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Crystal structure refinement and hydration behaviour of $3CaO \cdot SiO_2$ solid solutions with MgO, Al_2O_3 and Fe_2O_3

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Abstract

In this paper, analytical evidence on crystal structure and hydration behaviour of $3CaO \cdot SiO_2$ (C_3S) solid solutions with MgO, Al_2O_3 and Fe_2O_3 is presented. Samples were prepared using an innovative sol–gel process as precursor. The Rietveld refinements of XRDs show significant changes in the crystal structures for C_3S solid solutions with MgO and Al_2O_3, but only small changes for Fe_2O_3. Low concentrations of MgO do not change the hydration of C_3S, but 1.4 wt.% increases the reactivity after some days. With Al_2O_3 the initial and long-term hydration is activated, but the main reaction of C_3S decreases. Fe_2O_3 retards the hydration for several days, the long-term reaction is not affected or even activated. Altogether changes in hydration activity are more dominated by the type of oxide than by the height of changes in lattice parameters. The results can help to interpret the reactivity of different Portland cements and improve the quality control of the cement production.

Keywords: Chemical properties; Impurities; Silicate; Sol–gel process

1. Introduction

With 52–85 wt.% alite ($3CaO \cdot SiO_2 = C_3S$) is the most important constituent in all ordinary Portland cement (OPC) clinkers. Other main constituents of OPC clinker are belite ($2CaO \cdot SiO_2 = C_2S$; 0–27 wt.%), aluminate ($3CaO \cdot Al_2O_3 = C_3A$; 7–16 wt.%) and ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3 = C_4AF$; 4–18 wt.%).[1] In an OPC clinker, the four phases are not pure stoichiometric compounds but form solid solutions with other oxides. Alite, for example, is a solid solution of tricalcium silicate with different minor oxides, such as MgO, Al_2O_3, Fe_2O_3 and alkali oxides. Due to the fact that the hydraulic reaction of alite dominates the strength development of Portland cement, the influence of minor components incorporated in C_3S is very important for the production and use of OPC.

The amount of minor and trace elements that can be incorporated into the crystal structure of C_3S and its influence on the crystal structure has been analysed by several authors.[2–11] In Table 1, different analyses about the content of foreign oxides in C_3S are summarized. These data show that the content of MgO, Al_2O_3 and Fe_2O_3 can vary with the kind of clinker in a wide range. At room temperature, pure C_3S only exists in the triclinic I modification (T I). The other six modifications (two triclinic, three monoclinic and a rhombohedral) are stable only at higher temperature or as solid solutions with stabilizing foreign oxides.[2,3,12] Table 2 shows the changes in modification of tricalcium silicate with different kinds and amounts of foreign oxides and the respective type of substitution. Not all of the polymorphic transformations can be monitored by XRD, because for some transformations the changes in the crystal structure are very small. The type of substitution depends on the ionic radii and preferred coordination. The amount of MgO that can be incorporated into C_3S is higher than that of Fe_2O_3 or Al_2O_3, because the ionic radius of Ca^{2+} is closer to Mg^{2+} than to Fe^{3+} or Al^{3+}. Especially for the solid solution of MgO in C_3S the solubility limit depends on the temperature. At 1420 °C, 1.5 wt.% MgO is incorporated into

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Table 1
Analyses of foreign oxides in alite occurring in different OPC clinker[2–5]

	Fe_2O_3	Al_2O_3	MgO	Na_2O	K_2O
Minimum	<0.1	0.6	0.1	<0.1	<0.1
Maximum	4.5	2.7	2.1	1.2	0.9
Typical	0.7	1.0	0.8	0.1	0.1

All data are in wt.%.

Table 2
Modification of C_3S with foreign oxides and type of substitution[10–13,22,24]

Modification	Fe_2O_3	Al_2O_3	MgO (1500 °C)[*]
T I	0–0.9	0–0.45	0–0.55
T II	0.9–1.1	0.45–1.0	0.55–1.45
M I			1.45–2.0
M II			>1.2
Type of substitution	2 Fe for 1 Ca + 1 Si	Al for Ca, Si and hole	1 Mg for 1 Ca

All data are in wt.%.

[*] Solubility limit depends on temperature of synthesis.

C_3S, at 1500 °C it is 2.0 wt.% and at 1550 °C the limit is 2.5 wt.%.[13–15]

Despite a lot is known about the influence of foreign oxides on the crystal structure of C_3S, only few and often contradictory results have been published about the influence on the reactivity. They are presented and discussed together with the own results.

2. Experimental procedure

In order to synthesize pure C_3S solid solutions without any by-product (e.g., free lime or C_2S), the addition of foreign oxides was calculated according to the type of substitution given in Table 2. This procedure takes more time for the sample preparation than simple doping, but it is important because it is known that some by-products have a greater influence on the reactivity of C_3S than the incorporation of foreign oxides.

C_3S was prepared using a sol–gel process as precursor before the high temperature synthesis.[16] The concentrations of foreign oxides were chosen according to Table 2 in order to get different modifications of C_3S. The principle of the sample preparation via a sol–gel process is shown in Fig. 1. A solution of colloidal silica (Ludox AS 40, Grace Davison, Worms, Germany) containing 40.1 wt.% SiO_2 with a medium particle diameter of about 22 nm was mixed with a stoichiometric amount of a neutral $Ca(NO_3)_2$ solution that was freshly prepared from $CaCO_3$ (pa, Merck, Darmstadt, Germany) and HNO_3 (pa, Merck, Darmstadt, Germany). For doped samples, solutions of $Al(NO_3)_3$, $Mg(NO_3)_2$ and $Fe(NO_3)_3$ were added to the reaction mixture. The mixture was heated up to 70 °C and stirred in an open beaker at pH 5.5 for about 8 h until a gel resulted. After transferring the gel into platinum crucibles it was slowly heated to 900 °C whereby the water evaporated and $Ca(NO_3)_2$ and other nitrates decomposed to metal oxides. Finally the samples were heated to 1450 °C for 12 h. As the extremely fine particles in the sol–gel process are very reactive, pure C_3S with a content of free lime <0.1 wt.% was synthesized with only one intermediate grinding.

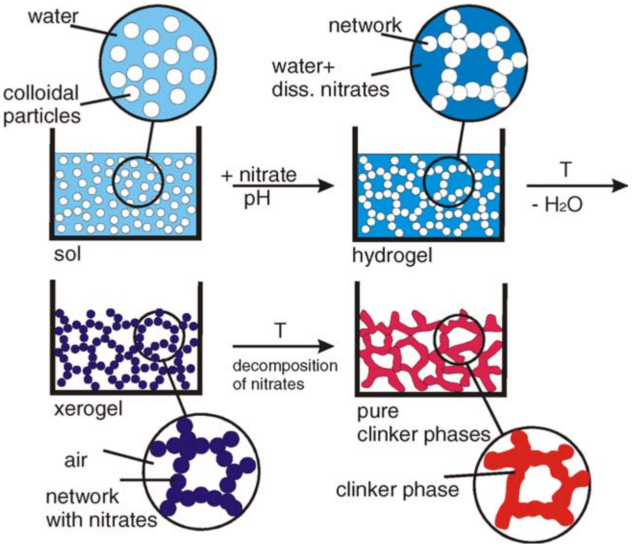

Fig. 1. Principle of sample preparation via sol–gel process as precursor.

All samples were ground under the same conditions in a planetary ball mill (planetary mono mill, pulverisette 6, Fritsch, Idar-Oberstein, Germany) until the particles had a fineness of 3000 ± 200 cm^2/g measured by the Blaine method.[17] The influence of different foreign oxides on the grindability of C_3S solid solutions is not the same. MgO seems not to have a significant influence on the grindability, whereas Al_2O_3 and Fe_2O_3 decrease the grindability of C_3S and these samples had be ground longer to get the same fineness.

All diffraction data were recorded with a X'Pert PRO X-ray diffraction system (PANalytical, Almelo, The Netherlands) in the range of 10–70° 2θ using Cu $K_{\alpha1,2}$ and a position sensitive detector (X'Celerator). The finely ground samples were prepared by back loading in order to minimize preferred orientation. The crystal structure refinement and quantification of by-products was done with the software X'Pert HighScore Plus (PANalytical, Almelo, The Netherlands) using the full range of data. The profile was fitted with the Pearson VII function. The following parameters were fitted: zero shift, background, scaling factor, Pearson VII coefficients, lattice parameters and preferred orientation. Because of the high number of atomic coordinates (29Ca, 9Si and 45O) other structural parameters like occupancy factor, position and thermal parameter of each atom, were not refined.

The hydration behaviour of samples with a water/solid ratio of 0.5 was investigated in an isothermal heat flow calorimeter (TAM air, Thermometric, Järfälla, Sweden) at 20.0 ± 0.1 °C. All samples were hydrated in two different ways: in the titration cell, the solid sample and water were thermostated for several hours before the reaction was started by injecting the water into the reaction vessel and stirring the sample in the calorimeter for several minutes. This procedure allowed monitoring the hydration from the very beginning when water was added to the sample. The hydration in the titration cell was monitored for 48 h. An other set of samples was mixed in the reaction vessel outside the calorimeter, transferred into the calorimeter within 3 min after mixing and then measured over a period of 9 days. The second method had the disadvantage that the measured heat flow in the calorimeter is disturbed for about 30–90 min, but eight samples could be measured simultaneously. Both data sets were combined for the evaluation of hydration.

3. Results and discussion

3.1. Crystal structure refinement

Based on the XRD data, the crystal structures of the samples were refined using structural models and calculations of Rietveld method. The structure data of Golovastikov et al.[18] (C_3S triclinic; ICSD = 4331) and Nishi et al.[19] (C_3S monoclinic; ICSD = 64759) were used for the refinement. The lattice parameters and changes of lattice parameters of doped C_3S in comparison with pure C_3S are given in Tables 3–5. Changes in the crystal structure of doped samples could mainly be monitored by changes in the lattice parameters b, c and α, while the other parameters changed only slightly. At the moment we have no explanation for this behaviour. In Fig. 2, the measured and calculated X-ray diffraction of pure C_3S in the most significant range 28–53° 2θ is shown together with the difference plot.

Solid solutions of MgO with C_3S always had a triclinic structure. The lattice parameters changed up to 1.4 wt.% of MgO and then kept nearly constant up to 2.05 wt.% of MgO. In samples with at least 1.95 wt.% of MgO, free periclase (MgO) was identified in the X-ray diffraction and considered as a second phase during Rietveld refinement. These samples should also contain traces of C_2S, but this by-product could not be identified in the X-ray diffraction because of strong peak overlaps from C_2S and C_3S. In the sample with 3.0 wt.% of MgO the lattice parameters again changed. For this sample, the fit of the monoclinic structure was better than for all other samples, but the fit for the triclinic structure was still much better. Concerning these data, the solubility limit of MgO in C_3S is about 1.4 wt.% at 1450 °C. Nearly the same solubility limit of 1.5 wt.% was detected by Katyal et al.,[20] who did the synthesis at the same temperature. As pointed out in the introduction, the solubility limit strongly depends on the temperature used during the synthesis. Obviously the synthesis temperature of 1450 °C is not high enough to incorporate the amount of MgO necessary to get a polymorphic transformation of C_3S from the triclinic to the monoclinic structure. Neubauer[21] reported that a concentration of 1.1 wt.% of MgO is enough to produce monoclinic C_3S if at least additionally 0.2 wt.% of Fe_2O_3 is present in the sample. C_3S containing 1.1 wt.% of MgO and additionally 0.7 wt.% of Fe_2O_3 resulted in a monoclinic structure, which fitted best with the structure typically found in OPC clinker. In Fig. 3, the measured and calculated X-ray diffraction of C_3S with 3.0 wt.% of MgO is presented in the region 28–53° 2θ.

The lattice parameters of C_3S solid solutions with Al_2O_3 changed up to a concentration of 0.95 wt.% and kept stable with higher concentrations. In the sample with 1.2 wt.% of Al_2O_3, a small amount of tricalcium aluminate C_3A was identified as a side product and considered as a second phase during Rietveld refinement. The present results confirm the solubility limit of about 1.0 wt.% given in the literature.[13]

For samples of C_3S with up to 1.5 wt.% of Fe_2O_3 only negligible changes in the lattice parameters were detected, but neither side products nor non-reacted Fe_2O_3 could be found. These results agree with the findings of Woermann et

Table 3
Refined structural parameters and changes in lattice parameters for C_3S with different amounts of MgO

	MgO (wt.%)							
	0	0.5	0.6	1.4	1.5	1.95	2.05	3.0
a	11.634	11.628	11.630	11.622	11.623	11.624	11.624	11.625
b	14.215	14.197	14.182	14.170	14.170	14.169	14.168	14.161
c	13.689	13.675	13.654	13.644	13.644	13.644	13.643	13.638
α	105.32	105.29	105.15	105.16	105.16	105.14	105.14	105.11
β	94.55	94.56	94.66	94.63	94.63	94.64	94.64	94.66
γ	89.84	89.88	89.88	89.88	89.88	89.89	89.88	89.91

	MgO_{free} (wt.%)							
	0	0.5	0.6	1.4	1.5	<0.5	ca. 0.8	ca. 1.7
Δa		−0.006	−0.004	−0.012	−0.011	−0.010	−0.010	−0.009
Δb		−0.018	−0.033	−0.045	−0.045	−0.046	−0.047	−0.054
Δc		−0.014	−0.035	−0.045	−0.045	−0.045	−0.046	−0.051
$\Delta\alpha$		−0.03	−0.17	−0.16	−0.16	−0.18	−0.18	−0.21
$\Delta\beta$		+0.01	+0.11	+0.08	+0.08	+0.09	+0.09	+0.11
$\Delta\gamma$		+0.04	+0.04	+0.04	+0.03	+0.05	+0.04	+0.07

a, b, c (Å), ±0.003; α, β, γ (°), ±0.02.

Table 4
Refined structural parameters and changes in lattice parameters for C_3S with different amounts of Al_2O_3

	Al_2O_3 (wt.%)				
	0	0.4	0.5	0.95	1.2
a	11.634	11.639	11.644	11.646	11.645
b	14.215	14.204	14.192	14.183	14.181
c	13.689	13.681	13.668	13.663	13.661
α	105.32	105.24	105.17	105.10	105.11
β	94.55	94.60	94.65	94.68	94.66
γ	89.84	89.86	89.87	89.87	89.86
	C_3A (wt.%)				
	0	0.4	0.5	0.95	0.4
Δa		+0.005	+0.010	+0.012	+0.011
Δb		−0.011	−0.023	−0.032	−0.034
Δc		−0.008	−0.021	−0.026	−0.028
$\Delta\alpha$		−0.08	−0.15	−0.22	−0.21
$\Delta\beta$		+0.05	+0.10	+0.13	+0.11
$\Delta\gamma$		+0.02	+0.03	+0.03	+0.02

a, *b*, *c* (Å), ±0.003; α, β, γ (°), ±0.02.

al.[22] who could also detect only very small changes in the X-ray diffraction data and therefore detected the solution limit of Fe_2O_3 in C_3S by reflected light microscopy.

3.2. Hydration

The hydration activity of C_3S has to be characterized for different reaction stages of C_3S hydration.[23] The time and intensity of the thermal power peak maxima characterize the rate of the initial and main hydration reaction. The cumulative heat gives an indication for the degree of hydration. It is well known that by-products can affect the hydration of C_3S. Therefore, results only from the hydration of pure phases are presented and discussed. The thermal power and cumulative heat of different C_3S solid solutions are given in Figs. 4–6.

The intensity of the initial reaction is not effected by the incorporation of MgO but the main reaction is accelerated slightly without affecting the rate of heat evolution. This can be interpreted from the position and intensity of the main peak and results in an increase of cumulative heat for all doped samples up to 12 h. After this time, C_3S with 0.5 and 0.6 wt.% of MgO hydrates a little bit slower than the pure sample and reaches the same cumulative heat of hydration after 9 days. The cumulative heat of the sample with 1.4 wt.% MgO is always above the level of the pure C_3S and after 9 days the cumulative heat is about 10% higher than for pure C_3S. Thompson et al.[24] studied the reactivity of alite with different amounts of MgO but investigated only the hydration up to 35 h. They found a decrease in the reactivity for alite containing up to 1.0 wt.% of MgO. Abdul-Maula and Odler[25] reported that the progress of hydration of C_3S was not altered between 1 and 90 days.

The initial reaction of C_3S with Al_2O_3 is dramatically increased compared with pure C_3S. Therefore, it can be concluded that the incorporation of Al_2O_3 generates active sites and accelerates the very early hydration of C_3S. The shape

Table 5
Refined structural parameters and changes in lattice parameters for C_3S with different amounts of Fe_2O_3

	Fe_2O_3 (wt.%)			
	0	0.85	0.95	1.50
a	11.634	11.635	11.635	11.634
b	14.215	14.207	14.206	14.203
c	13.689	13.683	13.682	13.679
α	105.32	105.28	105.27	105.27
β	94.55	94.58	94.58	94.59
γ	89.84	89.86	89.86	89.86
Δa		+0.001	+0.001	0.000
Δb		−0.008	−0.009	−0.012
Δc		−0.006	−0.007	−0.010
$\Delta\alpha$		−0.04	−0.05	−0.05
$\Delta\beta$		+0.03	+0.03	+0.04
$\Delta\gamma$		+0.02	+0.02	+0.02

a, *b*, *c* (Å), ±0.003; α, β, γ (°), ±0.02.

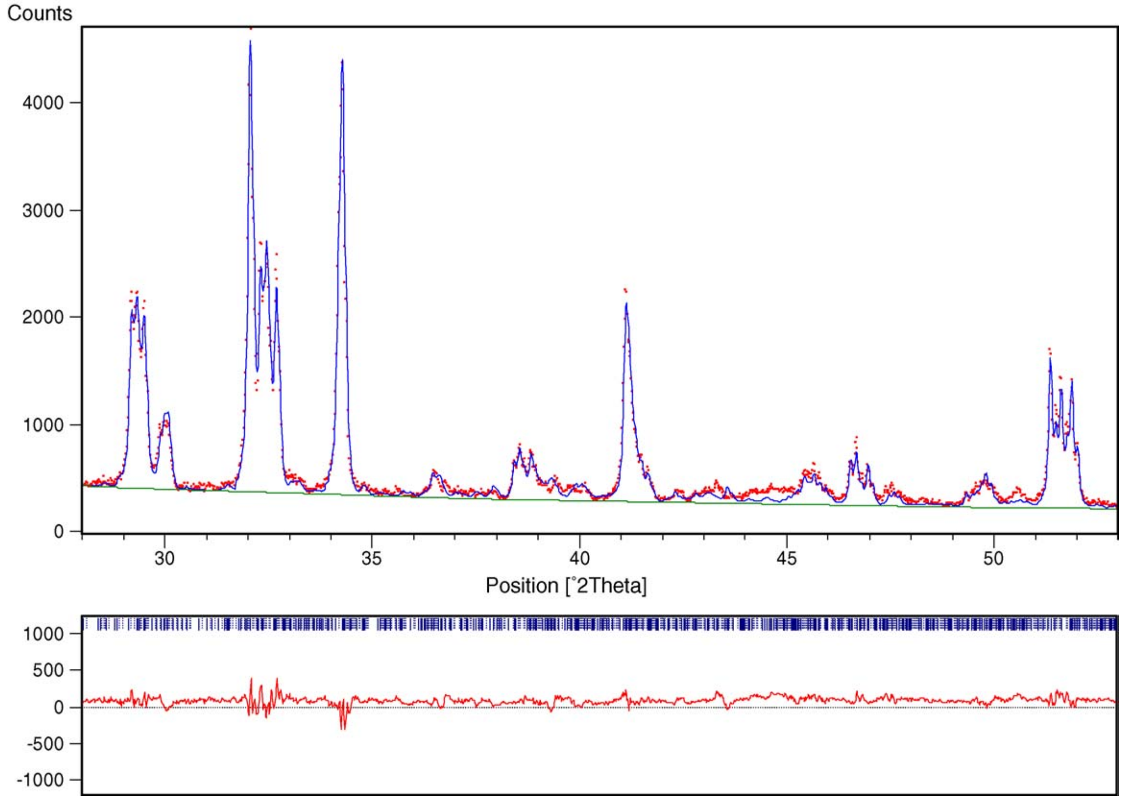

Fig. 2. Measured and calculated XRD pattern of pure C_3S after refinement with triclinic structural data of Golovastikov et al.[18]

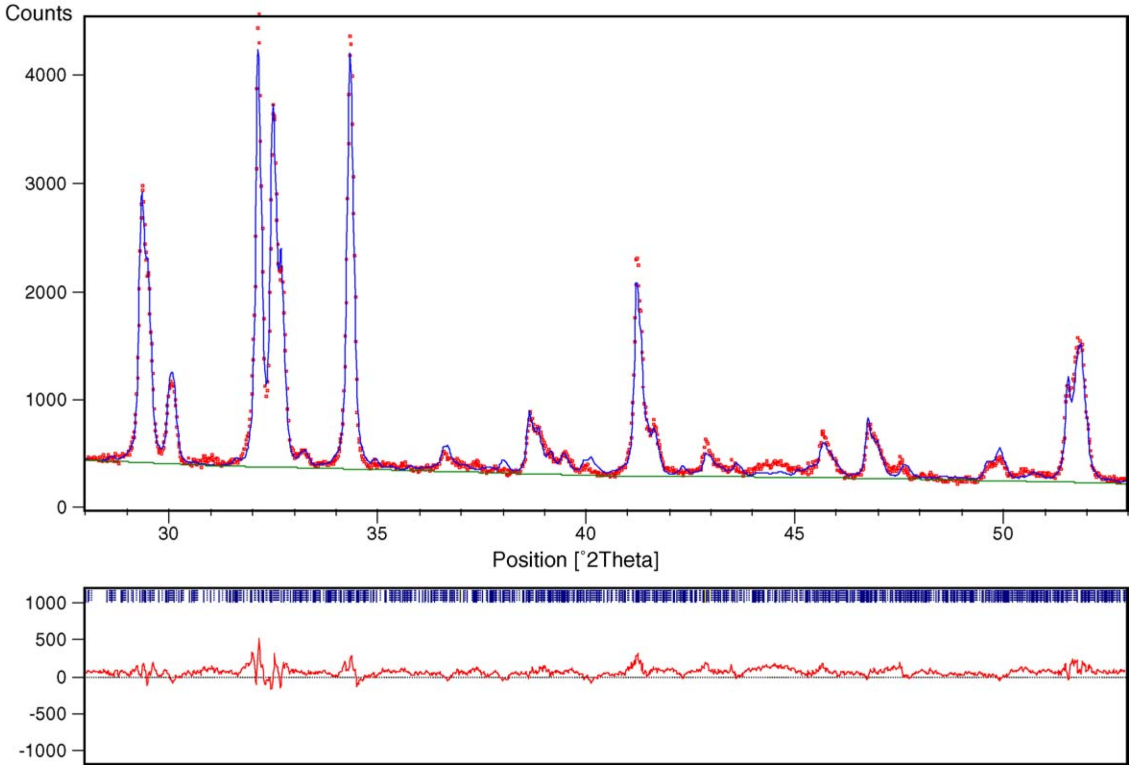

Fig. 3. Measured and calculated XRD pattern of C_3S with 3.0 wt.% of MgO after refinement with triclinic structural data of Golovastikov et al.[18] and MgO as a second phase.

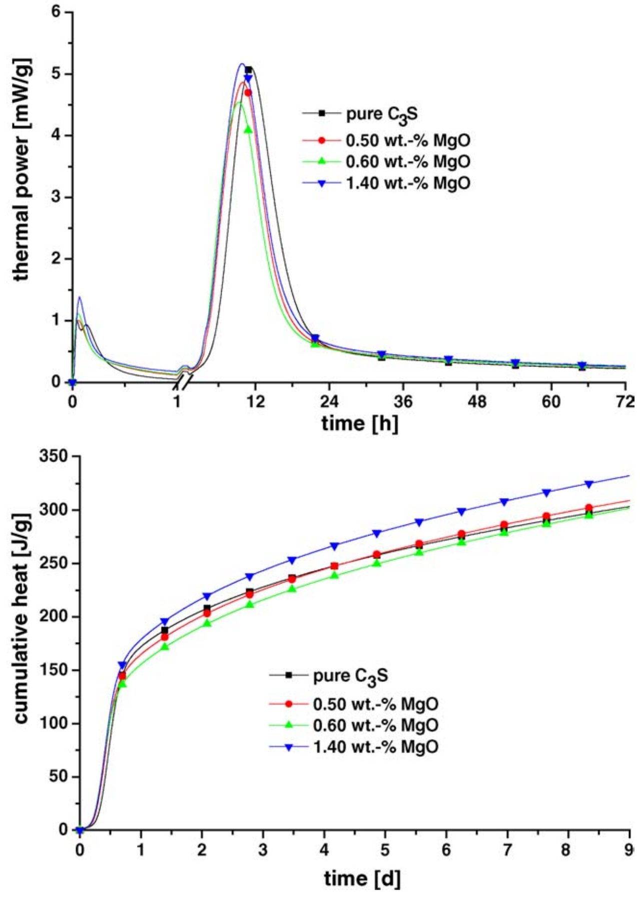

Fig. 4. Thermal power and cumulative heat of hydration for C_3S solid solutions with MgO.

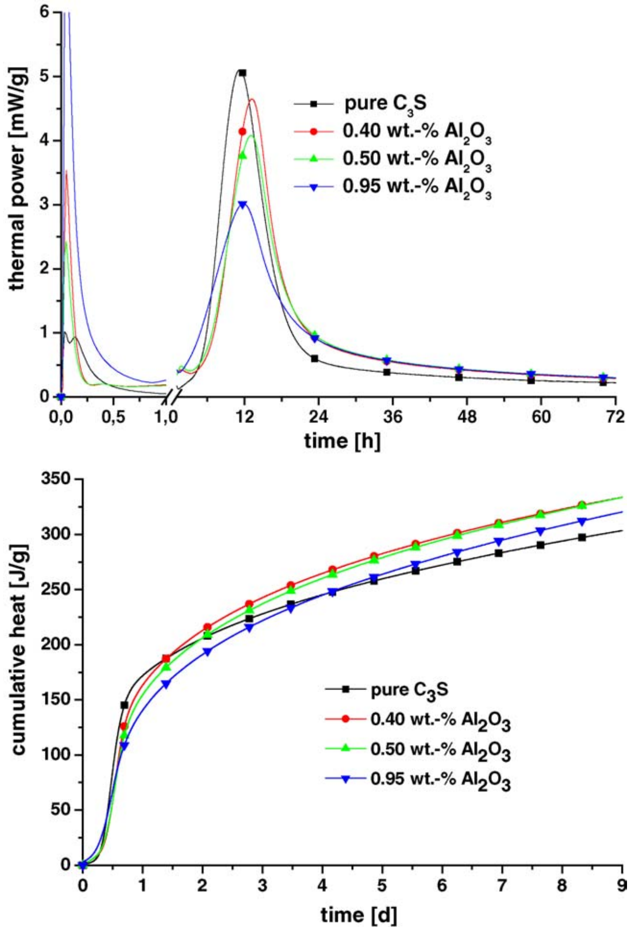

Fig. 5. Thermal power and cumulative heat of hydration for C_3S solid solutions with Al_2O_3.

of the main hydration curve of C_3S with higher amounts of Al_2O_3 is different from most other samples. There is no such strong drop in the rate of hydration after the initial reaction, but the slope of the reaction rate and the maximum rate of hydration is much lower than in the case of pure C_3S. This is also visualized in cumulative heat of hydration. After 6 h the heat of hydration of doped C_3S is higher than the control, but after 12 h the cumulative heat of the doped samples is 20–40% lower than the control. Depending on the concentration of Al_2O_3 this is changing during time of hydration and after 9 days all solid solutions with Al_2O_3 produced higher cumulative heat of hydration than pure C_3S. We assume that this effect can be explained by an intensified surface reaction caused by the complex substitution of Al that results in more lattice defects. After the reaction has proceeded, the higher reactivity is not that important, because the former hydration is diffusion-controlled. These results are different compared to the findings of Odler and Schüppstuhl[26] who observed a retarding effect of solid solutions of C_3S with 0.5 and 1.0 wt.% Al_2O_3, respectively.

The doping of C_3S with Fe_2O_3 caused the most dramatic changes in reactivity. The initial reaction was not affected by Fe_2O_3 but the main reaction was strongly retarded and also the hydration rate decreased. The cumulative heat of hydration of samples with 0.85 and 0.95 wt.% of Fe_2O_3 reached the level of pure C_3S after 4 or 7 days, respectively. After 9 days of hydration the sample with 1.5 wt.% of Fe_2O_3 also reached the level of pure C_3S and from the slope it can be presumed that the heat of hydration will exceed that of pure C_3S after a longer time of hydration. These findings give a better way to interpret the higher reactivity and faster strength formation of OPC with lower concentrations of Fe_2O_3. Normally it is interpreted that these differences are caused by the formation of less reactive ferrite instead of the very reactive aluminate, but the hydration products of aluminate and ferrite only have an insignificant influence on the strength development of hydrated OPC. Due to the fact that C_3S dominates the strength development of OPC, these changes in reactivity caused by the formation of C_3S solid solutions with Fe_2O_3 are more reasonable. Valenti et al.,[27] who investigated the influence of 1.0 wt.% Fe_2O_3 on the hydration of C_3S during the first 24 h, also observed a significant retardation of the hydration. The same result was published by Fierens et al.,[28] who studied the hydration of a solid solution containing 1.0 wt.% of Fe_2O_3 in C_3S by X-ray diffraction and scanning electron microscopy. Abdul-Maula and Odler[25] only observed moderate

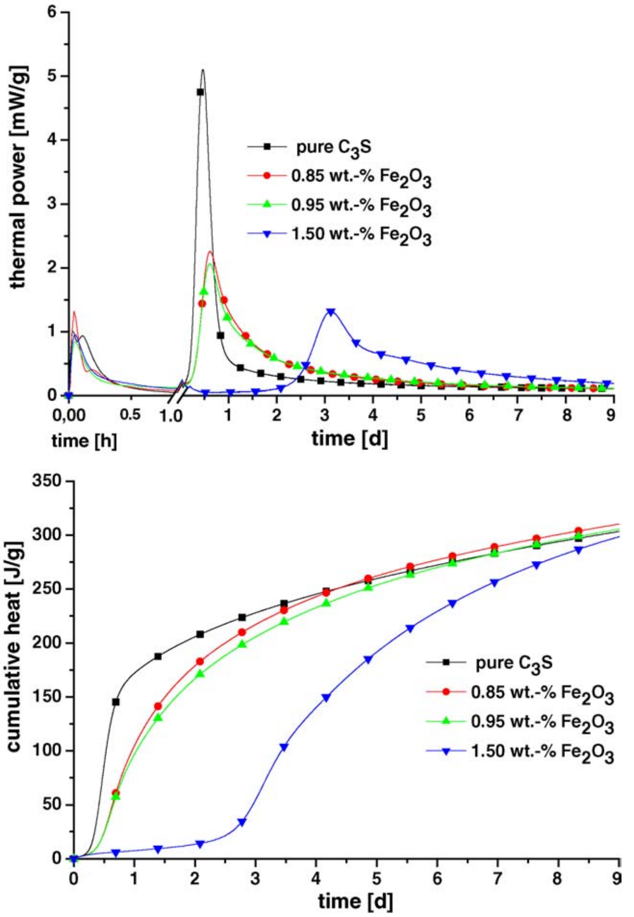

Fig. 6. Thermal power and cumulative heat of hydration for C_3S solid solutions with Fe_2O_3.

alteration for the hydration of C_3S doped with Fe_2O_3 during the hydration between 1 and 90 days.

In some cases, our own results, found for the hydration behaviour of doped C_3S, are in good agreement with results previously reported in the literature and are contradictory to others. One reason for contradictory results found in different studies is the purity of the C_3S solid solution used for the hydration, because by-products can seriously affect the hydration of C_3S and only single phase free from by-products give reliable results for the influence of the doping on the hydration behaviour of C_3S.

4. Conclusion

The crystal structure of C_3S solid solutions with MgO or Al_2O_3, respectively, is significantly altered. At 1450 °C the solubility limit for MgO in C_3S was found to be much lower than the limit of 2.0 wt.% given in the literature for a synthesis temperature of 1500 °C. Therefore, the amount of incorporated MgO was too low for a polymorphic transformation from triclinic to monoclinic. The changes in lattice parameters of C_3S doped with Fe_3O_3 are very small.

Despite MgO had the most significant influence on the crystal structure, the influence on the hydration was quite low. MgO accelerated the main reaction slightly but the most important finding is the improvement of the long-term hydration of the sample with 1.4 wt.% of MgO. The influence of Al_2O_3 on the hydration is more complex. The initial reaction of C_3S was essentially accelerated, but the hydration on a medium time scale was slightly slowed down. On the long-term range, all samples containing Al_2O_3 developed significantly more heat of hydration than pure C_3S. The activated hydration can be linked to the complex type of substitution of Al in C_3S, whereby more defects are introduced into the lattice. These defects can activate the hydration. Despite very small changes in lattice parameters brought about by the incorporation of Fe_2O_3 into C_3S, the doping brought about the highest change in reactivity. The initial reaction kept unchanged, but the most important main period of hydration was slowed down much more than by Al_2O_3 or MgO. Despite this strong retardation, after 9 days all samples with Fe_2O_3 generated at least the same cumulative heat of hydration like pure C_3S. These findings give a better interpretation for the reactivity of OPC with different concentrations of Fe_2O_3.

All in all, the changes in lattice parameters by doping C_3S with foreign oxides does not directly correlate with changes in hydration activity, but in some cases it could be used to identify the kind and amount of incorporated foreign oxide. The most important fact for the hydration activity of C_3S is the kind of incorporated ion and the type of substitution. One hypothesis is that foreign ions alter the number of active sites in the crystal system of C_3S and thereby directly influence the reactivity of C_3S. Another hypothesis is that the foreign ions have a significant effect on the durability of the protective layer that forms around the grains of C_3S after the initial reaction, but for both hypothesises more fundamental research has to be done to fully understand these phenomena. Especially the influence of a combination of different foreign oxides incorporated into C_3S on the reactivity is of great interest.

Understanding the interaction of changes in the lattice parameters of C_3S caused by a combination of different foreign oxides and changes in hydration reactivity would be a very powerful tool to predict the reactivity of cement from X-ray diffraction data and can significantly improve the quality control of Portland cement clinker production. It can also help to understand the interaction of different cements with additives and admixtures that are unpredictable at the moment.

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