



BOOK OF ABSTRACT



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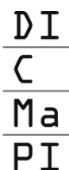
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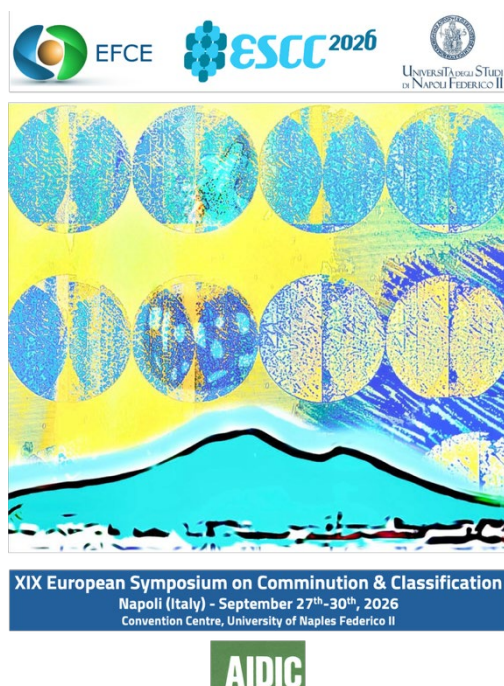
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PREFACE



The **XIX European Symposium on Comminution & Classification** (Napoli, Italy, September 27th-30th, 2026), is an event by EFCE (European Federation of Chemical Engineering, Working Party on Comminution and Classification), organised by AIDIC, the Italian Association of Chemical Engineering.

The Conference, the 19th in a series started in 1962, welcomes scientific and technological contributions on traditional and innovative aspects concerning: Fundamentals of particle breakage; Particulate characterisation; Mechanisms of grinding, dispersing and classification; Modelling of comminution and classification processes; Wear, erosion, contamination; Technological application fields of comminution and classification such as: chemical engineering operations and reactors, recycling industry and waste processing, environmental applications and renewable energy, mining, food, pharma, battery industry; Mechanochemical and mechanofusion

processes, bulk and surface mechanical transformations, mechanical alloying; Plant operation, control and energy optimisation in milling and classification processes; Innovative materials for comminution and classification; Powders flowability and floodability in milling operations, grinding aids; Cell disintegration and recovery of high added-value products; Application of machine learning, automation and artificial intelligence to comminution and classification processes.

The Conference is organised under the patronage of the University of Naples Federico II, the National Research Council, the Italian University Chemical Engineering Group, and the City of Naples, with the presence of several sponsors. It is structured into 3 Plenary Lectures, 6 Keynote Lectures, 14 parallel sessions bridging about 50 oral presentations, and poster sessions.

*Prof. Fabio Montagnaro
Conference Chair*

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Designing milling processes of pharmaceutical active ingredients for orally inhaled drug products

Andrea Benassi
Chiesi Farmaceutici R&D, Italy



Abstract

Jet mills are widely adopted to reduce pharmaceutical powder particles to the inhalable range (roughly 0.5–5 microns) owing to their ease of cleaning and absence of additives in the process. In these devices size reduction and classification occur at the same time; although convenient, this point makes their operating regimes highly non-linear, unstable and difficult to control. Pharmaceutical powders can be significantly expensive and the typical batch size quite small. Designing a size reduction process from scratch for a new product, solely based on trial-and-error approaches, can be very time and resource consuming. Therefore, predicting particle size and yield as a function of process and product parameters would be highly desirable during design and scale-up phases. Mechanistic models based on dimensional analysis and scale invariance have been demonstrated to fail when adopted in scale-up trials. Computational fluid/particle dynamics simulations have also been applied to the task showing significant limitations too. A third possibility is to adopt empirical approaches, based on the measurement of powder mechanical properties. All these methods will be reviewed, highlighting their pitfalls and limitations currently preventing us from achieving predictive capabilities.

The dark art of milling: optimising the milling of low carbon fuels for energy applications

Orla Williams
University of Nottingham, UK



Abstract

Milling is one of the largest consumers of energy globally and is widely used in material processing. This presentation demonstrates how recent advances in milling science from the power sector can inform more efficient and reliable milling practices. Over the past two decades, solid fuel combustion has shifted from coal to biomass in many countries. Most large-scale power station conversions have relied on adapted coal mills that use impact and abrasion to fracture brittle coal, even though biomass preferentially fails by shear fracture. This mismatch between fracture mechanisms and material properties has resulted in significant operational challenges, including mill choking and mill explosions. These challenges have driven advances in milling knowledge, including the development of novel milling metrics and increased recognition of the limitations of impact-based milling for ductile materials. Ball milling relies on impact fracture mechanisms, but the effectiveness of impact milling is fundamentally limited by a material's critical particle size for brittle fracture. This constraint is particularly problematic for biomass, leading to high energy consumption and poor particle size reduction. Recent work on the co-milling of brittle and ductile materials has demonstrated synergistic effects, enabled enhanced size reduction of the ductile fraction and eliminated the choking issues that can arise when ductile materials are milled alone. Laboratory scale milling trials also provide a powerful tool for diagnosing and mitigating problems observed in industrial systems. For example, olive residues transported through screw feeders in power stations frequently cake and cause blockages. By investigating ball milling conditions for olive cake, the influence of moisture content and temperature on the glass transition behaviour of olives was identified. Finally, this presentation shows how novel milling metrics can be used at laboratory scale to rank milling performance across materials and successfully correlate these results to full scale mills.

Green crushing? The potential of mechanical pathways to engineer powders from lignocellulosic biomass for energy, materials and green chemistry

Claire Mayer-Laigle

National Research Institute for Agriculture, Food and Environment (INRAE),
Montpellier, France



Abstract

Plant biomass, a vast yet underutilized resource, contains functional components embedded within a complex and resilient lignocellulosic structure. Reducing it to below cell size induces profound physical and chemical transformations that can be leveraged as valuable building blocks for advanced energy vectors, smart materials, and cosmetic or biomedical applications. This presentation will address the fundamentals of mechanical deconstruction from a physical perspective, with a focus on modes of energy transmission (type, intensity, and duration) and their impact on the physicochemical properties of powders. We will then show how controlling these mechanisms enables the design of tailored particles and the emergence of new functionalities, illustrated through applications such as plant-derived powdered fuels, fluorophore grafting onto plant powders for sensing, fully biobased materials for 3D printing, and hybrid strategies coupling milling with deep eutectic solvents for the targeted extraction of high-value molecules.

Understanding the symbiotic relationship between comminution and classification equipment in designing and optimising circuits for efficient operation

Aubrey Mainza
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Abstract

Comminution and classification are the main processes used to prepare particles for the downstream recovery methods such as flotation, magnetic separation, or leaching. Comminution equipment is primarily responsible for size reduction, while classification ensures that particles meeting downstream process requirements report to the recovery section and determines which particles are recycled for further size reduction. For a circuit to operate efficiently, the symbiotic relationship between comminution and classification must be considered during both design and optimisation. At the design stage, material flow must be simulated using dynamic models to capture variations arising from inherent feeding and equipment discharge mechanisms, which rarely operate under steady state conditions. Optimisation strategies that recognise the interaction between comminution and classification must be adopted for operating plants to ensure that products from each stage meets the required specifications. To process material at optimum energy efficiency and capacity, only particles requiring further size reduction should be recycled. Maximum recovery can be attained by allowing only liberated particles from the comminution circuit to enter the downstream recovery stages. For this to occur, the symbiotic relationship between comminution and classification devices in the circuit must form an integral part of the design and optimisation criteria. For example, in a circuit where a ball mill operates in closed circuit with hydrocyclones, design and optimisation must ensure that the circulating load remains within an acceptable range. This can be achieved by avoiding overloading of the ball mill circuit and by using hydrocyclones that provide sharp separation, minimal water recovery to the underflow, and a cut size that allows liberated particles to pass to downstream recovery processes. It is important to recognise that energy consumption depends not only on the operating parameters of the comminution devices but also on the performance of the classifiers within the circuit. Steady state models are often inadequate for identifying constraints related to

material flows in a circuit. Instead, models that account for the dynamic response of all devices in the circuit can be used to identify and evaluate potential solutions for circuits involving comminution and classification devices. This paper discusses the symbiotic nature of comminution and classification in different circuits and how associated challenges in those circuits can be addressed. Advances in comminution circuits, where comminution and classification duties are integrated in the same device, are also explored. Furthermore, optimisation strategies are presented alongside case studies demonstrating how circuits can be fine-tuned to produce desired products at the lowest possible energy consumption.

Defects in particles – the universe inside

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Abstract

An important trend in particle science and technology is aiming for a better understanding and design of systems of increasing complexity. The property function defines the target in product design and is understood along the five dimensions of size, shape, surface, composition and structure (i.e. amorphous, crystalline, internal pore size distributions and defects), and their respective distributions. The presentation will focus on defects in particles, the least understood and investigated dimension of the particle property space. Defects in particles occur inside of a particle or at its surface. Defects largely determine the fracture toughness of a material, the strength of a particle and the required energy to break it. A major challenge in studying defects is their in-depth characterization, which often requires sophisticated and expensive techniques including advanced spectroscopic and scattering techniques (e.g. RAMAN, ESR, XRD) or electron microscopy and tomography. We will discuss the role of defects in size reduction. Defects in crystalline particles are related to grain boundaries and crystal twins, dislocations, stacking faults and shear planes, all are related crystal disorder, whereas defects in amorphous materials depend on the local distributions of bonds and voids. Internal stresses are particularly high at local defects, facilitating crack opening. For energy efficient comminution, the defect density should be high. The grinding limit at the nanoscale strongly depends on the ability of nanoparticles to store defects. In contrast, process conditions for delamination of a bulk material to produce 2D materials (for instance, graphene, MoS₂, BN) must be tuned carefully to minimize any defect formation. Here, weak interactions between the crystal planes shall be overcome, while in-plane fracture should be avoided for the production of large sheets. Compression of particles below their brittle-ductile transition, such as bioglass for bone replacement or Si-Ge particles for battery electrodes, leads also to thin, plate-like morphologies, since these particles are plastically deformed without major fracture events. Based on the given examples, we will discuss white fields in particle science and technology to show unique opportunities for further research on fundamental questions and in pressing fields, such as the development of a sustainable, “green” particle technology.

When comminution and classification circuits start talking: Communicative process automation and the future of autonomy

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Abstract

Comminution and classification remain the most energy-intensive stages in mineral processing, yet they are also the least adaptable to variability and uncertainty. Traditional approaches – whether empirical, mechanistic, or advanced process control – have aimed to stabilise circuits within narrow performance windows. However, the increasing complexity of ores, circuits, and sustainability demands exposes the limitations of command-and-control paradigms. This talk introduces Communicative Process Automation (CPA) as a new framework for mineral processing automation. CPA treats the mill, cyclone, sensors, and operators not as isolated components but as agents in dialogue, negotiating trade-offs among throughput, recovery, energy, water, and wear. Drawing on principles from complexity science, advanced logic, and systems modelling, CPA extends beyond conventional optimisation by embedding explainability, adaptability, and value-sensitive decision making at the heart of circuit operation. Through case studies and conceptual demonstrations, the talk will illustrate how CPA reframes comminution and classification: from deterministic control problems to decision-centric, communicative systems capable of self-adjustment, transparency, and resilience. This paradigm shift opens new pathways towards truly autonomous, sustainable mineral processing and invites collaboration across engineering, computational, and social sciences to realise the next generation of mining autonomy.

On the measurement of the work-hardening effects of mechanical grinding

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Abstract. Mechanical milling induces strong work hardening and the formation of nanocrystalline domains in powders, challenging conventional microstructural characterization. This contribution reviews advanced X-ray diffraction line profile analysis methods that exploit the whole powder pattern, providing reliable insight into lattice defects and crystalline domain size. Examples from mechanically milled metals and ceramics illustrate state-of-the-art capabilities.

1. Characterization of mechanically ground powders by X-ray diffraction.

Mechanical milling is known to produce strong work hardening effects and crystalline domain size reduction. This enables the production of highly reactive, finely powdered inorganic materials for a variety of applications, from catalysis to additive manufacturing and advanced powder sintering. In this context, it is essential to understand the effects of grinding, especially under the most extreme conditions, which lead to the formation of nanocrystalline materials.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are essential tools, but can be limited in observing nanoscale crystalline domains with high defect density and strong agglomeration. Under these conditions, X-ray diffraction (XRD) is particularly useful and appropriate: Line Profile Analysis (LPA) – the study of diffraction peak width and shape – provides information on lattice defects (e.g., stacking faults, dislocations, etc.), and on the shape, size and dispersion of the crystalline domains down to few nanometres.

The most traditional approach to LPA uses only peak widths. Methods based on the Scherrer equation or the Williamson-Hall plot are very popular because they are simple to use, but they rely on crude approximations and provide limited information that can even be misleading [1].

2. Advanced methods for line profile analysis.

Over the last two decades, there has been a significant development in methods that utilize the entire XRD powder pattern information, including all the Bragg peak profiles and the diffuse scattering component. This provides detailed information on the microstructure of materials, particularly if they are nanocrystalline and highly deformed, such as those resulting from mechanical comminution. This new and more reliable approach can

be integrated into well-known powder diffraction methods, such as the Rietveld method. Various software programs are available, some of which are commercial and easy to use. [2–4]. This is well known in the XRD community, especially at the level of methodological developments, but reaches less the broad user community, which ranges from basic to applied research in various fields of chemistry, physics and engineering.

This presentation aims to help fill this gap by illustrating the state of the art of LPA methods, with examples applied to nanocrystalline powders obtained by high-energy mechanical milling.

Acknowledgement

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Automation of the Sieving Technique for Online Particle Size Analysis within a Milling Circuit

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Abstract. Particle size analysis plays a critical role in the mineral processing industry, especially on the milling circuit, which is an energy intensive process requiring optimal operating conditions. This paper presents a study undertaken to develop an online particle size analyser which is based on the sieving technique. A summary of the stages involved in the development of the instrument are outlined, which include preliminary testwork, conceptualisation and prototype design, assembly, and concept testing. Mechanical design principles were followed during the design process, and preliminary tests proved that the concept is feasible. Preliminary testing of the concept validated the design, demonstrating its capability of being robust. The proposed instrument is expected to be less expensive than currently existing instruments, and can be more reliable because it applies the sieving technique, which is typically used to validate most online particle size measurement instrument in the market. Once the concept was validated in the laboratory, a more advanced prototype was designed which is suitable to be tested in a mineral processing concentrator.

1. Introduction

Particle size analysis plays a critical role in the mineral processing industry as it enables the optimisation of energy intensive processes, especially milling. It is essential for maintaining product quality for downstream processes such as flotation and leaching, whilst ensuring profitable operations are achieved. Sieving is the oldest particle size measurement technique, and it is still utilised to verify modern particle size measurement instruments based on indirect methods such as microscopy, laser diffraction to name a few [1].

This study focuses on the development of a robust online particle size analyser based on the sieving technique. The traditional sieving method, is known for being accurate, but it is a manual and time consuming technique. The primary objective of the study is to design an affordable instrument, with high precision and accuracy, whilst optimising the time it takes to complete the particle size measurement, allowing the instrument to be online.

2. Experimental methods and concept design

2.1. Dry and wet sieving tests

Preliminary testwork was required to determine the feasibility of developing the concept of an online particle size analyser based on the sieving technique. The concept

revolved around the automation of the sieving technique, therefore certain stages of manual sieving were required to be eliminated, mostly the drying of the sample. It was therefore critical to conduct dry and wet sieving tests to determine how a PSD generated from dry solids particles differed from the one generated from wet solid particles.

This comparison test was conducted on samples collected from various mines, with the deviations being critically analysed. The analysis of these results determined if it was feasible to proceed with generating a concept design.

2.2. Concept design

Manual sieving method, requires the sample addition on top of the sieve stack, followed by shaking it with a sieve shaker, and emptying the retained particles on each sieve, while simultaneously weighing them. This involved moving the sieves in the X, Y and Z direction.

To automate this procedure, it was critical to simplify it, therefore the X and Y movements were eliminated, and the sieves were required to move in the Z direction (up and down).

Load cells played a critical role in simplifying the automation of the sieving procedure. Components such as the fork lifter, shelf, and sieves, were 3D printed using PLA material. Load cells were attached to a vertically moving shelf, which is actuated up and down. The fork

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lifter is directly attached to the load cell, and it is responsible for lifting the sieve up and down, whilst simultaneously measuring the weight of the sieve. The system automatically tared itself before each cycle begins. The thickness of the components were designed based on Equation 1[2] below:

$$h = \sqrt{\frac{6M}{b \cdot \sigma_{allowable}}} \quad (1)$$

This was also verified by conducting a Finite Element Analysis on all the critical components.

3. Results and Discussion

Figure 1 below illustrates results of the preliminary tests conducted to determine the feasibility of developing the particles size measurement instrument.

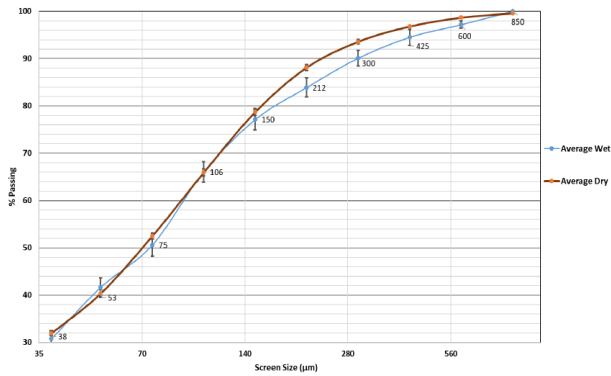


Figure 1. Zn Ore primary cyclone dry and wet averaged PSD curves

Since it was critical to optimise the analysis time, the PSD results were required to be calculated using the wet mass of particles retained on the sieves. Therefore it was critical to compare the PSD curves generated by the dry and wet solids particles. Figure 1 illustrates that the deviation between the two PSD curves was minimal and less than 5% on size classes between 150 to 600 µm.

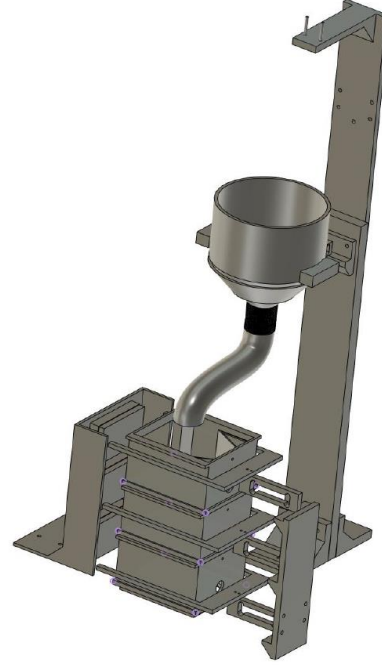


Figure 2. Preliminary design of the concept

Figure 2 illustrates a Fusion 360 design output of the final concept, with all the components assembled together.

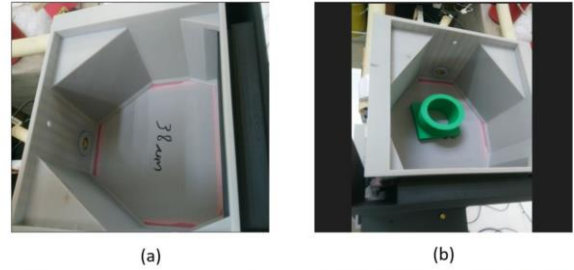


Figure 3. (a) Empty 3D printed sieve, (b) 3D printed sieve with a known mass object placed on it.

Figure 3 illustrates the sieve when it is empty and when a known mass object was placed on it. This experiment was conducted to test concept of the sieve lifting and mass measurement of retained solid particles.

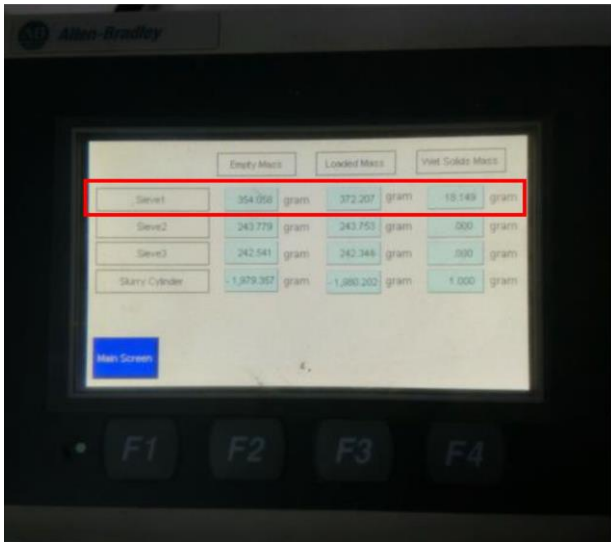


Figure 4. HMI results output from the PLC of the weight of the empty 3D sieve, sieve with known mass object positioned on it, and the difference between the two.

During the preliminary testing, the sieve lifting system tares the load cells by first weighing the empty sieve. This is followed by weighing the mass of the sieve with retained solids particles, in this case a known mass object positioned on top of the sieve. Figure 4 illustrates the captured masses of the sieves and the calculated mass of the object positioned on the sieve



Figure 5. The mass of the object measured with a calibrated scale

Figure 5 illustrates the measured mass of the object placed on the sieve, and the difference between the measured and the calculated mass of the object is less than 0.2 grams.



Figure 6. Assembled concept design of the density meter.

Figure 6 illustrates the assembled density meter which was used to measure the density of the slurry sample to be analysed by the system. The density measurement is required to complete the particle size distribution calculations for the sample, where the initial mass of the sample was automatically calculated.

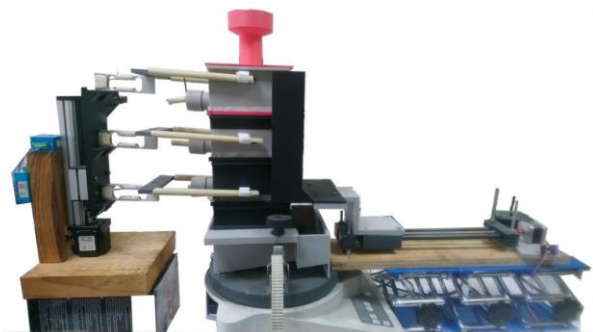


Figure 7. Assembled concept design of the sieve lifting and measurement system

Figure 7 illustrates the assembled sieve lifting and mass measurement system which was used to conduct preliminary testing of the concept.

4. Conclusion

The findings from this study demonstrated that the PSD calculated from dry and wet particle mass has minimal difference. This paved way to conclude that it is feasible to proceed with generating a concept for automating the sieving technique. The developed concept also demonstrated capability of accurately measuring the particle size distribution using the automated sieving technique.

Acknowledgement

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Laboratory-Scale Assessment of Shear and Impact Attrition of Carbamazepine Dihydrate Crystals during Agitated Filter Bed Drying

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Abstract. Agitated filter bed drying (AFBD) is a key pharmaceutical operation but can induce attrition in mechanically fragile crystals. Using carbamazepine dihydrate as a model, this study combines a lab-scale AFBD surrogate with an FT4 Powder Rheometer® and an aerodynamic dispersion method to probe shear- and impact-driven breakage. Results show progressive, multi-regime attrition, initial crystal snapping followed by surface chipping, governed by impeller clearance, consolidation load, solvent content, and energy input, providing a material-efficient framework for optimising AFBD process.

1. Introduction

In the pharmaceutical industry, agitated filter bed drying (AFBD) is a critical unit operation for isolating, dewatering, and drying potent active pharmaceutical ingredients (APIs). The inclusion of mechanical agitation is essential for promoting heat and mass transfer uniformity, preventing channelling, and ensuring homogeneous drying of the filter cake. However, the application of an impeller also introduces significant mechanical stresses into the particle bed, frequently resulting in undesirable particle size reduction through shear deformation, frictional contacts, and particle–particle or particle–impeller interactions. These effects are particularly pronounced for fragile crystalline materials, where uncontrolled breakage can compromise both product quality and downstream processability.

The behaviour of a particle bed during agitated drying is governed by a complex interplay of material properties and operating conditions, which together dictate the balance between particle breakage and agglomeration. Bagster and Bridgwater [1] investigated material flow in agitated dryers and demonstrated that bed dynamics are strongly influenced by impeller geometry and operating configuration, particularly blade height, blade angle, and bed depth. These geometric parameters affect local shear fields, stress distributions, and flow regimes within the bed. Complementary studies by Lekhal *et al.* [2, 3] further highlighted the sensitivity of crystal properties to key process variables, including agitation rate, temperature, and pressure. Their work showed that particle breakage is favoured under conditions of low drying rates and/or high shear rates, whereas agglomeration tends to dominate at high drying rates and/or low shear rates. They also reported that impact-induced breakage occurs primarily at high impeller speeds, while shear-induced breakage within the bulk of

the particle bed is the more prevalent and dominant attrition mechanism [4].

Despite the recognised importance of these mechanisms, experimental investigation of agitated drying remains challenging. Over the years, numerous laboratory-scale agitated dryers have been developed to study drying under controlled conditions [5–8]. However, most of these systems are in-house instruments designed within academic settings and are therefore not readily available to the pharmaceutical industry. Furthermore, laboratory setups intended to replicate industrial-scale heat and mass transfer behaviour and mechanical stress environments often require relatively large quantities of material, which are typically unavailable during early-stage process development. These systems also tend to lack operational flexibility, such as interchangeable impeller geometries or precise control over impeller motion, limiting their ability to probe the influence of individual process parameters systematically[9].

To address this limitation, a laboratory-scale agitated filter bed dryer was developed in collaboration with Freeman Technology as an auxiliary attachment for the FT4 Powder Rheometer®. This AFBD surrogate enables simulation of the agitated filter bed drying process under well-controlled conditions and allows particle attrition arising from bulk shear deformation, consolidation, and impeller-induced stresses to be directly observed and quantified. In the present work, carbamazepine dihydrate (CBZ·2H₂O) is selected as a model compound for systematically studying particle breakage phenomena during agitated drying. CBZ·2H₂O is particularly well suited to this role due to its acicular shape, high propensity for fracture, pharmaceutical relevance, and well-documented crystal structure and mechanical anisotropy.

To complement the FT4-based AFBD, which primarily interrogates breakage under shear and

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compressive loading, a second, orthogonal breakability assessment technique was developed to specifically examine impact-driven attrition. This method employs the aerodynamic dispersion unit of the Morphologi G3 to induce high-velocity particle impacts. This approach enables systematic evaluation of particle fragmentation as a function of impact energy while requiring only minimal quantities of material.

Together, these complementary techniques demonstrate that particle breakage in carbamazepine dihydrate is a multi-regime, progressive process. This combined experimental framework provides a powerful means of disentangling the relative contributions of shear- and impact-induced damage, offering valuable insight for the rational design and optimisation of AFBF processes for mechanically fragile pharmaceutical solids.

2. Carbamazepine dihydrate

Carbamazepine dihydrate crystals incorporate two water molecules within their crystal lattice, forming continuous channels that extend along the longest dimension of the macroscopic crystal and are aligned with the crystallographic c-axis. The crystal structure is monoclinic, belonging to the space group $P2_1/c$ [10]. The crystals typically display acicular and platy morphologies, which arise from anisotropic growth behaviour: the growth rates associated with the dominant crystal faces $\{h00\}$ and $\{0k0\}$ are significantly higher than those along the third crystallographic direction. As a result, the b and c axes correspond to the particle length and width of the formed crystals (Figure 1).

The ordered arrangement of water channels within the lattice gives rise to weak cleavage planes of the $\{0k0\}$ family, which are oriented perpendicular to the dominant $\{h00\}$ face. These cleavage planes are mechanically fragile and can be readily exposed during dehydration, as stress is relieved within the lattice [11]. Cracking on the $\{h00\}$ faces, aligned parallel to the c-axis, has been observed and is attributed to the removal of water molecules from the channel structure [12] (Figure 2). Material preparation have previously been prepared [13, 14].

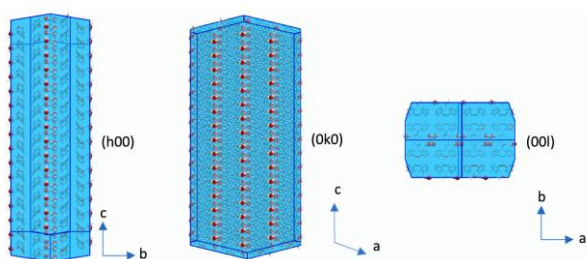


Figure 1. Calculated Bravais, Friedel, Donnay and Harker (BFDH) crystal morphology of carbamazepine dihydrate.[13]

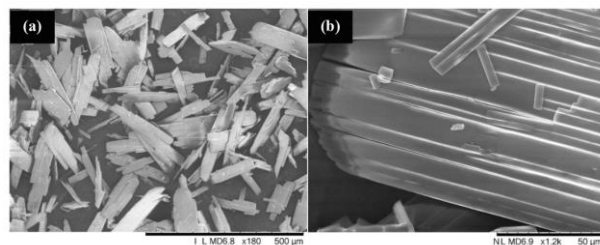


Figure 2. (a) Carbamazepine dihydrate crystals viewed by scanning electron microscope (SEM); (b) Formation of cracks on weak cleavage planes along $\{h00\}$ face under vacuum in the SEM chamber due to dehydration. [13]

3. Impact Breakage Assessment by Aerodynamic Dispersion Method

In our investigation into impact-induced breakage, we utilised the aerodynamic dispersion unit of a Morphologi G3 to subject carbamazepine dihydrate to controlled mechanical stress. This method employs a pulse of pressurised air, ranging from 0.5 to 5.0 barg, to accelerate minute powder samples against the internal walls of an entrainment spool. To establish a quantitative link between process parameters and breakage, we performed transient three-dimensional Computational Fluid Dynamics (CFD) modelling to predict the normal impact velocities of the particles within the disperser. By tracking particle trajectories through a Lagrangian approach, we were able to calculate average impact velocities for various size classes, which served as critical inputs for our modified version of the Ghadiri and Zhang impact breakage model.

$$R^* = \beta \rho \sum_{i=1}^n \phi_i D_i U_i^2$$

where R^* is the fractional mass loss, β the breakability index, ρ the particle density, i the bin number, ϕ the volume fraction of the particles, D the representative particle size, and U the corresponding particle impact velocity in bin i . Our analysis revealed that the breakage of these acicular crystals is inherently non-linear and operates across two distinct mechanical regimes. In the first regime, which corresponds to lower dispersion pressures, we observed rapid fragmentation where the crystals predominantly snap along their largest dimension. This "snapping" mechanism is driven by geometric bending moments acting on the high-aspect-ratio particles and was characterised by a breakability index of 0.47. As the particles became more equant through initial breakage, we identified a transition to a second regime dominated by chipping and surface erosion, which exhibited a significantly lower breakability index of 0.20 (Figures 3 & 4).

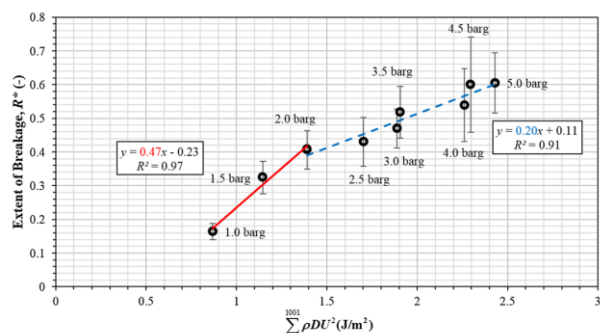


Figure 3. Extent of breakage as a function of ρDU^2 . [13]

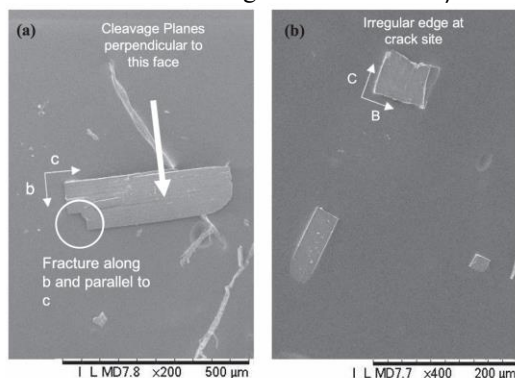


Figure 4. Snapping of carbamazepine dihydrate crystals. [13]

Furthermore, we gained significant structural insights into the interplay between external geometry and internal crystallographic planes of weakness. While the crystal lattice contains $\{0k0\}$ cleavage planes that are structurally vulnerable due to the presence of water channels, our results indicate that fracturing perpendicular to the crystal length remains the dominant failure mode under impact. This confirms that for highly acicular materials, the geometric effect of bending is a more powerful driver of attrition than the existence of weak cleavage planes. Collectively, this aerodynamic approach demonstrates its value as a rapid, material-efficient tool for assessing the attrition risk and grindability of fragile pharmaceutical solids.

4. Breakage during Agitated Filter Bed Drying

This study also introduces a novel, laboratory-scale AFBD unit developed as an auxiliary accessory for the FT4 Powder Rheometer, designed to bridge the technology gap in scale-down experimentation by accurately mimicking industrial conditions using minimal material quantities. The experimental prototype features a jacketed 25 mm vessel with interchangeable, 3D-printed impellers that provide precise control over rotational velocity, axial mixing, and temperature (Figure 5).



Figure 5. Experimental setup of the AFBD vessel. [14]

We quantified the extent of breakage (R^*) by measuring the positive shift in particle size distribution as a function of impeller clearance, rotational speed, and environmental conditions. The findings demonstrate that the impeller-base clearance is highly influential, with smaller gaps significantly increasing attrition due to intensified shear deformation in the failure zone. While increasing the number of impeller revolutions expectedly raised the breakage extent, the impeller tip speed within the tested range (0.04 to 0.15 m/s) did not significantly influence breakage for a constant number of rotations (Figures 6a & b). Notably, the application of vacuum suction to consolidate the cake increased the normal load on the powder bed, resulting in a dramatic rise in R^* (Figure 6c). Solvent content emerged as a major factor in particle durability, with crystals breaking more readily at high liquid contents (up to 50% water by mass) due to the formation of capillary bridges that increase inter-particle attraction and resistance to flow (Figure 6d). Shape analysis identified a transition in breakage mechanisms: crystals initially undergo fragmentation by snapping perpendicular to their longest dimension (the (001) plane) and subsequently transition to surface chipping as the particles become smaller and more equant. Ultimately, the study established a linear correlation between the extent of particle breakage and the specific mechanical energy expended by the impeller, confirming the new AFBD unit's value as a comparative assessment tool for optimising industrial drying protocols.

4. Conclusions

This work presents a systematic investigation of particle breakage during agitated filter bed drying using carbamazepine dihydrate as a model fragile pharmaceutical crystal. By combining a laboratory-scale AFBD surrogate with an orthogonal aerodynamic dispersion method, the study successfully disentangled the contributions of shear- and impact-induced attrition. The results demonstrate that particle breakage is a progressive, multi-regime process, transitioning from snapping-driven fragmentation of high-aspect-ratio crystals to surface chipping as particles become more equant.

The newly developed AFBD unit provides a material-efficient and scalable platform that reliably captures the influence of key process variables, including impeller clearance, consolidation load, solvent content, and mechanical energy input. Together with the Morphologi

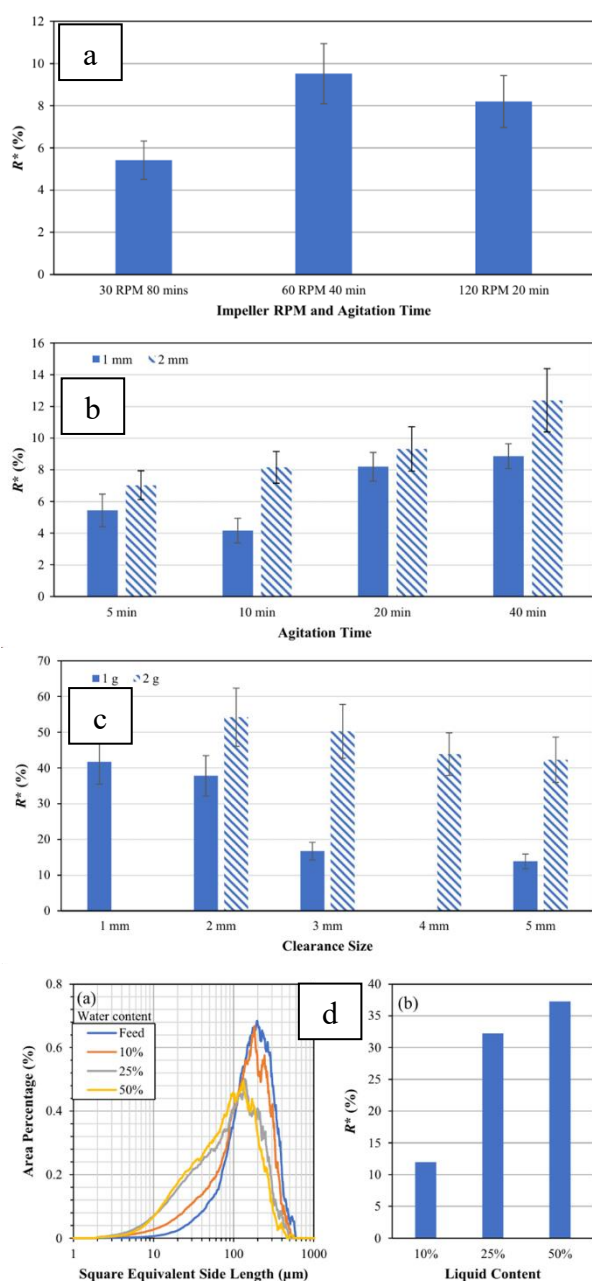


Figure 6. R^* as a function of (a) impeller RPM and agitation time (fixed number of rotations), (b) agitation time, (c) clearance size (with vacuum suction) and (d) liquid content. [14]

G3-based impact assessment, this integrated experimental framework offers valuable mechanistic insight into particle degradation during agitated drying and represents a practical toolset for the rational design and optimisation of AFBF processes for mechanically fragile pharmaceutical solids.

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Impact of Grinding Processes on the Microstructure and Porosity of Wheat Bran

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Abstract. Plant matrices such as wheat bran exhibit complex structures and compositions, where interactions between polymers, water, and solvents strongly influence fractionation and extraction efficiency. This study proposes analytical approaches (ATR-FTIR, Time-Domain NMR, and solid-state NMR) to characterize these interactions and support the optimization of grinding and extraction processes. The main objective was to test whether FTIR data describing water binding states in powdered wheat bran can be correlated with water mobility measurements obtained by NMR under two relative humidity conditions. The influence of grinding modes (shear versus impact) and particle sizes (300 and 500 µm) on hydration properties was investigated. Results support combining FTIR and NMR to characterize molecular interactions and structural changes within plant matrices. Overall, this integrated approach provides insights into relationships between grinding processes and fragmentation mechanisms. Mechanical stress leads to matrix breakdown, producing different water affinities. Despite similar grid sizes, significant differences in particle size distribution and functional properties were observed, reflecting distinct stresses applied. Experiments at two humidity levels show that comminution conditions strongly influence hygroscopic sensitivity, confirming the decisive role of milling. Thus, technological functionality cannot rely solely on composition and microstructure but must include mechanical deconstruction governing water interactions and resulting properties overall.

1. Introduction and context of the study

Wheat bran is a by-product of conventional wheat milling which is currently undervalued as only 10% is currently used for food applications [1]. To incorporate bran into food products and other materials, wheat bran is often reduced into a fine powder involving a milling step. During the milling, the bran is subjected to mechanical stresses generated by the grinder such as compression, impact, friction, shear and extension, [2] that can influence its functional properties and so the quality of the final products [3]. A better understanding of the influence of the milling step notably the effect of different mechanical loading modes on the hydration water properties could bring new insights for a better processing and valorization of this by-product.

Molecular-level understanding relies on ATR-FTIR, which revealed that milling alters particle size and molecular structure, modifying water interactions in wheat bran [4]. Complementary studies using DVS, NMR relaxometry, and solid-state NMR linked relaxation and molecular interactions parameters to water retention, structure, and porosity [5-8]. These methods are well-suited to describe lignocellulose-solvent interactions and predict their impact on system porosity. Previous work [4] applied a direct subtraction method adapted from [9] to isolate, in FTIR, the spectral contribution of interfacial hydration water. Subtracting the lyophilized spectrum from the native spectrum highlights absorption bands associated with different water types in the plant matrix. Corrected, normalized, and smoothed spectra were used to interpret the effects of milling on water bonding states. The ATR-FTIR and NMR methods were combined to

evaluate the binding strengths between water and the bran matrix.

2. Materials and methods

2.1. Wheat bran

Wheat bran from durum wheat bran (*Triticum durum*), was supplied by a French industrial miller, the Panzani Group. This batch consists of fine bran, made up of smaller particles from the inner layers of the husk. It is richer in starch and protein due to its proximity to the aleurone layer.

2.2. Grinding operations

Durum wheat bran batches were milled using processes dominated by specific mechanical stresses (impact, shear, friction) at varying sieve sizes.

Impact mill – UPZ (Hosokawa-Alpine, type 100 UPZ, Augsburg, Germany): Grinding was performed at room temperature at 18,000 rpm using 500 µm and 300 µm sieves, with impact as the predominant stress mode.

Ultracentrifugal mill – ZM200 (Retsch, Germany): Operating at 18,000 rpm with 500 µm or 250 µm sieves, shear dominates while impact also occurs. Bran was pre-frozen, and chamber temperature was monitored to avoid structural alterations. Milled material was collected via a cyclone equipped with a filter to limit fine particle dispersion.

2.3. Conditioning samples at different relative humidities

Prior to ATR-FTIR, NMR relaxometry and solid-state NMR analysis, the ground samples were equilibrated at two relative humidity levels (58% and 86%) achieved

using saturated solutions of NaBr and KCl, respectively, in accordance with standardized sorption conditions. A conditioning time of 14 days was required to reach mass stability.

2.4. Bran characterization

2.4.1. Particle size measurement by laser diffraction

The particle size distribution of the ground samples was measured by laser diffraction using a Mastersizer 2000 equipped with a Scirocco 2000 dry dispersion unit Scirocco 2000 (Malvern Instruments, Worcestershire, UK). The particle size distribution is expressed as % of total particle volume. The median particle size (D_{50}) and span ($(D_{90}-D_{10})/D_{50}$) were used as the primary descriptors. This measurement was performed only on ground material since the size of initial brans was outside the measurement range of the device. All measurements were performed in triplicate.

2.4.2. ATR-FTIR spectra

The FTIR spectra were collected in the 400–4000 cm^{-1} wavenumber range on a Bruker Vertex 70v Fourier Transform spectrometer (Bruker Optik GmbH, Germany) operating with a Global source in combination with a KBr beamsplitter and a DigiTect DLaTGS detector with integrated preamplifier. The optical cell was a Golden Gate diamond ATR system. The spectra were recorded with a resolution of 4 cm^{-1} , automatically adding 128 repetitive scans. Scans were corrected for the air contribution and were preprocessed using OPUS software (version 7.0) by performing a baseline correction, a 9 points smoothing and a vector normalization for taking into account the effective number of absorbers. Experiments were conducted on powders of native and ground brans previously equilibrated at 50% or 86% relative humidities in specific climatic chambers (at 25 °C). The spectra of freeze dried brans were subtracted following the direct difference method [9]. The resulting spectrum is supposed to correspond to interfacial hydration water. In ATR-FTIR, the parameter R_{multimer} is defined as the ratio of absorbance maxima for two water states: $R_{\text{multimer}} = A_{3600} / A_{3200}$. The 3600 cm^{-1} band corresponds to weakly coordinated “multimer” water MW (0–1 hydrogen bonds), while the 3200 cm^{-1} band represents strongly coordinated “network water” NW (up to four hydrogen bonds). An increased R_{multimer} indicates a higher proportion of weakly structured water interacting with the matrix.

2.4.3. Time-Domain NMR

T_2 measurements on powders were performed using a minispec 20-MHz Bruker spectrometer (Wissembourg, France). The temperature of samples at 20 °C was measured and controlled using a calibrated optical fiber. T_2 relaxation times were measured via the combined FID-CPMG sequence implementing 128 scans preceded by a 400 ms recycle delay. The FID duration was 141 μs . The echo time (TE) in the CPMG sequence was 0.05 ms for 2000 echoes. The fitting of FID-CPMG signals required the combination of exponential, Gaussian and SinC functions. The total NMR signal was well represented by a combination of a cardinal sinus function and a Gaussian broadening, followed by three or four exponential decreasing depending on the hydration level [10].

2.4.4. Solid-state NMR

A Bruker Avance NEO 400 WB spectrometer operating at a proton frequency of 400.13 MHz was used for all NMR spectra acquisition. The magic angle spinning (MAS) rate was set at 12 kHz. VCT-CPMAS ^{13}C NMR was performed using 160 contact times with 128 accumulations and a recovery time of 3 s. T_{CH} , T_{HH} and $T_{1\rho}^{\text{H}}$ parameters were determined as previous proposed [5].

3. Results and discussion

It is worth noting that, although similar grid sizes were used in both milling devices, the particle sizes measured at the outlet show significant differences as shown in table 1 (median diameters of 140.53 μm and 306.02 μm for the 300 μm sieve for ultracentrifugal and impact mill respectively for example). This highlights that, during deconstruction, the mechanical stresses specific to each mill (mainly shear in the centrifugal mill, and a combination of impact and shear in the impact mill) [11] influence the fragmentation mechanisms in different ways. Therefore, beyond the grid size alone, the nature of the applied stresses (impact, shear, compression) plays a key role in determining the resulting particle size distribution [4].

Table 1. Different parameters (D_{10} , D_{50} , and D_{90}) of the particle size distribution curves for wheat bran samples milled using ultracentrifugal and impact mills with different sieves.

	Ultracentrifugal mill		Impact mill	
	250 μm	500 μm	300 μm	500 μm
D_{10}	21.04	79.97	39.39	136.20
D_{50}	140.53	436.23	306.02	514.02
D_{90}	362.80	1001.37	651.85	1355.50

All ATR-FTIR spectra show three main absorption bands. The band at $\sim 3600 \text{ cm}^{-1}$ corresponds to weakly coordinated “multimer” (MT) water, forming few hydrogen bonds (0–1) and interacting mainly with the matrix. The $\sim 3450 \text{ cm}^{-1}$ band represents “intermediate water” (IW), with moderate structuring (2–3 hydrogen bonds), acting as a transition between disordered and structured states. The $\sim 3200 \text{ cm}^{-1}$ band corresponds to “network water” (NW), composed of strongly coordinated molecules (up to four hydrogen bonds), reflecting a well-organized hydrogen-bond network similar to highly structured or bound water. ATR-FTIR analysis revealed clear differences in the structure of water within ground durum wheat bran matrices, depending on the grinding conditions and relative humidity. The spectra obtained show a reproducible distribution of the three water populations (MW, IW, NW), with a higher overall intensity at 86% RH. Calculation of the R_{multimer} parameter confirmed these observations, revealing a predominance of disturbed water (MW) under high humidity, and a more pronounced structure (NW) under NaBr conditions. These results

illustrate the sensitivity of water states to the microstructure induced by milling processes and to hydration conditions. Table 2 presents the values of the R_{multimer} parameter, calculated for each experimental condition (grinder type, sieve size, relative humidity). This ratio reflects the balance between the populations of weakly structured water (MW) and strongly bound water (NW) in the matrix.

Table 2. Values of the R_{multimer} ratio (A_{3600}/A_{3200}) and water uptake for each ground sample and relative humidity condition.

	Ultracentrifugal mill		Impact mill	
	250 μm	500 μm	300 μm	500 μm
Water uptake at RH 86%	8.7%	2.86%	8.27%	1.95%
R_{multimer} RH 86%	1.38	1.09	1.12	1.28
R_{multimer} RH 58%	0.87	1.16	1.12	1.16
Water uptake at RH 58%	-3.2%	-0.75%	0.61%	-2.28%

In Table 2, we report the water uptake of the samples under the different conditioning conditions. At low humidity (58%), the samples tend to lose water, except for the sample produced with the impact mill using a 300 μm grid.

Under conditioning at 86% relative humidity, all samples absorb water, and the obtained values appear to be mainly related to the grid size used, with only minor differences between the milling devices. These first observations highlight that the mechanical stresses generated by the mills, beyond particle size reduction, also affect differently the various tissues composing wheat bran, leading to different capacities for hydrogen bond formation. The state of water within this matrix can be described using the multimer ratio (R). An R value below 1 indicates a higher proportion of interactions between water molecules and the surrounding water molecules (network water NW), whereas an R value above 1 suggests that, for the same water content, water molecules interact more with the matrix (Multimer water MW). This parameter therefore provides insight into the accessibility of the matrix to water molecules and, potentially, to solvents used during extraction processes.

Analysis of the values reported in table 2 also makes it possible to identify the dominant water population under different conditions. Under a relative humidity of 86%, all samples exhibit R_{multimer} values greater than 1, indicating a predominance of multimer water (MW). Under a relative humidity of 58%, one sample of ground wheat bran at 250 μm with ultracentrifugal mill show values less than 1, in which network water (NW) becomes the dominant fraction. The functional groups and/or their accessibility can be altered by the grinding loading mode

impacting the network water component situated at low wavenumbers.

As shown in Figure 1, for each sample, the kinetics were modeled, allowing the extraction of several parameters: T_{CH} , which characterizes interactions between macromolecules; T_{HH} , the spin diffusion time, which indirectly probes water–matrix interactions; and $T_{1\rho}^{\text{H}}$, which enables the assessment of the level of molecular order.

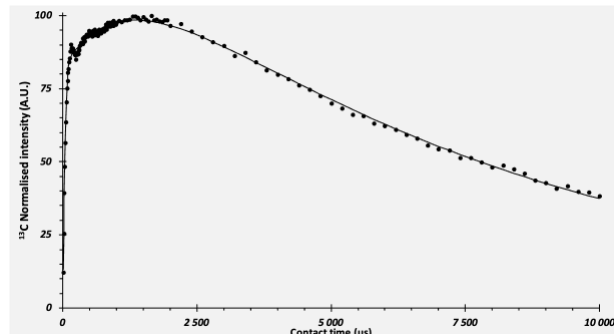


Figure 1. VCT profile of wheat bran milling with impact mill and conditioned at relative humidity of 59%. Each data point represents the signal intensity extracted from the ^{13}C CPMAS spectrum acquired at the corresponding contact time on the x-axis. Solid lines represent the results of modelling.

R_{multimer} correlates with solid-state NMR parameters such as cross-polarization transfer time (T_{CH}) and spin diffusion time (T_{HH}) (Figure 2), reflecting macromolecular interactions and water structuring in polysaccharides, as well as with T_{23} from NMR relaxometry, characterizing intermediate water mobility. Although both parameters evolve in a similar manner, the direct linear correlations remain moderate (0.46–0.53), likely due to sample heterogeneity and differences in hydration levels.

Indeed, wheat bran is a complex matrix composed of various plant tissues. While it is of great interest for extraction processes, its structural complexity must be considered. During deconstruction, mechanical stresses affect these tissues differently, which is precisely what this study aimed to highlight.

However, the chemical groups revealed by this differential deconstruction, depending on the milling process, likely do not respond in the same way across the analytical techniques used (FTIR, solid-state NMR, and NMR relaxometry). This suggests that other types of correlations need to be explored.

Biochemical analyses are currently underway to complement this study and refine the observed correlations.

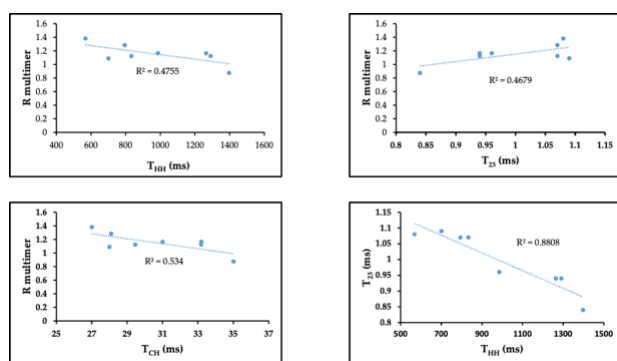


Figure 2. Observed interactions between Rmultimer measured by ATR-FTIR and T_{CH}/T_{HH} from solid-state NMR, as well as T_{23} from NMR relaxometry. All data obtained under the two relative humidity conditions were used.

4. Conclusion and perspectives

The complementary analysis done by ATR-FTIR and NMR showed results consistent with the observations of Barbar et al. (2023), who demonstrated a redistribution of water content depending on the grinding method and relative humidity. The link between more intense grinding (fine shearing) and an increase in multimer water is also consistent with the trends described by Cadden (1987), who had already suggested a correlation between particle fineness and the release of bound water in ground plant fibers. Complementary studies are needed to clarify the relation between the effect of the grinding mode on the dissociation of the tissues and on the accessibility of the constituents and their impact on the hydration properties. This will bring new elements to optimize the milling processability of wheat bran to target specific hydration properties as well as extraction efficiency by increasing solid–liquid surface area.

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Mutual Interactions in Multi-Component Comminution with Stirred Media Mills: Effects on Breakage Rate and Particle Transport

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Abstract. The comminution of multi-component systems is essential for processing ores and recycled materials, targeting size reduction and phase liberation. Heterogeneous feedstocks exhibit component-specific breakage strengths and transport behaviours, complicating selective comminution. Although high-pressure rolls, ball mills, and stirred media mills have been studied, detailed experimental data supporting population balance models (PBMs) remain scarce. This work investigates the comminution behaviour of a quartz–limestone mixture in a stirred media mill. Breakage rates for single-component and binary systems were measured using five narrow size fractions under varied stress conditions, showing component-specific interactions for both materials. Particle transport and classification by the stirrer deflector wheel reveal temporary accumulation of the harder component under certain conditions. Avoiding this buildup requires sufficient stress energy to fracture quartz and moderating classification intensity.

1. Introduction

Comminution of multi-component systems is critical in minerals engineering. With declining ore grades and increasingly stringent recycling regulations, research is focused not only on particle size reduction, but also on exploiting differences in material properties to achieve the selective enrichment of high-value phases, thereby improving process efficiency and sustainability [1]. Dry and wet comminution follow fundamentally different selectivity mechanisms. In dry operated mills – such as high-pressure grinding rolls and conventional ball mills – coarser, harder particles act as stress concentrators, promoting energy transfer from the mill to the product [2–4]. Conversely, in wet comminution in tumbling or stirred media mills the softer phase often breaks preferentially under relatively low stress energies and short residence times, while particles of the harder component mainly remain intact. Consequently, coarser, harder particles are more frequently captured by the media, which protects the fragments of the softer phase and thus lowers overall selectivity [5, 6]. Material-specific interactions thus open opportunities for tailoring comminution strategies toward valuable components.

In dry processes, these divergent breakage behaviors strongly affect particle classification and overall performance. Tavares & Kallembach [7] showed that comminution of basalt-limestone and copper ore-limestone mixtures in a Bond mill, the harder fractions accumulate under both open- and closed-circuit conditions. Dündar & Benzer [8] observed similar accumulation when dry grinding blended cements, where the lower breakage rates of clinker and porcelain –

combined with density differences – complicate process control. In wet stirred media mills, the deflector wheel of the stirrer enables separation of fines from coarse particles [9], yet its impact on multi-component feeds remains unexplored.

Developing predictive models for comminution design and optimization is a current priority. Population balance models have proven effective for multi-component systems, but they require accurate information on particle transport, breakage function, and breakage rate. The breakage function – describing size distributions post-breakage – is only marginally affected by the presence of other components [7]. By contrast, breakage rates – which express the probability that particles of a given size break during a comminution process – are highly mixture-dependent. Most PBM approaches for multi-component comminution build on Kapur & Fuerstenau's [10] energy split factor, which allocates the specific energy input among components based on their breakage behaviour as part of a mixture in relation to the breakage behaviour as a single-component. Zhao et al. [6] applied this concept to a quartz-chlorite slurry in a wet ball mill, finding the chlorite's energy split factor to be below a value of one but increasing linearly with chlorite content – implying reduced chlorite breakage in mixtures.

Despite these advances in modelling and comprehensive understanding of the basic mechanisms in multi-component comminution, key questions remain regarding how process parameters and stress energy levels affect breakage rates and material transport in stirred media mills. This study addresses these gaps via systematic

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experiments on a limestone-quartz mixture and with the help of the mechanistic stress energy model proposed by Kwade [11, 12].

2. Stress energy model

The stress energy model developed by Kwade [11, 12] links process parameters to achievable particle size via stress energy SE and stress frequency SF. It describes stress conditions in various mill types – especially wet-operated stirred media mills – and allows optimal conditions for product quality and energy efficiency to be identified with a limited number of experiments. The stress energy is the kinetic energy of colliding grinding media, depending on their relative velocity and mass. Because velocities are distributed, the maximum stress energy SE_{GM} is typically used to characterize grinding processes, calculated as follows:

$$SE_{GM} = d_{GM}^3 \cdot \rho_{GM} \cdot v_t^2 \quad (1)$$

where d_{GM} denotes the grinding media size, ρ_{GM} its density, and v_t the stirrer tip speed. The stress frequency is the number of media-particle collisions a feed particle experiences per unit time. According to Equation (2), it is calculated from the number of media contacts per unit time n_c , the capture probability P_{cap} and the total particle count n_p .

$$SF = n_c \cdot P_{cap} / n_p \quad (2)$$

The number of media contacts is assumed to be proportional to the stirrer speed n and the number of grinding media n_{GM} , while also accounting for the grinding chamber volume V_{GC} , the media filling ratio ϕ_{GM} and the porosity of the grinding media bulk ε (see Equation (3)). Assuming spherical particles, the total particle count can be determined from Equation (4) under consideration of the solids volume concentration c_v .

$$n_c \propto n_{St} \cdot n_{GM} = \frac{n_{St} \cdot V_{GC} \cdot \phi_{GM} \cdot (1-\varepsilon)}{\frac{\pi}{6} \cdot d_{GM}^3} \quad (3)$$

$$n_p = \frac{V_{GC} \cdot (1-\phi_{GM} \cdot (1-\varepsilon)) \cdot c_v}{\frac{\pi}{6} \cdot x^3} \quad (4)$$

3. Materials & methods

The breakage rates and transport behaviour were characterised using limestone (KSL Staubtechnik GmbH) and quartz (Quarzwerke GmbH) as individual components, as well as a 50:50 mixture of these two materials. Figure 1 shows the corresponding particle size distributions. With a Mohs hardness of 7, quartz can be considered the harder of the two components compared to limestone, which has a Mohs hardness of 3.

The breakage rate S was determined from the disappearance of material in the top size class m_1 as a function of comminution time t , using data obtained from batch experiments. The calculation was performed according to Equation (5), assuming first-order breakage

kinetics. To investigate the influence of particle size, the feed material was separated into five size fractions.

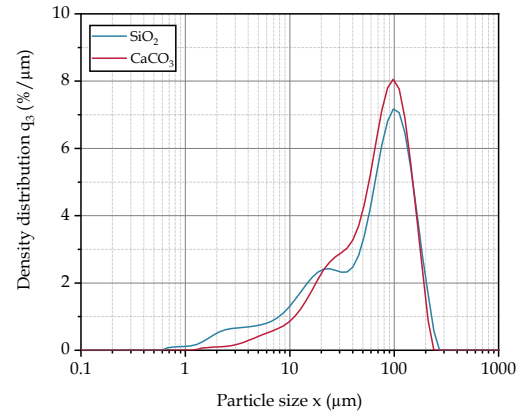


Figure 1. Particle size distributions of feed materials.

$$S = -\ln(m_1(t)/m_1(0)) / t \quad (5)$$

All batch experiments were conducted at laboratory scale in a horizontal stirred-media mill (PML 2, Bühler Group). A constant solid mass concentration of 20 wt. % and a media filling ratio of 80 % were maintained throughout. To evaluate the effect of stress conditions on breakage rate, both stirrer tip speed and media size were varied. As summarized in Table 1, four process parameter sets per material were tested, yielding grinding media stress energies between 0.032 mJ and 0.515 mJ. In every trial, zirconia grinding beads ($\rho = 6050 \text{ kg/m}^3$) were used.

Table 1. Process parameter combinations for determination of specific breakage rate.

Parameter set	v_t [m/s]	d_{GM} [μm]	SE_{GM} [mJ]
1	6	530	0.032
2	6	755	0.094
3	8	755	0.167
4	8	1100	0.515

The transport behaviour was characterised using experiments conducted in batch mode. The slurries were first prepared in a stirred vessel with a solids concentration of 20 wt.% and then continuously pumped through the mill at a flow rate of approximately 40 l/h. Samples were taken continuously at the outlet during the experiment and analysed for solids concentration, particle size and, in the case of mixture comminution, also for composition by x-ray fluorescence. In these investigations, only grinding media with a size of 755 μm were used, with the stirrer tip speed varying between 6 m/s and 12 m/s.

4. Results

To explore the mutual interaction of limestone and quartz during multi-component comminution, Figures 2 and 3 plot the breakage rates at grinding media stress energies of 0.032 mJ and 0.515 mJ against the volumetric energy

input. Following Fragnière et al. [13], this input is defined as the product of grinding media stress energy SE_{GM} and stress frequency SF divided by the total particle count n_p . In all cases, the breakage rate rises with energy input until it peaks at $SE_{GM} \cdot SF/n_p = 2 \times 10^{-24}$ J/s, demonstrating effective comminution regardless of the applied stress energy. Beyond this maximum, for $SE_{GM} \cdot SF/n_p > 2 \times 10^{-24}$ J/s, the breakage rate declines as coarser particles become increasingly resistant to breakage. Throughout the stress energy spectrum, quartz consistently shows lower breakage rates than limestone, owing to its greater hardness. Moreover, both minerals exhibit reduced breakage in the mixed system versus their single-component performance – limestone because of the protecting effect by harder quartz particles, and quartz because of its decreased capture probability under the short process times studied.

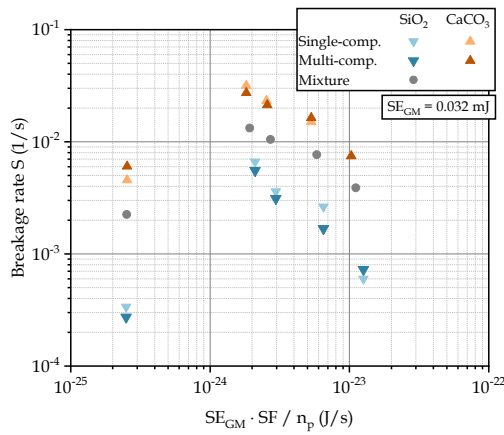


Figure 2. Breakage rate of quartz, limestone and their mixture as a function of $SE_{GM} \cdot SF/n_p$ for a grinding media stress energy of 0.032 mJ.

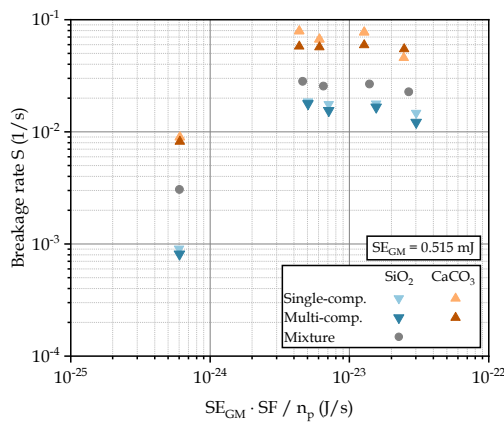


Figure 3. Breakage rate of quartz, limestone and their mixture as a function of $SE_{GM} \cdot SF/n_p$ for a grinding media stress energy of 0.515 mJ.

These interactions also strongly affect particle transport in passage mode operation. Figure 4 plots the quartz fraction in the mill discharge over time and shows that, at media stress energies up to 0.26 mJ, the harder quartz component

accumulates at relatively constant values inside the grinding chamber. Insufficient breakage of quartz particles means that the relatively coarse particles are held back by the centrifugal forces at the deflector wheel rather than being discharged. With a constant media size, higher stirrer speeds exacerbate this retention. By contrast, at a sufficiently high stress energy ($SE_{GM} = 0.375$ mJ), quartz is broken more effectively, weakening the deflector's classification effect and allowing the quartz fraction in the product to rise steadily toward the feed composition. In practice, as comminution continues and quartz particles become progressively weaker, even lower energy regimes will eventually deliver a product whose quartz content matches that of the feed mixture.

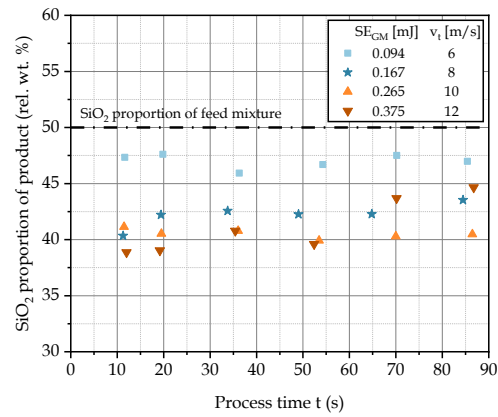


Figure 4. Quartz proportion of the product at the outlet of the stirred media mill as a function of process time for varying stirrer tip speeds and corresponding grinding media stress energies operating the stirred media mill in passage mode.

5. Conclusion

This study used quartz and limestone to investigate multi-component comminution in short-term batch tests, comparing single-component and multi-component systems. Breakage rates were directly correlated with grinding media stress energy, stress frequency and particle count. Limestone consistently exhibited higher breakage rates than quartz due to its lower hardness, both alone and in the mixture. In multi-component systems, both minerals break less efficient than in single-component tests – attributed to a protection effect of quartz on limestone and to a reduced capture probability for quartz. Different breakage kinetics also influenced material holdup: in 90 s passage mode tests, quartz accumulated in the mill regardless of stirrer speed, although higher stress energies mitigated this build-up. Future work will combine comminution and transport studies via residence time distributions to refine predictive PBM models.

Acknowledgement

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CO₂ Capture Performance and Particle Comminution Behavior of Brazilian Dolomite in a Lab-scale Dual Interconnected Fluidized Bed for Calcium Looping Application under Simulated Natural Gas Combustion Conditions

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Abstract. In this work, a Brazilian dolomite was investigated as a CaO-based sorbent in a Calcium Looping (CaL) process under a simulated natural gas exhaust atmosphere, to evaluate its potential for efficient CO₂ capture in low-concentration flue gas. The campaign was carried out in a bench-scale Dual Interconnected Fluidized Bed (DIFB) reactor, and the obtained key experimental parameters were optimized by a Rotatable Central Composite Design (RCCD) method. The performance in terms of sorbent capture capacity and its particle comminution by impact fragmentation was evaluated, considering the influence of gas velocity and temperature. Carbonation temperature was identified as the dominant operational parameter. When assessing overall performance, tests conducted in the presence of a simulated combustion gas derived from natural gas yielded trends in line with a typical CaL process but showing a reduced CO₂ capture efficiency compared to other data reported in the literature, although for different conditions. Under the most favorable operating conditions, at 675 °C and for a fluidization velocity of 0.5 m/s, a capture efficiency of 0.0177 g_{CO2}/g_{sorbent}, affected by sorbent thermal degradation and its rather severe elutriation behavior, was measured.

1. Introduction

Despite the increasing efforts towards the energy transition and the reduction of greenhouse gas emissions, fossil fuels will continue to play a relevant role in the global energy scenario over the coming decades [1].

In Brazil, where the role of fossil fuels is consistent with the global picture, the natural gas consumption is expected to rise in the coming years, given the policies aimed at promoting the development of offshore reserves and the industrial use of natural gas [2].

In this context, Carbon Capture, Utilization, and Storage (CCUS) technologies represent strategic short-term alternatives for mitigating CO₂ emissions while maintaining the reliance on fossil resources. Among these approaches, CaL represents a post-combustion CO₂ capture process based on the reversible reaction between calcium oxide (CaO) and carbon dioxide, forming calcium carbonate (CaCO₃) during carbonation and regenerating CaO during calcination. CaL is traditionally carried out in DIFB reactors with a carbonator where CO₂ is captured from the flue gas at temperatures around 600–650 °C, and a calciner, operating at approximately 900–950 °C to regenerate the sorbent and produce a

concentrated CO₂ stream suitable for storage or utilization [3].

The advantages of this technology rely in the use of low-cost, abundant and eco-friendly sorbents such as limestone and dolomite, and in a straightforward retrofitting of existing plants and relatively low efficiency penalties [4].

Several studies, focused on fluidized bed reactors, which allow solids circulation between the reactors and are favorable to provide efficient gas–solid contact, and heat and mass transfer, have addressed process intensification strategies, including indirect heating systems, integration with renewable energy sources, and the development of synthetic sorbents with improved cyclic stability [5].

One of the main technical challenges of CaL is represented by the sintering of the sorbent at high temperatures, especially during the calcination stage, with the consequent decay in CO₂ capture capacity over iterated cycles. In addition to sorbent deactivation, the sorbent loss due to comminution (attrition and fragmentation) occurring in fluidized beds calls for continuous fresh sorbent make-up. Among the various

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comminution mechanisms, fragmentation by impact damage – comparatively less scrutinized – due to high velocity collisions between fluidized particles and targets, can generate both elutriable and non-elutriable fragments [6].

Despite the extensive research conducted, the application of CaL to natural gas-fired power plants, that is, under low CO₂ concentrations (close to 4%), remains less explored when compared to coal-fired systems and derived flue gases with CO₂ concentrations above 12–15 vol.% [7].

Although most CaL studies had been focused on limestone performance, dolomite, a calcium–magnesium carbonate, is a cheap natural material with a price roughly 10% higher than limestone, presenting a more elevated resistance toward sintering, although its use implies larger sorbent feed rate to obtain the required Ca/S ratio and larger extent of attrition phenomena [8].

In this context, the present study investigated a Brazilian dolomite exposed to CaL tests at low CO₂ concentrations in a lab-scale DIFB apparatus, focusing on CO₂ capture and particle comminution by impact fragmentation.

2. Experimental

The experimental setup, specifically developed for looping experiments, consists of a laboratory-scale DIFB including two identical bubbling FB reactors (ID 40 mm), serving as the calciner and the carbonator, respectively. The reactors, although operating in batch mode, are interconnected by a transfer line enabling the rapid pneumatic transport of the sorbent between the two units by means of a valve-controlled system [9].

Each CaL test consisted of ten consecutive calcination/carbonation cycles, followed by a final calcination step performed prior to the spent sorbent discharge.

In both reactors, inert silica sand with a particle size of 0.8–1 mm was used as fluidizing and thermal ballast material. A dolomite sample of $m_0=20$ g, with particle size in the range 0.4–0.6 mm, was loaded at the calciner at the beginning of each test. Each stage lasted 10 minutes.

Calcination was conducted at 940 °C under oxy-combustion-like conditions, using a gas mixture containing 70% CO₂ in air. The superficial gas velocity during fluidization was maintained at 0.5 m/s.

The carbonator was fed with 4% of CO₂ (balance air) in tests investigating the effect of different carbonation temperatures and fluidization velocities on sorbent performance, according to a Rotatable Central Composite Design (RCCD) model.

The RCCD 2^k model (with $k=2$ in our experimental design) investigated two factors at five coded levels: a central (with replicated central experiments used to estimate experimental error), factorial and axial points, employed to characterize the curvature of the response surface. The experimental data were fitted with a quadratic regression model using matrix regression analysis, and response surface methodology was employed to evaluate the interaction between variables and process performance. Finally, analysis of variance (ANOVA) was applied to assess the statistical

significance of the parameters investigated. The methodology is described more in detail elsewhere [10]. Table 1 shows the design with the total number of experiments [11].

The amount of CO₂ captured during each carbonation step was determined by integrating the outlet CO₂ concentration profile, monitored using a mobile NDIR analyzer, over time. The CO₂ capture capacity (ξ) was defined as the mass of CO₂ captured per unit mass of the initial sorbent, according to the following expression:

$$\xi = \frac{\int_0^t [W_{CO_2}^{in} - W_{CO_2}^{out}(t)] dt}{m_0} \quad (1)$$

where $W_{CO_2}^{in}$ and $W_{CO_2}^{out}(t)$ are the CO₂ inlet and outlet mass flow rates, respectively, as a function of time t .

Since the DIFB could not reproduce the high-velocity conditions of industrial-scale systems, comminution by impact fragmentation was studied at room temperature using a dedicated apparatus [8]. Fragmentation experiments were carried out at five impact velocities ranging from 10 to 45 m/s using 1.2 grams of the pre-processed sample previously subjected to CaL test, re-sieved into the initial particle size range of 0.4–0.6 mm. After impact, considering as “fragments” the impacted particles finer than 0.4 mm, the mass fraction of fragments f , defined as follows, can be obtained for each sample as a function of velocity:

$$f = \sum_{d_i < 40 \mu m} [x(d_i)] \quad (2)$$

where $x(d_i)$ is the mass fraction of particles that fall into a size range with an average diameter d_i .

The fragmentation data were fitted using a linear model in which the slope represents the fragmentation intensity as a function of impact velocity. This parameter was selected as the response variable in the RCCD analysis.

3. Results

Overall, it should be noted that severe fragmentation and elutriation were observed throughout the tests, causing filter clogging and substantial material losses, which significantly affected the experimental methodology. Despite these challenges, the RCCD experimental design provided consistent data and enabled evaluation of the effects of temperature (T) and fluidization velocity on CO₂ capture performance. The sorbent exhibited a typical CaL deactivation trend, with higher CO₂ capture during the first cycles followed by rapid decay and stabilization after approximately five cycles (Figure 1). However, the overall capture capacity was considerably lower than values reported in the literature for CaO-based (i.e., limestone) sorbents. Moreover, unlike dolomites, which generally show a smoother deactivation trend and higher long-term stability, the dolomite sorbent investigated in this work behaved more similarly to limestone, displaying a pronounced decay in capture performance. These discrepancies may be associated with differences in operating conditions and sorbent composition. Particularly, the higher silica content of the Brazilian dolomite investigated here, around 27%, may have

negatively affected both capture efficiency and mechanical resistance compared to the dolomite tested in the reference study by Coppola et al. [12], for which the SiO₂ content was 0.91%. Among the tested conditions, the best performance was obtained at low fluidization velocity (0.23 m/s) and 675 °C, where longer gas residence time enhanced gas–solid interaction and improved carbonation, while no carbonation occurred at T of 750 °C or above, as thermodynamic equilibrium shifted toward calcination under these conditions.

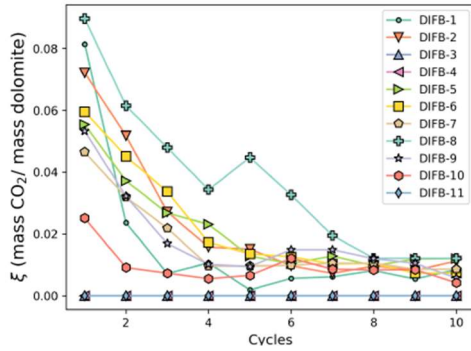


Figure 1. Specific CO₂ capture performance ζ (in g/g) as a function of the number of carbonation stages for DIFB tests.

In Figure 1, the tests numbered ‘1’ through ‘11’ in Table 1 are labeled ‘DIFB-1’ through ‘DIFB-11’. Test 11 was not conducted, but the capture capacity was assumed to be equal to 0 since the scheduled test was at the highest T considered (780 °C) and the experimental capture capacity for the test at 750 °C was already zero.

Response surface analysis revealed a saddle-shaped behavior, indicating the absence of a clear global optimum. Temperature was identified as the dominant parameter affecting process performance, whereas velocity showed a weaker statistical influence. Although the quadratic RCCD model captured the general trends, it could not accurately represent the sharp thermodynamic transition between carbonation and calcination at high temperatures. Response surface plot of ζ_{mean} experimental data by v and T is not reported here for the sake of brevity, while the values of ζ_{mean} can be found in Table 1 (where ζ_{mean} has been calculated as the average of ζ values referring to cycles from 6 to 10, i.e. when the sorbent capture capacity reaches a plateau).

The second-order polynomial used to model the response variable ζ_{mean} provided a moderate fit to the experimental data, with temperature emerging as the only statistically significant factor in the ANOVA analysis, suggesting that broader operating ranges or additional variables, such as fragmentation intensity, may be necessary to better describe and optimize the system. Impact tests to investigate particle comminution by fragmentation were designed with the label IPT. IPT-1 was performed on sorbent particles after having experienced 10 CaL cycles under DIFB-1 conditions, and so on up to IPT-10. The impact test-fitted results, with the fragmentation index (f) plotted as a linear function of impact velocity, are presented in Figure 2, being the

angular coefficient the response for the RCCD model applied. In Figure 3, the response surface plot is then reported.

Table 1. RCCD matrix of actual values and codification for two parameters, fluidization velocity (v) and carbonation temperature (T); and average CO₂ capture capacity (ζ_{mean}) for the tests in the DIFB system.

#	v (m/s)	T (°C)	x1	x2	ζ_{mean} ($\cdot 10^3$ g/g)
1	0.30	600	-1	-1	6.7
2	0.70	600	1	-1	9.2
3	0.30	750	-1	1	0.0
4	0.50	750	0	1	0.0
5	0.50	675	0	0	11.3
6	0.50	675	0	0	10.6
7	0.50	675	0	0	9.6
8	0.23	675	-1.41	0	17.7
9	0.78	675	1.41	0	11.6
10	0.50	570	0	-1.41	8.3
11	0.50	780	0	1.41	0.0

The figure highlights a region of low fragmentation occurring at T between 580–680 °C, which is the range where the experimental results give the higher capture capacities. When considering, in fact, the impact tests of Figure 2, the higher fragmentation was observed at the highest and lowest T considered, 750 °C (IPT-3, IPT-4) and 570 °C (IPT-10), where the capture capacities are essentially zero. In the range where the CO₂ capture occurs more significantly, with the formation of larger amount of in-bed fragment as well, presumably, the fragmentation index turns out to be the lowest, in particular at 675 °C, for the highest velocities considered of 0.5 and 0.78 m/s. When considering the fluidization velocity effect, the results show a reduction in the impact fragmentation tendency as the velocity increases. From the experimental impact tests, when considering the tests carried out at 600 °C, the curve of the test at the higher fluidization velocity, 0.7 m/s, such as IPT-2, is located in the low fragmentation indexes zone, whereas the IPT-1 test, at a velocity of 0.3 m/s, results in larger amount of fragments. This trend is also observed for the test at 675 °C, at the lowest velocity considered (0.23 m/s), which behaves differently from the tests at 0.5 and 0.78 m/s.

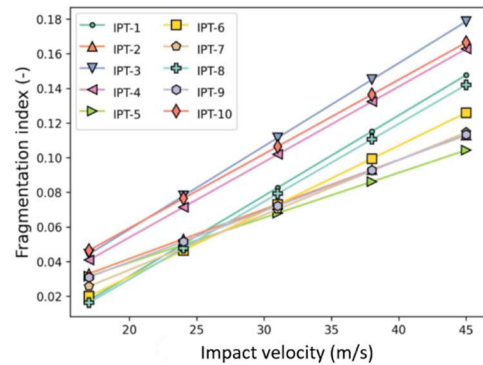


Figure 2. Linearly interpolated fragmentation index (f) curves as a function of impact velocity.

It is plausible that elevated fluidization velocities promoted the removal of fragile external layers by attrition or chipping, thereby exposing a mechanically more robust surface for the subsequent impact tests.

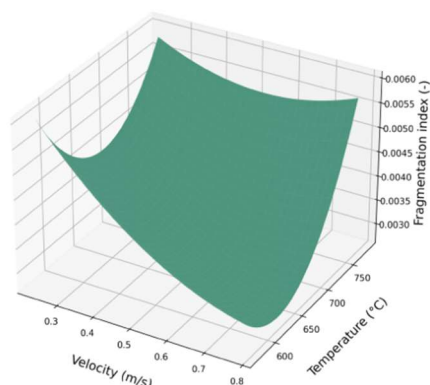


Figure 3. Response surface plot of fragmentation index (f) experimental data as a function of fluidization velocity and temperature.

4. Conclusions

This study evaluated a Brazilian dolomite as a sorbent for CO₂ capture in a CaL process using a bench-scale DIFB reactor under simulated natural gas exhaust conditions. The experimental campaign, designed through an RCCD model, enabled systematic assessment of the effects of carbonation temperature and fluidization velocity on sorbent performance and comminution by fragmentation behavior. Results showed that carbonation temperature is the dominant operating parameter governing CO₂ capture. The overall CO₂ uptake remained low compared to literature values for CaO-based materials, most of which, however, were obtained in experimental campaigns involving higher CO₂ concentrations. This reduced performance may also be attributed to thermal degradation, severe elutriation, and the high silica content of the dolomite, which likely weakened both chemical reactivity and mechanical stability. More in detail, the mean carbonation degree showed a strongly non-monotonic dependence on T , with a maximum around 675 °C and complete suppression above 750 °C, where the equilibrium of the exothermic CaO–CO₂ reaction is approached. The effect of the fluidization velocity v was non-linear and coupled with T : at the optimal temperature, lower v favoured conversion through the longer gas residence time, whereas at lower T higher v enhanced ξ through better mixing, suggesting a possible shift from kinetic and mass-transfer control to thermodynamic control as T increases. The optimum operating window is narrow and lies at moderate T combined with low v , with the highest measured conversion obtained at 0.23 m/s and 675 °C.

Impact tests revealed a non-trivial relationship between operating conditions and particle resistance, although it is necessary to emphasize that severe fragmentation and material losses significantly affected reactor operation. At intermediate temperatures (around 675 °C), associated to higher CO₂ capture capacities, and higher fluidization velocities, the extent of impact

fragmentation resulted to be reduced, suggesting a partial surface “conditioning” effect due to attrition of weak external layers. The most carbonated particles showed the lowest fragmentation, suggesting that a denser CaCO₃ layer mechanically stabilizes the sorbent. Secondary effects were also evident: a high v during carbonation enhanced in-bed attrition damage, while high T can degrade the microstructure, both raising particle fragility. The response surface analysis highlighted the limitations of a purely quadratic model in capturing the transition between chemical reactions regimes, suggesting that future optimization should consider other coupled performance variables, alongside classical parameters used to evaluate CO₂ capture.

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Rethinking breakage for mineral recovery

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Abstract. Many measures of breakage used in mineral processing are defined for conventional equipment and do not reflect the fundamentals of particle fracture or the purpose of the breakage. Simplistic single-point size indicators and laboratory breakage energy tests with low efficiency drive a backward-looking view of technology and risk.

Reassessing a target breakage size distribution related to mineral exposure and recovery routes, provides a new perspective on process efficiency. This enables redefinition of the ideal product size as a function of ore feed type and recovery processes, including staged recovery. The overall process efficiency can be assessed not only in terms of tons of metal produced but critically based on energy (including green energy), recovery, water use, and tailings production.

Utilising these fresh insights combined with the objectives of size reduction in mineral processing, has inspired a rethinking of the measures of breakage that can usefully be applied.

1. Introduction

Within mineral processing, the purpose of comminution is to expose minerals for separation from the gangue and other minerals, which themselves may be valuable or deleterious. Depending on the recovery process, the required form of exposure varies:

- Flotation: sufficient surface exposure for activation and bubble attachment.
- Leaching: access to the minerals on the surface or via cracks or porosity.
- Physical separation (e.g., gravity, electrostatic, or magnetic): sufficient volume fraction in a particle to differentiate from the barren particles.
- Sorting: detectable volume fraction within a particle.

Consequently, these have different breakage objectives. The common metric of product size to suit any process is the P80 value, a convenient single-point measure that can be quoted across projects. The cost and efficiency of different comminution process options to achieve this P80 may be used in trade-off studies to choose an optimal process over the life-of-mine. The problem is that this can be misleading, as different processes produce different size distributions and present quite different opportunities, or lack thereof, for staged upgrade of the minerals.

There is considerable value to updating the accepted simplistic practice of single-point size description, instead relating the product size to purpose.

2. Size distribution and recovery

The size distribution of comminuted product depends on the types of equipment used, as illustrated in Figure 1. Which shows product streams sampled along stages of a single comminution circuit, from run-of-mine (RoM) feed through stages of crushing and milling to the final cyclone overflow product. The product size distribution from a unit process is a function of the breakage modes, residence time, classifier, and method of operation.

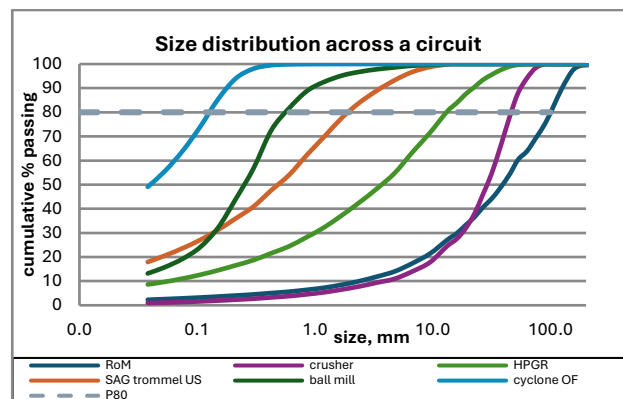


Figure 1. Different size distributions across a single circuit [9]

Infamously, ball milling was incorrectly considered to be more efficient than SAG milling as the operating work index was calculated to be lower based on the simple P80 values required by the Bond equation [5]. To address this, models compensating for the larger proportion of fines produced by the SAG mill, have been developed by investigators such as Morrell [8].

Comminution units are imperfect, so the products are sent to a classifier to direct particles to the next stage or recycle to the equipment. Classification is dependent on size, density and shape of particles. The higher density of mineralised particles results in a different size distribution of the mineralised to barren particles. Hence, the type of classifier and degree of recycle contribute to the liberation profile of the comminution product [6].

However, the attraction of a single-point comparison remains strong and still pervades the mining industry when developing target grind sizes, that are not related to the upstream process.

A brief overview of different recovery processes focussed on feed size distribution provides context for the purpose of ore preparation.

Flotation

Mineral recovery by flotation dominates many commodities in the minerals industry. Considering the

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typical form of a flotation recovery-by-size curve presented in Figure 2, it drops off below a fine size due to non-selectivity, and above a coarse size due to non-liberation and particle size effects.

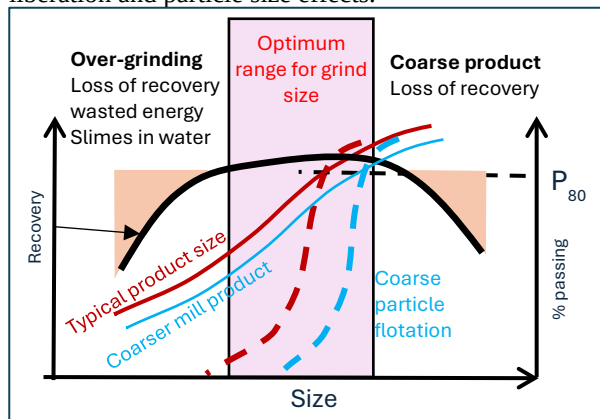


Figure 2. Recovery by size and feed size distributions

A typical product size distribution from a ball mill circuit is superimposed to illustrate that much of the product from the comminution circuit falls outside the optimum recovery size range. If a steeper size distribution can be produced with the same P80 as that of the ball mill circuit, shown by the dashed red line, more of the particles will fall within the optimum recovery range. For a coarse particle recovery system, the product can be coarsened further (blue dashed line) while still providing optimum recovery.

In a typical process specification, the two comminution processes with identical P80's would be considered identical in performance. However, the shape of the feed recovery size distribution has a significant impact on the recovery potential. Additionally, simplified energy calculations based on size P80 reduction relationships, may ignore the considerable energy reduction due to the steeper comminution product, where energy is not wasted on producing unwanted fines.

Coarse particle recovery offers the considerable advantage of reduced comminution energy, easily calculated by a coarser product P80. However, the ideal dashed blue line is not achieved in milling equipment. Instead, the coarser mill product (blue line) inexorably retains a high fraction of fines, as this is intrinsic to the SAG-ball milling and classification process.

Sorting

Particle-based sorting involves direct measurement of particle properties, such as by XRF, transmission X-ray, or colour. Gangue particles are ejected, based on a cut-off grade, thereby upgrading the feed to the final recovery process. Like any selection system, the process has inherent inefficiencies described by a probability distribution by size for a given ore. The detection method, data processing, and physical ejection (usually air jets), limit the system to processing a relatively narrow effective range of particle sizes. To enable efficient sorting, the feed has to be screened to a suitable mid-size.

Figure 3 illustrates the principle of sorting recovery for a system that is efficient in the 10-25 mm range, overlaid on measured product streams around a HPGR, SAG, crushing, and pebble crushing products.

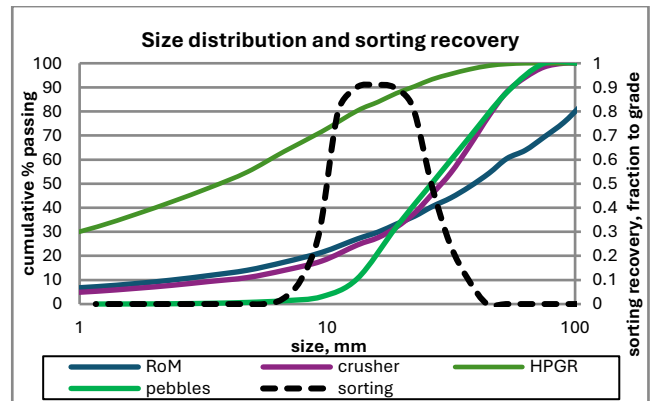


Figure 3. Overlap of sorting size range with product streams

All the streams have a limited fraction that can be sent to sorting:

- HPGR: 15%
- Crushed feed: 30%
- RoM feed: 20% (but expensive to screen)
- Pebble crusher: 50% x 20% of feed = 10%

As each of these conveyor streams is destined for a different part of the downstream process, this would entail multiple screening points, an expensive process. The underlying issue is that the feed is not conditioned to fall within the narrow size range required for efficient sorting.

Bulk ore sorting

Bulk sorting measures the average grade of a batch of rock. It is well suited to RoM feed on the main feed conveyor when ore properties are highly variable. Loss of grade is intrinsic to the approach, as decisions are made on parcels of ore. This is a low-cost sorting method, diverting rejected material out of the processing stream. The risk is that ores that show little spatial variability can lead to substantial losses of valuable material to the reject stream.

Heap leaching

Heap leaching allows recovery from low-grade feed streams that are not economic to process via the comminution and recovery circuit. Often this involves coarsely crushed ore which is stacked on the pad. Some sites partially screen or crush to better condition the size distribution for more consistent porosity and percolation of the lixiviant. Recovery is slow, typically over months, and can vary widely: often 50-70%, but significantly lower where permeability or mineral accessibility is poor. It is well understood that crushing, minimising fines, and careful distribution on the pad greatly enhance recovery, but at a substantial processing cost that often cannot be justified.

3. Shifting the paradigm

Having considered the link between particle size distribution and recovery, the potential inherent in designing the comminution process to enhance recovery can be considered.

Based on the liberation model of Hilden [7] fitted to a porphyry ore body, an upgrade curve has been compiled [3] as illustrated in Figure 4. This provides a smoothed mathematical description of the mass recovery for a range

of sizes for a target metal recovery, i.e. the ore upgrade or removal of mass. For this data, to recover 95% of the metal from the RoM ore, on average 80% of the mass would need to be recovered. For the material crushed to sub-1 mm, only 15% of the ore mass needs to be recovered to recover 95% of the metal. Clearly this will change according to ore type and process but can be fitted to testwork for particular ores and recovery processes.

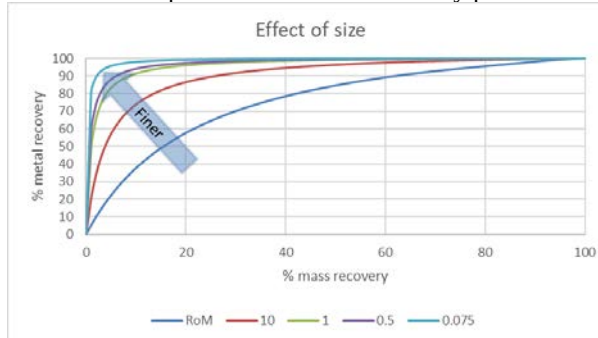


Figure 4. Recovery by mass for decreasing feed size [3]

Combining the energy usage figures with a metal recovery model, provides a method to calculate the overall relationship between energy used and total potential metal recovery. An analysis of the impact of removing 40% of the rock through a sorting or upgrade step at one of a number of size options is presented in Figure 5. All the values are relative to the standard process of milling the full feed to final size and the associated flotation recovery, both energy and recovery for the base case

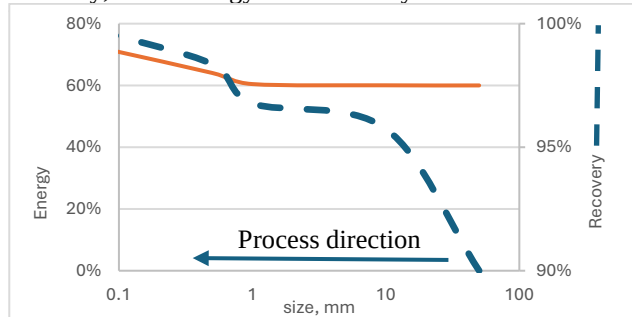


Figure 5. Relationship between metal recovery and energy usage for 40% mass removal at different sizes

If the upgrade is through coarse rejection ahead of comminution, then the energy consumption reduces to 60%, but with the penalty of recovery potential reducing to below 95% of current. The energy saved reduces as the 40% mass removal is conducted at finer sizes, with 70% energy usage at 0.1 mm upgrade size, but this provides a far superior 98% to 99% recovery. This shows there is a strong trade-off of recovery with upgrade size.

Figure 6 shows the outcome for progressive upgrade stages. Unlike Figure 5, the figures are cumulative to reflect progressive upgrade. This illustrates the advantage of removing a small amount of mass at multiple stages along processing, with 33% energy usage providing 96% potential recovery – representing a massive and economically viable saving in processing costs.

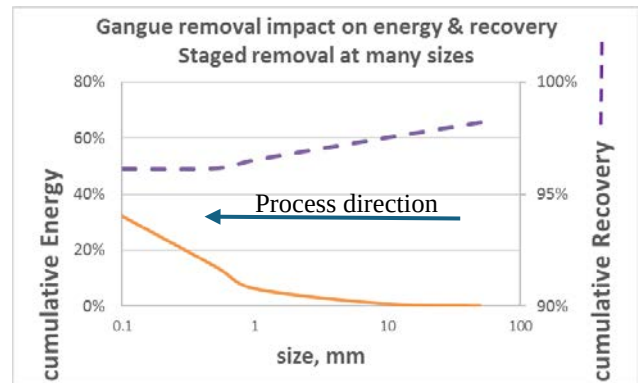


Figure 6. Cumulative recovery and energy usage for progressive upgrade

Progressive upgrading requires producing feed sizes suited to each stage of rejection or recovery, which renders the scenario in Figure 6 unachievable with conventional circuits.

4. Staged breakage

As seen in the size ranges in Figure 2 and Figure 3 for flotation and sorting, there is a strong driver to produce narrow feed size distributions to each stage of recovery or rejection. This does not favour conventional crushing-ball mill or SAG – pebble crush - ball mill (SABC) circuits. Additionally, most coarse waste rejection systems are dry processes. These factors suggest that comminution circuits should be redesigned for future process efficiencies. Stages of controlled breakage, that maximise appropriate material available in the next desired recovery/reject step, are required. This flies in the face of current approaches that embrace massive single-line processing with few stages of processing, a choice driven by capital and operating costs. To justify a change, it is necessary to fairly assess the energy and performance of lower-energy stages of breakage that are tuned to reduce the fraction of ore that requires final fine breakage.

An example of breakage data from ideal breakage product versus standard SAG milling of a porphyry ore is presented in Figure 7. Ideal breakage uses only 20% to 25% of the measured SABC circuit energy while placing most of the product in the optimal recovery zone.

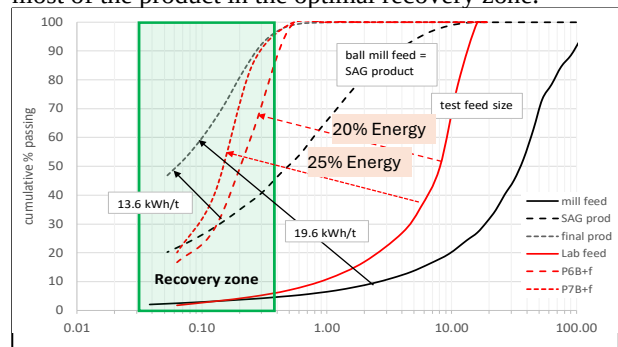


Figure 7. Ideal versus SAG milled product and energy

This provides an indication of the size of the of ideal breakage in terms of energy, with the recovery not quantified but expected to improve based on the ideal distribution of the feed for the flotation process.

5. Implications for energy and recovery

Modelling of energy use with such dramatically different outcomes, as shown in Figure 7, requires a valid approach outside methods employed in standard process design. The size specific energy (SSE) metric [4] is based on the energy to produce a fine size fraction, usually the final product size. A laboratory test has been developed to measure ideal minimum practical energy [1] quantified by SSE. This was applied to measured process data to quantify equipment efficiencies and thus allow laboratory characterisation data to be applied to real values for industrial equipment [2]. A more realistic energy use can then be applied to each chosen stage of breakage.

Figure 8 illustrates the impact on energy consumption of a hypothetical progressive upgrade scenario.

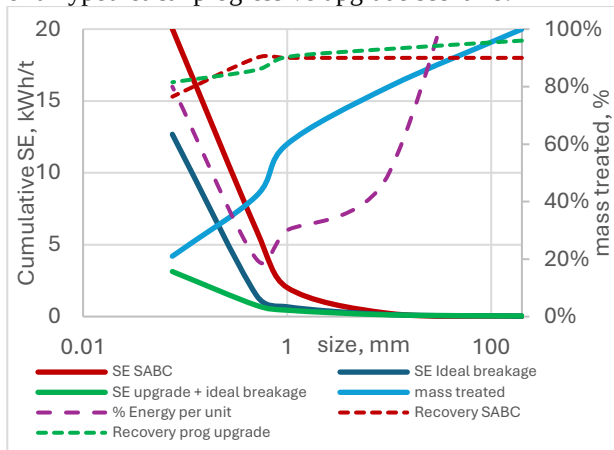


Figure 8. Progressive upgrade and energy-efficient equipment

The SABC energy trend represents business as usual with a total SE of 20 kWh/t. The energy per unit is the reduction in energy use for each stage of comminution. Doubling the energy used in blasting provides a better top-size control to the crushing stages. Applying realistic energies for ideal breakage methods across three stages enables substantial energy reduction in the size range of 10 to 0.5 mm. Below that down to 75 μ m, a stirred mill is used with 20% energy reduction compared to ball milling.

When staged upgrade is then added to the process, the total energy consumption plummets. The progressive mass treated shows how much is being cumulatively removed per stage, landing on only 20% being subjected to fine grinding. The impact provides a paradigm shift of dropping from 20 to 3.1 kWh/t. This corresponds in a matching reduction in the required processing capacity as the feed mass reduces.

Recovery simulations are based on typical site recovery figures for the SABC circuit. For the progressive upgrade circuit, recoveries are based on the calculated recovery potentials of Figure 4. There are recovery losses at every upgrade stage. This has been minimised by maximising the feed size into the optimum liberation and recovery zone for each stage of recovery. The emphasis is on gangue rejection, so a lower recovery grade can be prioritised to maximise recovery at each stage. This is important to minimise the progressive losses of staged upgrade. The final recovery should be higher than for conventional mining and flotation. The envisaged stages of recovery for this scenario can be:

1. RoM: closer spacing, variable distribution of explosives, timing for controlled heave to minimise dilution - reducing losses and increasing processing grade at the mining face.
2. 10 – 30 mm: ore sorting
3. 1– 2 mm: physical separation such as gravity, electromagnetic, or electrostatic.
4. 0.4 – 0.7 mm: coarse particle flotation.
5. -0.1mm: standard flotation on regrind product

Opportunities exist for recovery of the rejected coarse particles in the 1-30 mm range by directing them to a heap leach. This allows scavenging of low grade and of mis-directed higher-grade particles. Recovery will be high in a well-constructed pad built from this controlled feed size.

The benefits include a massive reduction in energy consumption; slashing the size or removing the need for tailings dams; increased water recovery reducing fresh water needs to potentially a quarter of current.

The opportunities outlined here can have a significant impact on the design and economic assessment of future circuits. To make this a reality, the mining industry will need to advance their mindset on conducting breakage for mineral recovery, underpinned by meaningful measures of energy and efficiency.

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Breakage Behavior of a Layer of Corn Kernels under Uniaxial Compression

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Abstract. Corn breakage is principal phenomenon in corn industrial processing. In the roller mills, or flakers material is loaded continuously controlled by the working gap. While several studies showed the different aspects of single kernel compression of corn kernels, a little is known about the differences in breakage between a single particle and a layer of corn kernels breakage as influenced by size and moisture content. The aim of the study was to assess the effect of moisture content and kernel thickness on breakage probability in cereal grain layer under monotonic compression, and to interpret the observed variability using energy-based modelling. The results showed that mechanical response of the layer is dependent on the moisture content and the thickness of kernels compressed. At lower moisture content, kernels tend to be more brittle and characterized by the higher breakage rates at lower energy levels. At higher moisture content, kernels have higher ability to dissipate energy through deformation, which cause the lower breakage rates at similar energy levels. These findings may support future analysis of grain processing operations where local variability of kernel affects the energy requirements.

1. Introduction

Mechanical damage, fracture and breakage occur frequently during handling and processing affecting cereal grains quality and market grade, processing efficiency including energy efficiency [1]. The importance of studying the breakage phenomenon for cereals can be considered twofold. The adequate and reliable model of particle breakage based on the stochastic distribution of primary fracture characteristic (force, deformation, strength, energy) will improve fracture predictions and decrease in mechanical damage and kernels losses as the operating conditions and mechanical design of machines can be optimized through usage of those models. In other hand, energy-based probabilistic models are highly relevant for size reduction operations to maximize their efficiency and lowering the energy demand, so operating in the minimum energy mode. Literature evidence shows that particle breakage is still far from the minimum-energy mode, as only less than 10% of the input energy is effectively utilised for particle disintegration [2,3]. This shows that breakage modelling remains highly relevant in food and particulate process engineering.

Till date research on cereals fracture has been focused on characterization of single kernel behavior during compression and impact demonstrating that material resistance to load and fracture mode depend on the grain

type, internal structure, moisture content and loading direction [1]. The existing empirical and energy-based probabilistic models relied on single particle fracture gives good consistency with experimental results, but require time consuming single-particle fracture characterization for high number of particles [4]. On the other hand, the complex particle behaviour in industrial applications, where groups of particles formed in dense streams, beds or monolayer, is not captured in the single particle compression.

In corn processing, roller mills, crushers, flakers, and other devices that utilize a working gap between compressing elements are frequently used [5]. In this type of equipment material is loaded as a layer of known thickness controlled by the working gap, not a single grain. This is a specific case of loading differing between single particle and particle beds. As shown in the study of Campos et al [6], the particle breakage mode differs between the single-particle and particle bed composed of different number of layers due to different stress and energy distribution within particles. While several studies showed the different aspects of particle beds behaviour for corn kernels [7–9] and other particulates [6,10,11], a little is known about the differences between single particle and monolayer breakage and interpretation of breakage probabilities obtained through these two approaches for corn kernels. Moreover, for cereals the influence of

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particle size and moisture content in the transition from single particle breakage to monolayer remains unexplored.

In this study the above gaps are addressed by exploring the breakage probability of single-particle and monolayer of 40 non-contacting corn kernels of different size ranges and moisture content subjected to monotonic compression. This creates a physically meaningful intermediate configuration, in which global loading can be related to partial fracture of a grain population rather than to failure of one isolated kernel or to collective breakage in a confined bed. This in turn could lay the foundation to go from time consuming single particle-characterization of breakage probability to monolayer tests.

The aim of the study was to assess the effect of moisture content and layer thickness on breakage probability in cereal grain layers under monotonic compression, and to interpret the observed variability using energy-based modelling.

2. Materials and methods

2.1. Materials

The study was conducted on the example of yellow dent corn with properties presented in Table 1 and four moisture content (MC) levels: 8.20%, 11.95%, 16.00%, 20.02%, as described elsewhere [12].

Table 1. Properties of corn kernels used in the study [12]

Property	value
Starch content	61.33% $\pm$ 0.76%
Protein content	6.63% $\pm$ 0.40%
Oil content	3.33% $\pm$ 0.15%
True density	1.220 $\pm$ 0.002 g/cm ³

2.2. Single particle static compression

To initially evaluate the mechanical properties of kernels, such as engineering failure stress, failure force, failure deformation, failure energy, monotonic compression test on single particle was conducted on universal testing machine (MTS systems) with 1 kN load cell. Kernels were placed in the natural rest position – germ down – and compressed one by one [13]. Loading of kernel was stopped when the primary fracture occurred visible as a sharp drop in force on the force-deformation profile.

2.3. Monolayer compression

This experiment was inspired by earlier work of Schönert [11] and Campos et al. [6] and involved the compression of grains in a monolayer, as previously described in [14]. Grains from samples with given moisture contents were divided into 4 narrow size fractions: 3.95-4.05 mm, 4.50-4.60 mm, 5.05-5.15 mm and 5.60-5.70 mm. Monolayers were created from 40 grains from each size range and moisture content level. The number of kernels in the layer resulted from the size of the compression piston and the arrangement of grains so that they did not overlap and formed a single layer (Figure 1).

The response of grains in the layer was analysed for defined load values from the range of 4500 N to 9000N. Loads were applied until the target load was reached, and

then the samples were unloaded. Force and displacement were recorded during the tests. The response to compressive loads of the particle layer was analysed using an energy-based approach involving strain energy analysis. The maximum energy during loading was calculated according to [12,15,16], assuming it is equal to the area under the force-deformation curve:

$$E = \int_0^{u_{max}} F(u) du \quad (1)$$



Figure 1. The arrangement of kernels in the particle layer

According to [11], the energy absorbed by the layer was defined as the portion of energy indicated by hysteresis loop, i.e., the portion of the surface area contained between the loading and unloading curves. This energy, related to the mass of the grains, was treated as the specific energy absorbed in the layer.

Additionally, grain damage in the layer was analyzed using a probabilistic approach. The fraction of damaged grains – the one for which primary fracture occurred – relative to the total number of grains in the layer was used as the determinant [17]:

$$P_b = \frac{n_b}{40} \quad (2)$$

This value was then related to the loading conditions, moisture content, grain layer thickness as well as the specific absorbed energy.

3. Results and discussion

The results of mechanical characterization of kernels during compression showed that the moisture content modify the mechanical response of material. In the Figure 2 the dependence between the specific fracture energy and deformation of individual corn kernels at different moisture content under monotonic compression was presented. It is apparent that the fracture energy increases nonlinearly, or rather, in a power-law manner. According to the Hertzian contact model [18], the force in the elastic region of contact increases approximately as $F \propto \delta^{3/2}$, which, when integrated with respect to displacement, leads to a proportionality of the strain energy to the displacement as $E \propto \delta^{5/2}$. The power-law exponents deviates from the ideal value of 5/2 due to complex contact topology for non-spherical particles, presence of friction, irreversible phenomena such as: microcrack initiation, plastic deformation, and crack propagation leading to energy dissipation. Noticeably, with increasing moisture content, grain deformability increases at comparable energy levels, and generally, moist grains

required more energy to initiate a crack, which is consistent with studies of other researchers [16,19,20].

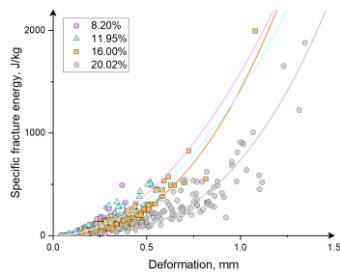


Figure 2. Specific fracture energy at single particle compression plotted against deformation. Solid lines represent fitted power curves

The results presented in Figures 3 and 4 confirm the effect of moisture content on grain breakage in the monolayer. The force-deformation curves (Figure 3) clearly indicate that at first phase of compression individual grains initially contact the compression piston, then deformation of particles in layer occurs with a rapid increase in force. The local changes in slope and irregularities are associated with load redistribution within the layer, while drops in force indicates sequential fracture of individual grains. It is noticeable that with increasing moisture content, the grain layer's deformability increases. Absorbed energy also increases, as indicated by larger hysteresis loops for grains with higher moisture content (20.02%). Increasing moisture content reduces the proportion of broken grains at a given energy level (Figure 4), which is consistent with the relationships observed for individual grains [12].

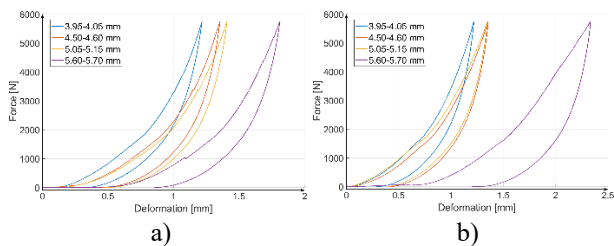


Figure 3. Force-deformation profiles of compression of monolayer of corn kernels with a) 8.20% MC, b) 20.02% MC

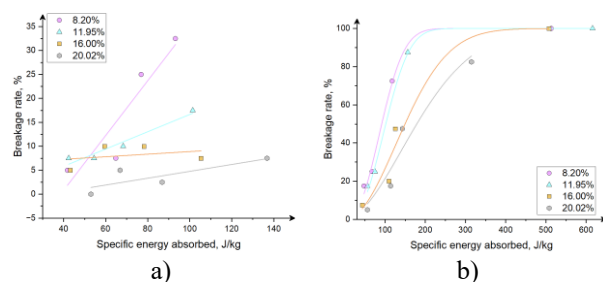


Figure 4. The dependence of breakage rate on specific energy absorbed in monolayer of corn kernels of different moisture content from narrow size range a) 3.95-4.05 mm b) 5.60-5.70 mm

Analysis of the curves in Figure 3 indicates that as the thickness of the grains forming the layer increased, the energy absorbed in the system (the hysteresis loop increased) increased when the same compressive force was applied. This is also confirmed by the results presented in Figure 4, where the increase in absorbed energy was accompanied by an increase in breakage rate. It can therefore be seen that a monolayer composed of thicker grains has poorer load-bearing capacity. This can be explained by the lower strength exhibited by larger grains [21,22] due to their tendency to have a higher likelihood of structural flaws (voids, cracks, or non-uniformities) compared to smaller ones [4]. When compressed, these act as areas where stress concentrates, leading to greater plastic deformation and a higher probability of breakage. Analysis of the change in breakage rate (Figure 4) also indicates that grains in the layer do not break simultaneously, but gradually, as individual energy thresholds are exceeded for each grain. This phenomenon results from the distribution of individual grain strengths and the uneven distribution of stresses in the monolayer [6,11].

4. Conclusions

In this study the effect of moisture content and particle thickness on breakage of corn kernels forming the monolayer was investigated.

The results showed that mechanical response of the layer is dependent on the moisture content and the thickness of kernels compressed. At lower moisture content kernels tend to be more brittle and characterized by the higher breakage rates at lower energy levels. At higher moisture content, kernels have higher ability to dissipate energy through deformation, which cause the lower breakage rates at similar energy levels.

These findings may support future analysis of grain damage in processing and handling operations where local variability of kernel properties and loading condition is important.

Acknowledgement

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In Situ Characterization of Deformation and Fracture Mechanisms in Bi-Component Agglomerates Using μ CT-Based Digital Volume Correlation and Spatial Statistics

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Abstract. Understanding breakage mechanisms of agglomerates is essential for optimizing comminution and handling processes in particulate systems. In this work, the composition-dependent mechanical behavior of cylindrical agglomerates composed of glass and polystyrene was investigated using a combined ex situ and in situ approach. Ex situ compression tests were conducted to determine fracture force, stiffness, and primary fracture energy. The results reveal a non-monotonic, M-shaped dependence of fracture energy on composition, highlighting the complex interplay between particle properties and binder-mediated interactions. To resolve internal deformation mechanisms, in situ μ CT experiments were combined with digital volume correlation (DVC), enabling full-field measurement of three-dimensional displacement and strain fields. Spatial strain localization was quantified using Local Indicators of Spatial Association (LISA) based on k-nearest-neighbor statistics. By combining volumetric and deviatoric strain clustering, distinct deformation regimes such as dilatational shear, pure shear, and compaction were identified. The presented methodology establishes a direct link between microscale deformation and macroscopic breakage behavior, providing new insights into agglomerate comminution processes.

1. Introduction

The breakage behavior of agglomerates plays a central role in comminution processes such as milling, granulation, and powder handling. Mechanical stability is governed by complex interactions between particle properties, binder bridges, and microstructural arrangement [1-4]. Conventional testing approaches provide macroscopic quantities such as strength or fracture energy but do not resolve the underlying deformation mechanisms. In contrast, X-ray computed tomography (μ CT) combined with digital volume correlation (DVC) enables full-field measurement of internal deformation, offering direct access to strain localization and damage evolution [5].

However, the interpretation of heterogeneous strain fields remains challenging. Spatial statistical approaches such as Local Indicators of Spatial Association (LISA) provide a quantitative framework to identify and classify localized deformation patterns [9,10]. The objective of this work is to link macroscopic breakage behavior with microscale deformation mechanisms in bi-component agglomerates by combining mechanical testing, DVC, and spatial statistical analysis.

2. Materials and Methods

2.1. Agglomerate Preparation

Cylindrical agglomerates were produced from binary mixtures of glass (GL) and polystyrene (PS) particles with varying volumetric compositions (PS100, PS75GL25, PS50GL50, PS25GL75, GL100), enabling a systematic investigation. The primary particles had a characteristic size of approximately 200 μ m, allowing particle-resolved imaging in subsequent in situ μ CT experiments (cf. Fig.1). Agglomeration was performed using a liquid

binder solution (7 w.% hydroxypropylmethylcellulose aqueous solution), with the absolute binder mass kept constant at approximately 15 mg after drying to ensure comparability between compositions and enable the analysis of composition-dependent breakage behavior.

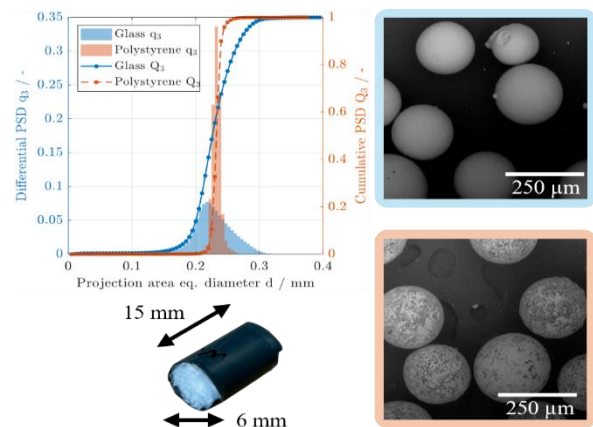


Figure 1. Particle size distribution (left) and SEM images (right) of the used primary particles with representation of an agglomerate in poly lactic acid (PLA) cover.

Particles were homogeneously mixed, followed by binder addition and compaction into cylindrical casings ($d = 6$ mm, $L = 15$ mm). After drying, solid binder bridges formed and the final binder mass was determined gravimetrically, similar to our previous work [1]. This procedure yields reproducible agglomerates with consistent binder content, enabling the isolated study of composition-dependent breakage behavior.

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2.2. In Situ μ CT and Digital Volume Correlation

In situ compression experiments were performed using X-ray computed tomography (μ CT) to capture the internal structure of the agglomerates at successive load steps (cf. Fig.2). A reference scan was acquired at an initial load level (5 N), followed by additional scans at increasing load increments (10 N). This enabled the tracking of internal deformation throughout the loading process (cf. Fig.3).

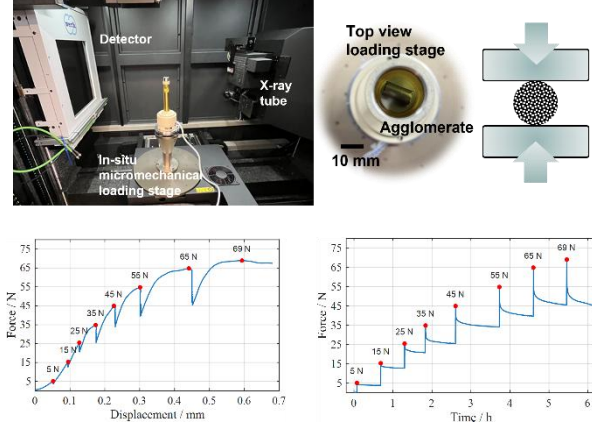


Figure 2. Experimental setup for the μ CT in situ compression tests (top) and representative force displacement and force time curves of the stepwise compression procedure.

Three-dimensional displacement fields were computed using digital volume correlation (DVC), which is based on the correlation of grayscale patterns between the reference image $I_0(x)$ and the deformed image $I_1(x)$ [5-8].

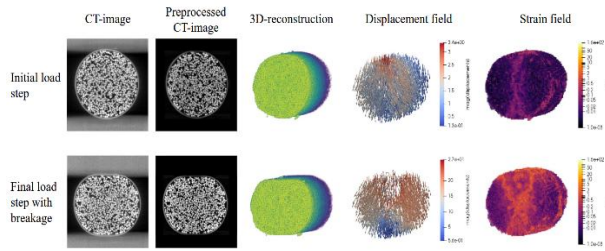


Figure 3. Representation of the workflow from grayscale image stack to the three dimensional displacement and strain fields.

An initial estimate of the displacement field $u(x)$ was obtained by maximizing the cross-correlation function. The displacement field was subsequently refined using an iterative optimization approach by minimizing the gray-value residual.

$$C\Phi(u) = \sum [I_0(x) - I_1(x + u(x))]^2 \quad (1)$$

Based on the resulting displacement field, the deformation gradient tensor F was computed as

$$F = I + \nabla u \quad (2)$$

from which the Green-Lagrange strain tensor E was derived

$$E = \frac{1}{2} (F^T F - I). \quad (3)$$

From E , both volumetric ϵ_{vol} and deviatoric ϵ_{dev} strain measures were calculated, forming the basis for the subsequent analysis of deformation and breakage mechanisms.

2.3. Spatial Statistical Analysis

To quantify spatial strain localization, a Local Indicators of Spatial Association (LISA) approach was applied to the normalized strain fields. The analysis is based on Local Moran's I_i , which evaluates the degree of spatial autocorrelation of a variable relative to its neighborhood [10].

$$I_i = z_i \sum_j w_{ij} z_j \quad (4)$$

Here, z_i denotes the standardized strain value at location i , and w_{ij} represents binary spatial weights defining the local neighborhood based on a k -nearest-neighbor (kNN) approach. In this study, the neighborhood includes the reference point and its ten nearest neighbors ($k = 10 + 1$). Positive values of I_i indicate spatial clustering of similar strain magnitudes (high-high or low-low), while negative values identify spatial outliers. Based on this classification, regions of strain localization can be distinguished from mechanically inactive zones.

This statistical framework enables a quantitative and spatially resolved identification of deformation patterns and provides the basis for linking strain localization to underlying breakage mechanisms [7,10].

3. Results and Discussion

The in situ μ CT-DVC analysis provides direct insight into the internal deformation processes governing breakage in agglomerates under compressive loading. The computed displacement and strain fields reveal highly heterogeneous deformation patterns that evolve significantly with increasing load (cf. Fig.3). Spatial statistical analysis based on Local Indicators of Spatial Association (LISA) enables a systematic quantification of strain localization within the agglomerates. The LISA plot matrices of the deviatoric (Fig.5) and volumetric (Fig.4) strain fields show pronounced composition-dependent differences in both the onset and spatial organization of high-strain clusters.

For mixed compositions (PS75GL25 and PS25GL75), high-high (HH) clusters emerge at comparatively low load levels and progressively localize into distinct regions that evolve into well-defined fracture planes. This behavior indicates a gradual accumulation of damage driven by localized deformation. In contrast, GL100 and PS50GL50 agglomerates exhibit a delayed formation of HH clusters, which remain more spatially diffuse until shortly before failure. This suggests a more abrupt

breakage behavior with limited precursory strain localization (cf. Fig.4 and 5).

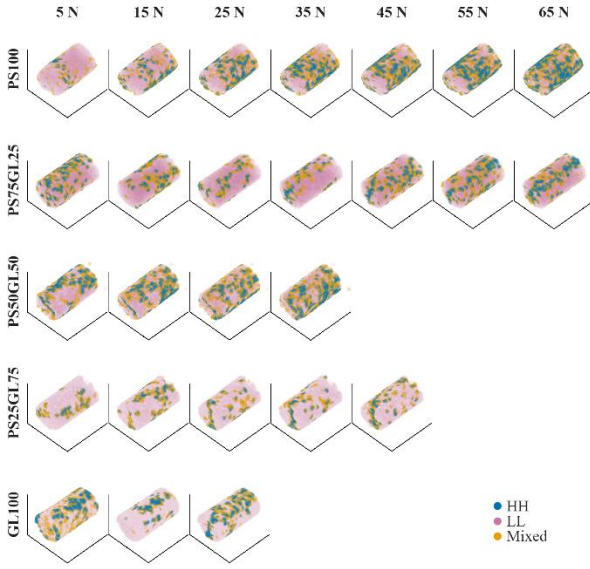


Figure 4. Local Indicators of Spatial Association (LISA) of the normalized volumetric response ϵ_{vol} for all compositions and load steps.

A fundamentally different deformation pattern is observed for PS100 agglomerates. Here, HH clusters appear early but remain spatially distributed throughout the entire volume, indicating a more homogeneous deformation process rather than localized fracture.

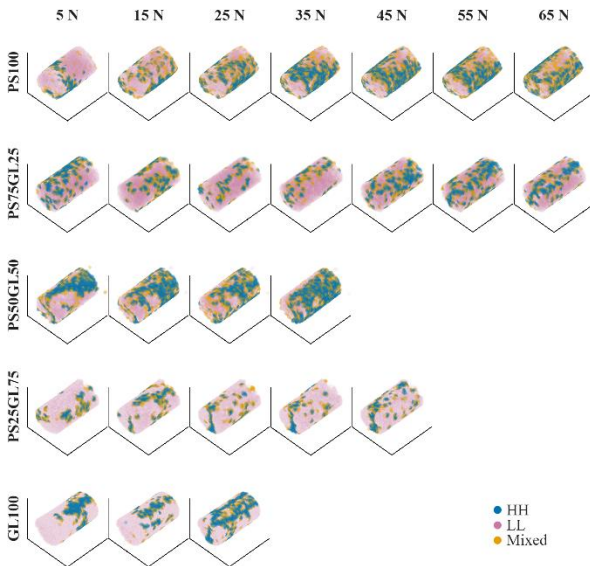


Figure 5. Local Indicators of Spatial Association (LISA) of the normalized deviatoric response ϵ_{dev} for all compositions and load steps .

This behavior reflects the more compliant nature of the polymer-based system and suggests a transition from fracture-dominated to deformation-dominated response. While the LISA plot matrices provide spatial insight into strain localization, the stacked bar and line plots enable a

quantitative assessment of cluster evolution. Across compositions, the fraction of HH clusters increases with load, reflecting the progressive development of localized deformation. However, the rate and extent of this increase differ significantly, highlighting the influence of composition on damage evolution (cf. Fig.4 and 5).

The combined evaluation of volumetric and deviatoric strain fields allows the identification of distinct deformation mechanisms. Regions characterized by high deviatoric strain and positive volumetric strain are associated with dilatational shear, indicating particle separation and crack initiation (cf. Fig.6). In contrast, negative volumetric strain indicates compaction-driven deformation, corresponding to local densification and load redistribution.

The breakage mechanism plot matrix reveals that mixed agglomerates exhibit a strong contribution of dilatational shear localized along emerging fracture planes, whereas glass-rich systems show a higher contribution of compaction prior to failure. Polystyrene-dominated systems are characterized by distributed deformation with less pronounced localization.

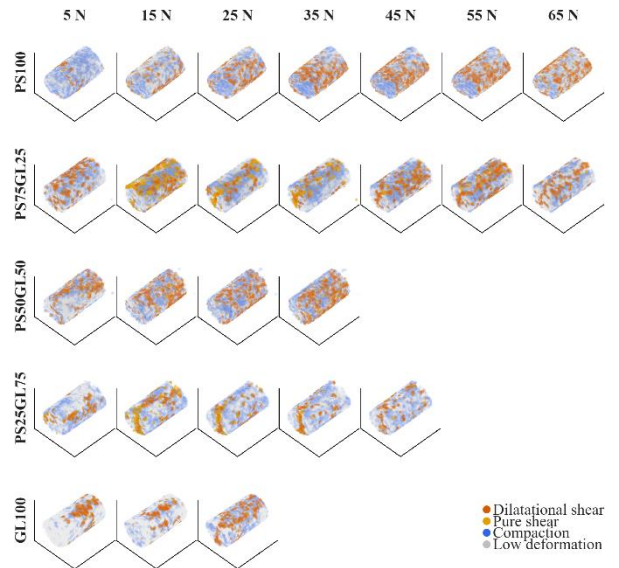


Figure 6. Spatial plot matrix of strain-based breakage mechanisms across all agglomerate compositions and load steps.

Overall, the results demonstrate that breakage in agglomerates is governed by the spatial organization and interaction of different deformation mechanisms rather than by a single dominant failure mode. The combination of in situ μ CT, DVC, and spatial statistical analysis provides a powerful framework to resolve these mechanisms and to establish a direct link between micro-scale deformation processes and macroscopic breakage behavior in particulate systems.

4. Conclusions

This study demonstrates that the combination of in situ μ CT, digital volume correlation, and spatial statistical analysis provides significant potential to enhance the information content obtained from tomographic

experiments and to resolve breakage processes at the microscale. By enabling the spatially resolved quantification of internal deformation, the approach allows detailed insights into the mechanisms governing fracture initiation and propagation within agglomerates.

The application of LISA to volumetric and deviatoric strain fields enables a quantitative identification of strain localization and its progression under load. By combining both strain measures, distinct deformation regimes such as dilatational shear, compaction, and distributed deformation can be identified and linked directly to breakage processes.

The results reveal strong composition-dependent differences in deformation behavior. Mixed agglomerates exhibit early strain localization and the formation of well-defined fracture planes, whereas glass-rich systems show delayed localization and more brittle behavior. Polystyrene-dominated systems, in contrast, are characterized by more homogeneous deformation.

Overall, the presented approach provides a mechanistic understanding of agglomerate breakage by linking microscale deformation patterns to macroscopic failure behavior. This framework offers significant potential for improving predictive models and optimizing comminution processes in particulate systems.

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From breakage initiation to fragmentation: structure-dependent breakage and modeling of multicomponent synthetic lithium slags

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Abstract. Synthetic lithium slags containing engineered artificial minerals (EnAMs) are a promising secondary resource for critical raw materials, yet their efficient processing requires a better understanding of breakage in multicomponent systems. This study investigates the structure-dependent breakage behavior of synthetic lithium slags from breakage initiation to fragmentation and subsequent modeling. Breakage initiation was characterized by single-particle microcompression using a nanoindenter, whereas fragmentation above the initial threshold was studied with a rigidly mounted two-roller breakage tester. The results show that the specific energy required for breakage initiation increases with decreasing particle size, with a markedly stronger rise below a characteristic critical size. Fragmentation experiments further reveal a transition from particle- or cluster-dominated breakage to a regime increasingly controlled by the internal material structure. At the same time, decreasing product particle size enhances phase liberation. A quantitative comparison of different slag systems shows clear differences in fragmentation sensitivity, indicating that both composition and microstructure govern the breakage response. Based on these findings, material-specific parameters were calibrated using a Tavares–King-type threshold model and $T_{10}-t_b$ relationships, providing the basis for DEM simulation and future process optimization of multicomponent synthetic slags.

1. Motivation and relevance of breakage characterization in multicomponent lithium slags

Metallurgical slags are still frequently treated as residues or low-value by-products, although they contain relevant amounts of critical elements and therefore represent a considerable resource potential. Within the context of the circular economy, this is particularly true for lithium-bearing slags from pyro- and hydrometallurgical process routes, in which lithium and other valuable elements can be concentrated in artificially engineered mineral phases. In the priority program SPP 2315 “Engineered Artificial Minerals (EnAM)”, this concept is pursued by deliberately adjusting composition and solidification conditions in order to generate structures that are favorable for downstream separation processes [1, 2].

For the mechanical processing of such multicomponent systems, breakage behavior is a key issue. Breakage initiation determines the stress or energy level required for crack formation, whereas subsequent fragmentation controls whether the resulting products are broad, fines-rich, or preferentially generated along structural weak zones. This coupling between structure, crack initiation, and fragment formation is crucial for the later liberation of EnAM phases and, thus, for the efficiency of subsequent separation steps [3, 4].

The topic is relevant from both a scientific and an economic perspective. Concepts established for single-component materials can only be transferred to heterogeneous, polycrystalline, and locally varying slag systems to a limited extent. At the same time, comminution remains one of the most energy-intensive process steps in mineral processing. A material-specific understanding of breakage behavior is therefore essential to avoid overgrinding, to identify suitable stressing mechanisms, and to design energy-efficient liberation routes [5, 6].

Against this background, the present work applies an integrated approach to the structure- and size-dependent characterization of synthetic lithium slags. The objective is to describe breakage on two coupled levels: first, the initiation of breakage by microcompression, and second, the fragmentation behavior above the initial breakage threshold using a rigidly mounted two-roller breakage tester. Based on both experimental levels, material-specific parameters are derived and transferred to DEM simulations.

2. Title Materials and experimental approach

2.1. Synthetic lithium slag systems with controlled composition and solidification conditions

The study focuses on the synthetic lithium slag systems S1, S5, and S6 produced within SPP 2315 in cooperation

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with partners from process metallurgy and mineral processing.



Figure 1. Schematic representation of the synthetic production route and the investigated slag systems

The designations S1, S5, and S6 refer to different slag batches that differ in both composition and solidification conditions. S1 was produced with a cooling rate of 50 °C/h, whereas S5 and S6 were solidified at 25 °C/h. In addition, the contents of Li₂O, MnO, Al₂O₃, SiO₂, CaO, and MgO vary between the systems. This allows both structural and compositional effects on breakage behavior to be analyzed. The detailed compositions are given in Table 1 [3, 2].

Table 1. Chemical composition of the investigated synthetic slag systems in wt. %

Slag	Li ₂ O	MnO	Al ₂ O ₃	SiO ₂	CaO	MgO
S1	8,5	0,5	41	27	23	-
S5	8,5	10	45	12	12	5
S6	8,5	10	45	17	17	-

2.2. Characterization of breakage initiation by single-particle microcompression

To characterize breakage initiation, single-particle microcompression tests were carried out using a nanoindenter. Individual particles of defined size classes were locally loaded between flat punch and substrate while force–displacement curves were recorded. The breakage point was identified by the first significant drop in the counterforce. The specific fracture energy was obtained by integrating the force–displacement curve up to that point. At least 40 particles were analyzed for each size class [3, 4].

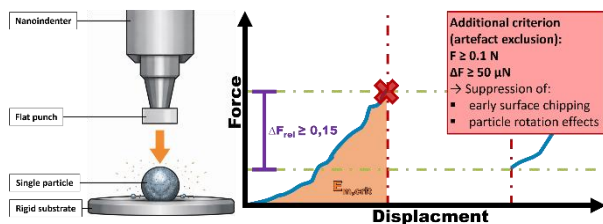


Figure 2. Schematic representation of the microcompression experiment and determination of the first breakage event from the force–displacement curve

2.3. Fragmentation experiments and modeling approach



Figure 3. Photograph of the two-roller breakage tester

To characterize breakage behavior above the initial threshold, fragmentation experiments were performed with a rigidly mounted two-roller breakage tester. The slags were classified into narrow size fractions and fed as a monolayer particle stream through a defined roll gap. The gap width was varied relative to the mean feed particle size x50 of the respective class. Based on the measured torque, the specific energy input was calculated. The comminuted products were then collected and analyzed with respect to their particle size distributions [5, 7, 4].

The experimental results were transferred into a modeling framework that explicitly distinguishes between breakage initiation and subsequent fragmentation. For the first breakage event, the size-dependent breakage threshold was described using a Tavares–King-type approach. The fragmentation behavior in the two-roller breakage tester was represented by T10–tn modeling. First, T10 was fitted as a function of the specific energy input; subsequently, the remaining tn values and thus the complete fragment size distribution were calculated using the incomplete beta function. On this basis, DEM-relevant breakage parameters were calibrated [6, 5].

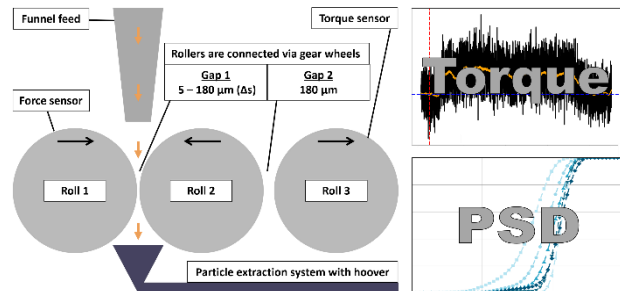


Figure 4. Schematic representation of the rigidly mounted two-roller breakage tester including particle feeding, sensor positions, and the evaluation of torque and product particle size distribution (PSD)

3. Results and discussion

3.1. Breakage initiation

The microcompression tests show that the specific energy required to initiate breakage increases with decreasing particle size. However, this trend is not equally pronounced over the entire size range. For coarser particles, the increase is rather weak, whereas below a characteristic critical particle size the required breakage energy rises more strongly. This indicates that different structural length scales become effective depending on particle size and that breakage initiation cannot be described by a single size-dependent relationship over the full investigated range [3, 6].

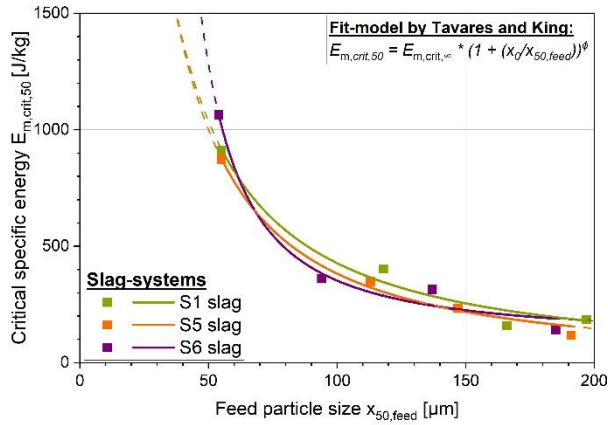


Figure 5. Critical specific breakage energy as a function of feed particle size for slag systems S1, S5, and S6 determined from microcompression experiments; solid lines represent the fitted Tavares–King model.

When comparing the three synthetic lithium slags S1, S5, and S6, only moderate differences are observed for breakage initiation. The deviations are visible, but not pronounced enough to identify a single structural or compositional parameter as the dominant factor. Nevertheless, a clear tendency can be recognized: the force required during pre-crushing increased from S1 to S5 to S6, and the same order is reflected in the microcompression results. Thus, S6 shows the highest resistance against breakage initiation, whereas S1 fails at the lowest stress or energy level. Overall, however, breakage initiation alone allows only a limited differentiation between these structurally related slag systems.

3.2. Fragmentation behavior

The fragmentation results reveal a characteristic behavior for multicomponent systems. At low specific energy inputs, fragmentation still depends strongly on the initial feed particle size, meaning that coarser feed particles initially produce coarser product particles. With increasing specific energy input, however, the trends of the different feed size classes converge until the resulting product sizes become nearly identical. This convergence indicates that above a certain energy level the breakage process is no longer governed primarily by the external particle size, but increasingly by the internal material structure.

A more detailed analysis suggests that fragmentation initially proceeds on the scale of the whole particle or of larger cluster agglomerates, whereas at higher energy input a smaller characteristic structural scale becomes dominant. The point at which the different trends converge lies slightly below the average grain size of the respective slag system. This supports the interpretation that fragmentation changes in this region from particle- or cluster-controlled behavior to grain-size-controlled behavior [3, 1]

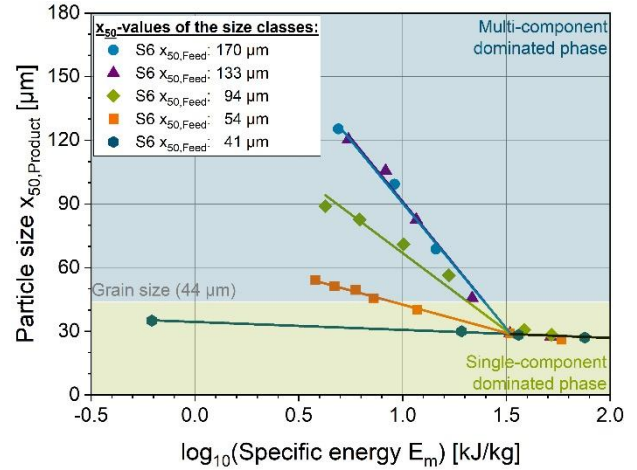


Figure 6. Product particle size $x_{50,product}$ as a function of specific energy input for different feed particle sizes, illustrating the transition from particle- or cluster-controlled breakage to a structure-controlled fragmentation regime

In addition, decreasing product particle size leads to a higher yield of fully liberated particles. Continued fragmentation therefore improves the liberation of the valuable phases and enhances their subsequent separability.

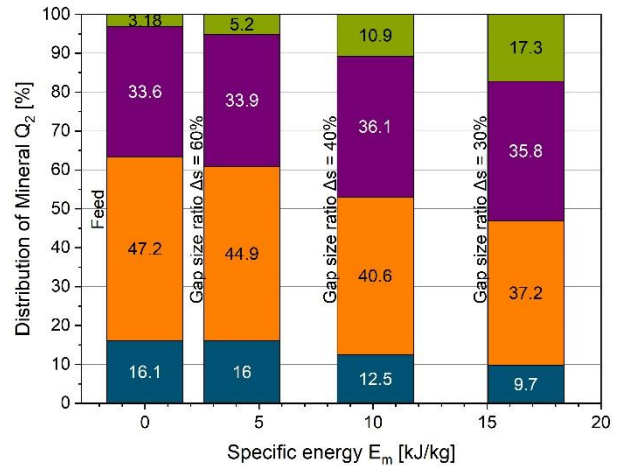


Figure 7. Mineral distribution as a function of specific energy input, showing an increasing fraction of liberated particles with progressing fragmentation.

For a quantitative comparison between the slag systems, the sensitivity of product size to increasing specific energy input was expressed by the slope k of the fragmentation curves. Clear differences are observed between the slag systems. S1 shows the lowest slopes over the investigated size range and therefore fragments comparatively moderately once the breakage threshold is exceeded. S5 lies mostly above S1 and thus exhibits stronger fragmentation. S6 differs most clearly from the other two systems, especially at larger feed particle sizes, and shows the highest sensitivity to additional energy input after breakage initiation. Accordingly, S6 exhibits the most pronounced fragmentation behavior.

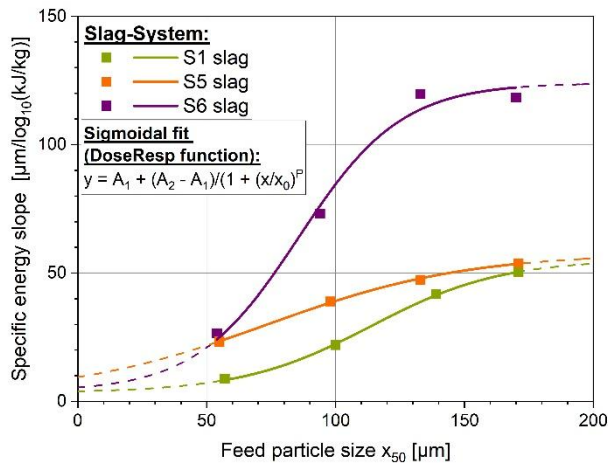


Figure 8. Slope k of the fragmentation curves as a function of feed particle size for slag systems S1, S5, and S6, describing the sensitivity of product size to increasing specific energy input.

These differences point to both structural and compositional influences. The comparison between S5 and S6 is particularly informative because both slags were produced at the same cooling rate and are therefore structurally more comparable than S1. Since S5 and S6 nevertheless differ significantly in their fragmentation response, chemical composition must have a substantial influence in addition to structure. Conversely, the comparison with S1 indicates that solidification conditions and the resulting microstructure also play an important role. Overall, the fragmentation behavior cannot be explained by a single parameter, but must be understood as the result of interacting factors such as composition, grain size, cluster structure, and probably also grain shape and orientation [3, 4].

3.3. Transfer to breakage modeling

The experimentally derived parameters form the basis for DEM simulations of the corresponding test setups. In the current state, polyhedral elastic particles with the original feed size distribution are used. Breakage is implemented by a Tavares-based breakage model, while fragment generation is described through the calibrated T_{10-t_n} relationships. This results in a consistent modeling framework that enables synthetic lithium slags to be described, compared, and, in the long term, optimized by simulation [3, 4].

4. Conclusions

The study shows that the breakage behavior of synthetic lithium slags cannot be described solely by chemical composition or by a simple particle-size dependence. Instead, it is governed by the interaction of particle size, grain size, cluster size, and local phase arrangement. Breakage initiation and the subsequent fragmentation process follow different, but coupled, mechanisms. While breakage initiation is strongly controlled by structural weak points, the resulting fragment size distribution is additionally governed by the active structural domain during comminution.

From a methodological point of view, the combination of nanoindenter-based microcompression and a two-roller

breakage tester provides a suitable route to systematically characterize both levels of the breakage process. The subsequent modeling based on a Tavares–King-type threshold description together with T_{10-t_n} relationships and the incomplete beta function establishes a robust basis for parameterized DEM simulations. At the same time, the results demonstrate that a direct structural comparison of complex slags remains challenging, because these systems are too heterogeneous to be represented by a single universal breakage function. Nevertheless, the present approach enables a material-specific characterization and therefore provides a basis for transferring the methodology to other multicomponent systems [3, 1, 5].

Acknowledgement

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Size Reduction, Classification, Spheronization, and Recycling of Electrode Active Raw and Recycling Materials

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Abstract. The rapidly growing demand for lithium ion batteries increases the need for efficient and sustainable processing of battery materials along the entire value chain. Across both first life material production and battery recycling, size reduction, classification, and spheronization represent key process steps governing material performance and process efficiency.

This contribution presents three exemplary applications illustrating the relevance of these unit operations:

- (i) grinding, classification, and spheronization of natural and synthetic graphite for anode active materials
- (ii) fine grinding and classification of lithium carbonate as a cathode precursor, and
- (iii) classification of black mass to recover anode graphite and subsequent respheronization for battery recycling applications.

Advanced NEUMAN & ESSER impact mill and classifier technologies (ICX, ICS, and DCX) are applied to address the specific process requirements of each application, enabling high energy efficiency, narrow particle size distributions, and controlled particle morphology. The presented approaches enhance material performance in first life batteries and enable the production of high quality secondary raw materials, supporting a circular “battery to battery” value chain.

1. Introduction

The accelerated transition toward renewable energy and electromobility has dramatically increased global demand for batteries. While lithium is often perceived as the key element, the graphite content in a single lithium-ion cell is typically 10–15 times higher than the lithium content, making graphite processing a central challenge in battery manufacturing. High-performance anodes require high purity, precise particle size, and particularly spherical morphology to ensure defined specified values for surface area, flake formation, and tap density as well as long cycle life.

Alongside first-life battery material production, the end-of-life treatment of batteries is becoming increasingly strategic. In addition to tightening EU recycling regulations, black mass recycling provides significant potential for recovering graphite and critical raw materials such as cobalt, enabling substantial CO₂ reductions and facilitating a closed-loop “battery-to-battery” value chain.

2. Grinding, Classification, and Spheronization of Graphite as Anode Active Material

The overall development goal for the NEUMAN & ESSER (NEA) spheronization system was to increase both yield and throughput in comparison to conventional plants, and to offer a system that can easily be adapted to different final product requirements and offers an easy scale-up. The resulting NEA system for the spheronization comprises merely two units. The size reduction, hereinafter referred to as micronization, occurs in the NEA ICX (Impact Classifier Mill eXtra) with an internal dynamic air classifier. The actual spheronization is conducted downstream of the NEA ICX in a NEA ICS (Impact Classifier Spheronization). Both machine types are available in various sizes offering a suitable plant size for any required output capacity.

Superfine comminution in the NEA ICX (Figure 1) requires increased grinding intensity. Therefore, the grinding zone geometry was designed accordingly. The size of the final product is determined by the intensity as well as the frequency of the mechanical stress during the grinding process. These factors are both strongly influenced by the fluid dynamics in the mill [1] [2] [3].

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The same applies to the development of the NEA ICS for spheronization. Grinding intensity must be adjusted carefully to ensure shaping within as few internal circulations as possible, without overstressing the product.

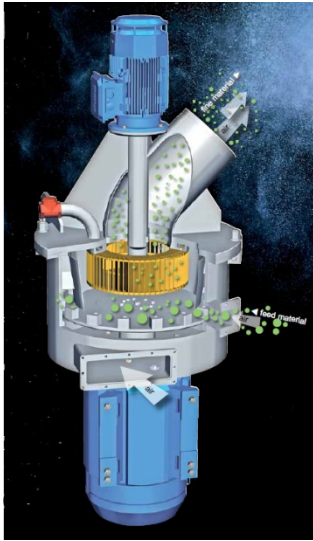


Figure 1: Impact Classifier Mill Extra (ICX)

The routing of the particles from the grinding zone towards the classifier wheel is of the same importance: It is crucial that the ground material is distributed homogenously across the classifier wheel flow cross-section.

For good classification results, both the radial and tangential velocity component of the process gas have to correspond to the desired cut condition at the outer circumference of the classifier wheel. The classification efficiency strongly depends on the inflow conditions of the dynamic classifier wheel [4] [5] [6] [7] [8]. The guide ring design takes this requirement into account. Furthermore, the classifier wheel was designed to enable superfine cuts. The design principle of both the classifier wheel and the guide ring correspond to the design of the NEA Deflector Classifier Extra (DCX, see Figure 2) [9], and the NEA Guide Ring Classifier (GRC) [10].

Production lines include the classifier NEA DCX. With additional classification steps in the production line, both residual dust as well as final product can be separated from the particle stream to avoid overloading the comminution and spheronization apparatuses, and overstressing of the product. This leads to an increase in final product yield.

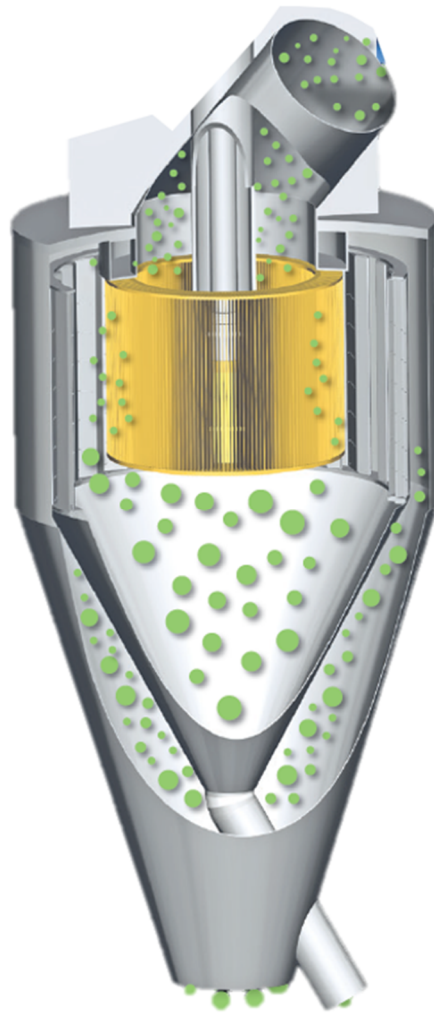


Figure 2: Deflector Classifier eXtra (DCX)

The presentation will show grinding and spheronizing results of the NEA spheronization system, which has been tested extensively in the NEA test center and successfully put into commercial operation. Key parameters determining the final product quality are particle shape (e.g., determined by flow cytometry), tap density, particle size distribution (PSD), specific surface area (SSA), combined with high yield and throughput. All of those can be adjusted by applying appropriate settings of the process parameters.

Spheronized product with a d_{50} between 5 μm and 20 μm and tap densities $> 1 \text{ g/cm}^3$ can be produced reliably at high yields.

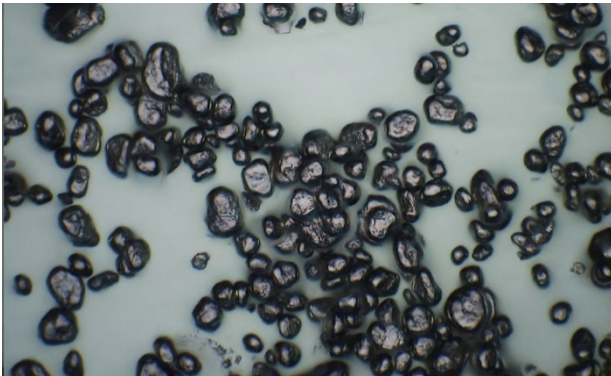


Figure 3: Shaped natural Graphite

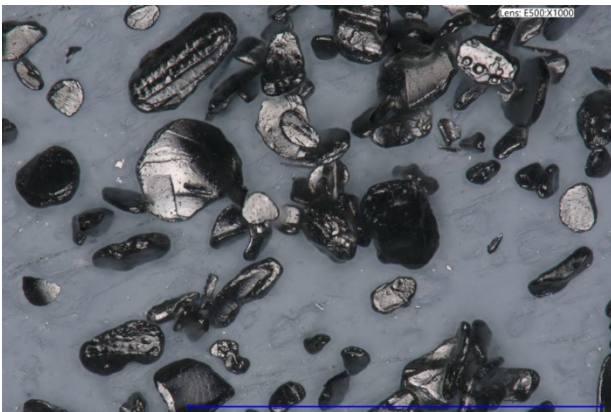


Figure 4: Synthetic graphite precursor; green/calcined coke

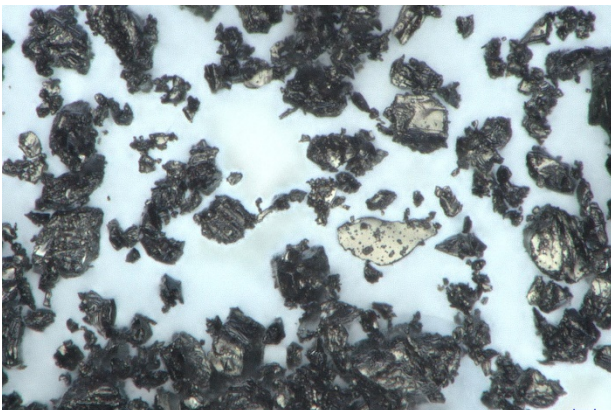


Figure 5: Hard carbons from biomass, suitable for Na-Ion battery

3. Grinding and Classification of Lithium Carbonate as Cathode Precursor

Lithium carbonate (Li_2CO_3) is a critical precursor for cathode active materials, particularly NMC, NCA, and LFP chemistries. Its fineness, PSD, and purity directly affect downstream processes such as calcination, solid-state reactions, and slurry rheology.

Lithium carbonate processing imposes several challenges:

- Agglomeration tendency: Li_2CO_3 often forms soft agglomerates, requiring controlled, low-stress grinding.
- Heat sensitivity: Excessive process temperature promotes caking and alters moisture levels.
- Ultra-fine PSD: Typical required top cuts are $d_{98} < 10\text{--}20 \mu\text{m}$, depending on cathode chemistry.
- Stable classification: Narrow PSD improves reactivity and homogeneity during cathode precursor synthesis.

The NEA ICX is also suited for lithium carbonate micronization. Its grinding zone can be configured for softer, brittle materials, minimizing excessive fines formation. Controlled rotor speed and classifier settings ensure:

- uniform breakage of soft agglomerates
- minimal generation of $< 1 \mu\text{m}$ dust
- stable product temperature ($< 70\text{--}80^\circ\text{C}$)

The NEA Classifier provides high-efficiency top cuts critical for cathode precursor performance.

The presentation will show grinding and classifying results on a small production size impact classifier mill NEA ICX at a $d_{50} < 5 \mu\text{m}$, and will provide an outlook to the processing of lithium carbonate on the largest available NEA ICX1600 with a grinding chamber diameter of 1600 mm!

4. Classifying Black Mass to Recover Graphite and Respheronization of Recovered Anode Material

Recycling black mass—generated from mechanical battery shredding—plays a central role in the sustainable battery industry. While most attention focuses on lithium, nickel, cobalt, and manganese, high-purity graphite is also recoverable and constitutes a major mass fraction.

The recycling of graphite imposes several challenges:

- contaminated with cathode particles, separators, carbon black, and metallic debris
- partially degraded and may have irregular morphology
- mixed across wide PSD ranges (d50 from 5 μm to >100 μm)

Effective and efficient separation requires a robust air-classification strategy.

The NEA Classifier provides

- fine separation between graphite (low density) and active cathode particles (higher density)
- narrowing of PSD for downstream processing
- reduction of heavy impurities (Cu, Al, Fe)

Through controlled air-classification, a refined graphite fraction can be isolated with higher purity, enabling reuse. Recovered graphite typically exhibits flake-like or crushed morphology. To reinstate its usability in battery anodes, the particles are rounded via the ICS spheronizer. This process yields recycled spherical graphite with:

- improved tap density
- reduced specific surface area
- restored electrochemical performance comparable to primary graphite

The presentation will show results from successful tests of classifying and respheronizations test of recovered black mass from recycled batteries.

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Thermochemical Storage of Solar Energy via Fluidised Bed Calcium Looping – Relationship Between Sorbent Properties and Process Performances under Variable Operating Conditions

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Abstract. Thermochemical storage of solar energy via fluidised bed calcium looping is emerging as a promising technology. In this work, the combined effect of carbonation and calcination temperatures on sorbent deactivation and energy storage in a directly irradiated fluidised bed reactor was assessed. Experiments were carried out over 10 calcination–carbonation cycles. Results show that increasing calcination temperature accelerates sorbent deactivation, whereas carbonation temperature plays a minor role. A larger temperature difference between calcination and carbonation enhances particle size reduction due to thermal and mechanical stresses. A compensation effect between sorbent reactivity and the process temperature gradient on energy storage density was observed. At higher cycle numbers, maximum energy storage density was achieved at $T_{carb} = 600^\circ\text{C}$ and $T_{calc} = 800^\circ\text{C}$, identifying these conditions as optimal for material performance. In terms of particle comminution, it emerges as one of the key phenomena governing the long-term evolution of the bed inventory in solar-driven calcium looping for thermochemical energy storage, with potential implications on fluid-dynamic stability, elutriation, and the effective sorbent residence time.

1. Introduction and aim of the work

Anthropogenic CO₂ emissions represent the primary driver of global climate change: in 2025, they reached approximately 38.4 Gt, with atmospheric CO₂ concentration of about 427 ppm [1]. In this context, the rapid implementation of decarbonisation strategies, including CO₂ capture, is essential to limit rising emissions. Calcium Looping (CaL) is a promising post-combustion CO₂ capture technology (currently, at TRL 6–7 on average) that can be integrated into combustion and gasification plants [2]. CaL consists of the cyclic carbonation and calcination of CaCO₃, typically carried out in two interconnected Fluidised Bed (FB) reactors [3]. During carbonation, CO₂-rich flue gas reacts with CaO at 600–700°C to form CaCO₃. The solid is transferred to a second reactor and calcined at 800–900°C, releasing concentrated CO₂ flue gas and regenerating the CaO sorbent [4]. Calcination is an endothermic process requiring high temperatures which can be directly supplied by Concentrated Solar Power (CSP) systems,

thus enhancing the process sustainability and environmental relevance. CaL-CSP systems have been widely studied for ThermoChemical Energy Storage (TCES) due to their high reaction heat and low-cost sorbent material [5]. The main drawback of CaL is the sorbent particles deactivation over cycles due to sintering and pore plugging, which reduce CO₂ capture and energy storage performance [6]. This depends on material impurities, CO₂ partial pressure, temperatures of carbonation (T_{carb}) and calcination (T_{calc}), and particle comminution. In this work, the reactivity of the sorbent is evaluated in a FB reactor coupled with a concentrated solar radiation simulator [7]. The effect of T_{carb} and T_{calc} on material performance is investigated, with emphasis on the role of comminution of sorbent particles.

2. Experimental campaign

2.1. Materials

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The FB inventory consisted of inert sand and reactive sorbent. Silica sand was used as inert material (particle density: 2600 kg/m³; size: 850–1000 μm). A natural Italian limestone (98.5%_{wt} CaCO₃) was used as sorbent (particle density: 2400 kg/m³; size: 420–590 μm), allowing easy separation from sand after each test.

2.2. Experimental conditions

Figure 1 depicts the experimental set-up adopted for CaL tests [6,7]. It consists of three sections: bubbling fluidized bed, wind-box and conical freeboard, which is closed by a ceramic glass optical window. Concentrated solar radiation is simulated by three short-arch Xe-lamps (4 kW_{el} each) coupled with elliptical reflectors. An electric heating system – comprising a gas preheater and radiant heaters – is used during non-solar operation.

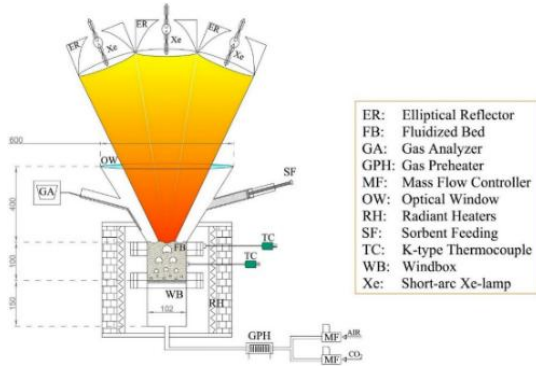


Figure 1. Layout of the concentrated solar FB reactor.

The experimental campaign investigated carbonation and calcination at 600°C, 650°C, 700°C, and 800°C, 850°C, 900°C, respectively, for ten reaction cycles (N). Carbonation was performed with CO₂ concentration in the inlet gas of 10%_v; while calcination was carried out using air as the fluidising gas. The fluidisation velocity was set at 0.6 m/s for all conditions. Carbonated particles recovered after cycles $N = 1, 4, 7$, and 10 were sieved into size fractions of 300–420, 200–300, and 100–200 μm to determine the Particle Size Distribution (PSD). Calcined particles from cycles 0 and 8 were collected for N₂ porosimetry analyses. The data were processed to evaluate the specific surface area, total pore volume, and pore size distribution.

2.3. Data analysis

The collected carbonated samples (after a given cycle N) were analysed to determine the carbonation degree following the procedure described in Di Lauro et al. [6]. After heating the sample (once FB-carbonated for N cycles) at 950°C in a muffle furnace, the carbonation degree $\bar{X}_{Ca}(N)$ was calculated using Eq. (1) as the ratio between the moles of CO₂ released (i.e., moles of CaCO₃ formed upon carbonation) and the total moles of CaO:

$$\bar{X}_{Ca}(N) = \frac{(m_b^N - m_a^N) M_{CaO}}{m_a^N x_{CaO} M_{CO_2}} \quad (1)$$

where m_b^N and m_a^N stand for the sample mass before and after heating in the muffle furnace, respectively; x_{CaO} is

the CaO mass fraction in the parent sorbent; M_{CaO} and M_{CO_2} are the molar mass of CaO and CO₂, respectively. The energy storage density (E_{SD}) [MJ/m³] at cycle N was calculated using Eq. (2), where $\Delta_r H$ is the reaction heat (standard value: 178 kJ/mol) at the corresponding carbonation temperature, ρ_{bulk} is the bulk density of limestone (1385 kg/m³) and x_{CaCO_3} is the mass fraction of CaCO₃ in the feedstock limestone, while $\bar{C}_p$ is an average value for the specific heat capacity of CaCO₃ (1 kJ/(kg °C)), and M_{CaCO_3} is the molar mass of calcium carbonate. Finally, in Eq. (2), $\bar{X}_{Ca,N}^{av}$ is the carbonation degree averaged up to the considered reaction cycle N (Eq. (3)).

$$E_{SD}(N) = \Delta_r H \bar{X}_{Ca,N}^{av} \frac{\rho_{bulk} x_{CaCO_3}}{M_{CaCO_3}} + \rho_{bulk} \bar{C}_p (T_{calc} - T_{carb}) \quad (2)$$

$$\bar{X}_{Ca,N}^{av} = \frac{\sum_{N=1}^N \bar{X}_{Ca}(N)}{N} \quad (3)$$

3. Results and related discussion

Figure 2 reports the effect of calcination and carbonation temperatures on the sorbent carbonation degree, whose trend is decreasing along N due to the progressive particle deactivation by thermal sintering.

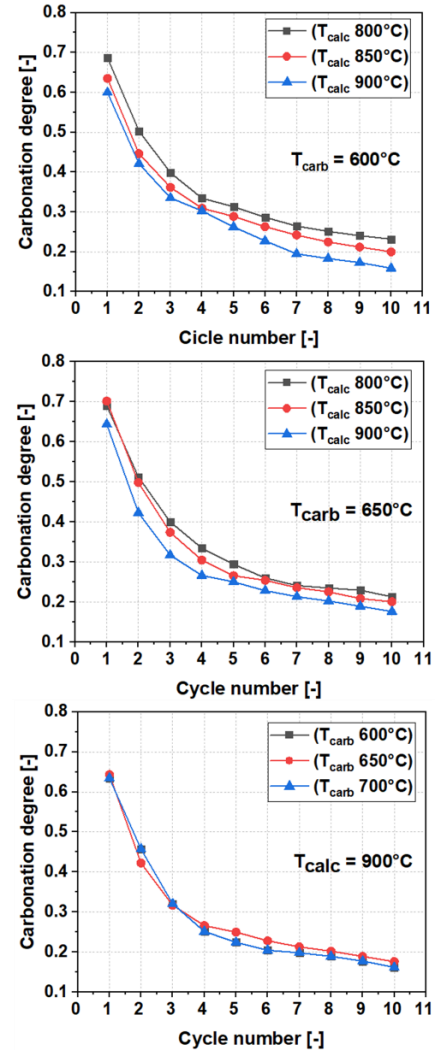


Figure 2. Evolution of carbonation degree (Eq. (1)) upon iterated CaL cycles for different T_{carb} and T_{calc} .

$\bar{X}_{Ca}$ drops markedly during the first five cycles, followed by a more gradual decrease thereafter. For example, at $T_{calc} = 800^\circ\text{C}$ and $T_{carb} = 600^\circ\text{C}$, it decreases from 0.69 ($N = 1$) to 0.31 ($N = 5$) and approaches 0.23 for $N = 10$. This can be ascribed to the agglomeration of CaO grains, to form a rigid and interconnected structure, further protected by an outer CaCO_3 layer, which limits further sintering as N increases on and on. However, agglomeration inevitably reduces porosity and specific surface area, enhancing CaO deactivation. These effects intensify with increasing T_{calc} , while rising T_{carb} has a marginal role.

The porosimetry analysis and specific surface area of the tests conducted at fixed T_{carb} (650°C) and T_{calc} of 800°C and 900°C are shown in Figure 3 and Table 1.

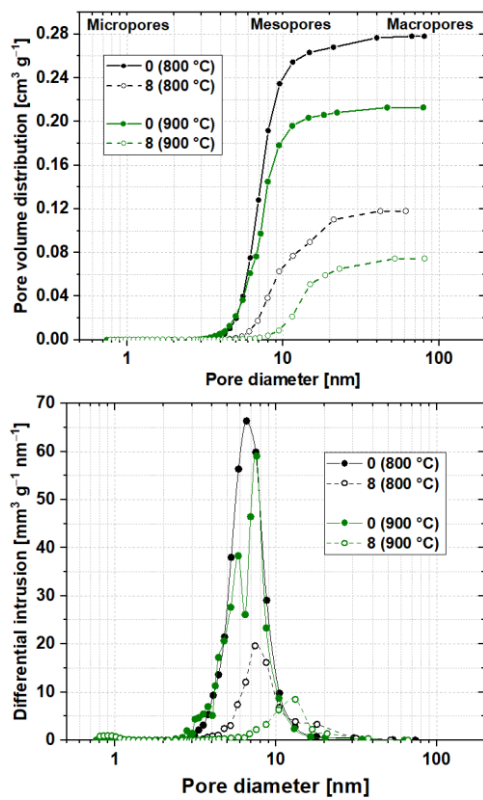


Figure 3. Cumulative specific pore volume (up) and differential intrusion curves (down) vs. pore diameter. Data refer to samples at different cycle numbers and calcination temperatures (keeping $T_{carb} = 650^\circ\text{C}$).

For each process condition, the specific surface area and total porosity after the eighth calcination are significantly lower than those after the initial calcination (labelled as $N = 0$). As T_{calc} increases, the samples show a relevant reduction in both specific surface area and total porosity. Furthermore, differential intrusion data reveal that higher calcination temperatures promote pore coalescence, leading to particle sintering. Specifically, increasing T_{calc} from 800°C to 900°C shifts the pore size distribution peak from ~ 7.5 nm to ~ 15 nm, an effect more pronounced after the eighth calcination. These results strengthen the view of loss in reactive porosity when calcination temperature (or reaction cycle) increases.

Table 1. Porosimetry data of samples in Figure 2.

$T_{calc} - N$	Specific surface	Total pore
	[m ² /g]	volume [cm ³ /g]
800°C – 0	21.9	0.27
800°C – 8	6.8	0.11
900°C – 0	18.6	0.20
900°C – 8	3.7	0.07

Now the results concerning particle comminution analysis will be presented. It is highlighted that, starting from a parent limestone size range of $420\text{--}590$ μm , particle fragmentation predominantly occurs within the $300\text{--}420$ μm fraction. Figure 3 reports the average mass fraction of particles in this range and the mean Sauter diameter, as a function of N and the temperature difference ΔT (i.e., $T_{calc} - T_{carb}$).

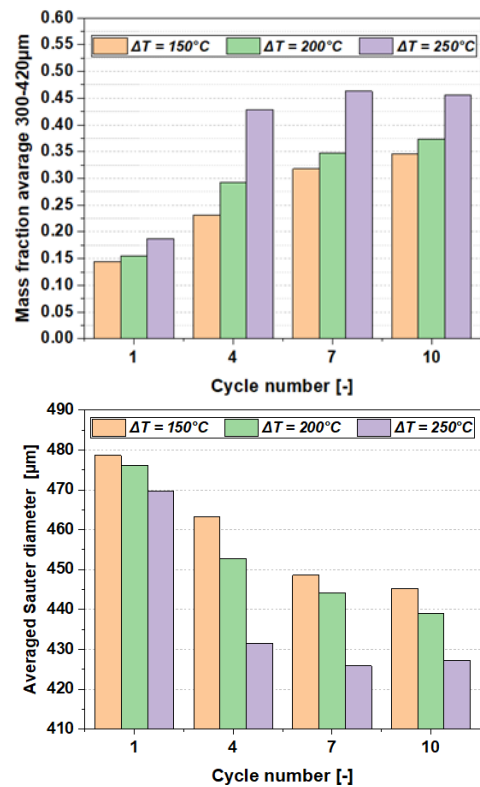


Figure 4. Mass fraction of $300\text{--}420$ μm particles (up), and averaged Sauter diameter for the whole PSD (down), for samples collected upon iterated cycles of calcination/carbonation; data parametric in the temperature difference between carbonation and calcination.

As N increases, the $300\text{--}420$ μm mass fraction rises, while the average Sauter diameter decreases for all the investigated conditions. Fragmentation is most severe during the first four cycles and weakens thereafter. This behaviour is attributed to a combination of different factors: i) thermal shock experienced by carbonated particles upon entering the calcination reactor; ii) attrition mechanisms, which initially smooth particle asperities and subsequently promote continuous material removal

through mechanical stresses; iii) rapid CO₂ release at higher calcination temperatures. More in detail, the PSD mean Sauter diameter decreases from ca. 478 to 445 μm when N increases from 1 to 10 ($\Delta T = 150^\circ\text{C}$), and from ca. 470 to 425 μm when N increases from 1 to 10 ($\Delta T = 250^\circ\text{C}$). A relevant feature is that, the higher the thermal gap suffered by the particles upon cycling (ΔT), the lower the mean diameter, namely the larger the extent of particle comminution. The $\sim 10\%$ reduction in Sauter diameter measured over 10 cycles, coupled with the progressive enrichment of the 300–420 μm fraction, could perturb the fluid-dynamic regime of the bed (e.g., minimum fluidisation velocity, segregation patterns) and enhance fines elutriation, thereby establishing comminution as a mechanism that, alongside chemical deactivation, influences the operability window of solar-assisted CaL at industrial scale.

Figure 5 presents the effect of calcination and carbonation temperatures on energy storage density for experiments at $T_{\text{carb}} = 600\text{--}650^\circ\text{C}$ and $T_{\text{calc}} = 800\text{--}900^\circ\text{C}$.

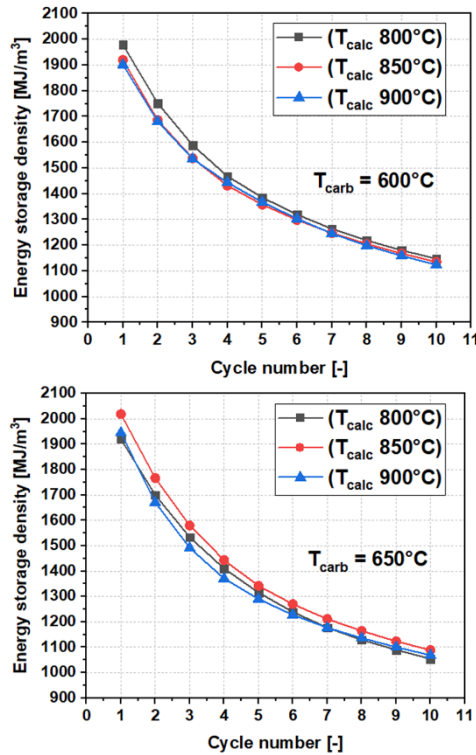


Figure 5. Effect of carbonation and calcination temperatures on energy storage density (Eq. (2)).

E_{SD} decreases with N , consistent with the trend observed for the carbonation degree. Overall, it declines from 1900–2020 MJ/m³ at $N = 1$ to 1050–1150 MJ/m³ at $N = 10$. Energy storage density depends on both $\bar{X}_{Ca}$ and ΔT ; therefore, lower $\bar{X}_{Ca}$ values (which tend to reduce E_{SD}) can be compensated by higher ΔT (which increases it). Indeed, for all plots of Figure 5, the curves are nearly overlapping due to a compensation effect between lower ΔT and higher reactivity. In detail, while a lower T_{calc} increases $\bar{X}_{Ca}$ (thus increasing E_{SD}), it simultaneously reduces ΔT , leading to a decrease in E_{SD} .

4. Conclusions

This study investigates the combined effect of carbonation and calcination temperatures in a solar-assisted CaL process, using a directly irradiated FB reactor coupled with a concentrated solar radiation simulator. Results show a rapid decrease in carbonation degree during the initial cycles, driven by sorbent sintering, as indicated by the reduction in specific surface area and porosity. The decline is amplified at higher calcination temperatures. It was also observed that a larger temperature difference between carbonation and calcination promotes greater particle size reduction, driven by increased thermal stresses. Energy storage data were evaluated across different process conditions, revealing a compensation effect between sorbent reactivity and ΔT .

In terms of particle comminution, it can be regarded as an intrinsic, and unavoidable, feature of solar-assisted CaL operation: its coupling with thermal shocks, attrition, and CO₂-release-driven mechanical stresses ultimately co-determines, together with sorbent chemical deactivation, the achievable energy storage density and the long-term operability of the technology.

Acknowledgement

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Development of an axial gap rotary shear for the sampling of sorted food waste sub-category

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Abstract. Extended Producer Responsibility (EPR) is an important regulatory instrument under which producers are required to pay a fee to cover the end-of-life management and treatment of their products. The Institute of Raw Materials Preparation and Environmental Technologies at the University of Miskolc developed an EPR related municipal solid wastes (MSW) sampling methodology based on the simultaneous application of manual sorting and sieving. A key principle of this methodology is that each particle must be classified in its as-found state according to the material component representing the largest mass fraction. Since food waste is typically present in a highly heterogeneous and contaminated form, it must be sorted in this condition into the appropriate category. This raised the question of how much EPR-relevant material is embedded in the food waste sub-category sorted in this way; therefore, a new methodology was developed to address this issue. The first step of the new procedure is liberation by means of an appropriate comminution device. Fundamental comminution tests were carried out using a cutting mill, a hammer crusher, an axial-gap rotary shear, and a radial-gap rotary shear. Based on the evaluation of the results, a new axial-gap rotary shear was designed and constructed. This paper presents the relevant sampling aspects, the fundamental comminution experiments performed on food waste using four different machines, the design and construction of the new axial-gap rotary shear, and the systematic mechanical and biological investigation of two particle-size fractions obtained from the sorted food waste sub-category of an average residual municipal solid waste average sample.

1. Introduction

Extended Producer Responsibility (EPR) has become an increasingly important policy instrument in modern waste management systems, as it shifts part of the financial and organizational responsibility for end-of-life products from municipalities to producers. In parallel with EPR, deposit return systems (DRS) also play a growing role in improving the separate collection and recovery of valuable material streams. The introduction of these regulatory frameworks requires reliable information on the material composition of municipal solid waste (MSW), including the occurrence and distribution of EPR- and DRS-related components.

In Hungary, the EPR system was introduced in 14th March 2023 by Government Decree 80/2023, creating a strong need for practical and scientifically sound methodologies for the characterization of relevant waste streams. In response, the Institute of Raw Materials Preparation and Environmental Technologies at the University of Miskolc developed a sampling and sorting methodology based on the combined application of manual sorting and sieving (Faitli et. al., 2024; Jaber et.

al., 2026). A fundamental principle of this approach is that each particle is classified in its original, as-found state according to the material component representing the largest mass fraction.

However, this principle raises specific challenges in the case of food waste sorted by the developed sampling methodology, which is typically highly heterogeneous and often contains adherent packaging residues and other EPR-relevant materials. According to Hungarian sampling standards the sorted food waste “fraction” is called waste sub-category. As a result, the apparent classification of food waste may mask the actual presence of recoverable material components. To address this problem, a new methodology was developed based on the liberation of the sorted food waste sub-category by comminution. The present study investigates the sampling-related aspects of this problem, compares the performance of different comminution devices, and presents the design of a newly developed axial-gap rotary shear. Figure 1 shows the technological flowsheet of the developed test protocol to examine the material composition of the sorted food waste sub-category. After the liberation by comminution and splitting, a subsample

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was soaked in water, where it split into three parts. Light particles floated up, heavy particles settled and biomaterials typically went into the suspension. This soaking served as a washing also and that facilitated further manual sorting and biological examinations not described here.

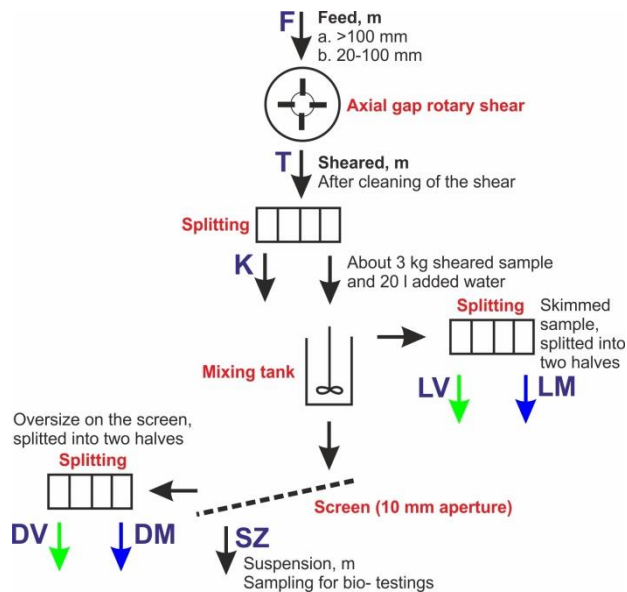


Figure 1. Technological flowsheet of the developed test protocol to examine the material composition of sorted food waste sub-category.

2. Development of the comminution machine

2.1. Preliminary comminution tests

Preliminary tests were carried out using packaged food products and vegetables to select the most suitable type of comminution equipment. The model materials were selected based on photographs of the real food waste sub-categories obtained during previous sampling campaigns. During the preliminary experiments, packaged bread rolls, packaged sliced cold cuts, and lettuce were processed in an axial-gap rotary shear, a hammer crusher (Figure 2), a radial-gap rotary shear, and a cutting mill. The results were evaluated and described based on photographs taken of both the products and the interior of the machines. In the axial-gap rotary shear the plastic-packaged food products were successfully liberated and the food separated from the plastic packaging. However, the plastic remained largely intact, which can be explained by the 0.5 mm shear gap applied in the machine. The food fraction itself was only moderately size-reduced, which can be attributed to the low rotor circumferential speed of 0.5 m/s. In the hammer crusher, liberation of the food material was achieved effectively, and all three materials were finely comminuted due to the high rotor circumferential speed (~40 m/s) and the combined action of impact and shear stresses. The plastic components, however, remained largely intact, and a considerable part of them stayed inside the machine (Figure 2). This can primarily be

explained by the small amount of feed material used. At the same time, small sample quantities may also occur during the operation of the final target equipment; therefore, this was identified as a disadvantage of the hammer crusher. In the radial-gap rotary shear, the vegetable material adhered to the inner wall of the machine, and only a minimal amount left the equipment.



Figure 2. Test comminution in a hammer crusher.

The bread roll was comminuted without difficulty; however, due to electrostatic charging, most of the plastic film also adhered to the interior of the machine. In this case, the film itself was comminuted effectively. The cutting mill successfully liberated the individual food products, but the packaging of the sliced cold cuts, similarly to the hammer crusher, did not leave the machine and remained inside. The thin plastic bag, on the other hand, passed through the machine without undergoing effective size reduction.

Based on the experience gained during these tests, and considering the required machine size and cleanability, the two-rotor type axial-gap rotary shear was finally selected for the task.

2.2. Design and construction of the axial-gap rotary shear

In the two-rotor axial-gap rotary shear, the feed material is drawn into the shearing zone by two counter-rotating shafts equipped with disc cutters. Comminution is achieved in the narrow axial gaps formed between the rotating discs and the opposing elements, resulting in efficient liberation and controlled size reduction of heterogeneous waste materials.

The process design of the equipment was performed according to the methodology originally proposed by Csőke et al. (1997), followed by the mechanical design and construction of the machine. For technological design calculations, the following approximate

relationships can be derived. The maximum shearing force is given by

$$F_{\max} = kA\tau_m [\text{N}] \quad (1)$$

The maximum torque is

$$M_{\max} = bF_{\max} = kA\tau_m b [\text{Nm}] \quad (2)$$

where, the shear cross-sectional area can be approximated as

$$A = \frac{w^2}{2 \tan \alpha} \quad (3)$$

In these equations, A is the cross-sectional area of the material being sheared, τ_m is the shearing resistance of the material, approximated by its shear strength, b is the lever arm, and k is a correction factor accounting for the differences between the conditions under which τ_m is determined and the actual shearing conditions, such as blade wear, cutting speed, and shear gap. In most cases, k lies in the range of 1.0 to 1.3.

By substituting the sheared cross-section into the torque equation, and considering that in a machine of working length L and disc width y , the number of discs mounted on one shaft is

$$N = \frac{L}{2y} \quad (4)$$

The total torque demand of the two-rotor machine, i.e. the combined torque demand of both shafts, can be expressed as

$$M = \frac{kLs^2\tau_m(D-t)}{4y} \quad (5)$$

The useful power demand of the machine drive is then

$$P_h = \frac{kL\pi ns^2\tau_m(D-t)}{2y} \quad (6)$$

In practice, the actual motor power demand is higher because of deformation-fracture effects associated with the front knives and due to friction losses. Therefore, the required motor power can be estimated as $P \approx cP_h$ where, $c = 1.5-1.9$. The rated motor power is then taken as $P_r = 1.2P$ (Csőke et. al., 1997).

The machine width was set to 0.25 m, considering the largest items expected in the feed material. Liquid-filled soft drink bottles were considered as the reference objects representing the upper size limit of possible feed pieces. Owing to the large feed size, the diameter of the shearing discs was selected as 0.20 m. The rotor circumferential speed was set to 0.5 m/s.

For the determination of torque and power demand, an extreme operating case was assumed in which the machine would be required to shear a 1.5 mm thick metal sheet. This intentionally conservative design approach was adopted because sorted food waste may contain a wide range of foreign materials, including bones and canned food products. Considering the losses

in the reduction gearbox, two 4 kW geared motors were selected to drive the machine.

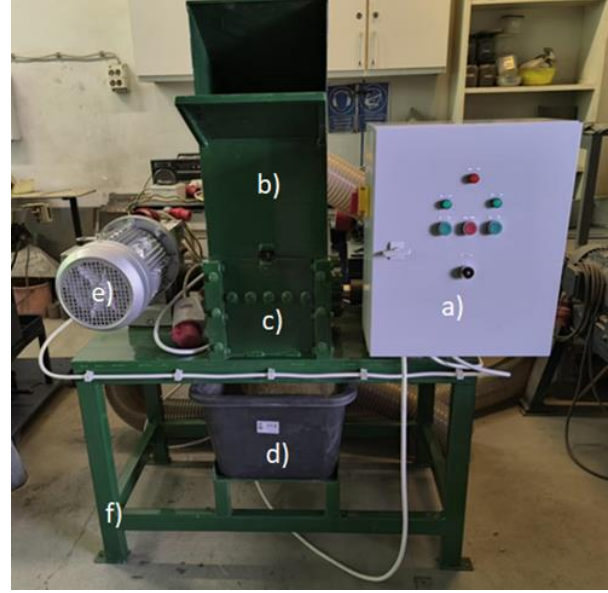


Figure 3. The constructed axial-gap rotary shear and its main units: (a) electrical control box, (b) feed hopper, (c) shearing chamber, (d) product collection container, (e) drive motor, and (f) supporting frame.

The shearing discs and spacers were surface-ground, making it possible to set a shear gap of 0.08 mm to ensure the effective comminution of plastic films. The completed equipment is shown in Figure 1 together with its main units. To improve cleanability, the machine was equipped with a partially rotatable comb assembly, which allows sample material adhering between the discs and remaining inside the machine to be removed easily.

The successful construction of the equipment confirmed the feasibility of integrating process design, mechanical design, and in-house manufacturing in the development of small-scale experimental comminution devices.

3. Results and conclusion

One pilot study had been conducted to test the methodology developed for examining the contamination of food waste (Figure 1) and the new axial-gap rotary shear. Sampling took place on May 16th, 2025, at the premises of MiReHu Kft. in Miskolc, Hungary as part of the national level MSW sampling campaign of SPRING 2025.

The total mass of the >100 mm and the 20-100 mm size fractions of the sorted 1.1 food waste sub-category of the residual MSW average sample of M-XI (balance sheet number: W17079-02509766) were delivered to the lab. The analysis of the two food waste size fractions was carried out according to Figure 1. Figure 4 shows the skimmed materials which were floated on the surface of the suspension in the mixing tank.

Table 1. Material composition of the examined sorted food waste category.

	2D plastics	3D plastics	Paper	Others	Bio	Water	Total		Ratio	
>100 mm	6.11	2.42	2.42	0.65	29.29	59.11	100.0	%	0.618	-
20-100 mm	4.30	0.59	0.47	0.21	37.85	56.57	100.0	%	0.381	-
									1	
Total	5.4	1.7	1.7	0.5	32.6	58.1	100.0	%		

Without further describing the other done physical, chemical and biological examinations, Table 1 shows the measured final material composition of the food waste sub-category of the examined RMSW average sample.

Another conclusion is that, the built axial-gap rotary shear has liberated the sorted food waste sub-category size fractions reliably.



Figure 4. The skimmed materials which were floated on the surface of the suspension in the mixing tank.

If water is considered to be food, then the total food content of the examined sorted food waste sub-category was 90.7 m/m%. And that means that the so called contaminants, namely materials - which should have been sorted into other waste categories - account for only 9.3 m/m% (Table 1). And this is the final conclusion that the key principle of the Hungarian MSW sampling methodology, - namely that each particle must be classified in its as-found state according to the material component representing the largest mass fraction – is correct. The mass balance of the waste materials can be correctly measured on the basis of this sampling principle, because the sorting errors of materials that do not belong to the actual category finally equalize. When the mass of the beverage in a PET bottle is greater, it should be classified as food waste, but PET bottles that only appear empty also contain beverage, so the resulting effect is balanced.

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Modification of Magnesium-Aluminate Spinel Powder for Thermal Spray Applications

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Abstract. Magnesium–aluminate spinel is a promising alternative to alumina for electrical insulation coatings in transport applications due to its high electrical resistivity and chemical stability. However, its low density, moderate hygroscopicity, and high melting point limit powder flowability, reduce molten particle formation in atmospheric plasma plume, and increase coating porosity. To address these issues, a novel transition-metal-doped magnesium–aluminate spinel powder was formulated and synthesized via an industrially scalable high-temperature solid-state route. Three different powder modification approaches were applied to improve flowability and tested in a standard thermal spray powder feeder to verify their transferability between thermal spray workshops. The first approach, based on chemical modification using binding or organic agents, had no effect on powder morphology and improved flowability only during the first spraying cycle. After interruption of the process, the powder accumulated in the feeding system, making this solution unsuitable for industrial scale-up. The second approach, spray drying, promoted partial spheroidization but exhibited similar flowability limitations. The third approach, thermal modification using two high-temperature prototype technologies, promoted initial powder spheroidization and the completion of residual phase reactions. Due to limited production capacity, only one variant was tested further. It demonstrated good powder flowability and high moisture resistance.

1. INTRODUCTION

Solid feedstock thermal spray powders can be classified as a specific group of functional application-driven materials, such as metals, composites, and ceramics, characterized by their guaranteed flow behaviour, a narrow particle size distribution from 25 to 150 μm , and highly scalable industrial production ranging from tens to hundreds of kilograms [1, 2]. However, even their number in terms of chemical compositions available on the market is quite limited, focusing mainly on major thermal spray application areas in the transport, energy, and general engineering industries. This demanding market is nowadays increasingly vulnerable and threatened by non-European countries in the delivery of raw materials, due to export license control [3].

Therefore, the development of new thermally sprayable solid feedstocks as alternatives to the existing ones becomes more important to ensure the sustainability of key industrial sectors in Europe. For the newly developed thermally sprayed powders, one key technological characteristic that must be achieved is

flowability, which provides the consistent powder feeding into a torch and directly impacts coating quality.

This is especially challenging for ceramic powders when compared to metallic and composite ones because the contribution of density, particle morphology, triboelectric charge and hygroscopicity is much greater, and therefore various approaches must be used to improve their flowability.

Magnesium-aluminate spinel is considered as an alternative candidate to conventionally used alumina electrical insulation thermal-sprayed coatings in bearing transport applications [4] because of its low density (3.58 g/cm³), wide band gap energy, low dielectric constant ($\epsilon=7.5$), high electrical resistivity, and high resistance against chemical attack [5]. To overcome the limitation of its high melting point (2135 °C), reduce the porosity of the thermally sprayed coating, and increase its electrical resistivity, a new formulation of spinel doped with a transition metal element was developed. However, after solid-state synthesis, milling, and sieving, the powder was observed to be non-flowable. Therefore,

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several different strategies for its modification were designed and further tested directly in the thermal spray powder feeder. In the end, only one exceptional route was identified, providing both smooth spinel powder flow and resistance to ambient moisture.

2. SYNTHESIS OF SPINEL POWDER

The reactants were purchased commercially and used as received without further purification: aluminum(III) oxide (Al_2O_3 , p.a., Lachner), magnesium(II) oxide (MgO , p.a., Penta), and a transition metal oxide MO_x (99.9%, Sigma Aldrich). The $\text{MO}_x\text{-Al}_2\text{MgO}_4$ powder samples were synthesized via a 2-step process composed of: (i) mechanochemical milling in a planetary ball mill (Pulverisette 6, Fritsch GmbH, Germany), and (iii) high-temperature solid-state reaction in a laboratory furnace (2017S, Clasic, Czech Republic) performed in platinum crucibles with volumes of 160 ml and 100 ml, as shown schematically in Figure 1. The reactants were weighed using a laboratory scale (Pioneer Plus PA, Ohaus Corporation, Switzerland) and subsequently milled in a planetary ball mill at 450 rpm for 10 minutes using a demineralized water as the milling medium. For milling, an agate milling jar with a volume of 0.5 dm^3 and 25 pieces of agate milling balls with a diameter of 20 mm were used. After milling, the milling balls were collected, and the suspension was poured into the stainless-steel bowl without additional rinsing. Before the next milling batch, the milling jar and balls were rinsed with demineralized water, and the process was repeated 7 times to obtain the required amount of ceramic suspension.

A mechanochemically prepared ceramic suspension was dried in a laboratory dryer (SLW 53-W STD, Pol-Eko Aparatura, Poland) at 105°C for 6 h, producing both highly agglomerated and less agglomerated powders. Based on the dried powder's appearance, the dried material was divided into 2 fractions, namely: (i) spinel bulks (approximately 700 g), (ii) spinel powder (approximately 350 g). These fractions were heat-treated separately at 1500°C with a 3-hour dwell time to promote the solid-state reaction between the oxides. Hypothetically, for solid-state reaction products, we presumed differences in phase composition between the sintered bulk and the sintered powder.

Sintered samples-spinel bulks and spinel powder were processed separately, firstly milled in a vibratory disc mill (RS200, Retsch GmbH, Germany) in a 200 ml stainless steel milling chamber for 13 seconds at 700 rpm. Then, the powders' rheological properties were enhanced in terms of flowability, necessary for the application in atmospheric plasma spray coating technology.

3. POWDER MODIFICATION

The synthesized powder was separated into two fractions, below $25 \mu\text{m}$ and $25\text{--}75 \mu\text{m}$, using an automatic sieving machine AS200 Control (Retsch GmbH, Germany) before further flowability modification. Powder particles larger than $75 \mu\text{m}$ were repeatedly milled in the planetary ball mill Pulverisette 6 (Fritsch GmbH, Germany) to reduce the particle size to fit the indicated range. Three different powder modification strategies were than used:

- (i) Modification by organic agents, where binding dispersion for the powder size in a range $25\text{--}75 \mu\text{m}$ was used, in a laboratory dryer (SLW 53-W STD, Pol-Eko Aparatura, Poland), and crushed in a agate mortar,
- (ii) Modification by spray drying, where an initial stable suspension containing a powder particles below $25 \mu\text{m}$ with polymeric binder was produced and spray dried using a Mini Spray Dryer B-290 (BUCHI Labortechnik AG, Switzerland), and
- (iii) Thermal spray processing route, where two developed prototype units with different temperature regimes were applied, including a non-isothermal high-temperature plasma (CEITEC, Czech Republic) and a low-temperature flame plume (FunGlass, Slovak Republic).

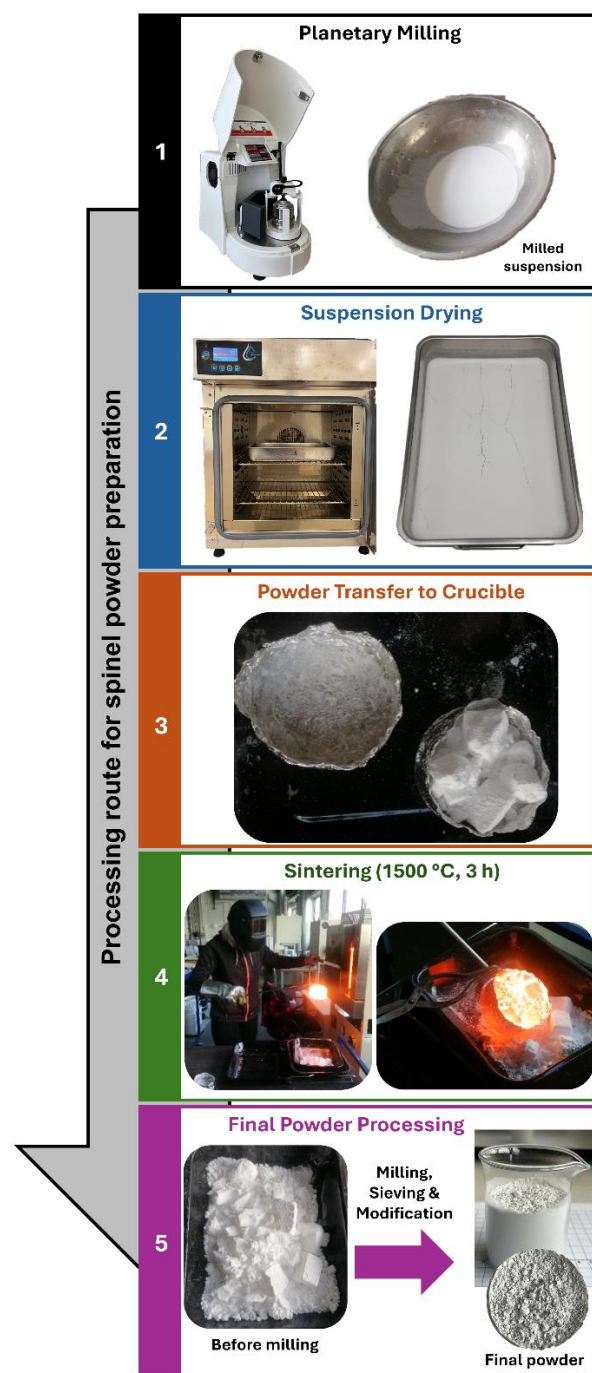


Figure 1. Processing route for spinel powder preparation.

4. POWDER CHARACTERIZATION AND TESTING

The powder morphology was examined and documented using scanning electron microscopy (SEM; Lyra3, Tescan, Czech Republic) in backscattered electron (BSE) mode.

Powder X-ray diffraction (PXRD) data at room temperature were collected in Bragg–Brentano geometry in reflection mode using monochromated Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) on a Rigaku SmartLab 3 kW diffractometer (Rigaku, Japan), operated at 30 mA and 40 kV. Data were recorded over a 2θ range of $15\text{--}90^\circ$, with a step size of 0.02° and a scan rate of $3^\circ \cdot \text{min}^{-1}$.

Thermogravimetric analysis (TGA) was performed using a TGA-Discovery thermogravimetric analyzer (TA Instruments, USA) under a pure nitrogen atmosphere ($25 \text{ ml} \cdot \text{min}^{-1}$). The sample was heated from 30 to 150°C at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ and held isothermally at 150°C for 30 min to avoid any decomposition of organic agents (e.g. decarboxylation). The sample mass was approximately 25 mg.

A PF-50 powder feeder (FST, Netherlands), equipped with a heating jacket, was used for modified powder flowability testing.

The powder obtained after synthesis, crushing and sieving consisted of irregularly shaped agglomerated particles (Figure 2a). Its phase composition was a nearly single phase having a transition metal-doped magnesium–aluminate spinel as a major phase (98.5 wt.%), and a small amount of unreacted initial phase of MgO was still detected. The as-synthesized powder without any further modification did not exhibit flowability.

The powder modified with organic agents showed partial spheroidization of the particles (Figure 2b) while maintaining the same phase composition. Initial signs of improved flowability were observed. However, testing in a thermal spray feeder revealed that, although the powder flowed satisfactorily after aeration and filling, its flowability deteriorated whenever the spraying process was interrupted. In subsequent spraying cycles, the powder accumulated within the feeder transport system unless additional cleaning was performed.

Spray dried powder produced from a fine powder suspension exhibited a more regular spheroidal particle morphology (Figure 2c), which was expected to improve powder flow due to reduced mechanical friction. However, the experimental flowability behaviour was found to be similar to that of the powder modified with organic agents, producing a powder buildup in the feeder system in the next cycle after interruption of the process. Powder accumulation in the transport system was observed for both variants, regardless of whether powder preheating in the feeder was applied.

The prototypes developed for thermal powder modification at CEITEC and FunGlass research centres enabled remelting of the powder particles into a highly spheroidal morphology. As apparent from Figures 2d and 2e, the melting temperature had a pronounced effect on the internal structure of the spheroidized particles. Both approaches also resulted in a noticeable purification of the spinel phase (Figure 3), showing a pronounced decrease

in MgO impurity content. Unfortunately, the powder modified at a lower temperature was produced in only a limited quantity, which was insufficient for further powder feeder testing. In contrast, the second approach promoted excellent flowability and, more importantly, high resistance to ambient moisture. This performance was maintained regardless of whether powder preheating was used and remained unchanged even after several months of storage.

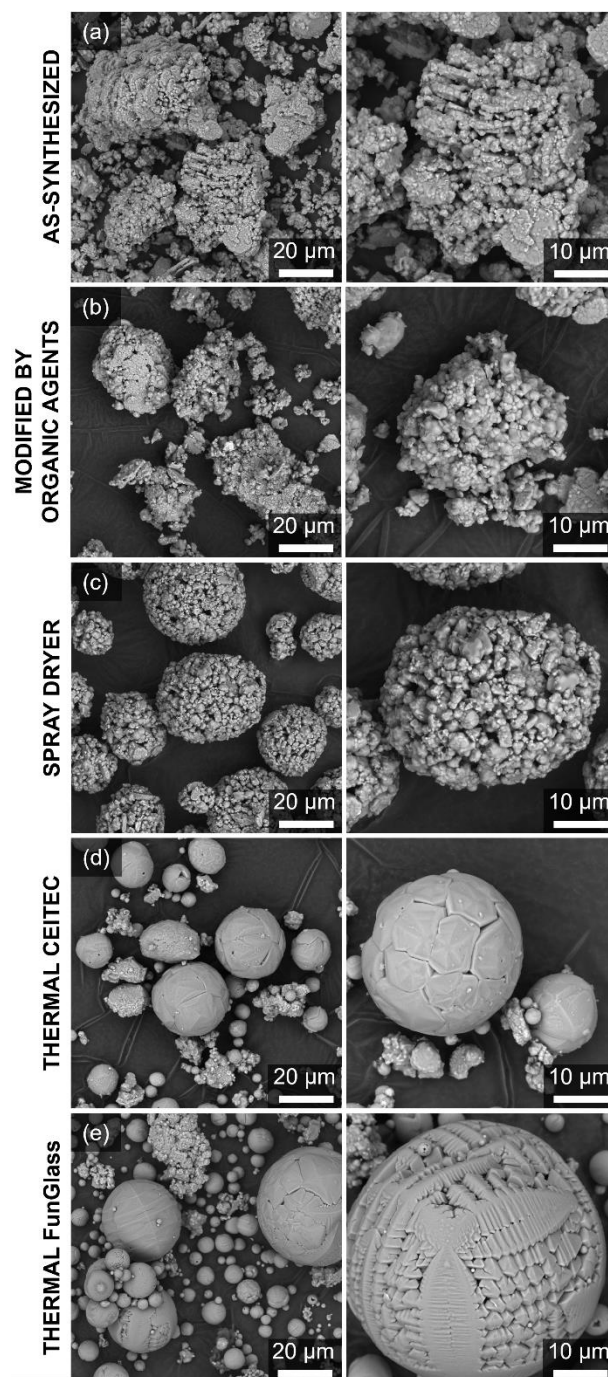


Figure 2. Surface morphology (SEM-BSE) micrographs of the transition-metal-doped magnesium–aluminate spinel powder in different states: (a) as-synthesized, (b) modified by organic agents, (c) processed by spray drying, (d) thermally treated using the CEITEC prototype, (e) thermally treated using the FunGlass prototype.

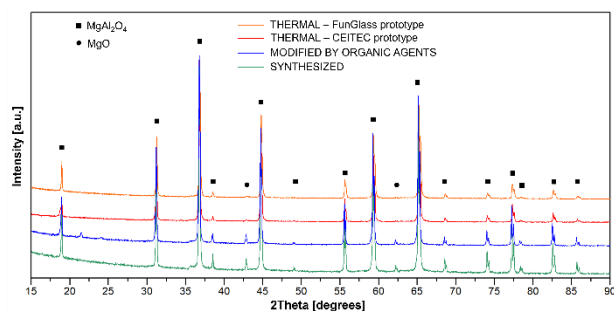


Figure 3. XRD diffractograms of transition-metal-doped magnesium–aluminate spinel powders in different states: as-synthesized (green), modified with organic agents (blue), thermally treated using the CEITEC prototype (red), and thermally treated using the FunGlass prototype.

The TGA measurements showed that the powder becomes more susceptible to moisture when an organic agent is used for its modification rather than the magnesium–aluminate spinel itself (Figure 4). Reducing the organic content to ensure the flowability of thermal spray powders is just as challenging as it is for pharmaceutical products [6]. It is clear that the lowest moisture absorption losses in the powder were measured for non-modified powders in their as-synthesized state and for thermally modified powders.

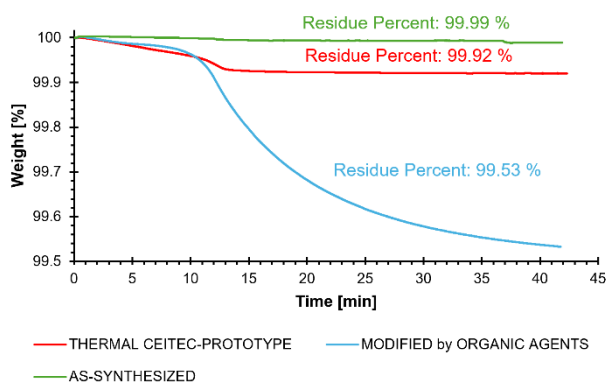


Figure 4. TGA curves of absorbed moisture loss in magnesium–aluminate spinel powders: as-synthesized (green), modified with organic agents (blue), thermally treated (red).

5. SUMMARY

A new formulation of a transition metal-doped magnesium–aluminate spinel powder was successfully synthesized. Three powder-to-powder modification approaches by (i) organic reagents, (ii) spray drying, and (iii) thermal technologies were designed to ensure the synthesized ceramic powder flowability. The first two approaches promoted temporary powder flow once the powder was filled into the feeder, but only until the thermal spray process was interrupted for the first time. The thermal approach enabled remelting of the synthesized spinel, resulting in particle spheroidization, enhanced purification through the completion of reactions with unreacted species, and revealed high resistance to ambient moisture, and ensured exceptional,

reproducible flowability even after several months of powder storage. The flowability of the thermally modified powder was predominantly ensured by its change into a highly spherical morphology, which reduced friction between particles, and by an insignificant amount of organic reagents capable to absorb moisture. The resulting synthesized and thermally modified thermal spray powder, with a particle size in the range of 25–75 μm , fulfils the purity and flowability requirements and can be further scaled up for industrial production.

Acknowledgement

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Mechanochemical clay activation: energy demand, stressing mechanics, and implications for industrial scalability

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Abstract. Mechanical activation of clays is a promising route to reduce clinker content in modern cements and to enable sustainable binder systems. However, the transfer of mechanochemical activation from laboratory scale to continuous industrial processing remains a major challenge. This study discusses the limitations of conventional batch-based mechanochemical approaches and presents dry agitated bead mills as a scalable and industrially proven solution. Based on stress energy considerations, contact frequency analysis, and comparison with conventional ball mills, the suitability of dry agitated bead mills for large-scale clay activation is demonstrated. Industrial reference data from the Pamir 12,000 meca-clay plant underline the feasibility of continuous mechanical activation at high throughput and energy density.

1. Introduction

Reducing CO₂ emissions in cement production requires a substantial decrease of the clinker factor, increasingly through the use of supplementary cementitious materials (SCMs). As conventional SCMs such as slag and fly ash become scarce, clay-rich raw materials have gained renewed interest due to their wide availability. Untreated clays usually exhibit low reactivity and therefore require activation prior to cement application [1].

Thermal activation by calcination is well established but associated with high energy demand and CO₂ emissions. Mechanochemical activation has therefore emerged as an alternative or complementary route, relying on intensive mechanical stressing to induce structural disorder and enhance reactivity [1]. Previous studies demonstrate that milling alters clay crystal structures and surface chemistry, but activation efficiency is strongly influenced by operating parameters and equipment type [2,3]. Most investigations rely on laboratory-scale planetary ball mills, which operate in batch mode and suffer from limited industrial scalability [1,3].

Agitated bead mills, in contrast, are widely used in industrial fine and ultrafine grinding and operate at high power densities with predominantly shear and compression stressing. Recent studies indicate that dry agitated bead mills can induce pronounced mechanochemical effects with superior energy efficiency compared to conventional ball mills [4–9]. This work therefore examines dry agitated bead mills as an industrially viable activation technology for clays.

2. Material & Methods

Clay-containing raw materials relevant for use as SCMs were processed in dried condition without prior thermal activation. Standard pre-crushing and drying ensured stable feeding. Wear-resistant ceramic grinding media were selected to enable intensive stressing under dry conditions.

For industrial scale-up, a dry agitated bead mill with a grinding chamber volume of 12,000 L was analysed (see Figure 1). Scale-up was based on maintaining dominant stressing mechanisms rather than strict geometric similarity. Stress intensity and stressing frequency—governed mainly by agitator tip speed, media size, and filling degree—were selected as key scale-up criteria.

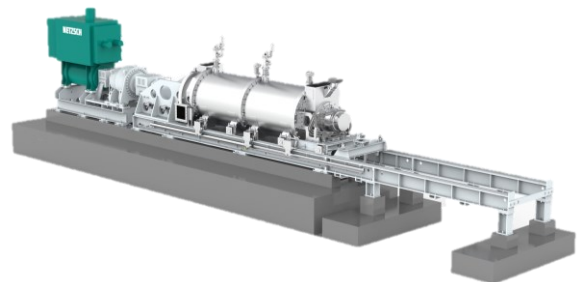


Figure 1. Industrial dry agitated bead mill (12,000 L grinding chamber volume) considered for the scale-up and evaluation of continuous mechanochemical clay activation.

Discrete Element Method (DEM) simulations were conducted to analyse grinding media motion, collision

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frequency, and stress energy distributions. The simulations provided qualitative insight into internal stressing conditions and supported comparison across mill sizes and operating points.

3. Results & Discussion

3.1. Energy demand and tunability of activation quality

Mechanochemical clay activation is governed by cumulative milling input energy rather than discrete activation events [1–3]. Literature data show that comparable activation states can be achieved at very different energy inputs depending on material system and milling configuration. Energy reductions of more than 50 %—and up to approximately 90 %—have been reported while still achieving sufficient reactivity for cement applications [3,10] (see Figure 2).

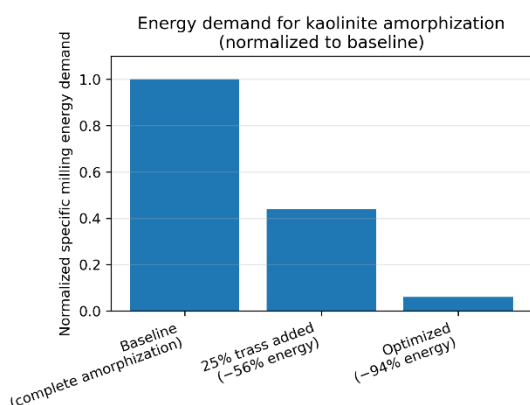


Figure 2. Normalized specific milling energy demand required to achieve comparable kaolinite amorphisation under different material and process configurations, illustrating that activation energy demand is not unique and can be significantly reduced through optimisation.

The energy–reactivity relationship is inherently non-linear. Reactivity increases rapidly at low energy input due to defect formation and early-stage amorphisation, followed by saturation at higher energies where additional input is increasingly dissipated [3] (see Figure 3). Consequently, activation quality is tunable by matching stress intensity and stressing frequency to a material-specific effective energy window, rather than maximising energy input.

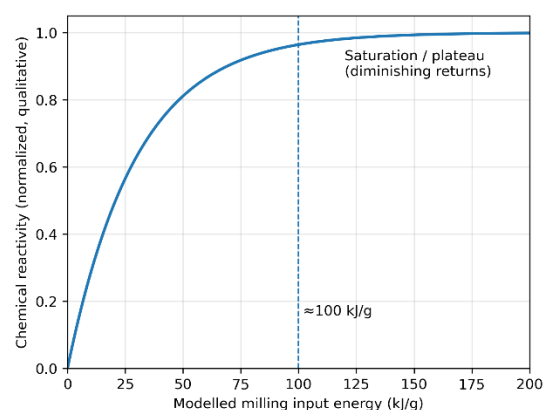


Figure 3. Schematic relationship between cumulative milling input energy and chemical reactivity of clays, showing rapid reactivity increase at low energy input and saturation at higher energy levels (qualitative).

3.2. Limitations of tumbling ball mills

Comparisons between tumbling ball mills and agitated bead mills at comparable scale show fundamentally different stressing characteristics [6,9] (see Figure 4). Ball mills exhibit low stressing frequencies and broad stress-energy distributions, resulting in long residence times to achieve activation-relevant cumulative energy input. Even large two-chamber ball mills require disproportionally large volumes to reproduce the stressing conditions readily achieved in small agitated bead mills.

This leads to unfavourable throughput-to-footprint ratios and restricts ball-mill-based activation to laboratory or pilot scale. While activation is technically possible, industrial implementation becomes impractical due to low achievable throughput relative to installed equipment size.

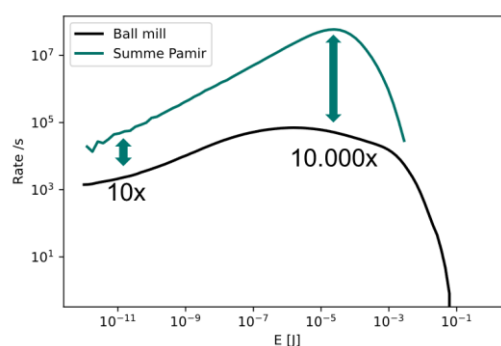


Figure 4. Comparison of stressing rates as a function of stress energy for a tumbling ball mill and an agitated bead mill at comparable mill size, highlighting fundamentally different stressing characteristics governed by the milling principle rather than geometric scale.

3.3. Industrial relevance of agitated bead mills

Figures 5 and 6 together convey a clear scale-feasibility argument for mechanochemical clay activation. Figure 5 illustrates the substantial size

difference between the investigated systems, comparing a large two-chamber tumbling ball mill ($\approx 125 \text{ m}^3$ grinding volume) with a laboratory-scale agitated bead mill (Pamir 40 L). Figure 6 subsequently compares the corresponding stress-energy distributions obtained in these two systems. The figures demonstrate that, in order to reach stressing conditions comparable to those generated in the small agitated bead mill, a ball mill of orders-of-magnitude larger volume is required.



Figure 5. Comparison of system scale between a two-chamber tumbling ball mill ($\approx 125 \text{ m}^3$) and a laboratory-scale agitated bead mill (Pamir 40 L), illustrating the large volume difference required to access comparable stressing regimes.

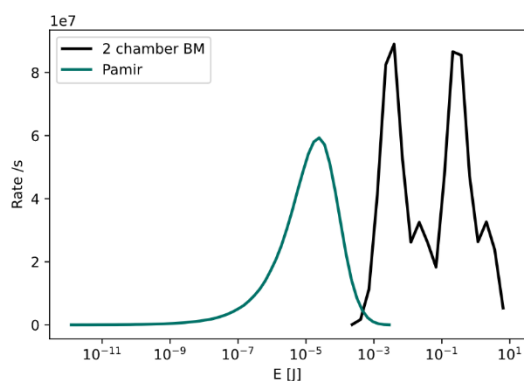


Figure 6. Stress-energy distributions of a large two-chamber tumbling ball mill and a small agitated bead mill (Pamir 40 L), showing that comparable activation-relevant stressing conditions in a ball mill require substantially larger equipment.

3.4. Influence of clay mineralogy

Activation efficiency strongly depends on clay mineralogy. Kaolinitic clays generally respond more readily to mechanochemical activation than 2:1 clays or mineralogically heterogeneous systems [3]. In such cases, stand-alone mechanical activation may be insufficient, and combined mechanical–thermal routes may be required [1–3].

Industrial activation technologies must therefore allow flexible adjustment of stressing conditions and

energy input to accommodate clay-specific responses and targeted performance levels.

4. Conclusions

Mechanochemical activation of clays is controlled by cumulative energy input, stressing mechanics, and mineralogy, resulting in a non-linear and tunable energy–reactivity relationship. Tumbling ball mills are intrinsically limited by low stressing frequency and unfavourable scale-up behaviour, restricting activation to non-industrial throughput.

Dry agitated bead mills provide activation-relevant stress intensities combined with very high stressing frequencies, enabling efficient energy utilisation at high throughput and compact scale. Their flexibility further allows adaptation to clay-specific activation requirements. Overall, industrial clay activation favours high-power-density agitated systems over conventional tumbling mills for scalable and energy-efficient mechanochemical processing.

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Stress-based modelling of mechanochemical reaction kinetics

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Abstract. Mechanochemistry is considered an emerging technology of the future, as its methods enable sustainable and solvent-free alternatives to conventional wet-chemical syntheses. While the exact mechanistic background of these reactions is still under research, quantification of the underlying stress conditions appears to be a promising approach to predict the outcome of a reaction. This study takes the first steps towards developing a model for the reaction kinetics of a mechanochemical reaction as function of mechanical stress conditions. The approach is based on experiments and DEM-simulations involving different types of ball mills and well-established stress modelling. Especially the specific energy input and stress intensity have shown to be significant parameters for the progress of the mechanochemical model reaction.

1. Introduction

Mechanochemistry is considered a technology of the future for environmentally friendly chemical reactions. Today, up to 80% of chemical industry waste consists of solvents rather than the valuable components themselves. Unlike conventional wet chemistry, mechanochemical reactions can be carried out without the use of solvents and are often more energy-efficient [1].

Mechanical stress causes defects and deformations in solids, thereby making the material chemically reactive. Additionally, effects such as particle deformation, fracture, and the formation of new contact surfaces, as well as frictional heat, play a role in the reaction's progress. Although the molecular processes in mechanochemical reactions are complex, certainly the input of mechanical energy is decisive for the reaction outcome. The mechanical energy is often provided by ball mills, in which grinding media are set in motion and transfer their kinetic energy to the entrapped reactant material when colliding. By means of experimental, simulation and modelling approaches, this work thoroughly analyses the stress conditions in different ball mills and correlates them with the according degrees of chemical conversion. The mass-specific mechanical energy input and the intensity of single stress events could be identified as significant parameters for the resulting reaction kinetics. Furthermore, initial steps towards the development of a scaling model for a mechanochemical model reaction were formulated.

2. Experimental

In this study, a simple inorganic metathesis reaction was used as a model reaction (1). The reaction is initiated by mechanical energy and was performed completely dry

without providing thermal energy in addition to the milling energy



The general suitability of this mechanochemical CaCO_3 synthesis as a model reaction has already been demonstrated in the past [2]. This model reaction has now been carried out in different laboratory scale ball mills, including a planetary ball mill (PM400, Retsch, 125 mL), a high-energy ball mill (Emax, Retsch, 125 mL), and a mixer ball mill (CryoMill, Retsch, 25 mL). The milling times and operating speeds were varied, while grinding media diameter and material (5 mm, SS), filling ratio and amount of reactant material were held constant.

Additionally, experiments were performed in a vertical stirred media mill (VSMM), a self-constructed batch-wise operated unit based on a Dispermat AE-06 (VMA-Getzmann, unit described in [3]). The VSMM was operated with 1 kg grinding media (SS) of 3.5 mm diameter at different milling speeds for up to 400 minutes. The ball-to-powder-ratio was the same as in the smaller mills.

In all experiments, the resulting reaction progress was quantified by purification of CaCO_3 from crude mixture via dissolution mechanics, subsequent drying and weighing of formed CaCO_3 . The purification procedure has been described in [2].

3. Stress model

Assuming that the mechanical stress is decisive for the reaction kinetics, the stress conditions need to be quantified, which is possible with a suitable stress model. To interpret the grinding media collisions, the stress model proposed by Kwade [4,5] was used. Accordingly,

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the grinding media transfer the so-called stress energy SE to the powder upon impact, which is dependent on their kinetic energy and, thus, a distributed parameter. The stress characteristics of a certain mill operation can be described by this stress energy distribution. It allows to calculate both the mean stress energy and the stress number SN, which counts all occurring stress events. Accounting for all stress events, the total energy input is described by the product of the mean stress energy and stress number. The mass-specific energy E_m also considers the total amount of the powder in the mill.

$$E_m = \frac{\overline{SE} \cdot SN}{m_p} \quad (2)$$

For a single collision, the stress intensity SI can be defined as in (3), considering the entrapped powder (“active powder mass”) within one collision.

$$SI = \frac{SE}{m_{p,act}} \quad (3)$$

3. DEM simulations

The stress energy distribution cannot or at least very hardly be measured in a real experiment, but it can be evaluated using the discrete element method (DEM). In DEM, particles are simulated as discrete elements. Newton’s second law is applied to determine the state of motion and a contact law is used to calculate a particle contacts. In this study, only the grinding media were simulated as particles. The reactant material was instead considered by calibration of damping and friction parameters and not included as particles in the simulations. The simulations were performed using the Rocky software (Ansys, Inc.) and analysis of the simulation results was supported by custom-made python routines.

The different mills are characterized by different motion patterns and, thus, different stress types and conditions. Therefore, impact (normal) and shear (tangential) stress in each mill were analysed separately. The information was used to compare mill-dependent stress conditions and to quantify the stress energy distributions. From this, the mean stress energy and stress number as well as mass-specific energy and stress intensity could be determined and correlated with the experimental product yields. For the stress intensity, the stressed particle mass was estimated according to the Schönert model [6].

4. Modelling of reaction kinetics

The simulation data was correlated with experimentally determined reaction yields, and it was demonstrated that the specific energy input is suitable for describing the reaction kinetics for the laboratory-scale mill types investigated and across a wide operating window. A minimum stress intensity is also a prerequisite for an efficient chemical conversion. The dominant stress mechanism varies depending on the mill type and operating conditions. During the stress processes, powder adheres to the mill chamber wall and the grinding balls, a phenomenon that depends on the stress conditions.

Conversely, the resulting powder layers on the grinding media and grinding chamber walls also influence the elasticity and restitution of the grinding media contacts and, consequently, the stress intensity

While these results mentioned were obtained for small, laboratory-scale mills, the results were then compared to the larger vertical stirred media mill (VSMM). It was found that the VSMM is less efficient in progressing the reaction than the smaller ball mills, so that the mass-specific energy alone was not a suitable parameter for predicting the reaction kinetics in the bigger VSMM. This could be traced back to the influence of the stress intensity, with a higher stress intensity being generally favourable for an efficient chemical conversion. As an example, Figure 1 shows the stress energy distributions for both the Emax and the VSMM at a certain operation speed. The stress frequencies are normalised to the mass of the used grinding media in the respective device to allow for a direct comparison. The ball-to-powder-ratio was kept constant in all devices.

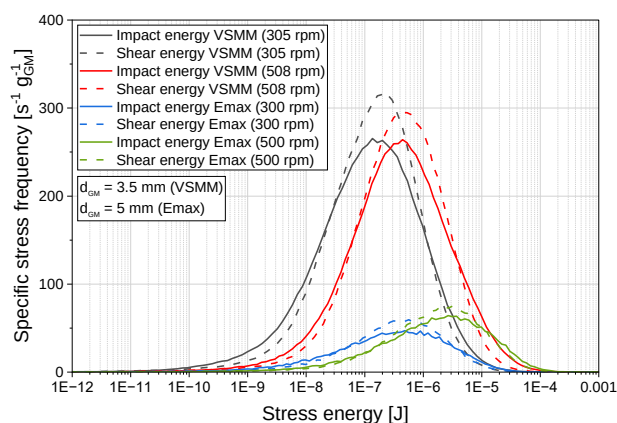


Figure 1. Exemplary stress energy distributions (impact and shear) for certain operation of the Emax and vertical stirred media mill from DEM simulations. The stress frequency is normalised to the grinding media mass.

While the vertical mill has significantly more stress events per grinding media mass and time, the distribution curve is also shifted to lower stress energies. Possibly, collisions of low stress energy are not effective in progressing the chemical reaction, indicating a minimum required stress intensity. To quantify the effect, a mathematical dependence of the chemical conversion on both the mass-specific energy and stress intensity had to be found. For this purpose, a Johnson-Mehl-Avrami-Kolmogorov (JMAK) model was applied to the data in the first step. Promoting the hypothesis of the significant role of the stress intensity, the JMAK approach was fitted for each mill operation at different stress energies and the fit parameters were interpreted physically. In the next step, the specific energy input was modelled using operation parameters and based on the idea of the presented stress model.

The result is a semi-empirical model for predicting the chemical conversion based on the stress conditions in different ball mills and across different laboratory scales. The validation graph in Figure 2 shows a good overall

agreement of modelled and experimentally assessed reaction progress.

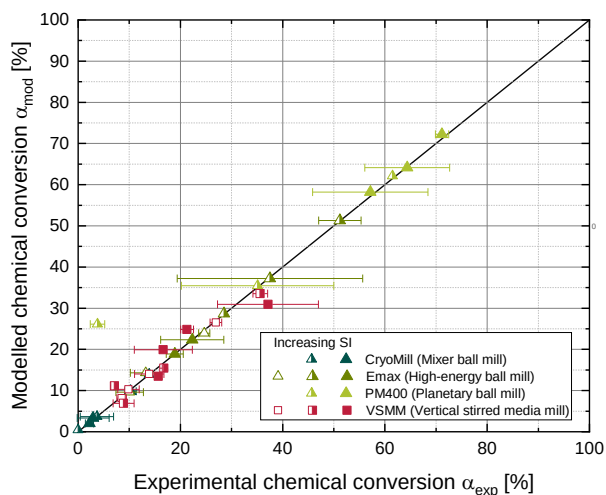


Figure 2. Exemplary model validation for the investigated mechanochemical reaction in the different ball mills including VSMM: The modelled chemical conversion is plotted against the experimentally measured degree of chemical conversion from purification

Acknowledgement

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Role of Milling Stress in the Mechanochemical Activation of Clay

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Abstract. The mechanochemical activation of clay has been successfully reported in quite a number of publications that employed planetary ball mills. Nonetheless, there is a deficiency in research regarding the necessary stress conditions for the mechanochemical activation of clay and the transfer to scale-able mills. This study utilized two types of media mills for mechanochemical activation: a planetary ball mill and a stirred media mill. Furthermore, discrete element method (DEM) simulations have been conducted to assess the stress energies resulting from the adjusted operating parameters. The findings indicate that the overall specific energy alone is insufficient to characterize the mechanochemical activation process. The most critical factor is the stress intensity resulting from the acting stress energies, as varying stress energies require significantly different specific energies to achieve the same level of material activation. Additionally, a minimum stress intensity is required to reach a high degree of material activation. Similar to traditional size reduction processes, an optimal stress intensity and with it stress energy has been identified for mechanochemical activation, which results in the same level of material activation with lower specific energy.

1. Introduction

A well-established approach for minimizing the environmental impact of the cement industry is the partial substitution of cement with supplementary cementitious materials (SCMs). Typical SCMs, including fly ash and blast furnace slag, cannot meet the increasing demand driven by the transition to renewable energy in electricity generation and the processes of green steel manufacturing, as well as the rising need for cement [1]. Calcined clay represents the most promising substitute for SCMs, demonstrating adequate pozzolanic properties and comparatively low environmental footprint due to its low to medium calcination temperature [2].

An effective method to enhance the environmental impact in producing calcinated clay is the mechanochemical activation (MCA) of it. By this approach, mechanical energy causes structural changes in the material, including delamination, dehydroxylation, and amorphization [3]. These modifications improve the clay's reactivity and enhance its pozzolanic properties. In the literature quite a number of studies on this topic exist, focusing on the impact of material properties, and milling parameters on the activation efficiency, as well as characterizing the activated material. Almost in all published studies exclusively planetary ball mills (PM) for MCA are used. For instance, [4] reported that a higher balls-to-powder ratio enhances the process efficiency. A higher rotating speed improved the clay amorphization while a longer processing time caused material agglomeration. For improving the energy efficiency of MCA, [5] could reduce the required specific energy by addition 25 wt.-% trass to the clay.

However, planetary ball mills are limited in application for small batches of material and are not reliable for industrial demand. Furthermore, understanding the required stress conditions for the MCA can enhance the application of different mill technologies and the choice of optimal operating parameters. This study aims on conducting batch grinding trials in PM and stirred media mill (SMM) with various operating parameters, utilizing the same material across all trials. The objective is to estimate the necessary stress energies that will facilitate effective activation of the material while minimizing the specific energy.

2. Materials and Methods

In this study, Kaolin was utilized for MCA. The Kaolinite content in the material constituted 75 % of the mineral composition. The particle sizes along with the BET specific surface area of the raw material are presented in Table 1.

Table 1. Particle sizes measured wet by Laser diffraction (Malvern Mastersizer 3000) and BET specific surface area of raw Kaolin

x_{10} [μm]	x_{50} [μm]	x_{90} [μm]	S_m [m^2/g]
4.5	14.3	38.5	6.5

The experimental trials were conducted in the planetary mill PM400 from Retsch with 250 mL jars. The trials were conducted with steel and aluminium oxide grinding media. For the variation of the stress energies, the size of the grinding media was changed while the

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rotating speed was kept constant for all trials at 400 rpm. Furthermore, additional trials were conducted with an inhouse constructed vertical orientated batch SMM. In this SMM series of experiments, grinding media made of steel and aluminium oxide were utilized. To vary the stress conditions, both the stirrer speed and the size of grinding media were altered. To calculate the stress energies resulting from all PM and SMM trials, DEM simulations were conducted. The assessment of the MCA of samples was performed using XRD measurement. To evaluate the performance, the degree of amorphousness (DOA) calculated with equ. 1 was considered.

$$DOA = 1 - \left(\frac{I_c}{I_c + I_a} \right) \quad (1)$$

Where I_c represents the integral area of crystalline peaks, and I_a is the integral area of amorphous humps.

3. Results and discussion

The raw material with a median particle size of 14.3 μm is already so small that no considerable change in particle size is expected. Nevertheless, the grains are composed of stacked layers of kaolin, which will result in a notable change in the specific surface area (SSA) during the grinding process as a result of the fracture and delamination of these layers and according to [6] also due to the increase in the porosity. For investigating the impact of operating parameters on the process, the resulted values of SSA over the grinding time for two sets of operating parameters in PM and SMM are plotted in Figure 1. Overall, the data of PM and SMM show a similar behavior regarding the SSA, where three regimes, as suggested by [7], can be distinguished. These consist of a Rittinger zone marked by a continuous increase of SSA, an agglomeration regime that shows a plateau, and a regime where the SSA decreases due to particle aggregation. Additionally, even in Rittinger zone material amorphization occurs. However, it was not possible to overcome this regime in every trial, i.e. no energy threshold could be identified that must be exceeded to achieve a significant levels of material amorphization. The data further indicate that both types of mills, PM and SMM, yield similar results, with the most critical factor being the stress energy resulting from the specified operating parameters.

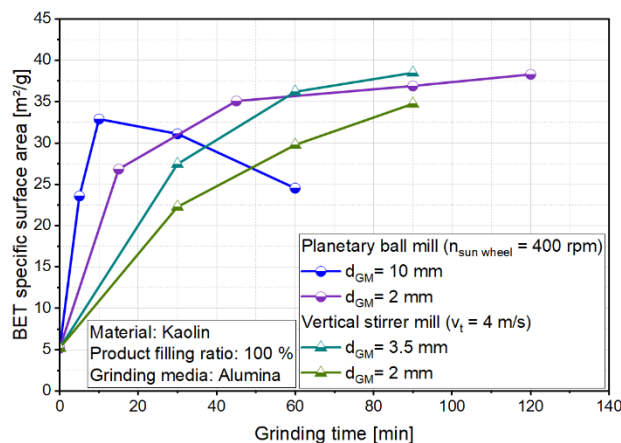


Figure 1. Values of BET specific surface area over the grinding time for trials with PM and SMM with two different grinding media size and constant rotating speed for each type of mills

Regarding the energy requirements for MCA, the data presented in Figure 2 depict the necessary specific energy in relation to the mean stress energy for various values of DOA. The figure indicates that there is an optimal stress energy at which the specific energy reaches its minimum. Furthermore, it is evident that comparatively to size reduction processes, a high stress energy is beneficial and required for amorphization of material.

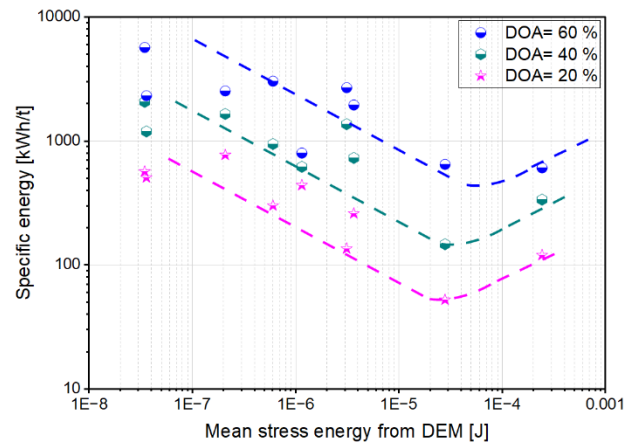


Figure 2. Required specific energy in relation to the applied mean stress energies acquired from DEM simulations for three values of degree of amorphousness.

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Improving Comminution Circuit Performance in an Iron Processing Plant: No-Capital-Investment Approach

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Abstract. To conserve energy, efforts are made to increase the efficiency of conventional comminution circuits. As a case study, this research conducted a process audit of the comminution circuit in an iron processing plant to identify low-cost solutions (i.e., with no capital investment) for improving product quality and reducing maintenance and operating costs. The main challenges were the crusher operation in a partially full condition, high-pressure grinding roll operation in a non-standard condition, and poor screen efficiency. Additionally, the makeup ball size regime and ball filling were significant issues for the ball mill. Following the initial study, a series of modifications were made to the operation of the crushing and grinding circuit. This consequently resulted in 9.3% increase in the crushing plant throughput after operating the crushers in choked condition. By increasing the HPGR operational pressure and the hopper level, the BBWI of the HPGR product was reduced by approximately 5%. By modifying the screen process, the circulating load decreased by about 20%, and the screen efficiency increased from 63.5% to 89.5%. Furthermore, a new combination of makeup ball size regime decreased the P80 of the grinding circuit from 133 to 96 microns, along with a 9.5% increase in production rate.

1. Introduction

Comminution is essential for liberating valuable minerals, improving material handling, and producing controlled particle sizes [1]. High-pressure grinding rolls (HPGRs) have recently emerged as an intermediate device between fine crushing and coarse grinding [2]. Since comminution accounts for the largest share of energy consumption in mineral processing, significant efforts have focused on improving equipment efficiency [3]. Cone crusher performance strongly influences downstream processes, making optimization critical [4-5]. The shift from conventional three-stage crushing to HPGR-based circuits has increased complexity, but HPGR offers advantages such as lower operating costs and higher energy efficiency [6]. Key HPGR parameters include hydraulic pressure, roll speed, and hopper level [7-9]. In grinding circuits, simulations combined with ball wear laws have shown that optimal ball size distribution is essential for efficient breakage and minimizing ultrafine particles. A mixed ball regime (80% 80 mm and 20% 60 mm) improved fines production by 4% compared to mono-sized balls [10].

This research investigates various faults and challenges in operating conditions that significantly impact process performance. The process audit in the case study plant was used to identify operating faults and propose appropriate solutions to enhance comminution circuit

performance. All the required modifications that had a significant impact on the process were implemented at minimal costs with no capital investment required.

1.1 Iron Ore Processing of Steel Iron Ore Complex

Figure 1 shows a process flowsheet of the Steel Iron Ore Complex processing plant. The comminution circuit has been provided to prepare the desired feed for two plants. The concentrator plants are designed to produce an iron ore concentrate with a Fe grade of 68%.

Three stages of crushing were considered to provide the proper feed for the concentration plant. Jaw crusher, standard head cone crushers, and short head cone crushers were used as the primary, secondary, and tertiary crusher units, respectively. In the concentration plant, an HPGR in closed circuit with a wet vibrating screen was used as the pre-grinding circuit. The final product of the HPGR circuit (screen underflow) is fed to a ball mill-hydrocyclones circuit.

2. Materials and Methods

Plant audit was selected as a monitoring method in order to standardize the whole crushing, pre-grinding and grinding process plant. The main troubles were as follows: all the crushers operated in a partially full condition, the HPGR operated in a non-standard condition, resulting in a high amount of reject materials

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in the HPGR circuit, and the screen operated in a low-efficiency mode. Also, the ball mill operated with low ball filling (%) - defective balls and hydrocyclones worked in high solid content.

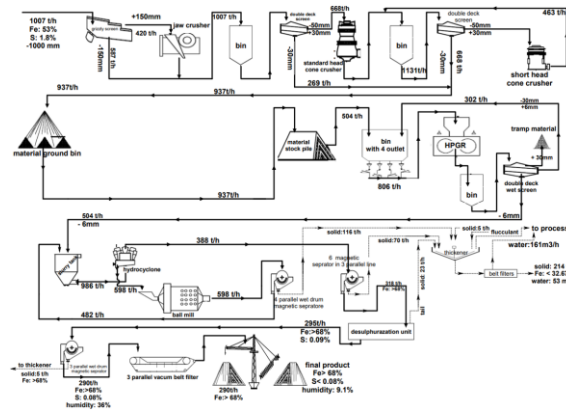


Figure 1. Process flowsheet of the Iron Ore Complex.

3. Results and Discussion

3.1. Crusher circuit

Three crushing stages were considered in the crushing circuit. Based on the design data, the feed rates of the primary, secondary and tertiary crushers were 433, 689, and 477 t/h, respectively, and the power draws of the crushers were 160, 315 and 315 kW, respectively. Process audit of primary (Closed Side Setting; CSS = 185 mm), secondary (CSS = 58 mm), and tertiary (CSS = 28 mm) crushers in 4 months showed that the average feed rates were 368, 510, and 405 t/h, respectively, and their average power draw were 115, 102, and 127 kW, respectively. The investigation results revealed that the crushers operated in a partially full condition. The reasonable solutions were to adjust the crushers' closed side setting (CSS), modify the feeders, and increase the feed rate to achieve a choke-fed operating condition. Two trials were conducted at the partially full and super-choked conditions (Figure 2). The results obtained indicated that the operating crushers in the super-choked condition reduced the P80 of the final (ground bin feed), secondary, and tertiary products by 15.2%, 17.5%, and 16.5%, respectively, compared to those in the partially full mode.

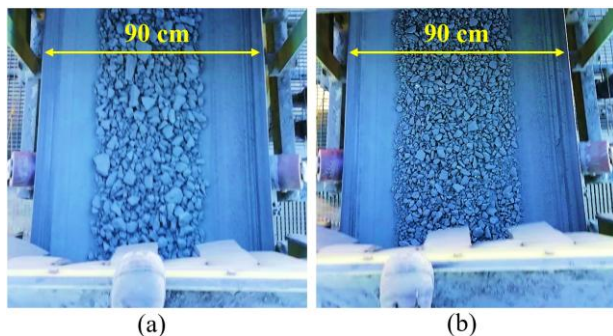


Figure 2. Product view of tertiary crusher in (a) partially full and (b) choke-fed operating conditions.

When operating the crushers in super-choked mode, as opposed to partially full, there was a 9.3% increase in plant throughput, and the size-specific energy at -32 mm decreased by 15.6%.

3.2. HPGR circuit

To increase the HPGR comminution efficiency, the operational pressure and hopper level were modified. The pressure and the hopper level were increased from 120 bar and 25% to 160 bar and 55%, respectively. Changing the operational pressure and hopper level caused an increase in the reduction ratio from 1.8 to 2.4. A snapshot view of the HPGR belt product in the operational pressures of 120 bar and 160 bar is shown in Figure 3. The ideal mode of the HPGR product is a compacted cake or flake. The product BBWI of the choked condition was obtained to be 15.2 ± 0.25 kWh/t as opposed to the BBWI of 16.1 ± 0.10 kWh/t for the partially full condition.



Figure 3. HPGR belt product in the operational pressures of 120 bar and 160 bar.

Wet screen audits showed that the upper deck's small apertures (14 mm) reduced open area, limiting fine particle passage and preventing effective stratification on the lower deck. This caused finer particles to recirculate to the HPGR, increasing the circulating load and reducing the screen product rate. Increasing two lower deck rows from 6 mm to 8 mm by operators reduced circulating load but introduced coarse particles to the underflow, raising wear by 7% and coarsening the hydrocyclone overflow. To improve efficiency and reduce rejects, increasing the upper deck aperture size to 30 mm is recommended (Figure 4).

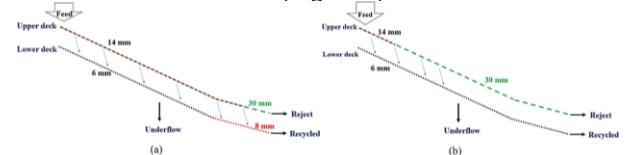


Figure 4. Wet double screen before (a) and after (b) modifications.

As the results indicated, the screen feed and underflow rate increased from 699 and 387 t/h to 738 and 463 t/h, respectively. The amount of the desired product (-6 mm material) and the material thickness on the second deck decreased from 46% and 47 mm to 20% and 33 mm, respectively. Therefore, by modification, the circulating load decreased from 79% to 59% and the screen efficiency increased from 63.5% to 89.5%. In addition, the down-stream results indicated a reduction of the ball consumption from 565 g/ton to 535 g/ton. A snapshot of

the recycled material before and after the modifications is shown in Figure 5.

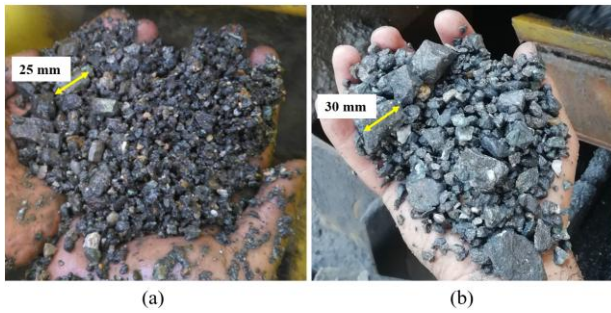


Figure 5. Recycled material of screen (a) before and (b) after modifications.

3.2. Grinding circuit

The operating parameters, such as overflow and underflow solid content, as well as operating pressure, were controlled and monitored. If the ball mill feed becomes too dilute, the wear rate of grinding media inside the ball mill increases. When it becomes too dense, it causes a reduction in the media kinetic energy and breakage efficiency. Increasing overflow solid content causes an increase in overflow d80 at the same operating pressure [10]. Table 1 shows the average operating data of hydrocyclones before and after modification.

Table 1. The average operating data of hydrocyclones before and after modification

	Design	Before modification	After modification
Underflow percent solid	75	77	76
Overflow percent solid	30	34	30
Pressure (kPa)	120	85	115

The filling charge of balls inside the mill was around 27%; it was increased to 30%. However, owing to some restrictions, it wasn't possible to reach the design by about 35%.

A random sample of balls from the mill showed that the percentage of defective balls was 29%. The defective balls were categorized into conical, holed, and layered types. These balls (broken) could cut the rubber lining of the mill due to their sharp edges and increase grinding media consumption.

Furthermore, none of the balls had a diameter of 25.4 mm (1 inch), which was supposed to be 15% of the total based on Rowland and Kjos formulas [40]. The quality of the balls is poor, as they lose their spherical shape at this size. In fact, the balls below 30 mm were deformed. The absence of small balls affects the grinding efficiency.

The optimum ball size distribution was determined to improve the operating efficiency of the ball mill through two techniques: theoretical modelling and a practical

approach. Thereupon, a new combination make-up ball size regime was proposed rather than using two-sized balls (60 and 40 mm). To decrease particles coarser than 0.5 mm (reject) 5% by weight was added to the 60 mm ball. Also, to obtain small spherical shaped balls, 15% of the 25mm ball was considered (Figure 6).

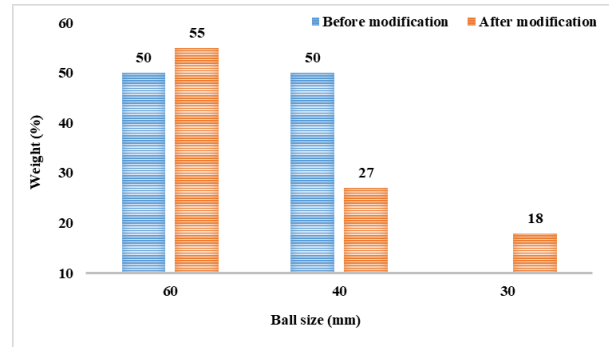


Figure 6. The old and new combination make-up ball size regime

Periodic observations from inside ball mills showed that the number of perfect balls smaller than 30 mm is observed in mills (Figure 7).

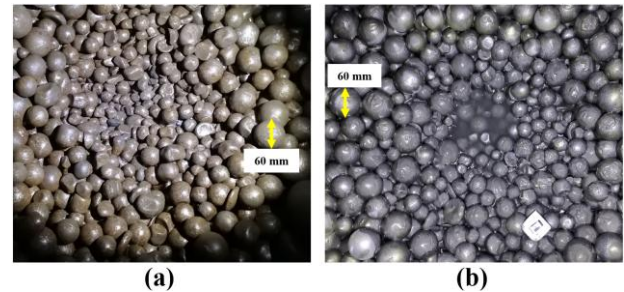


Figure 7. Balls inside mill (a) before and (b) after new combination make-up ball size regime

P80 of the final product during the optimization process decreased from 133 to 96 microns. Furthermore, the Blaine number of the final product not only increased from 980 to 1170 (g/cm²), but also the final production rate increased by around 9.5%.

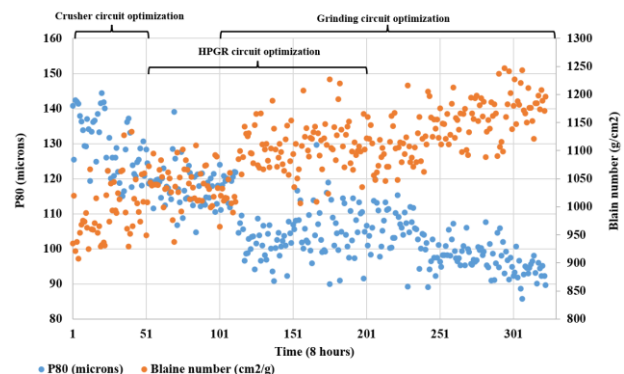


Figure 8. P80 and Blaine number of final product during optimization process

4. Conclusions

In this research work, to increase the comminution circuit efficiency, a process audit and several low-cost modification routes were presented and implemented at the iron ore crushing, pre-grinding, and grinding plant of the Steel Iron Ore Complex.

It was shown that the super-choked condition of the crushers reduced the P80 of the final product and the size-specific energy at -32 mm by 15.2% and 15.6%, respectively, compared to the partially full mode. Additionally, the crushing plant's throughput increased by 9.3%.

By increasing the HPGR operational pressure (from 120 bar to 160 bar) and the hopper level (from 25% to 55%), the particle grindability, measured as BBWI, decreased by 5.6%. In addition, the reduction ratio increased from 1.8 to 2.4.

By increasing the aperture size of the upper deck from 14 mm to 30 mm (useful area), the circulating load decreased from 79% to 59%, and the screen efficiency increased from 63.5% to 89.5%. Also, the amount of the rejected materials decreased from 1.6% to 0.5%.

By applying all previous modifications and combining the makeup ball size regimes, the P80 of the final product decreased significantly. Blaine number product during the optimization process increased from 980 to 1170 (g/cm²). Moreover, the final production rate increased by around 9.5%.

Acknowledgement

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A comparison between lab scale and pilot scale ball mill for the grinding of wet Switchgrass

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Abstract. Over the past two decades, lignocellulosic biomass has attracted growing interest for the development of second-generation biofuels. Among these, Switchgrass offers several advantages, including high sugar yields during fermentation processes and low water requirements for cultivation. To improve the accessibility of sugars to enzymes, new co-processing methods incorporating a grinding step between two fermentation phases are currently being developed to facilitate the mechanical breakdown of the material. Since drying steps are particularly costly in terms of energy and economics, the biomass must be ground to a moisture content corresponding to fermentation conditions, under which the material exhibits particularly complex rheological properties. This work proposes a combined DEM-experimental study to compare the grinding of wet Switchgrass in laboratory-scale and pilot-scale mills, with the aim of identifying the parameters governing the fragmentation processes.

1. Introduction

Dry and saturated milling processes have been extensively studied and are quite well now understood due to their numerous industrial applications, particularly in the mining and pharmaceutical industries [1,2]. However, growing interest has recently emerged in the milling of unsaturated materials, especially for biofuel applications involving the grinding of lignocellulosic biomass. Understanding the milling behavior of such unsaturated lignocellulosic biomasses requires accounting for the rheological variability of the material over a wide range of moisture content, from wet biomasses to concentrated suspensions. Although the presence of water can significantly affect grinding efficiency [3], the careful selection of process parameters remains crucial to achieve efficient feedstock milling in terms of both energy consumption and particle size reduction.

To address these two research questions, this paper presents a combined DEM modelling and experimental study, focused on the unsaturated grinding of Switchgrass. This work was conducted in the context of the American project “Center for Bioenergy Innovation”, which focuses on the development of second-generation biofuels for civil aviation from lignocellulosic biomass. Rajaonarivony et al. [4] demonstrated that ball mills are among the most efficient grinding devices for reducing particle size of fibrous materials, owing to the high frictional forces induced by grinding media. Building on this premise, the present study compares two ball mills at laboratory and pilot scales in order to evaluate the effects

of material rheology and process parameters on energy efficiency and particle size reduction.

2. Materials and Methods

2.1. DEM modelling

An in-house discrete element model implemented in C++ was developed to simulate the grinding chamber geometry of two ball mills: the laboratory-scale MM500 vibratory ball mill (Retsch®, DE) and a pilot-scale ball mill prototyped in the laboratory by Femag Industry®, FR. The discrete element method (DEM) was applied exclusively to the grinding media, using a Hertz contact model to analyse media dynamics and contact energy evolution during the grinding process. From these simulations, frictional and impact energies dissipated during contact were quantified and analysed.

2.2. Experimental framework

2.2.1. Raw material

The raw material used in this study is Switchgrass from Dartmouth College (NH, USA). Its initial D_{50} was measured to be 371 μm .

2.2.2. Milling process

In this study, two different mills were used. At the laboratory scale, experiments were carried out using a vibratory ball mill (MM500, Retsch®, DE) equipped with

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6 mm beads. The 125 mL grinding chamber is subjected to horizontal vibrations, with a frequency adjustable between 0 and 30 Hz.

At the pilot scale, a stirred ball mill prototype developed by Femag Industries®, FR, was used. The cylindric grinding chamber has a volume of 3 L, and bead motion is induced by the rotation of an impeller, with a speed adjustable between 0 and 300 rpm. The geometry of each mill is shown in Figure 1.

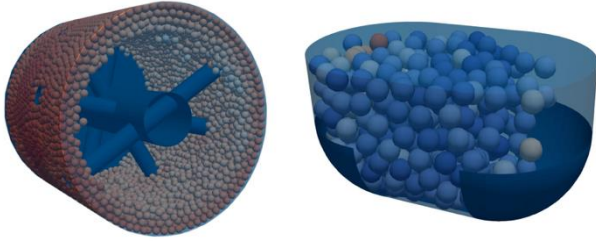


Figure 1. Grinding chamber geometries for pilot scale mill Femag (left) and lab scale mill MM500 (right).

2.2.1. Experimental design

A three-factor experimental design was conducted in each mill. The three factors selected for the study are: m_s , the dry mass of Switchgrass; m_b , the mass of 6 mm beads; and m_w , the mass of water. These parameters were chosen to cover a range of filling volumes (V_f), ratios between the dry mass of Switchgrass and the bead mass ($R = m_s/m_b$), and water contents (W). The values selected for V_f , R , and W are detailed in Table 1. For each water content, the cohesion of Switchgrass was measured using a Jenike shear cell [5], in accordance with the Mohr–Coulomb criterion. All determined values are reported in Table 2.

Table 1. Variables used in experimental design

Variables			
R	0.05	0.06	0.07
V_f (%)	27	50	73
W (%)	60	70	90

Table 2. Cohesion measurements performed at different water contents

W (%)	60	70	90
C (Pa)	147	330	4

Two response variables were chosen for this experimental design: E (in MJ), the energy consumed by the mill, and ΔS (in $\text{m}^2 \cdot \text{kg}^{-1}$), the specific surface area created after 2 h of grinding. Based on these response variables and factors, multivariable linear regressions based on the least squares method were performed according to the following expression:

$$y = \beta_0 + \sum_i \beta_i \cdot m_i + \sum_{i \leq j} \beta_{ij} \cdot m_i m_j + \epsilon \quad (1)$$

Where y is the response variable and $i, j \in \{s, b, w\}$

3. Results

3.1. Numerical modelling

Figure 2 shows the evolution of the dissipated friction energy and power for both mills as a function of the rotation speed and grinding frequency ranges allowed by each piece of equipment. The first notable observation is that the energy dissipated by friction is markedly higher in the pilot-scale mill compared to the laboratory-scale mill, with an increase of approximately a factor of 20. While the MM500 appears to reach a quasi-steady state almost instantaneously, the Femag requires a longer transient before the grinding media are fully set in motion and this regime is established.

In both cases, friction increases with increasing rotation speed or frequency following an exponential law. A significant rise in friction is observed above $\Omega = 150$ rpm, which can be attributed to the onset of the centrifugal regime leading to a maximization of frictional energy. Since efficient milling of fibrous materials such as lignocellulosic biomass relies on maximizing frictional energy, a grinding frequency of 25 Hz and a rotation speed of 300 rpm are selected for the experimental work.

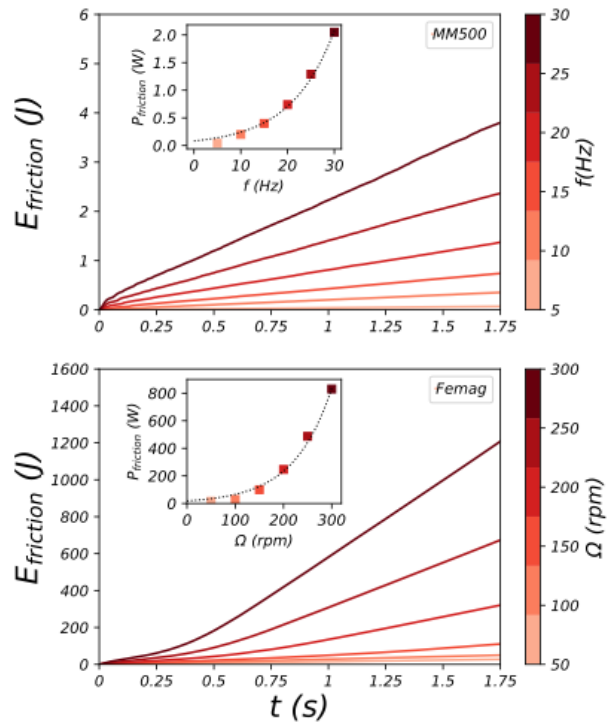


Figure 2. Dissipated friction energy and power in each mill as function of grinding frequency f or rotation speed Ω .

3.1. Experimental study

Figure 3 illustrates the linear regression performed on the response variables ΔS and E .

This regression highlights that the specific surface areas obtained with both mills are relatively similar and remain within a narrow range. In contrast, the energy consumption shows a markedly different behaviour: the laboratory-scale mill exhibits an almost constant energy demand across the tested conditions, whereas the pilot-scale mill displays three distinct clusters around 2 MJ, 3.5 MJ, and 6.5 MJ. Experimentally, these three groups correspond to the three levels of V_f .

Based on these observations, an efficiency indicator, denoted SPI (Score Power Index), was calculated for each mill as follows:

$$SPI = (\Delta S \cdot m_s)/E$$

This indicator is intended to account for the dry mass of Switchgrass processed during the comminution process. Linear regression was performed using this new indicator, and significant variables for each mill were identified based on a 5% significance level. Consequently, the following expressions relating ΔS and E were established for the two mills:

$$\frac{\Delta S}{E} \approx \frac{k}{m_b} (\text{Femag}) \quad (2)$$

$$\frac{\Delta S}{E} \approx m_s [ax^2 + (bm_b + c)x] \quad (\text{MM500}) \quad (3)$$

Where $x = \frac{w}{1-w}$ and a, b, c, k constants.

For the pilot-scale ball mill Femag (Equation (2)), particle size reduction is governed mainly by bead mass. This observation is consistent with the numerical simulations, which revealed very high frictional energy levels, likely dominating over the cohesion or drag forces associated with the presence of water.

For the lab-scale mill MM500 (Equation (3)), water appears to play a central role. The experimental results suggest that particle size reduction is enhanced at higher cohesion levels. Indeed, a more cohesive material tends to adhere to the walls of the milling chamber, facilitating its attrition by the grinding media. However, this beneficial effect of cohesion is moderated by the filling volume of the chamber as an excessively low filling ratio reduces the contact surface between the cohesive material and the beads.

Based on the previous observations, Figure 4 illustrates the relationship between the cohesion value (previously determined using a Jenike cell), the filling volume, and $\Delta S/E$ for the MM500. The data were fitted using the following expression (Equation 4):

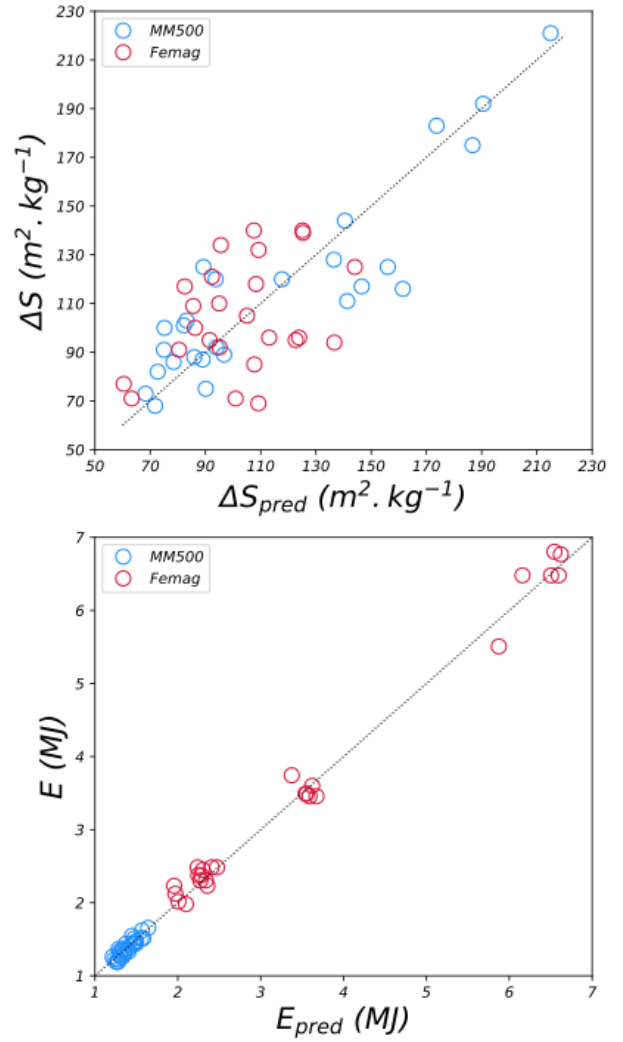


Figure 3. Measured response variables as function of the response variables predicted by the linear regressions.

$$\frac{\Delta S}{E} \approx f(C) \cdot V_f \quad (4)$$

Where $f(C) = 0.01 \cdot C^3 - 5.5 \cdot C^2 + 959 \cdot C$

Equation (4) shows that $\Delta S/E$ tends toward zero for very low values of C . In the case of Switchgrass, this condition is reached at very high-water contents, corresponding to highly diluted systems for which the creation of specific surface is difficult. To explain this, several hypotheses can be proposed.

First, the large amount of water may reduce bead velocity and, consequently, frictional energy, due to the presence of drag and lubrication forces. Moreover, in these diluted systems, the very low amount of dry Switchgrass significantly decreases the probability of interactions between fibers and grinding media, leading to poor particle size reduction.

Consequently, at the lab scale, rheology strongly impacts grinding efficiency but must be considered alongside the filling volume. While a diluted system will not be effectively ground regardless of the filling volume, cohesive materials require a high filling volume to maximize the contact surface between the beads and the feedstock, thereby ensuring efficient grinding.

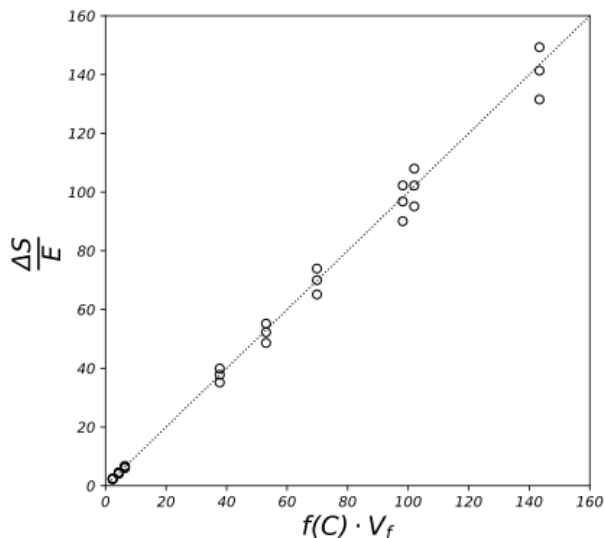


Figure 4. Relationship between the cohesion of the feedstock, the filling volume and the grinding efficiency for the lab-scale mill (MM500).

4. Conclusion

This combined DEM-experimental approach provides a deeper understanding of how process parameters and feedstock rheology affect the grinding efficiency of two ball mills. The numerical modelling was used to guide the selection of process parameters with the objective of maximizing friction.

Experimentally a relationship was established between water content, process parameters, and particle size reduction.

At the laboratory scale, water content and cohesion strongly influence particle size reduction. In contrast, in the pilot-scale mill, the change in geometry and the large number of grinding media, which generate substantial frictional energy, appear to dominate, largely overriding the rheological effects of the feedstock.

Acknowledgement

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Roller Press applications along the value chain of iron

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Abstract. Rollers Presses for Briquetting, Compaction and High Pressure Grinding Rolls (HPGR) offer variable flexible applications across multiple industries. This contribution will focus on examples along the production chain of iron from raw material in an ore mine to steel making process. High volume opportunities with HPGR and pellet feed activation between rollers are addressed in the field of comminution. In addition, basic theories of roll processing are explained to bridge them to circular economy applications like Briquetting of steel mill dust and inertisation during green steel DRI-HBI.

1. Basis

Global steel industries support significant customer needs as the basis supply for building materials, transportation and modern consumable goods. As recycling technologies and the life cycle preservation of metals are of growing interest, the majority of steel suppliers still depend on a high volume iron ore processing.

Various processing routes are available on the market [Stahl und Eisen]. Within highly optimized applications roller presses can often be found and are known for their low energy consumption, high throughput and availability, small factory footprint and preferable downstream effects [Heinicke]. By varying operating pressure and mechanical set ups (e.g. surface design), the machine can both comminute and agglomerate feed materials, even if these processes seemingly differ in physical nature. This contribution will detail roller press use cases in the production chain of iron ore and report on the linking of physical principles.

2. Physics principle

Figure 1 shows a state-of-the art Köppern type roller press. The machine consists of two counter rotating rollers, which are pressed against each other by hydraulic systems. Strong drive trains including variable speed drives and gear reducers deliver the torque needed to nip the material on the roller surface, transport it through the operating gap and perform the pressing process to enable agglomeration or comminution.

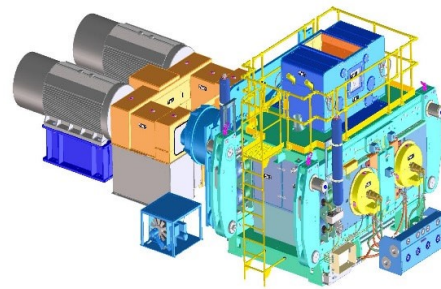


Figure 1. State of the art roller press

As every application has its own defining characteristics, regarding throughput, energy consumption and roller lifetime often determined by the feed material, a set of normalized scaling values can be used. These values are very ore dependent. Therefore, lab scale tests are done at suppliers' facilities. One major key factor is the pressure needed to transform the material within comminution or agglomeration process [Johanson].

The specific pressing force (F_{spez}), in units of kN/m^2 , is the total pressing force applied to the floating roll by the hydraulic system divided by the projected area of the roller [Schönert].

$$F_{spez} = F / (D \cdot L)$$

Where: F [kN] - total pressing force
 D [m] - roller diameter
 L [m] - roller width

Although the installed absolute forces differ significantly for different roller sizes the specific pressing force stays constant. The pressing process between the HPGR

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rollers requires about the same specific pressing force for lab scale and industrial size units to achieve the desired beneficiation effect. Therefore, a larger HPGR needs higher absolute forces.

In addition to this effect, roller press agglomeration uses significantly higher specific forces than grinding applications as per Figure 2.

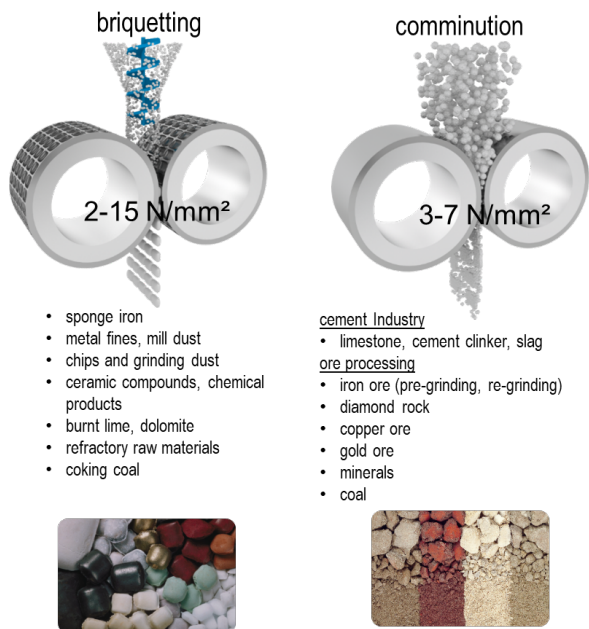


Figure 2. Differences in F_{spez} in agglomeration and comminution applications

In general, the roller press comminution process (known commonly as high pressure grinding roll, HPGR) focuses mainly on the breakage of particles along the grain boundaries while roller press agglomeration, known as briquetting, focuses on forming the single components into a compound of material. Nevertheless, agglomeration can also be found in the physics of comminution, especially if compound forming materials (e.g. clay) are included in the feed material (example for flake as per figure 3).

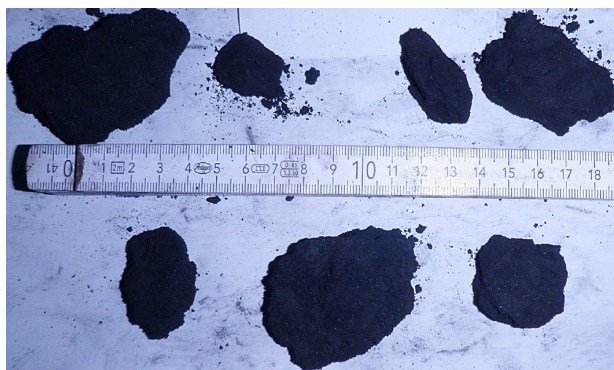


Figure 3. Example of flake from iron ore grinding

In this scenario however, the flake formation is not a goal and deagglomeration must be installed causing additional plant efforts and investment costs to overcome the problems of separation/screening downstream. Sometimes those effects are intended as they push downstream processability like stacking or pelletizing. One other option is to reduce the pressing force for this application with limiting effect for the grinding connected to it.

In the absence of those natural binders, formation of agglomerates can sometimes be problematic even at higher forces. Highly enriched iron ore normally tends not to agglomerate therefore binders must be added to assist the material processing. While bentonite has a long tradition in standard fine iron ore travel grate operations, new types are being heavily researched on the market in order to limit CO₂ emissions caused in iron ore processing [Vale]. Again, the specific pressing force can be used to limit consumables by applying higher forces. At those effects the force action scenario at the roller surface tends to force material out of the operating gap even more. Therefore, screws are introduced to guide the material in between the rollers, beneficiate deaeration of material and increase capacities of the press.

Other tricks are available to adjust the presses for comminution and agglomeration to the individual needs of the process. Experience in the detailed applications and test work is therefore a key challenge and offers the solution to overcome such limitations [Drzymala]. Some typical examples are given below.

3. Example Iron Ore PREGRINDING

A typical application for roller presses is in the tertiary crushing stage of iron ore processing. The key task is to reduce particle size for the downstream ball mill as per figure 4. Machines are operated at feed sizes of <30mm (<50mm for very big roller diameters) in open and closed circuit design. The advantage of closed circuit designs is the full limit of the maximum transfer size is sent to the downstream ball mill, as otherwise not possible in an open circuit environment.

As material passes the gap of the rollers in a full bulk scenario it might happen that coarse, top size particles are embedded in finer material which protects force introduction to those particles. Thereby there is still a statistical chance a coarse particle can survive in a HPGR and would report to downstream without introducing screen limitations.

One key advantage within the HPGR process is the introduction of so-called microcracks within the material. This means a deformation of the natural grain of the ore which reports to the downstream. The following fine grinding apparatus (e.g. ball mill) can therefore grind the materials at lower energy need and

thus much higher throughput rates are achieved. By changing of the applied pressing force those effects can be boosted and adjusted to the ore variability introduced into the system [Michaelis].

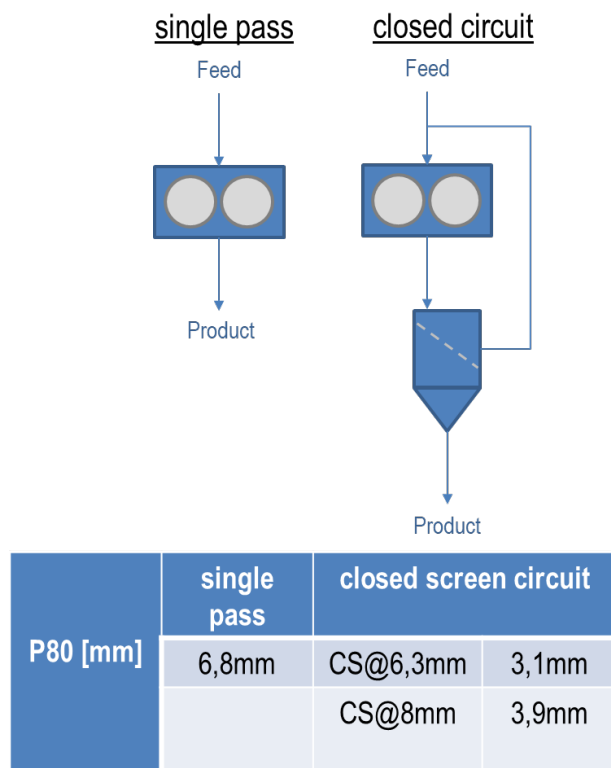


Figure 4. Examples of flowsheets for pregrinding application of HPGR and typical product sizes

4. Example Iron Ore REGRINDING

After fine grinding and beneficiation (sorting) stages for iron ore further processing of iron ore pellet feed is of major global interest. To transform iron ore pellets for ship transport and preparation for steel industries the material can be agglomerated. It is beneficial to introduce wide size distributions at high Blaine numbers to form good green pelletizing strength for rotating disks/tubes and roller presses are used to perform this task [Pietsch].

Iron ore pellet feed has special properties where water saturation and stickiness are of most interest. Figure 5 shows typical material behaviors and feeder solutions to overcome limitations [Gunter]

The pressing force again is an influencing factor as iron ore concentrate behaves like a sponge during the pressing process. If external pressure is applied, the internal pores are compressed and may be saturated with water. Thus, the internal water will drop off the material at too high forces and find its way to surfaces of the rollers then.



Figure 5. Stickiness of iron ore pellet feed and step feeder solution for HPGR

This will reduce nipping behavior of machines and limit their production. Detailed knowledge on internal structure and pressure/density behavior is one key understanding, which is accessed during test work in order to find the right optimization for the specific material [Staskiewicz].

5. Example Iron BRIQUETTING

Using iron ore concentrate in the sintering process demands for adding bentonite binder as standard process for travel grate applications and agglomeration disks. Disks are limited to gravity forces by building the compound of materials for the green pellets. To increase binding forces roller presses might be used to enable lower binder demand and ongoing research is being done in this field. This may also optimize the high temperature needs for the downstream beneficiation as well. Applications of roller presses for fine powders are not new as dust residues in steel mill plants have been processed for many decades.

One special application is the briquetting of direct reduced iron under inert conditions by roller presses to meet global shipping standards. Figure 6 shows a typical press and principle of a DRI-HBI application. Forces are very high as to form a solid unlimited agglomerate, which must be separated directly after the press for handling purposes. The briquetting forces deactivate highly reactive surfaces of the pure iron, so that the re-oxidation process is highly inertised and allows for long range transport without firing risk [Bergendahl].

Again, the specific pressure is set and checked during test work to clear safe densities for $>5 \text{ t/m}^3$. With respect to changing industries in the field of H2 operations, the agglomeration behavior needs consideration along with research into roller surface options and pressure ranges.

Nevertheless, these examples show again that the physical details of the process require adjustments of the roller press to the individual task in order to enable higher flexibility.



Figure 6. DRI-HBI application of roller presses

6. Summary

The value chain of iron is geographically dispersed and includes various processing facilities and methodologies across the globe. Roller presses can contribute to optimization of the production through the ability to adjust pressures during operation. This enables fine-tuning of the roller press to the local need of iron ore grinding, pellet feed preparation or agglomeration processes. Changing goal definitions towards future applications of H₂ routes or recycling technologies are boosted not only by this pressuring flexibility but also by expanding the range of specialty surface designs, which have been developed and proven through more than 100 years of experience in various roller pressing applications.

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Vale, ..^

Influence of microstructure on slag breakage behavior

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Abstract. This study investigates deformation, fracture propagation, and liberation mechanisms in lithium aluminate-bearing slags with varying cooling histories and resulting microstructures. In-situ compression experiments were conducted using X-ray computed tomography (XCT) combined with digital volume correlation (DVC) to quantify local deformation, fracture development and strain evolution during loading. Image-based analysis was used to quantify the relationship between fracture behaviour to microstructure, pore network and target phase features and liberation behavior and provides a framework to link the design engineered artificial minerals with improved comminution.

1. Introduction

Understanding the breakage and liberation behaviour of slags improves their recyclability and ensures that slag can serve as a secondary raw material for low concentrated valuable elements.

These elements are transferred to engineered artificial minerals (also called EnAM). To liberate the valuable mineral phases, comminution is needed. Besides generating smaller particles out of the parent particle and new surfaces, the valuable mineral phases (= target phases) become accessible for downstream separation processes. Since milling and crushing are cost-intensive processes in mineral processing, optimization of breakage behavior and liberation is needed to increase process efficiency.

The relationship between microstructure, fracture behaviour, and liberation can be described through fracture mechanisms. Early liberation theory is introduced by Gaudin to distinguish between liberation by detachment and liberation by comminution [1]. Liberation by detachment describes fracture along grain boundaries or interfaces where attachment forces between adjacent phases are weaker and result into selective fracturing. In contrast, liberation by comminution describes fracture propagation through mineral phases independent of their interfaces, where liberation occurs mainly through particle size reduction and surface generation. In practice, fracture behaviour usually lies between these boundary cases and is influenced by the local microstructure.

Microstructural features, e.g. grain size, phase intergrowth, pores, defects and crystallographic interfaces, influence local stress distributions and therefore can determine preferential fracture pathways [2]. Consequently, fracture propagation in heterogeneous materials is not random by default. Preferential breakage occurs when fractures interact more frequently with

specific phases, interfaces, or defects which lead to selective fragmentation of certain microstructural domains [3]. Such behaviour is relevant for engineered artificial minerals, where cooling and crystallization conditions determine target phase properties and therefore may affect comminution and liberation results [4].

This study investigates deformation and breakage mechanisms in lithium-bearing slag, a product of lithium extraction out of pyrometallurgical processes. In-situ X-ray computed tomography (XCT) compression and impact experiments are combined with digital volume correlation (DVC) to quantify internal strain and localize deformation during compression. The measured strain fields is then linked to the initial microstructure and mechanical properties of the slag sample.

2. Materials and methods

2.1. Materials

Synthetic lithium aluminate-bearing slags are produced at IME Process Metallurgy and Metal Recycling, RWTH Aachen. The slags vary in terms of cooling conditions and feed compositions which lead to different microstructures of lithium aluminate as a target phase.

Cylindrical samples were prepared to ensure reproducible sample geometry and stable positioning within the in-situ load cell during compression (Figure 1). The cylindrical geometry minimizes movement of the parent slag particle and provides more defined contact conditions between the sample and the compression pistons.

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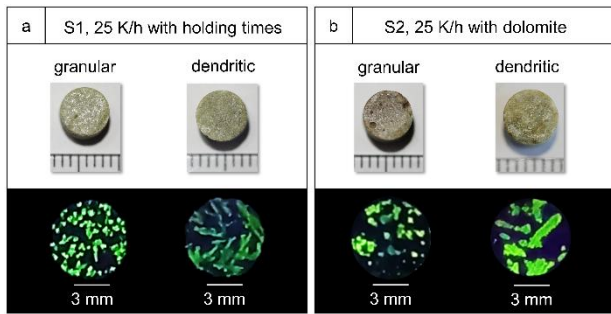


Figure 1. Cylindrical shaped slag samples, labelled as granular and dendritic under visible light and UV light conditions. The green fluorescent mineral phase is lithium aluminate (target phase). Slags come in different slag batches under different cooling strategies, e.g. a) 25 K/h with holding times, b) 25 K/h without holding times with dolomite.

2.2. Methods

2.2.1 Compression experiments

To compress slag samples, the CT5000 in-situ load cell (5 kN) from Deben UK Ltd. Was used and coupled with a Zeiss Xradia 510 Versa XCT system. Samples are positioned between two parallel silicon nitride ceramic pistons and compressed while force-displacement data and XCT projections were monitored simultaneously. The displacement rate is 0.1 mm/s and samples had a preload force of 5 N.

XCT settings are limited by the size of the load cell and attenuation coefficient of the ceramic, carbon-fiber window of the loadcell and the sample and lead to a voxel size of 8 μm .

2.2.2 Digital volume correlation

Dynamic and high-resolution scans from compression experiments on slag samples were acquired with CoreTOM in collaboration with UGCT, Ghent University – Centre for X-ray Tomography. Together with UGCT, a 4D image analysis workflow is developed and applied. The data is mainly processed using digital volume correlation (DVC) in Avizo. Image registration with respect to the initial scans prior to compression will be carried out to correct bulk motion and misalignment. Subsequently, dynamic scans will be analysed using DVC to derive displacement vectors and strain fields. The resulting displacement vectors will then be used to estimate the overall strain in the high-resolution scans.

3. Results and discussion

This study will provide quantitative insights into breakage mechanisms of lithium slag, including pore collapse, fragment rearrangement and fracture propagation. It introduces a reproducible workflow for large-scale 4D XCT analysis and generate HQ datasets for open access data management.

Recent findings are that lithium aluminate phase exhibit pre-damages prior to compression. In collaboration with Institute of Stochastics in Ulm University, three samples were virtually reassembled in three dimensions to investigate breakage mechanism quantitatively. It was shown that existing target phases can influence the

pathway of fractures, i.e. target phases may act as defects that connect multiple fractures. With the increase of pore number and size, the pore network will dominate the direction of the fractures instead of the localization of target phases. In that case, fractures occur mainly between pores and lead to breakage of solid phase bridges.

During compression, the target phases act as defects, can influence the trajectory of fractures and tend to break into finer fragments than the matrix phase. Compact (granular) microstructures support preferential breakage, i.e. fracturing within a specific mineral phase such as lithium aluminate. Dendritic target phases tend to show more random fractures (Figure 2).

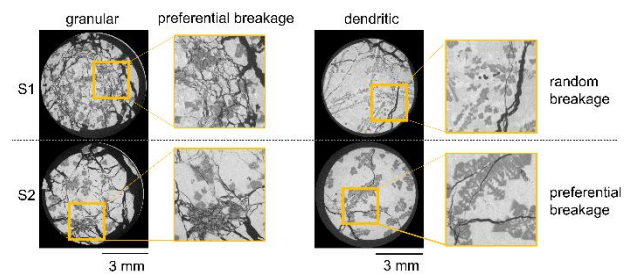


Figure 2. Qualitative image-based assumption of fracture mechanisms for different slag batches and microstructures.

Surface liberation increases with ongoing compression for all investigated slag types and microstructures. However, the increase is not proportional to the occurrence of fracture events. Small force drops usually lead to cracks on the periphery of the slag sample or fragments are generated without exposing the target phase substantially. Therefore, fracture initiation alone will not be sufficient enough to achieve effective liberation, although lithium aluminate may have shown features for more selective fracturing, e.g. containing pre-damages and producible in various microstructures.

Granular-labelled slag samples have shown to generate larger number of fine target phase domains with high surface liberation values. This indicates that fragmentation frequently intersected with lithium aluminate domains and lead to new accessible target phase surfaces. In contrast, target phase domains remain interconnected even after fracture beyond fracture events in dendritic samples and have shown lower overall surface liberation.

The image-based approach is able to approximate liberation behavior by means of geometric descriptors derived from segmented XCT data. Descriptors are able to quantify boundaries, fragmentation and connectivity and have enabled to put microstructure and fracture into relation to liberation. These image-based proxies are therefore suitable to estimate liberation trends between different microstructures.

However, image-based liberation descriptors are only an approximation of physical liberation. Surface liberation does not directly mean that there is a complete detachment because fine target phases can still be interlocked in the fragments despite appearing exposed in segmented data. This stems from segmentation uncertainty, voxel

resolution and partial volume effects that may influence the quantification of interfaces and small fragments. Therefore, image-based descriptors should be seen as proxies for liberation potential than direct measurements of the process recovery.

4. Conclusion

This study presents the combination of in-situ X-ray computed tomography with digital volume correlation to locate deformation, fracture propagation, and breakage mechanisms in lithium-bearing slags. The workflow enables three-dimensional analysis of displacement and strain evolution during compression and links local deformation behavior and the slag microstructure.

Overall, the results show that breakage behavior in slags can not be explained only by mechanical loading conditions but must be interpreted in combination of microstructure, defect distribution, and pore architecture. The presented methodology provides a framework for connecting microstructural characterization with comminution behavior and can support the design of engineered artificial minerals with improved liberation and improved recyclability in downstream processing approaches.

Acknowledgement

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Mechano-grinding of Platinum slags using stirred mills – key things to consider

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Abstract. The reprocessing of platinum-bearing slags presents significant opportunity for recovering residual platinum group metals (PGMs); however, the complex mineralogy and refractory nature of slag phases demand highly efficient comminution strategies. Smelting at high temperatures alters both the composition and grain structure of the material, significantly impacting their grinding response. In the reprocessing of platinum-bearing slags several technologies have been used. However, grinding of these slags using conventional ball mills have resulted in unresolved liberation challenges. Stirred milling technologies, with their capability for fine and ultrafine grinding, offer a promising alternative for processing these challenging secondary resources. This paper examines the grinding behaviour of platinum slags in stirred mills, focusing on key operational, mineralogical, and process-design factors that influence performance. A mechano-grinding approach is adopted to reduce activation energy and enhance particle breakage. Experimental studies were conducted on two platinum slags with different mineralogical characteristics sourced from platinum operations in South Africa. By integrating experimental findings with industry experience, this paper provides a practical framework for optimising stirred mill performance in slag reprocessing flowsheets, ultimately enhancing PGM recovery and improving the sustainability of smelting operations.

1. Introduction

The recovery of platinum group metals (PGMs) from secondary resources has become increasingly important due to declining primary ore grades and increasing pressure to improve the sustainability of metallurgical operations. Platinum bearing slags, generated during smelting operations, contain residual PGMs that are a potential economic benefit, but also present a processing challenge. These materials tend to have a complex mineralogy and often refractory nature [1], which results in poor liberation and inefficient downstream recovery.

Smelting at high temperatures alters the physical and chemical characteristics of the original concentrate, modifying the phase composition, grain size, and the textural association of PGMs within the matrix [2]. These transformations strongly influence the response of slags to comminution. Conventional milling has been applied in slag reprocessing circuits; however, such mills require a high energy input in order to achieve adequate liberation sizes. Thus, unresolved liberation challenges remain a key bottleneck in the effective treatment of platinum-bearing slags.

Stirred milling technologies, which have a high energy intensity and are more energy efficient at finer grinding sizes, are a promising alternative for processing challenging secondary materials. In particular, mechano-grinding approaches can promote enhanced particle breakage through increased stress intensity and potential

mechanochemical activation, leading to reduced activation energy requirements. However, limited systematic studies have examined the grinding behaviour of platinum slags in stirred mills coupled with recovery of valuable minerals using froth flotation. This paper investigates the mechano-grinding response of two platinum-bearing slags sourced from South African operations, with the aim of identifying key operational and material-related factors that influence stirred milling performance in slag reprocessing applications and their effect on metal recovery downstream.

2. Methodology

2.1. Equipment and materials

Experiments were conducted using a laboratory-scale vertical stirred mill, shown in Figure 1. The mill is fitted with a pin-type impeller consisting of two layers of two pins, which generate high shear and impact forces within the grinding chamber. This configuration promotes efficient energy transfer to the media-particle system through intense stressing conditions.

The selection of this mill was guided by the need to carry out controlled tests on small platinum bearing slag samples. The pin mill would allow small quantities of slag material to be processed while still maintaining stress environments that can be scaled up to what is encountered in industrial size mills.

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Two platinum-bearing slags were sourced from South African operations. Prior to slag testing, platinum-bearing ore and flotation tailings were used in preliminary campaigns to establish an operational envelope and understand mill response across a broader range of conditions. Tests with slag material were performed in the operational envelopment that had promising results for both platinum-bearing ore and tailings samples.



Figure 1. Laboratory scaled vertical stirred media mill, showing the stirrer and bucket beside it. Taken at the University of Cape Town.

2.2. Operational Parameters

A parametric study was conducted to evaluate the influence of stirrer speed and grinding media size on milling performance and energy consumption. Stirrer speeds of 448 and 558 rpm were investigated, in combination with media sizes of 3.5 and 5 mm.

All experiments were conducted in batch mode, with grinding durations of 15, 30, and 45 minutes. At each sampling interval, particle size distributions were measured, and specific energy consumption was calculated based on power draw and grinding time.

To link the comminution performance with downstream recovery, flotation tests were conducted on each milled product. Mass pull and PGM recovery were used as indicators of liberation efficiency and process performance.

The experimental matrix enabled the identification of operating conditions that balance energy efficiency with sufficient particle size reduction for effective downstream recovery.

3. Preliminary Results

The study demonstrates a strong dependence of specific energy on both stirrer speed and media size. A minimum energy consumption was observed at a media size of 3.5

mm and stirrer speed of 448 rpm, indicating an optimal balance between impact frequency and stress intensity.

The signature plot for platinum-bearing ore (Figure 2) shows that increasing stirrer speed leads to higher specific energy consumption, along with finer product sizes. This suggests that at higher speeds, energy input may exceed the necessary energy threshold to process the material economically.

Similarly, the use of smaller media resulted in higher specific energy consumption. Although smaller media increase the number of contact points and enhance fine grinding, the reduced stress intensity per collision appears insufficient to effectively break the relatively hard and refractory slag phases.

Conversely, larger media (5 mm) provide higher stress intensity but reduce the frequency of collisions, limiting overall breakage efficiency. These findings are consistent with a mechano-grinding framework, where both energy efficiency and breakage effectiveness are governed by the interaction between operational parameters and material characteristics.

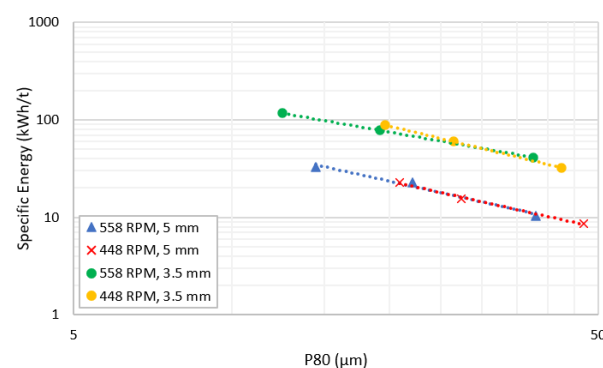


Figure 2. Signature plot showing specific energy as a function of particle size for different stirrer speeds and media sizes for platinum-bearing ore.

Tests conducted on platinum-bearing slags (Figure 3) within the identified operational window exhibited similar trends to those observed for the ore. In this case, the effect of media size was investigated at a fixed stirrer speed.

The use of larger media (5 mm) resulted in lower specific energy consumption at coarser product sizes; however, energy consumption increased more sharply as finer product sizes were targeted. In contrast the 3.5 mm media exhibited a more gradual increase in specific energy with decreasing product size.

This behaviour suggests that while larger media provide higher stress intensity suitable for coarser breakage, they become less efficient for grinding at finer product sizes due to reduced collision frequency. Smaller media, despite lower stress intensity, provide more frequent stressing events, making them more energy-efficient for achieving finer product sizes.

Froth flotation results for the ground slags are presented in Figure 4, highlighting the effect of media size used during feed preparation. Solids recovery increased with grind time for both media sizes, corresponding to increased energy input and finer particle sizes, which likely improved mineral liberation. This effect was more

pronounced for material prepared with 5 mm grinding media, with little difference in solids recovery observed between 45 minutes and 60 minutes for the 3.5 mm prepared feed. This feed also yielded lower solids recovery while maintaining comparable water recoveries. The consistently high water recoveries observed for both cases suggest significant entrainment of fine particles. The similarity in water recovery, despite differences in solids recovered may not be entirely due to true flotation, but rather due to entrainment. This points to limited selectivity under the tested conditions and highlights the need to better control froth stability and fine particle recovery. Further tests are being conducted to characterise the solids recovered in the froth flotation tests.

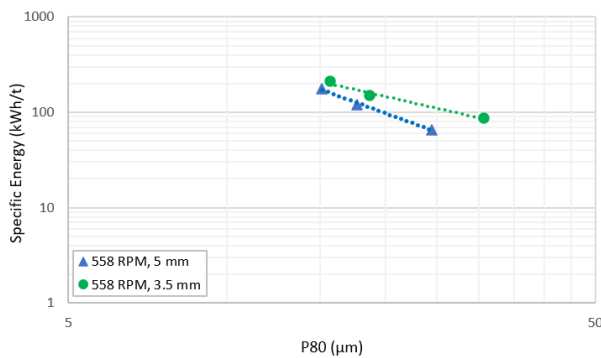


Figure 3. Signature plot showing specific energy as a function of particle size for optimal stirrer speed and different media sizes for platinum-bearing slags.

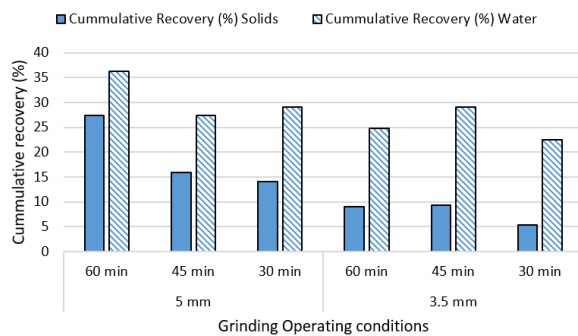


Figure 4. Cumulative recovery of solids and water in froth flotation tests for flotation feed prepared with 5 mm and 3.5 mm grinding media.

4. Conclusions

This study demonstrates stirred milling can be used in the comminution of platinum-bearing slags, particularly where conventional milling fails to achieve adequate liberation. The study highlights that both stirrer speed and media size play a critical role in determining grinding efficiency. For the pin mill size employed operating at a stirrer speed of 558 rpm and media size of 3.5 mm resulted in a higher specific energy, with limited corresponding gains in particle size reduction, indicating suboptimal energy consumption under these conditions. Froth flotation results showed consistently high water recoveries, suggesting significant entrainment of fine

particles and consequently reduced selectivity. This indicated that improved control of particle size distribution and froth conditions will be necessary to enhance downstream recovery performance.

The study provides insights into the mechano-grinding behaviour of platinum slags and establishes a basis for further investigation into the links between mineralogy, stress environment, and downstream recovery. These findings contribute to the development of more energy efficient and sustainable slag reprocessing flowsheets for enhanced PGM recovery.

Acknowledgement

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DEM simulation of the compaction behaviour of lactose powder combined with μ CT analysis

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Abstract. Powder compaction is a key step in many industrial processes, where the applied mechanical stresses can cause plastic particle deformation or breakage, which influences the packing behaviour and thus the mechanical strength of the bulk material. In this work, the compaction behaviour of lactose powder is investigated experimentally and numerically to improve the predictions of compressibility and the packing structure during the compaction process. The particles are compacted under different normal stresses in an in-situ micro-computed tomography (μ CT) compaction cell in a cylindrical die. The μ CT imaging allows local analysis of the packing structure, particle displacements, and contact development during compaction. The experiments are used to validate simulations with the Discrete Element Method (DEM), which enables a direct comparison of the porosity and stress development in the particle bed for different particle sizes between experiment and simulation at different compaction stresses.

1. Introduction

Powder compaction is a fundamental operation in many industrial processes such as tableting, briquetting, calendaring and extrusion, where the mechanical behaviour of the particles determines the final product properties. In practice, particulate products consist of particles that are not only distributed in size but also in their mechanical properties, as commonly observed in pharmaceutical formulations. This leads to a loading situation that strongly depends on local concentration, packing arrangement, and particle properties.

During compaction, the deformation of a particle bed typically progresses through three stages: particle rearrangement, elastic deformation, and plastic deformation or even particle fracture when exceeding the mechanical material strength. In order to understand and optimize this process, continuous methods such as finite element method (FEM) or discrete methods such as the discrete element method (DEM) are commonly used.

Experimental insight into micromechanical interactions can be obtained using in-situ micro-computed tomography (μ CT), which allows local analysis of the packing structure, particle displacements, and contact development during compaction.

In DEM simulations, contact forces and particle deformations can be directly resolved using suitable contact models, providing detailed insight into the micromechanical interactions that are not accessible in experiments. The elastic-plastic deformation can be described with our previous developed contact model [1] that captures the yield point at the transition from elastic to plastic deformation using measurable mechanical properties of the particles.

2. Materials and methods

The compaction behaviour of lactose powder was investigated experimentally and numerically. Lactose powder produced by spray drying was used in this study. The morphology of the lactose particles was analysed by light microscopy and scanning electron microscopy (SEM) (Figure 1).

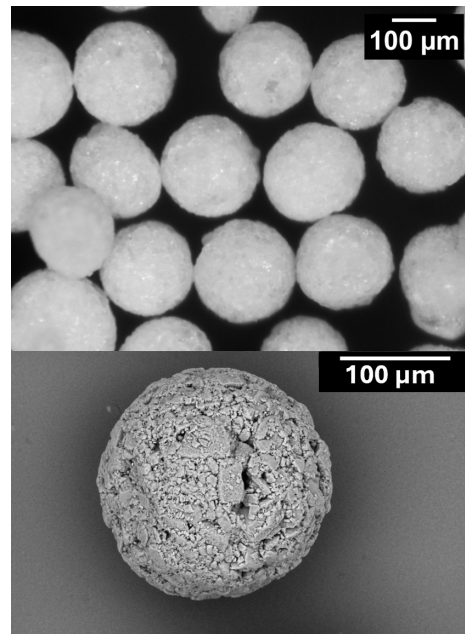


Figure 1. Optical analysis of the lactose particles with light microscope and SEM.

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The mechanical properties of the particles were conducted with single particle compression tests using a Nanoindenter (TI Premier Hysitron, Bruker). Additional compression tests were performed to investigate particle fracture behaviour under increased load.

Compaction tests were carried out with an in-situ force cell (Figure 2), which can be integrated into the μ CT (TomoScope L, Werth Messtechnik GmbH). The particle bed was subjected to different normal stresses to analyse the evolution of the packing structure and the particle displacements.

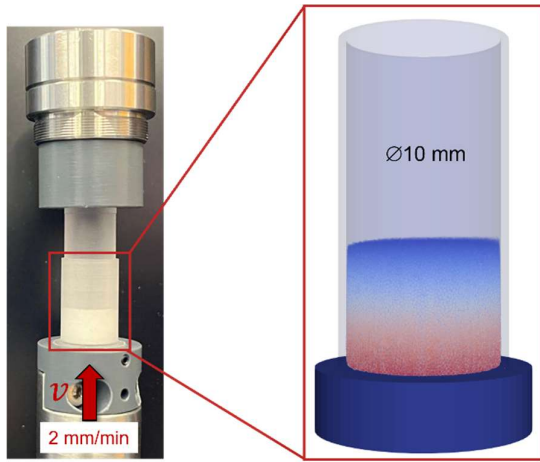


Figure 2. Experimental in-situ setup used for μ CT compaction tests.

3. Results

The results from single-particle compression tests reveal that particle deformation is initially governed by elastic and plastic behaviour, followed by fracture at higher stresses (Figure 3). This indicates that particle breakage becomes relevant at elevated compaction stresses and must be considered in the analysis of the compaction process.

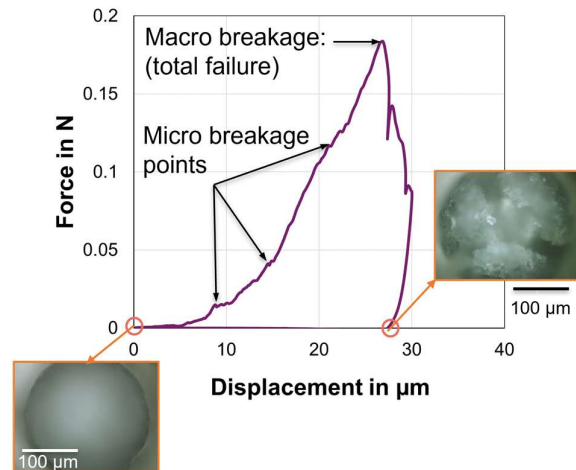


Figure 3. Typical force displacement curve of the particle compression test until breakage.

The μ CT experiments provide detailed insight into the packing structure during compaction. With increasing normal stress, a densification of the particle packing is observed, accompanied by particle rearrangement, plastic deformation, and a reduction in porosity. At higher stresses, particle fracture occurs at the surface of the bed. The DEM simulations show good agreement with the experimental results in terms of porosity and overall compaction behaviour (Figure 4).

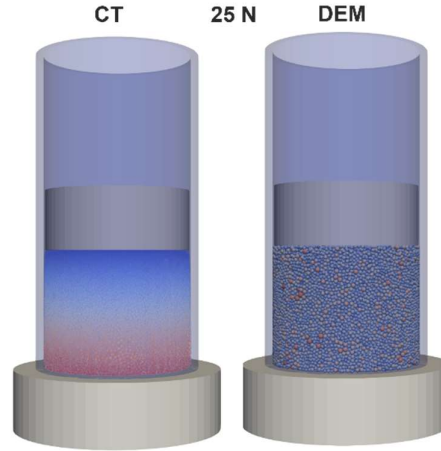


Figure 4. Compaction test at 25 N showing μ CT reconstruction (left) and DEM simulation (right).

The simulations provide information on contact forces, particle deformations and stress distributions within the particle bed. An increase in contact number and local stresses is observed with increasing compaction stresses. The distribution of plastic deformation within the particle bed and the porosity distribution over the particle bed height were analysed for increasing compaction stresses. Furthermore, good agreement between experimental and numerical compressibility was observed.

4. Conclusions

This study investigated the compaction behaviour of lactose powder using a combined experimental and numerical approach based on in-situ μ CT measurements and DEM simulations. The results show that compaction is governed by particle rearrangement, plastic deformation, and particle fracture at higher compaction stresses. The μ CT experiments provide detailed insight into the structural evolution of the particle bed, while DEM simulations provide access to particle deformations and stress distributions. The combined approach improves the understanding of compressible particulate systems and supports the development of more predictive models for industrial compaction processes.

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Wet grinding of thermoplastics

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Abstract. Fine microparticles made from engineering and high-performance thermoplastics are of great interest for modern manufacturing methods of Industry 4.0, i.e. additive manufacturing processes, such as powder bed fusion of polymers with a laser beam (PBF-LB/P). The production of very fine polymer particles with a size of less than 10 micrometers via dry grinding is difficult for amorphous plastics and nearly impossible for engineering and high-performance thermoplastics, such as polybutylene terephthalate, polyoxymethylene, or polyaryl ether ketone. However, fine polymer microparticles of the aforementioned plastics can be easily produced by wet grinding addressed here. For PBF-LB/P, in addition to flowability, the thermal properties of the thermoplastic, i.e. its melting and solidification temperatures as well as melt crystallization kinetics are crucial. Therefore, damage to the polymer during the comminution process and contamination of the product due to grinding media wear should be minimized. The ground products are thoroughly characterized using vibrational spectroscopy, X-ray diffraction, and differential scanning calorimetry. The dependency of product properties on stressing conditions and system composition is discussed in view of the necessary mass specific comminution energy and in view of minimization of grinding media wear. Experimentally determined grinding limits are discussed in relation to the mechanical properties of thermoplastics.

1. Breakage of plastics

Polymers are materials that are difficult to grind due to their viscous or viscoelastic properties. Size reduction of plastics or rubber by comminution is necessary, for example, in recycling or for polymer-based particulate products such as toner systems, powder coatings or powders used in laser powder bed fusion additive manufacturing of polymers (PBF-LB/P). In order to break a particle, the elastically stored energy within the material must be greater than the critical energy required for crack propagation [1]. The behaviour of viscoelastic materials can be described by the complex Young's modulus (E^*), which is made up of the elastic storage modulus (E') and the loss modulus (E''). Therefore, to efficiently break a viscoelastic material, it is necessary to ensure that the energy introduced into the particle by stressing in a mill is stored elastically rather than dissipated. Furthermore, a minimum stress energy must be applied to the material to allow for crack propagation. As E' and E'' of a polymer depend significantly on temperature and stressing velocity, fine comminution of thermoplastics is usually performed at reduced temperatures and high stressing velocity. Under these conditions, viscous dissipation can be significantly reduced. To improve the grindability of visco-elastic materials such as polymers or other organic matter, they can be pre-cooled using liquid nitrogen or carbon dioxide. Pre-cooling is particularly important for the comminution of rubber-elastic materials, especially for fine comminution. Impact mills, cutting mills, pin mills, jet mills or pan mills are employed for the

comminution of viscoelastic materials to account for high impact velocities. Pin mills and counter-rotating pin mills are recommended for fine comminution of polymers. The fine comminution of viscoelastic materials such as polymers is particularly costly: the mass-specific energy input required for a product fineness below 100 μm is estimated to be 10 to 50 times higher than that required for a brittle material of the same size.

Despite the widespread use of plastics, including fine polymer powders, few studies have systematically investigated the effect of process temperature on breakage and the size reduction process of thermoplastics. For dry comminution, for example, bin Ahmad and Ashby [2] investigated the failure mode of polymers in dependence on temperature and stress. They compiled fracture maps of failure for PMMA, PS, polyisobutylene and an epoxy resin, enabling the prevailing fracture mode in compression and tension to be assessed as a function of temperature (normalised to the respective glass transition temperature). They identified four modes of deformation and fracture: brittle fracture, ductile fracture, cold drawing, and viscous flow. Brittle fracture occurs at high stresses and low temperatures. Green et al. [3] exploited the temperature dependence of the failure mode of thermoplastics in impact comminution of PET-PVC mixtures in a hammer mill. PET and PVC flakes measuring between 4.6 and 7.4 mm in diameter and around 0.7 mm in thickness were subjected to dry comminution under identical stressing conditions at ambient temperature and at liquid nitrogen temperature.

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While PVC stressed at room temperature exhibited ductile fracture and a bimodal product particle size distribution, the IN₂ pre-cooled PVC exhibited brittle fracture and a monomodal product particle size distribution shifted towards smaller particle sizes. A more detailed discussion on breakage mechanism of polymers can be found in [4]. In own work wet comminution of thermoplastics in stirred media mills was investigated for amorphous plastics, such as polystyrene (PS) and semi-crystalline engineering and high performance thermoplastics including polybutylene terephthalate (PBT), polyoxymethylene (POM) and polyether ether ketone (PEEK) [5-8]. Depending on the thermoplastic and the mode of stressing, either a brittle or a ductile fracture was observed. In the case of PEEK, graze formation occurred prior to breakage. This increased the fracture toughness and led to unusual grinding kinetics [5]. The formation of crazes and viscous energy dissipation explain why polymers are harder to break than inorganic (brittle) matter. Upon reduction of the temperature, the formation of crazes is less pronounced, i.e. the material behaves more brittle leading to improved grindability. An advantage of the wet comminution process compared to dry grinding of thermoplastics is that it allows for very fine product particles at moderately reduced temperatures, which amongst other is due to the higher stress numbers [9] stirred media mills provide compared to impact comminution. In the case of PS product particles as small as 2 micrometers ($x_{50,3}$) could be obtained [5]. Within the conference contribution the process parameter dependencies during wet grinding of thermoplastics will be discussed in greater detail.

For this extended abstract we limit the discussion to the grinding limit of thermoplastics and the effect of grinding media wear on product properties relevant for PBF additive manufacturing of polymers, first and foremost the effect of grinding media wear on melt crystallization.

2. Grinding limit of plastics

There are different model pictures for the grinding limit of brittle matter. Brittle materials are known to become more ductile as the particle size decreases, cf. the brittle-ductile transition. Thus, the grinding limit can be defined as the critical particle size at which the brittle-ductile transition occurs. Another widely accepted explanation of the grinding limit for brittle materials is that the minimum size of a particle produced via comminution is given by the distance between two adjacent cracks. Kniecke et al. [10] have demonstrated that for brittle materials the ultimate grinding limit is independent of stressing conditions, but dependent on defect storage. In this model, size reduction continues until single-crystalline, defect-free nanoparticles are produced. For polymers, i.e. materials exhibiting viscous and plastic behaviour, the extension of the plastic zone δ_c according to Dugdale [11, 5] may serve as an estimate for the limiting particle size obtainable by grinding:

$$\delta_c = \frac{K_{Ic}^2}{2 \cdot \sigma_F \cdot E} \quad (1)$$

Here K_{Ic} is the fracture toughness, σ_F is the yield stress and E the Young's modulus. Particles of a size being smaller than δ_c were expected not to break in the model picture, but only be deformed plastically. The extension of the plastic zone according to Dugdale for the thermoplastics considered in own work and calculated for 20°C taking typical material parameters into account is summarized in Table 1. While the experimentally observed grinding limit for PS is close to the extension of the plastic zone, remarkably, for the semi-crystalline thermoplastics grinding products smaller than that characteristic length could be produced.

Table 1. Extension of the plastic zone δ_c calculated according to eq. 1 (at 20°C) and observed minimal product particles sizes ($x_{50,3, \min}$) in wet comminution of selected thermoplastics in ethanol (at given process temperature). The Young's modulus is between 2500 MPa and 3200 MPa for the investigated polymers.

	K_{Ic} [MPa·m ^{0.5}]	σ_F [MPa]	δ_c [μm]	$x_{50,3, \min}$ [μm]
PS	0.80	55	1.8	1.9 (-40°C)
PEEK	5	100	32.9	4.2 (-30°C)
POM	4	65	45.6	5.0 (-30°C)
PBT	5	55	37.7	8.0 (15°C)

3. Influence of grinding media material on wear and melt crystallization kinetics of the thermoplastic comminution products

In laser powder bed fusion of polymers the feedstock powders do not only have to fulfil certain demands with respect to particle and bulk solid characteristics, such as dense packing and good flowability during the additive manufacturing process, which can be controlled by a narrow particle size distribution and particles of (close to) spherical shape, which e.g. can be produced by a thermal rounding process and the application of flowing aids [6], but also thermal -cf. the so-called 'sintering window', which is the difference between melting and solidification onset temperatures or the melt crystallization kinetics- and rheological material properties have to be well-tuned and ideally should not deteriorate during powder formulation. In a study by Tischer et al [8], PBT was wet ground in a stirred media mill at 20°C using ethanol as the dispersing medium at identical mass-specific energy inputs by applying grinding beads of 2 mm size of different materials, namely silica (SiO₂), chrome steel, cerium-stabilised (ZrO₂ (Ce)) and yttrium-stabilised (ZrO₂ (Y)) zirconia. The product particle size showed the same dependence on the mass-specific energy input irrespective of the used grinding media material. Figure 1 a shows the portion of grinding media wear caused by abrasion during the grinding process for products recovered after 15 hours process time. The (maximum) stress energy $SE_{\max}$ (stress intensity) [9] was 0.9 mJ for all experiments.

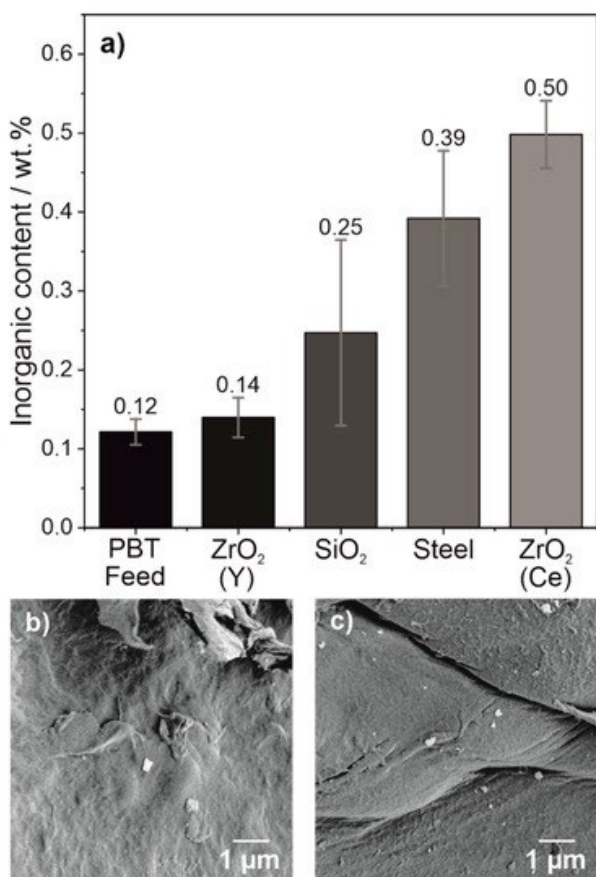


Figure 1. Inorganic content of (a) wet ground PBT particles ($SE_{max} = 0.9$ mJ, 20°C , 15 h) using different grinding media as determined by TGA with representative SEM images of the abrasion on the PBT particle surface comminuted with (b) ZrO₂ (Y) and (c) ZrO₂(Ce). Average of three measurements and standard deviation are shown. Reproduced from Tischer et al. [8] under the CC-BY 4.0 license.

Obviously, the abrasion content in the PBT product particles ground with yttrium-stabilized zirconia media (ZrO₂ (Y)) was the least and could not be discriminated from that of the feed material, which was 0.12 wt.-% (PBT Feed). Both, ceria-stabilized zirconia and steel media lead to substantial grinding media wear in the product and discolouration. The abrasion particles are sub-micron sized as confirmed by scanning electron microscopy (Figures 1 b and 1 c). In all cases the degree of crystallinity or the phase morphology did not change, as confirmed by differential scanning calorimetry (DSC) and X-ray diffraction.

In all cases, a consequence of the media wear particles being present in the PBT comminution product was a decrease of the ‘sintering window’ (difference between melting and solidification onset temperatures as determined by dynamic DSC) from around 21 K (PBT Feed) to 17 K to 13 K, where the smallest thermal process window was observed for the product obtained with steel grinding media. For PBF-LB/P a wide sintering window is desired. A too small thermal process window makes it more challenging to assure a stable manufacturing process. In the worst case a too narrow sintering window

can lead to distorted parts or cause a termination of the building process. That using steel grinding media is unfavourable in terms of the desired product properties and a stable PBF-LB/P process, also becomes obvious from isothermal DSC measurements (Figure 2).

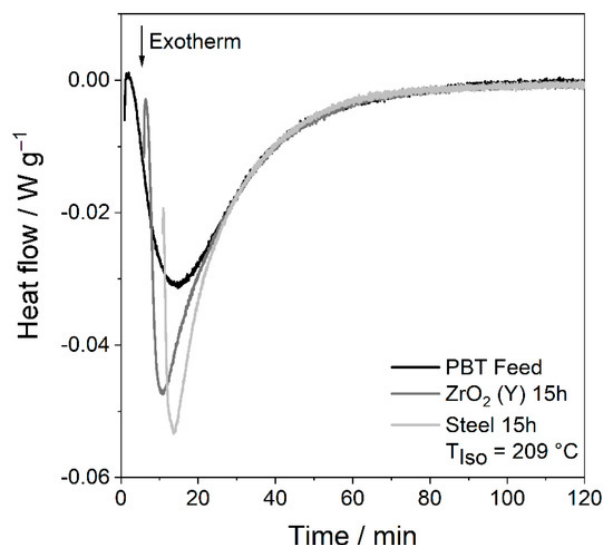


Figure 2. Isothermal crystallisation at 209°C of PBT feed material and wet ground powder with steel and ZrO₂ (Y) grinding beads ($SE_{max} = 0.9$ mJ, 20°C , 15 h), where wet ground samples have a time off-set. Reproduced from Tischer et al. [8] under the CC-BY 4.0 license.

Figure 2 shows the time course of the isothermal crystallisation of the PBT feed material and the wet ground PBT material with steel and ZrO₂ (Y) after 15 hours. The thermograms of PBT stressed with ZrO₂ (Y) and steel media have a given temporal offset, with the aim of overlapping the latter part of the thermogram where crystal growth occurs. This clearly illustrates that although nucleation is accelerated, crystal growth is hardly affected. In the case of wet ground PBT, the time taken to reach the peak is greatly reduced, as can be seen from the large temporal offset required. However, the thermogram behind the peak is almost identical to that of the PBT feed material. This proves that only nucleation, which takes place in the early stage of the crystallisation process, is accelerated. Crystal growth, which determines the later course of the thermogram, remains unchanged. A more detailed discussion and explanation can be found in [8]. An accelerated melt crystallization kinetics is undesired for PBF-LB/P feedstock powders, as it negatively can affect the process and lead to premature melt crystallization causing warpage and, consequently, in the worst case the abortion of the building process.

4. Conclusions

Within this contribution we will discuss wet comminution of various thermoplastics in stirred media mill from a fundamental perspective (grinding limit, process parameter dependencies) and from practical considerations in view of (undesired) changes of product properties being relevant for powder bed fusion additive manufacturing based on own work [4-8]. Wet

comminution of thermoplastics is especially interesting, if very fine product particles below 10 microns size are desired, which are hard to obtain by dry impact comminution. In wet comminution of thermoplastics, yttrium-stabilized zirconia media are recommended. Powders comminuted with ZrO₂ (Y) grinding beads exhibited reduced abrasion and slower accelerated crystallisation kinetics compared to ZrO₂ (Ce). Consequently, yttrium-stabilised ZrO₂ grinding media were found to be the most effective for the wet comminution of polymers amongst the tested materials, as they exhibited rapid comminution kinetics, no discolouration, and the least altered thermal properties of the ground thermoplastic in terms of dynamic and isothermal crystallisation.

Acknowledgement

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Modelling wet-operated stirred media mills with population balances based on mechanistic models

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Abstract. A fully mechanistic population balance model for wet-operated stirred media mills is presented and implemented into the Dyssol simulation environment. The framework consistently links material-specific breakage behaviour with machine-specific stressing and transport phenomena. Breakage functions are determined experimentally using a modified counter-rotating three-roller mill and combined with stress energy distributions obtained from CFD–DEM simulations to calculate physically based breakage rates. In addition, mechanistic sub-models for grinding media and particle transport are developed to account for back-mixing effects and the influence of internal classification devices. The model integrates four interacting components: breakage function, breakage rate, grinding media transport, and particle transport. Validation against experimental grinding results shows good agreement for batch, continuous, and circulation operation modes. The developed framework provides a robust basis for predictive simulation and future extension towards scale-up and alternative mill geometries.

1. Introduction

Stirred media mills are extensively used for fine and ultrafine wet grinding due to their high energy efficiency and capability to produce narrow particle size distributions. Nevertheless, comminution remains one of the most energy-intensive unit operations, motivating continuous efforts to improve process understanding and model-based optimization [1].

Previous studies have demonstrated that particle breakage in stirred media mills is governed by both the magnitude and frequency of stressing events, which are strongly influenced by mill geometry, operating parameters, and suspension properties [2–5]. Population balance modelling (PBM) provides a rigorous framework to describe comminution processes by tracking the evolution of particle size distributions [6]. However, many PBM approaches rely on phenomenological parameters and simplified descriptions of stressing conditions, limiting their predictive capability for stirred media mills [7–9].

To overcome these limitations, recent work has increasingly combined PBM with numerical methods such as the discrete element method (DEM) and computational fluid dynamics (CFD) [10–17]. Multiscale approaches linking CFD–DEM-derived stress energy distributions to PBM formulations have improved breakage rate prediction [18–20], but the consistent integration of material-specific breakage behaviour and transport phenomena remains challenging.

The objective of this work is therefore to develop a fully mechanistic population balance model for wet-operated stirred media mills, integrating experimentally determined breakage behaviour, CFD–DEM-based stressing conditions, and mechanistic descriptions of grinding media and particle transport. The model is implemented into the dynamic flowsheet simulation framework Dyssol [21,22].

2. Modelling Approach

2.1. Population Balance Framework

The model is based on the general population balance equation describing particle mass transfer between size classes due to breakage and transport. A key concept is the separation of material-specific properties from machine-specific stressing conditions. Material behaviour is described by breakage energies and breakage functions, while stressing conditions depend on operating parameters and internal mill dynamics. This modular structure facilitates parameter transfer between operating conditions and mill geometries.

The stirred media mill model is implemented into the dynamic simulation environment Dyssol, enabling both steady-state and transient simulations. This allows the investigation of start-up behaviour, parameter changes, and interactions between grinding, transport, and classification phenomena at flowsheet level.

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2.2. Breakage Behaviour of Particles

Particle breakage is characterised by the specific breakage energy and the breakage function. The specific breakage energy defines the probability of fracture under a given stressing condition, while the breakage function describes the resulting fragment size distribution. Figure 1 shows experimentally determined median breakage energies as a function of particle size.

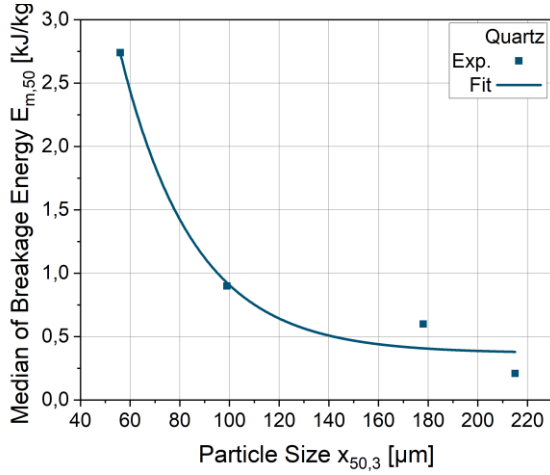


Figure 1. Breakage energies determined with single-particle breakage in nanoindentation experiments

Material-specific breakage functions are obtained using a modified counter-rotating three-roller mill, which enables controlled single-particle stressing under defined energy input. Experimental results are evaluated over multiple stressing events to capture cumulative breakage behaviour relevant for stirred media milling. The derived breakage functions are compared with established literature models (Figures 2 and 3) and serve as central input parameters for the population balance model.

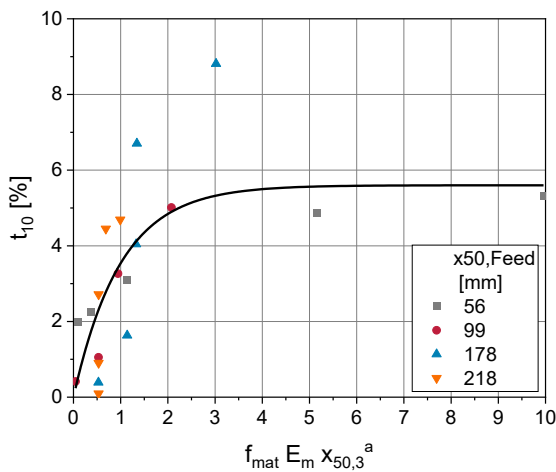


Figure 2. Prediction of t_{10} based on Shi et al. [9]

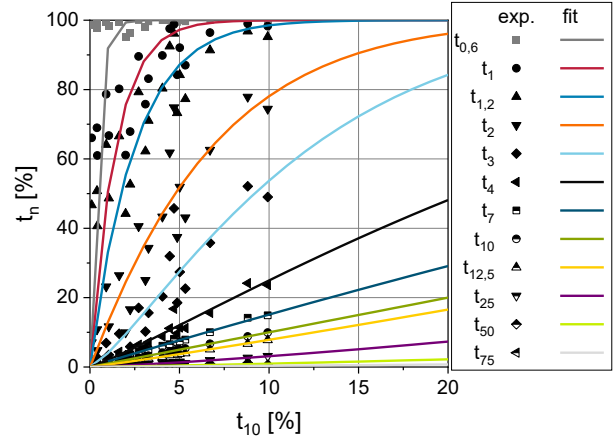


Figure 3. Modelling of breakage function based on $t_{10}t_n$ -Model

2.3. Stress Energy Distribution and Breakage Rate

While breakage functions describe the fragmentation behaviour, the breakage rate quantifies the frequency of breakage events. Breakage rates are calculated by coupling the material-specific breakage behaviour with stress energy distributions obtained from CFD–DEM simulations (Figure 4).

CFD–DEM simulations provide spatial and temporal distributions of grinding media collision energies and stressing frequencies. To account for the fact that not all stressing events contribute equally to breakage, effective stress energies are introduced. The breakage rate is then formulated as the fraction of particles breaking per unit time and size class, resulting in a physically consistent description linking numerical simulations with experimental material data.

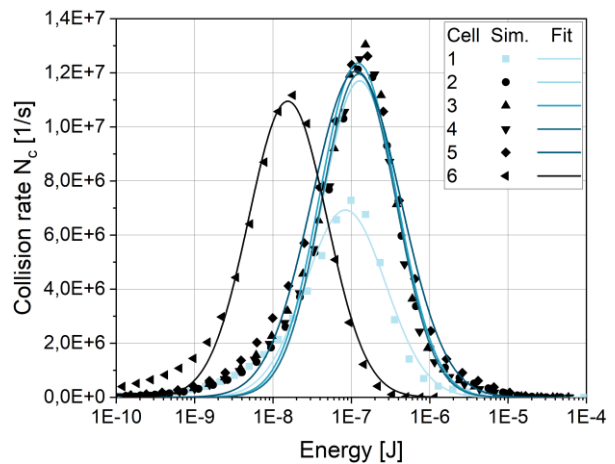


Figure 4. CFD–DEM-based stress energy distribution inside a stirred media mill.

2.4. Grinding Media Transport

Grinding media motion strongly influences stressing conditions in stirred media mills. A mechanistic model for grinding media transport is developed based on

force balances acting on individual beads, including centrifugal, drag, and contact forces. This approach enables the description of bead motion as a function of operating parameters and mill geometry.

The model is validated using CFD–DEM simulations and captures the influence of parameters such as tip speed, bead filling degree, and suspension viscosity. The presence of a deflector wheel is explicitly considered, as it induces reverse flow zones and significantly alters grinding media distribution and stressing conditions (Figure 5).

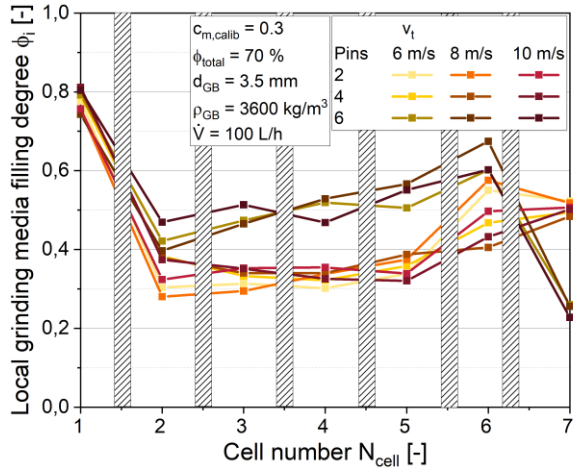


Figure 5. Simulated grinding media axial grinding media filling degree with deflector wheel.

2.5. Particle Transport and Residence Time Behaviour

Particle transport is described by axial and radial flow combined with back-mixing effects. Residence time distributions are measured experimentally using tracer methods and reveal pronounced material retention when a deflector wheel is installed.

To represent this behaviour within the population balance framework, a separation function is introduced (Figure 6). This function enables a mechanistic description of internal classification effects and their influence on particle transport and size distribution evolution.

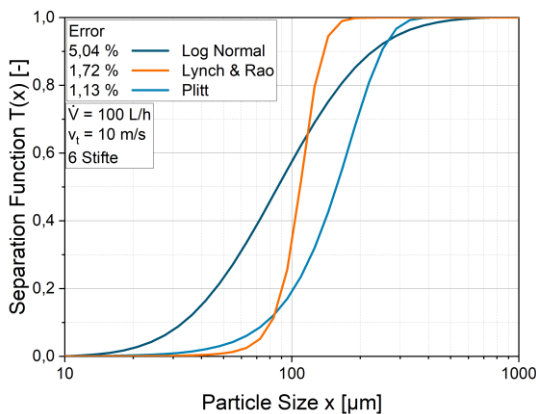


Figure 6. Modelled separation function and resulting error based on grinding results

4. Model Implementation and Validation

4.1. Implementation in Dyssol

Within Dyssol, the stirred media mill is represented using a cell-based population balance model, dividing the mill into ideally mixed compartments. Each cell is characterised by its local grinding media distribution, stress energy distribution, and transport behaviour. The breakage matrix is updated dynamically based on CFD–DEM results and experimentally determined breakage functions.

This formulation allows simulation of batch, continuous, and circulation operation modes, including transient effects and the influence of internal classification devices.

4.2 Model Validation

Model predictions are validated against experimental grinding results for glass and quartz in laboratory-scale stirred media mills. For batch operation, the model reproduces the overall shape of measured particle size distributions, with deviations for particles below approximately 10 μm attributed to experimental limitations in breakage characterization (Figure 7).

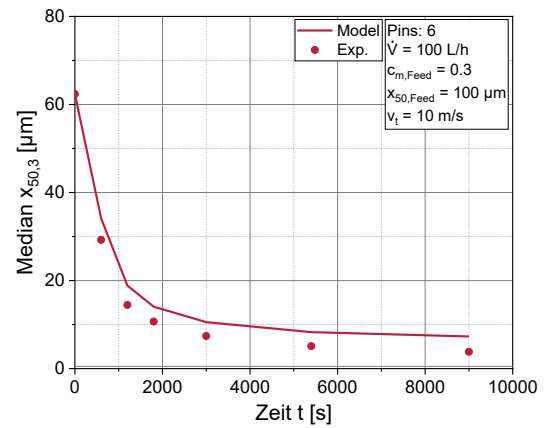


Figure 7. Validation of model for a mill geometry without internal classification

In continuous and circulation operation, the model captures the temporal evolution and final product size distributions with good agreement in the coarse and intermediate size ranges (Figure 8). The transferability of model parameters between different mill geometries demonstrates the benefit of separating material-specific and machine-specific model components.

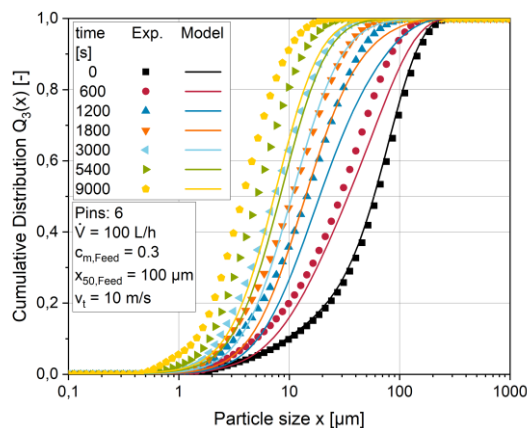


Figure 8. Validation of model for a mill geometry with internal classification

4.3 Conclusion

A fully mechanistic population balance model for wet-operated stirred media mills has been developed and implemented into the Dyssol simulation framework. By consistently integrating experimental breakage functions, CFD–DEM-derived stress energy distributions, and mechanistic transport models, the approach enables predictive simulation without reliance on purely empirical fitting parameters. The framework provides a solid basis for future extensions towards scale-up, alternative mill geometries, and enhanced internal classification modelling.

Acknowledgement

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Validating the Improved Energy Transfer Model in Stirred Media Mills with different Ores

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Abstract. In the past a range of mechanistic models have been developed to predict milling processes. A popular one for stirred media mills is the stress model for which recently the energy transfer was considered in greater depth. To better account for the effect of viscosity on the energy transfer coefficients a previous study was carried out using quartz. In contrast, most grinding processes involve more complex materials. In this work that further developed stress model is validated using ores as complex materials. Characterisation of the materials and their breakage behaviour is performed and a master curve for the prediction of the specific energy input established. The model's performance is evaluated by comparing experimental comminution data with model-based predictions of specific energy input.

1. Introduction

As energy costs rise, the energy optimization of industrial processes is becoming increasingly important. This is particularly true for energy-intensive comminution processes. In addition to numerical models, mechanistic models also offer the possibility of optimising comminution in large-scale plants based on a small number of Lab-scale experiments.

A well-known mechanistic model is Kwade's stress model [1], which has been further developed in the past [2, 3], to more accurately describe the behaviour of the mill. Energy transfer factors are a particular focus of their work. In the work of Sterling et. al. [3], the influence of viscosity on the energy transfer factors was reevaluated, and an improved master curve was established. This master curve can be used to determine the optimal operating conditions for multi-scale stirred media mills based on a limited number of experimental tests and knowledge of material properties.

Although these models have been well studied for homogeneous materials, heterogeneous materials are often encountered in practical applications. The study of multi-component comminution is gaining importance in context of sustainability concerns, such as recycling and the availability of critical raw materials. However, the stress model improvement by Sterling et. al. [3] is based on studies with silica as model material and will be validated using several copper and iron ores in this study.

2. Materials and methods

2.1. Experimental investigations

Laboratory-scale comminution studies are first conducted for each of the ores used. For this purpose, a horizontal

stirred media mill with a polyurethane lining and agitator is used. The suspension is cooled via the feed tank. At least six different parameter combinations are tested for each ore, with variations in agitator tip speed and grinding media (GM) density and size. The range of parameters used is shown in Table 1.

Table 1. Parameter variation for grinding experiments

Parameter	Symbol	Variation
GM size	d_{GM}	1,01 – 3,05 mm
GM density	ρ_{GM}	3,8 – 6,05 kg/L
Stirrer tip speed	v_t	6 – 12 m/s
GM filling ratio	φ_{GM}	80 %
Volumetric solids content	c_V	20 %

According to Kwade and Schwedes [1], this results in maximum stress energies ranging from 0,15 to 8,73 mJ. The comminution time is 20–60 minutes in circuit operation. From the GM filling ratio results the suspension volume inside the mill and therefore an average residence time t_r can be determined. In order to enhance reproducibility, the feedstock is added to the tank over a period of three minutes, with one-third of the total feedstock added each minute. Throughout the test duration, several samples are taken and analysed for particle size. Selected samples are additionally analysed for solids content, throughput, and rheology. Based on this data, the viscosity can be correlated with the particle size distribution of the suspension. Furthermore, it is possible to determine grinding-specific parameters such as the specific energy input E_m or the stress number SN .

In addition, nanoindentation tests are performed on the ores used. The Young's modulus Y can be determined from the elastic force-displacement curves according to

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Portnikov [4] using Eqs. (1–2). Here, F corresponds to the applied force for a total deformation Δ of the loaded particle with diameter d and effective Young's modulus Y^* . To then calculate the Young's modulus Y , the Poisson's ratio ν must be known.

$$F = \frac{1}{3} Y^* \cdot \sqrt{d} \cdot \Delta^{3/2} \quad (1)$$

$$Y^* = \frac{Y}{(1-\nu^2)} \quad (2)$$

The compressive strength of the materials σ_{cs} can also be determined from nanoindentation tests, when stressed until breakage. It can be calculated using Eq. (3) with the applied force F and a cross-sectional area A of the stressed particle. The latter is calculated using the longest and the smallest chord of the unstressed particle to form an ellipse.

$$\sigma_{cs} = \frac{F}{A} \quad (3)$$

It determines the minimum particle size and thus influences the stress intensity SI . The Young's modulus, on the other hand, is used for the calculation of the particle-related energy transfer coefficient ν_p .

2.2. Modelling

The master curve is modelled in accordance with the work of Sterling et. al. [3] following the determination of material properties and the grinding behaviour, respectively. Based on the experimental investigations, the average optimal stress intensity (stress energy related to stress mass) of the product $\overline{SI_{p,opt}}$ and subsequently also the product-specific stress number SN_p can be determined. The master curve, plotted as a function of $\overline{SI_{p,opt}}$ times SN_p versus $\overline{SI_{p,opt}}$, enables a backward calculation and thus a prediction of the comminution time t_c and the specific energy input E_m .

In contrast to Sterling et. al.'s work [3], the equation for determining the improved product-specific stress number $SN_{p,imp}$ was adapted in this study as shown in Eq. (4). The respective calculation of these variables as well as the power factor k_{susp} can be found in the model [3].

$$SN_{p,imp} = \nu_t \cdot \frac{m_{GM} \cdot t_r}{\frac{\pi}{6} d_{GM}^3 \cdot \rho_{GM} \cdot \sqrt[3]{k_{susp}}} \cdot \left(\frac{\overline{SI_{p,imp}}}{\overline{SI_{p,opt,imp}}} \right)^{1-\alpha} \quad (4)$$

3. Results and discussion

The following section presents the results for one of the copper ores used, referred to hereafter as Sample 1. After characterizing the material using a nanoindenter and analysing its fracture behaviour based on comminution tests as shown in Section 2.1, the master curve depicted in Figure 1 was obtained. The two grinding media materials used — zirconium dioxide (ZrO_2) and an oxide mixture consisting primarily of aluminium oxide (Al_2O_3) — are color-coded. The combined master curve, plotted in dark blue, follows the equation given in Eq. (5).

$$\overline{SI_{p,opt,imp}} \cdot SN_{p,imp} = 5,4 \cdot 10^{-18} \cdot \overline{SI_{p,opt,imp}}^{4,2} \quad (5)$$

The R^2 value of 0.96 indicates a good fit.

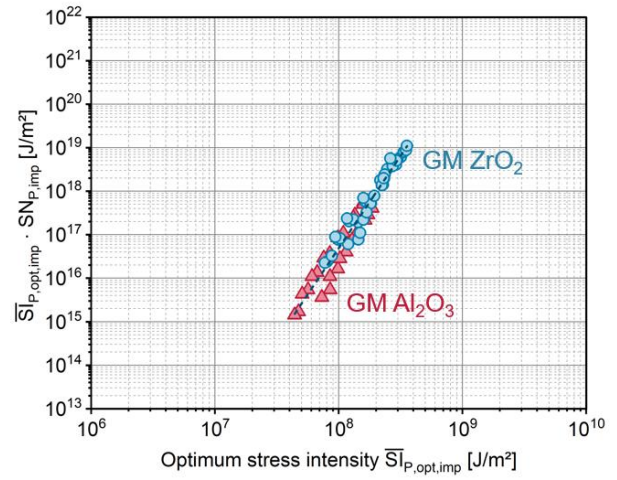


Figure 1. Master curve for Sample 1 with different grinding media (GM) materials used.

If the master curve is used to calculate the specific energy requirement for various target particle sizes for Sample 1 under given milling parameters, a model-based prediction of the grinding behavior can be made. A comparison with the experimentally collected data for a selected test is shown in Figure 2. This test was conducted using grinding media from the alumina mix at a stirrer peripheral speed of 6 m/s.

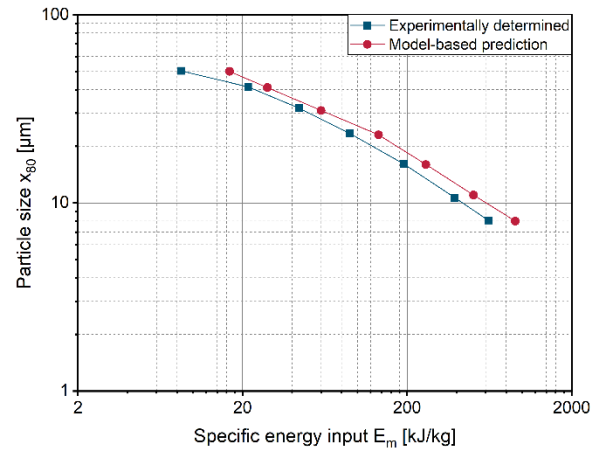


Figure 2. Comparison of comminution curves between experimental data and modelling approach for grinding of Sample 1 with GM size of 2,53 mm GM density of 3,8 kg/L and stirrer tip speed of 6 m/s.

The trends of the experimentally recorded and modelled comminution curves are generally similar. However, the model-based curve overestimates the specific energy input slightly compared to the experimental curve.

4. Conclusion

The model developed by Sterling et. al. provides a solid foundation for predicting the behaviour of real-world complex materials such as ores. However, the difference between the modelled specific energy input and the

experimentally determined value makes it clear that there is still room to refine the model's predictions.

Acknowledgement

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Investigation of Composition Dependent Breakage in High Pressure Grinding Rolls (HPGR) using a novel Breakage Model in Discrete Element Method (DEM) Simulations

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Abstract. The discrete element method (DEM) has been extensively used to model and investigate comminution, but few models consider the materials composition and microstructure during breakage events. Additionally, the interactions between different material phases during comminution are not yet well understood. Since experimental investigations of these relationships are complex and time-consuming, a texture inheritance model for particle breakage in the DEM has been developed. The model uses spherical particles to reduce computation costs which allows simulations with larger quantities of particles, while also conserving particle texture in breakage events. Using the developed texture and texture inheritance model, the breakage behaviour of an artificial magnetite-iron ore is investigated in high pressure grinding rolls (HPGR). By implementing and varying a composition dependence of a peak force breakage criterion, the effects of particle composition on comminution and liberation are investigated. Material with lower critical breakage strength results in more fines and liberation in the product due to more breakage events. Effects of the composition dependent breakage criterion were not observed, likely due to model limitations and a mismatch between comminution and mineral microstructure.

1. Introduction

Discrete element method (DEM) simulations are increasingly used to investigate and optimize processes in the field of granular materials, specifically with the increasing ability to model systems at industrial scale due to improved parallelization strategies, e.g. GPU based calculations, or computationally efficient scaling models, e.g. coarse graining approaches. This brings opportunities to investigate more complex topics that are experimentally time consuming and costly or entirely unfeasible.

In the field of comminution or particle breakage on the discrete level, the mode of breakage is a subject of ongoing discussion. Cracks forming predominantly intergranular could potentially result in better liberation behavior and reduced energy consumption of comminution processes. Additionally, it could increase the size of liberated material which in turn increases the efficiency of subsequent separation processes or enables entirely different ones. While experimental investigations give insights into fundamental breakage mechanisms, transfer to processes on industrial scale is challenging: the investigations are time consuming and changing materials or process geometries demand numerous examinations.

Modelling these mechanisms and incorporation them into a DEM simulation is a way to bridge the gap to industrial processes. Experimental investigations can be used to validate the fundamental breakage behavior of models to ensure realistic representation and the fast adaptability to changing geometric constraints and materials of simulations can be used to facilitate product and process design.

However, consideration of material microstructure in DEM simulations is sparse so far and only considered

in set-ups using non-spherical particles. DEM simulations using non-spherical particles have costly contact detection schemes and limited compatibility with coarse graining approaches both of which complicate the application to larger industrial system.

Breakage of spherical particles is usually modeled using the particle replacement method (PRM), which replaces a breaking particle by an array of fragments within the volume of the parent. Volume conservation is ensured by overlapping or shrunk fragments that subsequently push nearby fragments or particles aside or by growth procedures. These replacement schemes inherently pose a challenge for texture considerations: the texture information in void spaces between shrunk fragments is lost or duplicated in schemes with overlapping fragments. To circumvent this, the texture inheritance model was proposed [1]. In the model, a particle's texture is transformed to a cubical shape during breakage events. The cubical texture can be fragmented into cubical fragments without generating overlaps or void spaces. Subsequently, the textures are transformed back to spherical shapes which can be used in the replacement scheme. Previous investigations have shown good agreement of the model with random sampling in varying size classes, indicating the conservative properties of the model with regard to texture.

In this work, the application of the aforementioned model is tested in an industrial scale comminution process. A sensitivity study for the link between the composition of individual particles and their critical breakage strength is performed to investigate a simple connection of microstructure and breakage behavior. The results of the study are a first step in representing the complex interactions of microstructure and breakage

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behavior in breakage models for spherical particles in DEM simulations.

2. Methodology

2.1. Discrete element method (DEM)

The DEM is a Lagrangian numerical approach in which states of individual particles, such as position, velocity, and forces acting on them, are progressively modelled using time steps. To calculate the motion of particles and update their position accordingly Newton's and Euler's equations are solved. To model particle contacts the linear-spring-dashpot model is used [2].

2.2. Texture model

To enable a dependence on the composition of individual particles, the information of the particle's composition needs to be available. The composition of particles in this context is the volumetric parts of individual phases i compared to the total volume of the particle $C_i = \frac{V_i}{V_{total}}$.

However, to accurately model the inheritance of it to fragments in breakage events the microstructure is relevant. In this work, the particles' microstructure is represented as a voxel grid. A low-resolution example of such a grid is shown in Figure 1 (left). Each voxel in the grid is assigned a phase information. The composition can then be calculated as the number of voxels of a phase relative to the total number of voxels in the grid $C_i = \frac{V_i}{V_{total}} = \frac{N_i}{N_{total}}$. The number of voxels, i.e. the resolution, defines the accuracy with which the model is able to represent the texture volume. The texture volume is a digital representation of a real material and can be voxel based, e.g. similar to the slag texture in [1], or more abstract as positions of grains, e.g. the parameterizations by Wiegel [3] or Hilden & Powell [4]. The sampling procedure places the voxel grid of individual particles at random positions within the texture volume. The voxels within the grid then get assigned the phase in the texture volume they are closest to. An exemplary binary texture of a particle is shown in Figure 1 (right).

In this work, an artificial magnetite-iron ore texture following Hilden & Powell [4] is used as texture volume.

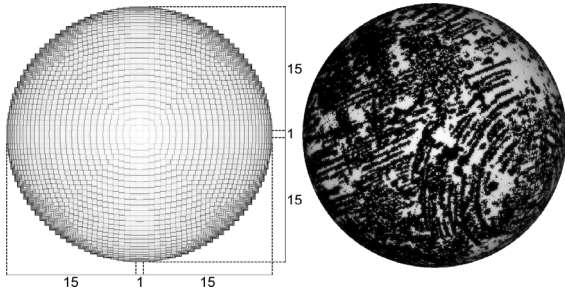


Figure 1. Depiction of a low-resolution voxel-grid (left) and an exemplary high-resolution binary particle texture (right).

2.3. Breakage and texture inheritance model

The breakage model used in this work is an implementation of the previously proposed texture

inheritance model [1]. In the model, particles are replaced by an array of spherical fragments within the volume of the breaking parent particle similar to other particle replacement method schemes. Volume conservation is ensured by uniformly shrinking and subsequently growing each fragment. The growth of the fragments is an iterative procedure during which the size of the fragments is increased in small increments if resulting overlaps with surrounding particles, fragments or walls do not exceed a threshold. The growth procedure continues until the fragment reaches the volume required for volume conservation. The threshold needs to be carefully calibrated to ensure resulting forces are large enough for fragments to generate the space necessary for their growth while remaining as small as possible to limit artificial energy input and the influence of the growth procedure on comminution behavior.

Usually, the void spaces between the spherical fragments in the replacement scheme impede the inheritance of texture since the texture information within the void spaces is lost. The previously proposed texture inheritance model [1] solves this issue by intermittently mapping the texture information of the parent particle to a cubical texture using transformations by Roşca et al. [5]. The cubical texture of the parent particle can be fragmented into cubical textures for the fragments without generating void spaces or overlaps. These textures are transformed back to spherical shapes which represent the inherited textures of the fragments. For more details see Hirschberger et al. [1].

2.4. Composition dependent breakage criterion

Cleary & Sinnott [6] use a list of discrete critical breakage forces for each individual size class as breakage criterion (see orange dots in Figure 3). An exponential function can be fit through these values to create a more versatile, size dependent breakage criterion $F_{CS}(x_p)$. The resulting breakage criterion, i.e. the critical breakage force as a function of particle size, is shown in Eq. (1) and Figure 3.

$$F_{CS}(x_p) = a \cdot x_p^b + c, \quad (1)$$

where a, b and c are fit parameters. Equation (1) is the basis of the size and composition dependent breakage criterion used in this work (see Eq. (2)). To include the influence of different phases, a term is created for each phase. Each of these terms describes the breakage strength of the phase using weightings of the size dependent breakage criterion $F_{CS}(x_p)$. The terms are weighted by the volumetric part of the phase C_i in the particles and the strength of the phase relative to the strength of a reference phase $f_{rel,i} = \frac{\sigma_i}{\sigma_{ref}}$:

$$F_{crit}(x_p, C_i) = \sum_i (F_{CS}(x_p) \cdot C_i \cdot f_{rel,i}). \quad (2)$$

In the binary case, i.e. a target material embedded in a matrix, Eq. (2) can be simplified to:

$$F_{crit}(x_p, C_{target}) = F_{CS}(x_p) \cdot (1 - C_{target}) + F_{CS}(x_p) \cdot C_{target} \cdot f_{rel,target}. \quad (3)$$

2.5. Simulation set-up

The simulation used to investigate the performance of the novel breakage model and the influence of composition dependence on breakage behaviour, is a recreation of the simulation by Cleary & Sinnott [6]. The high pressure grinding rolls (HPGR) are modelled using two opposing rolls with a chute above. The chute is filled with particles to feed the system with material. During the entire process the gap between the rolls remains constant and at the pinch-point the gap between them is 60 mm. The rolls rotate with a speed of 19.0 rpm and push the particles into the pinch-point to increase pressure and initiate breakage. A slice in the center of the mill sufficiently large to model particle particle and particle wall interactions is modelled. The slice has a thickness of 189 mm and uses periodic boundary conditions in y-direction. A depiction of the set-up of the simulation is shown in Figure 2 for the initial state.

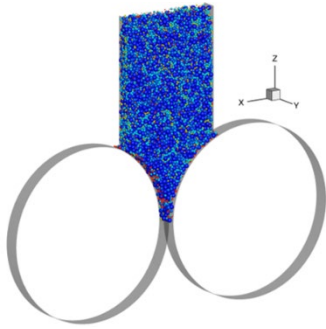


Figure 2. Simulation set-up of the HPGR with the chute filled with feed particles in the initial state.

Material properties of the bulk material used as feed are taken from [6]. For the microstructure, the following relative grain strengths were investigated in the composition dependent breakage criterion (Eq. (3)): $f_{rel,target} \in \{0.5, 1.0, 2.0, 4.0, 6.0, 13.21\}$. The value 1.0 represents the reference case using the strength used by Cleary & Sinnott [6] and the value 13.21 approximates the strength of magnetite grains (extrapolated from the values reported in [7]). Figure 3 shows the critical breakage forces of the particles for the various grain strengths as a function of particle size for an average particle composition $C_{target} = 0.233$.

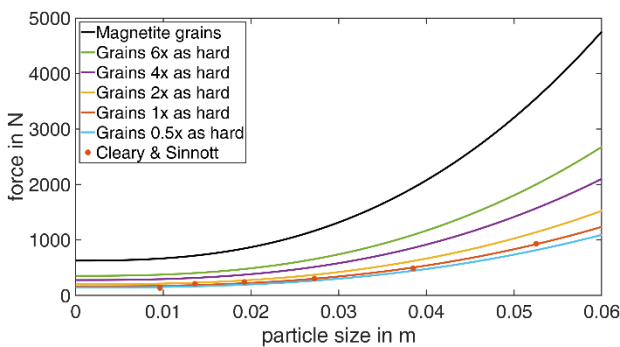


Figure 3. Critical breakage force as a function of particle size for different grain strengths at an average composition of $C_{target} = 0.233$.

To attempt to isolate the effect of the composition dependence in the critical breakage force on the breakage behavior, two additional cases were investigated. In these cases, for the strength of the grains similar values to the matrix material were selected, as is the case in the reference case using Cleary & Sinnott's [6] material properties. However, the strength of matrix and grain material is set to match the average material strength of the composition dependent cases using relative strength values for the grains of 4 and 13.21, respectively.

3. Results

Figure 4 shows the product size distributions of the different grain strengths. For grains with lower critical breakage strengths more fines are produced because more breakage events occur. A corresponding effect for the coarse material is less clear. Since few particles are in the larger particle size classes, larger fluctuations between the strengths are present.

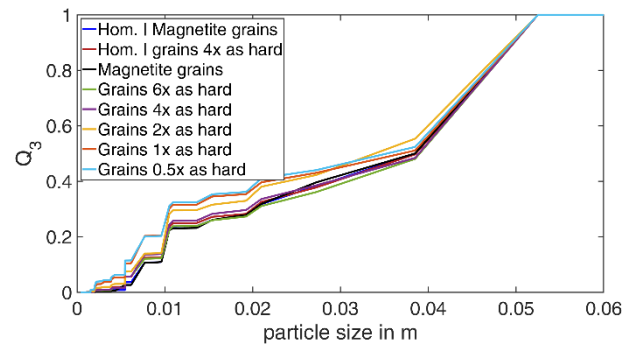


Figure 4. Product size distribution for the various grain strengths.

The size distributions of materials with homogeneous particle microstructures and their composition dependent counterparts show similar size distributions (blue and black, and purple and red curves, respectively). This indicates that the product size distribution is largely independent of the materials composition in the current set-up.

If the forces within the process are significantly larger than the critical breakage forces of either phase, the impact of composition dependence on the comminution behavior would be significantly reduced. For this reason, simulations with stronger grains (four times the strength of the matrix material) and the strongest grains (13.21 times the strength of the matrix material) were used in these investigations. In the simulations with stronger grains, breakage is reduced, which can be observed in the reduced fines in Figure 4. This indicates that the stress in the process is not significantly larger than the material strength. However, relevant difference between the homogenous and composition dependent case were not observed.

The progression over time of the liberation degree of the matrix material in the product is shown in Figure 5. The values approach a constant value after an initial rise, i.e. a stationary process is reached after enough material has exited the domain. Liberation degrees remain low for

each grain strength, indicating that the size reduction is not sufficient to liberate the material. Material for which the grains have lower breakage strengths systematically results in higher liberation degrees of the matrix material. Since liberated particles are primarily found in smaller particle size classes, cases with more fines result in higher liberation degrees. As observed for the product size distribution shown in Figure 4, the liberation degrees of materials with homogeneous particle microstructures and their composition dependent counterparts are similar (blue and black, and purple and red curves, respectively). In this set-up the liberation degree of the matrix material appears to be independent of the particle composition.

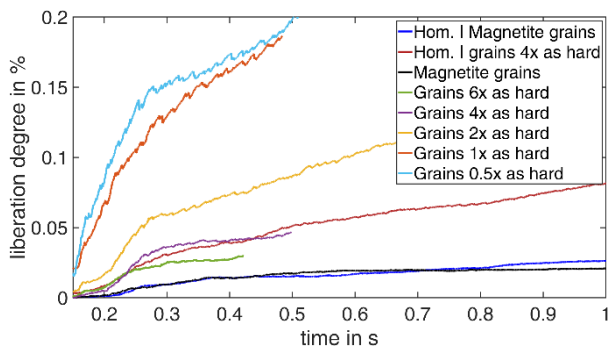


Figure 5. Liberation degree of matrix material in product particles over time for the various grain strengths.

Figure 6 shows the recovery of target material (grains) over the recovery of the matrix material. The angle bisector in the graph represents ideal mixing, i.e. the particles' microstructure does not undergo fundamental changes due to comminution. Weaker materials show marginally more deviations from the angle bisector, but overall the effect of the comminution on the microstructure appears negligible. The comminution in the HPGR set-up is therefore insufficient to liberate the grains for the modelled microstructure.

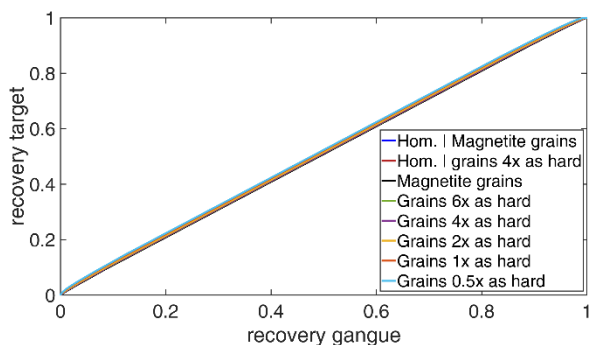


Figure 6. Recovery of target material over the recovery of gangue material for the various grain strengths.

4. Conclusion

The model was shown to be applicable to an industrial scale comminution process. Microstructure information of product material was investigated using size distributions and liberation degrees.

In the comparison of cases using homogeneous particle microstructures and those using a magnetite iron ore texture with a composition dependent breakage criterion only minor differences were observed. An effect of particle microstructure and composition dependence on product size distribution and liberation degree is expected due to the different breakage behavior of liberated particles of the respective phases.

As mentioned previously, composition dependence affects breakage behaviour when the composition of particles changes. Figure 6 indicates that the majority of the mass in the process does not undergo such changes. A more prominent effect of the composition dependence could potentially be observed in processes resulting in more liberation using e.g. a smaller gap size or by using a microstructure with larger grains.

Another aspect is a limitation to two generations of fragments in the employed breakage model. Changes in the breakage behaviour due to the composition dependence, such as weaker material breaking more often, can only be represented in the simulation, if the particles are able to break. However, fragments of the second generation cannot break in the current implementation of the model and any effects of changes in the composition of these fragments on the breakage behaviour cannot be observed in the simulation.

Acknowledgement

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Simulation of classification in a gravitational inertial air classifier using a fast CFD-DPM approach method

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Abstract. This work presents a fast CFD-DPM simulation approach for the simulation of a gravitational-inertial classifier, as operated in a gneiss quarry. Industrial surveys were carried out to gather data on the classifier performance under different operating conditions. The simulation approach consisted in the simplification of a CFD-DPM workflow to address the reduction of the computation time required to obtain a good representation of the classification performance. For this purpose, the simplification of the computational domain as well as a coarse graining approach were used to reduce the number of particles in the simulations and obtain results in an affordable computation time, presenting fairly accurate results compared to the industrial data.

1. Introduction

In the minerals industry, air classification is mainly used when the moisture content of the materials is low. The aggregate industry is a very good example, using air classification after crushing and sieving units to remove fine particles (Petit et al., 2018). Different designs of air classifiers are available (Shapiro and Galperin, 2005). Among them, the Gravitational-Inertial Classifier (GIC) has been adopted in the aggregate industry, drawing the attention of the academic community which started to study the classifier using experimental and numerical techniques (Johansson and Evertsson 2012a, 2012b).

The GIC presents a complex airflow, presenting two air inlets that can be adjusted to modify the contribution of each inlet on the overall airflow. The two airflows merge in the chamber passing through a set of classification channels designed to create a certain balance between gravity and centrifugal force on the particles. Also, it presents a recirculation zone where particles that were not classified have a second chance of reporting to either the coarse or the fine fractions.

The complexity of the air-laden flow inside the GIC chamber present a perfect case of study for computational modelling applications. In this regard, previous studies used a Eulerian-Eulerian Computational Fluid Dynamic (EECFD) approach to describe the air-laden flow inside the GIC (Johansson and Evertsson, 2012b). Other methods such as the Discrete Element Phase (DPM) or the Discrete Element Method (DEM) could be coupled to CFD solvers to recreate the particle trajectories inside the GIC chamber. However, the main issue seems to be the number of particles required to recreate the wide Particle Size Distribution (PSD) of the feed. Additionally, particles in the simulation should exchange momentum

with the fluid phase to model the pressure loss. In this regard, attempts to reduce the number of particles without accounting for the momentum exchange may result in poor resolution of the airflow and the classification performance. Thus, no previous attempts of using Eulerian-Lagrangian CFD (ELCFD) approaches to simulate the performance of the GIC have been published.

This work proposes a fast CFD-DPM simulation approach to obtain fairly accurate estimations of the performance of a gravitational inertial classifier in an affordable computation time. The subject of study is a GIC operating in a gneiss quarry. The fast simulation approach is based on the simplification of the computational domain and the utilization of a coarse graining method to reduce the number of simulated particles while still accounting for the effect of solids loading on the classification performance. Data, gathered during a field campaign at the industrial site, were also used for setting boundary conditions and for validation.

2. Materials and Methods

The GIC is installed in a gneiss quarry located in the metropolitan area of Rio de Janeiro. The quarry possesses three crushing schemes. The output of the tertiary crusher (VSI) is sent to a double screen deck, whose undersize (< 2.36 mm) is fed to the GIC (Fig. 1). The coarse product of the classifier is conveyed to a silo where it is stocked for later shipment. The fine product of the GIC is sent directly to a bag filter with no intermediate classification or dedusting equipment. The classifier presents a primary airflow that enters the separator at the top, and a secondary airflow that enters the equipment at the bottom.

The classifier performance is tuned by setting the overall flow rate, by means of a frequency controller

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linked to the fan power input and by adjusting the primary and secondary air valves. As such, different contributions of the primary and secondary airflows change the air velocity inside the classification chamber, modifying the classification performance.

An industrial campaign was carried out to characterize the fluid dynamics conditions and classification performance of the GIC as used at the site. Air static pressure and velocity were measured by setting probes in the primary inlet, secondary inlet, and outlet of the GIC (Fig. 1). The classification performance was changed by setting different conditions of the primary and secondary air valves, using a 2^2 design of experiments presented with central point, shown in Table 1. The nominal fan frequency of 1800 rpm was used in all cases.

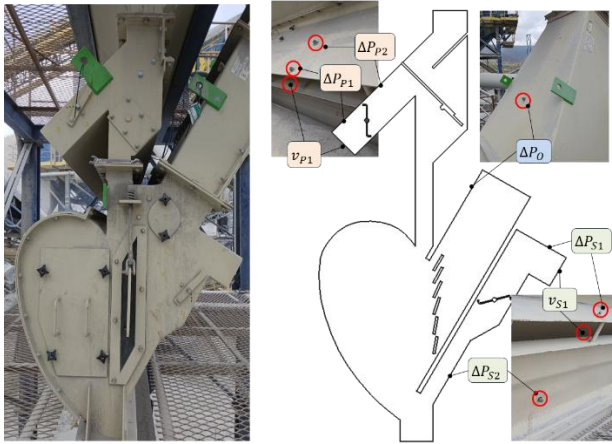


Figure 1. Gravitational-inertial classifier (left), pressure and velocity probe locations used on site (right).

Table 1. Design of experiments carried out during industrial campaign

Test	Primary airflow	Secondary airflow	Case
1	Minimum	Minimum	Min - Min
2	Maximum	Minimum	Max -Min
3	Minimum	Maximum	Min - Max
4	Medium	Medium	Mid - Mid
5	Maximum	Maximum	Max - Max

The fast CFD-DPM method used to simulate the GIC performance was executed using Ansys Fluent capabilities. The computational domain representing the GIC chamber was reduced to a 50 mm slice, as presented in Fig. 2. Only the most important features of the geometry were represented. Air was modelled using the RANS equations. Boundary conditions for the air were computed based on the mean average values obtained during the industrial campaign. Velocity values at the primary and secondary physical inlets were used to compute the mean velocity downstream at the computational model inlets.

Gneiss particles entering the classifier were simulated using the DPM method. DPM groups particles of same sizes in groups called parcels. The trajectory of each parcel is tracked in the domain considering the force

balance equations of a single particle but carrying the mass of the hole cluster of particles. This approach reduces the number of elements tracked in the simulation. Parcels do not interact with each other, and the volume of the particles is not accounted in the simulations.

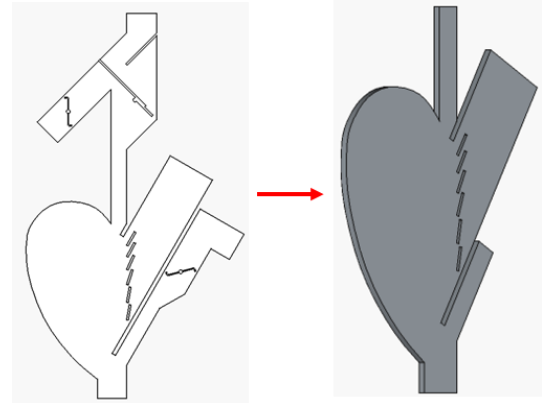


Figure 2. CAD of the full GIC geometry (left), sliced simplified domain used in the CFD-DPM simulations (right).

In principle, the number of parcels in the domain is too high for the simulation to run in an affordable time. This is due to the wide PSD of the feed and the necessity of simulating fine particles to have a good representation of the classification, which is expected to present cut sizes near 75 μm . In this regard, a coarse graining method was used to simulate the bulk behaviour of the particles inside the classification chamber. The wide PSD of the feed was replaced by particles presenting a single particle size. The density of the particles was maintained to conserve mass and volume. The size of the particles was computed to conserve the momentum exchange inside the chamber, calculated based on an estimation of particle and air velocities in the classification region. The coarse graining size resulted in 1 mm, presenting a reduction of the particle number of 92%. The computation of the partition curve was performed by adding a pulse of tracer parcels into the simulation. Tracer particle sizes covered the wide range of the feed PSD but with an arbitrary small feed rate; thus, with a small contribution in the overall number of particles added into the simulation.

The simulation of the classification started by simulating the fluid flow until stable velocity and pressure conditions were achieved. Then, bulk particles with the coarse graining size were injected into the simulation. The simulation was resumed until new stable conditions were achieved. Finally, tracer particles were injected into the simulation. The simulations were continued until classification of tracer particles were achieved.

3. Results and discussion

Results of the industrial campaign, in terms of the total flow rate and pressure loss of the GIC are presented in Fig. 3. Total airflow and pressure loss depends on the positions of the air valves and the feed of particles, as expected. The min–min case presents the lowest airflow and the highest pressure loss, while the max–max case

presents the opposite condition. Airflow and pressure losses are influenced by the presence of solid particles fed to the classification process, as observed in the air-laden conditions. Pressure loss increases due to the presence of particles, while airflow reduces, as expected. The overall results present consistent behaviour with a small deviation in the mid-mid case, which presents lower airflow and higher pressure flow compared to the overall trend in the results.

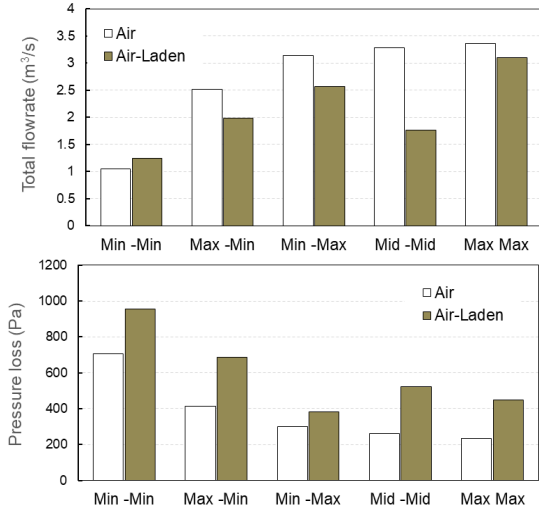


Figure 3. Experimental results for the study cases in terms of the total airflow (top), and pressure loss (bottom).

Results of the CFD simulations in terms of the air velocity magnitude are presented in Fig. 4 for the min-min and max-max cases. Results show the large differences in the velocity field inside the chamber depending on the positions of the air valves. Max-max case presents a more intense flow field and greater contribution of the secondary airflow. Fig. 4 also presents the results of the velocity field after injection of the particles. The effect of the solid loading is clearly visible in both cases, but more evident in the max-max case due to the interference with the more intense recirculation flow near the internal deflectors.

The effect of solids loading on the fluid flow inside the chamber is more evident in the results presented in Fig. 5. Pressure loss is plotted as a function of time for two selected study cases. Particles are injected in the simulation at 3 s, where a jump in the pressure loss occurs. As observed, CFD-DPM simulations can reproduce the effect of solid loadings but differences in the results are clear when compared to the presented experimental values. The min-min case presented considerable errors even in the absence of particles, while the max-max case presented fair representation of the experimental results for both the air and air-laden conditions.

Snapshots of instantaneous particle positions for two selected cases are presented in Fig. 6. The classification mechanism inside the chamber is clearly observed in both cases. Bulk particles (size ≈ 1 mm) descend through the chamber with negligible action because of air drag. Bulk particle trajectories are hardly modified even when passing through the secondary inlet

at the bottom. Thus, recirculation of bulk particles because of the secondary inlet is not represented, being a limitation of the modelling approach. Despite the apparent disconnection between air and particles, the pressure loss jump presented in Fig. 5 evidence that air-particle interactions are properly accounted for in the model.

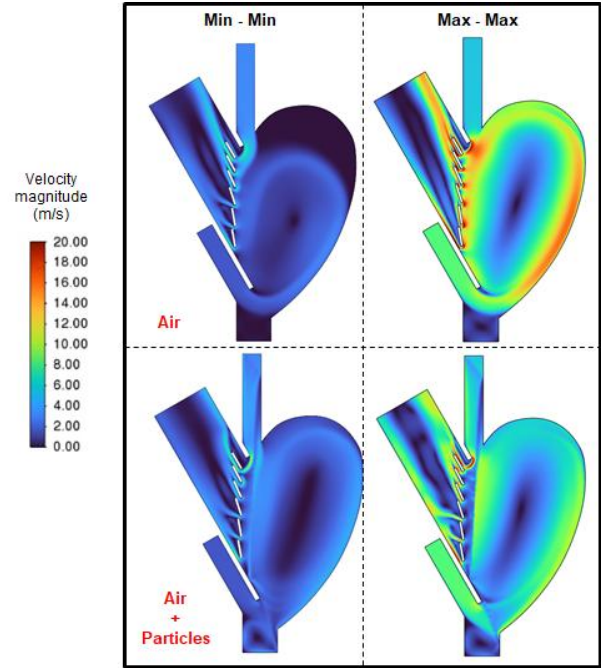


Figure 4. CFD velocity results (top) vs CFD-DPM results (bottom) for two of the study cases.

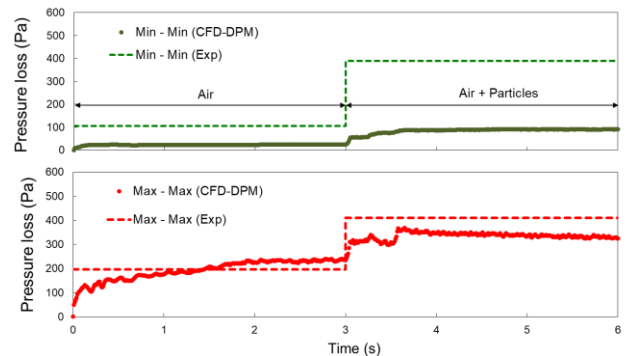


Figure 5. CFD-DPM results in terms of particle positions for two of the study cases.

The trajectories of tracer parcels (sizes ≤ 1 mm) are presented in Fig. 6, describing the classification inside the GIC. Comparison between the min-min and max-max cases present differences in the particle sizes that are dragged to the outlet of the classifier. Fig. 7 presents the classification performance in terms of the partition curves for two selected cases. Experimental results show that the cut size is near $75 \mu\text{m}$ for the max-max case, being the higher cut size found among the study cases. Other cases, such as the min-min case, present cut sizes finer than $50 \mu\text{m}$. Such fine cut sizes suggest that the GIC is operating at airflow rates lower than designed. Comparison between experimental and numerical results demonstrate that CFD-DPM results presents classification performance

close to ideal, with an overestimated sharpness of cut and neglecting the fishhook effect for the finer sizes.

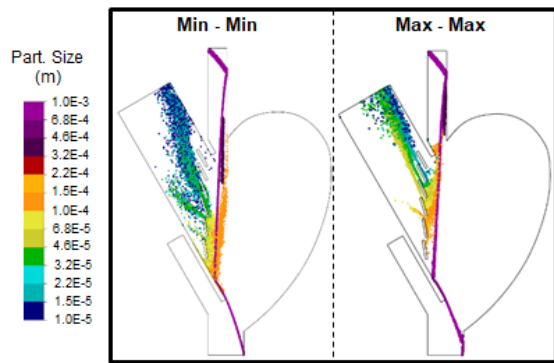


Figure 6. CFD-DPM results in terms of particle positions for two of the case studies.

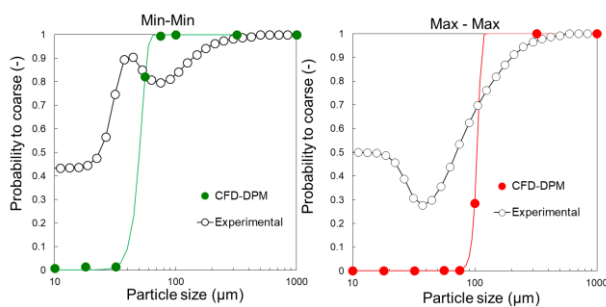


Figure 7. Comparison between experimental and predicted partition curves for two selected case studies.

Differences between simulated and experimental results were expected as the fast CFD-DPM approach was proposed to give fast simulation results at the risk of neglecting secondary but important physical behaviors such as the account of solids volume fraction inside the chamber or the adhesion / cohesion forces that affect classification of fine particles due to particle clustering. Such phenomena may be represented in more ambitious simulation approaches, but that demand considerably higher computation times.

Despite the evident errors, Fig. 8 shows good agreement between simulated and experimental results when comparing the x_{80} of the case studies. The value of x_{80} may seem arbitrary, but the x_{50} value could not be computed in some of the cases. Despite the simulation deviations, Fig. 8 shows that the fast CFD-DPM approach represents the trend in the x_{80} , proving that the method can be used to simulate industrial scenarios maintaining internal consistency and being of value to spot the effect of operating variables on classification performance.

Computation time resulted in approximately 60 hours using a workstation featuring an AMD Ryzen 2920X (12 Cores) and 64 GB of RAM, which is an affordable computation time, considerably shorter than a similar simulation using standard CFD-DEM methods in the same workstation.

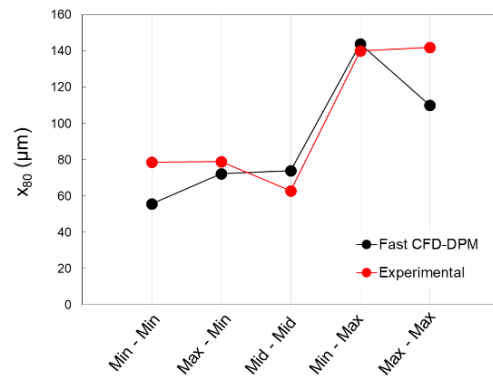


Figure 8. Summary of experimental versus predicted x_{80} .

4. Conclusions

A fast CFD-DPM simulation approach was used for the simulation of the classification of gneiss particles in an industrial GIC.

The method was able to give fairly accurate results when predicting the overall pressure loss with and without particles being fed to the process.

Partition curves obtained with the method present closer to ideal classification due to the physical effects neglected in order to accelerate the computation of the method.

Despite the deviations in prediction of the partition curves, the method showed consistent results preserving the trends in the experimental results.

Acknowledgement

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AI-Driven Surrogate Modelling of Wet Stirred Media Mills

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Abstract. Modelling of wet-operated stirred media mills (WSMMs) using coupled CFD-DEM simulations provides detailed insights into stress energy distributions and particle breakage mechanisms. However, the high computational cost of these simulations limits their applicability for dynamic process modelling and integration with population balance models (PBMs), which require continuous stress energy distribution inputs to capture evolving process conditions. In this work, an AI-based surrogate model is proposed to replace CFD-DEM simulations by predicting stress energy distributions, stress frequency, and power consumption as functions of key operating and material parameters, including grinding media size and filling degree, stirrer tip speed, as well as contact properties. The surrogate is trained on systematically generated CFD-DEM data using an active learning strategy to efficiently explore the high-dimensional parameter space. New simulation conditions are iteratively selected based on model uncertainty to maximize information gain while minimizing computational cost. The resulting framework enables rapid and physically consistent prediction of process behaviour, providing a pathway toward dynamic modelling, process optimization, and scale-up of WSMM systems.

1. Introduction

Wet-operated stirred media mills (WSMMs) are widely used for fine grinding applications, where process performance is governed by stress energy distributions and stress frequency [1,2]. High-fidelity modelling using coupled CFD-DEM simulations enables detailed resolution of bead-fluid and bead-bead interactions, providing valuable insight into breakage-relevant quantities [3-5]. However, the computational cost associated with such simulations limits their applicability for large-scale parametric studies and dynamic process modelling. In particular, population balance models (PBMs) require continuous inputs of stress energy distributions to capture evolving process conditions, which cannot be efficiently obtained through direct coupling with CFD-DEM simulations. Changes in process conditions, such as slurry viscosity, directly influence stress energy distributions and consequently affect breakage behaviour, requiring continuous updates of model inputs. To address this limitation, the present work proposes an AI-based surrogate modelling framework to replace CFD-DEM simulations and enable rapid prediction of key process descriptors across a wide operating space.

2. Methodology

2.1. CFD-DEM Simulations and Data Generation

A high-fidelity unresolved CFD-DEM framework [3,4] is employed to generate the dataset required for training the surrogate model [6-8]. The simulations are performed on

a laboratory-scale wet stirred media mill (PML-1), where bead-fluid and bead-bead interactions are resolved through volume-averaged fluid coupling (CFD) and soft-sphere contact mechanics (DEM). A representative simulation snapshot is shown in Figure 1, illustrating bead motion and velocity distribution within the mill.

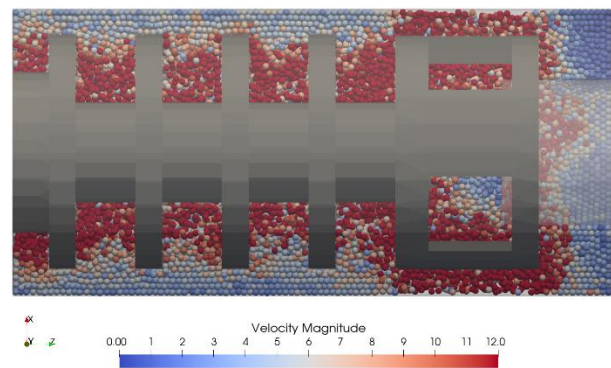


Figure 1. Instantaneous bead velocity distribution of PML-1. Case: stirrer tip speed (v_t) $\sim$ 12 m/s, bead diameter (d_{gb}) = 2 mm, filling degree (ϕ) = 80%

To systematically explore the operating space, key process and material parameters are varied over a representative range of operating conditions. These include stirrer tip speed, grinding media (bead) diameter, bead filling degree, bead density, slurry viscosity, and contact parameters.

For each simulation case, stress-based descriptors relevant for breakage (stress energy distributions, stress

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frequency, and power consumption) are extracted using customized post-processing routines. In particular, the stress energy per collision is evaluated based on relative bead velocities and effective mass considerations (as described in [4]):

$$SE = \frac{1}{2} m_{eff} v_{rel}^2 \quad (1)$$

where m_{eff} is the effective mass of interacting beads and v_{rel} is the relative collision velocity. From this, stress energy distributions (SEDs) and stress frequency are computed, along with mill power consumption.

The resulting dataset establishes a mapping between operating conditions and breakage-relevant quantities, forming the basis for surrogate model development.

2.2 AI-Based Surrogate Model and Active Learning

An AI-based surrogate model [6-8] is developed to approximate the nonlinear relationship between process parameters and stress-based descriptors obtained from unresolved CFD-DEM simulations. The model takes operating and material (DEM) parameters as inputs and predicts outputs including stress energy distributions,

stress frequency, and mill power consumption. Particular emphasis is placed on accurately capturing stress energy distributions over multiple orders of magnitude, as these directly govern breakage behaviour in WSMMs [1,2].

To efficiently explore the high-dimensional parameter space, the surrogate model is trained using an active learning strategy, as illustrated in Figure 2. Initially, a limited number of CFD-DEM simulations (Generation 0) is performed to construct a baseline training dataset. Based on the trained surrogate, regions of high prediction uncertainty are identified, and additional simulation points are selectively sampled in these regions.

This iterative loop, comprising simulation, training, uncertainty estimation, and resampling, continues until convergence criteria are met, such as stabilization of prediction accuracy or diminishing information gain. The approach enables targeted data generation, significantly reducing the number of required CFD-DEM simulations compared to exhaustive sampling.

The resulting framework is expected to deliver accurate predictions across the operating space while maintaining computational efficiency, thereby enabling rapid evaluation of process conditions.

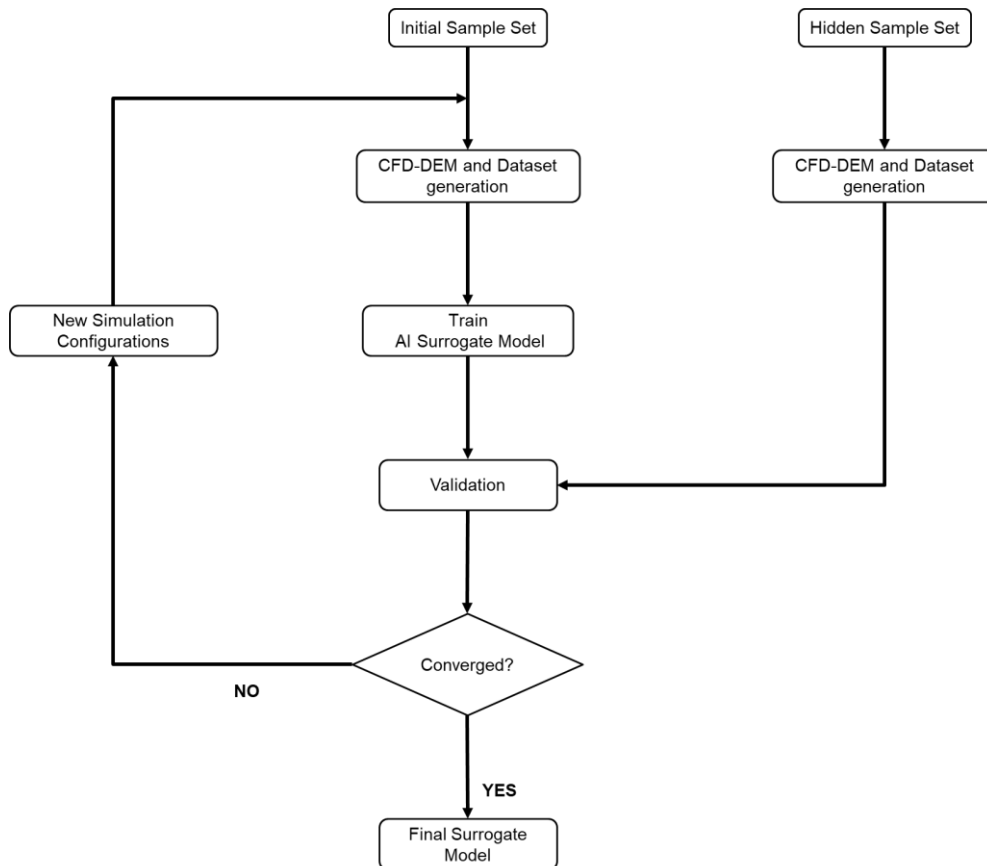


Figure 2. Active learning framework for AI-based surrogate modelling of wet stirred media mills. An initial set of CFD-DEM simulations is used to train the surrogate model. New simulation conditions are iteratively selected based on prediction uncertainty, while model performance is evaluated using a hidden validation set until convergence is achieved.

3. Conclusions

This work presents a framework for AI-driven surrogate modelling of wet stirred media mills, aimed at replacing

computationally expensive CFD-DEM simulations. The proposed approach integrates high-fidelity simulation data with machine learning techniques to predict stress

energy distributions, stress frequency, and power consumption across a wide range of operating conditions.

By incorporating an active learning strategy, the framework enables efficient exploration of the parameter space while minimizing simulation effort. The developed surrogate model is expected to facilitate rapid and physically consistent process modelling, enabling future integration with dynamic process models and population balance approaches.

Ongoing work focuses on generating the CFD-DEM dataset and validating the predictive capability of the surrogate model, with particular emphasis on generalization and robustness across operating conditions.

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Artificial Intelligence in Comminution: From Predictive Models to Agentic Discovery

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Abstract. Artificial intelligence (AI) is reshaping how comminution and classification processes are modelled, optimised and understood. Early applications centred on narrow predictive models trained on experimental or numerical data, followed by surrogate models that emulate expensive simulations at a fraction of their computational cost. The current wave of transformer-based systems extends this spectrum considerably. As general-purpose reasoning and transfer-learning architectures, they enable domain-specific expert systems, agentic workflows to autonomously set up and analyse simulations, and the combination of language models with symbolic regression for data-driven discovery of interpretable, mechanistically meaningful equations. Beyond comminution, recent developments in frontier AI research, including autonomous coding agents that improve their own algorithms, AI co-scientists that generate and test hypotheses, and systems whose autonomous task-completion horizon doubles every couple of months, represent a rapid trajectory whose implications target every field. This contribution provides an overview that bridges classical and generative AI in the context of comminution, illustrates the state of the art through case studies on stirred media mills and DEM surrogate modelling, and contextualises current frontier capabilities.

1. AI in Comminution: From Data to Understanding

Artificial intelligence (AI) has moved from an external trend to an increasingly necessary complement in experimentation, mechanistic modelling and numerical simulation in comminution. The first broad wave of applications centred on narrow AI, predictive models trained on experimental or numerical data to estimate quantities such as product fineness, stressing conditions, collision energies or process performance [1–3]. These approaches already demonstrated major reductions in modelling effort and opened routes towards optimisation, control and scale-up. A next logical step was the move from predicting selected target variables to emulating entire simulations through surrogate models, for example for the discrete element method (DEM). In this mode, AI acts as a fast digital-twin layer above established tools, accurately emulating simulation outputs while reducing computational costs by several orders of magnitude. Similar trajectories in other scientific domains, most prominently AlphaFold in protein structure prediction [4], illustrate the broader potential of data-driven emulation whenever first-principles computation is expensive.

2. Transformers, Agents and Interpretable Discovery

Recent transformer-based models broaden this landscape considerably [5]. Unlike classical neural networks that map fixed inputs to fixed outputs, transformers are

general-purpose architectures whose strength lies not only in language processing but in transfer and analogy learning across heterogeneous data, be it text, code, equations, images, sound, sensor-motor or measurement data, gene sequences and structured documents, or all of them combined. This generality makes them useful as reasoning engines and interfaces to scientific knowledge and engineering software. For comminution, this enables domain-specific expert systems for milling and classification knowledge, retrieval-enhanced access to literature and internal documentation, and agentic workflows that prepare simulation cases, operate software tools, execute analyses and summarise results with minimal human intervention.

In parallel, symbolic regression and related data-driven equation-discovery methods offer a complementary path towards interpretable, mechanistically meaningful relations rather than purely black-box predictions [6]. The combination is especially promising: language models can orchestrate data handling, hypothesis generation and workflow automation, while evolutionary symbolic or physics-guided methods identify compact equations with physical meaning. Applied to stirred media milling data, this hybrid approach converges on scaling-law families that are both predictively accurate and discussable by domain experts, opening a route towards automated assistance not only for reporting and knowledge access, but for model formulation itself.

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3. Where Frontier AI Stands Today

Beyond comminution-specific tools, the broader AI landscape is advancing at a pace the engineering community should be aware of. DeepMind's AlphaEvolve, an autonomous coding agent guided by evolutionary search, recently discovered the first improvement to Strassen's matrix multiplication algorithm in 56 years and optimised critical components of Google's data-centre infrastructure [7]. Sakana AI's AI Scientist produced a fully AI-generated research paper that passed blind peer review at an international machine-learning workshop [8]. Google's AI Co-Scientist and related multi-agent systems autonomously generate, test and refine scientific hypotheses, pointing towards a future in which AI contributes directly to the discovery process.

Benchmark data from METR quantifies this trajectory: the length of tasks that frontier AI agents can complete autonomously with 50 % reliability has been doubling approximately every couple of months over the past years [9]. Leading AI researchers estimate systems matching broad human-level cognitive capabilities within five to ten years, with some placing this horizon even sooner [10]. For comminution, where sparse data, changing feed materials and multiscale physics quickly expose modelling weaknesses, human validation remains essential for now. Yet the trajectory makes clear that the role of AI in engineering workflows is shifting from isolated prediction tools towards semi-autonomous collaborators.

4. Implications and Outlook for Comminution

The most immediate practical gains are likely to arise where general-purpose reasoning models are combined with fast, narrow digital twins. A frontier language model can formulate hypotheses, design parameter studies and interpret results, while surrogate models evaluate thousands of candidate configurations in seconds. With only the most promising solutions needing to be validated experimentally, a flywheel effect is established, massively accelerating iteration cycles. This paradigm applies across predictive models, DEM surrogates, transformer-based assistants, tool-using agents and interpretable equation discovery, each addressing different parts of the same workflow.

Longer term, the same trajectory points towards multimodal process understanding, closer integration with automated experimentation and laboratory robotics, and autonomous digital twins that continuously learn from operational data. At the same time, wider adoption requires clear guardrails, such as factual grounding, provenance of generated outputs, uncertainty awareness and expert review. The aim of the present contribution is to provide an overview of these developments and to outline where meaningful adoption for comminution can start today.

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Investigation on selected methods for condition and process monitoring in mineral processing of lithium ore

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Abstract. The European Union's goal of achieving climate neutrality by 2050 has accelerated the search for domestic lithium sources. As demand for lithium continues to rise, particularly in the fields of electromobility and energy storage, innovative mineral processing technologies are essential for the efficient exploitation of Li-ores from European deposits. This study presents a comprehensive investigation in the field of condition and process monitoring special in the comminution of Li-ores from European deposits. Optimization goals for machines in the mining sector include increasing throughput and improving product quality, taking into account the varying properties of the raw materials. Fast feedback on the product quality like the size range and ore content would allow for control optimizations to achieve both energy efficiency and an optimized product size range. Methods for determining the product quality and key figures of comminution machines are being investigated in this research.

1. Introduction

Condition and process monitoring is becoming an increasingly important factor in raw material beneficiation, driven in particular by the steadily growing demands for efficiency, product quality, and sustainability. While industrial manufacturing processes typically handle homogeneous feed materials, raw materials within a single deposit often exhibit significant spatial and temporal variability in their properties. Producing a consistently high-quality final product therefore requires besides a flexible and adaptable design of the individual process steps a constant monitoring of relevant specifications.

Most processing machinery consists of stationary installations designed for operating lifetimes of several decades. As a result, it is often not economically viable for operators to replace them entirely with costly new equipment. In industries with narrow profit margins, it is therefore all the more worthwhile to enhance the efficiency of existing machines by retrofitting them with intelligent sensor systems. The ability to transform the acquired data into actionable information and decisions through advanced software solutions further enables upgraded machines to be integrated seamlessly into a modern, highly automated, and technologically sophisticated production process.

Changes in the particle size distribution (PSD) within the feed stream can be detected in one part of the study using a system setup based on a passive-intrusive acoustic sensor system. The focus is placed on monitoring the material flow on a conveyor belt, using the particle size distribution as an illustrative example. A large number of studies exist on the online detection of particle

size distributions using various systems [3,4], including approaches based on passive-intrusive acoustics [5-7]. The system presented here is deliberately simplified and is designed only to detect deviations in product quality, such as changes in the particle size distribution. Its commissioning and calibration are therefore significantly easier.

To separate valuable from barren material sensor-based sorting can be implemented and has already been investigated in different papers [8-10]. Sensor data in crushers is analysed to get an idea about the content of valuable material in a sample, particle size and wear.

2. Materials and Methods

2.1. Material

The investigations focused on low-grade or mineralogically complex ores from underutilized deposits in Europe. Each ore sample contained one of the lithium-bearing micas: zinnwaldite, lepidolite, or petalite. The selected ore samples from various European deposits were systematically characterized in [11] with respect to their mineralogical and physical properties to identify the most suitable mineral processing strategy.

2.2. Systems for condition and process monitoring

A prototype was developed that is capable of detecting changes in the particle size distribution (PSD) of a conveyed material. The system is operated through a simple user interface designed specifically for the present application. In addition, a wireless data transmission link

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was established between a microcontroller and the Raspberry Pi via a WLAN network. Figure 1 illustrates the basic structure of the monitoring system.

The system enables the transmission of the MPU-6050 accelerometer data to the Raspberry Pi. One advantage of this transmission method is that the data can be accessed simultaneously by any device connected to the network, such as a laptop or desktop PC. For wireless data transfer, the ESP-32 microcontroller is used. It is connected to the accelerometer and reads its raw data. In addition, it provides an HTTP server that supplies the acceleration measurement data. The accelerometer is attached to an impactor that is in contact with the material stream, conveyed on a belt conveyor. When the particles in the mass flow collide with the waveguide at mass and velocity, they create an impulse. The height of this impulse depends on the volume of the particles, assuming the same impact velocity and particle density. The vibrations resulting from the collision are measured by an acceleration sensor on the oscillator. Through data processing and analysis, conclusions can be drawn about the particle size distribution.

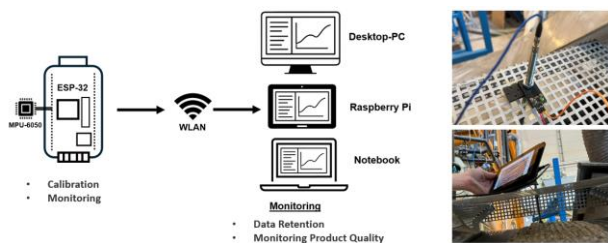


Figure 1. Monitoring system for quality control of the material.

Figure 2 shows the used laboratory jaw crusher. The crusher has jaw dimensions of 110 mm x 160 mm, a crushing chamber height of 300 mm, and a stroke of 10 mm. To measure the occurring crushing forces, four load cells with a measuring range of up to 20 kN are installed in the fixed jaw. As shown in Figure 2, two load cells are positioned in the upper section and two in the lower section of the jaw, allowing the forces in each region to be measured separately.

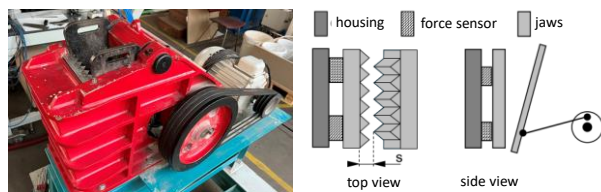


Figure 2. Laboratory jaw crusher (left) & sketch of crusher and force sensors (right)

The following investigations focus on determining the crusher fill level and the lithium content based on sensor data obtained from force measurements.

3. Results and discussion

Different fractions of petalite lithium ore were conveyed under identical operating parameters, including conveying speed. For each fraction, three measurements of 10 seconds each were recorded. The measured values are shown in Figure 3. Smaller particle size distributions result in lower signal values. Measurement accuracy decreases as the material becomes finer. Studies using other sensor types indicate that each particle-size range has a suitable sensor and that the appropriate sensor should be selected according to the specific application.

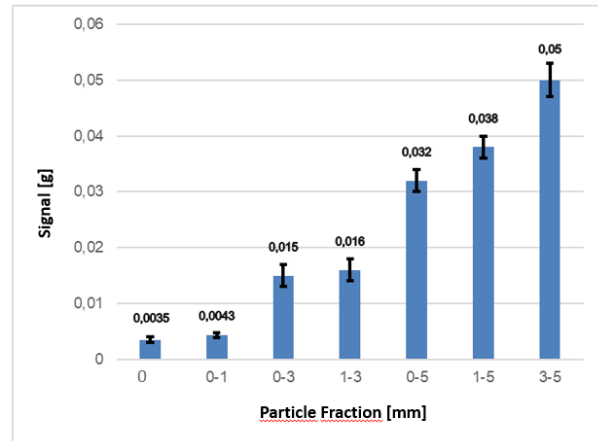


Figure 3. Average values for the measured signals depending on the size fractions

The test material was conveyed and the system was calibrated accordingly. For this purpose, the average signal over a measuring period of 10 seconds was used as the reference value. Samples were taken downstream of the sensor to analyse the PSD by conventional screening. During continuous measurement, using the same 10-second interval, the system computes the average values and compares them with the calibrated reference. If a deviation exceeding the defined limit is detected, the system alerts the operator. In this study, a threshold of 20% of the signal was set. When the measured value dropped by 22%, a sample was taken for further analysis. The results are shown in Figure 4.

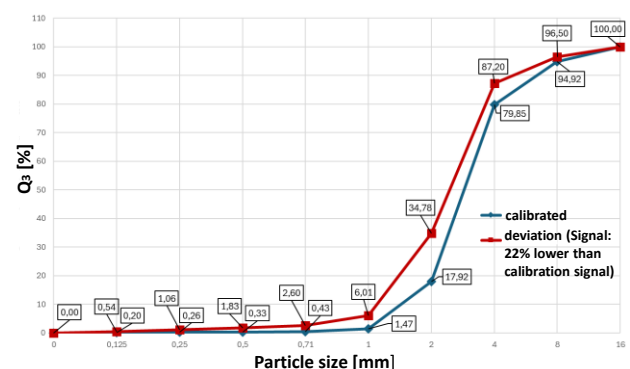


Figure 4. PSD's for calibration and testing after it failed the quality control of the system

To prevent the jaw crusher from becoming overloaded, it is helpful to know the filling level of the crushing chamber.

In tests with Zinnwaldite and Petalite, the influence of the crusher fill factor on the crushing forces at the top and bottom was investigated. The mean values of the respective measured forces are shown in Figure 5. On average, all crushing forces during the comminution of Petalite were about three times as large as those for Zinnwaldite. For all forces, clear trends as a function of the filling ratio f_B are discernible. The forces in the lower region increased only slightly with the filling degree; the regression lines shown serve only to illustrate the trend and would not intersect the origin if extended. This is because, as the single-grain tests show, even a very low filling degree can lead to high forces at the bottom. Since, as the fill level increases, the forces acting on the upper load cells increase, and since the forces increase more slowly because less crushing occurs in the upper region, the increase in the lower force is nonlinear when considering the entire fill level range. For the average forces at the top $F_{m,o}$, linear increases were observed for both ores, and their regression lines could be extended to the origin with very good accuracy. They are described by the following equations:

$$f_{B \text{ Zinnwaldite}} = 0,5022 \cdot f_B \quad (1)$$

$$f_{B \text{ Zinnwaldite}} = 1,6311 \cdot f_B \quad (2)$$

The R^2 of equation 1 is by 0,998 and from equation 2 by 0,995. The compressive forces in the upper section can be considered a suitable indicator of the crusher's fill level, provided that a sufficiently large data basis is available to make the variation of these forces predictable as a function of the material properties, such as strength and particle size.

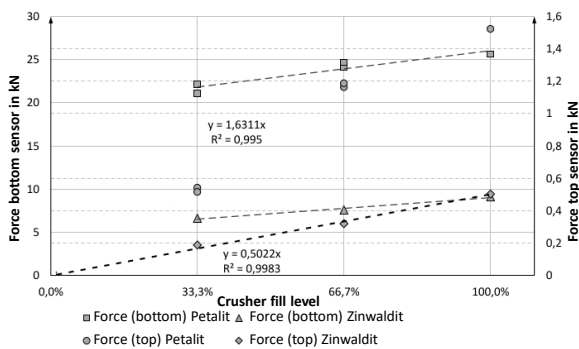


Figure 5. Change in crushing forces in the upper and lower regions of the crushing chamber as a function of the filling ratio for Petalite and Zinnwaldite, feed particle size: 15–30 mm

Figure 6 shows the mean peak forces during the comminution of the 30/50 mm fraction of Zinnwaldite High Grade and Zinnwaldite Low Grade at a gap width of 11 mm. Consistent with the strength values obtained from the Point Load Tests, the measured forces for the High-Grade material are significantly lower than those for the Low-Grade material. An evaluation of sensor data

from force measurements or power measurements can therefore provide information about the lithium content of the zinnwaldite.

Results of the sensor-based sorting of Zinnwaldite are published in [10]. The lithium content in the High-Grade class is approximately 2.4 times higher than in the barren class.

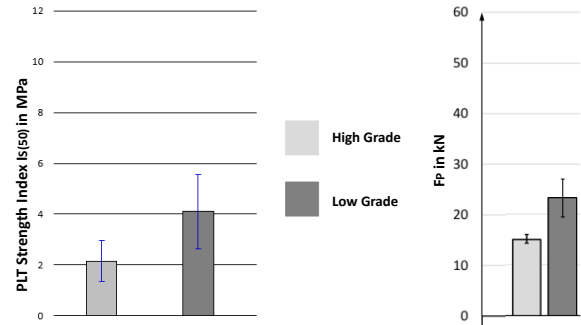


Figure 6. PLT Strength Index (left) and measured force in the jaw crusher (right)

4. Conclusion

The study focused first on detecting changes in product quality, such as the particle size distribution, using a system based on intrusive passive acoustics. A change in PSD can indeed be detected with this approach.

A second focus was the determination of the crusher filling degree using sensor data from the crushing force. The compressive forces in the upper section of the jaw crusher proved to be a suitable indicator of the fill level. The force-measurement data also provided insights into the lithium content of the crushed zinnwaldite, since the compressive strength of the high-grade material is lower than that of the barren fraction.

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Different top-down approaches to two-dimensional nanoparticles with plate-like geometry

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Abstract. We present two approaches for production of two-dimensional (2D) nanoparticles with plate-like geometry in a stirred media mill. The first method is stirred media delamination. It relies on overcome of weak van-der-Waals interactions between the layers of layered materials due to shear forces generated by collisions of the particles with the milling beads. This results in delamination of nanosheets with a thickness of few atomic layers from layered materials. The second method for nanoplatelet generation is based on plastic deformation of ductile particles in a stirred media mill by compression forces. Process parameter studies for production of 2D nanomaterials require fast in-suspension particle size analytics with high statistical significance. Generally, in-suspension size analysis of 2D nanoparticles is challenging. Size-distributions of 2D nanomaterials with size- and shape-dependent optical properties can be measured by Analytical Ultracentrifugation with multiwavelength detector (MWL-AUC). For nanomaterials without size-dependent light absorption, scattering of a laser beam in forward and sideward direction can be exploited to distinguish between nanoparticles of different geometry.

1. MoS₂ nanosheet formation by stirred media delamination

2D nanomaterials with plate-like geometry like graphene, MoS₂, WS₂ or GeS exhibit unique optical and electronic properties and are therefore, promising for applications as visible light photocatalysts, for Li-ion batteries and sensing [1-3].

Delamination of sheets with a thickness of only few atomic layers from layered materials in liquid phase is a versatile approach to plate-like 2D nanoparticles. In layered materials there are strong covalent and/or ionic bonds within the layers, but only weak van-der-Waals interactions between the layers. The van-der-Waals forces between the layers can be overcome by applying shear forces parallel to the layers. In this way thin nanosheets are peeled-off. If the delaminated nanosheets are sufficiently stabilized against agglomeration and re-stacking, suspensions of nanosheets are accessible by liquid phase delamination processes. The shear forces required for delamination of layered materials can be generated by ultrasound [4], by rotor-stator devices [5], high pressure homogenization [6] and stirred media mills [7-11]. We investigated the stirred media delamination of layered materials in detail for graphene [6-9], hexagonal boron nitride [10] and molybdenum disulfide [11] as this method is in principle scalable to industrial relevant amounts of material. We found that for sufficiently low

stressing energy of the milling beads delamination of nanosheets dominates over lateral fracture [8].

In this contribution, we show the delamination of molybdenum disulfide in a stirred media mill as this material is an interesting semiconductor with size-dependent optical properties [12], see Figure 1.

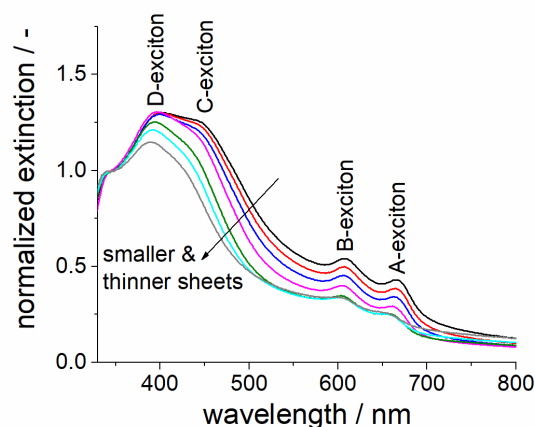


Figure 1. Size-dependent UV/Vis spectra of molybdenum disulfide nanosheets with excitonic transitions [11].

Backes et al. exploited the size-dependent optical properties of molybdenum disulfide nanosheets to develop a method for determination of mean values for

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the lateral diameter L and for the number of layers per particle N [13]. By correlating UV/Vis spectra of different molybdenum disulfide size fractions with the nanosheet dimensions obtained from statistical TEM and AFM analyses they obtained the following empirical equations [13]:

$$L = \frac{3.5 \mu\text{m} \cdot \frac{E_B}{E_{345}} - 0.14 \mu\text{m}}{11.5 - \frac{E_B}{E_{345}}} \quad (1)$$

$$N = 2.3 \cdot 10^{36} \cdot e^{-\frac{54888 \text{ nm}}{\lambda_A}} \quad (2)$$

with $E_{345\text{nm}}$: extinction at 345 nm, E_B : extinction at the B-exciton and λ_A : wavelength of the A-exciton (see Figure 1).

We demonstrate, how to extend the method of Backes et al. so that distributions for L and N can be obtained. For that purpose, we classified the delaminated samples from the stirred media mill by centrifugation to obtain different size-fractions. These size fractions were analysed by MWL-AUC, which is the gold standard for size and shape analytics in suspension [14-16]. As this method yields the distribution of the sedimentation coefficient (sedimentation rate normalized to the relative centrifugal force) in combination with the UV/Vis spectrum of each settling component of the sample, distributions for L and N can be extracted from a single AUC measurement.

Based on the distributions for L and N obtained from MWL-AUC, the classification by preparative centrifugation is described quantitatively by determination of a separation efficiency curve for each size dimension.

2. Plastic deformation of spherical silica particles

Compression experiments on single particles in a SEM micromanipulator revealed that spherical silica particles with sizes below a critical value – the brittle-ductile-transition – do not show brittle fracture when exposed to compression forces. Instead, the shape of the particles transforms from spherical to plate-like due to plastic deformation. During processing in a stirred media mill, particles are exposed to compression forces when captured between two colliding milling beads. As expected from SEM micromanipulation, the formation of plate-like silica nanoparticles in a stirred media mill is observed for feed particles with sizes in the ductile range [17]. We processed spherical amorphous silica particles in an organic dispersing medium in a stirred media mill to prevent dissolution. The size of the feed particles and the process conditions were varied. The shape transformation from spherical to plate-like was investigated by statistical analysis of SEM micrographs as well as in suspension by single-particle light scattering in forward (FSC) and sideward (SSC) direction, see Figure 2.

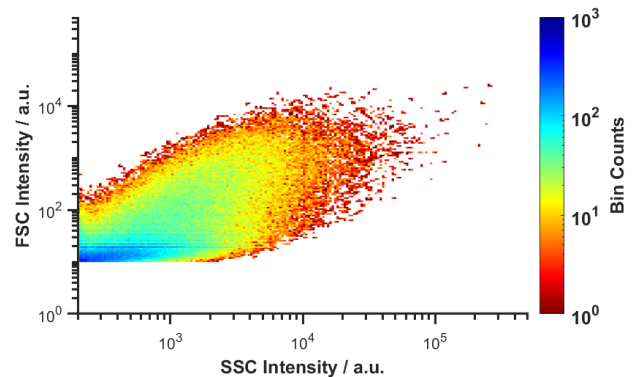
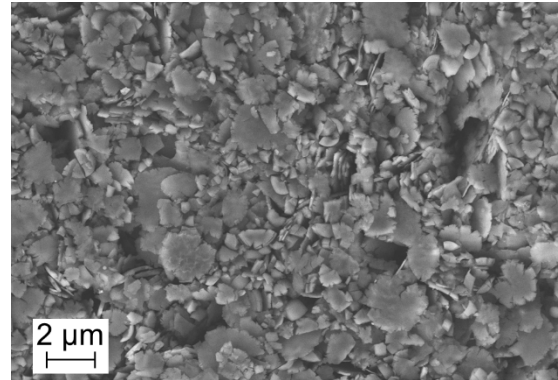
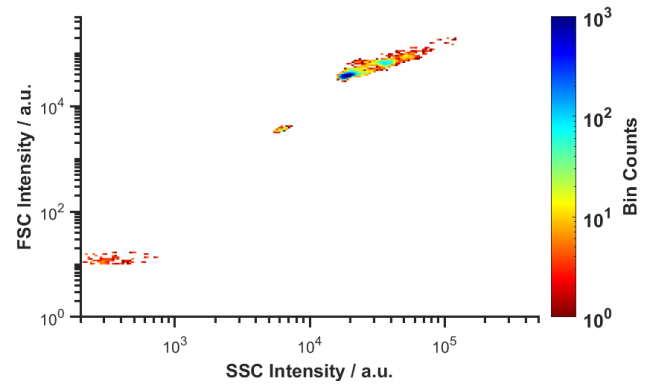
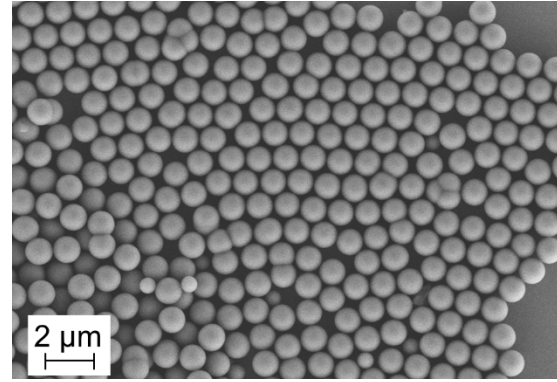


Figure 2. SEM micrograph and 2D scatter histogram of the spherical feed particles (above) and of plate-like particles formed by plastic deformation in a stirred media mill (below).

Within 10 h the spherical particles are completely transformed to platelets with a thickness of about 100 nm or even thinner. As the light scatter behaviour of spherical and plate-like silica particles is quite different, see Figure 2, a quantitative evaluation of the scatter histograms

provides access to the relative fraction of spheres and platelets in the sample. The used laser light scattering device “LUMiSPOC” (Single-Particle Optical Counter from LUM GmbH) enables analysis of the scatter behaviour of thousands of particles within few minutes. Thus, this method provides fast shape analysis in suspension with high statistical significance and will be further developed for more detailed size and shape analysis in future.

Acknowledgement

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A Digital Ecosystem for Environmental Benchmarking and Decision Support in Aggregate Production

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Abstract. Mass balancing of raw material regional supply is a particular challenge for the quarry and construction industry. This includes both virgin and recycled material, aggregates and soil in many cases, small to large infrastructure projects, multiple suppliers and entrepreneurs, and over multiple data systems. Supply and demand are not always synchronized; demand is tight on both economic and environmental choices, which sometimes leads to suboptimal decisions that favour economic benefits. Current practices are often fragmented, with limited integration between process data, environmental assessments, and supply chain planning tools.

This paper presents research and development efforts to enable a digital ecosystem with seamless data transfer, visualization, and benchmarking of aggregate production and supply. The framework brings together multiple industry-oriented methods and tools developed within ongoing research initiatives, demonstrating their potential for interoperability and coordinated use. This includes process and environmental calculation platforms Plantsmith, a GIS-based system (QuarryGIS) for visualization of environmental benchmarking and logistics in infrastructure projects, and an AI assistant based on a retrieval-augmented generation (RAG) system supporting the development of Environmental Product Declarations (EPDs). Other relevant digitalization efforts will also be highlighted to enable a wider digital ecosystem for the aggregates supply system.

The proposed approaches demonstrate how digital integration can support mass-balance consistency, improve transparency in material flows, and enable data-driven decision-making across production and supply chain levels. The results highlight the potential for improved resource efficiency, reduced environmental impact, and more informed selection of aggregates supplier in infrastructure projects.

1. Introduction

Aggregate production is essential for any urban development and maintenance. Aggregate production shares various similarities with coarse-dry mineral processing, as crushers and screens are applied for comminution and classification methods to achieve the desired product quality based on the intended application of the aggregates.

Both industries face similar challenges and opportunities regarding digitalization and improved resource efficiency. It has been estimated that up to 90% of generated data is not utilized for analysis or decision-making [1], and that only covers the data collected. In industrial production systems, data is frequently incomplete or not collected due to acquisition costs and lack of standardized data infrastructures [2]. In addition, the human factor plays a critical role. Operators and engineers must understand both the underlying system behavior and the limitations of digital tools in order to develop trust in their outputs. The effectiveness of

decision-support systems depends, therefore, not only on data availability but also on user trust, which governs whether such systems are accepted and used in practice [3]. Often, the lack of transparency is the cause of mistrust.

All of these aspects are limiting the potential improvements for the aggregate and minerals industries. There are, of course, several good examples of digitalization efforts within the field, such as vision systems, advanced process control, soft sensors, various digital support systems, etc. Two examples of such initiatives are the EU Horizon projects DigiEcoQuarry (Grant No. 101003750) and Rotate (Grant No. 101058651), which address multiple perspectives of digitalization and improved sustainability of aggregate production. However, these applications are not widely used in the field, and standalone applications often lack interoperability with other systems, hindering digital integration and a complete digital infrastructure. This limits the potential for improving resource efficiency and

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environmental performance. Together, these challenges: limited data utilization, incomplete data collection, and insufficient trust in digital systems, form a critical barrier to the effective implementation of data-driven decision-making in the aggregates industry. The data generated is also not only associated with the production. Besides the machine and process data, there is substantial data generated on organisational and market level.

This paper aims to give an overview of the work done on integrating environmental information into decision-making for aggregate production and supply. The effort is a multi-tier approach, including integration of process and environmental calculations.

2. Environmental Impacts of Aggregates

The reporting of environmental impacts for aggregate production is changing from being market-driven to being a regulatory requirement. In the nordics, there has been a rapid development in the number of Environmental Product Declarations (EPDs) published, and the amount of publicly available data is just going to increase. An EPD is a comprehensive document that provides transparent and verified information on the environmental impact of a product or service throughout its entire life cycle, from raw material extraction to disposal, as described by EN 15804. These can be used for benchmarking, as demonstrated by Gowda et al [4]. Currently, the European aggregate industry is in a transition phase following the recent revision of the Construction Products Regulation (CPR). The CPR introduces requirements to declare environmental performance as part of the Declaration of Performance (DoP), thereby extending the basis for product evaluation beyond technical and economic criteria. This shift places new demands on data availability, quality, and integration, as environmental indicators are largely derived from life cycle assessment methodologies in accordance with EN 15804. Starting with Global Warming Potential (GWP) as a required indicator from 2026–2027, with a gradual expansion to the full set of EN 15804 core indicators by 2030.

3. System Frameworks

A digital ecosystem needs to consist of multiple modules that enable the user to evaluate the process performance from multiple perspectives and provide feedback that the user can apply for data-informed decision-making. The proposed digital ecosystem can be understood as an iterative loop between analysis, synthesis, and decision support, see Figure 1. This conceptualization is consistent with established Decision Support System frameworks, where data is transformed into actionable insights through processes of analysis and integration [5].

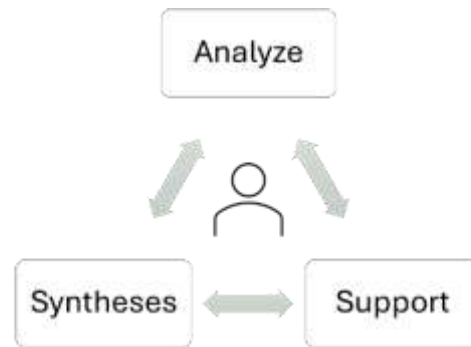


Figure 1. General framework for a user-centred digital ecosystem.

3.1. Plantsmith

The core of the system is the online process and environmental platform Plantsmith [6] for quantifying and evaluating the process and environmental performance. The platform is under verification as an EPD tool by EPD International. See Figure 2 for an example of the user interface.

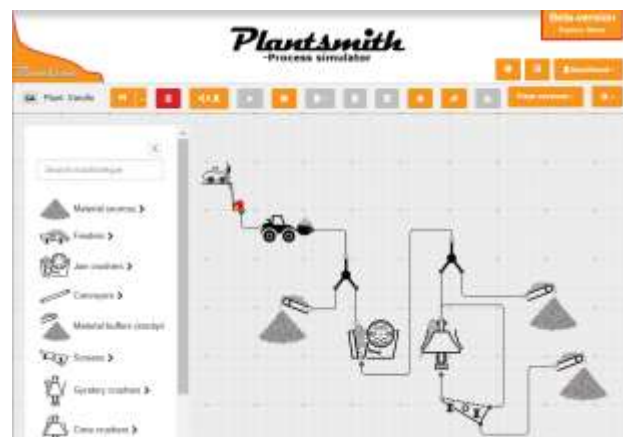


Figure 2. User interface of the online process and environmental flowsheet platform, Plantsmith.

The platform provides a steady-state flowsheet simulation from drilling and blasting, and down to fine comminution and wet processing. Users can access different levels of models based on their modelling background and user access level; these can include, for example, OEM-specific models and empirical models.

The environmental module enables the user to generate EPDs based on company-specific information from production. This includes annual product quantities and corresponding consumption of resources in the form of fuel, energy, and other auxiliary materials needed to maintain stable operation. Utilizing the process simulation environment to automatically generate the allocation of resources to different product groups based on mass and energy balance.

3.2. Quarry-GIS

The interpretation and synthesis of EPD data remain challenging, even for experienced LCA practitioners. To enable improved evaluation of the EPD results, a Quarry-GIS was developed, see Figure 3.



Figure 3. The QuarryGIS for the interpretation and benchmarking of EPD results.

The QuarryGIS provides an overview of the quarries with available EPDs in an SQL web server, mapped out with their coordinates in a Geological Information System (GIS) interface. The user can select the visualization of the national distribution of different impacts for different product groups, as well as evaluate potential logistical alternatives for different infrastructure projects. Enabling benchmarking with other producers and products, as well as supporting the interpretation of the impacts from Plantsmith. Providing reference values to minimize the risk of incorrect data entry and calculations.

3.3. EPD AI Assistant

The third aspect is the supporting functionality. All documents for the involved standards and platform details are accessible. However, the consolidation of the relevant section is time-consuming and difficult to navigate, as some information could be contradictory, as some standards are general while others are application-specific in certain conditions. All associated documentation has been centralized in a MediaWiki as a document and data repository. See example in Figure 4.



Figure 4. Wiki for the Plantsmith platform with an integrated LLM AI trained on the associated documents.

To further enhance the supporting functionality, a Retrieval-Augmented Generation (RAG) architecture has been implemented, using the MediaWiki repository as a knowledge base. A retrieval module selects relevant documents via lexical or embedding-based search, which are then used by a Large Language Model (LLM) to generate context-aware responses. This approach enables

the integration of fragmented data into actionable insights while improving transparency and trust through grounded, traceable outputs. This reduces the cognitive load on users and improves consistency in the interpretation of standards and documentation. A schematic overview of a RAG is illustrated in Figure 5.

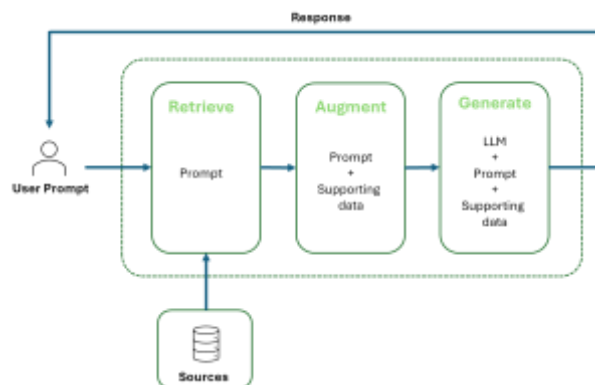


Figure 5. RAG schematic overview.

3.4. Third-party Integration

On top of the local system framework, broader deployment of any digital solution requires compatibility and seamless integration with third-party systems. Plantsmith utilizes a REST API for external communication and has been implemented within larger digital infrastructures, such as DigiEcoQuarry IQS and the Rotate platform. The REST API serves as the interface through which external applications, devices, and services can send, retrieve, and configure data using standardized protocols and formats, ensuring interoperability between systems.

4. Application Example

The most common application will be the flowsheet simulations and the generation of data and documentation for publishing EPDs for the quarry and products. An experienced user will be aware of the data and configuration needed to generate reliable results. While an inexperienced user will need support. A query on product group will result in a combination of responses from the platform manual as well as the standard definition from the GPI with exact location in those documents which it is referring to.

4.1. Design and Evaluation

The primary use case of flowsheet simulations is the design and evaluation of process layouts and configurations, as demonstrated by Bhadani et al. [7]. The platform's user profile and subscription level determine which models are available and they can be customized to specific needs, such as marketing, engineering, research, or training. This enables the development of both custom and generic models for targeted applications. Process evaluation can be conducted based on mass balance, energy balance, cost analysis, or the environmental impact of different products resulting from the selected process configuration.

4.2. Benchmarking

Comparing the result after the process configuration and environmental calculations, the user can go over the to Quarry GIS and evaluate the performance of the circuit with others. A recently published EPD had, for example, a Global warming potential of 1.37 kg CO₂ eq., Acidification of 0.009 Mol H⁺ eq., Eutrophication of 0.04 mol N eq., and Water depletion of 0.22 m³/ton. This results in a percentile of 87%, 85%, 85% resp. 52% over the published EPDs. This is within the expected range, reducing the likelihood of data inconsistencies or input errors. The lower performance in water depletion is attributed to both foreground and background datasets. Within the contribution analysis, it is estimated that the largest contributor to the WP for this product group is the source of electricity, which accounts for 89.6 % of the contribution.

4.3. Improvements

A part of having a platform to assess different operational strategies and resource use. The users can alter process configuration and resources. Given the same process and product group as in the previous example. If the user would like to compare the impact of changing from fossil-based diesel to bio-based diesel, HVO. The dataset can be adjusted for each consumable. A full transition to HVO diesel results in a 41% reduction in GWP, while increasing fuel costs by approximately 33% under current market conditions in Sweden. Additional changes to electrical source. With a green electrical contract for hydropower the GWP would be additionally reduced by 24% to a total of 75% improvements in GWP.

5. Conclusions

This study demonstrates how a digitally integrated ecosystem combining process simulation, environmental assessment, spatial analysis, and AI-based decision support can improve operational planning and environmental efforts in the aggregates industry. By linking operational data with environmental performance metrics and providing user-centered decision support, the proposed framework addresses key challenges related to data fragmentation, underutilization, and trust in digital systems. The results highlight the potential for improved resource efficiency, reduced environmental impact, and enhanced decision-making aligned with emerging regulatory requirements such as the CPR.

Acknowledgement

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Using an innovative size-exclusion extraction system aimed at the isolation of plant-derived exosomes

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Abstract. Exosomes are nanosized extracellular vesicles abundantly found in biofluids and plant biomass, capable of transmitting biological signals and participating in intercellular communication, immune regulation, tissue regeneration, and tumor development. The scientific community's strong interest in the biological effects of exosomes and their various clinical, nutraceutical, and cosmetic applications has driven the search for efficient, simple, and cost-effective methods for isolating and purifying exosomes.

This work introduces an innovative extraction system using a refrigerant solvent in sub-critical conditions that could serve as a straightforward, effective, and scalable alternative to traditional methods currently used for isolating exosomes from both human and plant sources. Extraction trials were conducted on wet and partially dried broccoli sprouts using a lab-scale, semi-automated plant equipped with an on-site homogenizing system to promote disruption of the solid cellular structure and the availability of exosomes in the plant matrix; moreover, a suitable filtration unit was investigated to obtain their size-based separation from the extract.

Although the initial setup included two polycarbonate filters in sequence with decreasing mesh size downstream of the extraction chamber, using a single stainless steel filter and recovering the extract in a preserving phosphate-buffered saline solution proved to be the best approach in terms of process feasibility and recovery of intact, non-aggregated vesicles.

1. Introduction

Recently, exosomes have attracted growing interest in applied life sciences and biotechnology research.

They are extracellular vesicles produced by eukaryotic cells and originate from endosomes, with diameters ranging from 50 nm to 200 nm [1, 2].

They play an important role in intercellular signaling by facilitating the transfer of bioactive compounds, thereby regulating both normal physiological processes and various pathological conditions [3].

In particular, plant-derived exosomes can serve as a natural nanodelivery system, offering advantages such as greater immune tolerance, diversity of origin, and safety compared to animal-derived exosomes [4].

The main plant-based matrices with high exosome concentrations include ginger, grapefruit, broccoli, pomegranate, apple, and orange [5].

Current techniques for exosome recovery include ultracentrifugation, ultrafiltration, precipitation, immunoaffinity capture, and size-exclusion chromatography [3]. However, these methods are difficult to implement industrially due to sample loss, low isolation efficiency, low exosome recovery and purity, and extremely high costs, highlighting the need for innovative solutions [6].

This research project aimed to demonstrate the feasibility of isolating exosomes from moist and partially dried broccoli sprouts using a novel semi-automated extraction

apparatus that employs subcritical fluid R1234ze, a solvent whose potential has already been demonstrated for the recovery of lipophilic substances from natural matrices [7].

However, in the present work, it was proposed as a drag fluid, without dissolving the exosomes and maintaining their lipophilic membrane intact by installing a homogenization system, thereby ensuring an adequate turbulence regime in the extraction chamber.

Additionally, the implementation of an appropriate filtration system downstream of the extraction chamber was examined to enhance extract purification and minimize exosome aggregation.

Extracts were characterized for sample size heterogeneity, vesicle membrane integrity, and exosome identity by confocal fluorescence microscopy, followed by Western blot analysis to evaluate the expression of Tetraspanin 8 (TET-8), a specific marker of plant-derived exosomes.

2. Materials and Methods

2.1. Raw materials

Wet broccoli sprouts (*Brassica oleracea*) were cultivated in vitro and provided by Arterra Bioscience SpA for experimentation (initial moisture content, 90% w/w). Before extraction, coarse grinding was performed using a commercial miller; in addition, partially dried samples were obtained by incubating the samples at 40°C

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in an oven for 24 h to reach a final moisture content of 30% w/w.

The refrigerant R-1234ze Solstice® (purity grade > 99.8 %) used for extractions was purchased from General Gas (Milan, Italy).

A purified exosome extract (10¹⁰ particles per mL) was provided by the Research Group belonging to the Biology Department, University of Tor Vergata (Rome) and used as a positive control for analyses.

2.2. Extraction system and experimental trials

The lab-scale extractor used for experiments is based on a patented process [8], described by Colucci Cante et al. [7], with some configurational adaptations.

The liquid percolates through the solid matrix, previously loaded into an extraction chamber and appropriately homogenized through an in-line Ultra Turrax system.

After purification through a filtration unit, it reaches a jacketed expansion chamber; here, it evaporates due to depressurization while the extract is released to the bottom, is sucked by a compressor, and is recondensed and recirculated, being fully regenerated.

Table 1 presents the system configurations and operating conditions used for the extraction tests.

Table 1. Extraction trials (T) performed on Broccoli sprouts using the solvent R1234ze.

PC: Polycarbonate; PBS: phosphate buffer saline; EP: extraction pressure; VP: vaporization pressure.

#T	Filters	Collection fluid	Time (min)	Matrix	EP (bar)	VP (bar)
#1	PC: 200 nm PC: 30 nm	-	30	wet	6	3
#2	PC: 200 nm PC: 30 nm	-	30	semi-wet	6	3
#3	PC: 200 nm	PBS	30	semi-wet	6	3
#4	No filter	PBS	30	semi-wet	6	3
#5	Stainless steel	PBS	30	semi-wet	6	3

2.3. Analytical methods

Extracts from each extraction run were collected using 4 mL of PBS (10 mM, pH 7.2), taking care to recover all residues from the walls of the expansion chamber.

Therefore, all samples were analysed both without any pretreatment (fresh samples, F) and after centrifugation at 50000 rpm for 2 h using a Beckman Optima L-90K ultracentrifuge (Beckman Coulter) equipped with an SW55 rotor.

The resulting pellets were resuspended in 100 µL PBS and stored at -20°C (ultracentrifuged samples, UC).

To assess extracellular vesicle properties, a multi-analytical approach was applied.

After a preliminary Dynamic Light Scattering (DLS) analysis to determine particle size distribution and sample heterogeneity, PKH26 staining combined with confocal microscopy was used to evaluate vesicle membrane integrity and their visualization.

Finally, a Western Blot (WB) of TET8, a plant-derived extracellular vesicle-associated tetraspanin involved in vesicle formation and membrane organization, was performed to confirm vesicle identity.

For confocal microscopy, samples were stained with PKH26 (Sigma-Aldrich), a lipophilic carbocyanine dye that intercalates into the lipid bilayer of extracellular vesicles, enabling stable membrane labeling without altering vesicle structure.

PKH26 emits in the red spectrum (excitation ~551 nm, emission ~567 nm) and was detected using a red fluorescence channel. Imaging was performed using a ZEISS LSM 900 confocal microscope with a 63× objective. Subsequently, the protein content of all preparations was determined using the Bradford assay [9], and Western blot (WB) analysis was performed to evaluate TET8 protein expression [10].

WB was performed using 10% SDS-PAGE to detect a ~31 kDa protein. Membranes were incubated with anti-plant Tetraspanin 8 antibody (TET8; PhytoAB, Cat. No. PHY1490A, Lot 094102).

Up to 35 µL of sample was loaded per well due to low protein concentration. Signal was detected using ECL ONE STAR (EuroClone, Cat. No. EMP003250) and visualized with a ChemiDoc MP Imaging System (Bio-Rad).

3. Results and Discussion

Trials #1 and #2 were initially conducted on wet and semi-dried broccoli, respectively, using a double-layer polycarbonate filtration system (0.2 – 0.03 µm mesh size) to recover exosome-rich extracts from the smaller filter. This setup revealed a filter failure due to excessive packing of the wet matrix and/or high pressure drops across the 0.03 µm filter, resulting in slow filtration and difficulty in operating the equipment at full capacity.

Since the nonpolar refrigerant could compromise vesicle integrity due to its affinity for the exosomes' double lipid membrane, the presence of residual water and turbulence within the extraction chamber was necessary to ensure adequate dispersion and entrainment of particles by the extracting fluid, without achieving effective dissolution. Therefore, it was necessary to redesign the filter housing to increase the filter surface area while reducing pressure drops. As a result, double filters were replaced with a single 0.2 µm filter (in PC and stainless steel for trials #3 and #5, respectively), and the exosome-rich extracts were collected in PBS to prevent particle aggregation [11].

DLS results revealed partially overlapping size distributions for stainless steel filter samples, with detectable particle populations in the 50 – 250 nm range and acceptable correlation profiles.

In contrast, polymer-filter and no-filter samples exhibited broad, poorly defined distributions, dominated by large particles (>1 µm) and high polydispersity, indicating aggregation and poor sample quality, with minimal representation of nanoscale vesicles.

As shown in Figure 1, confocal fluorescence microscopy revealed the presence of large aggregates in extracts from trial #3 (panels A and B) and in fresh samples from trials

#4 (panel C); smaller aggregates were also visible in ultracentrifuged samples from #4 (panel D). In contrast, the absence of aggregates and the visualization of distinct particles is evident in Panels E and F (trial #5).

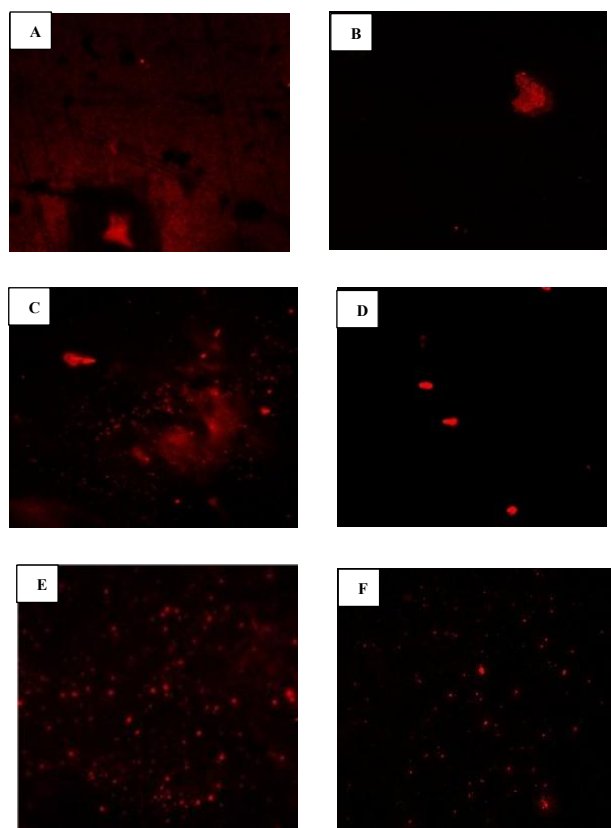


Figure 1: Immunofluorescence images. A: fresh polymer filter extract; B: ultracentrifuged polymer filter extract; C: fresh no-filter extract; D: ultracentrifuged no-filter extract; E: fresh stainless steel filter extract; F: ultracentrifuged stainless steel filter extract.

Western blot analysis targeting TET8 confirmed these findings, as observed in Figure 2.

Polymer-filter and no-filter samples exhibited a pronounced nonspecific fluorescence and substantial aggregation, which hindered vesicle detection.

In contrast, the use of a stainless filter facilitated the identification of vesicles with defined morphology and minimal background, as represented in Panels E and F.

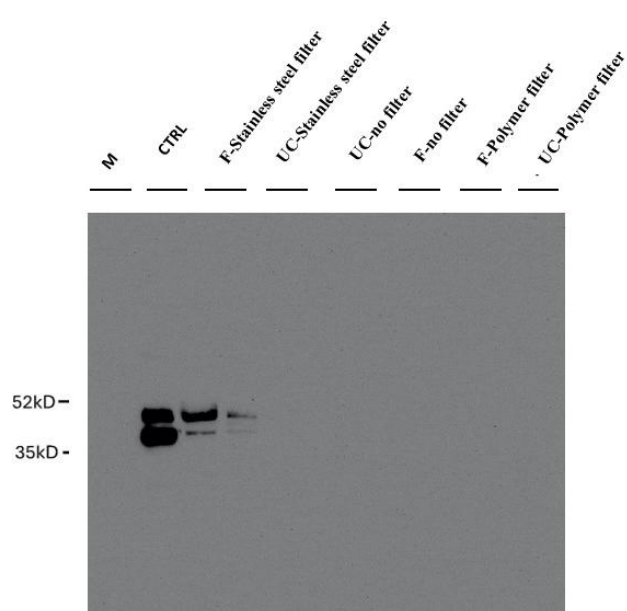


Figure 2: Western blot results. M: marker; CTRL: purified exosome extract used as a positive control; *F*: *Stainless steel filter*: fresh extract using a stainless steel filter; *UC-Stainless steel filter*: ultracentrifuged extract using a stainless steel filter; *UC-no filter*: ultracentrifuged extract without using a filter; *F-no filter*: fresh extract without using a filter; *F-Polymer filter*: fresh extract using a polymer filter; *UC-Polymer filter*: ultracentrifuged extract using a polymer filter.

A specific TET8 signal was detected in the positive control and in stainless steel filter samples, both fresh and ultracentrifuged, while polymer filter and no-filter samples showed no detectable signals.

In particular, the TET8 band detected in the *F*-stainless steel filter sample was slightly more intense than that observed in the *UC* extract prepared with a stainless steel filter, suggesting possible vesicle damage during ultracentrifugation.

Overall, these results indicated that polymer-based filtration likely retains vesicles within aggregates, preventing their detection across all analytical techniques. The exosome retention on the polycarbonate membrane, compared to the steel filter, could be attributable to the hydrophobic/aromatic interactions between the polymeric phenyl groups and the galactolipids present on their membrane [12].

In no-filter samples, vesicles were not physically retained but were highly diluted within the total recovered material, limiting their detectability.

In contrast, the stainless-steel filter enabled efficient recovery of vesicles, preserving their integrity and allowing consistent detection across DLS, confocal microscopy, and Western blot analysis.

4. Conclusions

This study demonstrates the potential of an innovative extraction system that utilizes a refrigerant solvent under sub-critical conditions as a straightforward, effective, and

scalable alternative to conventional methods for isolating exosomes from plant sources such as broccoli.

The system included an integrated homogenizing unit for processing the solid matrix and a filtration module designed for size-based separation of the extracts.

Using a stainless-steel filter yielded exosome preparations comparable to those obtained by the classical ultracentrifugation method (positive control).

This approach preserved material integrity, reduced nonspecific adhesion, and minimized background contamination, as demonstrated by confocal microscopy.

Western blot analysis of TET8 protein further confirmed the identity of the vesicles present in extracts from the stainless-steel filter configuration. Future studies will focus on optimizing exosome recovery and purification by refining the filtration unit to improve size-exclusion efficiency.

Acknowledgement

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Mechanochemical Leaching of Lithium from Battery Slags: Balancing Recovery and Processability

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Abstract. This work, conducted within the DFG Priority Program SPP 2315, investigates mechanochemical leaching as an approach for lithium recovery from engineered artificial minerals derived from synthetic battery slag. Different leaching strategies combining comminution and chemical treatment are evaluated, including stirred media milling, basket milling, and ultrasonic-assisted systems. Mechanical activation enhances lithium extraction by increasing surface area, inducing structural disorder, and improving mass transport. However, conditions that maximise lithium yield simultaneously promote the formation of gel-like structures, which severely impair processability by increasing viscosity and preventing solid–liquid separation. The influence of particle size, energy input, acid type, and chemical environment is systematically analysed. Sulfuric acid provides the highest lithium yields, particularly under combined mechanochemical activation and ultrasonication, but also induces pronounced gel formation. The addition of citric acid enables suppression of gel formation by maintaining $\text{pH} < 2$ and complexing dissolved gangue ions, resulting in both high lithium recovery (up to 91.6%) and stable slurry behaviour.

1. Introduction

The recovery of critical raw materials, particularly lithium, from secondary resources has gained increasing importance in recent years [1]. Engineered artificial minerals (EnAMs), derived from synthetic battery slags, represent a promising feedstock due to their defined composition and the presence of concentrated lithium-bearing mineral phases [2].

Mechanochemical leaching combines comminution and chemical dissolution in a single process step and has been shown to enhance reaction kinetics through increased surface area and structural activation [3]. However, the simultaneous dissolution of gangue phases introduces significant challenges with respect to processability. A major limitation is the formation of gel-like structures during leaching, which originate from the polymerisation of dissolved silica species. These gels lead to a significant increase in slurry viscosity and ultimately prevent solid–liquid separation, thereby limiting the applicability of the process [4].

2. Materials and methods

2.1. Leaching strategies

Different leaching strategies were investigated to assess the influence of mechanical and chemical process parameters on lithium recovery and slurry behaviour. Experiments were conducted under stirred conditions as a reference and under combined conditions including ultrasonication and mechanochemical activation.

Mechanochemical activation was carried out in a stirred media mill (SMM) (NETZSCH LabStar Alpha®Lab) at a stirrer tip speed of 9 m/s. A basket mill (BM) (TORUSMILL® TML) was used for simultaneous comminution and leaching under ultrasonic treatment at 3000 rpm. In both systems, the grinding media filling degree was 80% using 1 mm SiLibeads® Type ZY 6.0 yttria-stabilised zirconia beads. Ultrasonication (US) was applied with an ultrasonic probe.

Various leaching agents were evaluated, with focus on sulfuric acid (H_2SO_4) and citric acid. Temperature, ultrasonic intensity, milling duration, and additives were systematically varied.

The solid–liquid ratio was 10% and the acid concentration 1 mol/L for all experiments. All tests were performed using the same pre-comminuted battery slag (S6) with a median particle size of $x_{50,3} \approx 49 \mu\text{m}$. The phase composition is given in Table 1.

Table 1. Phase composition of battery slag (S6)

Mineral phase	Chemical formula	Mass fraction (wt%)
Lithium aluminate	LiAlO_2	8.4
Eucryptite	LiAlSiO_4	8.9
Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	30.9
Lithium manganese silicate	$\text{Li}_2\text{MnSiO}_4$	14.9
Mn–Al spinel	–	35.8
Quartz	SiO_2	1.0

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2.2. Analytical methods

During the leaching experiments, samples were taken at defined time intervals. The particle size distribution was determined by laser diffraction using a Mastersizer 3000 (Malvern Panalytical). The pH value was monitored continuously throughout the experiments. Lithium concentrations in the filtrate were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an iCAP 6000 series instrument (Thermo Fisher Scientific). This approach enables a direct correlation between particle properties, chemical conditions, and lithium recovery.

3. Results and discussion

3.1 Effect of Process Parameters on Lithium Recovery

The yield $Y(X)$ was calculated according to Eq. (1), where β represents the concentration of ion X in the volume of the liquid phase V_{Solvent} , while m_{Slag} and $w_{\text{Slag}}(X)$ denote the slag mass and the mass fraction of element X in the slag, respectively.

$$Y(X) = \frac{\beta(X) \cdot V_{\text{Solvent}}}{m_{\text{Slag}} \cdot w_{\text{Slag}}(X)} \quad (1)$$

Sulfuric acid provides significantly higher lithium recovery than other investigated acids. This behaviour can be attributed to its ability to maintain low pH values due to its two-proton donation, as well as to the precipitation of calcium sulfate, which reduces solution saturation and thereby enhances the dissolution of valuable ions. Accordingly, the following results focus on sulfuric acid as the primary leaching agent.

Figure 1 shows the lithium and aluminium recovery obtained under different leaching conditions. The investigated process configurations include stirred conditions (Stirring), stirred media milling (SMM), basket milling (BM), and ultrasonication (US). All experiments were conducted using sulfuric acid, with selected experiments including citric acid as an additive.

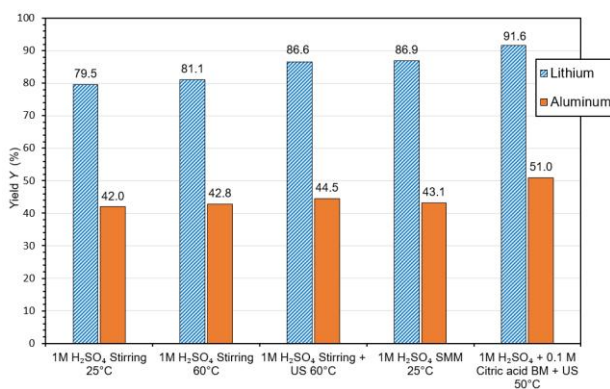


Figure 1. Lithium and aluminium recovery for different leaching conditions using sulfuric acid. Citric acid was added in selected experiments.

As shown in Figure 1, temperature has only a minor influence on lithium recovery. Increasing the temperature from 25 °C to 60 °C under stirred conditions results in

only a slight increase in yield from 79.5% to 81.1%, indicating a negligible effect on extraction performance.

In contrast, the application of ultrasonication leads to a noticeable increase in lithium recovery, from 81.1% to 86.6%, which can be attributed to cavitation effects enhancing mass transport and promoting mineral dissolution through localised pressure and temperature fluctuations [5].

Mechanochemical activation in the stirred media mill further increases lithium recovery to 86.9%, due to continuous particle size reduction, increased specific surface area, and the generation of structural defects.

The highest lithium recovery of 91.6% is achieved in the basket mill, where comminution and ultrasonication are combined, highlighting the strong synergistic effect of mechanical and ultrasonic activation. The addition of citric acid in this system enables stable operation and is discussed in detail in the following section.

3.2 Gel Formation and its Impact on Processability

A critical process limitation was identified in the form of gel formation, which occurs during extended milling and leaching. As shown in Figure 2, particle size measurements reveal a drastic increase in apparent particle size after approximately one hour of processing, indicating the onset of gelation. This phenomenon is irreversible and leads to the formation of highly viscous, gel-like suspensions that prevent further processing, including filtration, and require termination of the experiment. The physical appearance and rheological behaviour of this resulting gel are illustrated in Figure 3.

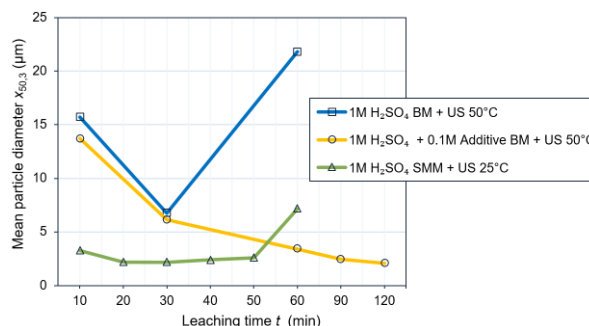


Figure 2. Evolution of mean particle diameter $x_{50,3}$ during leaching under different process conditions. Gel formation is indicated by a sharp increase in particle size, while stable particle size reduction reflects good processability.

Gelation is particularly pronounced for the BM + US system using H₂SO₄, where a sharp increase in particle size is observed after approximately 60 min. This behaviour can be attributed to the elevated temperature of 50 °C, which accelerates gel formation [6]. A similar trend is observed for the SMM + US system, where a gradual increase in particle size begins after about 30 min and becomes more pronounced after 60 min, indicating progressive gel formation.

In contrast, no increase in particle size is observed when citric acid is added to the sulfuric acid system. Instead, the particle size continuously decreases over the

entire leaching period of 120 min, demonstrating the complete suppression of gel formation under these conditions.

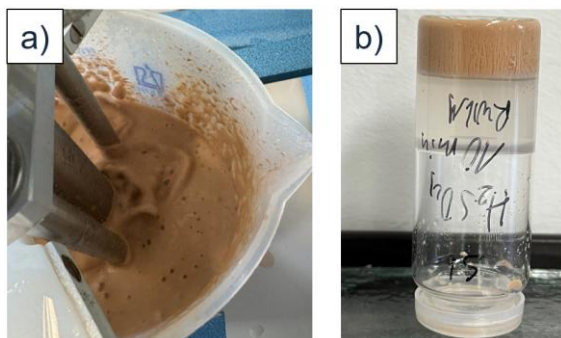


Figure 3. Visual appearance of gel formation during leaching. (a) Highly viscous suspension in the basket mill, resulting in impaired fluid motion and transport within the grinding chamber. (b) Formation of a stable gel network after leaching, preventing flow even when the container is inverted.

The formation of gel-like structures during leaching can be attributed to the polymerisation of dissolved silicic acid species. During acid leaching, silicate phases dissolve and release monomeric silicic acid ($\text{Si}(\text{OH})_4$), which subsequently undergoes condensation reactions to form oligomeric and polymeric silica species [6]. These species further aggregate into a three-dimensional network, entrapping liquid and solid particles and ultimately forming a highly viscous gel [6, 7].

This process is strongly influenced by the pH value. Silica exhibits an isoelectric point at approximately $\text{pH} \approx 2$, where the surface charge of particles approaches zero, minimising electrostatic repulsion and promoting particle aggregation [8]. Consequently, gel formation is favoured when the pH approaches this value.

Mechanochemical activation enhances this effect, as overgrinding increases the dissolution of silicate phases, leading to higher silicic acid concentrations. At the same time, the increased consumption of acid can result in a rise in pH towards the isoelectric point, further promoting aggregation and gel formation.

In addition, dissolved gangue ions such as Al^{3+} and Ca^{2+} promote flocculation and enhance silica polymerisation, further accelerating gel formation [8].

The addition of citric acid effectively suppresses gel formation by maintaining the pH below the isoelectric point and by complexing dissolved metal ions. Citric acid is known to chelate a wide range of divalent and trivalent metal ions, thereby reducing their reactivity and interaction with silica species [9]. This reduces flocculation and stabilises the suspension, preventing gel formation even during extended processing.

The evolution of pH during leaching confirms the importance of maintaining sufficiently low pH values. As shown in Figure 4, significant differences in pH behaviour are observed depending on the applied process conditions.

In the stirred H_2SO_4 system, the pH increases gradually but remains below the critical value of $\text{pH} \approx 2$ over extended leaching times, indicating limited acid

consumption due to the absence of intensive comminution. This explains the absence of gelation in stirred beaker conditions.

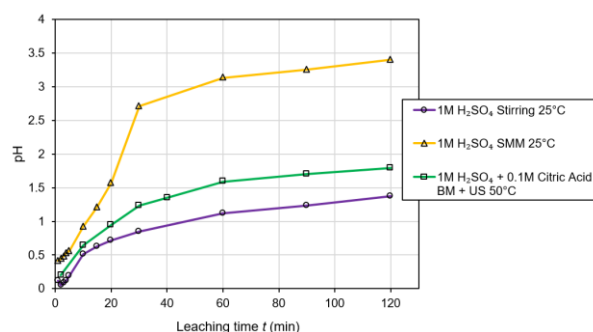


Figure 4. Evolution of pH during leaching under different process conditions. Mechanochemical activation leads to a rapid increase in pH, while the addition of citric acid stabilises the pH below the isoelectric point of silica.

In contrast, mechanochemical activation in the stirred media mill results in a rapid increase in pH. The pH exceeds a value of 2 within the first 30 minutes and reaches values above 3 after 60 minutes, indicating strong acid consumption caused by enhanced dissolution of mineral phases. This behaviour directly correlates with the onset of gel formation observed in Figure 2.

When citric acid is added, the pH remains below 2 throughout the entire leaching period. This stabilisation can be attributed to the buffering capacity of citric acid as well as the complexation of dissolved metal ions, which together suppress silica polymerisation and prevent gel formation.

These observations are in excellent agreement with the proposed gelation mechanism, highlighting the critical role of pH control in maintaining processability.

4. Conclusions

The results demonstrate that mechanochemical activation significantly enhances lithium recovery, particularly when combined with ultrasonication. However, it should be noted that the feed material was already relatively fine ($x_{50,3} \approx 49 \mu\text{m}$), and lithium-bearing phases were largely liberated. As a result, the overall improvement potential was limited, while more pronounced effects can be expected for coarser feed materials, where liberation is progressively achieved during comminution.

Processability is strongly limited by gel formation, which is induced by the dissolution of silicate phases and subsequent silica polymerisation. The experiments show that gel formation is governed by the interplay of pH, mechanical energy input, and temperature. Overgrinding increases acid consumption, thereby shifting the pH towards or above the isoelectric point of silica, which in turn promotes aggregation and gel formation. In addition, elevated temperatures further accelerate these processes and should therefore be avoided.

The addition of citric acid proved to be an effective strategy to suppress gel formation by stabilising the pH below the isoelectric point and by complexing dissolved

metal ions, thus maintaining processability even under intensive processing conditions.

Overall, the results highlight that efficient lithium recovery from engineered battery slags requires a careful balance between mechanical activation and controlled chemical conditions.

Acknowledgement

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Sustainable Mechanochemical Engineering of Biochar for Advanced Hydrophobic Coatings

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Abstract. This study presents an innovative and sustainable approach for the functionalization of biochar through mechanochemical amidation in the presence of octadecylamine. The proposed methodology represents an attractive alternative to conventional solution-based processes, as it reduces solvent consumption, operational costs, and environmental impact while offering excellent scalability. The obtained material was extensively characterized by spectroscopic and morphological techniques, which confirmed the successful formation of amide functional groups on the biochar surface and excluded the simple adsorption of amine molecules onto the carbon matrix. The introduction of long alkyl chains significantly enhanced the hydrophobicity of the biochar, owing to both the exposure of hydrophobic moieties and the increased surface roughness. These features make the modified material particularly suitable for the development of water-repellent coatings for hemp fibers. Through a dip-coating process, the treated hemp fibers exhibited remarkable hydrophobic behavior, reaching a water contact angle of 126° after only one deposition layer. Furthermore, the biochar-coated hemp fibers demonstrated excellent oil absorption performance from emulsion systems,

1. Introduction

Hydrophobic materials are of growing interest in materials science due to their wide range of applications, including self-cleaning surfaces, anti-stain textiles, separation systems, and functional coatings.[1]

Hydrophobicity can be achieved either through chemical modification of surfaces [2] or by applying hydrophobic coatings.[3] Surface functionalization provides strong and stable binding but often requires complex procedures and may have environmental drawbacks. In contrast, coatings are more versatile, cost-effective, and applicable to different substrates, although their long-term stability can be limited by possible leaching. Among coating techniques, dip-coating is widely used due to its simplicity and scalability.

Carbon-based materials, such as graphene derivatives, are commonly employed because of their tunable surface chemistry and suitability for hydrophobic applications in textiles, corrosion-resistant coatings, and glass surfaces.[4]

Functionalization of carbon materials typically requires the introduction of oxygen-containing groups, often via graphite oxidation (e.g., Hummers method), which is effective but environmentally demanding. More sustainable approaches may reduce functionalization efficiency.

Biochar, a biomass-derived carbon material, represents a sustainable alternative with high porosity and tunable

properties. It is widely used in environmental applications and can be chemically modified to enhance its functionality. [5] Compared to graphite, biochar can be oxidized under milder conditions, enabling further chemical transformations such as esterification or amidation to tune surface polarity.

However, most functionalization strategies rely on solvent-based processes that require large reagent consumption and long reaction times.[6] To address these limitations, this work proposes a solvent-free mechanochemical approach using planetary ball milling to functionalize biochar with octadecylamine, aiming to produce hydrophobic materials in a more sustainable and efficient way.

The modified biochar is further evaluated as a coating for hemp fibers, a renewable material with good mechanical and thermal properties but intrinsic hydrophilicity. Surface modification is expected to enhance their hydrophobic and oleophilic behavior, enabling efficient oil uptake from aqueous systems.

2. Results and discussion

2.1. Biochar selection

Octadecylamine (ODA) was selected as a long-chain alkyl amine suitable for imparting hydrophobic properties to the coatings. [6]

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To determine the functional groups present in pristine biochar (BC), oxidized biochars (oBC), and the milled one (oBC_{BM}) a comprehensive characterization was performed using elemental analysis (EA), Fourier-transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) surface area measurements, and pH analysis. The corresponding results are reported in Table 1 and Figure 1.

Table 1. Elemental analysis, surface area, and pH of the biochar and its derivatives

Sample	C (%)	H (%)	O (%)	N (%)	O/C	SA (m ² /g) ^a	pH ^b
BC	78.9	2.7	18.0	0.4	0.23	81	7.97
oBC	72.7	2.8	24.0	0.5	0.33	<1	4.30
oBC _{BM}	69.7	1.3	28.9	0.1	0.41	103	4.00

The FTIR spectrum reported in Figure 1 shows a distinct absorption band at around 1700 cm⁻¹, attributed to the C=O stretching vibrations of carbonyl groups. This band becomes more intense and broadened with increasing oxidation degree. The marked decrease in pH further confirms the carboxylic nature of the carbonyl functionalities, which are essential for the subsequent amidation step. It has to be noted that the additional milling step performed on the oxidized powder, reducing the particle size of the carbon material, increases the surface area and exposes a greater number of functional groups, thereby improving their availability for subsequent reactions.

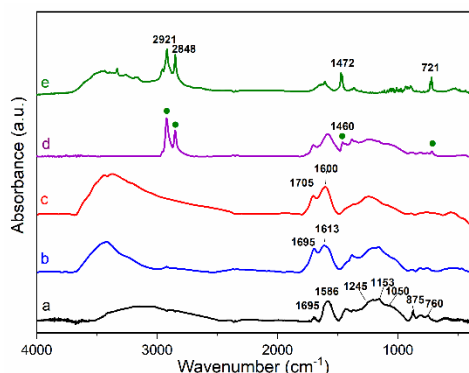


Figure 1. FTIR of a) Biochar (BC), b) Oxidized biochar (oBC), c) milled oxidized Biochar (oBC_{BM}), d) oBC_{BM}/ODA, e) ODA. Solid dots showing the wavenumbers related to ODA.

2.2. Mechanochemical functionalization and characterization of oBC_{BM} with ODA

The reaction was performed in the same conditions lately reported. [7] In a silicon nitride jar, oBC_{BM} and ODA in a ratio of 1 to 1 were added and milled for 2h at 300 rpm in a planetary ball milling. The resulting powder, oBC_{BM}/ODA, was recovered without any solvent and washed three times with 30 ml of ethanol to remove the

excess amine residue. After drying at 60°C for 12h, the powder was characterized first by WAXD and TGA.

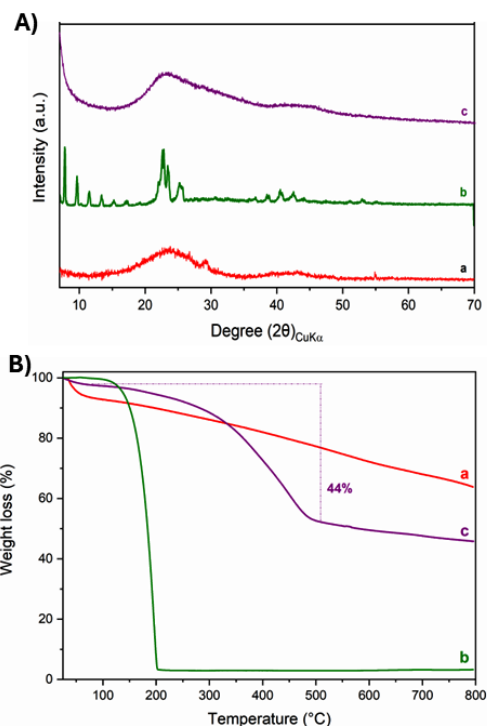


Figure 2. A) WAXD and B) TGA of a) oBC_{BM}, b) ODA and c) oBC_{BM}/ODA

Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were conducted on the obtained powder. As illustrated in Figure 1d, the spectrum exhibits characteristic absorption bands attributable to octadecylamine (ODA) at 2916, 2845, and 717 cm⁻¹, corresponding to the –CH₂ stretching vibrations of the alkyl chain. Furthermore, a noticeable shift is observed from 1472 cm⁻¹ in the pristine amine to 1463 cm⁻¹ in the functionalized powder, which can be ascribed to modifications induced by the grafting process.

TGA analysis (Figure 2B) confirms a high degree of functionalization, with a weight loss of up to 44%. This result is supported by elemental analysis, which shows a significant increase in nitrogen content from 0.1% in the starting oBC_{BM} to 2.4% in the oBC_{BM}/ODA material after reaction.

Furthermore, the WAXD analysis (Figure 2A) shows the absence of crystalline peaks and the appearance of a broad amorphous halo.

XPS analysis was performed on oBC_{BM}/ODA as the best sample to rule out a simple sorption mechanism and ensure the formation of a new covalent bond. For the sake of comparison, further analyses were also carried out for BC/ODA, to verify the different nature of the covalent bond formed.

From the fit outcomes (Figure 3), it was observed that nitrogen reacted differently depending on whether the biochar had undergone prior oxidation. Specifically, when the ODA treatment was performed on pristine BC,

pyridinic groups constituted the predominant fraction among all nitrogen-containing groups. Conversely, when biochar was oxidized and milled before functionalization, the nitrogen distribution shifted toward pyridone/amine groups, suggesting distinct reaction pathways and thus confirming the amide formation.

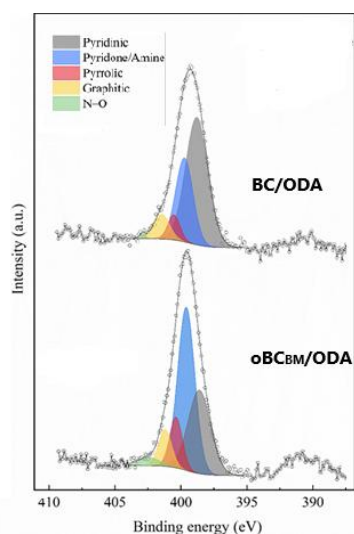


Figure 3. N1s spectra peaks fit of the two ODA-modified carbons

2.3 Application of oBCBM/ODA as hydrophobic coating

A dip coating of the oBCBM/ODA was performed on hemp fiber to evaluate a possible application in removing oil from the emulsion. The dip coating was chosen as the coating technique because it is a quick, easy, affordable, and high-quality method that, being economical and well-managed, represents a useful approach to providing a sustainable water-repellent coated fiber. Limonene was chosen as green solvent. (Figure 4)

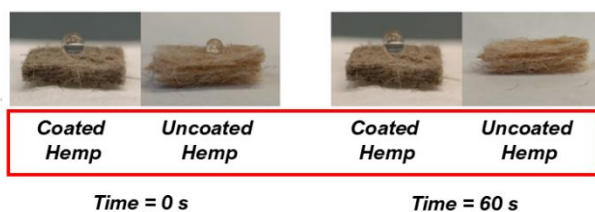


Figure 4. Contact angles of hemp fibers before and after dip-coating in limonene dispersions

Contact angle measurements provide insight into the polarity changes induced by the coating. As shown in Figure 4, uncoated hemp exhibits an initial contact angle of 123°, which decreases to zero within 60 s due to water penetration into the inherently hydrophilic fiber structure. In contrast, hemp fibers coated with oBCBM/ODA using a limonene-based dispersion display a comparable initial contact angle of 126°, but only decrease to 117° after 60 s, indicating a transition to hydrophobic behavior.

The notably reduced affinity for water suggests the possibility of removing apolar molecules in a water emulsion. Therefore, to demonstrate the absorption capacity of the oBCBM/ODA composite, an oil/water separation experiment was performed

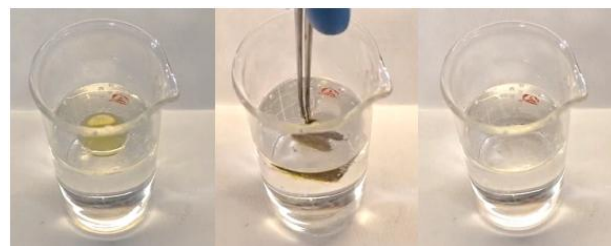


Figure 5. Oil adsorption by hydrophobic coated hemp.

As evidenced by Figure 5, the coated fibers demonstrated a remarkable oil absorption capacity (up to 1400%), outperforming previously reported approaches, highlighting their potential for environmental cleanup applications, especially in oil-water separation systems

3. Conclusions

This work presents an innovative, low-cost, scalable, and fully sustainable strategy for biochar functionalization via a solvent-free mechanochemical amidation process using octadecylamine (ODA). The approach replaces conventional solvent-based methods, operating at room temperature with minimal reagent use and leveraging renewable carbon feedstocks, thereby significantly reducing environmental impact.

Successful covalent grafting of ODA was confirmed through spectroscopic and morphological analyses. The mechanochemical treatment increases the degree of functionalization and yields a hydrophobic carbon-based material suitable as a filler for water-repellent coatings. When applied to hemp fibers via dip-coating, the modified biochar imparts strong hydrophobicity, reaching a contact angle of up to 126°. The treated fibers also exhibit excellent oil absorption capacity (up to 1400%), outperforming previously reported systems and highlighting their potential for oil–water separation and environmental remediation applications. Overall, the renewable nature of the material, the green synthesis route, and the achieved multifunctional properties make this system promising for anti-wetting, anti-icing, and antifouling coatings in marine and outdoor environments.

Acknowledgement

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Effects of high-energy kinetic milling conditions on the mechanochemically assisted synthesis of lanthanum cobalt oxide

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Abstract. This study presents an experimental investigation of the synthesis of perovskite-type lanthanum cobalt oxide (LaCoO₃; LCO) powders using different mechanical milling approaches. The study explores the effects of processing parameters for planetary ball milling and attrition ball milling, including the employment of a wetting agent, milling rate, material of milling media and milling jar, and calcination temperature, on the resulting microstructure and phase composition of the obtained LCO powders. The main focus during the synthesis was to obtain a phase-pure powder with the minimum possible content of secondary phases. For planetary milling, dry milling conditions and calcination at 850 °C for 2 h turned out to be the most effective regime, yielding the highest LCO content and the lowest amounts of residual La₂O₃ and Co₃O₄ phases. In the case of attritor milling, phase-pure perovskite was successfully obtained using dry milling in a SiN-lined milling jar with ceramic balls and at a relatively low calcination temperature of 650 °C. Among the investigated mechanochemical milling approaches, attritor milling proved the most promising process, offering the greatest efficiency and scalability.

1. Background

Lanthanum cobalt oxide LaCoO₃ (LCO) is ABO₃-type perovskite well-known for its unique physical and chemical properties based on A-site and B-site atoms association. Being environmentally friendly, relatively accessible, and highly active in various redox reactions, LCO has proved its high application potential for environmental catalysis [1], [2], photocatalysis [3], catalytic oxidation [4], [5], [6], hydrogen purification [7], and cathode materials of oxide fuel cells [8], [9], [10]. As is well-known, the microstructure and physicochemical properties of perovskite powders are highly dependent on the synthesis method chosen. While traditional solvent-moderated synthesis routes, such as hydrothermal, sol-gel, or co-precipitation [11], [12], were widely used to prepare LCO perovskite powders, mechanically assisted synthesis routes based on high-energy kinetic milling have been rarely explored. Among the indirect mechanochemical synthesis, the report by Sompech et al. [13] can be mentioned, who used mechanochemically activated synthesis of LCO through planetary ball milling of LaCl₃ · 7H₂O, CoCl₂, and Na₂CO₃ precursor powders. The mixture was milled at 300 rpm for 2 h in a Retsch PM 100 ball mill using a stainless-steel jar and stainless-steel balls. The obtained powder was subsequently calcinated at 600, 700, and 800 °C at a heating rate of 10 °C/min for 90 min. So far, only Ito et al. [14] reported a direct LCO

synthesis in a planetary ball mill at 700 rpm, using zirconia balls and a zirconia pot.

Therefore, in this study, we aimed to fill the knowledge gap related to the preparation of LCO-based perovskites using the mechanochemical activation approaches. The main feature of the current work is the employment of two alternative grinding methods, namely planetary grinding and attrition milling, to clarify the effects of milling parameters on the resulting microstructure and phase composition of the obtained LCO powders. Among the studied milling parameters, the influence of wetting agent, milling rate, milling media and milling jar materials, and calcination temperature was considered in detail, with the focus on synthesizing phase-pure LCO.

2. Experimental

2.1. Initial materials

The rare-earth lanthanum oxide (La₂O₃; 99%; Nanoshel) and cobalt(II) hydroxide (Co(OH)₂; 99.9%; ThermoScientific) were used as initial precursors for mechanochemical syntheses. Prior to milling experiments, the precursors were homogeneously mixed at a molar La:Co ratio of 1:1.

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2.2. Mechanochemically activated synthesis

Two milling devices were employed for mechanochemical synthesis, namely (a) a planetary ball mill (Pulverisette 6, Fritsch) and (b) a horizontal attritor (Simoloyer CM-01, Zoz) (Figure 1). The planetary ball mill is a benchtop device used for milling and mixing of various materials as well as for mechanical alloying or reactive grinding of different powders, including LCO perovskite [14], [15]. At the same time, the horizontal attritor is considered the most advanced tool for lab-scale high-energy fine grinding, mixing, dispersing, mechanical alloying, or reactive grinding [16], especially designed for the preparation of nanostructured materials, which was not previously employed for the mechanochemical synthesis of LCO perovskite.

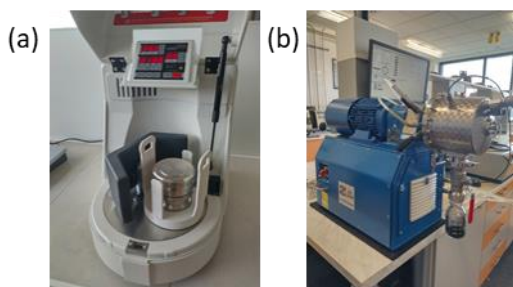


Figure 1. (a) The planetary ball mill Pulverisette 6 and (b) the horizontal attritor Simoloyer CM-01 used in the study.

The sample description and selected milling parameters are summarized in Table 1. As a wetting agent for wet planetary milling of the LCO-PW sample, the isopropyl alcohol (Penta, 99.5%) was used. After milling using both planetary and attritor mills, the powders were calcinated in a laboratory muffle furnace (LH 15/13, LAC) at temperatures of 550-850 °C for 2h in air.

Table 1. Sample designation and selected milling conditions.

Sample marking	Milling type/ Condition	Milling jar/ media	Milling speed/ time
LCO-PW	Planetary/ Wet	Steel balls / steel jar	350 rpm/2 h
LCO-PD	Planetary/ Dry	Steel balls / steel jar	350 rpm/2 h
LCO-A-Zr	Attritor/ Dry	ZrO ₂ balls/SiN jar	1000 rpm/2h
LCO-A-S-1000	Attritor/ Dry	Steel balls / steel jar	1000 rpm/ 2h
LCO-A-S-1400	Attritor/ Dry	Steel balls / steel jar	1400 rpm/4h

2.3. Materials characterization

The diffraction patterns of initial powder precursors, as-milled and calcinated powders were obtained using the

X-ray diffractometer (XRD; Rigaku 3kW) using Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA) in a 2θ range from 10 to 100 ° with a step size of 0.02° and a time per step of 1.5 s. The Rietveld refinement was performed using High Score Plus software supplemented with the ICDD Database. High-resolution scanning electron microscopy (SEM; Verios 460 L, FEI) coupled with energy dispersive X-ray spectroscopy (EDS) was used in back-scattered electron (BSE) mode to characterize powders' microstructure, elemental composition and elemental distribution of the powder samples. The specific surface area of the LCO samples was determined from the measured adsorption/desorption isotherms using a Micro 300 C1 surface area analyser (3P Instrument, BET-ANAMET). Prior to measurements, each calcined sample was degassed at 150 °C for 10 h under vacuum. Nitrogen served as the adsorbate gas, with the bath temperature maintained at liquid nitrogen temperature.

3. Results and discussion

3.1. Milling in the planetary mill

Both wet and dry planetary milling of La₂O₃ and Co(OH)₂ precursors produced well-homogenized mixtures consisting of La₂O₃, La(OH)₃ and Co(OH)₂ compounds (Figure 2). The formation of LCO perovskite with R3c rhombohedral structure was achieved in those mixtures after their following calcination at 750 °C for 2h. The sample LCO-PW contained 83.7 wt% of LCO, while the LCO-PD showed a higher LCO content of 87.5 wt.%. In addition to LCO, La₂O₃ and Co₃O₄ compounds were present as secondary phases in both calcinated powders, resulting from the unreacted fraction of precursors. The sample LCO-PW contained 10.7 wt% of La₂O₃ and 5.6 wt% of Co₃O₄, while the LCO-PD sample contained 10.7 wt% of La₂O₃ and 5.6 wt% of Co₃O₄, respectively. Although neither wet nor dry milling resulted in direct perovskite formation during milling, dry milling produced a larger amount of LCO in the calcinated powder, so the sample LCO-PD was chosen for further optimization of the calcination temperature.

Calcination studies (Figure 3) showed that the proportion of the secondary La₂O₃ and Co₃O₄ compounds relative to the desired LaCoO₃ decreased with the increase of calcination temperature. Within the investigated temperature range, the highest amount of LCO was formed at 850 °C, indicating that a higher temperature is required to obtain phase-pure LCO.

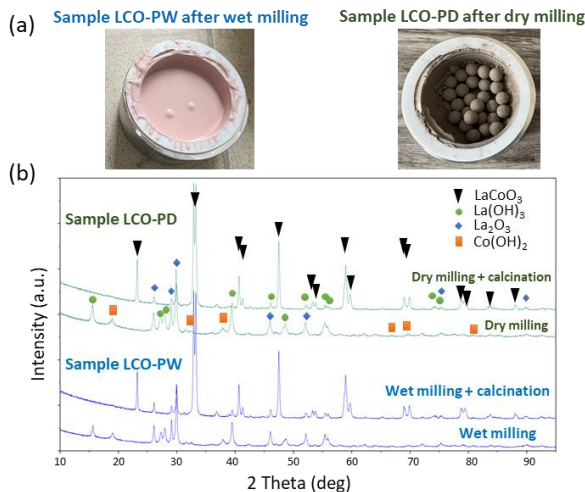


Figure 2. (a) The appearance of the milled products after wet and dry milling in the planetary mill, respectively, and (b) XRD patterns of LCO-PW and LCO-PD powders in the as-milled condition and after calcination at 750 °C for 2 h.

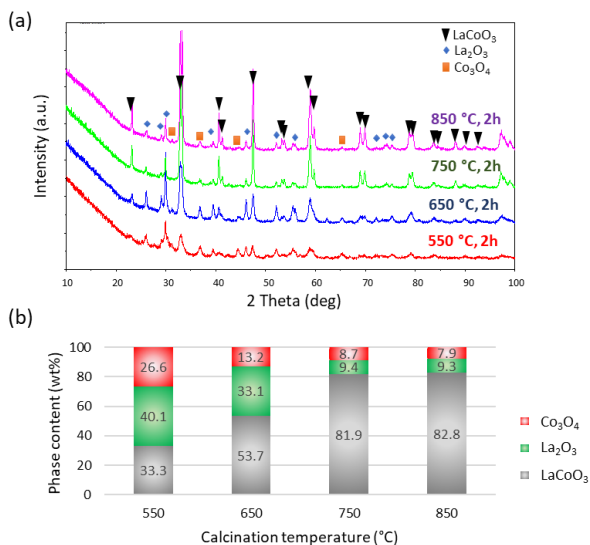


Figure 3. (a) XRD patterns of LCO-PD calcinated at 550, 650, 750, and 850 °C for 2 h and (b) the corresponding quantitative phase analysis of calcinated powders as a function of calcination temperature.

3.2. Milling in the attritor mill

In contrast to planetary ball milling, the attritor milling exhibited *in-situ* formation of 13.5 wt% of LCO in the LCO-AZ sample when using a mill configuration with a SiN-lined jar and ZrO₂ balls. In contrast, no LCO formation was detected for the mill configuration employing a stainless-steel jar and steel balls at 1000 rpm (sample LCO-A-S-1000), the formation of LCO was not detected. Only under more intensive high milling conditions used for the same mill configuration (milling speed of 1400 rpm and a longer milling time of 4h), *in-situ* LCO formation was achieved, although resulting in lower LCO content of 7.0 wt%. Based on these results, the LCO-AZ sample was selected for further optimization of

the calcination temperature.

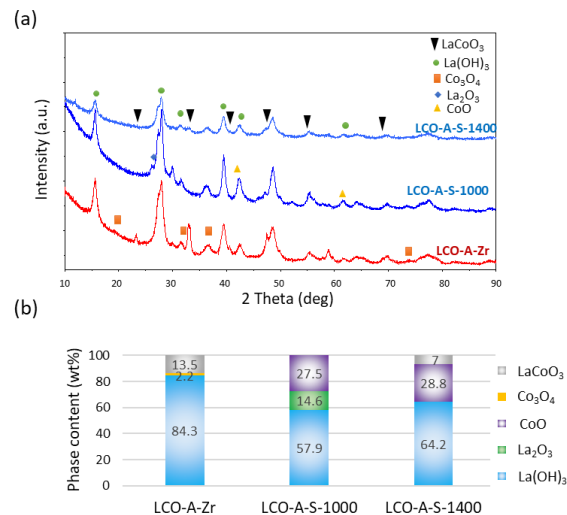


Figure 4. (a) XRD patterns of LCO-AZ, LCO-A-S-1000 and LCO-A-S-1400 powders milled at different conditions and (b) quantitative phase analysis of as-milled powders.

Study of the effect of calcination temperature on the phase composition of the as-milled LCO-AZ powder showed that the presence of secondary La₂O₃ and Co₃O₄ phases was only observed at 550 °C (Figure 5a-b). In contrast, at temperatures above 650 °C, LCO was a primary phase (>99.5wt%) with a minor admixture of secondary La₂O₃ oxide. After calcination, the sample had nanosized microstructure (Figure 5c) with the crystalline size of 22.7 nm and a surface area of 3.9 m²/g.

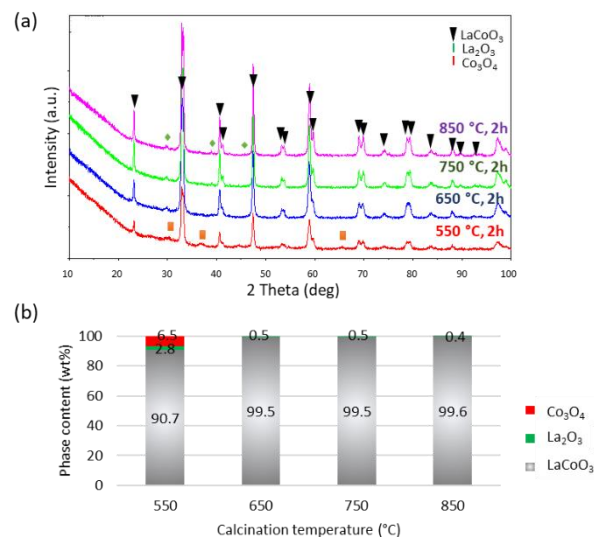


Figure 5. (a) XRD patterns of LCO-AZ powder calcinated at different temperatures and (b) quantitative phase analysis of calcinated LCO-AZ powder as a

function of calcination temperature, (c) and SEM BSE micrograph of LCO-AZ calcinated at 650 °C for 2h.

4. Summary

In this study, LCO perovskite was synthesized through mechanochemically assisted synthesis using different mechanical milling methods, including planetary ball milling and milling in the horizontal attritor, and varying synthesis parameters (wetting agent, milling rate, material of milling media and milling jar, and calcination temperature). The key findings are as follows:

- Milling in the planetary mill led to homogenization of the precursor mixture of initial $\text{La}(\text{OH})_3$, La_2O_3 and $\text{Co}(\text{OH})_2$ components, showing no substantial difference between wet and dry milling. The synthesis of LCO was achieved during subsequent calcination. Acquiring phase-pure LCO requires calcination temperatures above 850 °C.
- Direct mechanochemical synthesis of LaCoO_3 perovskite was achieved using a horizontal attritor due to its higher mechanical energy input in comparison with planetary milling. The mill configuration with SiN-lined jar and ZrO_2 balls produced the highest proportion of synthesized LCO in the powder's structure of 13.5 wt%, while the rest consisted of $\text{La}(\text{OH})_3$ and Co_3O_4 compounds. Calcination of the milled powder in the temperature range 550-850 °C prompted subsequent LCO formation, with a purity of 99.5 wt%, achieved already at temperatures as low as 650 °C.

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An Overview of Attrition in the Jetting Region of Fluidised Beds

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Abstract. The work on particle attrition in the jetting region of fluidised beds is reviewed. The rate of attrition is shown to depend on the orifice gas velocity to a power index, which could be much greater than the dependence of single particle attrition on impact velocity. This is predictable by coupling the extent of single particle impact breakage with jet hydrodynamics. More recent analyses by the use of CFD-DEM simulations, coupled with a model of the single particle breakage data, confirm the previous work and shed further light on the dependence of the effect of jet velocity, orifice size and transition velocity above which attrition is observed.

1. Introduction

Attrition in the jetting region of fluidised beds is a critical phenomenon governing particle lifetime, fines generation, and process efficiency. To provide a uniform gas distribution in fluidised beds, the distributor is designed to operate with a sufficiently high level of pressure drop, yielding a relatively high orifice gas velocity. This could cause significant surface damage even for strong particles, such as sand, and breakage for weak particles, such as spray-dried powders. A good example is particle attrition in Fluid Catalytic Cracking (FCC) operation in oil refining, where a few tons of debris are produced daily as a result of attrition.

There are numerous test methods developed for attrition testing, which are briefly reviewed here, followed by the characterisation of the attrition propensity of particles due to collision. This information is then used to analyse the rate of attrition in the jetting region of fluidised beds, by coupling with a hydrodynamic model of the jet region. Recent developments in the numerical simulation by Computational Fluid Dynamics (CFD) and Discrete Element Method (DEM) quantify the effect of the important factors which affect the attrition rate therein.

Early comprehensive reviews have established that high-velocity collisions play a dominant role in dilute regions such as the jet [1] and propose that single-particle impact testing provides a fundamental measure of particle strength, offering a bridge between intrinsic material properties and bulk attrition behaviour. Boerefijn et al. [2] frame the process as a multi-scale problem involving particle properties, fluidised bed hydrodynamics, and operating conditions. The jet region is identified as a hotspot for impact-driven attrition due to elevated slip velocities and frequent particle acceleration. A predictive understanding requires coupling material response to impact with solids circulation patterns, an idea that underpins subsequent modelling efforts [1,2]. A range of experimental techniques has been developed to

characterise attrition, though their relevance to jet-region conditions varies significantly. Jet cup testers [3] and air-jet apparatuses [4] are among the most representative, as they subject particles to high-velocity gas streams, similar to the jet environment. These methods capture both collision frequency and impact intensity, making them representative of the jet conditions. In contrast, standardised fluidised bed tests such as the ASTM method [5] provide reproducible benchmarks but often operate in bubbling regimes, where shear and low-energy collisions dominate, limiting their direct applicability to jet attrition.

Other devices probe complementary aspects of particle degradation. The UNC dustiness tester [6] and vortex shaker [7] primarily evaluate fines generation under dispersive or vibrational stresses, offering insight into particle fragility but not the high-energy impacts characteristic of jets. Similarly, stirred fluidisation systems [8] focus on dense-phase behaviour, where interparticle friction and shear prevail. While these methods are useful for broader attrition characterisation, they may underestimate breakage rates in jetting regions.

More targeted approaches have been developed to isolate impact-driven mechanisms. Particle jet impact studies [9] directly replicate high-velocity collisions, enabling controlled investigation of fragmentation thresholds and breakage modes. Likewise, impact breakage experiments [10] and plate impact tests [12] provide detailed information on energy-breakage relationships, which are essential for mechanistic modelling. Cyclone-based attrition testing [11] introduces repeated high-speed impacts and particle recirculation, offering a closer analogue to industrial systems, though with less control over individual collision events.

At the single-particle scale, the seminal work of Yüregir et al. [13] established the single particle impact tester as a robust tool for quantifying impact attrition. This method isolates particle strength and fracture behaviour, providing key parameters such as critical impact velocity and the extent of breakage. More recent developments,

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such as the shear and impact tester by Ahmadian and Ghadiri [14], extend this capability by incorporating combined loading modes.

The integration of these experimental insights is formalised in the model proposed by Ghadiri and Boerefijn [15], which specifically addresses attrition in the jetting region. The model links single-particle impact data with solids flux and collision frequency, enabling prediction of attrition rates based on both material properties and hydrodynamic conditions. This framework provides an approach to scaling laboratory measurements to reactor performance.

Earlier studies on FCC catalysts [16,17] laid the groundwork by identifying the importance of particle size distribution evolution and attrition mechanisms in industrial units. These works underscore the practical significance of understanding jet-region attrition, particularly for maintaining catalyst activity and minimising fines losses.

In summary, the literature demonstrates that attrition in the jet region of fluidised beds is predominantly governed by high-energy impacts, which can be effectively characterised through a hierarchy of experimental techniques. While bulk tests provide useful benchmarks, single-particle and jet-based methods are essential for capturing the underlying physics. The coupling of these data with hydrodynamic models provides a predictive capability for optimising industrial processes.

2. Single Particle Impact Attrition

In our laboratory, we have characterised the single particle impact attrition of a wide range of particles, most notably FCC and reforming catalyst particles, common salt and ingots of NaCl, KCl and MgO, ammonium nitrate, spray-dried powders of detergents, coffee, burkeite, agglomerates and granules, pharmaceutical crystals of aspirin, paracetamol, and additively-manufactured agglomerates. The main mechanism of attrition is by the propagation of sub-surface lateral cracks, as shown in the SEM images in Figure 1.

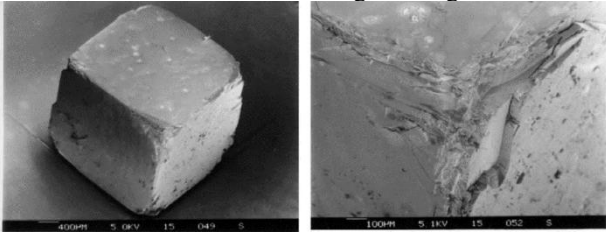


Figure 1. Attrition damage to an ingot of salt crystal [18].

The results for burkeite and MnO_2 particles, the latter used as a chemical looping catalyst (CLC), are shown in Figures 2 and 3, and in Table 1 for fresh and equilibrium FCC particles. The model of Ghadiri and Zhang [19] is used to analyse the results

$$\xi = \alpha\eta = \alpha \frac{\rho V^2 DH}{K_c^2} \quad (1)$$

where ξ is the fractional loss from the mother particles.

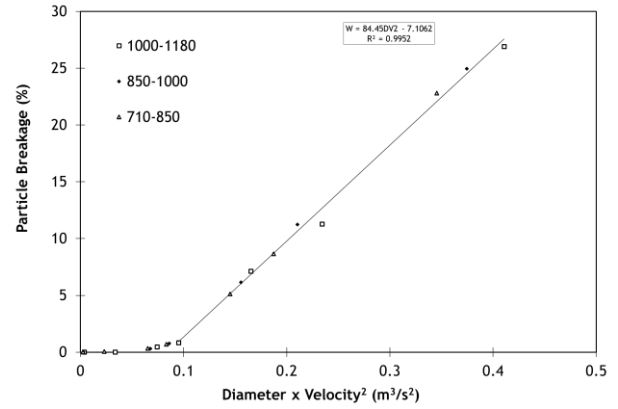


Figure 2. Impact attrition of spray-dried burkeite particles [20].

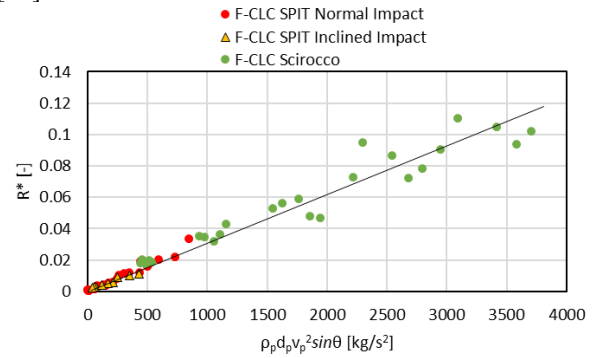


Figure 3. Impact attrition of crushed naturally-occurring MnO_2 particles [21].

Table 1. The attrition power index, n , for fresh and equilibrium FCC particles ($\xi = CV^n$) [1].

Material	Size range (μm)	C	n
F-cat	75-90	5×10^{-4}	1.93
F-cat	90-106	2.4×10^{-3}	1.79
F-cat	106-125	1.3×10^{-3}	2.06
E-cat	75-90	7.0×10^{-5}	2.03
E-cat	106-125	8.0×10^{-4}	1.79

3. Attrition in the Jetting Region of Fluidised Beds

Reported works in the literature show diversity in the dependence of jet attrition on the orifice gas velocity and size, as shown in Table 2, due to differences in the physical and mechanical properties of particles.

3.1. Jetting Hydrodynamic Model of Donsi *et al.* [22]

The jet model of Donsi *et al.* [22] gives the functional dependence of particle velocity, concentration, and hence the particle flux, in the jet region, as a function of particle properties and orifice size, i.e.

$V_p = f(u_o, d)$; $C_p = h(u_o, d)$ Flux, $W_s = g(u_o, d)$
Therefore:

➤ Effect of Orifice velocity: (constant d)

$$V_p \propto u_o^\alpha \text{ and } W_s/W_g \propto u_o^\beta$$

➤ Effect of Orifice size: (constant u_o)

$$V_p \propto d^n \text{ and } W_s/W_g \propto d^m$$

Table 2. Dependence of the overall and jet attrition rate on the orifice size and superficial/orifice gas velocity [1].

Author	Material	Attrition rate W (kg hr ⁻¹)	Attrition rate W (kg hr ⁻¹)
Blinichev et al. (1968)	Salt granules	$W_{\text{overall}} \propto U^{5.8}$	$W_{\text{overall}} \propto d^3$
Kono (1981)	Alumina-Silica	$W_{\text{overall}} \propto U^{2.3}$	
Patel et al. (1986)	Urea	$W_{\text{overall}} \propto U$	
Contractor et al. (1989)	Catalyst particles	$W_{\text{jet}} \propto U^{2.45}$	
Ayazi Shamlou et al. (1990)	Glass agglomerates	$W_{\text{overall}} \propto (U - U_{\text{mf}})$	
Seville et al. (1992)	Sand agglomerates	$W_{\text{jet}} \propto (U - U_{\text{mf}})$ $W_{\text{bed}} \propto (U - U_{\text{mf}})$	
Ghadiri et al. (1992)	NaCl Salt	$W_{\text{jet}} \propto U^{5.1}$ or	
Werther & Xi (1993)	FCC	$W_{\text{jet}} \propto U^3$ or	$W_{\text{jet}} \propto d^2$

3.2. Analysis of Jet Attrition: Effect of Orifice Velocity

Coupling the flux in the jet region with the single particle attrition, we get the attrition rate in the jet region, A_j , as follows:

$$A_j \propto W_s \times A_p \propto u_0^k$$

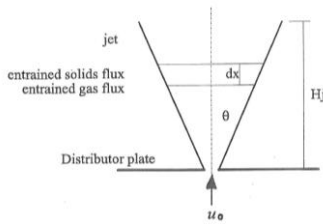


Figure 4. Schematics of the jet geometry and its features.

The results of the analysis by Ghadiri et al. [23] is shown in Table 3. The power index of the orifice gas velocity, k , is predicted to vary with orifice size. This has not been acknowledged in the previous works. The prediction is very sensitive to the jet half-angle θ .

Table 3. Prediction of the dependence of the jet attrition on the orifice velocity and size [23].

Material	Orifice diameter (mm)	Jet half-angle (°)	Prediction based on H_j from Yates et al.			Prediction based on max particle velocity		
			n	m	k	n	m	k
FCC	0.5	8	1.23	1.03	3.91	1.30	1.07	4.11
FCC	1.0	9	1.00	1.21	3.55	1.06	1.27	3.75
FCC	2.0	9	0.86	1.30	3.31	0.65	1.56	3.08
NaCl	1.0	6	1.00	0.92	3.52	1.86	0.42	5.26
NaCl	2.0	6	0.88	1.10	3.34	1.79	0.60	5.26
NaCl	3.0	6	0.81	1.13	3.24	1.63	0.68	4.92

3.3. Analysis of Jet Attrition: Effect of Particle to Orifice Size Ratio

Ghadiri *et al.* [23] carried out a systematic investigation of attrition of FCC powder in the jetting region of a fluidised bed, quantifying the dependence of the attrition rate on the orifice velocity and size. Boerefijn [24] subsequently showed that the orifice size dependency arises from differences in the mechanics of interparticle interaction arising in turn from the size ratio of the orifice to the particles, as schematically illustrated in Figure 5: (a) small dor/dp, fresh FCC; (b) small dor/dp, used FCC; (c) large dor/dp, fresh FCC, (d) large dor/dp, used FCC.

4. Analysis of Jet Attrition by CFD-DEM Method

Fulchini [25] carried out such an analysis using the EDEM software package. The input data are shown in Table 4. A snapshot of the simulations is shown in Figure 6, showing the maximum particle velocity of about 2 m/s for an orifice velocity of 40 m/s. Spherical particle shape

is used, but other properties are for two types of MnO_2 material, fresh F-CLC and equilibrium E-CLC particles. The attrition results are shown in Table 5 and Figure 7.

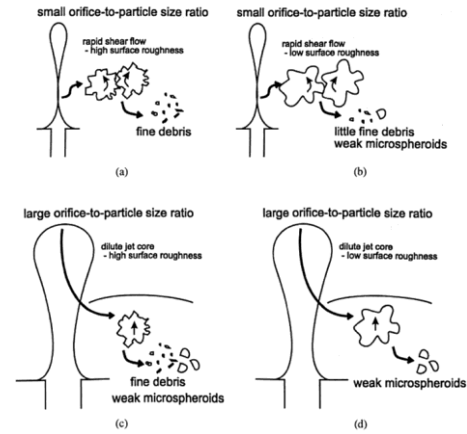


Figure 5. Schematics of interparticle interactions depending on the size ratio of orifice and particles [1].

5. Conclusions

Coupling jet hydrodynamics and attrition kinetics provides a means to identify the influence of material properties and operating conditions on attrition in the jetting region of fluidised beds. The attrition rate in a jet per unit mass of gas flowing through the orifice depends on the orifice diameter as well as velocity. This dependency may be a contributory factor for the existence of differences in reported results in the literature. Numerical simulations by CFD-DEM confirm the mechanics model of jet attrition.

Table 4. CFD-DEM simulation input data [25].

Particle size [μm]	925
1. Particle shape	Spherical
Particle density [kg/m ³]	3300
Bed dimensions [mm×mm×mm]	100×10×600
Orifice to particle size ratio	12
Number of particles [-]	20000
Air velocity inlet [m/s]	40
Temperature [°C]	25
Mesh cell size [mm]	2.5
Number of cells	38400
Turbulent model	k-ε
Drag model	Gidaspow
CFD-DEM coupling	4-way
Contact model	Hertz-Mindelin (no slip)

Acknowledgement

This paper is dedicated to the memory of the late Professor Giorgio Donsi, a great friend and inspiring scientist, whose model of jet penetration in fluidised beds was coupled with the Ghadiri and Zhang model of single particle impact attrition to predict particle attrition in the jet region. The work was conducted with some ten scholars, with support from BP Research, Shell Research, FCC manufacturers, and Total, in collaboration with Institut Francaise du Petrole in Lyon.

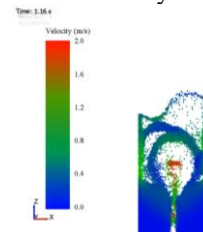


Figure 6. A snapshot of simulations showing the particle velocity range in the jet region [24].

Table 5. Simulation results showing the dependence of the attrition rate on the orifice velocity and size, according to the notation of Equation 2 [24].

Jet attrition			
Symbol	description	F-CLC	E-CLC
c_{jet}	Jet attrition index	5.5×10^{-7}	1.4×10^{-9}
u_{jet}^*	Jet velocity power index	2	6
d_{or}^*	Orifice size power index	1.7	3.6
$u_{jet,0} \text{ m/s}$	Jet transition velocity	13.5	4.2

$$\dot{R}_{jet} = \alpha \frac{H}{K_c^2} c_{jet} n_{or} \rho_p u_{jet}^x d_{or}^y \quad (2)$$

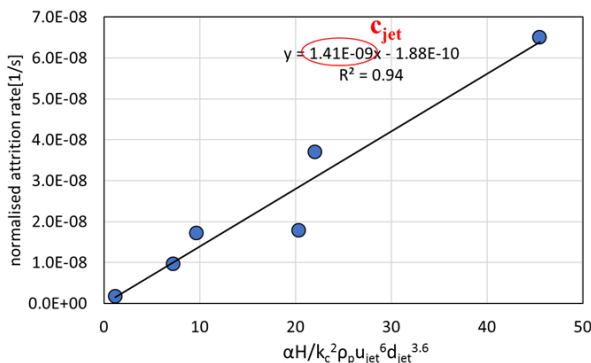


Figure 7. Attrition rate of a single jet in a fluidised bed [24].

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Surface finishing of Additively Manufactured Aluminum parts through Fluidized Beds

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Abstract. This study investigates the potential of fluidized bed finishing (FBF) of square specimens manufactured via Laser-Powder Bed Fusion additive manufacturing technology. Rotation-assisted FBF tests are carried out for two different specimens materials, AlSi10Mg and AA6061 alloys using irregular steel abrasive particles as bed material. Experiments are performed with an average relative tangential speed between the exposed surface of the specimen against the abrasives of 2 m/s, while varying the tilt angle of the specimen. Results are reported and compared between the two materials in terms of finishing parameters like mean areal surface roughness, skewness and finishing process indicator. Results highlight that rotation-assisted FBF represents a viable finishing treatment for both the AlSi10Mg and AA6061 alloys. The tilt angle is a key operating parameter, as it allows to maximize sliding and shear. In particular, at low tilt angle the best results are obtained, with a reduction of surface roughness of 67% and 47% for AlSi10Mg and AA6061 alloys, respectively.

1. Introduction

Additive Manufacturing (AM) represents one of the most intriguing manufacturing processes to fabricate objects directly from CAD 3D models [1]. AM covers the production of complex, composite and hybrid structures with several advantages compared to traditional manufacturing technologies, such as rapid prototyping, design flexibility, high level of customization and high materials efficiency [2].

The most widespread AM technologies for metals, i.e. Laser-Powder Bed Fusion (L-PBF), Electron Beam-Powder Bed Fusion (E-PBF) and Laser Metal Deposition (LMD), use powders as the material feedstock [3]. One of the main reasons that hampers the expected high employment of these technologies is the high surface roughness of the as-built parts, due to the well known staircase effect and the balling effect [4], resulting in rough surfaces with overhangs and sintered powders. For this reason, a consistent series of pre- and post-process operations are required to meet the desired final product specifications, as for instance, operations aimed at controlling the powder properties [5], post-process heat treatments to increase parts density and to achieve the desired microstructure [6], post-process surface finishing to improve the surface quality [7]. The most common finishing methods such as CNC machining, shot peening, electrochemical polishing and laser polishing have high limitations just for parts characterized by high geometrical complexity which represent the most

promising objects achievable with Additive Manufacturing. In the field of finishing methods based on mechanical interaction, the Fluidized Bed Finishing (FBF) technology is gaining more and more attention. As the abrasive particles used are brought in the fluidized state, their subsequent interaction with the part leads to the desired surface re-modeling and roughness reduction [8,9]. Rotation-assisted fluidized bed finishing (R-FBF) proved to be more efficient in comparison to the case of the static dipping of the part into the fluidized abrasive, as it helps to establish the proper relative speed conditions between the part and the abrasives required for a satisfactory roughness reduction [10]. In this study R-FBF is investigated for flat square specimens produced by L-PBF. Two different specimens materials have been studied, namely AlSi10Mg and AA6061 alloys. Experiments are carried out with irregular steel abrasive particles, at fixed relative tangential velocity, while varying the tilt angle of the specimen. The experimental tests aim at investigating the effectiveness of the finishing process for different materials and the optimal operating parameters.

2. Experimental

2.1. Materials

The R-FBF experiments were carried out on square flat specimens (20 mm x 20 mm x 1.5 mm) produced through L-PBF orthogonally to the build platform and starting

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from AlSi10Mg and AA6061 powders supplied by EOS GmbH. The printing parameters for AlSi10Mg were the following: laser power $P = 370$ W, hatch spacing $h = 0.19$ mm, scanning speed $v = 1300$ mm/s and layer thickness $LT = 30$ μm , while for AA6061 specimens they were: Laser Power = 400 W; Scanning speed = 230 mm/s; Layer thickness = 30 μm ; Hatch spacing = 110 μm .

Steel abrasive particles with irregular shape are used in this work as bed material, as their balance between density and hardness compared to the ones of the alloys to be processed proved to be effective in the smoothing of aluminum parts. The characteristics of the particles are: density equal to 4.2 kg/m³, mean size 0.53 mm, $d_{10} = 0.33$ mm, $d_{50} = 0.57$ mm, $d_{90} = 1.04$ mm.

2.2. R-FBF apparatus and operating conditions

The experimental setup used for the FBF experiments is reported in Fig. 1 [10]. It consisted of a Plexiglas fluidization column (inner diameter 0.21 m) which comprises a windbox and an upper section, 1.4 m high, where the abrasive material was located. The fluidizing gas, technical air, was fed at the bottom of the windbox and flowed through a steel bubble caps plate acting as gas distributor to the fluidization section of the column. The carrier gas was controlled by a mass flow meter with a maximum operating flow rate of 45 Nm³/h. The specimen clamping system was inserted into the column from the side and connected to an inverter-controlled electrical motor. The specimens were clamped on a custom fixture mounted on the motor rotation axis, that allowed therefore the rotation of the specimen as well as to fix its tilt angle.

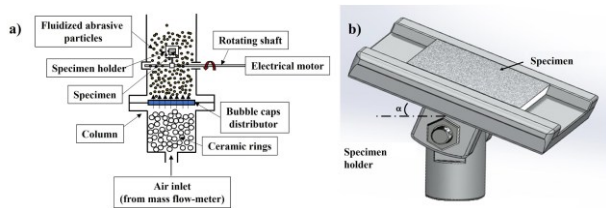


Figure 1. Scheme of the experimental apparatus used for the R-FBF experiments (a) with an inset of specimen positioning and tilt angle (b).

Experiments were carried out to investigate the effect of target inclination (α) on the finishing process during the rotation-assisted FBF tests at fixed average relative tangential speed (v) between the exposed surface of the specimen against the abrasives of 2 m/s. The bed was operated under incipient fluidization conditions and the processing time was fixed at 30 min for each test. The operating conditions and process parameters used in the experimental campaign are reported in Table 1.

Table 1. Process parameters and operating conditions used of rotation-assisted FBF experiments for both AlSi10Mg and AA6061 parts.

Tilt angle [°]	v range [m/s]	Process time [min]
25	2±0.18	0.15
65	2±0.5	0.25
90	2±0.6	0.90

2.3. Characterization of the specimens

Before the R-FBF tests, the specimens were accurately cleaned in ethanol by means of an ultrasonic bath for 15 min and then dried at 80°C for 1 h. Before and after FBF tests, a quantitative description of the surface texture was obtained by confocal microscopy (Leica DCM3D). For each acquisition, an 8×8 mm² area was considered, taking the sample center as a reference point. The acquired surfaces were then post-processed to correct tilt errors, to fill the missing points and to extract the surface texture parameters by means of the software Leica Map® v7. In particular, the surface quality was analyzed through the following parameters, all defined by the ISO25178 and ISO4287 standards: the mean areal surface roughness, S_a ; the areal skewness, S_{sk} ; the root mean square of the primary profile slope, P_{dq} . Moreover, on the basis of the values of the parameter S_a , the indicator of finishing performance I_{fp} was considered, defined as the change of S_a during the finishing step divided by S_a of the untreated specimen. For the sake of repeatability, each evaluation was carried out on three specimens for each investigated condition.

3. Results and discussion

The comparison of the selected texture parameters before (NT) and after (T) the R-FBF experiments at fixed rotation speed and for different tilt angles of the specimen are reported in Table 2 and 3 for AlSi10Mg and AA56061 specimens, respectively. Mean values of the selected parameters are reported with standard deviation.

Table 2. Surface texture parameters of AlSi10Mg specimens (results are reported as mean $\pm$ σ).

	Tilt angle [°]	NT	T
S_a [μm]	25	21.7±1.1	7.2±0.2
	65	20.9±3.7	9.0±2.9
	90	19.7±0.6	11.9±0.4
S_{sk}	25	0.02±0.0	-0.89±0.04
	65	-0.01±0.13	-1.94±0.34
	90	-0.2±0.14	-1.66±0.2
P_{dq} [°]	25	36±3.2	9±3.1
	65	36±2.6	8±2
	90	34±2.8	12±2.6

Table 3. Surface texture parameters of AA6061 specimens (results are reported as mean $\pm$ σ).

	Tilt angle [°]	NT	T
S_a [μm]	25	9.4±1.1	5.0±0.8
	65	8.8±0.7	5.3±0.8
	90	9.3±0.9	7.1±0.6
S_{sk}	25	0.39±0.21	0.15±0.39
	65	0.82±0.3	-0.15±0.30
	90	1.35±0.11	0.09±0.08
P_{dq} [°]	25	7.2±2.2	2.7±0.1
	65	7.3±2.6	2.9±0.2
	90	7.9±3.6	4±0.9

Results showed an appreciable and robust improvement of all the surface quality parameters for both the materials, even considering the chemical composition and the texture parameters of the untreated specimens were very different for the two alloys. In fact, for AlSi10Mg specimens initial S_a was around 20 μm , while for AA6061 specimens initial S_a was around 9 μm . Also P_{dq} values of the untreated specimens were very different, around 36° and 7.5° for AlSi10Mg and AA6061 specimens, respectively. The best results were achieved when adopting a tilt angle of 25°, for which sliding and shear between the specimen and the abrasive bed material are maximized. In fact, under these operating conditions, all the investigated texture parameters were remarkably improved. Instead, for the 90° angle condition, the smoothing ability of the abrasives decreased significantly.

Results in terms of the finishing parameter I_{fp} are reported in Figure 2 as a function of the specimen tilt angle for both the materials, AlSi10Mg and AA6061. Data showed that for a small tilt angle maximum values of I_{fp} are obtained, i.e. around 67% and 47% for AlSi10Mg and AA6061 materials, respectively. This result confirms that, although the two alloys are very different, being AlSi10Mg a more brittle material, while AA6061 a more ductile material, R-FBF can be still effective, especially using small tilt angles, i.e. maximizing sliding and shear.

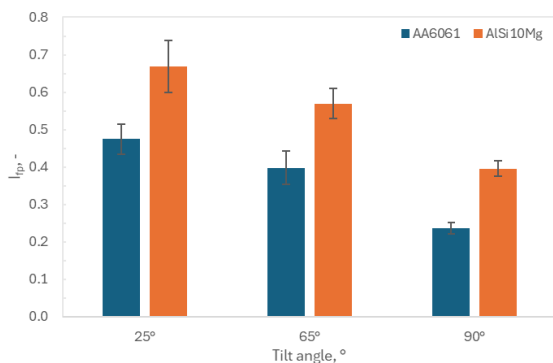


Figure 2. Surface finishing parameter I_{fp} as a function of the specimen tilt angle for AlSi10Mg and AA6061 alloys.

4. Conclusions

Rotation-assisted Fluidized Bed Finishing (R-FBF) of specimens manufactured by the Laser-Powder Bed Fusion (L-PBF) AM technology has been investigated under a variety of operating conditions. Two different specimens materials were considered, AlSi10Mg and AA6061. The effectiveness of R-FBF has been assessed, as a function of the nature of the abrasive material and of the tilt angle of the specimen with respect to the prevailing motion of the fluidized particles, at fixed mean relative tangential speed of 2 m/s between the surface and the abrasives.

Results confirm R-FBF is an effective treatment aimed at improving the surface texture parameters of metal parts made through AM. In particular, for both the specimen materials and regardless of the initial values of texture parameters, surface finishing depends on the orientation of the specimen with respect to the prevailing flow of the

fluidized particles. Surface finishing is maximized when plain shear flow of fluidized particles is established close to and past the specimen. In fact, for tilt angle equal to 25° a surface roughness reduction of 67% and 47% was achieved for AlSi10Mg and AA6061 materials, respectively.

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Optimization of the Specific Energy Consumption of Fluidized Bed Opposed Jet Mills for High-Performance Materials

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Abstract. Fluidized bed opposed jet mills are a well-established technology for the production of ultra-fine, contamination-free powders in high-value applications, including industrial minerals, advanced ceramics, rare-earth materials, and chemical products. Their ability to deliver narrow particle size distributions while preserving particle morphology makes them indispensable for high-performance materials. However, high specific energy consumption (SEC), largely driven by compressed gas generation, remains a key limitation. This contribution reviews major application areas of fluidized bed opposed jet milling and focuses on strategies to significantly reduce SEC while increasing throughput. Process optimization measures are discussed with emphasis on increasing grinding gas temperature to enhance jet velocity and compressor efficiency, as well as on upstream pre-grinding using high-pressure grinding roller (HPGR) mills. The results demonstrate that a single HPGR pre-grinding step can reduce the SEC of subsequent jet milling by more than 20% and, in many cases, enable comparable increases in system capacity. These approaches not only improve economic performance but also contribute to greater ecological sustainability and can be retrofitted into existing production plants.

1. Background

Fluidized bed opposed jet mills represent a cornerstone technology for the production of ultra-fine, contamination-free powders in numerous high-value industrial sectors. With more than 800 installations in Europe and over 1,500 globally delivered by HOSOKAWA ALPINE Aktiengesellschaft, these mills have established themselves as a versatile and robust solution for comminution processes requiring precise particle size distribution (PSD) control at high throughput.

However, the specific energy consumption of jet mills is relatively high, which is also due to the low efficiency of the compressors. Therefore, optimizing the specific energy consumption (SEC) is a key objective for the further development of these mills. Moreover, the operating parameters have a significant impact on the SEC.

2. Applications of fluidized bed opposed jet mills

2.1. Industrial minerals

A central advantage of fluidized bed opposed jet mills is their ability to generate ultra-fine fillers while preserving particle morphology—critical for industrial minerals such as talc, wollastonite and other engineered fillers.

For example, very fine talc fillers are produced in large quantities in large fluidized bed opposed jet mills, which are operated using compressors in the Megawatt

range. At the Hosokawa Alpine AG pilot plant, a TDG 200/400 was used to produce talc with a d_{97} of 1 μm . Despite these fine particle sizes, the SEM image shows platelet-shaped particles with a high aspect ratio (Figure 1).

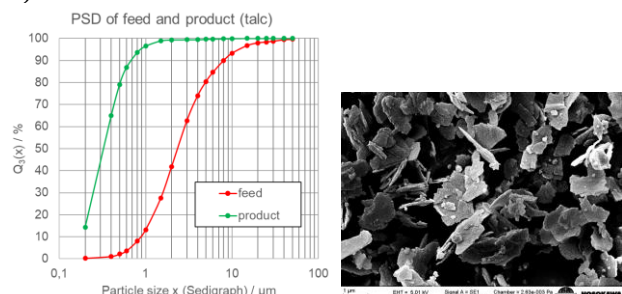


Figure 1. Particle size distribution (left) and SEM image (right) of a talc filler produced at the test centre using a TDG 200/400 fluidized bed opposed jet mill.

2.2. Ceramics and hard materials

For ceramics and hard materials, such as ATH, Al_2O_3 , ZrO_2 , SiC, B_4C , etc., fluidized bed opposed jet mills provide contamination-free grinding. Although no tools come into contact with these abrasive materials during grinding, the surfaces in the mill and its peripheral components that come into contact with the product must be protected against wear. For this purpose, linings made of ceramics or suitable polymers are used. The grinding wheels of the mills can also be made of solid ceramic or coated with ceramic.

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2.3. Rare-earth material

For the manufacturing of strong NdFeB-magnets the material needs to have a particle sizes and steep particle size distributions. In rare-earth processing, particularly pyrophoric neodymium used in permanent magnets, fluidized opposed jet mills support controlled-atmosphere milling with nitrogen circuits and low-oxygen environments. Due to the high demand of these materials, the scalability from lab- to industrial-scale is of vital importance.

2.4. Chemical products

In chemical applications, fluidized opposed jet mills are used to efficiently micronize temperature-sensitive materials, polymers, organic compounds, but also battery cathode active materials (LFP, NMC). Additionally, special design adaptations enable processing of low-bulk density materials such as silica and recovered carbon black, improving dispersion, bulk density, and material handling.

3. Optimization of the SEC

Although fluidized bed jet mills offer many advantages, their use is limited to high-quality materials. This is primarily due to their high specific energy consumption. Optimizing the SEC is therefore a key focus for many operators. In many cases, measures to reduce the SEC also led to higher mill throughputs, which results in improved utilisation of the equipment and profitability.

3.1. Grinding gas temperature

One essential measure is increasing the milling gas temperature. On the one hand, this increases the efficiency of the compressors. On the other hand, the jet speed, and thus the jet power, increases with temperature at the same pressure, resulting in a higher energy density in the mill. As can be seen in Table 1, the increase in temperature has a higher effect on the jet speed than the increase of the grinding gas pressure.

Table 1. Jet speed at different grinding gas pressure values at 20°C and 150°C, respectively.

Grinding gas pressure p_{abs} [bar]	Jet speed at nozzle [m/s]	
	@ 20 °C	@ 150 °C
2	325	391
3	398	478
4	439	527
7	501	602
9	524	629
11	540	649

3.2. Pre-grinding by HPGR mill

Another interesting option for reducing the SEC is the pre-grinding of feed materials using high-pressure grinding roller (HPGR) mills. Similar effects are already known in other applications, such as the grinding of cement in ball mills or of ores in wet stirred media mills. The combination of pre-grinding in an HPGR mill, e.g., the Alpine Ecoplex mill ECP, with fine grinding in a fluid bed jet mill is shown in Figure 2. A single pass of

the feed material through the HPGR mill is sufficient to reduce the SEC of the subsequent fine grinding in the fluidized bed opposed jet mill by more than 20%, which represents a significant savings potential given the high energy costs of jet milling alone.

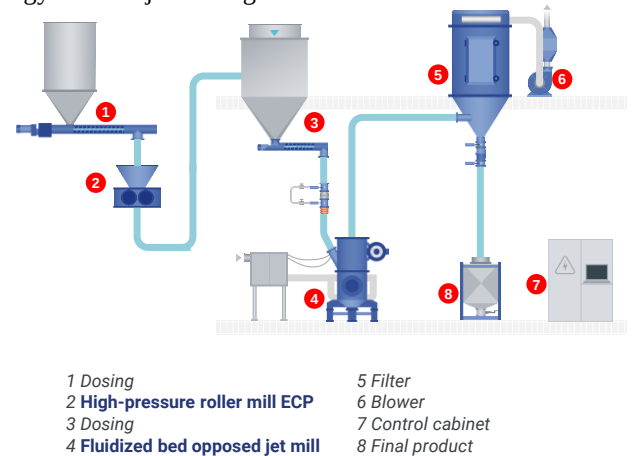


Figure 2. Combination of HPGR mill ECP and fluidized bed opposed jet mill AFG

This effect can be observed for brittle materials such as hard materials (SiC, B₄C etc.) or minerals (talc, limestone etc.). In many cases this reduction in SEC can be used to increase the capacity of the system by up to 20 % resulting in an improved utilization and profitability (Figure 3). Due to the higher output of the production line, the higher investment costs are amortized within a short time.

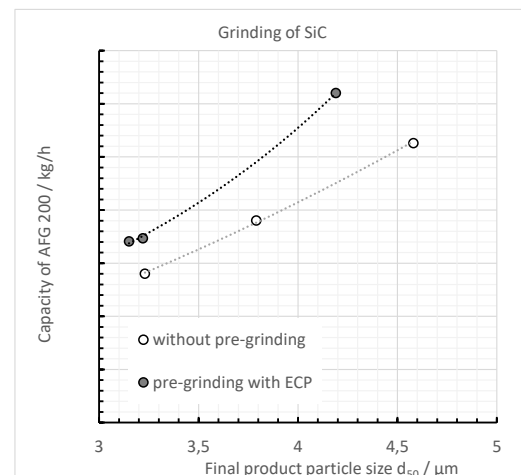


Figure 3. Throughput as a function of product fineness for the grinding of SiC with and without pre-grinding using an Alpine ECP HPGR mill

3. Conclusion

Fluidized bed opposed jet mills continue to evolve as enabling technologies for advanced powder engineering. There are various ways to significantly reduce the SEC (separation pressure) and thus increase the efficiency and ecological and economic sustainability of these grinding systems. Interesting approaches include increasing the grinding gas temperature and pre-grinding the feed material with HPGR mills. These mills can also be retrofitted into existing plants.

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Modelling and calibration of the Andrews-Mika diagram with a texture-dependent liberation model

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Abstract. Mineral liberation modelling has advanced from simple geometrical approaches to frameworks capable of describing ore texture variability and breakage-liberation phenomena. However, current models still present important limitations, either due to the large experimental effort required for calibration or the lack of direct coupling between texture, phase conservation, and breakage mechanics. This study uses a texture-dependent liberation model (TLM) in virtual experiments in calibration of an Andrews–Mika diagram model for a conceptual binary copper ore. Calibration of the Andrews-Mika diagram model showed that some of the model parameters vary significantly with particle grade, contrasting with the assumption that they were constant in the original formulation. The proposed approach bridges the gap between realistic TLMs and practical and phenomenological comminution models, thereby facilitating the integration of comminution and liberation models for full circuit simulations.

1. Introduction

Mineral liberation modelling has evolved considerably over the last century, progressing from purely geometrical approaches [1] to advanced frameworks incorporating mineral texture and breakage mechanisms [2-5].

Early liberation models aimed to describe the three-dimensional geometry of intact particles and predict the distribution of liberated and middling particles after breakage, although without a clear representation of the coupling between fragmentation and liberation phenomena [1]. While these approaches represented important advances in the phenomenological understanding of liberation, their application in comminution modelling remained limited. Significant progress was achieved in the early 1970s with the introduction of the Andrews–Mika diagram, a two-dimensional representation capable of mapping the distribution of progeny particles in the size-by-grade phase space after breakage [2]. Despite its relevance, the practical application of the diagram in comminution models was restricted by the complexity associated with its mathematical description [6].

A major advancement was only achieved in the late 1990s with the work of King and Schneider [6-7], who proposed a quadrivariate function capable of fully describing the Andrews–Mika diagram. This phenomenological framework provides a direct and practical representation of the diagram by separately predicting its boundaries, the internal distribution of middling particles, and the liberated fractions represented by Dirac functions at the extremes. This model directly

interfaces with population balance formulations, enabling the coupled simulation of breakage and liberation.

Despite its advantages, the King and Schneider model requires a large amount of experimental data for calibration [6-7]. In parallel, geometric-textural approaches have also been proposed to explicitly represent mineral textures. Among these, the stochastic texture-dependent liberation model (TLM) proposed by Hilden and Powell [5] stands out by generating abstract intact ore textures calibrated from mineralogical image analysis. This approach enables the prediction of liberation spectra under different textural conditions and provides a realistic representation of texture variability effects. However, the model does not explicitly account for particle breakage mechanics and cannot meaningfully be incorporated in process simulators with recycle streams.

The present study considers a conceptual copper ore texture and applies the TLM [5] to perform virtual experiments aimed at supporting the calibration of the Andrews–Mika diagram model.

2. Modelling overview

2.1. Andrews-Mika diagram

The Andrews-Mika diagram is a graphical representation of the phase space available to progeny particles produced when a single parent particle breaks during comminution. The diagram is constructed in a two-dimensional space whose axes are particle size and grade. Any progeny particle in a population can be located as a point in this space and the diagram addresses where a fragment from a

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broken parent particle at a known position (grade g' , size d_p') realistically appears in the phase space [2].

The key insight is that the progeny population is not free to occupy the entire phase space below the parent. Instead, it is strictly constrained by the conservation of mineral and gangue volumes. Because no progeny particle can carry more mineral than the mineral present in the parent and, equally, no progeny can carry more gangue than the gangue present in the parent, these two conservation requirements define jointly a bounded sub-region of the phase space. This sub-region of the phase space, called attainable region, has been modelled using a quadrivariate function that varies with grade and size of both parent and progeny particles [6-7].

A discretized model for the attainable region was proposed as [6-7]:

$$p_i(g|d_p; g', d_p') = L_m[I_{\xi(g_{i+1})}(\alpha^M, \beta^M) - I_{\xi(g_i)}(\alpha^M, \beta^M)] \quad (1)$$

where g and d_p are the grade and size of the progeny particle, g' and d_p' are the grade and size of the parent particle, $\xi(g_i)$ the transformed grade variable and α^M and β^M are parameters of the incomplete beta function I .

Application of Eq. (1) requires: (1) calculating the boundaries of the phase-space; (2) defining the inner distribution based on the fraction of middling particles; (3) calculating the fraction of liberated mineral (L_1) and gangue (L_0). The upper (g_u) and lower (g_l) bounds of the Andrews-Mika diagram are calculated as:

$$g_u \leq \max \left[g' \left(\frac{d_p'}{d_p} \right)^{\delta_{u,1}}, g' \left(\frac{D_{lib}}{d_p} \right)^{\delta_u} \right] \quad (2)$$

$$1 - g_l \leq \max \left[(1 - g') \left(\frac{d_p'}{d_p} \right)^{\delta_{l,1}}, (1 - g') \left(\frac{D_{lib}}{d_p} \right)^{\delta_l} \right]$$

where δ_u , $\delta_{u,0}$, δ_l and $\delta_{l,0}$ are fitting parameters, while D_{lib} is the size where liberation starts to become statistically relevant. These parameters indirectly capture the relationship between grain and particle size in the liberation behaviour. King [6] suggested $\delta_{u,1}$ and $\delta_{l,1}$ with constant value as 0.2, while δ_u and δ_l are predicted as:

$$\delta = \min \left[\delta_0 \left(\frac{D_{lib}}{d_p'} \right)^{\frac{1}{2}}, 3 \right] \quad (3)$$

where δ_0 is a fitting parameter.

After properly defining the boundaries of the Andrews-Mika diagram (Eqns. (2) and (3)), the inner distribution may be defined by the incomplete beta function, shown in Eq. (1). At this stage it is worth noting that the inner distribution will extend only from g_l to g_u , which may not consider the entire range from 0 to 1. This situation is handled by assuming the transformed variable $\chi = \frac{g - g_l}{g_u - g_l}$ as an input to the model [6-7].

Parameters α^M and β^M (Eq. (1)) must be chosen to ensure that the average grade of the inner distribution ($\bar{g}^M$) matches the grade of the parent particle as:

$$\begin{aligned} \alpha^M &= \bar{g}^M \gamma \\ \beta^M &= (1 - \bar{g}^M) \gamma \end{aligned} \quad (4)$$

where γ is the standard deviation of the distribution given by $\gamma = \frac{1 - f(d_p)}{f(d_p)}$. The term $f(d_p)$ is given as:

$$f(d_p) = \frac{1}{1 + \left(\frac{d_p}{D_{lib}} \right)^\lambda} \quad (5)$$

where λ is a fitting parameter.

The average grade of the inner distribution is then given as [6-7]:

$$\bar{g}^M = \int_{g_l}^{g_u} gp(g|d_p; g', d_p') dg = \frac{g' - L_1}{1 - L_1 - L_0} \quad (6)$$

Eq. (7) relies on the fraction of liberated mineral (L_1) and gangue (L_0) in each size class. These fractions are also predicted using an incomplete beta function defined at the boundaries and based on the transformed variables as:

$$\begin{aligned} L_0 &= I \left(\frac{-g_l}{g_u - g_l}, g' \gamma, (1 - g') \gamma \right) \\ L_1 &= 1 - I \left(\frac{1 - g_l}{g_u - g_l}, g' \gamma, (1 - g') \gamma \right) \end{aligned} \quad (7)$$

2.2. Texture-dependent liberation model (TLM)

TLMs have been investigated by different authors since the early 2000s [4-5]. These frameworks combine detailed image analysis of the unbroken ore to characterize and model the ore texture, thus aiming to improve the prediction of liberation behaviour.

The TLM, proposed by Hilden and Powell [5], creates an abstract intact texture to capture the liberation distribution and properties of the fragmented particles. The model is designed to handle complex ores with different grades and grain size distributions, where the volume texture is characterized by [5]: phase type, modal mineralogy, grain shape, grain size distribution and spatial distribution.

The model considers particle shapes as spheres or orthogonally oriented cubes, while the grain size distribution is described using the Rosin-Rammler distribution [5]. The spatial distribution of grains within the parent particle is modelled based on the degree of clustering in the different axes, where the distribution considered is defined only by a filling factor [5]. The process of populating the texture volume involves randomly inserting primary grains into a 3D space using a random number generator. Progeny fragments are formed by sampling the texture volume to generate simulated particles in 2D or 3D, spanning various size classes. The breakage process assumes independence

from grain boundaries or mineral properties, thus describing only random and non-selective breakage.

This modelling framework does not mechanically describe particle breakage. Instead, it considers the intact texture as having an infinite size and randomly selects samples within it for each progeny size. Initially, the progeny particle size to be sampled is defined. The model then uses a Monte Carlo algorithm to randomly select a coordinate within the intact texture, where a cube with an edge length equal to the progeny size and centred at this coordinate is generated. This cube represents a progeny particle of the selected size, and its composition is subsequently calculated. This procedure is typically repeated 10,000 times per size class to reliably estimate the liberation distribution for the given progeny size [5].

3. Materials and methods

3.1. Conceptual ore texture

The present work investigates the liberation behaviour of a hypothetical bornite copper ore. The ore texture is assumed to be a binary mixture of bornite and gangue, with specific gravities of 5.1 and 2.7 t/m³, respectively. 80% of the grains are finer than 1 mm, while the Rosin-Rammler slope of the distribution was equal to 2. As such, the minimum and maximum grain sizes varied from 16 μ m to 2 mm, respectively. The texture filling parameter (Section 2.2) is assumed to be equal to 1.

3.2. Virtual experiments

Virtual experiments are then conducted using the TLM [5] discussed in Section 2.2, and the ore texture presented in Section 3.1.

These virtual experiments were initially performed considering the ore texture parameters as presented in Section 3.1 and assuming a texture size of 10 mm. A total of thirteen simulations were performed by varying the grade of the parent particle from 5 to 65% by volume. Since the model does not allow grains to overlap, the grade of 65% by volume, which represented 77.8% by weight, was the maximum achieved given the packing limit [5]. All simulations were carried out by considering progeny sizes varying from 8 mm to 0.29 μ m. Parent particle size was assumed as 50 mm in these simulations.

3.3. Calibration of the Andrews-Mika diagram

From the virtual experiments described in Section 3.2, parameters in the attainable region equations presented in Section 2.1 were calibrated. In particular, the following model parameters were fitted: D_{lib} , $\delta_{0,u}$, $\delta_{0,l}$, $\delta_{l,1}$, $\delta_{u,1}$ and λ . Parameters $\delta_{0,u}$ and $\delta_{0,l}$ from Eq. (3) may assume different values for the upper and lower boundaries of the Andrews-Mika diagram.

The parameters are fitted separately by first describing the boundaries of the Andrews-Mika diagram using Eqns. (2) and (3), which depend on D_{lib} , $\delta_{0,u}$, $\delta_{0,l}$, $\delta_{l,1}$ and $\delta_{u,1}$. The remaining parameter, λ , is subsequently fitted using the extracted values of the liberated ore mineral and gangue fractions (L_1 and L_0) through Eq. (7). The optimal parameter estimation is carried out using a nonlinear optimization method based on Sequential Quadratic Programming.

4. Results and discussions

Figure 1 presents the 3D liberation spectrum predicted using the TLM for a particle with 20% grade by volume.

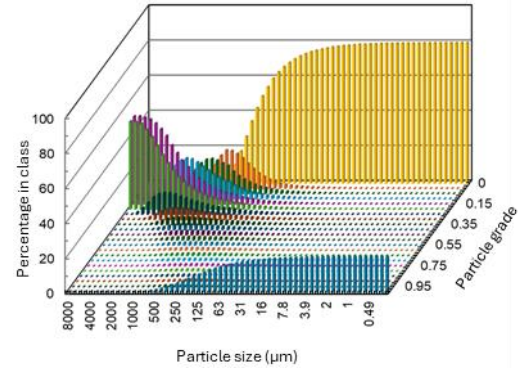


Figure 1. 3D liberation spectrum predicted using the TLM from breakage of a 20% grade by volume particle.

Data from Figure 1, which was generated by simulating a texture with 80% of the grains finer than 1 mm, is presented in Figure 2 to construct the boundaries of the Andrews-Mika diagram. Markers in Figure 2 represent the virtual experiment predicted with the TLM and lines the fitting of Eqns. (2) and (3). Good agreement is observed between them, with optimal values of parameters $\delta_{0,u}$ as 2.3, $\delta_{0,l}$ as 0.7, $\delta_{u,1}$ as 0.03, $\delta_{l,1}$ as 0.073 and D_{lib} as 6 mm.

Figure 2 also presents a comparison between the boundaries of the Andrews-Mika diagram by considering textures with different grain size distributions. Interestingly, results were well normalized in respect to grain size, where d_g in Figure 2 represents the 80% passing size of the grain size distribution.

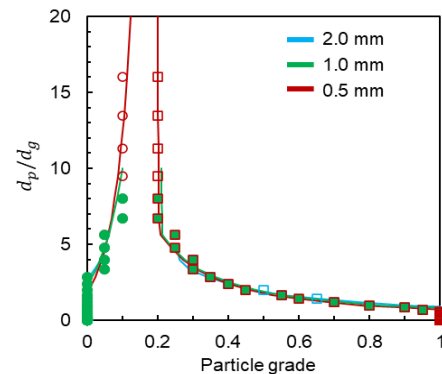


Figure 2. Comparison between the boundaries of the Andrews-Mika diagram predicted by the TLM and fitted with Eqns. (2) and (3) for a parent particle with 20% grade by volume and different grain size distributions.

The model that describes the attainable region [6-7], presented in Section 2.1, assumes that parameters from Eqns. (2), (3) and (6) must remain constant in respect to the parent grade, being then assumed as global ore texture parameters. However, results in Figure 3 demonstrate a strong dependence of $\delta_{0,u}$ and $\delta_{0,l}$ with the parent grade.

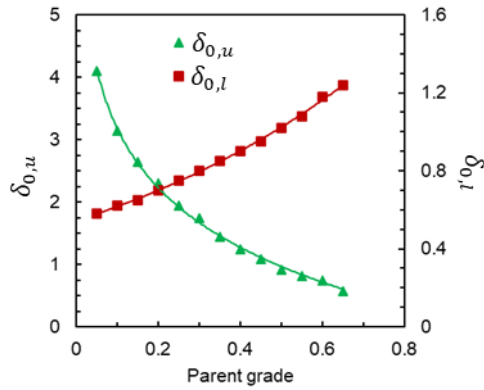


Figure 3. Relationship between optimal parameters $\delta_{0,u}$ and $\delta_{0,l}$ and the parent particle grade (in volume).

The parameters presented in Figure 3 are mainly associated with the tails of the curves shown in Figure 2, thus controlling the dispersion of the population of particles that can be found after breakage. When particles with lower grades are fragmented, the lower boundary tends to become more uniform and closely concentrated around lower grades. In contrast, the upper boundary exhibits higher dispersion, increasing the phase space in which progeny particles may be distributed after breakage. Figure 3 shows exponential decay trend for $\delta_{0,u}$ and an approximately exponential relationship for $\delta_{0,l}$, both in respect to the parent particle grade.

The relationships between the optimum values of $\delta_{u,1}$ and $\delta_{l,1}$ and the parent grade are presented in Figure 4. Parameter $\delta_{l,1}$ showed strong similarities to $\delta_{0,l}$, while $\delta_{u,1}$ remained nearly constant for parent grades below 45%, followed by an exponential decay at higher grades. These parameters control the curves associated with progeny sizes significantly larger than the liberation size (D_{lib}).

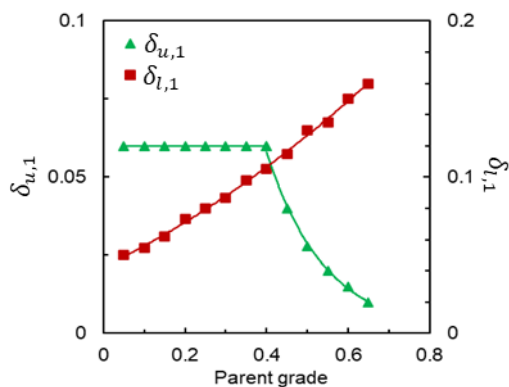


Figure 4. Relationship between optimal parameters $\delta_{u,1}$ and $\delta_{l,1}$ and the parent particle grade.

Finally, fitting of parameter λ (Eq. (6)) is presented in Figure 5 as a function of the parent grade. Results highlight a nearly parabolic relationship with maximum values for λ as 0.54, which was obtained for parent particles with 35% grade by volume. Increment in λ values correspond to a higher standard deviation of the inner distribution describing the population of middling particles. As such, results in Figure 5 demonstrate that particles with average composition are likely to produce a more dispersed population of particles in the different

grade classes, while breakage of low- and high-grade parent particles tend to produce progenies with grades closer to the parent particle grade.

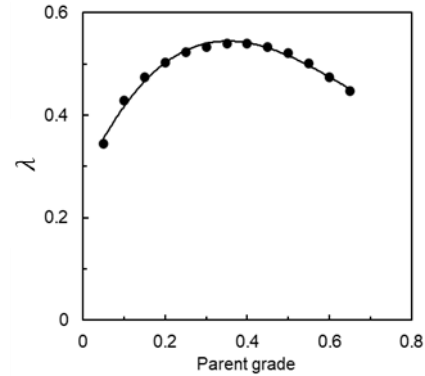


Figure 5. Relationship between optimal parameter λ the parent particle grade.

5. Conclusions

The present work uses a texture-dependent liberation model to calibrate a theoretical mathematical description of the Andrews-Mika liberation diagram.

The TLM simulates a conceptual ore texture and is used in virtual experiments. These experiments are performed varying the grade of the parent particle to map the liberation behaviour of the ore. Liberation spectra obtained from the TLM are then used as the basis to calibrate the boundaries and the internal distribution of the Andrews-Mika diagram. Results demonstrate a strong dependence of the model parameters with the grade of the parent particles, even though they were originally supposed to be constant [6,7], globally describing the ore texture.

Acknowledgement

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Mathematical Modelling of a Vertical Shaft Impact Crusher in Size Reduction of Aggregate Rock

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Abstract. Vertical shaft impact (VSI) crushers were introduced in the 1970s and achieved great popularity in some important applications, with a highlight in the aggregate industry, primarily owing to their ability to produce material with good cubicity. A VSI crusher (Barmac B7150SE from Metso) was installed in an aggregate plant in Rio de Janeiro in size reduction of a gneiss rock for manufactured sand production. Owing to varying production demands and the dynamics of the circuit, the crusher may be fed with material contained in a variety of size ranges, with particle sizes that may be as coarse as 45 mm and as fine as below 1 mm. Because of the importance of identifying the optimal conditions for operating the circuit, a mathematical model of the crusher was sought. After attempts to use published models were not successful, the need to develop a customized model became evident. The work describes the development of a crusher model, based on modification of the traditional Whiten crusher model. It recognizes that the VSI crusher may be described as two crushing processes operating in parallel: one represented by particles ejected by the rotor and the other by particles cascading through the ejected particles. Data from a total of 19 surveys with the crusher operating under a variety of conditions were used to fit the model. Results demonstrated that the model was able to capture the effects of feed throughput, feed size distribution, rotor opening and rotation frequency in predicting the product size distribution with high fidelity.

1. Introduction

Vertical shaft impact (VSI) crushers were introduced in the 1970s [1] and have since found a variety of applications in the minerals, aggregate and cement industries [2]. One of its most successful applications has been on manufactured fine aggregate production, owing to its ability to generate good aspect ratio material [3]. Different types and models of VSI crushers have been proposed, with the original being the Barmac, in which particles are projected against a bed of crushed rock deposited on the impact chamber of the machine, while a cascading curtain of rock crosses the projected flow from the crusher. Unlike compression crushers, whose throughput is highly limited by the gap, this type of crusher can tolerate highly variable feed rates, owing to the ability of the crusher to bypass material to the cascade flow.

Various attempts have been made to mathematically model the performance of VSI crushers. These have varied from phenomenological models, based on the concepts of breakage and selection/classification functions [4-6] to, more recently, the Discrete Element Method (DEM) [7,8]. In spite of the potential fidelity of the latter in describing microscale phenomena, its large computation demand prevents its use in integrated circuit simulations. Phenomenological models remain the only practical option in this task.

Whiten and White [9] considered that particle breakage in vertical shaft impact crushers could be described by a combination of a classification function followed by breakage of the selected particles. Bengtsson and Evertsson [5] used a similar approach but further discriminated volume and surface breakage, in a model that also described breakage of particles projected by the rotor and a bypass through the cascading flow. The authors demonstrated to be able to predict, with confidence, crusher power and product size distribution. More recently, Grunditz et al. [10] built on the same approach, only changing the classification/selection function by an energy-dependent function.

Some authors used the Whiten crusher model [11], which considers that particles are subjected to repetitive stressing events, to simulate the VSI. Justification for its use in VSI crushers was provided, indirectly, by Cunha et al. [7], who demonstrated that particles both projected by the rotor and cascading are subject to multiple impact events. Kojovic et al. [4] proposed this approach, with the breakage function being described as a function of specific impact energy. Segura-Salazar et al. [6] then considered that both the breakage and the classification functions were dependent on feed throughput, whereas the latter was also dependent on rotor frequency.

After unsuccessful attempts to represent results from an industrial-scale VSI crusher with models from the

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literature, a new approach is hereby proposed for a cascade-type crusher. It recognizes that the crusher can be optimally described as two parallel crushing processes: the primary that corresponds to breakage by projection of particles from the rotor and the secondary that represents breakage of material that falls under gravity cascading around the rotor. The model has been developed and fitted to data collected in an industrial circuit in operation with gneiss rock.

2. Modelling background

The framework of the model is illustrated in Figure 1, showing that the feed is split in two streams inside the crusher, depending on the feed rate, the feed coarseness, besides the opening of the hopper slit. Each of the flows is modelled as an individual crusher following Whiten's model [11]. As demonstrated by Cunha et al. [7], the severity of impacts varies significantly if the material is projected from the rotor or if it cascades, being this captured in the energy-dependent breakage functions (B). Particles entering the cascade flow are subjected to breakage by particles projected from the rotor. Therefore, the greater the amount of material projected by the rotor, the higher the probability of breakage of the cascading particles. This behaviour is captured by the cascade classification function (C_c) being a function of rotor feed rate.

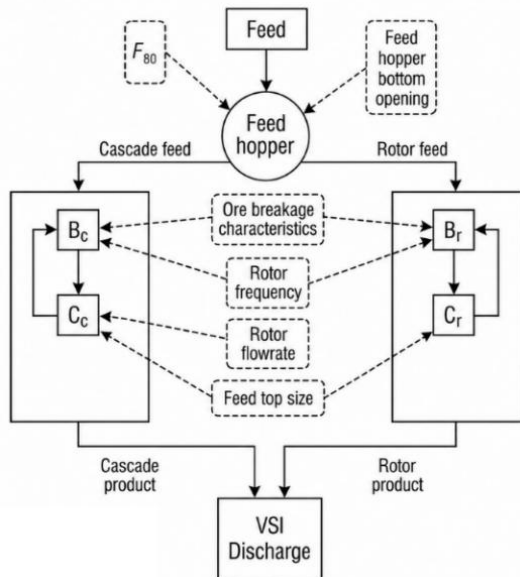


Figure 1. Model framework for the VSI crusher. B_c/B_r indicate the breakage functions of cascade/rotor and C_c/C_r indicate the classification function of cascade/rotor, respectively.

3. Materials and methods

The VSI crusher has been installed in an aggregate plant located in Itaguaí, a city in the metropolitan area of Rio de Janeiro. It is a Barnac B7150SE from Metso, with 320 kW power motor, which allows changing the rotor hopper opening and frequency of rotation, this later in real time during operation. It is part of a circuit that crushes rock to produce manufactured sand and filler for applications that include concrete and mortars. Besides the crusher, the

circuit also contains several vibrating screens, conveyor belts and an air classifier (Figure 2). Depending on circuit configuration, the crusher may operate in open or closed circuit, this later with recycle of material contained in different size ranges.

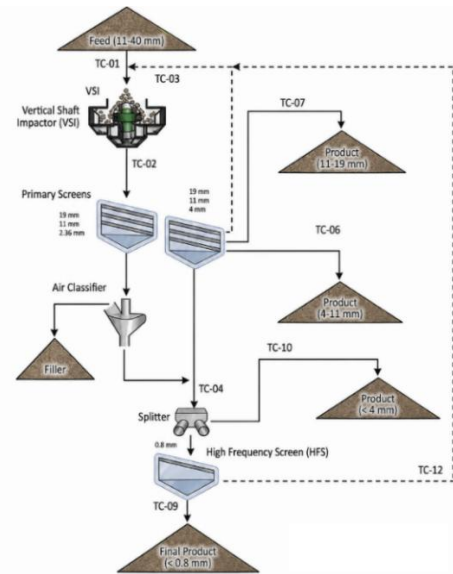


Figure 2. Simplified circuit flowsheet. Dashed lines represent de variable recirculation flow.

Nineteen surveys were carried out of the circuit when operating under a variety of conditions, including different feed size distributions, throughputs (51 to 540 t/h), openings of hopper slit (74 to 100%) and rotor frequencies (1100 to 2100 rpm). From each survey, samples from relevant streams were collected and subjected to size analyses by sieving. This, along with estimates of flowrates of the various streams of the circuit, were reconciled, serving as the basis for the development of the model. In addition, power drawn by the crusher in operation and running empty were measured.

Figure 3 shows composite feed size distributions to the crusher, which shows that it varied from nearly 45 mm down to below 1 mm, with 50% passing sizes varying from 28.6 to 12.4 mm. Such wide range is the result of differences in fresh feed size distribution, besides the stream in the circuit that is being recycled (Figure 2).

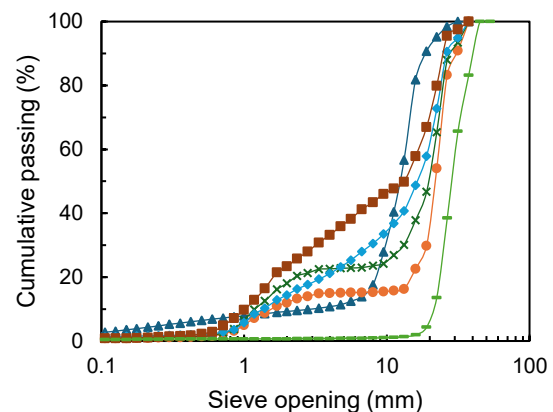


Figure 3. Composite feed size distributions to the VSI crusher from selected surveys

A sample of the material from the feed to the circuit was then subjected to drop weight tests with the aim of analysing the breakage characteristics of the rock.

4. Results and discussion

Results showing the variation in crusher power is a function of feed throughput are presented in Figure 4. It suggests that, as soon as the flowrate surpasses a minimum value, dictated by the feed hopper bottom opening and the feed particle size, a fraction of the feed starts to cascade. This behaviour was already demonstrated in earlier studies of VSI crushers [6,12].

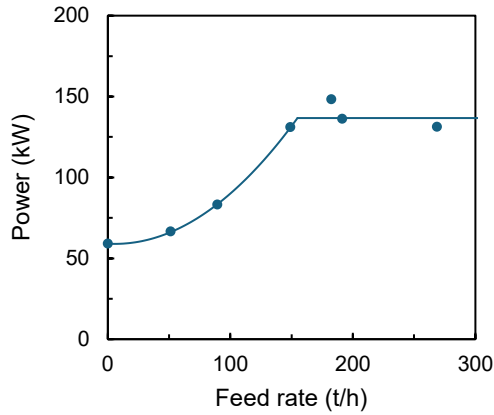


Figure 4. Variation in crusher power as a function of composite feed throughput (hopper slit opening of 91 %, 80% passing feed of 15.8 mm and frequency of 2100 rpm).

At first, the model was fit to data in which the power has not yet reached the plateau shown in Figure 4, suggesting no cascade flow. In this case it was possible to model the classification (C_r) and breakage (B_r) functions of the rotor. A typical result is shown in Figure 5, which shows the excellent agreement, evidence of the ability of the model to represent the main breakage mechanism inside the crusher. While here the breakage function from the drop weight test and the t_{10} procedure were used, a need was identified to modify the relationship of t_{10} with t_2 and t_4 , to account for the more limited rebreakage when particles are projected against a target, which is the case of the VSI crusher, in contrast to the drop weight test.

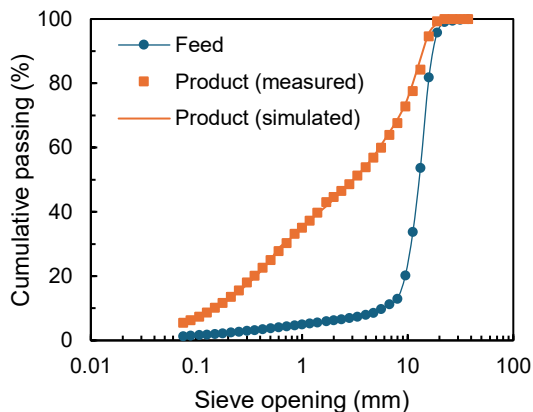


Figure 5. Comparison of experiments and predictions for a selected test (hopper slit open at 91 %) where all the particles from the feed is ejected by the rotor.

Now assuming that parameters from the classification and breakage functions remain unchanged for the rotor flow as the cascade flow appears, it then became possible to model parameters from the classification (C_c) and breakage (B_c) functions of this secondary flow. Figure 6 illustrates a case in which the model predicts separately the contributions from the rotor and cascade products. The rotor stream generates a finer product, since particles projected by the rotor undergo more intense impact conditions. In contrast, the cascade flow produces a coarser product, as particles in this flow are subjected to substantially lower impact energies [7]. The resulting overall product is then a combination of two distinct breakage processes, which is consistent with the physical behaviour of the crusher. This result supports the central assumption of the model, namely that the VSI crusher can be represented as two parallel comminution processes operating simultaneously.

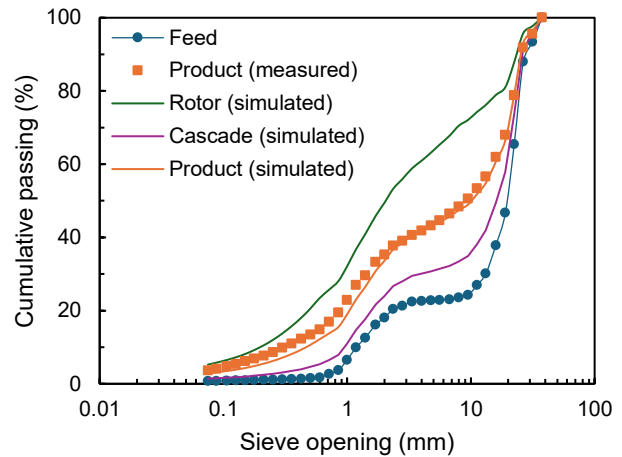


Figure 6. Comparison of experiments and predictions for a selected test, showing the predicted size distributions from the rotor and the cascade products.

A further examination of the model predictions of the cascade flow is shown in Figure 7. While the product of the rotor (omitted for clarity) remained unchanged, significant differences are observed in the predicted cascade product. As the hopper slit opening decreases, a smaller fraction of the feed is directed to the rotor, reducing the number of projected particles to impact the cascading material. As a result, the predicted cascade product becomes coarser, indicating lower breakage intensity in the secondary flow. This behaviour is result of the assumption that breakage of particles in the cascade stream depends strongly on the amount of material projected by the rotor.

An overall comparison of the model fit to experiments is possible in Figure 8, which shows the parity plots for both the 20% and 80% passing sizes, representative of both extremes of the product size distributions. While the agreement for the 80% passing sizes is excellent, the one for the 20% passing is only good, with the model tending to underestimate the content of fines in the product. The generally good agreement is particularly relevant, since the same set of model parameters was able to cover a broad range of operating

conditions. The satisfactory agreement obtained for both coarse and fine size descriptors suggests that the model captures not only the overall product size distribution, but also the sensitivity of the crusher response to changes in operating conditions.

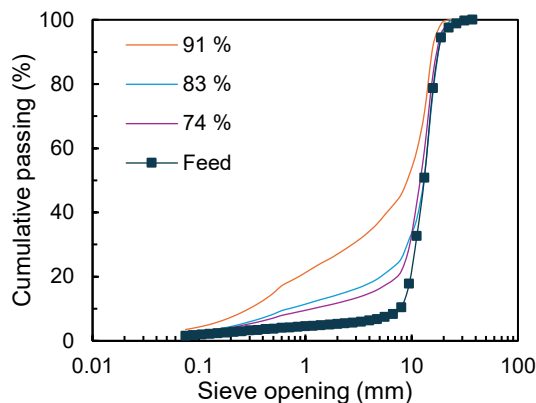


Figure 7. Comparison of predictions showing the predicted size distributions from the cascade products with different openings of the hopper slit from a feed throughput of 195 t/h.

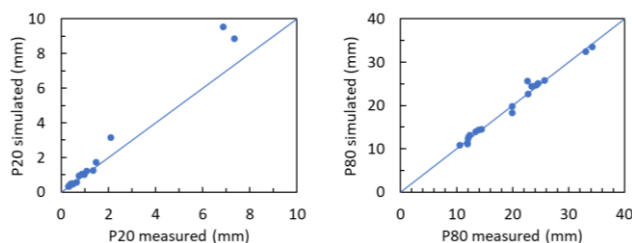


Figure 8. Parity plots of model predictions of 80% and 20% passing sizes in the product.

From a practical standpoint, the model provides a useful tool for predicting the influence of operational variables on VSI performance. The results show that the rotor and cascade contributions must be treated separately in order to properly describe the product size distribution. A single breakage environment would not be capable of reproducing the observed behaviour of the industrial crusher.

The proposed cascade-type VSI crusher model demonstrates strong predictive capability under varying operating conditions, which suggests its potential for integration into dynamic plant simulations. By incorporating both rotor and cascade contributions, the model can serve as a reliable unit operation within full-circuit simulations to optimize throughput, energy efficiency, and product quality across complex industrial processes.

5. Conclusions

A model of a cascade-type VSI crusher has been proposed that responds to variation in feed throughput and size distribution, rotor frequency and feed hopper slit opening, being capable to deal even with highly bimodal feed size distributions. By treating rotor and cascade breakage as two parallel comminution processes, the model was able to predict the product size distribution with good fidelity.

The parity plots showed good agreement for both P20 and P80, indicating that the model provides a reliable description of both the fine and coarse fractions of the product. This suggests that the proposed formulation is a practical tool for simulating and optimizing cascade-type VSI crushers in industrial circuits.

6. Acknowledgement

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Potential of Air Classification in Process-Plant Dust Recycling: A Mini-Review

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Abstract. Steel and cement plants, as well as biomass-based combustion plants, generate substantial amounts of fine dust that are removed from off-gases by de-dusting systems. The resulting residues are typically enriched in components that are volatile under process conditions, such as zinc and alkali salts. Due to volatilization at high temperatures and subsequent re-deposition during off-gas cooling, these species preferentially accumulate in the finest particle-size fractions. The presence of such components often restricts the utilization and recycling potential of de-dusting residues. Particle-size classification represents an effective strategy to address this challenge, as it enables the selective separation of the enriched finest fractions, thereby reducing the concentration of volatile components in the coarser bulk material. In addition, the fine fraction enriched in volatile species may, in certain cases, constitute a suitable feedstock for their targeted recovery. Owing to the characteristic cut sizes in the micrometre range, air classification is particularly well suited for this purpose, offering precise separation under dry processing conditions. This mini-review discusses the potential of air classification as a key processing step in the utilization and recycling of dust residues from industrial process plants, with a focus on applications in metal and mineral production.

1. Introduction

Large quantities of dust are generated in the minerals and metals industry as well as during the combustion of solid fuels (Table 1) [1-5]. The residues collected during off-gas de-dusting consist of fine granular materials that must either be valorized or disposed of in landfill sites. These residues are typically enriched in components that are volatile under process conditions, particularly heavy metals such as zinc and lead, as well as alkali salts. During high-temperature processing, these species vaporize and subsequently re-deposit onto existing particles as the off-gas temperature decreases. Because finer particles exhibit a higher specific surface area, the concentration of re-deposited material increases with decreasing particle size [6].

In recycling applications, such volatile components are generally undesirable because they tend to accumulate within the process through internal recirculation. However, for external utilization, for example for the targeted extraction of volatile components, their particle size-dependent enrichment can be advantageous for downstream recovery processes. Owing to the pronounced dependence of volatile component concentration on particle size, classification represents a viable approach to reducing their content in the bulk material by separating the enriched finest fractions. A well-established example is the treatment of sludge from wet off-gas cleaning of blast furnaces using

hydrocyclones, where a zinc-enriched fine fraction is separated from the coarser sludge fraction [7,8]

Table 1. De-dusting residues in the process industry; quantities calculated from production volume and mean specific dust emission rates

Process	Quantity of de-dusting residues [10^6 t/a]	Source
Sinter plant	0.18 (EU, 2004)	[1]
	1.5 (China, 2010)	[2]
Blast furnace (BF)	1.9 (EU, 2004)	[1]
	18 (China, 2010)	[2]
Steel converter (BOF)	1.5 (EU, 2006)	[1]
Electric arc furnace (EAF)	1.6 (EU, 2006)	[1]
Biomass combustion plants	3 (EU, 2003)	[3,4]
Cement mill	33 (EU, 2006)	[5]
	320 (World, 2006)	[5]

For dry de-dusting residues, air classification has been proposed previously [9,10]. In one study, also technical

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realization of air classification unit for zinc enrichment and depletion of BF dust has been reported [11].

2. Possible fields of Application

2.1. Dust recycling in Integrated Steel Mills

In integrated steel mills, dust streams arising from the sinter plant, the blast furnace (BF), and the basic oxygen furnace (BOF) must be recycled to ensure resource efficiency. The primary internal recycling route is via the sinter plant. However, the recycling capacity of the sinter plant is limited by the acceptable input levels of zinc and alkali chlorides. Consequently, substantial amounts of dust are still disposed of in landfills.

Air classification offers a suitable method to overcome these limitations by separating dusts into size fractions with different chemical compositions. For sinter plant dust, air classification can be used to produce a coarser particle size fraction with a reduced alkali chloride content, enabling increased recycling via the sinter plant [12]. Similarly, BF and BOF dusts with low to medium zinc concentrations can be air classified to obtain coarser fractions with reduced zinc contents, which are suitable for internal recycling [13,14].

In contrast, BOF dusts with high zinc concentrations cannot be recycled via the sinter plant due to restrictive zinc limits. These dusts can either be processed in external pyrometallurgical recycling facilities [15,16] or recycled internally via the BOF after appropriate agglomeration. In both cases, air classification can be applied to optimize the overall material flow by selectively separating zinc-rich fine fractions. This approach reduces the number of zinc volatilization and redeposition cycles within the steelmaking process, thereby lowering energy demand and process inefficiencies, while simultaneously producing fine fractions with elevated zinc concentrations that are suitable for secondary zinc recovery [17].

2.2. Dust recycling in mini mills

In mini mills (EAF steel mills), the zinc concentration in dusts varies widely, primarily depending on the composition of the scrap charge. Under these conditions, air classification can be applied in a manner analogous to the treatment of high-zinc dusts in integrated steel mills, enabling selective routing of zinc-rich fine fractions to external recycling and improved internal material utilization [18].

2.3. Dust recycling in cement mills

In some cement plants, cement kiln dust (CKD) or cement kiln by-pass dust (CKBD) can be reintegrated into the production process, whereas in other plants these dusts are discharged to landfill sites [3]. The reintegration of CKD and CKBD is primarily limited by their high chloride content, as the maximum permissible chloride concentration in cement is typically 0.1%. CKBD is particularly enriched in chlorides, with reported contents ranging from approximately 7.5% to 17% [19,20], which often prevents its direct recycling. In some plants, CKBD is therefore used as a raw material for the production of potassium chloride fertilizers [20,21]. Laboratory studies

have shown that air classification can significantly enrich potassium chloride in the fine fraction while simultaneously reducing the chloride content of the coarse fraction [22]. This approach can improve both the economic efficiency of the leaching process and the potential for recycling the chloride-depleted coarse fraction into the cement manufacturing process.

2.4. Fly ash from biomass combustion

Fly ash from biomass combustion is increasingly recognized as a potential secondary resource for potassium fertilizer production. Biomass fly ash often contains substantial amounts of water-soluble potassium compounds formed by the volatilization of alkali metals during combustion and their subsequent recondensation on fine particles. Several studies have shown that potassium can be recovered from biomass fly ash by water leaching, yielding potassium-rich solutions suitable for fertilizer production. However, experimental results indicate significant limitations of this approach. In a study with straw combustion fly ash potassium leaching efficiencies with water of less than 50% with only moderately higher recoveries under acidic conditions were reported [23]. Such low extraction efficiencies question the feasibility of producing potassium fertilizers via leaching compared to the direct agricultural application of fly ash. As an alternative, air classification has been demonstrated to enrich potassium in the fine particle fraction of biomass combustion fly ash. This approach has been successfully validated both in laboratory experiments [24] and at industrial scale [25], improving the potential for targeted potassium recovery while supporting circular economy strategies.

3. Conclusions

Industrial de dusting residues from steelmaking, cement production, and combustion processes present both challenges and opportunities due to their enrichment in volatile constituents such as zinc and alkali chlorides. As discussed in this mini review, the pronounced particle size-dependent enrichment of volatile components provides a systematic basis for optimizing recycling and utilization pathways for these materials. Air classification represents a technically robust and flexible dry separation method that enables the selective separation of fine fractions enriched in volatile components - particularly zinc and potassium salts - while simultaneously depleting the coarser bulk material. Across integrated steel mills, mini mills, cement plants, and biomass combustion systems, air classification has demonstrated clear benefits in reducing process limitations, improving resource efficiency, and enabling targeted recovery of valuable components. Both laboratory scale studies and industrial applications confirm its technical feasibility. Overall, air classification constitutes a versatile and scalable process that can support circular economy strategies by improving residue utilization and reducing landfill disposal.

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Methodological Advances in DEM-based Bulk Solids Handling Simulation for Predicting Particle Degradation

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Abstract. Mechanical degradation during bulk solids handling can significantly affect the performance of mineral processing and ironmaking operations by generating fines and reducing product quality. Although Discrete Element Method (DEM)-based approaches combined with mechanistic breakage models have been successfully applied to predict particle degradation, important limitations remain regarding the representation of energy transfer mechanisms and impact-angle effects, particularly for irregular particles. This work proposes methodological improvements to the Advanced Bulk Solids Handling Simulation framework by introducing algorithms capable of calculating impact angle, effective energy transfer through contact networks, and the minimum energy required for abrasion. Laboratory degradation tests were performed using charcoal briquettes subjected to screening and tumbling conditions representative of industrial handling operations. DEM simulations were conducted using EDEM and collision histories were post-processed through Monte Carlo procedures coupled with mechanistic breakage models. The proposed methodology accurately reproduced impact-angle measurements and significantly improved degradation predictions compared with previous approaches developed for spherical particles. The model successfully predicted fines generation in both screening and tumbling tests, achieving relative errors below 3% during the initial stages of degradation. Results demonstrate the potential of the methodology for predicting mechanical degradation of irregular granular materials in industrial bulk handling systems.

1. Introduction

Bulk solids handling operations are widely employed in mining and metallurgical industries through conveyors, transfer chutes, silos and stockpiles. During transport, particles are subjected to repeated compressive and shear stresses that may induce breakage and abrasion. Several empirical and mechanistic approaches have been proposed to estimate degradation during handling operations; however, no universally accepted methodology currently exists.

The development of DEM-based breakage models has substantially improved the understanding of particle degradation mechanisms. In particular, the Tavares breakage model has been successfully applied to a wide range of granular materials [1,2]. More recently, the approach named as Advanced Bulk Solids Handling Simulation [3] has enabled degradation prediction without explicitly replacing particles after breakage, significantly reducing computational requirements. In work by Cavalcanti et al., the impact angle in collisions was estimated indirectly from dissipated collision energies for spherical particles [4]. While this simplification proved adequate for iron ore pellets, its applicability to irregular particles remains uncertain. Therefore, the objective of this work is to develop and demonstrate an improved methodology capable of accurately describing degradation mechanisms of irregular particles through explicit impact-angle obtained from DEM and energy-transfer calculations.

2. Methodology

2.1. Advanced Bulk Solids Handling Simulation Framework

The proposed methodology is based on a hybrid approach combining DEM simulations and mechanistic breakage modelling [5]. In this approach, DEM is employed exclusively to reproduce particle motion and record collision histories, while degradation calculations are performed during a subsequent post-processing stage.

For each collision registered during DEM simulation, relevant variables are extracted, including particle and geometry identities, relative velocities, energy losses and collision geometry.

Since this approach preserves the original particle population during DEM calculations, the computational burden associated with explicit breakage models that continuously generate fragments during simulation is avoided. Consequently, large industrial handling systems can be analysed while maintaining physically based degradation predictions.

In a post-processing step outside DEM environment, virtual particles are created and then subjected to a particle breakage model based on Tavares and King work [6-8] as shown in Figure 1. The collision may result in either particle damage and surface breakage or complete disintegration of the particle, generating a distribution of fragments.

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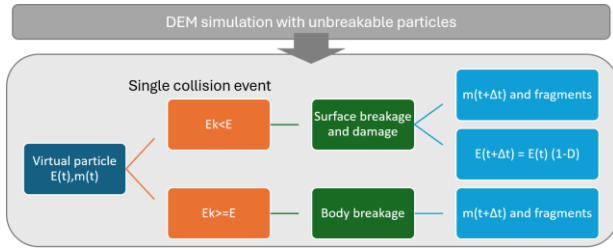


Figure 1. Model framework for breaking virtual particles outside DEM environment.

2.2. Explicit Determination of Impact Angle

Previous approaches estimated impact conditions indirectly through relationships between dissipated energy and collision orientation. While adequate for spherical particles, such approximations become unreliable when irregular particle geometries are considered.

In the present work, the impact angle is calculated directly from the collision normal vector and the relative velocity between colliding bodies. The procedure provides a geometrically consistent description of the collision event and remains independent of particle orientation and shape.

Because the formulation is derived directly from contact kinematics, the methodology can be applied to spherical, non-spherical and multi-sphere particle representations without additional calibration. The approach has been tested with controlled simulation of particle drop against inclined planes (Figure 2).

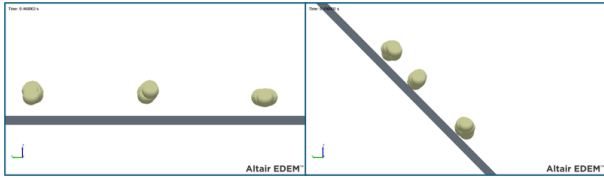


Figure 2. Snapshots of DEM simulations of multiple particle drop against a plane at two angular positions.

2.3. Energy Transfer Through Contact Networks

Conventional approaches typically associate breakage exclusively with the kinetic energy of particles directly involved in a collision. However, in confined systems such as silos, stockpiles and packed beds, energy may propagate through contact networks and induce breakage in particles that possess little or no individual kinetic energy.

To represent this phenomenon, a new algorithm was developed to evaluate energy transmission through overlapping contact events. The approach allows impact energy to propagate through neighbouring contacts, similarly to the behaviour observed in Newton's cradle systems. As a result, particles can receive fracture-inducing energy indirectly through the granular assembly, providing a more realistic representation of degradation in dense particle systems.

2.4. Abrasion Modeling

While impact breakage has been extensively studied, abrasion mechanisms depend on local contact

conditions and generally require a minimum level of stress or energy before material removal occurs. In the recent application of the model, Cavalcanti et al. [4], the abrasion model was proportional to collision energy losses. In this scenario, particles would still generate fragments, even in the case of very low energy losses. In the proposed framework, abrasion is activated only when the energy associated with a collision exceeds a minimum threshold value.

This concept introduces a mean for distinguishing ineffective contacts from contacts capable of producing measurable surface degradation.

3. Demonstration of Application

The methodology was evaluated using 22.4 mm x 19.2 mm charcoal briquettes subjected to controlled degradation experiments. Two handling environments were considered: Ro-Tap screening and tumbling tests in a 30x60 cm (length x diameter) drum.

The corresponding experimental systems were reproduced in DEM using EDEM 2025 and are shown in Figure 3. Collision histories extracted from the simulations were processed using the proposed framework and subsequently used as inputs for mechanistic degradation calculations.

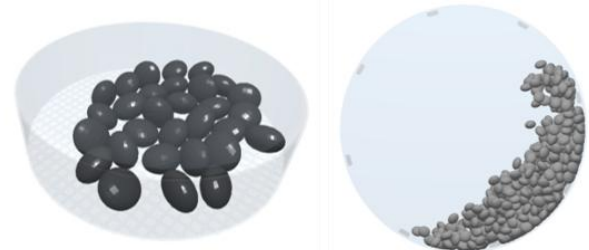


Figure 3. Snapshots of DEM simulations of Ro-tap (left) and Tumbling test (right).

The developed impact-angle formulation accurately reproduced collision geometry over a wide range of impact conditions. Furthermore, the incorporation of energy-transfer mechanisms enabled the identification of degradation events that would not be captured using conventional approaches.

Simulations results considering different values for the minimum abrasion energy are shown in Figure 4 for both systems. A common fitting factor of 0.25 J/kg has been found for both systems considering the 5 minutes mark as reference.

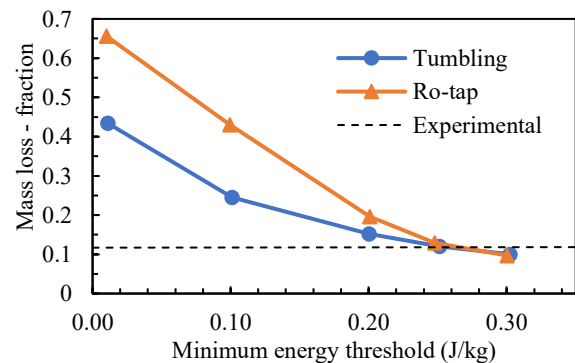


Figure 4. Mass lost due to abrasion at 5 min mark as function of the minimum energy threshold.

Finally, predictions of fine generation over time are presented in Figure 5. It was observed a good agreement to the experiments results, especially at the five-minute mark for the two different systems, being the Ro-tap the most intensive in terms of collision frequency, while the tumbling test the one with the highest collision energies. For longer times, the number of surviving particles reduces, so the original DEM simulation no long represents the actual hold-up of the systems. At some point a new DEM simulation would be required in order to generate new collision histories to be used with the breakage model.

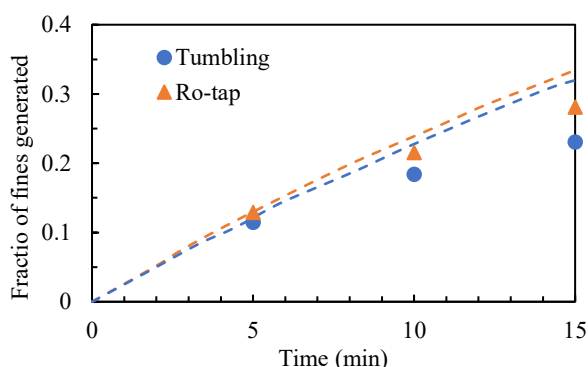


Figure 5. Evolution of mass lost due to abrasion for Ro-tap and tumbling. Dashed lines represent simulation results.

Fortunately, breakage levels exceeding 10% are uncommon in most bulk solids handling operations. Therefore, the results demonstrate the applicability of the proposed Advanced Bulk Solids Handling Simulation.

4. Conclusions

The results demonstrated that the methodological improvements proposed for the Advanced Bulk Solids Handling Simulation framework increased its capability to predict the mechanical degradation of irregular particles. The algorithm developed for impact angle calculation provided consistent results, while the incorporation of energy transfer between particles and the concept of a minimum energy required for abrasion allowed the representation of additional physical mechanisms associated with degradation during handling operations.

These developments extend the applicability of the methodology to irregular particles and dense granular systems where limited breakage occurs, addressing limitations associated with previous approaches originally developed for spherical particles. Furthermore, the proposed framework preserves the computational advantages of methodologies based on collision history while introducing descriptors that can be coupled with mechanistic breakage models.

Application of the methodology to tumbling and oscillating system such as Ro-tap screening using

charcoal briquettes showed agreement with the main degradation trends observed experimentally, indicating its applicability to the prediction of degradation of granular materials during bulk solids handling operations.

Acknowledgement

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Concrete as a Simulant for Selective Comminution and Material Recovery in Vertical Roller Mills

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Abstract. Recycling waste concrete is key to improving resource efficiency in construction. This study investigates parameters influencing selective comminution of homogeneous waste concrete in a vertical roller mill (VRM), aiming to produce clean coarse recycled aggregates for reuse. The fine fraction can be further processed to recover cement paste and fine aggregates, with the cement paste usable as a reactivatable binder or CO₂ sink. Waste concrete is also identified as a cost-effective simulant for studying VRM comminution selectivity. Parameter studies examined milling pressure, feed size distribution, process mode, and dry vs. wet conditions. Results show promising potential but indicate a need for further optimization.

1. Introduction

The construction industry is the largest market for domestically produced raw materials in Germany, including sand and gravel (211,000 Mt), crushed stone (167,000 Mt), and limestone (42,990 Mt) [1]. A substantial share is used in concrete, composed of cement paste, coarse aggregates, and fine aggregates.

Reducing carbon dioxide (CO₂) emissions and conserving non-renewable resources requires more efficient concrete recycling. Clinker production is a major concern, generating about 60% of cement-related CO₂ emissions [2]. In Germany, cement production reached 32.9 Mt in 2022, with € 3.4 billion in revenue, supplied entirely by domestic facilities highlighting significant potential for emission reduction through optimisation and recycling [3].

The “BeBreSaRec” project addresses this by improving selective comminution in vertical roller mills (VRMs) to preserve aggregates while liberating them from the cement paste. The aim is to recover high-quality aggregates for reuse and utilise the separated cement paste for reactivation or as a CO₂ sink.

2. Concrete Recycling – State of the Art

Aggregates for concrete are regulated under DIN EN 12620, which defines coarse aggregates as particles > 4 mm and fine aggregates as < 4 mm. In addition, it provides specifications exclusively for coarse recycled aggregate fractions. Consequently, the appropriate reuse of coarse crushed concrete as recycled aggregate has already been demonstrated at full industrial scale in construction practice [4]. By contrast, the recycling of crushed sand, constituting approximately 25–32 % by mass of crushed concrete, remains largely unexplored.

In Germany, over 78.8% of construction and demolition waste is recycled, but recycled concrete is mainly used in road frost blanket layers due to fine fractions containing adhered cement paste. [5]. This increases the water–cement ratio and reduces strength in new concrete, preventing true closed-loop recycling [4, 6]. Limited demand for fines leads to mixed materials (0–45 mm) being produced instead of high-quality coarse aggregates, wasting valuable resources.

Primary comminution occurs on-site, followed by secondary processing using impact, jaw, or cone crushers [4]. Among these, impact crushers exhibit a particularly high potential for selective comminution due to their force-limited operating principle [7]. They are predominantly utilised to exploit their general comminution characteristics, which are well suited to meeting the granulometric requirements for frost protection layer materials. In parallel, jaw crushers have increasingly become the subject of investigation in recent years concerning their suitability for selective concrete comminution [8].

In order to enable effective recycling of the fine fraction, VRMs have also gained attention in current research and development activities. A process developed by Loesche has demonstrated promising results by employing the force-controlled milling system in conjunction with both internal and external classification stages [9]. The process is capable of generating three distinct product fractions: coarse aggregates, fine aggregates, and a finely divided cement paste fraction.

Current systems are limited by feed moisture variability, highlighting the need for more robust processes as well as a deeper understanding of comminution mechanisms to optimize and advance concrete recycling technologies.

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3. Methodology

3.1. Material and Pretreatment

The experiments used 23-year-old homogeneous concrete composed of 15.7 % CEM I cement, 49.1 % coarse aggregates (8–22 mm crushed stone), and 35.2 % fine aggregates (0–4 mm sand). Material characterisation included strength, micro-hardness, and fracture toughness. A point load test yielded $I_{S(50)} \approx 2.45$ MPa, corresponding to a compressive strength of $\sigma_D \approx 61.2$ MPa (conversion factor 25) [10]. Vickers hardness (VHN) was measured on prepared sections, and fracture toughness (K_{Ic}) was determined [11]. Fracture toughness of the cement paste and base mass could not be reliably determined due to insufficient brittleness. Nevertheless, the obtained results indicate a pronounced disparity in microhardness and fracture toughness between the aggregate particles (Feldspar: VHN = 800 N/mm², Quartz: VHN = 1180 N/mm²) and the hardened cement paste (VHN = 100 N/mm²). This disparity promotes combined compressive and shear stresses under loading, favouring selective comminution.

About 10 t of concrete waste was pre-crushed by REMEX GmbH to 0–45 mm using an impact crusher (28 m/s, 35 mm gap), from which a 2 t representative sample was taken. The remaining 8 t was further crushed to 0–8 mm by recirculating > 8 mm particles, with size limits defined by the downstream VRM. Both fractions were sent to the Institute for Mineral Processing Machines and Recycling Systems Technology (IART), where representative sub-samples were obtained via systematic splitting and rotary division, covering both comminution stages. For the investigations presented in this study, the 0–8 mm particle size fraction was utilized as the primary feed material. Additional trials excluded fines (< 2 mm) by pre-screening the material with at a external sieving machine at a mesh size of 2 mm, producing a feed without fine particles.

3.3. Experimental Setup

The pilot-scale overflow VRM with external sieve classification at IART, originally designed for ore processing, was used for both wet and dry milling [12]. The screening unit (2 mm mesh) enabled recovery of the coarse fraction and supported aggregate liberation. A simplified flowsheet is shown in Figure 1.

Each experimental run produced process and material data, including mass flows (fresh feed $\dot{m}_F$ and circulating load $\dot{m}_C$ in kg/h), water input flow rate, torque (M , in Nm) and the rotational speed of the milling table (n , in 1/min), material bed height and the applied hydraulic pressure. Particle size distributions were obtained via sampling at defined points. The bed height was measured indirectly using calibrated magneto strictive sensors.

Each run included parameter adjustment, a stabilization phase, and a 10-minute measurement interval with synchronized multiple sampling. In batch mode, feed samples were taken only before and after the interval. Mean values were calculated from continuous data, and specific energy consumption was determined from mill throughput ($\dot{m}_M$, sum of fresh feed and circulating load) and mill power (mechanical torque and rotational speed

of the mill table. Particle size distributions were analysed by sieve analysis.

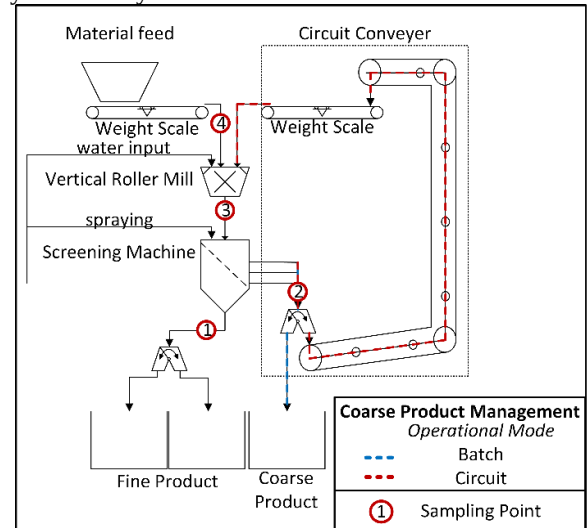


Figure 1. Simplified Flowsheet of the pilot plant, modified according to [12]; Sampling Points: ① screening fines, ② screening coarse, ③ milling product, ④ fresh feed

The overall methodology applied for data acquisition at the pilot plant has been previously validated in an independent study and demonstrated to provide a high level of reliability [12].

The scope of the present work encompasses results evaluated with respect to the system boundary of the mill. The influence of selected parameter combinations (see Table 1) is examined accordingly. Where required by process conditions, repeated measurements (RM) were conducted to ensure reproducibility and statistical robustness of the results. Variations in milling table speed and feed throughput were tested but are not included here. For all reported experiments, mill throughput was fixed at $\dot{m}_M = 500$ kg/h and table speed at $n = 35$ 1/min.

Conical rollers (15° inclination) were used to apply combined compressive and shear stresses, promoting selective comminution.

Table 1. Milling parameter combinations discussed in this paper

No	RM	hydr. Pressure [bar]	Feed fraction [mm]	Process	
				Wet/ Dry	Batch/ Circuit
1	1	14	0-8	Dry	Batch
2	2	24	0-8	Dry	Batch
3	2	24	2-8	Dry	Batch
4	3	24	2-8	Dry	Circuit
5	2	24	2-8	Wet	Batch
6	1	43	0-8	Dry	Batch
7	1	74	0-8	Dry	Batch
8	1	110	0-8	Dry	Batch

3.4. Determination of the composition and selectivity

Assessing comminution selectivity requires reliable and rapid determination of product composition. While X-ray diffraction (XRD) is standard for phase analysis, it is too time-intensive for high-throughput studies.

Instead, this study used pixel-based colour analysis, exploiting the contrast between cement paste and aggregates. Samples were analysed by size fraction, and images processed in MATLAB (Colour Thresholder), enabling fast and reproducible evaluation.

A higher proportion of darker tones indicates increased coarse aggregate content. Analysis focused on size fractions 2–8 mm. The method was validated against XRD using a Bruker D8 Advance and TOPAS program with Rietveld analysis, showing a relative deviation of about $\pm 2\%$ in aggregate content [13]. Further validation is beyond this study's scope, though limitations remain due to colour similarity and image resolution.

The selectivity of comminution is evaluated using mass recovery (R) and aggregate concentration (c) [14]. Analysis focuses on size fractions 2–8 mm, with components defined as cement paste, aggregates, and the mixture. The composition of each fraction ($c_{i,x}$) is determined based on the results obtained from the image analysis. In contrast, the mass proportion of the mixture ($\mu_{3i,m}$) is derived from the sieve analysis. Giving the option to calculate the overall concentration of the components in the coarse fractions. Aggregate mass recovery is based on the mass proportion of the aggregates in coarse product and their concentration relative to coarse feed and concentration.

This approach imply that comminution can be regarded as fully selective when the concentration of aggregates in the coarse fraction reaches $c_{a,CF} = 1$, and the corresponding mass recovery of aggregates attains $R_{a,CF} = 1$. Under these conditions, a complete separation of aggregates from the cement paste is achieved by screening, indicating ideal selectivity of the comminution process.

4. Results and Discussion

First, the PSDs of the milling products are analysed in relation to the applied parameters. Figure 2 shows the PSDs for all parameter combinations alongside the feed PSD, with mean values reported for repeated measurements.

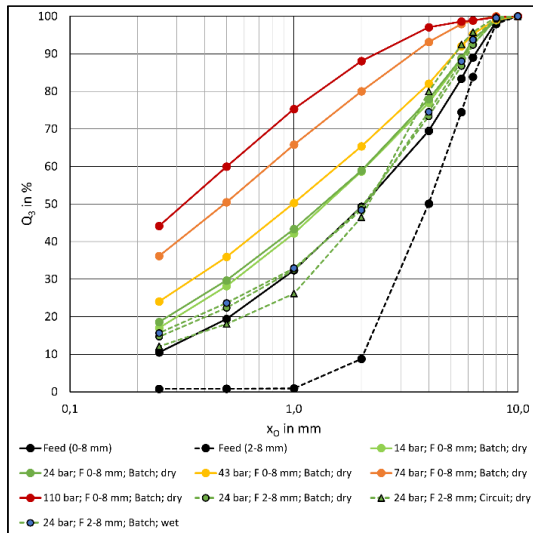


Figure 2. Particle size distribution (PSD) of the milling product and the fresh feed

For a 0–8 mm feed, increasing hydraulic pressure (43 to 74 bar) significantly alters the PSD while maintaining a similar slope, accompanied by a drop in bed height (12.43 to 7.94 mm). This indicates a transition from aggregate preservation at low pressure to increased breakage at higher pressure. At equal pressure (24 bar), comparing 0–8 mm and 2–8 mm feeds show reduced bed height (13.63 to 9.25 mm) but similar PSD slopes above 4 mm, indicating comparable comminution behaviour to coarser material. However, overall slope of the milling product is steeper with 2–8 mm feed. Comparing wet and dry milling, no notable difference in PSD despite reduced bed height (9.25 to 6.75 mm) can be recognized. This suggests bed height has limited influence under these conditions.

To further assess parameter effects, aggregate concentration and mass recovery in the coarse fraction are presented in Figure 3.

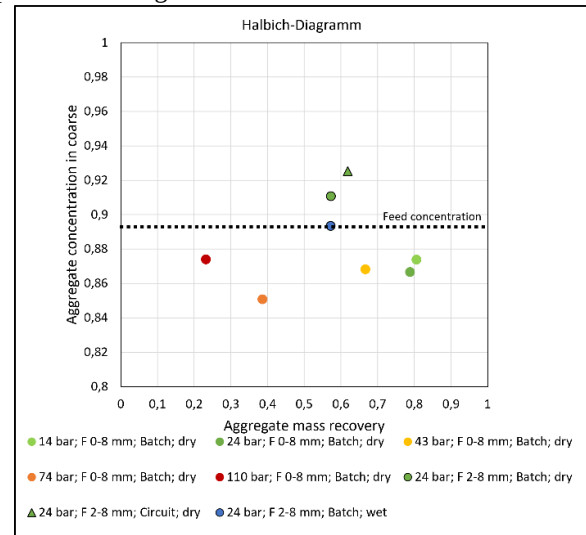


Figure 3. Aggregate concentration and mass recovery into coarse fraction

For all trials with a 0–8 mm feed, aggregate concentration decreased relative to the feed, and higher milling pressure reduced aggregate mass recovery, consistent with PSD trends.

In contrast, 2–8 mm feed trials achieved higher aggregate concentration in the coarse fraction with relatively good mass recovery, indicating effective selective comminution, though with some material loss. The highest aggregate concentration ($c_{a,CF} = 0.92$) occurred under circuit operation, but with reduced mass recovery due to continuous recirculation, representing an upper enrichment limit without additional sorting.

Figure 4 compares aggregate mass recovery with specific energy consumption. Increasing hydraulic pressure (14 to 110 bar) leads to a substantial rise in specific energy consumption. In contrast, excluding fine material from the feed and operating under wet conditions show no significant influence on the overall energy demand.

The relationship between specific energy consumption and aggregate mass recovery is further illustrated by evaluating their ratio in discrete intervals. This allows the incremental energy input to be interpreted

in terms of the energy required to recover the coarse aggregate fraction.

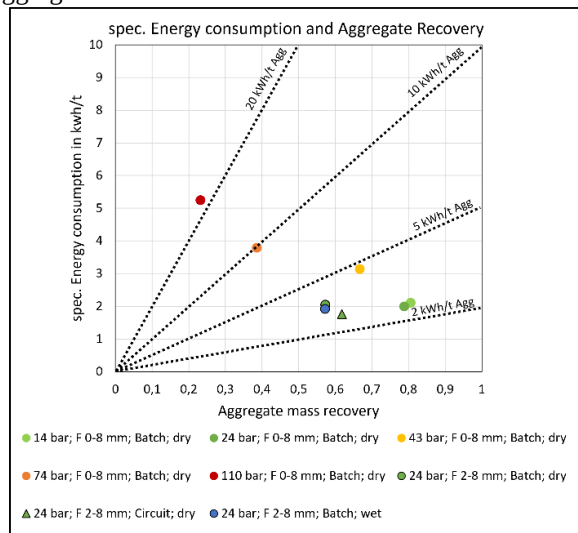


Figure 4. Comparison of aggregate mass recovery to specific energy consumption of the mill

Under this perspective, the most favorable efficiency is achieved at low pressures (14–24 bar) with a 0–8 mm feed, yielding approximately 2.5 kWh/t per recovered aggregate. Trials with a 2–8 mm feed show a slightly less favorable ratio of about 3.5 kWh/t, indicating higher energy demand per unit of recovered aggregate.

It should be noted that this evaluation is limited to the coarse aggregate fraction. A comprehensive assessment, including cement paste and fine aggregates, is still pending, and the overall conclusions may change once these additional material streams are considered.

5. Summary and Outlook

This study investigates key VRM milling parameters for waste concrete, including milling pressure, feed PSD, recirculation, and wet vs. dry operation. Comminution selectivity was assessed using an image-based colour analysis method, evaluating particle size distribution, aggregate concentration, mass recovery, and specific energy consumption, with focus on the 2–8 mm fraction.

Results show that milling pressure and feed PSD strongly affect aggregate recovery and purity. Low milling pressure is essential to preserve coarse aggregates and maintain selective comminution. Further fundamental research is needed to clarify mechanisms and account for material variability (e.g. aggregate type and cement). The developed method will be refined and compared with established techniques, with potential for future in situ process monitoring.

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Recycling of Lithium-Ion Battery Cells – Modelling the Crushing and Mixing Process

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Abstract. A variety of different process routes have been established for the recycling of lithium-ion batteries. To compare and optimize these routes effectively, a high process understanding is important. To take a closer look at the mechanical processes used for the recycling, models for the various sub-processes will be developed. This work focus on the modelling of the crushing of lithium-ion batteries in a cutting mill and the subsequent drying of the material in a mixing device. These models must consider the complex material behaviour of the crushed battery materials as well as the initial conditions of the materials within the battery cell. For example, the primary particle size distribution of the individual materials in the battery prior to the first comminution in the cutting mill is unknown. Based on these conditions, the first process step was described as a black-box model. Using this initial model, the input conditions for the subsequent process steps can be determined, enabling the development of physical models such as population balances for the subsequent processes.

1. Introduction

The recycling of Li-ion batteries is becoming increasingly important due to the rising demand of electric cars and the request for more independence from global raw materials markets. Therefore, a range of recycling processes have been implemented in industry. Especially in the context of the recycling of end-of-life batteries, there are several ways to recover the valuable materials via mechanical, hydrometallurgical or pyro-metallurgical process routes. The processing via a mechanical process chain, which this work focuses on, contains several comminution and separation steps. For these comminution and separation operations, various processes can be used as well as different process sequences, which can both affect the recovery rates. One way of recycling Li-ion batteries is based on the LithoRec process [1] shown in Fig. 1. First, the cells or modules are crushed in a shredder. The shredded battery fragments are then dried and stressed in a mixing and drying unit before the heavy parts of the cells such as the casing are removed using a zig-zag-sifter. After the electrolyte evaporation and separation of the heavy components, the remaining fragments consist mostly coated and uncoated electrode foils as well as separator foils and the detached black mass. These fragments can be stressed a second time to increase the yield of black mass in the subsequent screening step. A cutting mill or an impact mill can be used for this second comminution. At the end of the process chain the separator foils are removed from the copper and aluminum foils using a second air classification.

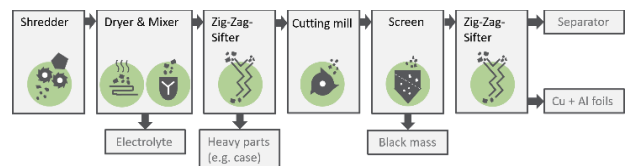


Figure 1. Mechanical process chain based on LithoRec [1]

A high process understanding and a large database are important to optimize a process chain and compare it with other recycling routes. To get this large database, the dynamic flowsheet simulation is beneficial. With this simulation it is possible to investigate the influence of several operating parameters of the single processes as well as the influence of these parameter changes on the subsequent processes and finally on the mass recovery of the different battery materials, whereby the so-called black mass (anode and cathode coating) represents the most valuable fraction. For the simulation, it is essential to develop process models that can be used in corresponding simulation software like Dyssol. In this work the focus is on the modelling of the first two process steps (crushing the cells and mixing/drying the fragments) and the required series of experimental studies.

2. Experimental

To develop the process models, a large database is required in advance. Accordingly, parameter studies are conducted for each individual process step. A key challenge here is the complex mixture of materials used in the battery cells. For this reason, the same type of

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cylindrical battery cells, whose cell composition is known from cell analysis [2], was consistently used for experimental data (exp. data) collection. To minimize the impact of fluctuating process conditions on data collection, the experiments were initially conducted on a laboratory scale. To do this, the battery cells were first crushed in a cutting mill. After comminution, the fragmented material was analyzed using analytical sieving. The material with a particle size of less than 500 μm was defined as black mass. The parameter study, which compared different bottom screen sizes of the cutting mill and different rotational speeds, showed an increase in black mass recovery at higher rotational speeds and with smaller screen sizes. Since small amounts of other materials can also end up in the <500 μm mesh fraction, the black mass was also analyzed using X-ray fluorescence (XRF) to determine the levels of impurities from Cu, Fe, and Al components. This shows a corresponding increase in impurities in the BM as the screen size decreases (Fig. 2), though there is only a slight change at varying speeds.

To investigate the subsequent mixing and drying step, a standard setting was selected in the cutting mill for cell crushing (700 rpm, 10 mm bottom mesh size). The crushed material was further processed in the mixing and drying unit at different circumferential speeds and at different drying temperatures. To ensure a sufficient data set for subsequent modeling, different processing times were also examined in this step in order to characterize the change in the particle size distribution (PSD) of the individual materials over time. While the change in drying temperature had no significant effect on black mass recovery, increasing the mixer's circumferential speed resulted in a higher black mass yield. However, the proportion of impurities in the black mass is also increasing. The mixing process has a significantly greater impact on the impurity content in the black mass than the cutting mill process, even at lower circumferential speeds (Fig. 2). However, after subtracting the proportion of impurities from the total mass of the black mass fraction, there is still a net recovery of about 90% of the black mass present in the cell.

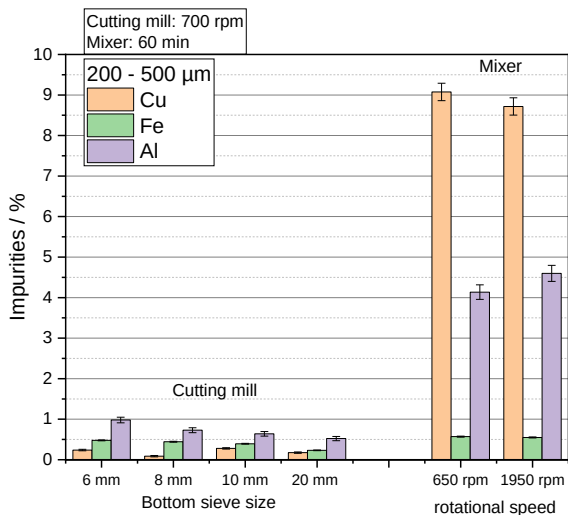


Figure 2. XRF Analysis of impurities in the black mass

3. Modelling

Models for the individual process steps will be developed based on the experimentally determined data. These models will be used to calculate the incoming and outgoing material flows. This primarily requires data on the size distributions of the individual materials. On this basis, the mass flows of the individual materials and, consequently, the recovery rates can be determined during subsequent separation processes. In addition to the particle size distribution, the proportion of black mass detached from the electrode foils is another important factor. Only the black mass detached from the foils can be separated later; furthermore, residual coating on the foils influences the material behaviour during separation processes such as sifting processes.

3.1. Crushing of battery cells

In the cutting mill, the first crushing of the whole cells into individual fragments is carried out. Since the process starts with crushing entire battery cells, the primary particle size distribution of the battery materials inside is not known. For this reason, a black-box model is used for the first process step. In the chosen modelling approach, the resulting particle size distributions following the comminution process are described using Weibull distributions (Eq. (1)).

$$Q_3\left(\frac{x}{d_s}\right) = 1 - e^{-\left(\lambda \left(\frac{x}{d_s}\right)\right)^k} \quad (1)$$

These Weibull-Distributions have two material specific parameters λ and k . Furthermore, it includes the bottom screen mesh size of the mill d_s . This allows calculating the resulting particle size distribution for each material component depending on the used bottom screen size [3]. In Fig. 3 these results for different screen sizes are shown for Cu foil compared to the experimental data.

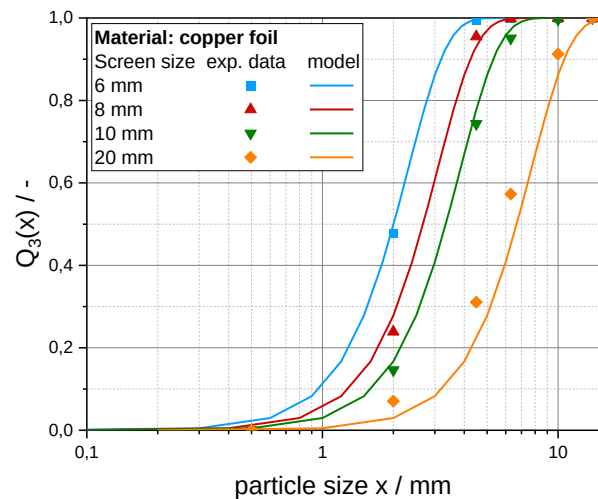


Figure 3. PSDs for Cu foil, exp. data and Weibull-model

3.2. Mixing and drying process

Contrary to the first cell crushing step, for the mixing and drying process, the initial particle size distribution of the

individual materials is known. As a result, working with a black-box model is no longer necessary. Changes in the particle size distributions can be modelled here using a population balance model (Eq. (2)).

$$\frac{dm_i}{dt} = \sum_{j=i}^{i_{max}} S_j b_{ij} m_j - S_i m_i \quad (2)$$

The corresponding breakage functions S and distribution functions b for this balance equation must be determined individually for each material. This requires data on the temporal changes in particle size distributions during the mixing process. A challenge in this determination is the mutual influence of the materials on one another. The larger, heavy housing components have an abrasive effect on, for example, the coated foils and can cause additional stress here, meaning that the fracture functions cannot be determined from individual material tests.

Using the population balance equations, it is possible to display the particle size distributions over time (Fig. 4). Calculating the particle size distributions is one of the most important steps in modelling, as these provide the basis for the subsequent separation processes and thus, for example, allow us to estimate the expected yield of black mass after the sieving process. In addition, by analysing changes in the particle size distribution of other materials, such as copper and aluminium foils, the proportion of these materials in the <500 μm fraction can be determined, thereby also providing information about the purity of the black mass fraction.

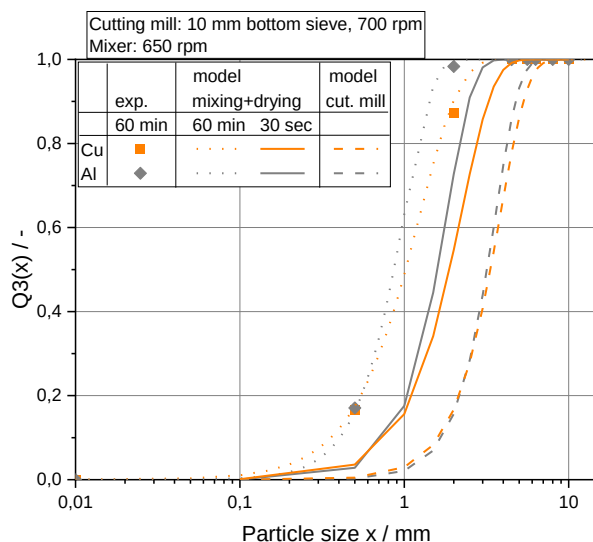


Figure 4. Modelled PSDs for Cu/Al foil after crushing and different mixing times compared to experimental data

4. Summary

The mechanical recycling of Li-Ion batteries consists of several comminution and separation steps. Due to the complicated material behaviour, it is often not possible to use literature models for most process steps. Thus, models must be developed or existing models must be adapted to the present material system consisting of foil materials, powders, and solid metal components.

While the cells are initially crushed in the first process step with partial detachment of the black mass from the foils, the second process step significantly increases the delamination of the black mass due to the additional stress applied by the mixer during material drying.

For modelling purposes, the various battery components must be considered separately. For each material, separate models or functions are created to calculate the resulting particle size distribution. By analysing the changing size distributions, it is possible to calculate the expected material recovery rates in the separation processes, such as the recovery rate of the valuable black mass and the proportion of impurities from other battery components in this size range.

By combining these models with other process models, an entire process chain can be represented through simulations, thereby reducing the need for time-consuming experimental studies and thus provides an efficient way to compare and optimize processes and process chains.

Acknowledgement

The projects SIMTEGRAL, LOWVOLMON and ElRec on which this report is based were funded by the German Federal Ministry of Research, Technology and Space (BMFTR formerly BMBF) under the funding codes 03XP0331A, 03XP0354B and 03XP0571A-D. The author is responsible for the content of this publication.

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Electrical Impulse Fragmentation Pre-Treatment of Hard Rock Li-Ores

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Abstract. The need for battery grade lithium has increased continuously due to the growing demand for Lithium-Ion Batteries (LIBs), but the supply for this critical raw material remains a challenge. The main source for hard rock lithium until now has been spodumene ore, which results in a strong dependency on the import from non-european countries. The Li4Life project focuses on the evaluation of complex Li-ores such as zinnwaldite, lepidolite and petalite from underutilised european sources. Since these ores exhibit a complex microstructural composition, mineral processing poses a challenge. Hence, innovative pre-treatments such as electrical impulse fragmentation are also evaluated as potential technologies to be implemented in the mineral processing flow sheet. In this work, three different european hard rock ores (zinnwaldite, lepidolite and petalite) are characterized and their behaviour after electrical impulse fragmentation pre-treatment as single particle and multiple particle testing is evaluated. Multiple particle testing included the evaluation at two energy levels. Preliminary results show that zinnwaldite ore is more suitable for the electrical impulse fragmentation pre-treatment.

1. Introduction

The need for Lithium has increased steadily in the last years, mainly driven by the increasing demand for LIBs[1]. Alone the demand for Lithium in Europe for the battery sector is expected to grow ninefold by 2040[2].

Li resources are distributed around the world but the supply chain for Li has focused on spodumene hard rock, which beneficiation routes are well defined. Other Li-bearing ores are underutilised and have not yet been developed industrially as their Li contents are lower and have complex microstructures that pose a challenge for the mineral processing.

Within the EU Li4 Life project, potential alternative european Li sources are investigated and the entire value chain, including mineral processing and beneficiation is evaluated. The possibility of using innovative technologies, such as the high voltage electrical impulse fragmentation (EIF) as pre-treatment in the mineral processing is evaluated.

This work presents the preliminary investigations for evaluating EIF on three european Li-bearing ores. The material characterization results and the results after single and multiple particles testing with EIF are also presented in the following sections.

2. Experimental Procedure

The selected materials were characterized regarding their mineralogical composition by using the Quantitative Microstructural Analysis (QMA). The mechanical properties were determined by using a point load tester (PLT). Additionally, the Li-contents was determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.1. Materials Characterization

Three european hard rock Li-ores were selected: zinnwaldite (Cinovice, CZ), lepidolite (ES) and petalite (ES).

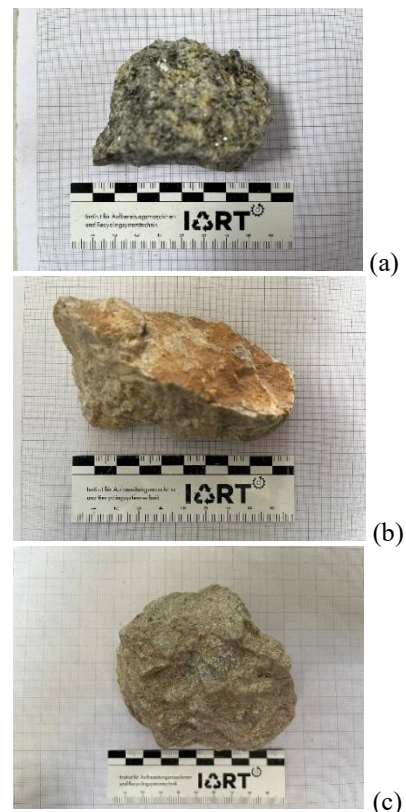


Figure 1. Selected Li-ores: (a) zinnwaldite, (b) lepidolite, (c) petalite.

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The Li-contents was determined to range between 1518 and 4301 ppm Li for the zinnwaldite ore and between 3409 and 4462 ppm for the lepidolite ore. The results for the petalite ore are not yet available.

Furthermore, the samples were evaluated regarding their microstructural composition by using the QMA [3]

and the mechanical properties, the uniaxial compressive strength (UCS) evaluated by means of Point load testing (PLT). The results are presented in Table 1.

Table 1. Materials Characterization

Ore/Varieties	Mineral Phases present	Median grain size [mm]	Is50, MPa	UCS, MPa
Zinnwaldite: Greisenised Granite (GCW) Greisen (GCG)	Quartz, Feldspar, Mica	Zinnw. GCW: 1,32 mm Zinnw. GCG: 0,75 mm	GCW: 4,10 GCG: 2,15	GCW: 102,5 GCG: 53,8
Lepidolite Lepidolite bearing aplite (LSA) Lepidolite felspar pegmatite (LSR)	Quartz, Feldspar, Mica	Lepid. LSA: 0,10 mm Lepid. LSR: 0,25 mm	LSA: 4,59 LSR: 5,13	LSA: 114,7 LSR: 128,2
Petalite	Quartz, Feldspar, Mica, petalite	Heterogeneous Petalite up to 6 mm Quartz-feldspar mica: 0,3-0,6 mm	2,0	50

2.2. High Voltage Electrical Impulse Fragmentation

High Voltage electrical impulse fragmentation refers to the treatment of materials with high voltage electrical impulses. Although the technology has been known for several decades [4-7] and laboratory machines have found their way into geological laboratories [8], the transfer into industrial applications has not been completed. New concepts have been introduced towards the development of new machines working with high voltage electrical impulses [9-10].

Characteristic from EIF is the introduction of cracks in the microstructure of the material through the electrical impulse discharge [11-12]. The introduction of cracks in the material leads to a weakening of the material, which means less energy needed for subsequent processing. Another advantage of this process is the selectivity, which can be used for selective liberation of mineral phases of interest.

As it can be seen in **Fehler! Verweisquelle konnte nicht gefunden werden.**, several elements are needed for the EIF to function : a high voltage electrode, the material to be treated, a dielectric medium (typically water), and a ground electrode. These are the basic components in the processing area.

The discharge through the material occurs when the impulse rise time, e.g. the time needed to reach the high voltage, is extremely fast, in the order of ns (usually below 500 ns) This is what is known as electrical impulse fragmentation, i.e. the high voltage discharge occurs through the solid material.

For generating the impulses, a Marx generator is used. The Marx Generator consists of several stages of capacitors. The charging of the capacitors occurs in parallel and the discharge in series, hence adding the energy of each stage in the final discharge.

The use of a Marx generator allows to regulate the amount of energy that is discharged with every impulse. Two different EIF-tests were conducted: single particle testing with individual particles ranging between 5 and 7 cm by using a 5-stages Marx Generator (max. Energy pro impulse: 90 J and max. output voltage 200 kV) and multiple particle testing (bulk) with a closed initial particle size distribution (PSD) from 20 to 25 mm by using a 12-stages Marx Generator (impulse energy: 140 J and output voltage 360 kV), see Figure 3.

The samples used for EIF single particle testing were inspected prior to the test and directly after.

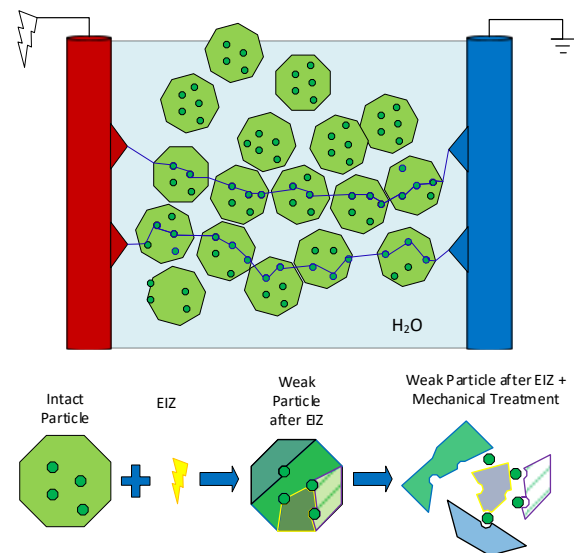


Figure 2. Electric Impulse generation and processing area (Source: M.Mezzetti/TUBAF-IART)

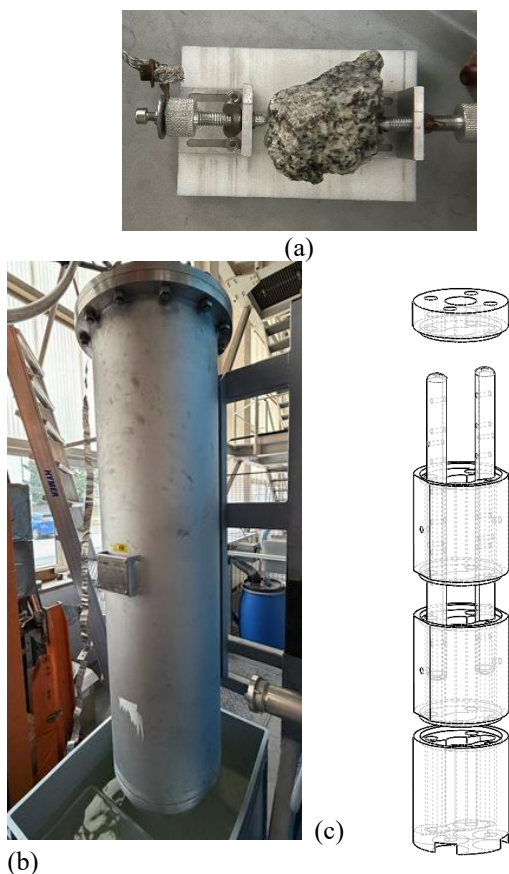


Figure 3. (a) Set up for single particle testing (as an example zinnwaldite ore sample), (b) 12-stages Marx Generator for multiple particle testing, (c) Test chamber for multiple particle testing.

3. Results

The Single particle tests were conducted by introducing initially 10 Impulses (90 J/Impulse) into the material. In the case of zinnwaldite, for most of the samples was this enough to introduce cracks into the material or break it either partially or completely.

The lepidolite samples exhibited a completely different behavior and required up to 300 impulses to exhibit cracks on the material.

The behavior of lepidolite could be described somewhere in between. For the petalite sample, some of the samples required only 10 impulses, but some others required more than 100 impulses for introducing cracks into the material.

An example of the evaluation of the samples after single particle testing can be observed in Figure 4.

Based on the observations and results gathered after single particle testing, testing with bulk material with initial particle size in the fraction 20-25 mm was evaluated.

As zinnwaldite ore seem to be more suitable for the EIF pre-treatment, several energy levels were evaluated, namely 1,16 kWh/t, 3,1 kWh/t and 6,1 kWh/t.

For lepidolite and petalite, the evaluation was conducted on material without pre-treatment and the highest energy level from 6,1 kWh/t.

The samples of material were dried after testing and the resulting PSD was evaluated. The results can be observed in Figure 5.

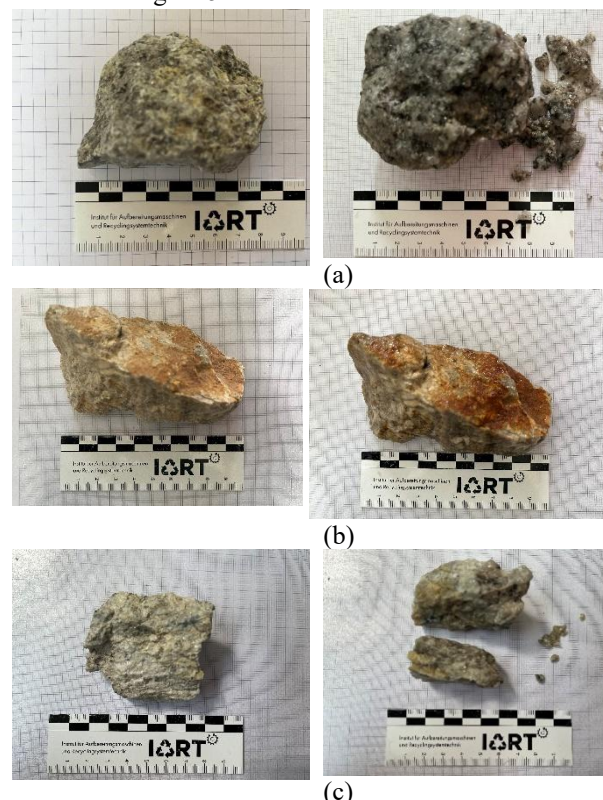


Figure 4. Single particle testing (left: before the test, right: after the test). Tests on (a) zinnwaldite ore (10 Imp-90J) (b) lepidolite ore (150 Imp-90J) and (c) petalite ore (15 Imp-90 J).

4. Conclusions

Three different Li-bearing ores have been evaluated regarding their suitability to EIF pre-treatment. Through the initial single particle testing it was possible to assess the susceptibility. The preliminary results showed that the zinnwaldite ore had the better response and only a few impulses, meaning low energy, was needed to introduce cracks into the material.

The bulk testing results confirmed the positive response from the zinnwaldite ore, resulting in the finer PSD when comparing testing among the three ores at the same energy level (6,1 kWh/t). The least susceptible material after bulk testing on this fraction was the petalite.

The difference in the response to EIF is presumably related to the microstructural features. The differences can be seen for example in the median grain size of the mineral phases present as well as in the mechanical properties. While zinnwaldite exhibits a relatively coarse microstructure (median grain size up to 1,32 mm), the lepidolite exhibits a much finer median grain size with only 0,1-0,22 mm.

The heterogeneous microstructure of petalite was also reflected on the single particle testing. In the bulk testing, petalite showed the less susceptibility.

Further investigations include the evaluation of the mineral liberation, the correlation to the microstructural features as well as the crack propagation behavior.

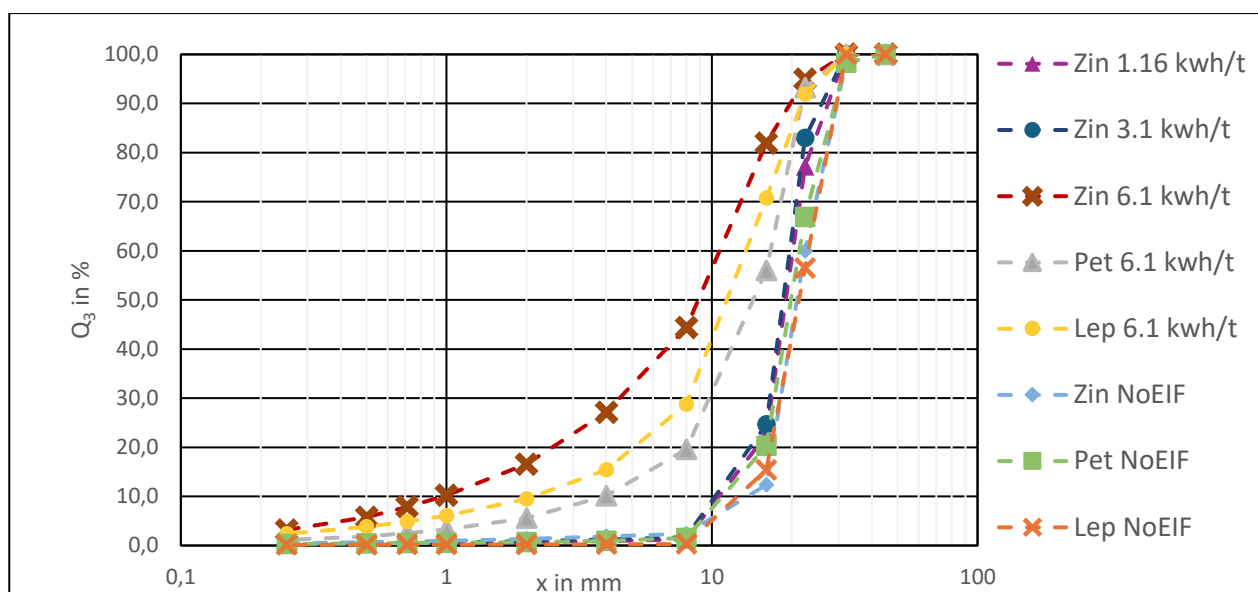


Figure 5. Particle size distribution of test materials after bulk EIF-testing.

Acknowledgement



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Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or the European Climate, Infrastructure and Environment Executive Agency (CINEA). Neither the European Union nor CINEA can be held responsible for them.

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Effect of Dry vs. Wet Grinding on the Catalytic Performance of Pyrite (FeS₂) in NaBH₄ Methanolysis for Hydrogen Generation

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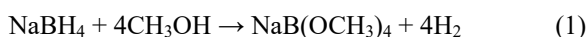
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Abstract. Catalysts play a critical role in hydrogen energy systems, and the development of low-cost, sustainable, and highly active alternatives remains a priority. In this study, pyrite (FeS₂) mineral prepared by dry and wet grinding was investigated as a catalyst for NaBH₄ methanolysis. At 30 °C, hydrogen generation rate (HGR) values of 2256 and 3221 mL·min⁻¹·gcat⁻¹ were determined for wet-ground (PW1) and dry-ground (PD1) samples, respectively. Characterization results revealed that dry grinding yields a higher BET specific surface area (1.23 vs. 0.61 m²/g), attributed to the deposition of iron oxyhydroxide species on pyrite surfaces during wet milling through galvanic interactions, which reduce accessible surface area and catalytic activity. Under optimised conditions (0.025 g catalyst, 0.125 g NaBH₄, 10 mL methanol, 60 °C), PD1 achieved an HGR of 19990 mL·min⁻¹·gcat⁻¹ with an activation energy of 38.07 kJ·mol⁻¹, demonstrating that dry grinding preserves chemically reactive fracture surfaces and enhances catalytic performance.

1. Introduction

Growing global energy demand and environmental concerns have intensified research into hydrogen as a clean energy carrier. Among chemical hydrides, NaBH₄ offers notable advantages including non-toxic and non-flammable nature, high stability, recyclability, and a theoretical H₂ storage capacity of up to 10.8 wt% [1]. In methanolysis, NaBH₄ reacts with methanol to release hydrogen according to Equation (1):



A catalyst is necessary to accelerate this reaction efficiently. With suitable catalysts, high-purity H₂ can be produced from NaBH₄ at room temperature [1]. Iron-containing catalysts have shown considerable activity in this context. Fe-B nanoparticles (Fe-B NPs/Ni foam) were supported on porous Ni foam. The catalyst exhibited an activation energy of 7.02 kJ·mol⁻¹ at 20–50°C [2]. Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@NH₂ nanoparticles were found to be effective catalysts for the methanolysis reaction of NaBH₄. The reaction, which takes 30 minutes to complete without a catalyst, was completed in 16, 10, and 20 minutes, respectively, using Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂@NH₂ catalysts. Using Fe₃O₄@SiO₂@NH₂, a HGR of 13188 mL·min⁻¹·gcat⁻¹ and an Ea value of 24.4 kJ·mol⁻¹ were calculated in the temperature range of 258–318 K [3].

The use of catalysts, particularly those containing metals, is crucial for controlling and accelerating hydrogen production via the methanolysis of NaBH₄ due to their high reactivity and reaction rates; however, their application is limited by cost [4].

Pyrite (FeS₂), one of the most abundant metallic sulfide minerals in the Earth's crust, is the primary gangue mineral in complex sulfide ores; its content in porphyry copper ores ranges from 0.3% to 14.9% [5]. It is commonly found alongside sphalerite, chalcopyrite, galena, and gold-bearing minerals [6]. An important factor affecting the surface properties of pyrite is the grinding environment and the galvanic interactions that occur between minerals [7]. The grinding environment employed in catalyst preparation therefore directly determines the surface chemistry and catalytic potential of pyrite through distinct mechanochemical and electrochemical processes.

Grinding not only reduces particle size but also alters physicochemical surface properties through mechanochemical activation [8]. Secondary processes such as agglomeration and recrystallisation may partially offset these gains over extended milling times [9].

The grinding environment, whether dry or wet, plays a decisive role in determining the extent and nature of these changes. Dry grinding consistently produces deeper structural distortions than wet grinding at equivalent energy input, as the absence of water allows freshly fractured, high-energy surfaces to be preserved rather than immediately passivated. In wet grinding, the aqueous medium promotes surface hydroxylation, which passivates reactive sites and limits the extent of mechanochemical activation [10]. For sulfide minerals, galvanic interactions between steel media and pyrite release Fe²⁺ and Fe³⁺ ions that hydrolyze and precipitate as iron oxyhydroxide species on mineral surfaces, reducing chemical activity [11], [12], [13]. Dry grinding

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eliminates this electrochemical pathway, preserving mechanically activated fracture surfaces [10].

In this study, pyrite ore was ground by both methods and used as a catalyst in NaBH_4 methanolysis. The surface properties of samples obtained under different grinding conditions were characterized, and the effect on hydrogen production performance was experimentally determined. Although the effects of grinding environment on particle size and surface morphology are well established in ore processing, its impact on catalytic performance in H_2 production remains insufficiently addressed. This study evaluates the potential of natural waste ores as a low-cost and sustainable catalyst alternative.

2. Experimental

2.1 Characterization Methods

The surface areas of the catalysts were calculated using the BET (Brunauer, Emmett and Teller) equation in the relative pressure range of 0.01–1. Crystal structures were determined by XRD analysis using a PANalytical Empyrean device with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over $2\theta = 10^\circ$ – 90° .

2.2. Materials and Chemicals

NaBH_4 (99% purity, AFG Bioscience) and methanol (Emsure®) were used without further purification.

2.3. Grinding Methods

Pyrite samples from Central Anatolia were crushed, ground with an agate mortar and pestle, and dry-sieved to below $425 \text{ }\mu\text{m}$. To minimise oxidation, material was sealed and stored at -18°C . For each experiment, 5 g of pyrite was ground in a stainless steel mill ($\varnothing 40 \times 75 \text{ mm}$) with 30 steel balls (6 mm diameter) mounted on a Retsch sieve shaker. For wet grinding, 5 ml of distilled water was added. Milling times were established from preliminary experiments to yield comparable product d_{50} , 10 min for dry and 6 min for wet grinding. Particle size distributions were measured by laser diffraction (Malvern Mastersizer Hydro 2000 MU).

2.4. Hydrogen Production

Dry- and wet-ground pyrite samples were designated PD1 and PW1, respectively, and used as catalysts in NaBH_4 methanolysis. Specific amounts of NaBH_4 and catalyst were placed in a sealed flask in a water bath; methanol at the same temperature was then injected. Released H_2 displaced water in a buret, and the gas volume was recorded over time. The hydrogen generation rate (HGR, $\text{mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$) was calculated from the initial slope of a polynomial fit to the volume–time data using Equation (2):

$$\frac{1}{W_{\text{cat}}} \left(\frac{dV_{\text{H}_2}}{dt} \right) = r_{\text{H}_2} \quad (2)$$

Experiments were conducted under identical conditions for PD1 and PW1. For the superior catalyst, the effects of catalyst amount, NaBH_4 amount, and temperature on HGR were then systematically investigated.

3. Results and Discussion

3.1. Characterization of Catalyst

XRD analyses were performed for both samples using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over approximately 5° – 90° (2θ). As shown in Figure 1, characteristic diffraction peaks of both samples are consistent with the pyrite phase (ICDD 00-042-1340, FeS_2). Peaks at approximately $2\theta = 28.5^\circ$, 33.0° , 37.0° , 40.8° , 47.5° , 56.3° , and 61.3° correspond to crystal planes (111), (200), (210), (211), (220), (311), and (222). The absence of secondary phase peaks indicates high purity in both samples.

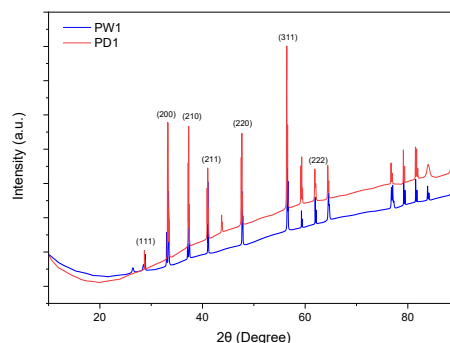


Figure 1. XRD patterns of pyrite samples

Crystallite sizes were approximately calculated using the Scherrer equation ($D = K\lambda / \beta \cos\theta$). In the calculations, $K = 0.9$ and $\lambda = 1.5406 \text{ \AA}$ were used, with the peak of highest density, approximately 56.3° (plane 311), used as a reference. Based on the approximate values obtained from the peak widths (FWHM), the crystallite size in the dry-ground sample is approximately in the range of 40–50 nm, while in the wet-ground sample this value decreases to the range of 20–30 nm. This result shows that wet grinding significantly reduces the crystallite size. The peaks appear sharper and more intense in the dry-ground (PD1) sample. This indicates that the crystal structure is better preserved and the crystallite size is larger. In the wet-ground sample (PW1), it was observed that the peaks were wider and their intensities were relatively reduced. The presence of a liquid medium during wet grinding causes interparticle collisions to be more effective and homogeneous, leading to distortions in the crystal lattice and smaller crystallite sizes. However, despite the smaller crystallite size observed in the wet-ground sample, its catalytic activity is lower than that of the dry-ground sample.

The surface properties of two different pyrite samples prepared using dry and wet grinding methods were investigated using the Brunauer–Emmett–Teller (BET) method. The grinding process is a critical parameter that significantly affects not only the crystal structure of minerals but also their surface area and pore structure. A regular increase in the amount of adsorbed gas was observed for both samples as the relative pressure increased. It is evident that both samples possess a mesoporous structure. It was observed that the dry-ground sample adsorbed a higher amount of gas compared to the wet-ground sample. This can be explained by effects such as surface rearrangement, agglomeration, or partial pore

blockage that occur during the grinding process in a wet environment. This finding confirms that the dry grinding process provides a higher specific surface area or a more developed pore structure.

BET analysis confirmed that both samples exhibit Type IV isotherm behavior (IUPAC), indicating mesoporous structures. PD1 has a BET surface area of 1.228 m²/g compared to 0.607 m²/g for PW1. Since particle size distributions under both conditions are nearly identical (Figure 2), the difference in surface area cannot be attributed to comminution efficiency. Rather, galvanic interactions during wet grinding precipitate iron oxyhydroxide species on freshly formed pyrite surfaces [11], [13], blocking accessible sites for N₂ adsorption and reducing the measured BET surface area. In dry grinding, the absence of an aqueous medium prevents such surface precipitation, preserving clean and reactive fracture surfaces. This interpretation is consistent with previous reports showing that wet-ground pyrite surfaces exhibit higher heterogeneity due to iron hydroxide and oxide deposits, which can be removed by EDTA washing to reveal the underlying sulfur-enriched surface [14].

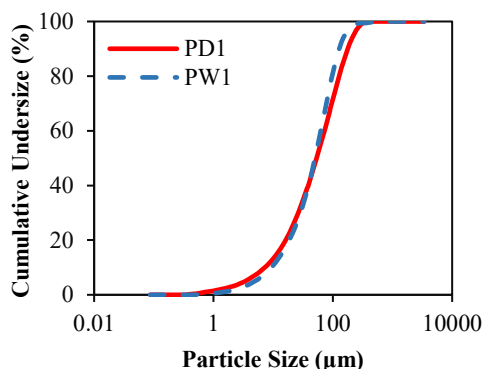


Figure 2. Particle size distributions of ground pyrite samples

3.2. Hydrogen Production Results

The time-dependent hydrogen production rates of the PD1 and PW1 catalysts were compared using 0.05 g of catalyst, 0.125 g of NaBH₄, 10 mL of methanol, and at 30°C. Both catalysts produced hydrogen at the theoretical hydrogen volume. However, the highest hydrogen production rate (HGR) was achieved with the PD1 catalyst. PD1 yielded an HGR of 3221 mL·min⁻¹·g_{cat}⁻¹, while PW1 yielded 2256 mL·min⁻¹·g_{cat}⁻¹. The effects of reaction parameters on the hydrogen production rate were investigated using the catalyst exhibiting higher activity.

The effect of catalyst amount was investigated at 30 °C using 0.125 g NaBH₄ in 10 mL methanol with 0.025, 0.05, 0.125, and 0.250 g catalyst (Figure 3). Although increasing catalyst amount raises the absolute reaction rate, HGR (calculated per gram of catalyst) was highest at the lowest catalyst amount (0.025 g). HGR values of 5136 mL·min⁻¹·g_{cat}⁻¹, 3221 mL·min⁻¹·g_{cat}⁻¹, 1381 mL·min⁻¹·g_{cat}⁻¹, and 1074 mL·min⁻¹·g_{cat}⁻¹ were obtained for catalyst amounts of 0.025 g, 0.05 g, 0.125 g, and 0.250 g, respectively. Based on these findings, 0.025 g was determined to be the optimal catalyst amount to balance reaction efficiency and catalyst quantity in the methanolysis of NaBH₄.

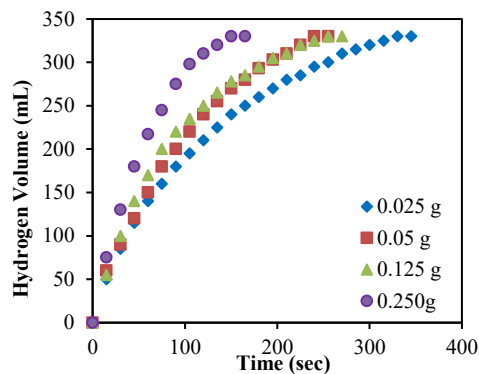


Figure 3. Effect of catalyst amount

To investigate the effect of the NaBH₄ amount, methanolysis reactions were carried out using 0.05 g, 0.100 g, 0.125 g, and 0.150 g of NaBH₄. These experiments were conducted in 10 mL of methanol solution in the presence of 0.025 g of catalyst at 30 °C. The results are presented in Figure 4. HGR values of 2207, 3855, 5136, and 10503 mL·min⁻¹·g were obtained, respectively. 0.125 g of NaBH₄ was considered the most suitable reactant amount.

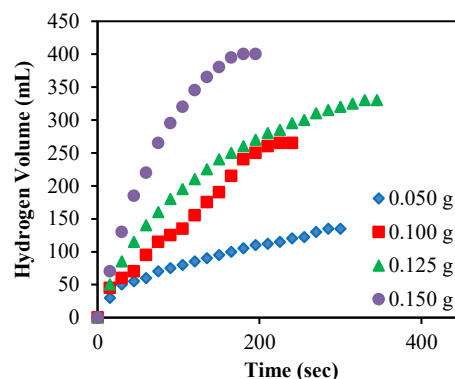


Figure 4. Effect of NaBH₄ amount

The effect of temperature was investigated at 25, 30, 40, 50, and 60 °C with 0.025 g catalyst, 0.125 g NaBH₄, and 10 mL methanol (Figure 5). HGR values increased with temperature: 2634, 5136, 11353, 12835, and 19990 mL·min⁻¹·g_{cat}⁻¹ at 25, 30, 40, 50, and 60 °C, respectively. Activation energy was calculated from the Arrhenius equation (Equations 3):

$$\ln k = \ln A - E_a/RT \quad (3)$$

Here, *k* represents the reaction rate constant, *T* the Arrhenius constant, *E_a* the activation energy, *R* the gas constant, and *T* the absolute temperature in Kelvin.

E_a is calculated as 38.07 kJ·mol⁻¹. This relatively low *E_a* indicates that the catalyst may allow for efficient hydrogen production under suitable conditions by reducing the energy barrier for the methanolysis reaction of NaBH₄. Under optimised conditions (0.025 g catalyst, 0.125 g NaBH₄, 10 mL methanol, 60 °C), PD1 achieved an HGR of 19990 mL·min⁻¹·g_{cat}⁻¹. This compares favourably with pyrite modified with polyethylenimine (PEI), which yielded 2883 mL·min⁻¹·g_{cat}⁻¹ [15]; CS/FeS₂ composites, which achieved 8000 mL·min⁻¹·g_{cat}⁻¹ at 25

°C [16]; and Fe₃O₄/FeS₂ hybrid structures at 8480 mL·min⁻¹·g_{cat}⁻¹ at 20 °C [17].

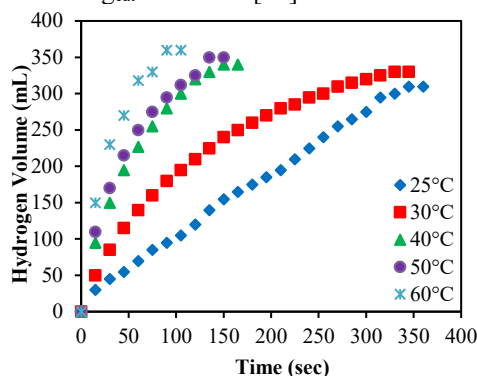


Figure 5. Effect of temperature

4. Conclusions

This study demonstrated the feasibility of using dry- and wet-ground pyrite (FeS₂) as a catalyst for NaBH₄ methanolysis. At 30 °C, dry-ground PD1 significantly outperformed wet-ground PW1.

The superior performance of dry-ground pyrite is attributed to the preservation of chemically reactive, high-energy fracture surfaces in the absence of aqueous passivation and galvanic interactions with steel grinding media. Characterization confirmed that the grinding environment alters mineral surface properties and that these changes directly influence catalytic performance. These findings establish the grinding environment as a critical parameter in mineral-based catalyst preparation for hydrogen generation. Furthermore, naturally occurring minerals offer a low-cost and earth-abundant alternative to synthetic catalyst systems. From a mineral processing perspective, dry grinding presents an additional advantage for sustainable operations in water-scarce regions.

Acknowledgement

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Characterization of impact-induced fracture in copper ore specimens using compact instrumentation as an alternative to the Hopkinson bar method for application in discrete element breakage models

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Abstract. Comminution accounts for 36% of a mining operation's energy consumption and is indispensable for extracting copper from its ore. Optimizing this stage requires measuring specific primary breakage energy under representative dynamic loading conditions. However, reference single-particle testing devices based on Hopkinson bars are often expensive and difficult to replicate, which limits the generation of comparable data. In this work, a compact drop-weight test rig is built and instrumented with a piezoelectric force sensor and a load cell. In addition, a reference long rod with strain gauges (based on Hopkinson bars) is built, and the measurements are benchmarked against it. Cylindrical copper ore and cement-based specimens with diameters between 7 and 13 mm are prepared with an aspect ratio of 1:1. Impacts are carried out at impact speeds between 1.0 and 1.5 m/s, while maintaining identical conditions, including material type, specimen geometry, impact energy, and striker shape. A total of 336 tests are conducted on copper ore and 252 on cement-based samples. The primary breakage energy is successfully measured using the three measurement systems, and it is shown that the most portable systems allow the measurement of primary breakage energy without a significant loss of accuracy.

1. Introduction

Copper is an indispensable material for technologies associated with electrification, power transmission, and electromobility, which is driving a sustained increase in global demand [1-3]. To produce copper from its ore, comminution is required, and it constitutes a critical stage due to its high energy consumption, accounting for 35–50% of the total energy used in a mining operation, equivalent to about 1.3% of global electricity consumption [4,5]. Therefore, improving comminution efficiency requires a more accurate understanding and quantification of the fracture mechanisms occurring at the single-particle scale.

The size reduction of particulate materials originates from microscopic events of crack initiation and in particular, primary breakage—understood as the first macroscopic rupture event that produces appreciable fragmentation of a particle under dynamic loading [6]—is relevant because it defines a physical threshold at which the applied energy begins to be converted into the creation of new surfaces [7]. Accordingly, the energy absorbed up to the instant of primary fracture is a key quantity to characterize the mineral response and to inform or validate breakage models in numerical simulations [6,10].

Reliable measurement of dynamic loads and energy in high-rate impacts has traditionally been addressed

using instrumented configurations such as Hopkinson bars and high-frequency load cells (Ultra Fast Load Cell, UFLC), which provide high temporal fidelity and have been widely used for dynamic characterization [10,11]. However, their implementation requires large-scale infrastructure (on the order of 3–5 m long) and strict alignment and calibration procedures, which prevents their use as portable or in-situ characterization tools and concentrates testing capabilities in a handful of dedicated facilities. In response to these limitations, compact instrumentation alternatives have emerged, including piezoelectric sensors and reduced-size load cells, which promise portability and ease of implementation without sacrificing access to high-frequency signals [11-14].

Despite these advances, a gap remains, there is a lack of consistent experimental evidence comparing specific primary breakage energy under dynamic conditions obtained with compact instrumentation against reference configurations [11], while keeping identical conditions such as material type, geometry, impact energy, striker shape, size, and sampling rate. In this context, this work proposes an experimental methodology to quantify the response associated with primary breakage in individual copper ore specimens using compact instrumentation consisting of a piezoelectric force sensor (PFS) and load cells (LC), assessing its performance as a practical alternative to standard systems [7], namely based on strain-gauge with a long rod (LRS), and its potential

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application in the calibration/validation of breakage models within the discrete element method.

2. Method

2.1. Materials

Two materials will be used: copper ore and cement-based samples. Homogeneous material such as cement-based will be used first to compare the different test benches (LC vs PFS vs LRSG) changing with four impact velocity while keeping the impact energy constant using four steel spheres with different masses M_s as reported in Table 1. The diameter of the ball is d_s , the drop height is h , and the impact velocity is v .

Table 1. Configurations to achieve a constant impact energy.

d_s [cm]	M_s [kg]	h [cm]	v [m/s]
7.32	1.588	11.1	1.48
7.96	1.955	9.0	1.33
8.59	2.395	7.4	1.20
9.23	3.050	5.8	1.07

In cement-based tests, a single specimen diameter of 13 mm will be selected. Twenty-one tests with cement-based will be performed at each impact velocity and each measurement system giving a total of 252 tests. The samples of cement-based are cast in 3D-printed molds to obtain a cylindrical shape, as presented in Figure 1.

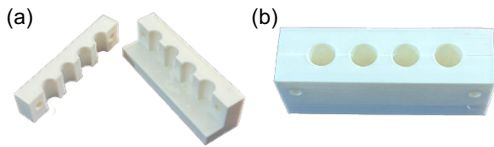


Figure 1. 3D printed mold for the manufacture of cement-based samples: (a) Parts of mold, (b) 3D mold.

Figure 2 shows the manufacturing methodology for copper ore samples. The first step is to cut it into 25 mm-thick slabs to ensure stability while scoring with a hole saw to obtain cylindrical geometry. For copper ore and cement-based materials, the samples must be trimmed with an angle grinder to achieve an aspect ratio of 1:1; then, each specimen will be weighed.

For the copper ore are selected four diameters for the samples, and four impact velocities of the striker with the same considerations maintaining of the impact energy constant, the summary of configuration shows in Table 2.

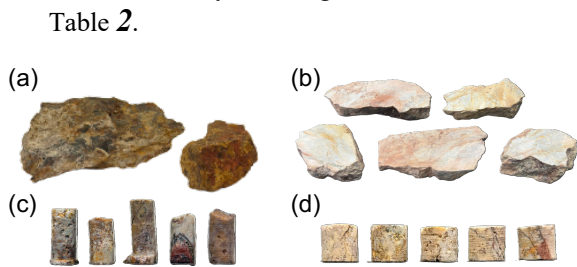


Figure 2. Steps for manufacturing the samples of copper ore: (a) Run-of-mine copper ore, (b) ore cutting in slabs, (c) cylindrical samples, (d) samples with aspect ratio 1:1.

Table 2. Configurations for the test of samples copper ore.

v [m/s]	Diameter [mm]			
	7	9	11	13
1.48	21	21	21	21
1.33	21	21	21	21
1.20	21	21	21	21
1.07	21	21	21	21
Total				336

2.2. Tests bench

The reference test bench is a long bar instrumented with strain gauges, as shown in Figure 1. The design is based on other test bench available in the literature [3]. The bar is made of ASTM 4340 steel, measures 3.05 m in length and has a diameter of 25.4 mm. The measurement is performed with semiconductor strain gauges, model KSPH-4-2K-E4 from Kyowa and with a Picoscope 5442D oscilloscope measuring at 8 MHz.

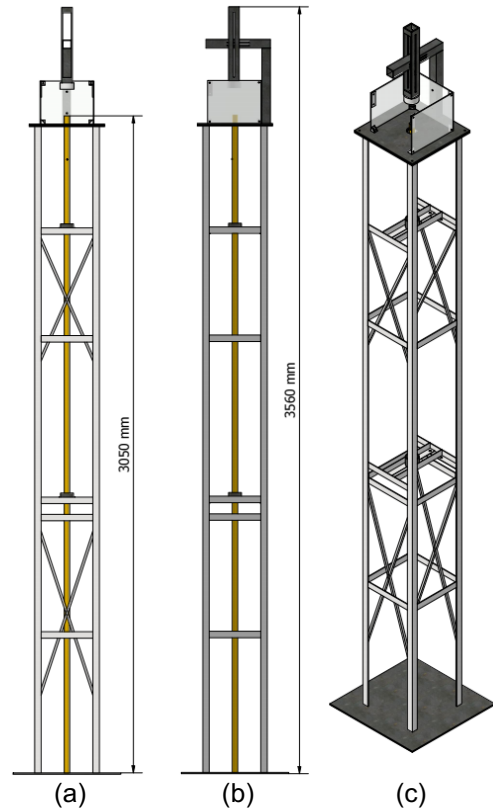


Figure 3. Design of test bench reference long rod with strain gauges (LRSG). (a) Front view. (b) Side view. (c) Isometric view.

The compact versions of the test benches are based on measurement with commercial load cells, and can use either, the DYM-102 load cell of 2000 kg or PCB 208C05 piezoelectric force sensor of 5000 lb, as shown in Figure 4. The release system of the steel ball is the same of the LRSG.

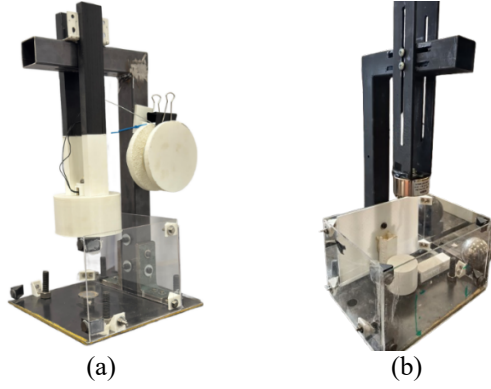


Figure 4. Proposed compact test bench to measure primary breakage energy. (a) Piezoelectric PCB 208C05. (b) Load cell DYMH-102.

2.3. Primary breakage energy

In both the reference system and the proposed compact system, the primary breakage energy cannot be directly measured. Figure 5 shows a diagram of the tests to be performed. In (a) the initial moment is shown where the steel ball is at a height h_i , and in (b) the moment of impact is shown, where the ball is in contact with the sample and the primary fracture is generated. To calculate the primary breakage energy, an energy balance is performed on the system, as presented in the following equation:

$$E_{i,p} = E_{i,r} + E_c + E_m \quad (1)$$

where $E_{i,p}$ is the potential energy of the steel ball before the impact, $E_{i,r}$ is the potential energy of the steel ball after the impact; i.e. the energy that the ball retains after the impact, E_c is the energy absorbed by the load cell (or force sensor) obtained from the measurements, and E_m is the energy absorbed by the sample up to the moment of the fracture, namely, primary breakage energy.

For the case when the LRSF is used, the energy balance equation can be calculated as [9]:

$$E_m = v_0 \int_0^{t_c} F(\tau) d\tau + g \int_0^{t_c} F(\tau) \tau d\tau - \frac{1}{2m_b} \left(\int_0^{t_c} F(\tau) d\tau \right)^2 - \frac{1}{\rho_r A_r C_r} \int_0^{t_c} F^2(\tau) d\tau \quad (2)$$

In the case of LC and PFS, the calculation is performed using the impulse absorbed by the sensor.

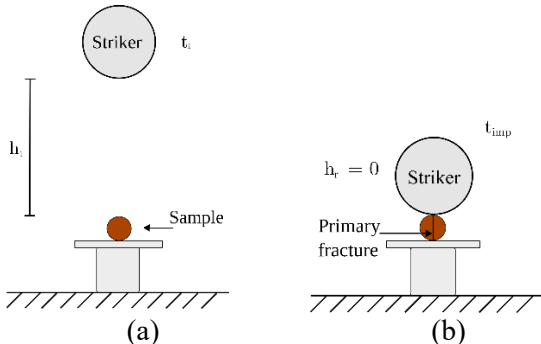


Figure 5. Impact load cell. (a) Start of the test. (b) Time at which the primary fracture occurs.

3. Preliminary results

Figure 6 shows impact test results using PFS and copper ore. Force versus time graphs are shown, identifying the start of the impact and the instant of the primary breakage.

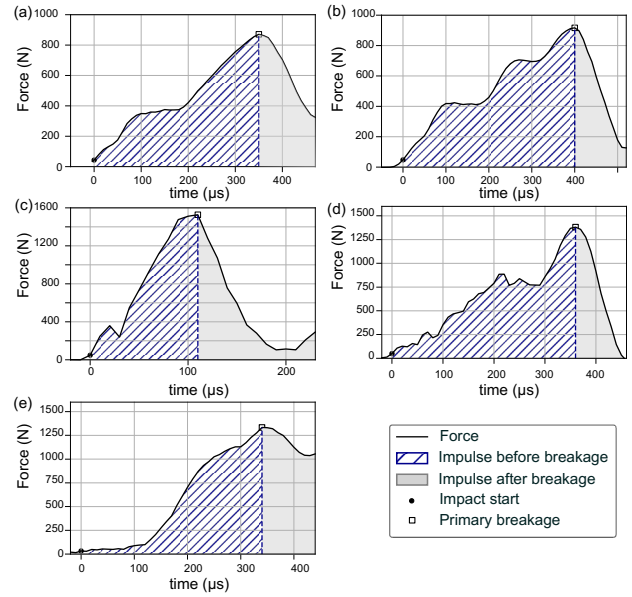


Figure 6. Impact load cell using PFS for different copper ore samples tested at 1.4 m/s using (a-b-c), and 1.08 m/s (d-e) with a diameter of 13 mm. (a) Test 45. (b) Test 49. (c) Test 53. (d) Test 80. (e) Test 85.

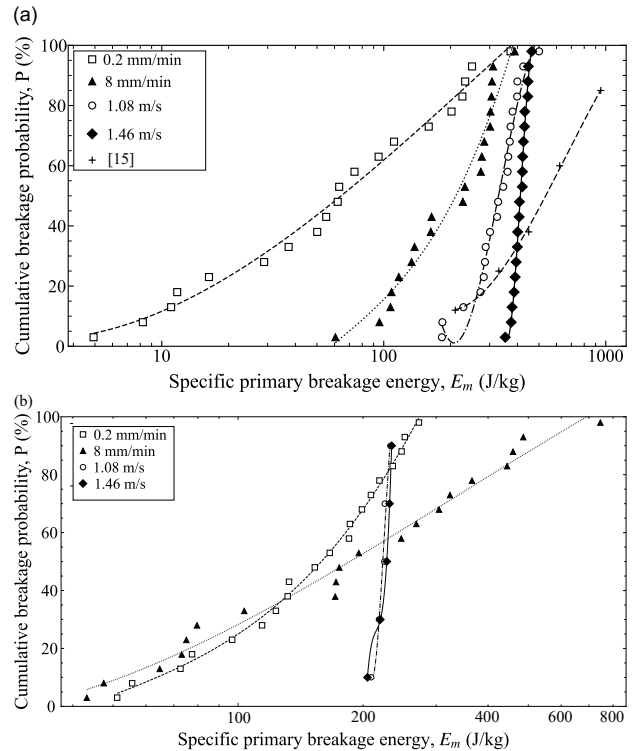


Figure 7. Specific primary breakage energy of copper ore versus its primary fracture probability tested at different impact and compression velocities. (a) 13 mm diameter samples compared with literature [15]. (b) 7 mm diameter.

Tests were conducted at different speeds as shown in Figure 7 for both diameters to demonstrate the influence of impact velocity on specific primary breakage energy.

4. Conclusions

A compact drop-weight test rig instrumented with a piezoelectric force sensor (PFS) and a load cell (LC) was designed, manufactured, and benchmarked against a long rod strain-gauge system (LRSG) based on Hopkinson-bar principles. The compact system reliably captures the force-time signature to primary fracture in a single copper-ore specimens and is approximately three times cheaper to build than outsourcing equivalent testing services, making it suitable for laboratories with limited structures.

Preliminary measurements on 130 copper-ore specimens (80 at $d = 13$ mm and 50 at 7 mm) confirm a clear dependence of specific primary fractured energy on impact velocity in the 1.07–1.48 m/s range. The median breakage energy E_{50} obtained with the PFS increased from 327 J/kg at 1.08 m/s to 408 J/kg at 1.46 m/s for 13 mm samples and reached values up to 8 times higher than those obtained under quasi-static compression at 0.2 mm/min (62 J/kg) using a Zwick Roell Z005. At the lower-velocity end, the measured E_{50} for 13 mm samples agrees within 2% with the value of 333 J/kg predicted by the breakage model of Tavares et al. [16].

The proposed methodology provides a portable and reproducible route to generate the size and rate dependent in breakage energy distributions required to calibrate and validate single-particle breakage models within the discrete element method. The remaining test on copper ore and cement-based, together with the full LC vs PFS vs LRSG cross-validation under identical conditions, are currently in progress and will allow quantifying the relative accuracy of each compact system against the strain-gauge reference, which is the central hypothesis of this study.

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Comparison of Industrial and Laboratory Grinding Specific Energies in Magnetite Ore Processing Using Donda's Approach

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Abstract. This study evaluates the grinding performance of two magnetite beneficiation plants operated by ArcelorMittal in Ukraine, with the aim of identifying opportunities to reduce energy consumption in comminution. An adaptation of Donda's methodology—a laboratory grinding procedure originally developed for itabirite ores from Brazil's Ferriferous Quadrangle—was selected as a diagnostic tool to compare laboratory-estimated specific energies with industrial values. The method relies on determining an ore-dependent parameter, K, from the relationship between cumulative oversize at a control screen and the specific energy applied at the mill pinion shaft. Representative samples from the primary, secondary, and tertiary grinding circuits of both plants were tested under adapted laboratory conditions, respecting the key principles of Donda's protocol. Industrial retained-mass values (R_F and R_P) were used to check whether laboratory-derived K values could approximate plant performance. The results show significant discrepancies, indicating notable potential for process improvement. Differences were most pronounced in the finer grinding stages, reflecting the increased difficulty of size reduction for higher-grade, finer concentrates. The outcomes demonstrate that Donda's methodology can effectively highlight inefficiencies in industrial grinding circuits, supporting targeted optimisation initiatives and potential reductions in energy consumption.

1. Context

ArcelorMittal has a global network of mining and steelmaking sites, supplying customers in 126 countries [1]. Committed to innovation and sustainability, ArcelorMittal owns 14 research centres (R&D) placed in Europe, North, South America and Asia [2].

With the growing global need for steel, having dependable, high-grade raw materials has become increasingly crucial. As one of the world's leading iron ore producers, ArcelorMittal relies on its own mines to ensure a consistent supply of top-quality ore for its steel production [3]. The Primary Department, part of Global R&D Maizières in France, aims to support the company's mining assets by optimizing existing processing routes and developing new ones.

This case study examines a beneficiation plant operated by ArcelorMittal in Ukraine, where the current process is being evaluated to reduce the energy consumption associated with comminution. For this purpose, *Donda's methodology*—a laboratory grinding test—was selected to assess the performance of the industrial grinding circuits. This methodology originates from a procedure used for primary grinding at the *Germano* concentrator operated by *Samarco Mineração*

in Brazil [4]. Further details on *Donda's methodology* will be presented in a dedicated section.

2. Materials and Methods

2.1. Donda's methodology

This methodology was originally developed to estimate the grinding energy demand of itabirite ores from Brazil's Ferriferous Quadrangle. Donda [4] formalized the approach and demonstrated its strong correlation with industrial data, showing that the specific energy required at the ball mill pinion shaft can be calculated using Eq.(1), where [4], [5], [6]:

$$E = \frac{1}{K} * \ln \frac{R_F}{R_P} \quad (1)$$

E refers to the specific energy applied at the motor's pinion shaft (kWh/t), K is an ore-dependent constant defined for a given screen size (t/kWh). R_F represents the percentage of material retained on a selected screen in the feed, while R_P is the percentage retained on the same screen in the product. The parameter K is value characteristic of each ore type for a given mesh size and set of grinding conditions. Higher K values indicate

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greater grindability and improved grinding performance [4], [5], [6].

The laboratory determination of K is based on at least four grinding tests, with standardized parameters, using representative samples of the same ore, each subjected to a different specific energy level (within the industrially relevant range). The applied energy is calculated by dividing the power at the mill's pinion shaft by the test ore mass. The power itself is estimated using *Rowland's* equation for small-diameter mills, multiplied by the ball charge mass, as expressed in Eq. (2) [4], [5], [6]:

$$Kwb = 6.3 * \sin(51 - 22 * (\frac{2.44-D}{2.44})) * (3.2 - 3 * V_p) * C_s * (1 - \frac{0.1}{(2^{(9-10*C_s)})}) \quad (2)$$

The cumulative oversize mass at the selected screen for the feed and product streams is measured, and these data are then used to obtain the value of K through an exponential regression fit of Eq. (1) [4], [5], [6].

Whenever standardized laboratory tests are performed and the laboratory K values are compared with the industrial K values, if the industrial K is lower than the one obtained in the jar tests, it indicates that the industrial grinding process can be improved. In other words, if the energy consumed in the plant is much higher than the energy measured in laboratory tests, it means that the industrial energy use can be optimized [7].

2.2. Samples

The iron ores in this asset are associated with Banded Iron Formations (BIF) and have an average grade of approximately 36% Fe. Magnetite-rich ore extracted from two open pits supplies two beneficiation plants, A and B. Plant A produces an iron ore concentrate containing 65% Fe and 8% SiO₂ and D80 around 60 µm, while Plant B produces a concentrate with 68% Fe and 5% SiO₂ and D80 around 40 µm. Both plants achieve these grades through three stages of ball milling followed by magnetic separation (Figure 1).

The feeds of the three grinding circuits were sampled (indicated in the Figure 1) to perform the grinding laboratory tests. Industrial data, such as mass balance and operational variables were shared by the plant.

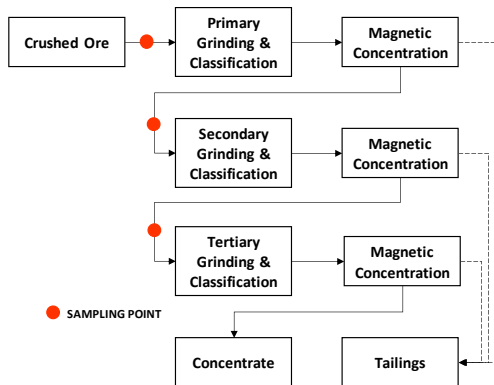


Figure 1. Schematic view of processing stages

Because Donda's methodology was originally developed for a specific ore and grinding circuit [7], some operating parameters—such as mill speed, mill filling, and others—do not fully match the conditions of the process evaluated here. Therefore, adaptations were required, integrating the plant's actual operating variables into the original testing protocol, except for the primary grinding stage. The primary grinding feed had to be crushed to 10 mm before testing, since its original size (D80 ≈ 20 mm) was much coarser than what is typically used in primary ball-mill circuits. The ball top size also had to be adjusted, as the industrial 120 mm balls are incompatible with the diameter of the laboratory-scale mill.

The objective with these tests were to compare the industrial expended energy with the laboratory estimated energy, like it was mentioned: *“if the energy consumed in the plant is much higher than the energy measured in laboratory tests, it means that the industrial energy use can be optimized”* [7].

To evaluate the grinding performance, the percentage of material retained in each control screen of both feed (R_F) and product (R_P) of industrial case was based on the mass balance of the plant. The R_F and R_P were the industrial values since it was wanted to compare if the K found in laboratory was comparable to the industrial K (the deviation is in the order of 10% [7]). If this hypothesis is true, then the energy calculated using Eq. (1) would approximate the industrial energy.

Table 1 presents some industrial data and the tests parameters adapted to the industrial case are presented on Table 2, Table 3 and Table 4.

Table 1. Industrial Data

Grinding Circuit	Control Screen (µm)	*R _F (%)	*R _P (%)
1ary (A)	212	93.4	17.2
2ary (A)	75	44.1	16.6
3ary (A)	53	27.3	12.2
1ary (B)	212	93.4	17.2
2ary (B)	53	62.6	27.3
3ary (B)	38	38.7	22.6

*Mass Balance reconciliation

Table 2. Primary grinding tests parameters

Plant	A	B
Parameter	Primary Grinding	
Mill inner diameter (m)	0.30	
Mill inner length (m)	0.30	
Mill load (%)	38.0	38.0
wt.% solids	77.4	77.2
% of critical speed	77	79
Energy on pinion shaft (kWh/t)	5, 8, 12, 15	5, 8, 12, 15
	Diameter (mm)	Proportion (%)
Charge distribution	63.5	35.0
	50.8	41.0
	38.1	18.0
	25.4	6.0

Table 3. Secondary grinding tests parameters

Plant	A	B
Parameter	Secondary Grinding	
Mill inner diameter (m)	0.30	
Mill inner length (m)	0.30	
Mill load (%)	38.0	35.0
wt.% solids	65.3	65.1
% of critical speed	67	74
Energy on pinion shaft (kWh/t)	6, 9, 12, 15	6, 9, 12, 15
	Diameter	Proportion
Charge distribution	40.0 mm	29.5 %
	30.0 mm	38.0 %
	25.0 mm	20.2 %
	20.0 mm	12.3 %

Table 4. Tertiary grinding tests parameters

Plant	A	B
Parameter	Tertiary Grinding	
Mill inner diameter (m)	0.30	
Mill inner length (m)	0.30	
Mill load (%)	38	35
wt.% solids	57.3	58.1
% of critical speed	67	74
Energy on pinion shaft (kWh/t)	2, 4, 7, 8.5	2, 4, 7, 8.5
	Diameter	Proportion
Charge distribution	40.0 mm	29.5 %
	30.0 mm	38.0 %
	25.0 mm	20.2 %
	20.0 mm	12.3 %

3. Results

The laboratory tests results are depicted in Figure 2 and Figure 3. Both plots show the cumulative oversize percentage at the respective control screen in function of the energy (kWh/t) applied in the mill pinion.

Table 5 shows the laboratory K value for each grinding stage, the mill pinion energy and the estimated motor energy, considering 5% of energy loss.

It was expected to have closer K values for the primary grinding, since Rp and Rf for plant A and B are practically the same, as indicated in Table 1. This K difference can be explained by several errors, like industrial and laboratory sampling errors, tests execution errors, and the fact that the sample had to be crushed at 10 mm, influencing the ball mill breaking mechanisms.

On the other hand, K values for secondary (0.2357 – plant A and 0.1288 – plant B) and tertiary grindings (0.1631 – plant A and 0.1175 – plant B) indicate the difficulty of reducing the grains' sizes: as predicted, the concentrate with 68% Fe and 5% SiO₂ is finer, requiring more energy to be grinding, thus, presenting smaller K.

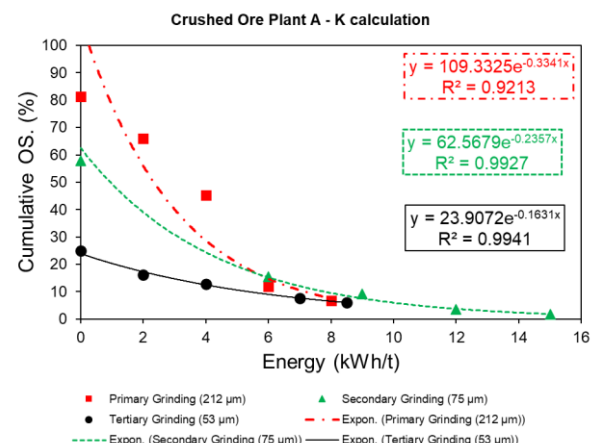
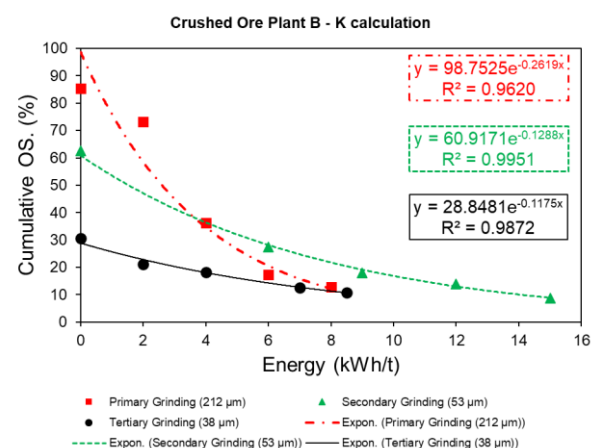
**Figure 2.** Curves for K calculation - Plant A**Figure 3.** Curves for K calculation - Plant B

Table 5. Laboratory tests results

Grinding Circuit	K (t/kWh)	Mill Pinion Specific Energy (kWh/t)	Mill Motor Specific Energy (kWh/t)
1ary (A)	0.3341	5.06	5.33
2ary (A)	0.2357	4.15	4.36
3ary (A)	0.1631	4.94	5.20
1ary (B)	0.2619	6.46	6.80
2ary (B)	0.1288	6.44	6.78
3ary (B)	0.1175	4.58	4.82

If the hypothesis that the laboratory K was close to the industrial K, then the specific energies would approximate. When industrial specific energies are compared to the laboratory specific energies it is observed that the industrial K is far from the laboratory K values. The percentual difference between the industrial and laboratory specific energies consumptions for each stage were shared to stakeholders to discuss further improvement actions since the laboratory and industrial K diverge.

4. Conclusions

This study applied Donda's methodology to evaluate the grinding performance of two magnetite beneficiation plants. Laboratory-derived K values and specific energy estimates were compared to industrial values to assess the potential for reducing comminution energy consumption.

The results show that laboratory-estimated specific energies are consistently and substantially lower than those measured in the plant. Such gaps suggest significant inefficiencies in the industrial grinding circuits. Differences were most pronounced in the finer grinding stages, reflecting the increased difficulty of size reduction for higher-grade, finer concentrates.

Overall, the findings demonstrate that Donda's methodology is a useful diagnostic tool for identifying optimisation opportunities. The substantial differences between laboratory and industrial energy values highlight the potential for improved process control, enhanced milling efficiency, and meaningful energy savings.

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Effect of Particle Size and Processing Conditions on the Production of Powdered Collagen from Arapaima Gigas Scales and its Application in Functional Products

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Abstract. This research aimed to determine the effect of particle size and processing conditions on the yield and physicochemical characteristics of powdered collagen obtained from paiche scales (*Arapaima gigas*). For this purpose, hydrobiological residues from the Peruvian Amazon were used, considering their valorization as a sustainable alternative for obtaining value-added functional ingredients.

The experimental procedure included washing, removal of non-collagenous proteins, demineralization, thermal hydrolysis, and drying under controlled conditions. Different particle sizes and processing temperatures were evaluated during the process. The variables analyzed included extraction yield, protein content, moisture percentage, solubility, and antioxidant activity of the powdered collagen. The results showed statistically significant differences among the treatments applied ($p < 0.05$), demonstrating that particle size reduction directly influences recovery efficiency and the functional properties of the final product.

The most favorable experimental condition achieved an extraction yield of 23.8%, protein content of 89.6%, moisture content of 5.4%, and solubility of 82.1%, while antioxidant activity reached approximately 68%. Likewise, the statistical analysis presented a coefficient of determination of $R^2 = 0.80$, evidencing a significant relationship between processing conditions and the functional quality of the obtained collagen. Overall, the results confirm the potential of *Arapaima gigas* scales as a sustainable raw material for the production of powdered collagen intended for nutraceutical and functional food applications.

1. Introduction

The fishing industry generates large volumes of waste during the processing of aquatic resources, including scales, skins, bones, and viscera, which are frequently discarded or used in low-value applications. However, these by-products contain bioactive compounds of industrial interest, particularly structural proteins such as collagen, whose valorization contributes to the integral utilization of fishery resources and the reduction of environmental impacts associated with inadequate waste disposal [1–3].

Arapaima gigas scales constitute an important source of collagen due to their high proportion of fibrillar proteins and minerals. In recent years, collagen of aquatic origin has attracted increasing interest in the food, pharmaceutical, and nutraceutical sectors because of its biocompatibility, bioavailability, and functional potential as an ingredient for the development of health-promoting products [2,4].

Furthermore, the utilization of residues from Amazonian species represents a sustainable alternative for generating added value within regional production chains.

Several studies have demonstrated that processing conditions significantly influence extraction efficiency and the physicochemical characteristics of the collagen obtained. Among the most relevant factors are temperature, processing time, and raw material particle size, since these parameters affect mass transfer, protein release, and collagen structural stability during extraction and drying stages [3,5]. Adequate particle size reduction increases the surface area available for chemical and thermal treatments, promoting protein recovery and improving the functional properties of the final product.

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In this context, the production of powdered collagen from *Arapaima gigas* scales represents a technological alternative with potential for the development of functional ingredients intended for nutraceutical and food applications. Therefore, the present study evaluated the effect of particle size and processing conditions on extraction yield and the physicochemical properties of powdered collagen obtained from *Arapaima gigas* scales, aiming to identify the most favorable conditions for its utilization as a high-value functional ingredient.

2. Materials and Methods

2.1. Raw Material Preparation and Collagen Extraction

The *Arapaima gigas* scales used in this study were obtained from facilities dedicated to the processing of aquatic resources in the Peruvian Amazon. Initially, the raw material underwent a manual selection process to remove impurities, muscle tissue residues, and foreign materials that could affect extraction quality.

Subsequently, the scales were washed with running water and conditioned through controlled drying until suitable conditions for mechanical processing were achieved. Once dried, they were ground and classified according to particle size to obtain different granulometric fractions, which were used to evaluate their influence on extraction yield and the physicochemical characteristics of the collagen obtained.

The collagen extraction process included the removal of non-collagenous proteins, demineralization, thermal hydrolysis, and drying. The elimination of non-collagenous proteins reduced interfering compounds present in the raw material, while demineralization facilitated the release of the protein matrix contained in the scales.

Subsequently, the material was subjected to thermal hydrolysis under different processing conditions to promote collagen extraction. Finally, the extract obtained was dried and conditioned to produce powdered collagen for subsequent analyses.

2.2. Evaluation of Physicochemical Properties of Collagen

The powdered collagen obtained was characterized through the determination of physicochemical and functional variables considered relevant for evaluating its potential application in nutraceutical products and functional foods. The variables analyzed were extraction yield (%), protein content (%), moisture (%), solubility (%), and antioxidant activity (%).

Extraction yield was calculated as the percentage ratio between the mass of recovered collagen and the initial mass of processed scales. Protein content was used as an indicator of the purity and quality of the product obtained, while moisture content was used to evaluate the stability and preservation conditions of the powdered collagen. Solubility was employed to determine the functional behavior of the product in aqueous systems, and antioxidant activity was used to estimate its potential capacity to neutralize free radicals.

The experimental data obtained were subjected to statistical analysis to determine the effect of particle size and processing conditions on the evaluated variables. Analysis of variance (ANOVA) was applied to identify significant differences among treatments, considering a significance level of 5% ($p < 0.05$). Additionally, regression analysis was performed to establish the relationship between processing conditions and the functional quality of powdered collagen through the estimation of the coefficient of determination (R^2).

3. Results and Discussion

The results obtained demonstrated that particle size and processing conditions significantly influenced extraction yield and the physicochemical properties of powdered collagen obtained from *Arapaima gigas* scales. Analysis of variance revealed statistically significant differences among the evaluated treatments ($p < 0.05$), indicating that the modifications applied during raw material conditioning and processing had a direct effect on the quality of the final product.

Particle size reduction promoted greater exposure of the protein matrix within the scales, facilitating mass transfer during demineralization and thermal hydrolysis stages. Consequently, collagen recovery efficiency increased and some of its functional properties, particularly solubility and antioxidant activity, improved. Likewise, processing conditions exerted a significant influence on the stability of the extracted proteins and on the final characteristics of the product obtained. These findings are consistent with previous studies reporting improvements in collagen extraction yield and functional properties when the available surface area is increased through particle size reduction [6,8].

The most favorable experimental condition presented an extraction yield of 23.8%, protein content of 89.6%, moisture content of 5.4%, solubility of 82.1%, and antioxidant activity of approximately 68%. These results demonstrate efficient recovery of protein compounds and confirm the potential of *Arapaima gigas* scales as a raw material for the production of high-value functional ingredients. The values obtained are consistent with studies conducted on collagen from aquatic sources, which report high protein contents and bioactive properties associated with its potential application in nutraceutical products and functional foods [5,8].

Furthermore, regression analysis showed a positive relationship between processing conditions and the functional quality of powdered collagen, yielding a coefficient of determination of $R^2 = 0.80$, which evidences a strong association between processing variables and the functional quality of the collagen obtained.

Table 1. Physicochemical Properties of Powdered Collagen Obtained from Arapaima gigas Scales Under Optimal Experimental Conditions.

Parameter	Unit	Value
Extraction yield	%	23.8
Protein content	%	89.6
Moisture	%	5.4
Solubility	%	82.1
Antioxidant activity	%	68

Table 2 presents the behavior of the physicochemical properties of powdered collagen obtained from Arapaima gigas scales under different particle sizes and processing conditions. An increasing trend was observed in extraction yield, protein content, solubility, and antioxidant activity as particle size decreased, with the best results achieved in treatment T4. In contrast, moisture content showed a progressive decrease, indicating greater drying efficiency and improved potential product stability.

These results demonstrate that an adequate reduction in particle size promotes the release and recovery of protein compounds while simultaneously improving the functional properties of powdered collagen obtained from Amazonian aquatic residues.

Table 2. Physicochemical Properties of Powdered Collagen Obtained from Arapaima gigas Scales under Different Processing Conditions

Treat ment	Part icle Size	Extra ction Yield (%) (%)	Prot ein Con tent (%)	Mois ture (%)	Solub ility (%)	Antioxi dant Activit y (%)
T1	Coar se	16.8 ± 1.2	80.4 ± 1.6	7.8 ± 0.4	68.5 ± 1.8	54.2 ± 1.5
T2	Med ium	19.7 ± 1.1	84.3 ± 1.4	6.7 ± 0.3	74.8 ± 1.5	59.6 ± 1.3
T3	Fine	21.9 ± 0.9	87.1 ± 1.2	5.9 ± 0.2	79.3 ± 1.2	64.1 ± 1.1
T4	Very fine	23.8 ± 0.8	89.6 ± 1.1	5.4 ± 0.2	82.1 ± 1.0	68.0 ± 1.0

Values correspond to mean ± standard deviation of the evaluated variables.

4. Mathematical Relationships and Process Evaluation

The properties evaluated during powdered collagen production were determined through mathematical relationships used to quantify extraction efficiency and the functional characteristics of the product obtained.

$$RE = \frac{M_c}{M_i} \times 100$$

Where:

RE = extraction yield (%)

Mc = mass of collagen obtained (g)

Mi = initial mass of processed scales (g)

$$H = \frac{M_h - M_s}{M_h} \times 100$$

Where:

H = moisture (%)

Mh = wet mass of the sample (g)

Ms = dry mass of the sample (g)

$$R^2 = 1 - \frac{\sum(y_i - \hat{y}_i)^2}{\sum(y_i - \bar{y})^2}$$

Where:

R^2 = coefficient of determination

y_i = observed values

$\hat{y}_i$ = values estimated by the regression model

$\bar{y}$ = mean of observed values

Equation (1) was used to determine the extraction yield of collagen obtained from Arapaima gigas scales. Equation (2) was used to evaluate the moisture content of the final product, while Equation (3) was employed to analyze the relationship between particle size, processing conditions, and the functional properties of powdered collagen. Regression analysis yielded a coefficient of determination of $R^2 = 0.80$, demonstrating a significant relationship between processing variables and the functional quality of the product obtained.

5. Conclusions

Particle size and processing conditions significantly influenced extraction yield and the physicochemical properties of powdered collagen obtained from Arapaima gigas scales, with statistically significant differences observed among the evaluated treatments ($p < 0.05$).

The most favorable experimental condition achieved an extraction yield of 23.8%, protein content of 89.6%, moisture content of 5.4%, solubility of 82.1%, and antioxidant activity of approximately 68%, demonstrating that appropriate particle size reduction promotes the recovery of protein compounds and improves the functional properties of the final product.

Likewise, regression analysis showed a coefficient of determination of $R^2 = 0.80$, indicating that the variations observed in the functional quality of powdered collagen are closely related to the processing conditions applied during extraction and raw material conditioning.

The results obtained confirm that *Arapaima gigas* scales constitute a sustainable and technically viable source for the production of powdered collagen with potential applications in nutraceutical products and functional foods, contributing to the integral utilization of Amazonian aquatic residues and the generation of high-value ingredients.

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Optimization of Cellular Disintegration and Particle Size of *Musa Paradisiaca* Rachis for Ecological Paper Production

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Abstract. This research focused on utilizing lignocellulosic agro-industrial waste as a sustainable alternative for manufacturing biodegradable materials with a reduced environmental impact. In this context, the potential of *Musa paradisiaca* rachis as a raw material for producing eco-friendly paper under conditions typical of the tropical Amazon was evaluated. The experimental procedure included washing, drying, particle size reduction, alkaline treatment, and pulping. Subsequently, sheets of eco-friendly paper were produced, and properties such as basis weight, tensile strength, moisture absorption, and fiber yield were assessed. The results showed statistically significant differences between the applied treatments ($p < 0.05$), demonstrating that adequate particle size reduction promotes fiber compaction and improves the paper's mechanical properties. The most efficient experimental condition yielded an average basis weight of 84 g/m², a tensile strength of 0.146 kg/15 mm, a moisture absorption of 69.8%, and a pulp yield of approximately 79.5%. Furthermore, the statistical analysis showed a coefficient of determination of $R^2 = 0.78$, indicating a significant relationship between the level of cell disintegration and the mechanical behavior of the eco-friendly paper.

1. Introduction

The increasing generation of agro-industrial waste has driven the search for sustainable alternatives that allow for the valorization of these materials and reduce the environmental impacts associated with their final disposal. Lignocellulosic waste represents an important source of renewable raw materials due to its high content of cellulose, hemicellulose, and lignin, structural components with potential for the production of biodegradable materials and paper products [1–3].

Among these residues, the rachis of *Musa paradisiaca* stands out, a byproduct generated during the harvesting and marketing of bananas, which is generally discarded or used for low value-added purposes. Several studies have demonstrated that residues derived from banana cultivation possess favorable physicochemical characteristics for obtaining cellulosic fibers, due to their high content of structural polysaccharides and their ability to form materials with mechanical properties suitable for industrial applications.[2,4].

Particle size reduction and cell disintegration are fundamental operations in the processing of lignocellulosic materials, as they promote fiber release,

increase surface area, and improve the efficiency of subsequent chemical treatments. These structural modifications facilitate the partial removal of lignin and hemicellulose, promoting greater cellulose availability for the formation of interfibrillar bonds during papermaking [1,4]. Consequently, significant improvements can be achieved in properties such as basis weight, mechanical strength, moisture absorption, and pulp yield.

Furthermore, recent research has indicated that the valorization of banana waste for the production of sustainable materials constitutes a viable alternative within the principles of the circular economy, contributing to the reduction of agricultural waste and the development of production processes with less environmental impact. [3,5,6].

Therefore, the present study evaluated the influence of cell disintegration and particle size of the rachis of *Musa paradisiaca* on the physical and mechanical properties of ecological paper, with the aim of identifying the most favorable conditions for its use as an alternative raw material in the production of sustainable materials

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2. Materials and methods

2.1. Preparation of raw materials

The rachis of *Musa paradisiaca* used in the research was collected from plantations located in the Amazon region of Peru. Initially, the material underwent a manual selection process to remove impurities, soil debris, and deteriorated plant material. Subsequently, it was washed with running water to remove particles adhering to the surface and ensure the uniformity of the raw material used in the process.

Once cleaned, the rachis was cut into smaller fragments and dried until it reached suitable conditions for mechanical processing. The dried material was then shredded and classified to obtain different particle sizes, which were used to evaluate the influence of size reduction on the properties of the eco-friendly paper.

Subsequently, the resulting particles underwent an alkaline treatment designed to promote cell disintegration and the partial removal of non-cellulosic compounds, primarily lignin and hemicellulose. This stage favored the release of cellulosic fibers and improved the conditions for pulp production. After treatment, the material was washed to remove chemical residues and then defibrated to obtain a homogeneous suspension of cellulosic fibers

The pulp obtained was used to produce sheets of eco-friendly paper through forming, pressing, and drying processes under controlled laboratory conditions. The samples produced were conditioned prior to physical and mechanical evaluation to ensure uniformity in the tests performed.

2.2. Evaluation of paper properties

The sheets of eco-friendly paper obtained were conditioned prior to testing and subsequently characterized by determining physical and mechanical properties considered relevant for evaluating the quality of the finished material. The response variables analyzed were basis weight (g/m^2), tensile strength (kg/15 mm), moisture absorption (%), and pulp yield (%).

Basis weight was determined from the ratio between the mass of the samples and the corresponding area of the sheets produced. Tensile strength was used as an indicator of the paper's mechanical behavior under tensile stress, allowing for the evaluation of the degree of bonding and compaction achieved by the cellulose fibers during sheet formation. Moisture absorption was used to determine the hygroscopic capacity of the material, while pulp yield was calculated as the percentage ratio between the mass of

pulp obtained and the initial mass of raw material processed.

The experimental data obtained were subjected to statistical analysis in order to evaluate the effect of cell disintegration and particle size on the properties of ecological paper.

An analysis of variance (ANOVA) was applied to identify significant differences between the evaluated treatments, considering a significance level of 5% ($p < 0.05$). A regression analysis was also performed to determine the relationship between the degree of cell disintegration and the mechanical behavior of the material, by estimating the coefficient of determination (R^2).

3. Results and discussion

The results showed that the level of cell disintegration and particle size reduction significantly influenced the physical and mechanical properties of the eco-friendly paper made from the rachis of *Musa paradisiaca*. Analysis of variance revealed statistically significant differences between the treatments evaluated ($p < 0.05$), indicating that the modifications applied during the conditioning of the raw material had a direct effect on the quality of the final product.

It was observed that decreasing particle size favored the release of cellulosic fibers and promoted a more homogeneous distribution of the fibrous matrix during sheet formation. This behavior contributed to greater structural compaction of the paper, increasing the interaction capacity between fibers and improving the mechanical properties of the resulting material. The most efficient experimental condition yielded an average basis weight of 84 g/m^2 , a tensile strength of 0.146 kg/15 mm , a moisture absorption of 69.8%, and a pulp yield of approximately 79.5%, values that reflect a suitable balance between biomass utilization and the physical-mechanical performance of the eco-friendly paper.

Furthermore, the regression analysis showed a positive relationship between the degree of cell disintegration and the mechanical resistance of the product, obtaining a coefficient of determination of $R^2 = 0.78$. This result indicates that 78% of the variability observed in the mechanical behavior of the paper can be attributed to the structural modifications generated by the reduction in size and the release of fibers during the processing of the raw material.

The results obtained suggest that optimizing size reduction and cell disintegration processes is a determining factor in obtaining eco-friendly paper from lignocellulosic waste. Improved fiber compaction and interfibrillar bond formation yielded materials with properties suitable for sustainable applications, demonstrating the potential of *Musa paradisiaca* rachis as an alternative source of cellulosic fibers for eco-friendly paper production in the tropical Amazon.

Table 1. Physical and mechanical properties of ecological paper made from the rachis of *Musa paradisiaca* under the optimal experimental condition.

Parameter	Unit	Worth
Weight	g/m ²	84
Tensile strength	kg/15 mm	0.146
Moisture absorption	%	69.8
Pulp yield	%	79.5

Table 2 presents the behavior of the physical and mechanical properties of the eco-friendly paper made from the rachis of *Musa paradisiaca* under different levels of cell disintegration. An increasing trend is observed in basis weight, tensile strength, and pulp yield as the degree of cell disintegration increases, with the best results achieved in treatment T4 (very high). In contrast, moisture absorption showed a progressive decrease, suggesting greater compaction and cohesion of the cellulosic fibers. These results demonstrate that greater fiber release favors the formation of a more homogeneous and resistant structure, improving the quality characteristics of the resulting eco-friendly paper.

Tabla 2. Physical and mechanical properties of ecological paper obtained from the rachis of *Musa paradisiaca* under different levels of cell disintegration.

Treatment	Level of cell disintegration	Weight (g/m ²)	Tensile strength (kg/15 mm)	Moisture absorption (%)	Pulp yield (%)
T1	Low	74.2 ± 1.8	0.091 ± 0.005	75.4 ± 1.6	70.8 ± 1.7
T2	Half	78.6 ± 1.5	0.114 ± 0.004	73.1 ± 1.4	74.3 ± 1.5
T3	High	81.9 ± 1.3	0.132 ± 0.003	71.5 ± 1.2	77.2 ± 1.3
T4	Very high	84.0 ± 1.1	0.146 ± 0.003	69.8 ± 1.1	79.5 ± 1.2

The values correspond to means ± standard deviation of the evaluated variables.

The results presented demonstrate a positive relationship between the level of cell disintegration and the tensile strength of the eco-friendly paper, with a progressive increase in this property observed as the release of

cellulosic fibers increases. Furthermore, the regression analysis showed a coefficient of determination of $R^2 = 0.78$, confirming a significant association between the two variables.

4. Mathematical relationships and process evaluation

The properties evaluated during the production of ecological paper were determined using mathematical relationships used to quantify the process performance and the physical behavior of the material obtained.

$$RP = \frac{M_p}{M_i} \times 100$$

Donde:

RP = rendimiento de pulpa (%)

Mp = masa de pulpa obtenida (g)

Mi = masa inicial de raquis procesado (g)

$$AH = \frac{M_h - M_s}{M_s} \times 100$$

Donde:

AH = moisture absorption(%)

Mh = wet mass of the sample(g)

Ms = dry mass of the sample(g)

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2}$$

Donde:

R^2 = determination coefficient

y_i = observed values

$\hat{y}_i$ = values estimated by the model

$\bar{y}$ = mean of the observed values

Equation (1) was used to determine the pulp yield obtained from the rachis of *Musa paradisiaca*, while Equation (2) allowed for the evaluation of the moisture absorption capacity of the produced eco-friendly paper. Equation (3) was used to analyze the relationship between the level of cell disintegration and the mechanical strength of the material, yielding a coefficient of determination of $R^2 = 0.78$.

5. Conclusions

Optimizing cell disintegration and reducing the particle size of the *Musa paradisiaca* rachis significantly influenced the physical and mechanical properties of the ecological paper produced, showing statistically

significant differences between the treatments evaluated ($p < 0.05$).

The experimental condition with the highest level of cell disintegration showed the best results, reaching a weight of 84 g/m², a tensile strength of 0.146 kg/15 mm, a moisture absorption of 69.8% and a pulp yield of 79.5%, which demonstrates that adequate fiber release favors structural compaction and improves the quality of the material obtained.

Furthermore, the regression analysis showed a coefficient of determination of $R^2 = 0.78$, indicating that the mechanical behavior of the paper is closely related to the degree of cell disintegration achieved during the processing of the raw material.

The results obtained confirm that the rachis of *Musa paradisiaca* constitutes a viable and sustainable alternative as a source of lignocellulosic fibers for the production of ecological paper, contributing to the use of agro-industrial waste and the generation of materials with less environmental impact.

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Kinetics and Adsorption Isotherms of Pb (II) In Soils using Zero-Valent Iron Nanoparticles Functionalized with Quinoa Residual Biomass

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Abstract. Lead (Pb(II)) contamination in soils is a major environmental concern because of its toxicity, persistence, and adverse effects on ecosystems and human health. This study evaluated the use of zero-valent iron nanoparticles functionalized with quinoa residual biomass as an efficient adsorbent for Pb(II) removal from contaminated soils. The synthesized nanoparticles were characterized by Fourier Transform Infrared Spectroscopy (FTIR), which confirmed the presence of carboxyl, hydroxyl, and amino functional groups involved in the adsorption process.

Batch adsorption experiments were carried out to evaluate the adsorption kinetics and equilibrium behavior. The kinetic data showed the best fit with the pseudo-second-order model, presenting a correlation coefficient of $R^2 = 0.9901$, indicating that chemisorption is the dominant mechanism controlling Pb(II) uptake. Equilibrium studies demonstrated that the Langmuir isotherm model best represented the experimental data, with $R^2 = 0.9946$, suggesting homogeneous monolayer adsorption on the adsorbent surface.

The separation factor RL was 0.1142, confirming a favorable adsorption process ($0 < RL < 1$). In addition, the maximum adsorption capacity (Q_{max}) reached 322.58 mg/g, while the Langmuir constant K_L was 1.347, demonstrating high affinity between Pb(II) ions and the adsorbent material. These results highlight the potential application of this sustainable nanomaterial for soil remediation.

Keywords: adsorption, isotherms, kinetics, Pb(II), zero-valent iron nanoparticles, quinoa residual biomass, soil remediation.

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Pressure Oxidation of Refractory Tailings in an Autoclave for Gold Recovery Optimization

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Abstract. The treatment of refractory tailings through pressure oxidation in an autoclave is an efficient alternative for improving gold recovery in mining processes. This study evaluated the effect of oxidation pressure and pyrite particle size on gold recovery from refractory tailings using an autoclave system. Experimental tests were conducted under operating conditions of 4.8 PSI and a particle size of 200 mesh. The results showed that, under these conditions, gold recovery reached 96.8%, whereas at lower pressure values (2 PSI), the recovery decreased to 85%. The pressure oxidation process significantly enhanced sulfide oxidation and facilitated subsequent gold extraction. The experimental data demonstrated that the variable with the greatest influence on the process was oxidation pressure, followed by particle size and residence time. Furthermore, the study confirmed that appropriate control of operating variables is essential to optimize oxidation efficiency, reduce processing costs, and maximize gold recovery from refractory ores. These findings highlight the potential application of autoclave technology as a sustainable and effective method for refractory gold processing in the mining industry.

1. Introduction

Refractory tailings, characterized by the presence of sulfides (pyrite and arsenopyrite), encapsulate gold and silver, making their recovery through direct cyanidation difficult. Pressure oxidation in an autoclave (POX) is a more efficient and environmentally friendly alternative to roasting, as it reduces the emission of SO₂ and gaseous arsenic.

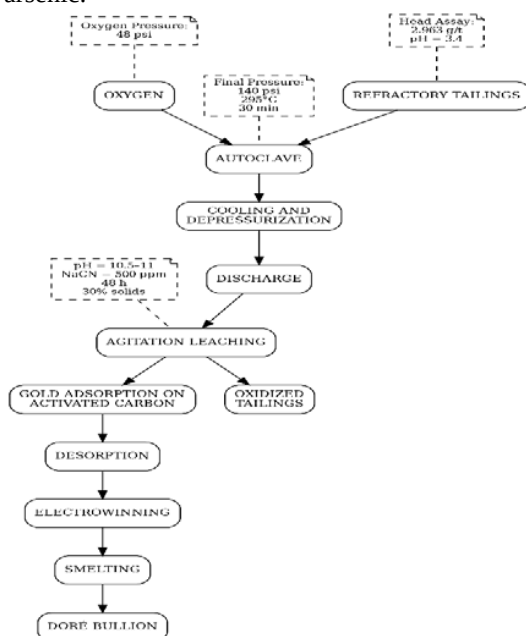


Figure 1. Flow diagram of sulfide oxidation and gold leaching

2. Materials and Methods

2.1. Materials and Equipment

Materials

- Refractory tailings composed mainly of pyrite and arsenopyrite.
- Stainless-steel vertical autoclave equipped with pressure and temperature control systems.
- Industrial oxygen cylinder fitted with a pressure gauge.
- Mechanical agitator with rotational speed (rpm) control.
- Digital pH meter.
- Burette.

Reagents

- Sodium cyanide (NaCN).
- Potassium iodide (KI).
- Silver nitrate (AgNO₃).
- Sodium hydroxide (NaOH).

2.2. Experimental Procedure

2.2.1. Sample Preparation for Metallurgical Tests

The refractory gold tailings used in this study were obtained from a pyrite- and arsenopyrite-bearing mining area located in the Conga Community, Cajamarca, Peru.

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The material served as the feed sample for all metallurgical tests.

Table 1. Weight of refractory tailings used for metallurgical testing.

No.	Sample	Weight (kg)
1	Tailings	8

2.2.2. Head Grade of the Tailings

Table 2. Head grade of the refractory tailings.

Sample	Element	Grade (g/t)
Tailings	Au	2.963

2.2.3. Autoclave Oxidation of the Refractory Tailings

Pressure oxidation experiments were carried out using industrial oxygen with a purity of 99.5%. The oxidation tests were conducted in a laboratory-scale autoclave reactor equipped with an electrically heated jacket. Oxygen was injected into the reactor through a dedicated gas inlet line connected to the autoclave.

Homogenized samples were used throughout all experiments. Each test commenced upon oxygen injection into the reactor. Prior to each experiment, the oxygen feed pressure was adjusted considering the sum of the water vapor pressure at the operating temperature and the desired oxygen overpressure.

Operating Conditions for Pressure Oxidation Tests

For each oxidation test, 1 kg of refractory tailings with a gold grade of 2.963 g/t, moisture content of 5.8%, and an initial pH of 3.4 was used.

Table 3. Operating conditions for pressure oxidation tests.

Test No.	O, Pressure (psi)	Final Pressure (psi)	Temperature (°C)	Time (min)
01	30	65	285	15
02	48	65	285	30
03	30	140	285	30
04	48	140	285	15
05	30	65	295	30
06	48	65	295	15
07	30	140	295	15
08	48	140	295	30

2.2.4. Cyanide Leaching Tests

Operating Conditions for Leaching Experiments

Agitated cyanide leaching tests were performed using the dried oxidation residues obtained from the autoclave treatment. Sodium cyanide was employed as the leaching reagent at a concentration of 500 ppm. The pH was maintained between 10.5 and 11.0 using sodium

hydroxide, and the pulp density was adjusted to 30 wt.% solids. All leaching experiments were conducted under continuous agitation for 48 h.

3. Results and Discussion

3.1. Results

3.1.1. Cyanide Leaching Tests

The results obtained from the cyanide leaching experiments performed on the refractory gold tailings are summarized in Table 4. The pregnant leach solutions obtained after 48 h of leaching were analyzed for gold content.

Table 4. Gold concentration in pregnant leach solutions.

Sample ID	Element	Result	Unit	Time
M001	Au	0.469	mg/L	48 h
M002	Au	0.533	mg/L	48 h
M003	Au	0.813	mg/L	48 h
M004	Au	0.724	mg/L	48 h
M005	Au	0.635	mg/L	48 h
M006	Au	0.698	mg/L	48 h
M007	Au	0.838	mg/L	48 h
M008	Au	0.940	mg/L	48 h

As shown in Table 4, the highest gold concentration in the pregnant solution was obtained for sample M008, reaching 0.940 mg Au/L after 48 h of leaching under a sodium cyanide concentration of 500 ppm.

3.1.2. Metallurgical Balance of the Leaching Process

Table 5. Metallurgical balance of gold recovery during cyanide leaching.

No.	Ore Weight (g)	Head Grade (g Au/t)	Au Content (mg)	Solution Grade (mg Au/L)	Au Recovered (mg)	Tailings Grade (g Au/t)	Au in Tailings (mg)	Recovery (%)
1	942.0	2.69	2.791	0.469	1.032	1.693	1.758	37
2	942.0	2.69	2.791	0.533	1.172	1.593	1.618	42
3	943.0	2.69	2.793	0.813	1.788	0.967	1.006	64
4	940.3	2.69	2.785	0.724	1.588	1.156	1.198	57
5	941.0	2.69	2.787	0.635	1.394	1.344	1.394	50
6	942.0	2.69	2.791	0.698	1.535	1.209	1.256	55
7	943.7	2.69	2.795	0.838	1.845	0.913	0.950	66

No.	Ore Weight (g)	Head Grade (g Au/t)	Au Content (mg)	Solution Grade (mg Au/L)	Au Recovered (mg)	Tailings Grade (g Au/t)	Au in Tailings (mg)	Recovery (%)
8	942.6	2.69	2.792	0.940	2.066	0.698	0.726	74

The metallurgical balance indicates that gold recovery increased substantially following pressure oxidation pretreatment. The highest recovery was achieved in Test 8, reaching 74%, whereas the lowest recovery corresponded to Test 1 with 37%. These results demonstrate the effectiveness of autoclave oxidation in enhancing gold accessibility during subsequent cyanide leaching.

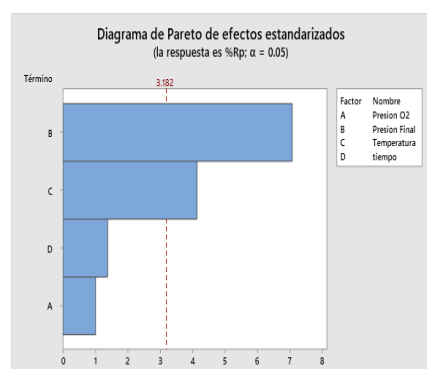
3.1.3. Analysis of Variance (ANOVA) and Pareto Chart

Table 6. Analysis of variance (ANOVA) for gold recovery as a function of oxygen pressure, final pressure, temperature, and retention time.

Source	DF	Adj SS	Adj MS	F-value	p-value
Model	4	1037.50	259.38	17.54	0.020
Linear	4	1037.50	259.38	17.54	0.020
Oxygen Pressure	1	15.13	15.13	1.02	0.386
Final Pressure	1	741.13	741.13	50.10	0.006
Temperature	1	253.13	253.13	17.11	0.026
Time	1	28.12	28.12	1.90	0.262
Error	3	44.38	14.79	—	—
Total	7	1081.88	—	—	—

The ANOVA results presented in Table 6 indicate that final pressure and temperature significantly affected gold recovery, with p-values of 0.006 and 0.026, respectively ($p < 0.05$). In contrast, oxygen pressure ($p = 0.386$) and retention time ($p = 0.262$) did not show statistically significant effects on the response variable.

Figure 2. Pareto chart of the standardized effects of oxygen pressure, final pressure, temperature, and retention time on gold recovery.



According to the Pareto chart, factors B (final pressure) and C (temperature) exceeded the significance threshold of 3.182, indicating a statistically significant influence on gold recovery. In contrast, factors A (oxygen pressure) and D (retention time) remained below the threshold value and therefore were not statistically significant within the experimental range evaluated.

3.2. Discussion

The experimental results demonstrated that pressure oxidation efficiency strongly depended on the operating conditions applied during the autoclave treatment. Under the optimum conditions of 295 °C, a final pressure of 140 psi, and an oxygen pressure of 48 psi, oxidation was completed within approximately 30 min, resulting in the highest subsequent gold recovery. In contrast, experiments performed at temperatures below 285 °C combined with a final pressure of 65 psi and an oxygen pressure of 30 psi exhibited slower oxidation kinetics and only partial sulfide conversion after 15 min of treatment. These findings indicate that elevated temperature and pressure favor sulfide decomposition and improve the liberation of encapsulated gold particles.

The metallurgical balances revealed a significant increase in gold recovery after pressure oxidation pretreatment. Test 8 achieved the highest recovery (74%), whereas Test 1 showed the lowest recovery (37%). This behavior confirms that adequate oxidation conditions improve the accessibility of cyanide to gold-bearing minerals and increase extraction efficiency.

The analysis of variance (ANOVA) demonstrated that final pressure and temperature were the most influential variables affecting gold recovery. Final pressure significantly enhanced oxygen availability within the slurry, accelerating oxidation reactions, while temperature increased reaction kinetics and sulfide conversion efficiency. Conversely, oxygen pressure and retention time exhibited lower statistical significance, suggesting that these parameters may be maintained within fixed operating ranges without considerably affecting process performance.

The Pareto chart supported the ANOVA results by identifying final pressure and temperature as the dominant variables governing gold recovery. Similar observations have been reported in previous studies, where pressure oxidation efficiency was strongly associated with operating pressure and temperature conditions.

These findings are in agreement with those reported by Soto-Urbe et al. [1], who demonstrated that pressure oxidation significantly improves gold extraction from refractory sulfide concentrates. Likewise, Gudyanga et al. [2] reported that oxidative pretreatment under acidic

conditions increases mineral liberation and enhances subsequent cyanidation efficiency. Furthermore, Lemos et al. [3] concluded that pressure oxidation represents one of the most effective technologies for processing refractory gold ores because of its rapid kinetics and improved metallurgical performance.

Compared with conventional roasting, pressure oxidation offers important environmental advantages, including lower atmospheric emissions and reduced formation of hazardous compounds. According to Soto-Urbe et al. [1], pressure oxidation minimizes sulfur dioxide generation while maintaining high oxidation efficiencies. Therefore, the application of autoclave technology represents a sustainable alternative for refractory gold processing.

From an industrial perspective, the results obtained in this study demonstrate that pressure oxidation in an autoclave can substantially improve gold recovery while optimizing operating conditions. Consequently, this technology has considerable potential for increasing the economic viability of refractory ore processing and promoting more sustainable mining practices.

4. Conclusions

1. Pressure oxidation (POX) pretreatment in an autoclave proved to be a more efficient and environmentally safer alternative than conventional roasting for the treatment of refractory gold tailings.
2. The optimum operating conditions identified in this study were 295 °C, a final pressure of 140 psi, an oxygen pressure of 48 psi, and a retention time of 30 min.
3. Final pressure and temperature were the most significant variables influencing gold recovery, whereas oxygen pressure and retention time exhibited comparatively lower statistical significance.
4. Precise control of the operating variables is essential to maximize sulfide oxidation efficiency and enhance subsequent gold recovery during cyanide leaching.

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Optimization of Hydrothermal Synthesis of Lanthanum-Cobalt Perovskite (LaCoO₃): Influence of pH, Stoichiometry, and Sintering Temperature

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Abstract. The aim of this study was to synthesize high-purity LaCoO₃ (LCO) using a wet-chemistry hydrothermal route and to systematically evaluate how synthesis parameters affect phase purity and material properties. The effects of the reactant molar ratio, pH, and calcination temperature on the microstructure, morphology, and phase composition of LCO were investigated. Particular attention was given to the formation of the La₂O₃ impurity phase, as even small amounts can significantly influence the physicochemical behaviour of the perovskite. Characterization by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis showed that the reactant molar ratio La:Co:citric acid is the most critical factor for reaching phase-pure LCO. Nearly single-phase LCO was achieved at a molar ratio of 1:1.2:1. Calcination at 750 °C resulted in higher phase purity and improved crystallinity as compared to 1150 °C, indicating that excessive temperatures may promote decomposition or impurity phase formation. Furthermore, pH had a significant effect on the final phase composition. A basic pH led preferably to LCO phase formation rather than La₂O₃. Overall, the study demonstrates that careful optimization of reactant ratios, starting mixtures pH, and calcination conditions is essential for obtaining high-purity, nearly single-phase LCO.

1. Introduction

Lanthanum cobaltite (LaCoO₃, LCO) is a rare-earth ABO₃ perovskite-type oxide widely studied for its catalytic, magnetic, semiconducting, and oxygen ion-conducting properties [1-5]. Due to its structural flexibility, high chemical and hydrothermal stability, and excellent oxygen mobility, LCO is considered a promising material for catalytic, photocatalytic, and electrochemical applications. The physicochemical properties of LCO strongly depend on the synthesis route, which influences crystallinity, morphology, particle size, surface area, and especially phase purity [6-8]. However, obtaining phase-pure LCO remains challenging because secondary phases, such as La₂O₃ or Co₃O₄, are frequently formed during synthesis.

As recently examined, La₂O₃ impurities enhance cefixime degradation ($k_{app} = 3.25 \times 10^{-3} \text{ min}^{-1}$) as co-catalysts in impurity-modulated LCO samples [9]. Although several studies have reported phase-pure LaCoO₃ synthesized via citrate methods [10], sol-gel approaches [11], freeze-drying-assisted precursor routes [12], and hydrothermal methods [13-14], a systematic understanding of the relationship between synthesis conditions and phase evolution is still limited. Therefore, this work investigates

the influence of the reactant molar ratio, pH, and calcination temperature on the phase composition and morphology of hydrothermally synthesized LaCoO₃ powders.

2. Materials and LCO synthesis

The reactants were purchased commercially and used as received without further purification: lanthanum(III) nitrate hexahydrate (La(NO₃)₃·6 H₂O, ≥96%, Merck), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6 H₂O, 99.2%, Lach-ner), citric acid anhydrous (C₆H₈O₇, ≥98.5%, Lach-ner), polyethylene glycol 400 (PEG 380-420, Ph.Eur., Roth), ammonium hydroxide solution 24.0% (NH₄OH, 99.2%, Penta), and ethyl alcohol (C₂H₅OH, 99.8%, Lach-ner). The LCO powder samples were synthesized via a citric acid-assisted hydrothermal route as schematically depicted in Figure 1. The La(NO₃)₃·6 H₂O and Co(NO₃)₂·6 H₂O were separately dissolved at room temperature (RT) in demineralized water under vigorous magnetic stirring to prepare 0.5 mol·L⁻¹ solutions. Citric acid (CA), acting as a chelating agent, was added to the mixed solution, which was then stirred for the next 1 h. The initial pH, measured with a digital pH meter (pHénoménal 1100 L, VWR, USA), was acidic (1.30-

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1.60). While maintaining continuous stirring, the pH was gradually adjusted dropwise with ammonium hydroxide solution to 7.05-10.0, depending on the design of the experiment. Immediately after pH adjustment, the mixture was transferred to a 50 mL PTFE-lined stainless-steel autoclave filled to approximately 80 % of its volume, sealed, and heated at 150 °C for 20 h in a laboratory dryer (SLW-53-W STD, POL-EKO Aparatura, Poland). The autoclave was then allowed to cool naturally to RT. The resulting precipitates were collected by centrifugation, sequentially washed with ethanol and demineralized water, and air-dried at 120 °C for 12 h. The dried powders were manually ground in an agate mortar and calcined in alumina crucibles under 2 different conditions: (i) 750 °C for 2 h, and (ii) 1050 °C for 10 h (LHS 08/15, LAC, Czech Republic) without controlled cooling. The final black LCO powdery samples were collected in vials and stored in a glovebox under an inert N₂ atmosphere to preserve any phase formed during synthesis. Milled precipitates and calcined powders had electrostatic surface charging, which required appropriate handling.

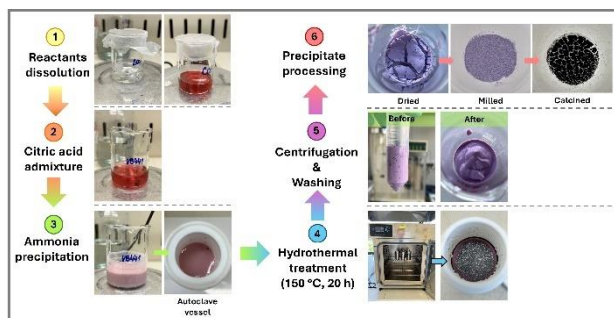


Figure 1. Schematic diagram illustrating the stepwise LCO synthesis.

3. Characterization techniques

The powder X-ray diffraction (PXRD) data at RT were collected in reflection mode with monochromated Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) on a Rigaku Smartlab 3 kW diffractometer (Rigaku, Japan) operated at 30 mA and 40 kV. Data were collected over a 2θ range of 10–100° with a step size of 0.02° and a scan rate of 3°·min⁻¹. Quantitative phase analysis was performed using the Rietveld method. Surface morphology imaging was performed using a field-emission scanning electron microscope (SEM) Verios 460L (FEI, Czech Republic) operating in immersion mode at an accelerating voltage of 5 kV and a probe current of 0.2 nA. SEM images were obtained using secondary electron (SE) and backscattered electron (BSE) detection modes. To prevent electrostatic charging of the studied powders, a 20 nm thick carbon layer was deposited on their surfaces using the EM ACE600 (Leica Microsystems, Germany).

The specific surface area of the LCO samples was determined from the measured adsorption/desorption isotherms using a Micro 300 C1 surface area analyser (3P Instrument, BET-ANAMET). Prior to measurements, each calcined sample was degassed at 150 °C for 10 h under vacuum. Nitrogen served as the adsorbate gas, with the bath temperature maintained at liquid nitrogen temperature.

4. Results and discussion

4.1. Hydrothermal synthesis of LCO

LCO samples were successfully synthesized using an autoclave hydrothermal method followed by calcination. In total, 11 samples listed in Table 1 were synthesized in order to obtain a single-phase LCO sample. Basically, 4 experimental conditions were investigated: (i) variation of the molar ratio of reactants, (ii) adjustment of the pH before autoclave treatment, (iii) selection of the calcination temperature in air, (iv) choice of the type of chelating agent. The obtained sample yields and calcination losses are listed in Table 2.

Table 1. Experimental conditions used for LCO samples synthesis.

Sample	La:Co:CA reactant molar ratio*	La:Co:PEG400 reactant molar ratio*	Calcination temperature [°C]	Final pH
LCO1	1:1:1	-	750	8.46
LCO2	1:1:0.5	-	750	8.46
LCO3	1:1:1	-	1050	8.46
LCO4	1:1:1	-	750	10.0
LCO5	1:1:1	-	750	7.05
LCO6	1:1.2:1	-	750	8.50
LCO7	1:1.2:1	-	750	8.51
LCO8	1:1.2:1	-	750	7.96
LCO9	1:1.3:1	-	750	8.49
LCO10	1:1.2:2	-	750	5.70
LCO11	-	1:1:0.005	750	8.27

*reactants: La - La(NO₃)₃·6 H₂O;

Co – Co(NO₃)₂·6 H₂O, CA - citric acid anhydrous.

Table 2. Summary of yields and calcination losses of synthesized LCO samples.

Sample	Yield after drying [g]	Yield after calcination [g]*	Calcination loss [%]
LCO1	1.7	0.8	45
LCO2	1.2	0.7	40
LCO3	1.8	0.8	45
LCO4	1.1	0.5	36
LCO5	1.6	0.7	51
LCO6	1.9	0.7	57
LCO7	1.9	0.7	57
LCO8	1.9	0.9	44
LCO9	2.0	1.0	43
LCO10	2.0	1.0	45
LCO11	0.65	0.28	29

*major amount of dried sample was used for calcination, a minor amount of sample, approximately 200 mg was stored for further analysis under an inert atmosphere of a glovebox, as their metastability was proved further.

4.2. Phase analysis using X-ray diffraction

Hydrothermally synthesized powders were amorphous; in contrast, the calcined samples exhibit high crystallinity of the detected phases. The summary of quantitative phase analysis obtained from the Rietveld refinement is listed in Table 3.

Table 3. Quantitative phase analysis results of calcinated LCO samples.

Sample	Phase fraction [wt.%]		Sample	Phase fraction [wt.%]	
LCO1	LCO	92.2	LCO7	LCO	99.2
	La ₂ O ₃	7.8		La ₂ O ₃	0.8
LCO2	LCO	68.1	LCO8	LCO	97.8
	La ₂ O ₃	31.9		La ₂ O ₃	2.2
LCO3	LCO	87.8	LCO9	LCO	~ 99.0
	La ₂ O ₃	12.2		La ₂ O ₃	~ 1.0
LCO4	LCO	69.7	LCO10	LCO	85.2
	La ₂ O ₃	30.3		La ₂ O ₃	14.8
LCO5	LCO	56.5	LCO11	LCO	75.6
	La ₂ O ₃	43.5		La ₂ O ₃	24.4
LCO6	LCO	99.2			
	La ₂ O ₃	0.8			

Examination of the molar ratio effect of citric acid as a chelating agent ranged from 0.5 to 2.0. It was found that

the optimum value for synthesizing high-purity LCO is 1.0, corresponding to an equimolar ratio of lanthanum metal salt. In the case of sample LCO10 with a citric acid molar ratio of 2.0, pH adjustment was stopped at a value close to 6, since a further increase in pH either led to dissolution of the precipitate or to precipitation itself. It was also found that the molar ratio of the cobalt reactant significantly affected phase formation. An equimolar ratio of metal salts resulted in up to 90 wt.% LCO phase, while slightly higher Co-salt ratios of 1.2 and 1.3 in samples LCO6, LCO7, and LCO9 produced nearly single-phase compositions. An interesting fact is that, in addition to lanthanum oxide, the sample LCO9 also contained traces of lanthanum carbonate. In addition to the effect of the molar ratio, the hypothesis that cobalt ions could be washed out using demineralized water was examined. The comparative PXRD study of samples LCO6 and LCO7 after 1 and 4 washing cycles, respectively, showed no difference in their phase composition, therefore, the impact of this factor was determined to be insignificant. Precise pH control of the reaction mixture prior to hydrothermal treatment proved to be an important processing step. LCO samples were synthesized at pH values ranging from 5.7 to 10.0. The lowest pH of 5.7 applied for sample LCO10, in combination with a higher Co ratio, produced 85.2 wt.% of LCO phase. A slightly higher pH of 7 (LCO5), in combination with an equimolar reactant ratio, resulted in the lowest LCO content (56.5 wt.%), while the highest pH of 10 in the LCO4 sample produced 69.7 wt.% of the LCO phase. Based on these results, a pH of 8.5 was found to be optimal for the formation of nearly single-phase LCO perovskite. A higher calcination temperature of 1050 °C promoted the formation of the lanthanum oxide phase, indicating that the perovskite phase is metastable and transforms into a binary oxidic phase with increasing temperature. The above-presented results show that citric acid is an effective chelating agent that promotes the formation of nearly single-phase perovskites. Additionally, PEG 400 was used as a neutral agent for its complexation capability in comparison with citric acid. Unlike citric acid, PEG 400 does not provide significant buffering capacity, resulting in a rapid pH increase upon ammonia addition (three drops increased the pH from 3.2 to 7.5, followed by a slower increase to 8.3). PXRD analysis revealed that sample LCO11 contained 75.6 wt.% LCO, indicating that LCO crystal formation is still promoted with this type of chelating agent, although at a lower yield compared to the citric-assisted synthesis. The highest-purity samples synthesized with an excess of Co reactant (LCO6 and LCO7) at pH 8.5 exhibited the largest calcination loss of 57%, which may be related to stronger chelation agent activity and, according to PXRD results, to total combustion.

4.3. Surface morphology using scanning electron microscopy (SEM)

Figure 2 shows micrographs of the LCO samples. The calcined powders exhibit well-developed submicron structures composed of nearly spherical particles with a high pore density. Samples LCO1 and LCO9 show minimal particle agglomeration, whereas LCO3, LCO4,

LCO5, and LCO6 exhibit larger particle aggregates. Sample LCO2 consists of larger particles due to the higher calcination temperature (1050 °C). Well-defined grain boundaries and multiple junctions were observed in all sample morphologies except LCO4, where grain boundaries are merged.

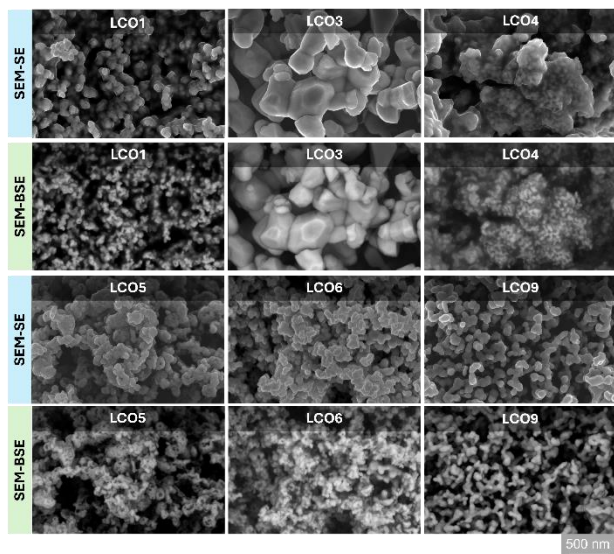


Figure 2. SEM micrographs of LCO samples acquired in SE and BSE imaging modes.

4.4. Brunauer-Emmett-Teller (BET) surface area analysis

Surface area characteristics determined by BET analysis of the selected calcined LCO samples are listed in Table 4. The surface areas ranged from 3.56 to 21.58 m²/g, with the highest value determined for LCO5 (pH 7, 1:1 La:Co cation ratio). As expected from the SEM and PXRD measurements, LCO3 (calcined at a temperature of 1050 °C) showed the lowest surface area (3.56 m²/g) and pore volume (~0.01 cm³/g). On the other hand, LCO5 and LCO9 exhibited significantly higher surface areas (21.58 and 10.14 m²/g, respectively) and pore volumes, both several times greater than those of LCO3.

Table 4. Surface area and porosity characteristics of selected calcined LCO samples.

Sample	Surface area [m ² /g]	Total pore volume [cm ³ /g]	Average pore diameter [nm]
LCO3	3.561	0.009	9.9
LCO5	21.584	0.056	10.3
LCO9	10.136	0.020	7.8

5. Summary

In recent years, perovskite materials have attracted the attention of materials scientists worldwide due to their exceptional catalytic and magnetic properties. In this study, the hydrothermal synthesis of LCO was investigated in detail, introducing a method for producing an exceptionally phase-pure crystalline LCO material.

Optimization of synthetic parameters yielded optimal molar ratios, pH, and calcination temperature for the production of a nearly phase-pure perovskite, specifically a La:Co:citric acid ratio of 1:1.2:1, a pH of 8.5, and a calcination temperature of 750 °C.

Acknowledgement

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The Role of Powder Size Distribution on the Flowability of Ceramic Thermal Spray Powders

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Abstract. Thermal spray technologies require powders with sufficient flowability to ensure stable feeding and reliable injection into the spray plume. However, ceramic powders, particularly those in the fine particle size range, exhibit different flow behaviour compared to metal powders due to lower density, higher interparticle friction resulting from surface morphology, stronger electrostatic charging, and sensitivity to ambient moisture. This contribution investigates the flowability of agglomerated and sintered prototype yttrium-stabilised zirconia (YSZ) powder and evaluates the suitability of commonly used powder metallurgy methods for thermal-spraying applications. The YSZ ceramic powder was sieved into five particle size fractions ranging from below 25 µm to above 75 µm. Powder flowability was evaluated using Hall, Gustavsson, and Carney flowmeters, Carr indices, angle of repose measurements, and GranDrum rheometry. Practical flowability was additionally verified using an industrial powder feeder for thermal spraying. The results showed that powder flowability generally improved with increasing particle size. Powders below 35 µm were not flowable through Hall and Gustavsson cups, while the Carney cup enabled flow measurement for all fractions except those below 25 µm. However, all fractions exhibited stable feeding behaviour in an industrial powder feeder. Moisture significantly increased the cohesivity of fractions with medium particle sizes.

1. INTRODUCTION

For almost five decades, thermal spray technologies have been successfully used to convert solid powder feedstocks into functional coatings [1]. However, these powders are available on the market only in a relatively limited range of chemical compositions, which directly determines their current industrial application. To enable thermal spray technologies to respond sustainably to current challenges and opportunities related to raw materials while expanding into new areas of application, it is necessary to develop new materials or alternatives to existing ones that are well-suited to the spraying process.

The ideal particle size range for powders used in thermal spray technologies is typically between 25 and 150 µm [1,2], often within a narrower particle size distribution. Powder particles larger than 150 µm are difficult to melt in the spray plume, whereas particles smaller than 25 µm tend to agglomerate and accumulate within thermal spray system hardware. Consequently, commercial powders classified by manufacturers for thermal spray applications predominantly belong to this particle size range and, with only a few exceptions, fulfil the requirement for sufficient flowability.

Powder flowability represents one of the most critical parameters in thermal spraying because powders are

commonly transported over medium or long distances from powder feeders, typically located outside the spray booth, to powder injectors mounted on plasma spray guns. These powders are subsequently injected into the plume under a compressed inert gas atmosphere. Powder flowability is influenced by numerous single-particle characteristics and interparticle interactions, including material density, particle shape, mechanical interactions, electrostatic forces, and reactivity with the surrounding environment, among many other less significant factors [1–3]. In general, powders with particle sizes below 25 µm are easier to feed when they are metallic or cermet materials, primarily due to their higher density, easier spheroidisation, lower electrostatic charging caused by friction, and lower atmospheric reactivity compared to ceramic powders.

Over time, a variety of methods have been developed and standardised for the characterisation of powder flow properties. Among the most commonly used techniques in powder metallurgy are the Carr indices [2–4], including angle of repose, aerated and tapped bulk densities, compressibility, cohesion, and uniformity. Additional commonly applied methods include particle size distribution analysis, powder rheometry, and powder

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charge analysis, all of which are among the most popular in the field of powder metallurgy [4–6].

The contribution focuses on the flowability of an agglomerated and sintered yttrium-stabilised zirconia (YSZ) ceramic powder and evaluates the reliability of commonly used powder metallurgy methods for the characterisation of thermal spray powders.

2. MATERIALS AND METHODS

2.1. Preparation of Ceramic Powder

An agglomerated and sintered prototype YSZ powder (Treibacher Industrie AG, Austria) was sieved using an AS200 Control sieve shaker (Retsch GmbH, Germany) into six thermal spray powder fractions: below 25 µm, 25–35 µm, 35–45 µm, 45–75 µm, above 75 µm. The powders were measured both in the as-received state and after heat treatment in a laboratory drying oven (SLW-53-W STD, POL-EKO Aparatura, Poland) at 200 °C for 8 h prior to measurement. Each fraction was examined both from the surface and in cross-section by means of scanning electron microscopy (SEM; Lyra3, Tescan, Czechia). The powder morphology was observed and documented in the secondary electron (SE) mode, while the cross-sectional micrographs were acquired in backscattered electron (BSE) mode. Cross-sections of the powder metallographic samples were prepared using standard metallographic procedures, including cold mounting, wet grinding, and polishing using diamond suspensions.

2.2. Laboratory Testing of Powder Properties

The Hall [7], Carney [8], and Gustavsson [9] flowmeters, different in funnel cone angle and calibrated orifice diameter (Figure 1), were used to evaluate the flowability of each prepared powder fraction. The flow time required for the entire standardised powder volume to pass through the flowmeter orifice was recorded. In addition, the angle of repose was measured using light projection recording, and the obtained data were subsequently analysed using ImageJ software (v1.54t, NIH, USA). The aerated bulk density (ABD) was determined using a standardised volume container and a precision laboratory balance (PA214CM/2, OHAUS Europe GmbH, Switzerland). Subsequently, a graduated cylinder was filled with the same volume of aerated powder and subjected to 50 taps to determine the powder packed bulk density (PBD). Based on ABD and PBD values, the compressibility Eq. (1) and Hausner ratio Eq. (2) were calculated:

$$\text{Compressibility [\%]} = \frac{\text{PBD} - \text{ABD}}{\text{PBD}} \times 100 \quad (1)$$

$$\text{HR} = \frac{\text{PBD}}{\text{ABD}} \quad (2)$$

Additionally, a new rheometer type GranuDrum (GranuTools, Belgium) was used for rotational powder cohesion testing. Forward rotational speeds in the range of 2 to 32 rpm were applied. The rheometer software, based on the integrated image analysis, provided cohesive index values of the ceramic powder.

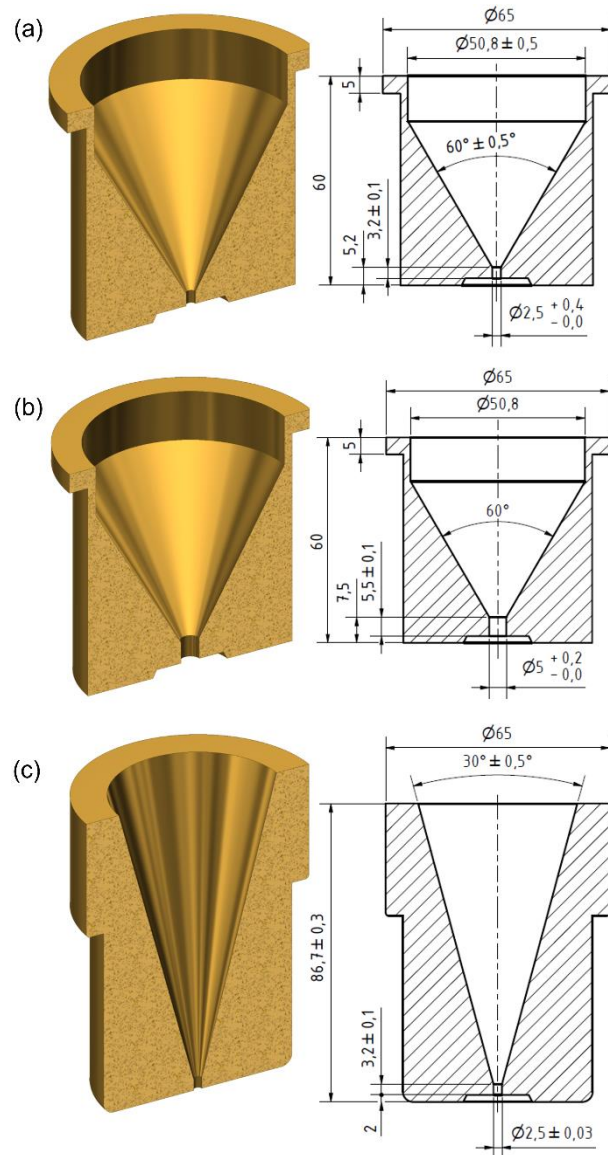


Figure 1. Schematics of the (a) Hall, (b) Carney, and (c) Gustavsson flowmeters.

2.3. Powder Feeder Testing of Powder Flowability

The flowability of the individual powder fractions was further tested directly using the industrially widespread thermal spray powder feeder PF 2/1LC (GTV GmbH, Germany) in order to verify the laboratory measurement results.

3. RESULTS AND DISCUSSION

The prototype YSZ ceramic powder exhibits a predominantly spherical morphology and, as apparent from its microstructure (see Figure 2), consists of individual particles that are sintered together. Typically, in every particle fraction, besides the particles of the specific sieved fraction, small satellite particles attached to their surface are also visible.

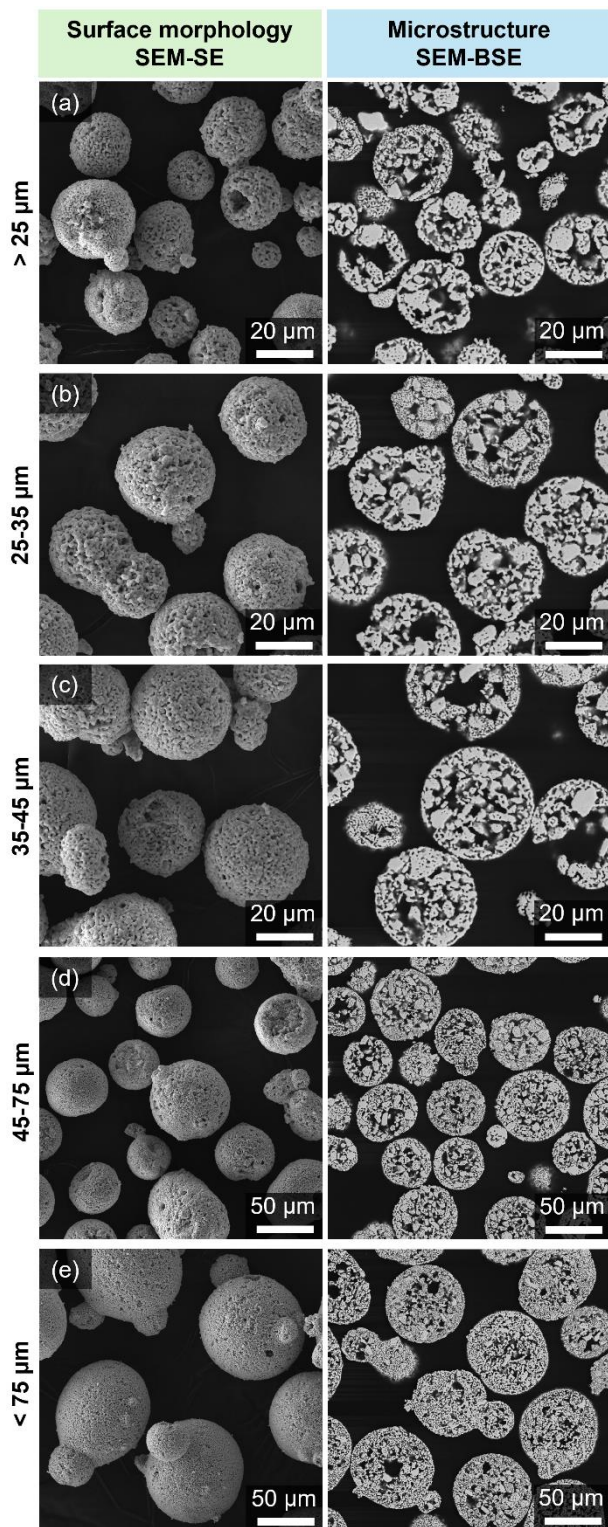


Figure 2. Surface morphology (SEM-SE, left) and cross-sectional microstructure (SEM-BSE, right) micrographs of the YSZ powder fractions: (a) below 25 μm , (b) 25–35 μm , (c) 35–45 μm , (d) 45–75 μm , and (e) above 75 μm .

The Carr indices provided confusing and not fully relevant results for the measured properties of the thermal spray powder. As can be seen in Figure 3, powder fractions with particle sizes below 35 μm were not flowable through the Hall and Gustavsson cups due to the

small orifice diameter. Surprisingly, after several taps, the ultrafine powder with particle size below 25 μm started to flow through the Gustavsson cup, likely due to its lower cone angle. Nevertheless, since initial tapping was required to initiate flow, the measurement was considered invalid. In the case of the Carney cup, powder flow was observed for almost all prepared size fractions except for the fraction below 25 μm . The results generally confirmed easier, faster powder flow with increasing particle size.

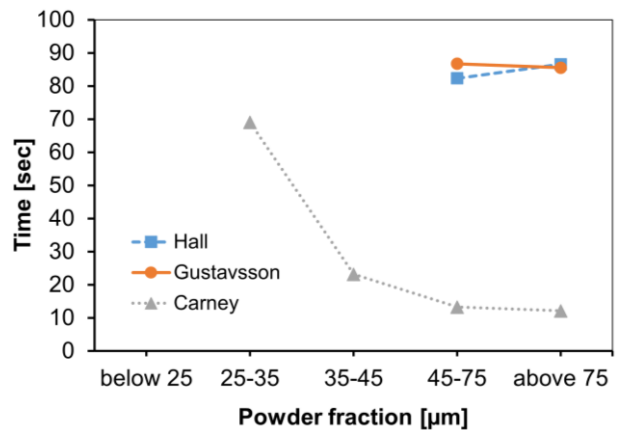


Figure 3. Powder flowability of all size fractions measured with different flowmeters (Hall–blue square, Gustavsson–orange dot, Carney–grey triangle).

The angle of repose ranged from 31° to 36°. Based on aerated and tapped bulk density measurements across all powder size fractions (Figure 4), the Carr Index was calculated, varying from 79–81%, suggesting good flowability. However, the Hausner ratio (4.6–5.2) indicates highly cohesive, non-flowing behaviour. Overall, the Carr indices suggest that for ceramic thermal spray powders, only the Carney cup provides limited and non-conclusive information on flowability.

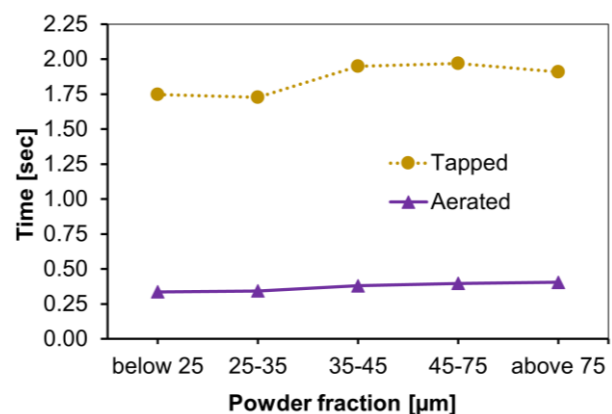


Figure 4. Comparison of aerated (purple triangle) and tapped (yellow dot) bulk density across powder size fractions.

The cohesive index values (Figure 5) measured using a GranuDrum rheometer [10] suggest acceptable flowability of the YSZ powders across all investigated

size fractions. The lowest values of cohesivity index, corresponding to the best flowability, were observed for the fraction above 75 μm . The highest cohesivity was found for the 25–35 μm and 35–45 μm fractions. In these size ranges, the highest moisture contribution was also observed, and the cohesivity index decreased significantly after prior powder pre-heating. This pre-heating effect was less pronounced for fractions below 25 μm and above 75 μm .

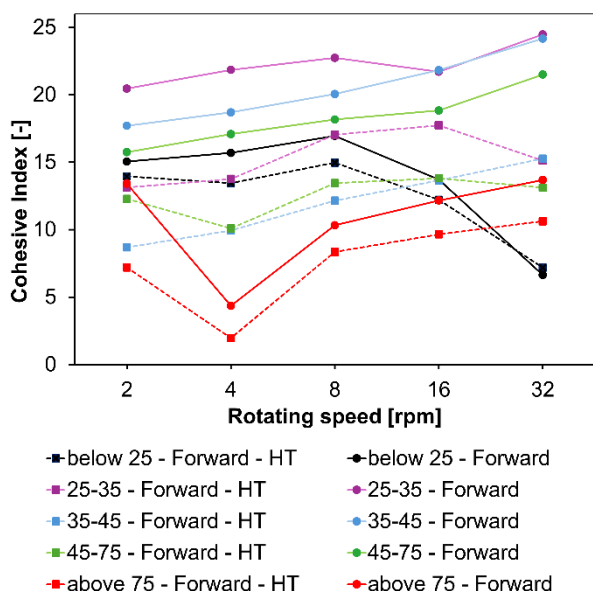


Figure 5. Cohesive Index (CI) across all particle size fractions, including powder, before (dot) and after heat treatment (HT, square).

For powder flow validation, the thermal spray powder feeder was used within a relatively short process window, typically applied by the thermal spray technology operator for powder feeding into the plume. The results showed excellent flowability for all powder sieve ranges, including the fraction below 25 μm , which was not observed to be flowable in the Carney cup flowmeter.

4. SUMMARY

The flowability of thermally sprayable ceramic powders decreases with a decreasing particle size compared to that of metals or cermets, where powder density can be considered the main critical parameter affecting powder flow.

The flowability of ceramic powders can be improved by modifying particle morphology, where particle spheroidization reduces mechanical interlocking, and by increasing particle size, resulting in a higher particle weight.

Electrostatic charge becomes more important for smaller particles below 25 μm , where particles tend to agglomerate.

Powder pre-heating prior to spraying, or heating the powder feeder vessel during spraying, significantly improves YSZ powder flowability by reducing moisture content in the particle size range of 25–75 μm .

Further investigation of powder flow mechanisms based on the initial powder compaction state and powder aeration prior to testing and thermal spraying is needed.

The Carr Index, Hausner Ratio, and avalanche angle measurement methods do not clearly describe the flow behaviour of YSZ ceramic thermal spray powders. Among the tested methods, only the Carney cup flowmeter provides information on guaranteed powder flow, although the results are still not entirely conclusive. Therefore, a reliable and rapid test method for ceramic thermal spray powder flowability still needs to be developed.

Acknowledgement

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Recycling of Lithium-Ion Batteries – the UPRAISE Project

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Abstract. The rapid growth in the production of electric vehicles and the stricter European Union (EU) recycling targets of 65 % (2025) and 70 % (2030) mean that end-of-life and production scrap from lithium-ion batteries are becoming an important source of secondary raw materials. In order to achieve these recycling targets in hydrometallurgy, efficient mechanical pre-treatment is particularly important. This work focuses on optimising mechanical pre-treatment using a combined vacuum grinding and drying unit. The material is dried in a mixing vessel, where the mixing blade applies additional stress to the shredded material, in particular the electrode foils. By optimising the stress intensity on the electrodes, the recovery rate of the black mass can be maximised whilst keeping impurities to a minimum. The aim of the UPRAISE project is to achieve black mass impurity levels of less than 3 wt %.

1. Introduction

The importance of recycling lithium-ion batteries is growing as the popularity of electric vehicles increases, production at the Gigafactories expands and regulations affecting the recycling industry become increasingly stringent due to the demand for greater independence from global raw materials markets. End-of-life (EoL) batteries and manufacturing waste now represent a major secondary supply of critical raw materials such as lithium, cobalt, and nickel.

A variety of recycling methods are already employed in industry, and for end-of-life batteries the valuable metals can be reclaimed through mechanical, hydrometallurgical or pyrometallurgical routes. The present study focuses on the mechanical pathway, which comprises a series of comminution and separation operations. A representative example is the LithoRec process [1] (see Fig. 1). The key stages are:

- Inert shredding – cells or modules are shredded in a nitrogen-purged chamber to suppress ignition
- Drying of the shredded fragments
- Mixing to increase the delamination of the electrodes
- First air classification – a zig-zag sifter removes heavy components (e.g., casings)
- A second grinding stage can be carried out to increase the black mass yield
- Sieving – Separation of the black mass fraction
- Second air classification – Separate the electrode foils from the separator

While this mechanical chain efficiently recovers the bulk of valuable materials, it shares the typical limitations of conventional mechanical recycling like high inert-gas consumption and a black-mass product that remains contaminated with copper and aluminum. Thus, the described mechanical process provides a practical

pathway for extracting critical raw materials from EoL batteries, but further optimization - particularly in electrolyte recovery and contaminant reduction - is required to meet the European Union's (EU) expanding recycling demand.

The UPRAISE project will provide a detailed understanding of the interdependencies between the individual stages of the recycling and recovery processes – from diagnosis and safe dismantling, through the processing of the black mass, to the production of high-performance battery materials. Within this project the mechanical pre-treatment of NMC- and LFP batteries will be investigated regarding black mass yield and purity, electrolyte recovery and energy consumption. The EU has set targets for overall recycling rates of 65% by the end of 2025 and 70% by the end of 2030. The objective of the UPRAISE project is to achieve an overall recycling rate of 75% for NMC processes and 77% in the LFP process.



Figure 1. Mechanical process chain LithoRec [1]

2. Methods and Objectives

The pre-treatment concept in UPRAISE aims to generate a high-purity black-mass from NMC and LFP batteries while lowering the environmental footprint. In conventional mechanical recycling the entire module is shredded and then dried whereby the volatile electrolyte solvents are often completely burned off. The yield of black-mass commonly contains Cu- and Al-impurities. In contrast, the approach which is used in UPRAISE employs a rapid, vacuum-based shredding and drying stage that separates the shredded materials from the

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volatile fraction in a single sealed chamber. The aim of process optimization in UPRAISE is to reduce the black mass impurities (Al and Cu) to < 3 wt %, increase the black-mass yield by roughly 15 % through optimized delamination from the electrode foils, and increase the recovery of the volatile electrolyte components by up to 80 % compared to non-vacuum processes.

For LFP batteries the process is refined further: crushing is performed on electrode stacks alone, leaving the remaining module parts, which can account for half the module weight, out of the feed stream. This selective comminution shall enable the production of a LFP black mass fraction with about 90 % purity.

In order to optimize the alignment of the mechanical pre-treatment with the subsequent thermal and hydrometallurgical processes, flow diagrams are first developed to define the key input and output parameters required for specific process steps. Therefore, cell analyses of the used modules are carried out first to determine the input composition; during the process, the recovered material fractions are analyzed and, where necessary, the processes are adjusted and optimized accordingly to ensure that the target parameters are achieved.

The mechanical pre-treatment process starts with the shredding of the discharged and short-circuited battery modules or electrode stacks to separate the individual components of the batteries. The use of an integrated vacuum shredding and drying unit offers a simultaneous fragmentation and drying of the modules under vacuum in a sealed chamber. This results in a reduced process time and energy consumption. In this process the shredded material falls into the mixing vessel where it is dried whilst being mixed. In this combined pre-module (Fig. 2), the volatile electrolytes are evaporated and condensed, which delivers a separate liquid stream with an efficient electrolyte recovery of 90–96 %. The use of a vacuum drying process also reduces the inert gas demand. Only a small, continuous nitrogen purge is required to protect the vacuum pump and manage vapors. This dramatically lowers nitrogen consumption and cost.

This combined pre-module also improves the separation and purity of the black mass. Real-time drying combined with optimized mechanical parameters (stress intensity) produces a black-mass with far fewer contaminants. The stress applied to the shredded material in the mixer ensures that, during this drying step, further stress is applied to the coated electrode foils thereby increasing the detachment of the coating from the foils. A high recovery rate of the black mass is particularly important here, as this is where the valuable components are found.



Figure 2. Used pilot plant, with pre-module (left) and product module (right)

A deeper understanding of the process is intended to identify the optimum stress conditions for comminution and mixing. Among other things, the kinetics of the detachment of the black mass from the electrode foils are to be investigated. The stress intensity must be sufficient to detach the coatings from the foils, but not so high that the foils themselves are further comminuted to sizes that fall within the size range of the black mass. Another factor in the mixing step is the evaporation of the electrolyte; it must therefore also be ensured that the material is thoroughly mixed to facilitate complete drying. Furthermore, the mixing time must be sufficiently long to guarantee complete drying. Preliminary investigations have already shown that a large proportion of the black mass is detached after a relatively short mixing time, and that further mixing only leads to the formation of additional impurities. Therefore, various requirements must be balanced against one another in this process step.

Following the pre-module, the various battery materials can then be separated from one another through subsequent separation steps in the product module (Fig. 2). The complex material system, comprising hard/compact materials, foil-like components, powders and liquid, makes this process especially complex. Once at least the volatile battery components have been removed from the shredded material in the mixer, the heavy components – such as parts of the module casing – are then separated using a zig-zag sifter. The remaining material is then passed through an air-jet tumbling sieve to separate the valuable black mass. A 500 µm sieve is planned to be used for this purpose. The use of an additional 2 mm sieve results in a total of three fractions. The black mass fraction (< 500µm) is then analyzed using XRF or ICP to determine the proportion of impurities, which mainly originate from crushed Cu and Al components. The aim is to achieve the highest possible yield of the black mass present in the modules, with the lowest possible level of impurities (< 3%).

In addition to the black mass, the copper and aluminum electrode foils are also valuable materials for which recovery is worthwhile. This recovery can be achieved, for example, using a zig-zag sifter. Once the heavy components, as well as the electrolyte and the black mass, have been separated, the remaining shredded

material consists mainly of copper, aluminum and separator foils. As the separator foils have a very low density, it is possible to separate them using a second sifting process. This as well requires appropriate parameter studies to be carried out to achieve the best possible separation of the materials for the given material system, in accordance with the modules used.

3. Summary

In order to recover as much of the critical raw materials from a battery as possible during battery recycling – and thereby also meet EU targets – efficient mechanical pre-treatment is especially important. The used mechanical pre-treatment consists of several comminution and separations steps like a combined shredder and mixer pre-module with a single vacuum unit. This offers a number of advantages in this respect such as the recovery of the electrolyte.

Key challenges in the process are determining the optimum energy input to detach the coating, as well as handling and separation of this complex material system, which consists of compact materials, foils, powders and liquid. If the electrode material does not receive sufficient stress, the black mass does not detach completely from the electrode foils; if the stress is too high, foil material is fragmented and contaminates the resulting black mass. The objective in UPRAISE is to produce a black mass with a contamination level of less than 3 wt %.

Through a cascade of different separation steps, it is possible to recover not only the electrolyte and the valuable black mass, but also the copper and aluminium components of the batteries in order to achieve a high overall recycling rate.

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