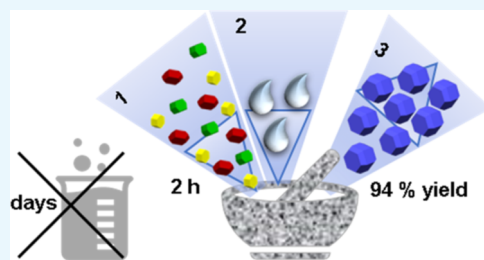


Ettringite via Mechanochemistry: A Green and Rapid Approach for Industrial Application

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ABSTRACT: Here, we report on a first mechanochemical synthesis of ettringite, an important cement hydrate phase. The mineral compound ettringite ($[\text{Ca}_3\text{Al}(\text{OH})_6]_2 \cdot (\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) occurs rarely in nature, but is common for cement-based materials. Ettringite has wide technical application in the ceramic and paper industry. However, its typical wet-chemical synthesis is cumbersome and produces waste water and CO_2 emissions. Here, we investigate the first mechanochemical synthesis of ettringite for developing an easy and sustainable alternative for industrial application. The mechanosynthesis was monitored in situ by coupled synchrotron X-ray diffraction (XRD) and infrared thermography (IRT). The consumption of the reactants and the formation of the reaction product were monitored with time-resolved XRD. IRT showed the temperature increase based on the exothermic reaction. The reaction conversion was significantly improved changing the strategy of the mechanosynthesis from a one- to a two-step process. The latter included neat pregrinding of solid reactants followed by a delayed addition of the stoichiometric amount of water. Thus, an increase of reaction conversion from 34 to 94% of ettringite could be achieved.



1. INTRODUCTION

Mechanochemistry has experienced significant development over the last decade. A variety of organic and inorganic materials and compounds were successfully synthesized via mechanochemical routes, including cocrystals, metal–organic frameworks, pharmaceuticals, alloys, and composites.^{1–19}

The increasing use of these mechanosyntheses benefits from their high efficiency, which allows improved reactivity and higher yields.^{15,20–23} Products of sufficient-to-high purity can be obtained, making additional purification steps redundant.²⁴ Solvent usage and chemical waste can be avoided, thus designating mechanochemical syntheses as “green chemistry”.

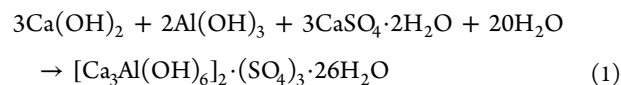
We applied mechanochemistry to synthesize ettringite, a significant constituent of the cementitious materials.^{25,26} Besides the importance for cementitious materials, ettringite is further used as a mineral filler and gloss-white pigment in ceramic and paper industry.²⁷ Furthermore, the channel structure of ettringite causes its high ion exchange capacity. This property can be exploited for the treatment of industrial wastes. Ion exchange properties can adversely influence the reliability of cement-based hazardous waste storages.^{28–36} Industrial synthesis of ettringite includes precipitation from the reactant containing suspension, along with product purification and dehydration.²⁷ Typical laboratory syntheses follow similar routes, thus remaining time and energy consuming and generating CO_2 emissions and waste water.^{36–39} Hence, a sustainable and clean synthesis of ettringite could be an alternative or a complementary way for the industrial applications.

The aim of this study is to explore the mechanochemical synthesis of ettringite toward possible industrial application. The mechanosynthesis was followed in situ by coupled

synchrotron X-ray diffraction (XRD) and infrared thermography (IRT) analyses. Consumption of reactants, possible intermediates, and products was monitored using time-resolved synchrotron XRD. On the basis of these data, intermediate stages can be identified and insights into the mechanism of the reaction can be obtained. Simultaneous tracking of temperature changes with IRT visualizes the heat release during the exothermic reaction as an additional indication of the reaction progress (Figure 1).

2. RESULTS AND DISCUSSION

The mechanosyntheses were performed according to the reaction (eq 1) in a vibration ball mill Pulverisette 23 (Fritsch, Germany) at the frequency of 50 Hz. The grinding experiments were carried out in the 10 mL poly(methyl methacrylate) (trade name: Perspex) grinding jar. The common use of the steel mill balls was avoided due to the possible incorporation of iron into the structure of ettringite through the replacement of aluminum. Instead, two zirconia balls with the diameter of 10 mm and the weight of 3 g each were used. Aluminum hydroxide $\text{Al}(\text{OH})_3$ (Kraft, $\geq 99\%$), calcium sulfate dihydrate $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (Kraft, $\geq 98\%$), calcium hydroxide $\text{Ca}(\text{OH})_2$ (Sigma-Aldrich, $\geq 96\%$), and water (Milli-Q, 18.2 $\text{M}\Omega \cdot \text{cm}$) were used as reactants.



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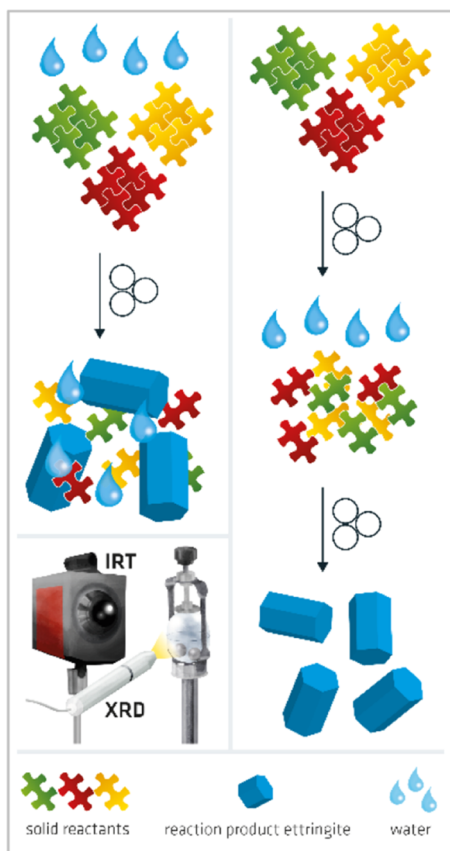


Figure 1. Schematics of the syntheses: left: one-step mechanochemical synthesis, right: two-step mechanochemical synthesis. Both processes were followed in situ by coupled IRT and synchrotron XRD analyses using the setup shown on the bottom left. Solid reactants include $\text{Ca}(\text{OH})_2$ (yellow), $\text{Al}(\text{OH})_3$ (green), and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (red).

The coupled in situ synchrotron XRD–IRT experiments were performed at Bessy II (HZB, Berlin). For further details on the setup and procedure of the coupled XRD–IRT analyses, the reader is referred to our previous publication.⁴⁰ The synchrotron beam with the energy of 12.4 keV was applied for the XRD analysis in transmission geometry. The diffractograms were detected with a time resolution of 30 s. An infrared camera was simultaneously used to detect temperature development on the surface of the grinding jar. Thermograms were recorded with a frame rate of 10 Hz. The relative temperature change ΔT was calculated as a difference between the temperature of the jar and room temperature.

The one-step mechanochemical synthesis includes filling in stoichiometric amounts of all reactants including water into the grinding jar and continuous grinding for 2 h. The product was a damp claylike mixture consisting of reactants and ettringite (Figure 2, left). It should be emphasized that the total amount of added water becomes incorporated into the structure of the formed ettringite if the complete reaction is achieved. Thus, the consistency of the resulting product indicates the presence of free water in the product mixture additionally suggesting the incomplete reaction. To assess the conversion of the mechanochemical synthesis, the XRD data were refined using the Rietveld method. The results show the formation of 34% ettringite and remaining 44% calcium sulfate dihydrate, 9% calcium hydroxide, and 13% aluminum hydroxide.

To improve the reaction conversion, a two-step mechanochemical synthesis with delayed water addition was carried out. First, solid reactants ($\text{Al}(\text{OH})_3$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$) were neatly ground for 90 min. Then, a stoichiometric amount of water was added directly into the grinding jar and the grinding was continued for the next 30 min. As a result, the formation of a fluffy white powder containing ettringite and a remaining low amount of gypsum was observed (Figure 2, right). From the

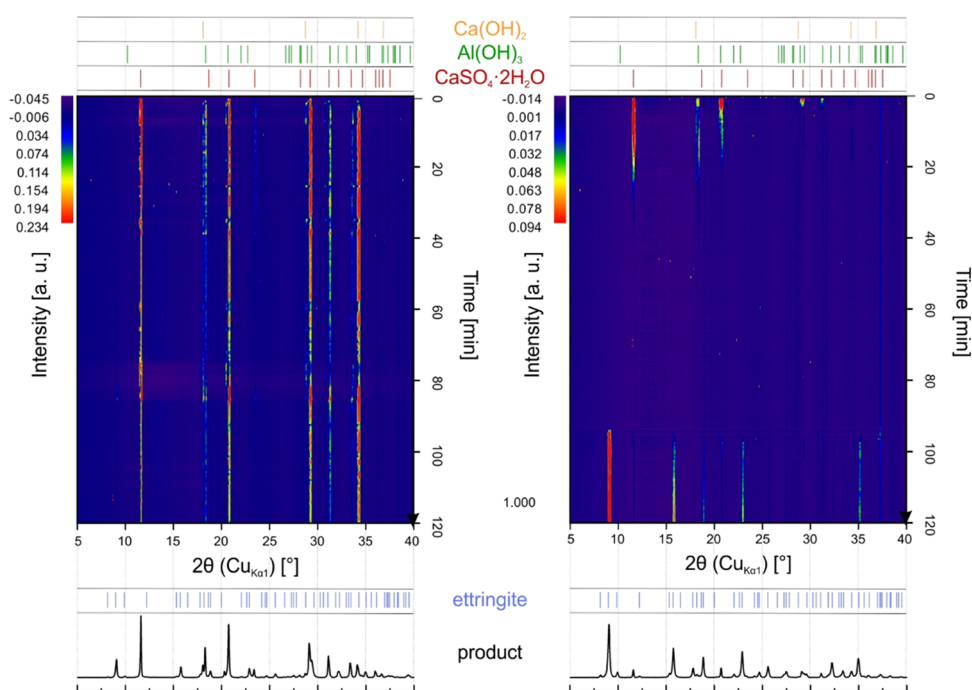


Figure 2. In situ XRD data of the mechanochemical ettringite formation. Left: one-step mechanochemical synthesis; right: two-step mechanochemical synthesis with delayed water addition after 90 min of neat grinding of solid reactants. Reflection positions of the reactants and ettringite are shown as barcodes. Bottom: the diffractograms of the product mixtures.

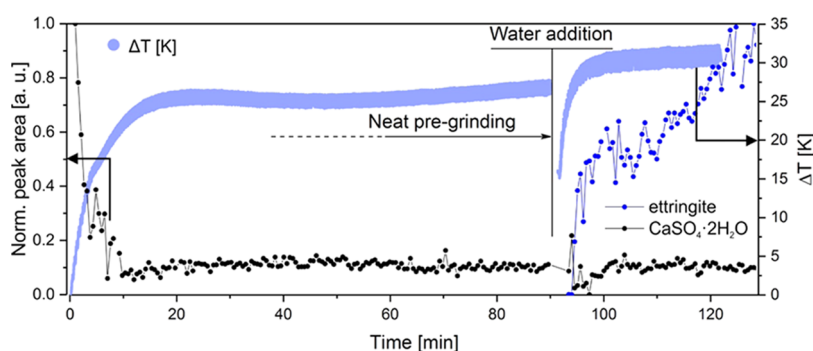


Figure 3. Time evolution of the temperature and the amounts of reactant and product in the reaction mixture. The temperature is shown as a difference to the room temperature (ΔT). The amounts of the compounds were assessed by calculating peak areas of their normalized diffraction signals: ettringite, reflection (1 0 0) at 9.1° ($\text{Cu K}\alpha_1$); calcium sulfate dihydrate, reflection (0 2 0) at 11.6° ($\text{Cu K}\alpha_1$).

Rietveld refinement, 94% of ettringite and 6% of gypsum were calculated. The formed ettringite can be assigned to PDF 00-037-147628 (PDF-2 2016). Disappearance of all reactant reflections after 30 min of the neat pre-grinding indicates the amorphization process. The influence of the neat pre-grinding duration on the reaction conversion is a subject of current research. The preliminary results indicate the insufficient reaction conversion similar to that in the one-step synthesis, if the pre-grinding duration is shorter than 90 min.

On the basis of XRD data, we estimated the amounts of some components of the reaction mixture, calculating the area of their main reflections. The amounts of the reactant, exemplarily gypsum, and ettringite in the reaction mixture were plotted over time and compared with temperature development (Figure 3). Addition of water into the jar causes a timely short abrupt decrease of the temperature. This is followed by the sharp rise of the temperature due to continued grinding and the intensive exothermic formation of ettringite. This observation allows concluding that neat pre-grinding of the solid reactants for 90 min leads to their activation. Thus, ettringite can be formed rapidly if the stoichiometric amount of water is added. Conversely, the availability of water at the beginning of the one-step mechanochemical synthesis strongly decelerates this reaction.

3. CONCLUSIONS

Summarizing, the strategy of the mechanochemical ettringite synthesis was optimized and the reaction conversion could be dramatically improved. The key factor is the delayed addition of water as liquid reactant after neat pre-grinding of the solids. Research is needed for a detailed understanding of the observed reactant amorphization during the neat pre-grinding, identification of amorphous intermediates, and their role in the mechanism of the mechanochemical reaction. The influence of the pregrinding duration on the reaction conversion is needed to be further observed.

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Notes

The authors declare no competing financial interest.

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