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Properties and Performance of Tricalcium Silicate Milled in a Planetary Ball Mill

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The focus in this study is on the effect of high energy milling on tricalcium silicate, the main constituent of ordinary Portland cement. Changes in the performance, e.g. hydration heat release, due to milling in a planetary ball mill (Pulverisette 5, Fritsch, Germany) were observed. For comparison, carefully milled tricalcium silicate was produced with the almost exactly same particle size distribution by mortar grinding (KM100, Retsch, Germany). In summary, the results indicate that due to high energy milling the performance of tricalcium silicate can be improved significantly: the hydration heat release is much higher at early hydration time. Also the peak and duration of the dormant period was shifted due to high energy milling. The X-ray diffraction analysis shows that the structure of the material changed in such a way that the amorphous content increases. Further results of surface analysis are shown in this study.

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1. Introduction

Ordinary Portland Cement (OPC) is one of the most commonly used building materials in the world. Its fabrication comes along with a resource- and energy-intensive process. On the one hand, there is an increasing requirement for cement (from today 2.5 up to 4 billion tons p.a. [1]) and a need for reduction of CO_2 emissions to slow or even stop global warming, on the other hand.

Many technics and methods are applied to reduce the Portland cement consumption, e.g. using composite material (granulated blast furnace slag, fly ash) or alternative binder systems (belite cement) [2, 3].

The possibility of an enhancement of cement performance due to high-energy milling to save OPC was investigated in this study.

2. Experimental

The main constituent of OPC, tricalcium silicate, was milled in two ways: first, high-energy milling via planetary ball mill was applied. For comparison with a moderate milling process a mortar grinder was used. After that, the specific surface areas according to Blaine were measured. At several finenesses hydration heat releases were recorded and taken in a relation to the specific surface areas. Here, hydration heat release was used as an indicator of hydraulic reactivity of tricalcium silicate.

2.1. Material

Tricalcium silicate $3CaO{\cdot}SiO_2$ was synthetically produced by burning process. Its chemical composition was analyzed by energy disperse X-ray spectroscopy (EDX) and is shown in Table I. EDX is a standard method for analyzing chemical composition of solid materials using the unique X-ray properties of the contained elements.

TABLE I

Chemical properties of used tricalcium silicate $3CaO{\cdot}SiO_2$ (EDX).

Component	wt.%
CaO	74.7
SiO_2	24.5
Al_2O_3	0.4
Fe_2O_3	0.2
SO_3	0.1
Rest	0.1

2.2. Grinding devices

For high-energy milling a Pulverisette P 5 (Fritsch, Germany) with hardened steel vial 250 ml and steel balls 20 mm were applied at 300 rpm and 80 g as well as a milling aid (diethylene glycol DEG). The mortar grinder KM 100 (Retsch, Germany) was used for careful milling of $3CaO{\cdot}SiO_2$.

2.3. Characterization methods

X-ray diffraction (XRD) was performed using a Siemens/Bruker D5000 θ-2θ-instrument with a CuK_α tube at 40 mA and 40 kV. For calculation of the amorphous content the external standard method with zincite was used [4]. Specific surface areas were measured with "hand-Blaine" apparatus. For DCA (isothermal heat flow calorimetry) measurement a ToniCal Trio (Zwick/Röll, Germany) and a water-binder ratio of 0.5 were applied at 25 °C.

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3. Results and discussions

In Table II specific surface areas according to Blaine are given. In planetary ball mill finenesses up to about 9.600 Blaine could be produced. In the opposite with mortar grinder much longer grinding times are necessary to reach these finesses.

TABLE II

Specific surface area of milled $3CaO{\cdot}SiO_2$.

$3CaO{\cdot}SiO_2$ milled in [min]	Milling time [cm^2/g]	Blaine
planetary mill	1	3430
planetary mill	5	5800
planetary mill	10	6380
planetary mill	20	7350
planetary mill	30	9630
mortar grinder	10	3600
mortar grinder	60	5100
mortar grinder	120	6030

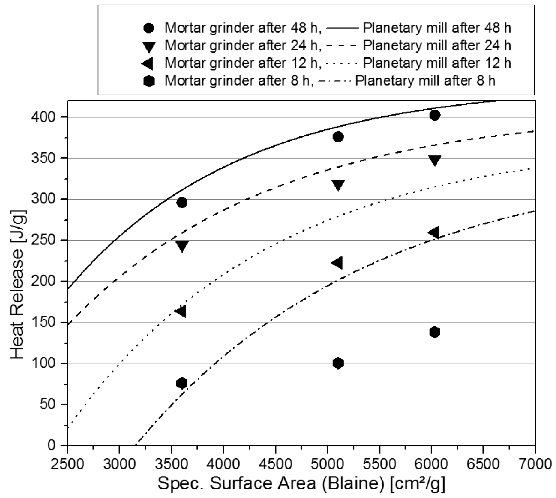

Fig. 1. Hydration heat releases of tricalcium silicate after planetary ball milling and mortar grinding.

Hydration heat release was measured up to 48 h. A combined illustration of fineness and hydration heat releases are shown in Fig. 1. Heat releases of $3CaO{\cdot}SiO_2$ milled in planetary mill at different finesses were fitted to one curve for better overview. It is notable principally that at high finenesses high-energy milling produces higher hydration heat releases than careful milling (mortar grinding). In fact, the dormant period of tricalcium silicate is shortened due to high-energy milling and following processes occurring much earlier with related hydration heat. At lower surface areas the differences between high-energy and carefully milled material are smaller. It seems that advantages of high-energy milling are neglected at low surface areas caused by very short milling and the associated small amount of crystal defects brought into the material structure. Another tendency is that the influence of high-energy treatment decreases with ongoing hydration time, which might be caused by relaxing effects like surface saturation.

TABLE III

Rietveld calculations of milled $3CaO{\cdot}SiO_2$.

	Planetary ball milling	Mortar grinding
micro strain [-]	0.31 ± 0.03	0.12 ± 0.02
crystallite size [nm]	$a = 44 \pm 9$	$a = 130 \pm 42$
	$b = 38 \pm 7$	$b = 69 \pm 11$
	$c = 36 \pm 7$	$c = 114 \pm 39$
amorphous content [wt.%]	8.2	6.2

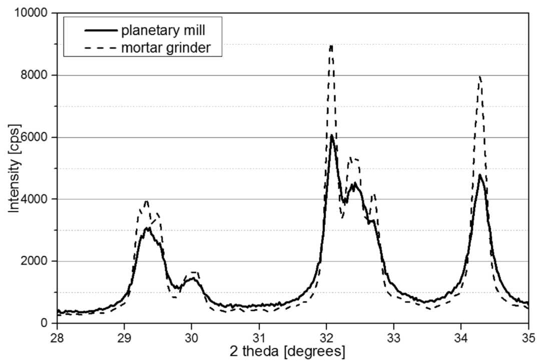

Fig. 2. X-ray diffraction patterns of milled tricalcium silicate.

X-ray diffraction patterns (Fig. 2) show a significant broadening of ball milled material. The Rietveld calculations are supporting these empirical impression. Results are presented in Table III. However, the micro strain is about three times higher due to high-energy milling. Even the calculated amorphous content as well as the crystallite size differ a lot from values of the material, milled in mortar grinder.

4. Conclusions

This paper was focused on the influence of high-energy milling on the reactivity and performance of tricalcium silicate. It was found that in relation to released hydration heat and structural parameters like micro strain or amorphous content the high-energy milling process in a planetary ball mill can significantly influence the milling product. However, in comparison with mortar grinder a much higher impact occurs at the same finenesses. These effects are recognizable at high specific surface areas. At low Blaine values these effects are almost disappearing.

References

[1] *Cement Technology Roadmap: Carbon emissions reductions up to 2050*, IEA International Energy Agency, 2009.

[2] H.-M. Ludwig, *Cement Int.* **10**, 80 (2012).

[3] G. Habert, C. Billard, P. Rossi, C. Chen, N. Roussel, *Cement Concrete Res.* **40**, 820 (2010).

[4] D. Jansen, C. Stabler, F. Goetz-Neunhoeffer, S. Dittrich, J. Neubauer, *Powder Diffr.* **26**, 31 (2011).