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 [m²/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_c 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 consists 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.

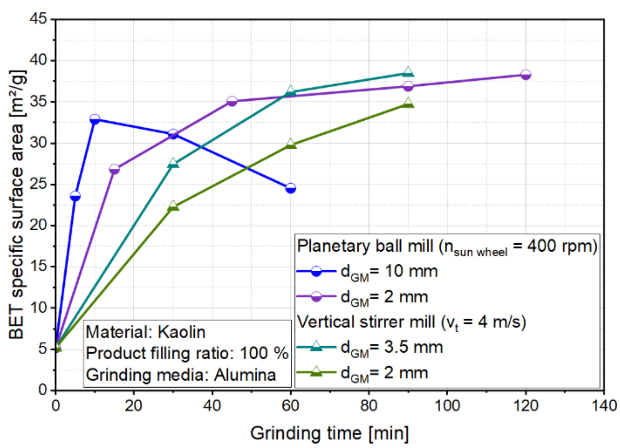

Figure 1. Values of BET specific surface area over the grinding time for trials with PM and SMM with two different grinding media size and constant rotating speed for each type of mills

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.

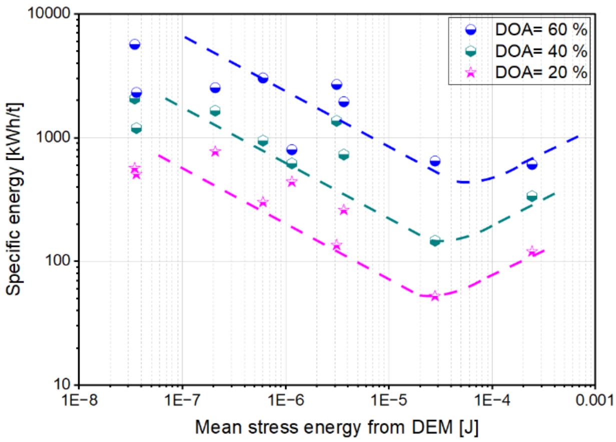

Figure 2. Required specific energy in relation to the applied mean stress energies acquired form DEM simulations for three vales of degree of amophousness.

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