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

Julia Stroh,*†‡ Naveed Z. Ali,*‡ Christiane Maierhofer,‡ and Franziska Emmerling*†‡

Department of Structure Analysis and Reference Materials, Federal Institute for Materials Research and Testing (BAM) Berlin, Richard-Willstätter-Straße 11, 12489 Berlin, Germany

ABSTRACT: Here, we report on a first mechanochemical synthesis of ettringite, an important cement hydrate phase. The mineral compound ettringite ([Ca₃Al(OH)₆]₂·(SO₄)₃·26H₂O) 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 CO₂ 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 cocystals, metal–organic frameworks, pharmaceuticals, and composites. The increasing use of these mechanosyntheses benefits from their high efficiency, which allows improved reactivity and higher yields. Products of sufficient-to-high purity can be obtained, making additional purification steps redundant. 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. Besides the importance for cementitious materials, ettringite is further used as a mineral filler and gloss-white pigment in ceramic and paper industry. 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. Industrial synthesis of ettringite includes precipitation from the reactant containing suspension, along with product purification and dehydration. Typical laboratory syntheses follow similar routes, thus remaining time and energy consuming and generating CO₂ emissions and waste water. 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 Al(OH)₃ (Kraft, ≥99%), calcium sulfate dihydrate CaSO₄·H₂O (Kraft, ≥98%), calcium hydroxide Ca(OH)₂ (Sigma-Aldrich, ≥96%), and water (Milli-Q, 18.2 MΩ-cm) were used as reactants.

\[
3\text{Ca(OH)}_2 + 2\text{Al(OH)}_3 + 3\text{CaSO}_4\cdot2\text{H}_2\text{O} + 20\text{H}_2\text{O} \\
\rightarrow [\text{Ca}_3\text{Al(OH)}_6]_2\cdot(\text{SO}_4)_3\cdot26\text{H}_2\text{O}
\] (1)
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. 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 $\Delta T$ was calculated as a difference between the temperature of the jar and room temperature.

The one-step mechanosynthesis 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 mechanosynthesis with delayed water addition was carried out. First, solid reactants (Al(OH)$_3$, CaSO$_4$$\cdot$2H$_2$O, Ca(OH)$_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 1. Schematics of the syntheses: left: one-step mechanosynthesis, right: two-step mechanosynthesis. Both processes were followed in situ by coupled IRT and synchrotron XRD analyses using the setup shown on the bottom left. Solid reactants include Ca(OH)$_2$ (yellow), Al(OH)$_3$ (green), and CaSO$_4$$\cdot$2H$_2$O (red).

Figure 2. In situ XRD data of the mechanochemical ettringite formation. Left: one-step mechanosynthesis; right: two-step mechanosynthesis 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.
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 amorization 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 mechanochemistry 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 amorization 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.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: julia.stroh@bam.de. Phone: +49 (0) 30 8104 5849 (J.S.).
*E-mail: franziska.emmerling@bam.de. Phone: +49 (0) 30 8104 1133 (F.E.).

ORCID
Julia Stroh: 0000-0003-1153-0894
Franziska Emmerling: 0000-0001-8528-0301

Present Addresses
*Federal Institute for Materials Research and Testing (BAM), Department of Structure Analysis and Reference Materials, Richard-Willstätter-Straße 11, 12489 Berlin, Germany (J.S.).
*National Centre for Physics, Quaid-i-Azam University Campus, 45320 Islamabad, Pakistan (N.Z.A.).

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. Rainer Krankenhagen for the support in conducting the IRT measurements and for valuable discussion on the IRT data evaluation strategy.

■ REFERENCES

(1) Frisič, T. Supramolecular concepts and new techniques in mechnochemistry: cocrystals, cages, rotaxanes, open metal-organic frameworks. Chem. Soc. Rev. 2012, 41, 3493–3510.
(2) Batzdorf, L.; Fischer, F.; Wilke, M.; Wenzel, K. J.; Emmerling, F. Direct in situ investigation of milling reactions using combined X-ray diffraction and Raman spectroscopy. Angew. Chem., Int. Ed. 2015, 54, 1799–1802.
(3) Batzdorf, L.; Zientek, N.; Rump, D.; Fischer, F.; Mayer, M.; Emmerling, F. Make and break - Facile synthesis of cocrystals and comprehensive dissolution studies. J. Mol. Struct. 2017, 1133, 18–23.
(4) Fischer, F.; Heidrich, A.; Greiser, S.; Benemann, S.; Rademann, K.; Emmerling, F. Polymorphism of mechanochemically synthesized cocrystals: A case study. Cryst. Growth Des. 2016, 16, 1701–1707.
(5) Fischer, F.; Scholz, G.; Benemann, S.; Rademann, K.; Emmerling, F. Evaluation of the formation pathways of cocrystal polymorphs in liquid-assisted syntheses. CrystEngComm 2014, 16, 8272–8278.
(6) Kulla, H.; Greiser, S.; Benemann, S.; Rademann, K.; Emmerling, F. In situ investigation of a self-accelerated cocrystal formation by grinding pyrazinamide with oxalic acid. Molecules 2016, 21, No. 917.
(7) Chow, E. H. H.; Strobbridge, F. C.; Friscic, T. Mechanochemistry of magnesium oxide revisited: facile derivatisation of pharmaceuticals using coordination and supramolecular chemistry. Chem. Commun. 2010, 46, 6368–6370.
(8) Huang, Y. H.; Lo, W. S.; Kuo, Y. W.; Chen, W. J.; Lin, C. H.; Shieh, F. K. Green and rapid synthesis of zirconium metal-organic frameworks via mechanochemistry: UiO-66 analog nanocrystals obtained in one hundred seconds. Chem. Commun. 2017, 53, 5818–5821.
(9) Matoga, D.; Oszajca, M.; Molenda, M. Ground to conduct: mechanochemical synthesis of a metal-organic framework with high proton conductivity. Chem. Commun. 2015, 51, 7637–7640.
(10) Atkinson, M. B. J.; Bucar, D. K.; Sokolov, A. N.; Friscic, T.; Robinson, C. N.; Bilal, M. Y.; Sinada, N. G.; Chevannes, A.;...
MacGillivray, L. R. General application of mechanochemistry to templated solid-state reactivity: rapid and solvent-free access to crystalline supermolecules. *Chem. Commun.* 2008, 5713–5715.

(11) Bačič, P.; Achimovicova, M.; Balaž, M.; Billik, P.; Chekerzeva-Zeleva, Z.; Criado, J. M.; Delogu, F.; Dutkova, E.; Gaffet, E.; Gotor, F. J.; Kumar, R.; Mitov, I.; Rojac, T.; Senna, M.; Streletskii, A.; Wieczorek-Ciurowa, K. Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem. Soc. Rev.* 2013, 42, 7571–7637.

(12) Xu, C. P.; De, S.; Balu, A. M.; Ojeda, M.; Luque, R. Mechnochemical synthesis of advanced nanomaterials for catalytic nanoparticles to technology. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1970, B26, 386–393.

(13) Poellmann, H.; Auer, S.; Kuzel, H. J.; Wenda, R. Solid solution of ettringites: Part II: Incorporation of B(OH)₄⁻ and CrO₄²⁻ in 3CaO·Al₂O₃·3CaSO₄·32H₂O. *Cem. Concr. Res.* 1993, 23, 422–430.

(14) Garay, A. L.; Pichon, A.; James, S. L. Solvent-free synthesis of metal complexes. *Chem. Soc. Rev.* 2012, 41, 523–531.

(15) Balaž, M. K.; Clausen-Schaumann, H. Mechanosynthesis: The mechanical activation of covalent bonds. *Chem. Rev.* 2005, 105, 2921–2948.

(16) Munch, B.; Giroud, N. A natural cement analogue study to alternative to Portland cement. *Cem. Concr. Res.* 2009, 39, 1333–1339.

(17) Zhang, Q.; Saito, F. A review on mechanochemical syntheses of functional materials. *Adv. Powder Technol.* 2012, 23, 523–531.

(18) Mi, G.; Saito, F.; Hanada, M. Mechanochemical synthesis of tobermorite by wet grinding in a planetary ball mill. *Powder Technol.* 1997, 93, 77–81.

(19) Zhong, L. H.; Qu, J.; Li, X. W.; He, X. M.; Zhang, Q. W. Simultaneous synthesis of ettringite and absorbate incorporation by aqueous agitation of a mechanically prepared precursor. *RSC Adv.* 2016, 6, 35203–35209.

(20) Boldyrev, V. V.; Tkacova, K. Mechanochemistry of solids: Past, present, and prospects. *J. Mater. Synth. Process.* 2000, 8, 121–132.

(21) Boldyrev, V. V.; Tkacova, K. Mechanochemistry of solids: Past, present, and prospects. *J. Mater. Synth. Process.* 2000, 8, 121–132.

(22) Boldyrev, V. V.; Tkacova, K. Mechanochemistry of solids: Past, present, and prospects. *J. Mater. Synth. Process.* 2000, 8, 121–132.

(23) Nasser, A.; Minglegrin, U. Mechanochemistry: A review of surface reactions and environmental applications. *Appl. Clay Sci.* 2012, 67–68, 141–150.

(24) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. Mechanical activation of covalent bonds by acoustic agitation: a mechanochemically prepared precursor. *RSC Adv.* 2016, 6, 35203–35209.

(25) Lavrentyev, V. V.; Tkacova, K. Mechanochemistry of solids: Past, present, and prospects. *J. Mater. Synth. Process.* 2000, 8, 121–132.

(26) Liu, Y. J.; Xu, Y. M.; Geng, C. L. Sulfoaluminate cement: An alternative to Portland cement. *Adv. Mater. Res.* 2012, 368–373, 478–484.

(27) Lehmkuhl, J.; Wendt, A. D.; Bing, H. Mineralischer Füllstoff und Baustoff-Additiv auf Basis von Calciumaluminiumsulfat und deren Herstellung und Verwendung. Google Patent DE19611454A1, 1997.

(28) Alvarez-Ayuso, E.; Nugteren, H. W. Synthesis of ettringite: a way to deal with the acid wastewaters of aluminum anodising industry. *Water Res.* 2005, 39, 65–72.

(29) Gou, X.; Shi, H. Microstructure and heavy metal adsorption mechanisms of hydrothermally synthesized Al-substituted tobermorite. *Mater. Struct.* 2017, 50, 245.

(30) Martin, L. H. J.; Leemann, A.; Milodowski, A. E.; Mader, U. K.; Munch, B.; Giroud, N. A natural cement analogue study to understand the long-term behaviour of cements in nuclear waste repositories: Maqarin (Jordan). *Appl. Geochem.* 2016, 71, 20–34.

(31) Moore, A. E.; Taylor, H. F. W. Crystal structure of ettringite. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1970, B26, 386–393.