19th European Symposium on Comminution & Classification (XIX ESCC)
September 27–30, 2026, Naples - Italy

Stress-based modelling of mechanochemical reaction kinetics

Victor Marcus Oldhues[1,*], Sandra Breitung[2] and Arno Kwade[1]

[1] Institute for Particle Technology, Technische Universität Braunschweig, Brunswick, Germany
[2] Department for Mechanical Process Engineering / Particle Technology, Technische Hochschule Nürnberg, Nuremberg, Germany

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

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2\ NaCl \qquad (1)$$

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,

* Corresponding author: v.oldhues@tu-braunschweig.de

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.

$$E_m = \frac{\overline{SE} \cdot SN}{m_P} \tag{2}$$

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

$$SI = \frac{SE}{m_{P,act}} \tag{3}$$

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.

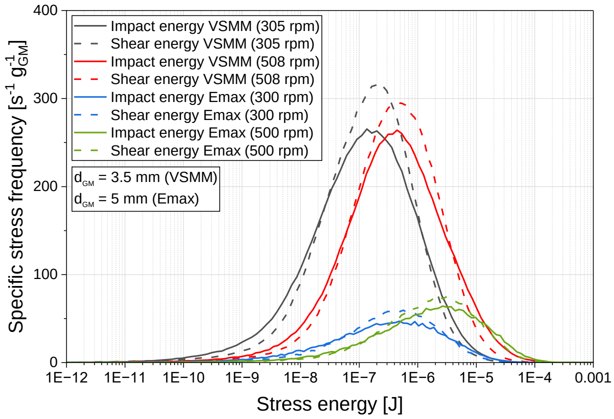

Figure 1. Exemplary stress energy distributions (impact and shear) for certain operation of the Emax and vertical stirred media mill from DEM simulations. The stress frequency is normalised to the grinding media mass.

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.

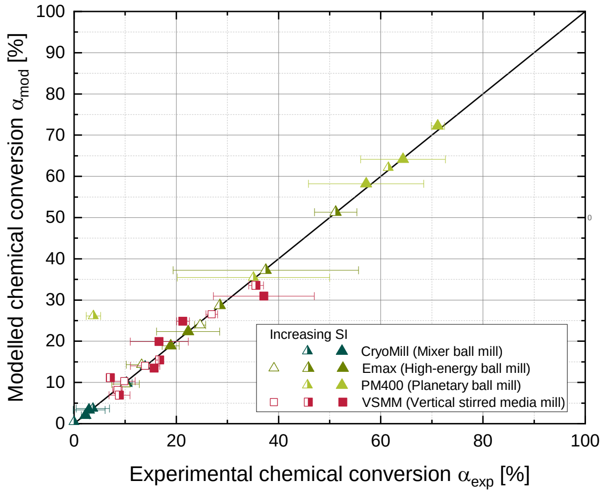

Figure 2. Exemplary model validation for the investigated mechanochemical reaction in the different ball mills including VSMM: The modelled chemical conversion is plotted against the experimentally measured degree of chemical conversion from purification

Acknowledgement

The German Research Foundation (DFG) is gratefully acknowledged for funding a significant part of the research in this work.

References

[1] James, S., Adams, C., Bolm, C., Braga, D., Collier, P., Friščić, T. et al. (2012) Mechanochemistry: opportunities for new and cleaner synthesis. Chemical Society Reviews, 41, 413–447.

[2] Oldhues, V. M., Dobreva, D., Borchardt, L., Kwade, A., & Breitung-Faes, S. (2025) Influence of different stress types on the mechanochemical CaCO3-synthesis. Powder Technology, 466, 121449.

[3] Prziwara, P., Hamilton, L. D., Breitung-Faes, S., & Kwade, A. (2018). Impact of grinding aids and process parameters on dry stirred media milling. Powder technology, 335, 114-123.

[4] Kwade, A., Schwedes, J. (2002) Breaking characteristics of different materials and their effect on stress intensity and stress number in stirred media mills. Powder Technology, 122, 109–121.

[5] Kwade, A. (2003) A Stressing Model for the Description and Optimization of Grinding Processes. Chemical Engineering & Technology, 26, 199–205.

[6] Schönert, K. (1991): Advances in comminution fundamentals and impacts on technology. Aufbereitungs-Technik, 32(9), 487-494.