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Crystal structure refinement and hydration behaviour of doped tricalcium aluminate

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Abstract

In this paper analytical evidence on crystal structure and hydration behaviour of C_3A solid solutions with MgO, SiO_2, Fe_2O_3, Na_2O and K_2O is given. Samples were prepared using an innovative sol-gel process as precursor, examined by X-ray powder diffraction, infra-red spectroscopy and the crystal structure was refined by the Rietveld method. A significant shift of lattice parameters was found for C_3A solid solutions with SiO_2, Fe_2O_3 or Na_2O but only minor changes were detected for K_2O. The hydration of C_3A solid solutions in the absence of $CaSO_4$ was accelerated for samples doped with SiO_2 or K_2O and it was retarded in the case of MgO, Fe_2O_3 or Na_2O. The hydration in the presence of $CaSO_4$ was accelerated when C_3A was doped with K_2O or Na_2O, whereas Fe_2O_3 strongly retarded the hydration. The doping with SiO_2 nearly had no influence on the hydration, the effect of MgO was not straight forward.

Keywords: Calorimetry; X-Ray diffraction; Crystal structure; $Ca_3Al_2O_6$; Solid solution

1. Introduction

Ordinary Portland cement (OPC) is a mixture of the clinker phases alite, belite, aluminate, ferrite, calcium sulfate and other minor constituents. Some properties of cement such as setting behavior and strength development are not only influenced by the proportion of the individual clinker phases but also by the composition of the phases themselves, because the clinker phases are not pure compounds but form solid solutions with other oxides in the clinker.

Although there are several clinker phases present in OPC which altogether react with water, the hydration of aluminate and alite are the most important ones for the early properties of cementitious products. A detailed study on the influence of MgO, Al_2O_3 and Fe_2O_3 on the crystal structure and hydration of tricalcium silicate (C_3S) solid solution was published elsewhere [1]. The crystal structure of C_3S solid solutions with MgO and Al_2O_3 significantly changed, but only small changes for the incorporation of Fe_2O_3 were detected. Low concentrations of MgO did not change the hydration of C_3S, but 1.4 wt.% increased the hydration activity after some days. With Al_2O_3 the initial and long term hydration was activated, but the main reaction of C_3S decreased. Fe_2O_3 retarded the hydration for several days, but the long term hydration was not affected or even activated. Altogether changes in hydration activity were more dominated by the type of oxide than by the height of changes in lattice parameters.

This paper deals with the crystal structure and hydration activity of tricalcium aluminate ($3CaOAl_2O_3 = C_3A$) solid solutions. The aluminate present in OPC clinker is a solid solution of C_3A with several other oxides like MgO, SiO_2, Fe_2O_3, Na_2O and K_2O occurring in the clinker. The amount of minor and trace elements that can be incorporated into the crystal structure of C_3A and their influence on the crystal structure has been discussed by several authors [2–7]. In Table 1 different analyses on the content of foreign oxides in C_3A are summarized.

Table 1
Analyses of foreign oxides in wt.% in aluminate occurring in different OPC clinker [2–5]

	SiO_2	Fe_2O_3	MgO	Na_2O	K_2O
Minimum	3.1	2.9	0	0.2	0.2
Maximum	6.6	8.3	2.1	4.6	3.85
Typical	3.9	5.0	1.4	1.0	0.7

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Table 2
Type of substitution

Modification	Fe_2O_3	SiO_2	MgO	K_2O	Na_2O
Simple substitution	$Fe^{3+} \rightarrow Al^{3+}$	$2Si^{4+} + \square_V{}^* \rightarrow Ca^{2+} + 2\ Al^{3+}$	$Mg^{2+} \rightarrow Ca^{2+}$	$2\ K^+ \rightarrow Ca^{2+} + 1\ \square_H{}^{\#}$?	$2\ Na^+ \rightarrow Ca^{2+} + 1\ \square_H{}^{\#}$
Reference	[22]	[27]	[24,25]		[18]
Coupled substitution		$Na^+ + Si^{4+} \rightarrow Ca^{2+} + Al^{3+}$		$K^+ + Si^{4+} \rightarrow Ca^{2+} + Al^{3+}$?	$Na^+ + Si^{4+} \rightarrow Ca^{2+} + Al^{3+}$
Reference		[8]		[3]	[8]

* $\square_V$ denotes vacancies.
\# $\square_H$ denotes holes.

Despite uncertainties about the accuracy of some of these results, the data shows, that the content of foreign oxides can vary widely. At room temperature pure C_3A only exists in the cubic modification, but several other polymorphs are known as a function of Na, Fe and Si content [8].

The structure of C_3A is built up of hollow rings of six corner sharing AlO_4 tetrahedra that are held together by Ca^{2+} ions. Two Al sites can be distinguished, although the environment of these is very similar. From the six Ca^{2+} ions three are six-coordinated, the other three have higher coordination numbers and a more disordered geometry [9,10]. Prodjosantoso et al. [10,11] found in their studies, that the occupation of the different Ca sites by foreign ions is distinguished by the diameter of the foreign ion. Smaller ions preferentially occupy the smaller six-coordinated sites, whereas larger ions occupy the eight- and nine-coordinated sites in C_3A.

Although the content of Na_2O in C_3A is quite low, it is the most influential foreign oxide on the crystal structure of C_3A. Many studies have been published about the influence of Na_2O on the crystal structure of C_3A. [12–16] and these results were summarized by Locher [17] as followed:

- The cubic modification C_I is stable up to a Na_2O content of 1.0 wt.%, C_{II} is stable up to 2.4 wt.%. There are only small differences in the crystal structure of both cubic modifications.

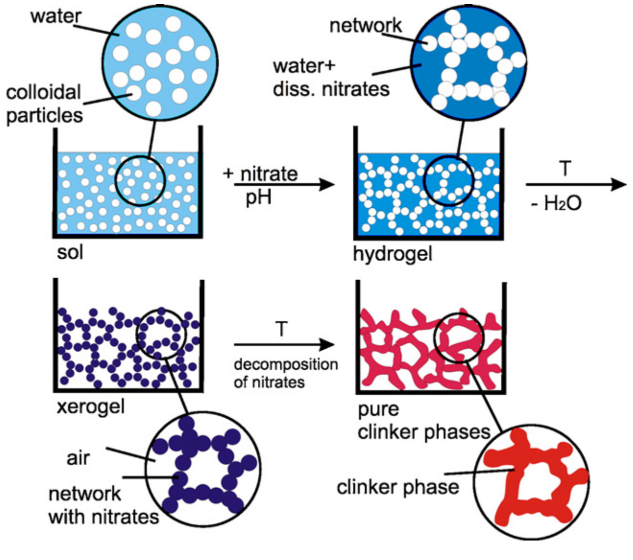

Fig. 1. Principle of sample preparation via the sol-gel process.

Table 3
Quantification of K_2O in reaction mixture and burned samples

Reaction mixture K_2O [wt.%]	Burned samples K_2O [wt.%]	Loss in K_2O [%]
1.24	0.10	92
3.64	0.52	86
5.40	1.44	73
6.83	2.35	66

- Between 2.4 and 3.7 wt.% of Na_2O, the cubic C_{II} and the orthorhombic O modification coexist.
- From 4.6 to 5.7 wt.% of Na_2O only the orthorhombic O modification is stable.
- Solid solutions between 5.9 and 7.6 wt.% of Na_2O only exist in the presence of silicon.

Na^+ substitutes for Ca^{2+} (the irregularly coordinated Ca(5) position is preferred) and another Na^+-ion occupies an otherwise vacant site in the centre of rings formed by $Al_6O_{18}^{18-}$ [18]. This substitution reaction gives a solid solution with the general formula $Na_{2x}Ca_{3-x}Al_2O_6$.

Maki [19] and Pollitt and Brown [20] failed to prepare solid solutions of C_3A with K_2O, but additional doping with SiO_2 favours the formation of the orthorhombic or monoclinic phase. This can be explained by the combined incorporation of SiO_2 and K_2O in the C_3A of OPC clinker.

Detailed studies were also done on the influence of Fe^{3+}-doping on the crystal structure of C_3A and different authors [21–23] have reported the existence of solid solution with the general formula $C_3(A_{1-x}F_x)$, but the limits of composition obtained for the solid solutions are different. In the most recent study

Table 4
Refined structural parameter for C_3A with different amounts of MgO, Fe_2O_3, SiO_2, K_2O or Na_2O [wt.%]; a, b, c [Å]±0.003

MgO	wt.%	0	0.5	1.0	1.5	2.0
a	Å	15.262	15.242	15.246	15.249	15.251
Δa	Å		−0.021	−0.016	−0.013	−0.012
MgO_{free}	wt.%	0	–	0.6	1.8	2.3
$C_{12}A_7$	wt.%		0.5	2.4	3.3	5.4
SiO_2	wt.%	0	1.0	2.0	3.0	4.0
a	Å	15.262	15.253	15.245	15.244	15.240
Δa	Å		−0.009	−0.017	−0.018	−0.022
Fe_2O_3	wt.%	0	1.0	2.0	3.0	4.0
a	Å	15.262	15.270	15.277	15.284	15.276
Δa	Å		0.008	0.015	0.022	0.014
K_2O	wt.%	0	0.10	0.52	1.44	2.35
a	Å	15.262	15.262	15.266	15.270	15.270
Δa	Å		0.000	0.004	0.008	0.008
CaO	wt.%		0.3	0.9	2.1	4.1
$C_{12}A_7$	wt.%		2.0	5.5	7.9	4.4
Na_2O	wt.%	0	1.30	3.86	5.40	6.83
a	Å	15.262	15.251	10.869	10.864	10.869
b	Å			10.843	10.853	10.854
c	Å			15.120	15.127	15.138
Δa	Å		−0.011		−0.005	0.000
Δb	Å				0.010	0.010
Δc	Å				0.007	0.018

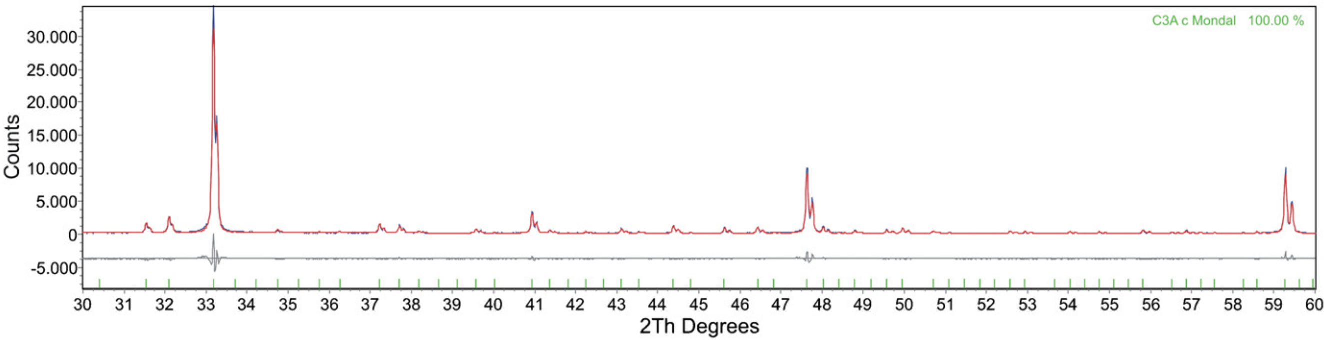

Fig. 2. Measured and calculated X-ray pattern of pure C_3A after refinement with cubic structural data of Mondal and Jeffrey [9].

Kemethmüller et al. [23] determined an increase of the lattice parameter *a* with increasing iron ratio up to the solubility limit of 3.5 ± 0.1 wt.% Fe_2O_3. Above this concentration no further changes in lattice parameters were detected.

According to Müller-Hesse and Schwiete [24], the solubility limit of MgO in C_3A is about 2.5 wt.%, Miyazawa and Tomita [25] reported a solubility limit of about 0.4 wt.%, but all authors agree, that MgO is substituted for CaO giving the general formula $Ca_{3-x}Mg_xAl_2O_6$. Prodjosantoso and Kennedy [11] prepared compounds in the series $Ca_{3-x}Mg_xAl_2O_6$ with $x=0$ to 0.5 and observed small amounts of mayenite ($C_{12}A_7$), the amount of this phase increasing as the Mg content was increased. For $x=0.25$ and 0.5 additional peaks for MA ($MgAl_2O_4$) were observed. They interpreted that Mg may stabilize $C_{12}A_7$ over C_3A.

Moore [26] and Terrier and Hornain [27] found that Si replaces Al in the solid solution C_3A+SiO_2 and the solubility limit is 5–6 at.%. If the number of oxygen atoms is considered to be unchanged, the replacement of Al^{3+} by higher charged Si^{4+} creates vacant sites of Ca^{2+} in the crystal structure. This substitution reaction leads to the general formula $Ca_{3-y}(Al_{1-y}Si_y)_2O_6$. Han et al. [28] reported, that the uptake of Si^{4+} into C_3A is favoured if Na^+ is also present in the mixture. In the system $CaO–Al_2O_3–SiO_2–Na_2O$ the solubility limit of SiO_2 is <0.5 wt.%, whereas solid solutions with characteristically higher SiO_2 content can be produced from melts, if additionally Fe_2O_3 is present. Fukuda et al. [29,30] reported about the effect of multiple substitution on the polymorphism of the C_3A phase. These results show, that the chemical variation of cationic substitution in tricalcium aluminate is constrained by excellent correlations between Al+Fe and Si as well as Ca+Mg and Na+K.

Among the minerals present in OPC, C_3A is the most reactive one. More than with other mineral phases the hydration mechanism and hydration products depend on whether gypsum is present during hydration. In both cases extensive studies have been done [17,31,32]. Despite a lot being known about the influence of foreign oxides on the crystal structure of C_3A, only a few and sometimes contradictory results were published about their influence on reactivity [16,17,23,31,33]. These will be discussed later on, together with the results of this work.

2. Experimental section

The aim of the synthesises were pure C_3A solid solutions without by-products. Therefore the composition of the starting material with foreign ions was calculated taking the type of simple substitution into account (see Table 2). This procedure is important, because otherwise the by-product(s) can have a stronger influence on the reactivity of C_3A than the incorporation of foreign oxides.

The C_3A was prepared using an innovative sol-gel process as precursor before the high temperature synthesis [34]. Four concentrations of foreign oxides were chosen according to the solubility limit or in order to get different modifications of C_3A. The principle of the sample preparation via a sol-gel process is shown in Fig. 1. A solution of colloidal alumina (VP disp. W630, Degussa, Hanau, Germany) containing 29.7 wt.% Al_2O_3 with a medium particle diameter of about 200 nm was mixed with a stoichiometric amount of a neutral $Ca(NO_3)_2$ solution, that was freshly prepared from $CaCO_3$ and HNO_3 (pa, Merck, Darmstadt, Germany). For doped samples solutions of $Mg(NO_3)_2$, $Fe(NO_3)_3$, $NaNO_3$, KNO_3 (pa, Merck, Darmstadt, Germany) or colloidal silica (Ludox AS 40, Grace Davison, Worms, Germany) were substituted for colloidal alumina or $Ca(NO_3)_2$ solution, depending on the mechanism of substitution. The mixture was heated to 70 °C and stirred at pH 8 for about 10 to 12 h until a gel resulted. After transferring the gel into platinum crucibles it was slowly heated to 900 °C while the water evaporated and $Ca(NO_3)_2$ and other nitrates decomposed to metal oxides. Finally, the samples were heated to 1350 °C for 9 h with two intermediate grindings. Since the particles in the sol-gel process are extremely fine, they

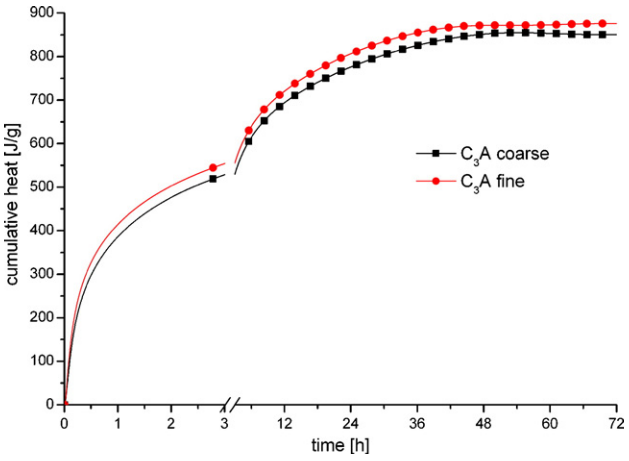

Fig. 3. Cumulative heat of hydration for pure C_3A with different finenesses; C_3A coarse=3150 cm^2/g, C_3A fine=4200 cm^2/g.

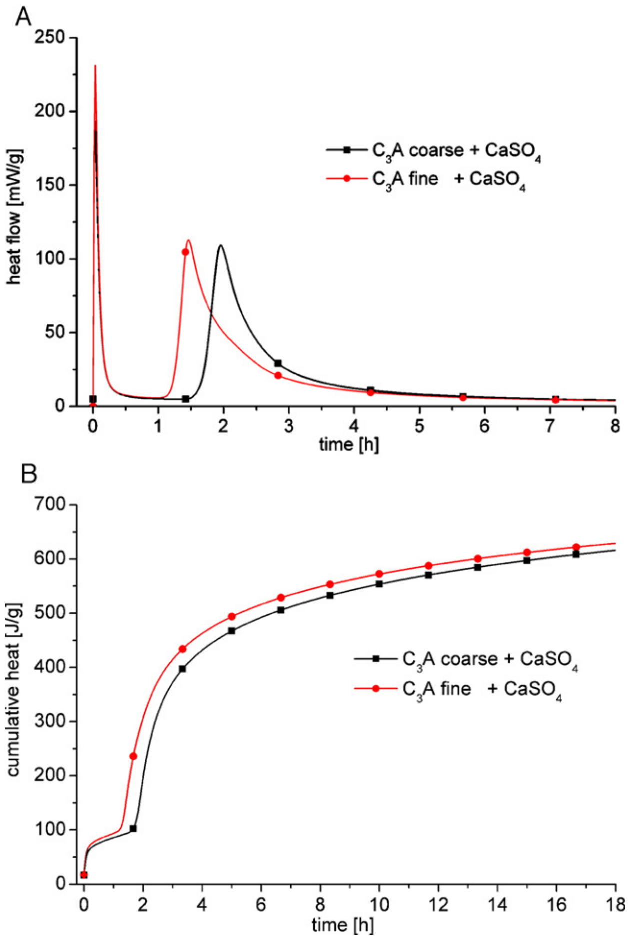

Fig. 4. A) Thermal heat and B) cumulative heat of hydration for pure C_3A with different finenesses in the presence of $CaSO_4$; C_3A coarse = 3150 cm^2/g, C_3A fine = 4200 cm^2/g.

are very reactive and therefore pure C_3A resulted after only 3 cycles of burning. Alkali oxides are more volatile than the other oxides used in this study, and therefore solid solutions with alkalis were only heated to 1200 °C for 8 h, but this process was repeated four times with intermediate grindings. Following the preparation of other authors [15,35] a certain excess of alkali oxides was used to counteract the evaporation of alkalis and the content of Na_2O and K_2O was analysed by X-ray fluorescence analysis. Under the conditions used there was no loss in Na_2O, but the amount of K_2O found in the burned samples was well below the added amount, because the vapor pressure of K_2O at 1200 °C is much higher than that of Na_2O and therefore some K_2O is lost by evaporation. The percentage of lost K_2O is decreasing with the content of K_2O in the sample, because with higher amounts of K_2O, the partial pressure of K_2O in the burning atmosphere is getting higher. This gives a higher absolute loss in K_2O but lower percentage of K_2O that is lost through evaporation. The amount of K_2O in the original sample and the burned samples is shown in Table 3.

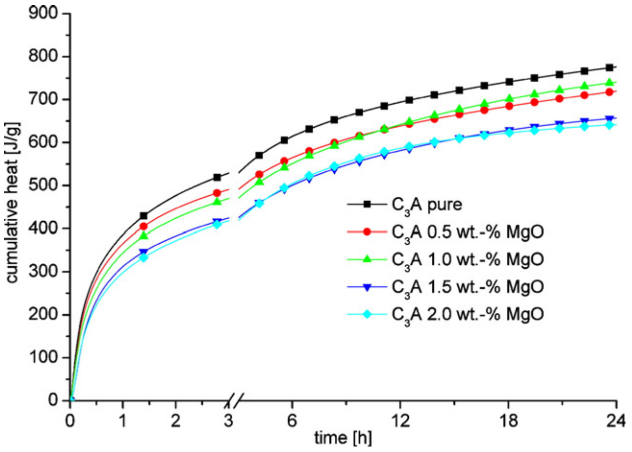

Fig. 5. Cumulative heat of hydration for C_3A solid solutions with MgO.

After the synthesis all samples were ground under the same conditions in a planetary ball mill (planetary mono mill, pulverisette 6, Fritsch, Idar-Oberstein, Germany) for 10 min and the fineness and particle size distribution was analysed by laser diffraction (Cilas 1064, Cilas, Marcoussis, France) and the Blaine method [36]. The samples doped with MgO, SiO_2 or Fe_2O_3 had a Blaine fineness of approximately 2800 cm^2/g and a mean size of D_{50} = 10.4 μm, samples containing Na_2O or K_2O were even finer. Since the samples that had been heated to different temperatures had different finenesses, pure C_3A was ground for a different duration of time to get samples of comparable fineness.

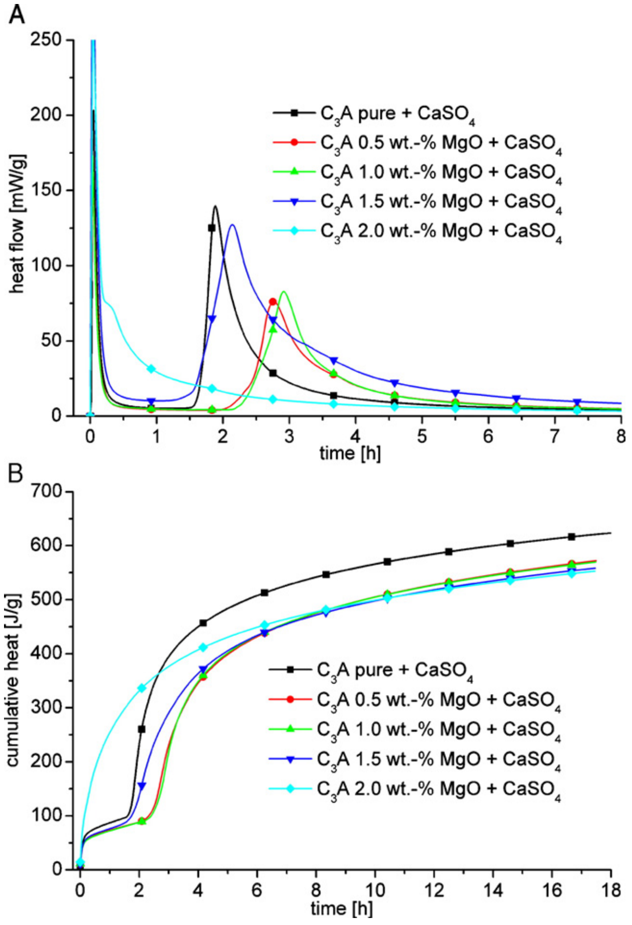

Fig. 6. A) Thermal heat and B) cumulative heat of hydration for pure C_3A solid solutions with MgO in the presence of $CaSO_4$.

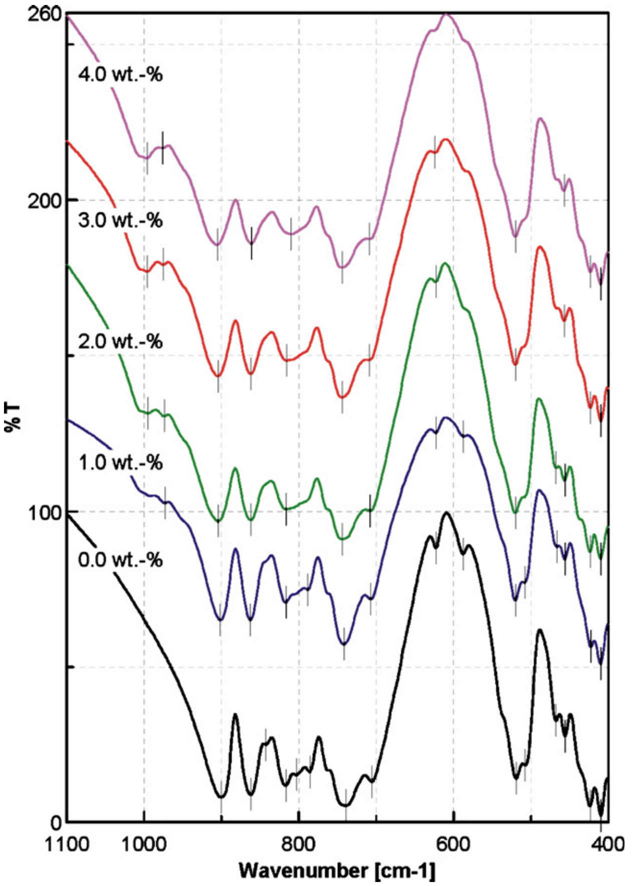

Fig. 7. IR spectra of C_3A solid solutions with SiO_2.

All powder diffraction data were recorded with a Bruker D8 Advance X-ray diffraction system (Bruker AXS, Karlsruhe, Germany) in the range of 10–100° 2θ using $CuK_{\alpha 1,2}$ and 2-dimensional detector (Vantec-1®, Bruker AXS, Karlsruhe, Germany), divergence slit: 0.3°, detector slit: 3°, 30 kV, 40 mA. The XRD patterns were edited with Diffrac® Plus Evaluation software (Bruker AXS, Karlsruhe, Germany). The crystal structure refinement and the quantification of by-products was done with the software Topas® 2 (Bruker AXS, Karlsruhe, Germany), whereas a fundamental parameter approach was used. Infra-red (IR) spectra of the C_3A solid solution series were recorded on the JASCO FT/IR-460 Plus using the KBr disc method.

The hydration behaviour of pure C_3A and C_3A together with $CaSO_4$ was investigated in an isothermal heat flow calorimeter (TAM air, Thermometric, Järfälla, Sweden) at 20.0±0.01 °C. In the titration cell the solid sample and the 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 1 min. This procedure allowed to monitor the hydration from the very beginning when water was injected into the sample. The hydration in the titration cell was monitored for at least 18 h. The pure C_3A was hydrated with a water/solid ratio of 0.5. In order to find the adequate sulphate content for the hydration control of C_3A, samples with different amounts of retarder (mixture of $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 0.5\ H_2O$ and $CaSO_4$) were hydrated. A mixture of C_3A/retarder = 12/1 and a water/solid ratio of 0.75 gave the best results for pure C_3A. The water/solid ratio was higher than for mixtures of C_3A with water, because the potential products ettringite and monosulphate have a very high content of water and can only be formed in mixtures with a high water content. The reactivity of C_3A solid solutions with K_2O was so high, that the amount of retarder had to be doubled (C_3A/retarder = 6/1). The results of the hydration of mixtures C_3A/retarder = 12/1 or 6/1 is not representative for reactions going on during hydration of OPC, but is applicable to study the influence of different foreign oxides on mixes of C_3A/retarder.

3. Results and discussion

Based on the X-ray diffraction data the crystal structures of pure and doped C_3A were refined by the Rietveld method. The structural data of Mondal and Jeffrey [9] (C_3A cubic, ICSD = 1841) and Nishi and Takeuchi [18] (C_3A orthorhombic ICSD = 1880) were used for the refinement. The lattice parameters, shifts of lattice parameters according to the solid solution series of C_3A and the quantification of by-products are given in Table 4. In Fig. 2 the measured and calculated X-ray diffraction of cubic C_3A is shown together with the difference plot.

The lattice parameter a of the undoped sample is in good accordance with the data given in literature. The IR spectrum of pure C_3A is in accordance with the data given by Boikova et al. [16] and Varma and Wall [37]. The hydration of pure C_3A with different finenesses in the absence and presence of $CaSO_4$ is shown in Figs. 3 and 4. The cumulative heat of hydration of the two samples without $CaSO_4$ only show insignificant differences and also the hydration in the presence of $CaSO_4$ is only slightly faster for the finer sample.

3.1. Influence of MgO

There is a significant decrease in the lattice parameter a with the addition of 0.5 wt.% of MgO but a is increasing again with higher additions of MgO. In all samples with a doping of at least 1.0 wt.% MgO free periclase and mayenite were detected as by-products. From this result it can be concluded that the solubility limit of MgO

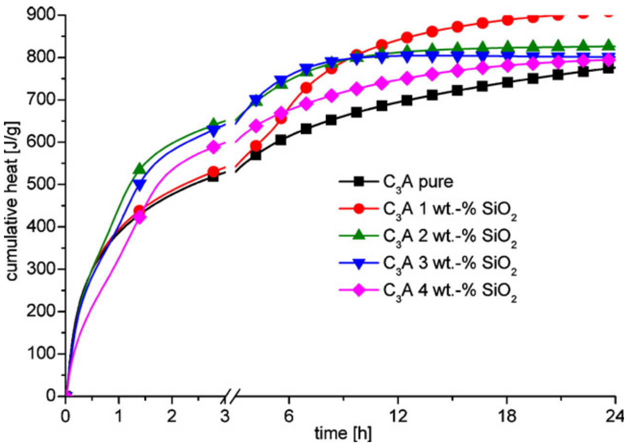

Fig. 8. Cumulative heat of hydration for C_3A solid solutions with SiO_2.

in C_3A is clearly below 1.0 wt.%. This is supported by the finding of Miyazawa and Tomita [25], who found a dissolution limit for MgO of 0.4 wt.% which is in contrast to the findings of Müller-Hesse and Schwiete [24] who found a solution limit of 2.5 wt.%. The IR spectra gave no evidence for the incorporation of Mg into the lattice of C_3A.

As a result of the non hydraulic by-product MgO and compared to C_3A slightly less reactive $C_{12}A_7$ the cumulative heat that developed during hydration of C_3A in the absence of $CaSO_4$ decreased with increasing amounts of MgO (Fig. 5). The hydraulic reaction of C_3A in the presence of $CaSO_4$, which is shown in Fig. 6, is retarded with 0.5 and 1.0 wt.% of MgO. Again, the retardation is most likely attributed to the increasing portion of non or less reactive by-products. With concentrations of 1.5 or 2.0 wt.% of MgO, there is a gain in reactivity. At first sight this seems to be inconsistent, but one has to take into account, that the hydration of C_3A in the presence of $CaSO_4$ is much more complex than without due to the formation of sulfoaluminates. The gain in reactivity of samples with free periclase and mayenite may be generated by changes in the morphology of the protective layer of ettringite that is formed on the surface of C_3A during the first minutes after contact with water and $CaSO_4$. If not the whole grain consists of C_3A but some parts are non-reactive periclase or less reactive mayenite, no continuous coating can be formed around the grains and the protective layer is disrupted, resulting in a renewed hydration of C_3A.

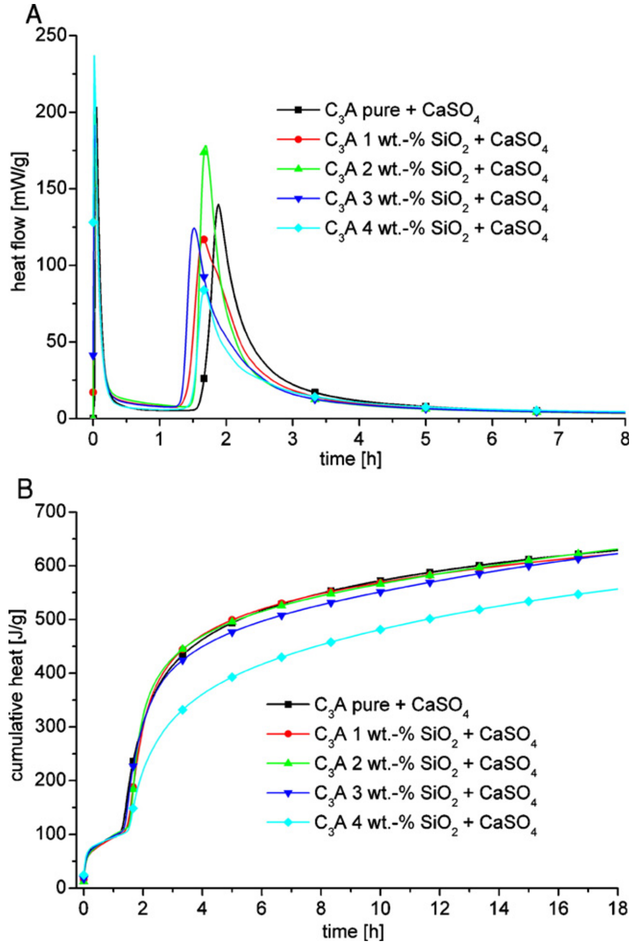

Fig. 9. A) Thermal heat and B) cumulative heat of hydration for pure C_3A solid solutions with SiO_2 in the presence of $CaSO_4$.

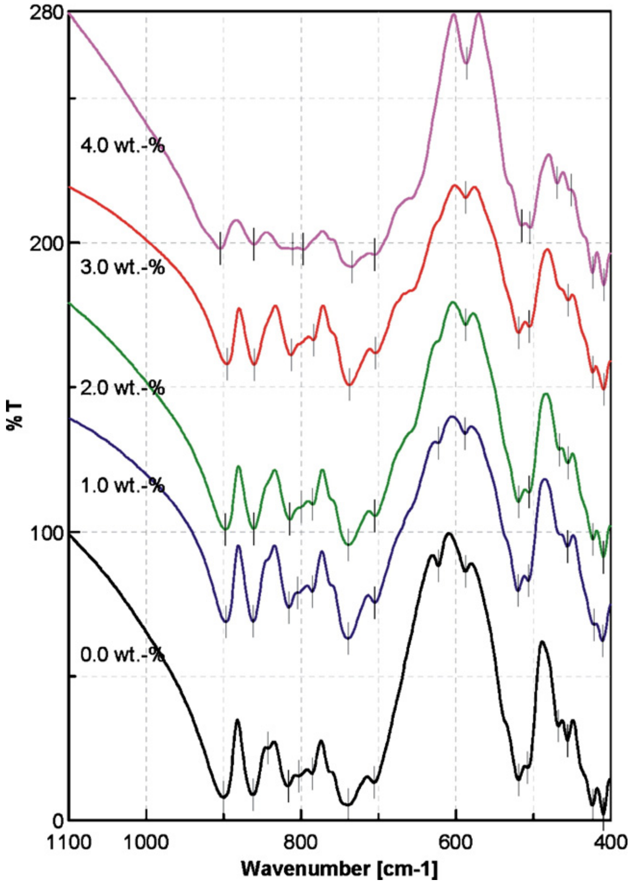

Fig. 10. IR spectra of C_3A solid solutions with Fe_2O_3.

3.2. Influence of SiO_2

The doping of C_3A with SiO_2 resulted in a small but continuous decrease in the lattice parameter *a* and no by-product could be detected. Most likely the dissolution limit of SiO_2 in C_3A is higher than previously reported in the literature, but it is also possible that some unreacted amorphous SiO_2 is present in the mixture. The IR spectra given in Fig. 7 also indicate, that SiO_2 is incorporated into C_3A. With a rising content of SiO_2 bands are broadening and the maxima at 623 and 587 cm^{-1} disappear, while at the same time two new bands at 996 and 976 cm^{-1} appear, which are in the typical region of SiO_4-bands. These bands could not be assigned to potential by-products like C_2S, C_3S or $C_{12}A_7$ and therefore are another indication for the incorporation of SiO_2 into C_3A.

In the absence of $CaSO_4$, the cumulative heat of hydration of pure C_3A is higher than for all solid solutions during the first 40 min. Later on this changes and the hydration of C_3A is accelerated by the doping with SiO_2 (Fig. 8). Up to 3 h the influence of 1.0 wt.% SiO_2 is very small, but then the hydration is more activated than with higher amounts of SiO_2. The cumulative heat of hydration of pure C_3A and samples with 2, 3 or 4 wt.% of SiO_2 is comparable after 18 h of hydration, but the cumulative heat for the sample with 1.0 wt.% SiO_2 is higher than that for all other solid solutions. The influence of doping with SiO_2 on the reactivity of C_3A in the presence of $CaSO_4$ is different from the reactivity in the absence of $CaSO_4$. The calorimetric measurement is presented in Fig. 9. Up to 3.0 wt.% of SiO_2 the main reaction was accelerated a little bit, but the influence on the cumulative heat of hydration was negligible. Only the cumulative heat of the sample with 4.0 wt.% SiO_2 was well below all others.

3.3. Influence of Fe_2O_3

The lattice parameter *a* is increased continuously up to 3.0 wt.% Fe_2O_3. In the sample with 4.0 wt.% of Fe_2O_3 the parameter decreased slightly, but this might be an analytical mistake caused by an excess of Fe_2O_3, because Kemethmüller et al. [23] reported a continuous increase in *a* up to the solution limit of 3.5±0.1 wt.%. The IR spectra of the solid solution series are shown in Fig. 10. The broadening of bands are due to structure disordering as a result of the substitution by Fe^{3+}. In correspondence with previously reported results from Varma and Wall [37], the most obvious change in the spectra can be seen in the region around 600 cm^{-1}. The peak at 623 cm^{-1} gradually disappears, whereas the peak at 587 cm^{-1} does not change in intensity up to 3.0 wt.% of Fe_2O_3 and is dramatically increased with 4.0 wt.% of Fe_2O_3 when all other peaks in the region 700 cm^{-1} to 900 cm^{-1} get much broader. All in all the IR data give an independent proof, that Fe_2O_3 is incorporated into the lattice of C_3A up to more than 3.0 wt.%.

The reactivity of C_3A solid solutions with Fe_2O_3 are significantly altered, both, in the presence and absence of $CaSO_4$ (see Figs. 11 and 12). In the absence of $CaSO_4$ the cumulative heat is reduced depending on the concentration of Fe_2O_3. In the presence of $CaSO_4$ the induction period is prolonged and in addition a strong loss of cumulative heat was detected. Kemethmüller et al. [23] did not detect differences in the reactivity of C_3A solid solutions with Fe_2O_3 hydrated in the absence of $CaSO_4$ but they obtained similar results to this study in the presence of $CaSO_4$. The reduced reactivity and extended induction period are interesting concerning the lower reactivity of sulphate resisting cement made from iron rich OPC clinker. Often the lower reactivity is only attributed to the complete absence of aluminate, but regarding the results of the hydration of C_3A solid solution with Fe_2O_3, the lower reactivity could also be based on a higher uptake of Fe_2O_3 into the C_3A.

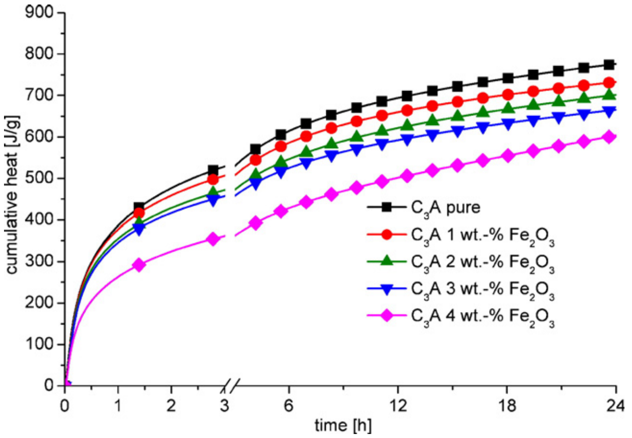

Fig. 11. Cumulative heat of hydration for C_3A solid solutions with Fe_2O_3.

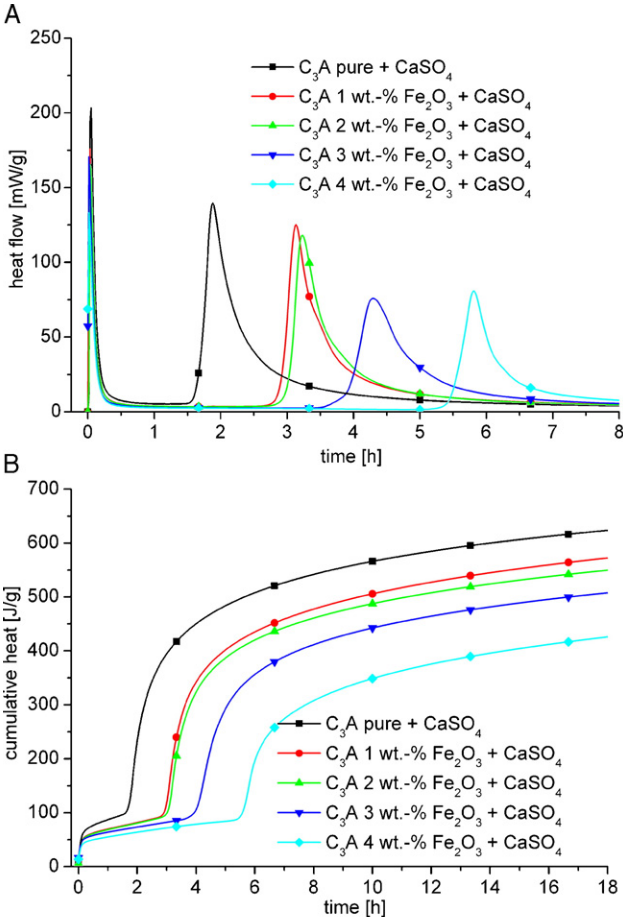

Fig. 12. A) Thermal heat and B) cumulative heat of hydration for pure C_3A solid solutions with Fe_3O_3 in the presence of $CaSO_4$.

3.4. Influence of K_2O

Even the doping with high amounts of K_2O only resulted in minor changes in the lattice parameter *a*, but the amount of by-products rose with the concentration of K_2O. It is possible that the pyrolysis of KNO_3 resulted in very fine particles that are X-amorphous and therefore can not be detected by XRD. Furthermore, the IR spectroscopy gave no evidence for the incorporation of K_2O into the lattice of C_3A.

Despite the incorporation of K_2O into the lattice being uncertain, the hydration of C_3A in the presence and absence of $CaSO_4$ is substantially altered. Changes in reactivity are most likely brought about by the by-products. In Fig. 13 it is visible that the reaction of C_3A with water in the absence of $CaSO_4$ was activated for all concentrations of K_2O. The mechanism of activation was not investigated in detail, but most likely the higher content of free CaO is one reason, because the reaction of free CaO with water is very fast. The cumulative heat of hydration after 24 h is very similar for all samples. The reaction of C_3A in the presence of $CaSO_4$ was so fast, that the dosage of $CaSO_4$ had to be doubled compared to all other measurements. The results in Fig. 14 show that the reactivity during the first several hours of hydration is rising with the concentration of K_2O and by-products, but the cumulative heat of hydration is decreased. This shows a parallel to the reaction previously discussed for the doping with MgO. The by-products might prevent the formation of a dense protective layer around the C_3A grains and therefore the layer is disrupted and the hydration is intensified.

3.5. *Influence of Na_2O*

With the addition of 1.30 wt.% of Na_2O the lattice parameter of the cubic structure is slightly decreasing. With 3.86 wt.% of Na_2O the symmetry of the crystal structure changes from cubic to orthorhombic and the lattice parameters *a*, *b* and *c* are increasing with rising amount of Na_2O up to 6.83 wt.%. This result is in good accordance with data published by Boikova et al. [16]. The IR spectra shown in Fig. 15 show the most obvious changes. Compared to undoped C_3A the bands get broader, weaker peaks and the peak at 623 cm^{-1} disappear, whereas the peak at 587 cm^{-1} is strongly increased. With higher concentration of Na_2O bands in the region between 700 and 920 cm^{-1} get broader again, some peaks are shifted and around 500 cm^{-1} two new peaks occur at different wavelengths than the two in the pure C_3A. According to Boikova et al. [16] the changes in the spectra indicate a change in the ring configuration and support the results found by XRD.

The calorimetric data of Na_2O doped C_3A in the absence of retarder is shown in Fig. 16. The early hydration of C_3A with 1.30 wt.% of Na_2O is not affected but the hydration is retarded with higher amounts of Na_2O. This corresponds to a great extend with the analytical results of Boikova et al. [16], who assigned the retardation caused by Na_2O to the occupation of holes in the C_3A structure with Na^+ for charge compensation. The occupation of the holes in the centre of $(Al_6O_{18})^{18-}$-rings makes the interaction with water more difficult and therefore retards the hydration during the first hours of hydration. The influence of Na_2O on the cumulative heat of hydration after 1 to 3 days is negligible. From Fig. 17 it can be seen that the first period of hydration of C_3A in the presence of $CaSO_4$ is substantially activated with rising amounts of Na_2O, but after one day the cumulative heat of hydration is nearly the same for all samples. Most likely the high amount of Na_2O which is incorporated into the crystal structure of C_3A has a negative effect on the durability of the protective layer that is formed on the surface of the C_3A grains. The morphological changes in the protective layer caused by Na_2O lowers the barrier for diffusion of water, resulting in a fast disruption of the layer and a strong gain in hydration of C_3A in the absence of $CaSO_4$.

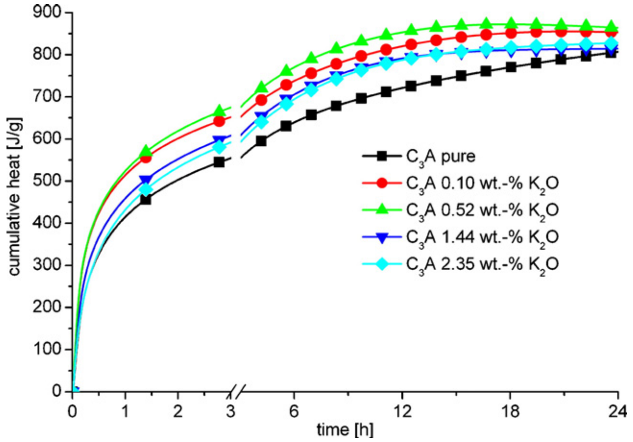

Fig. 13. Cumulative heat of hydration for C_3A solid solutions with K_2O.

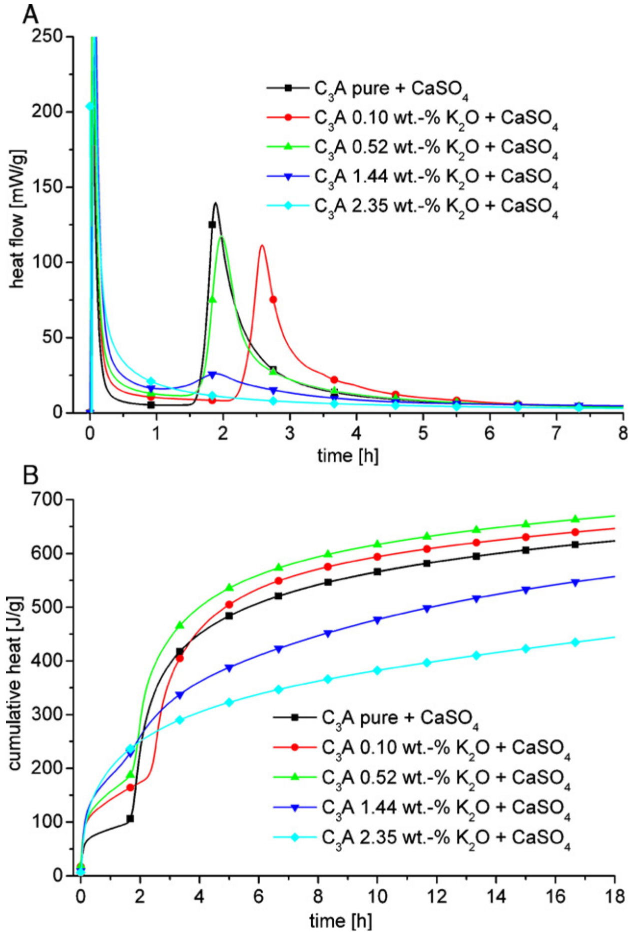

Fig. 14. A) Thermal heat and B) cumulative heat of hydration for pure C_3A solid solutions with K_2O in the presence of $CaSO_4$.

4. Conclusions

It is well known that foreign ions alter the crystal structure and the hydraulic activity of OPC clinker phases, but little work has been done so far to find a link between both influences. In this work C_3A was doped with MgO, SiO_2, Fe_2O_3, Na_2O and K_2O in different concentrations respectively. IR spectra were recorded and the crystal structure was determined using the method of Rietveld refinement. The hydration of all samples was compared using isothermal calorimetry. The results can be concluded as followed:

1. The crystal structure of C_3A was altered by SiO_2 and the hydration in the absence of $CaSO_4$ was accelerated. In the presence of $CaSO_4$ SiO_2 had nearly no influence on the hydration.

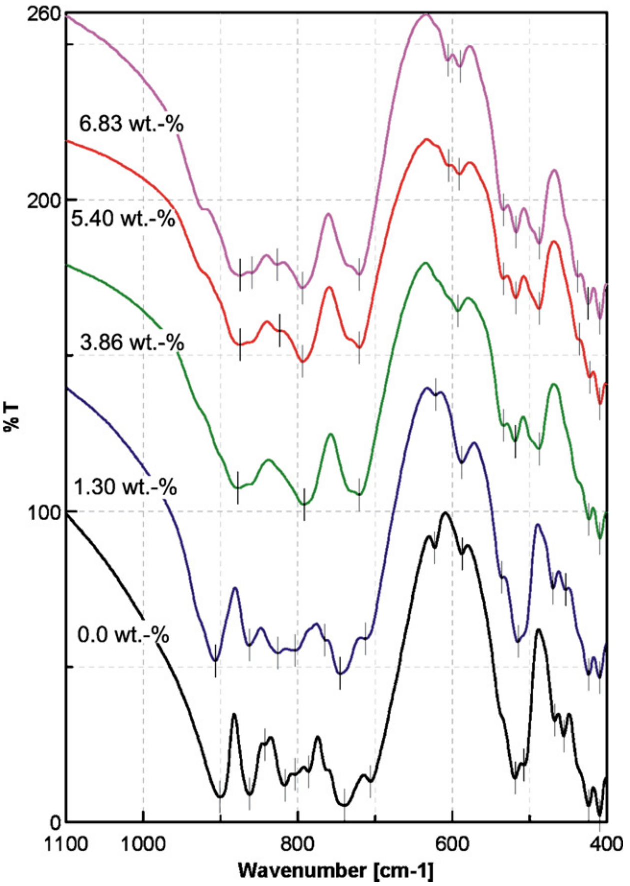

Fig. 15. IR spectra of C_3A solid solutions with Na_2O.

2. Fe_2O_3 changed the crystal structure of C_3A and had a retarding effect on the hydration, both in the presence and absence of $CaSO_4$.
3. Na_2O was the only oxide that changed the crystal structure from cubic to orthorhombic, but also within one crystal system the crystal structure was altered by the amount of Na_2O. The hydration of C_3A in the absence of $CaSO_4$ was retarded during the first hours but had nearly no effect on the long term.

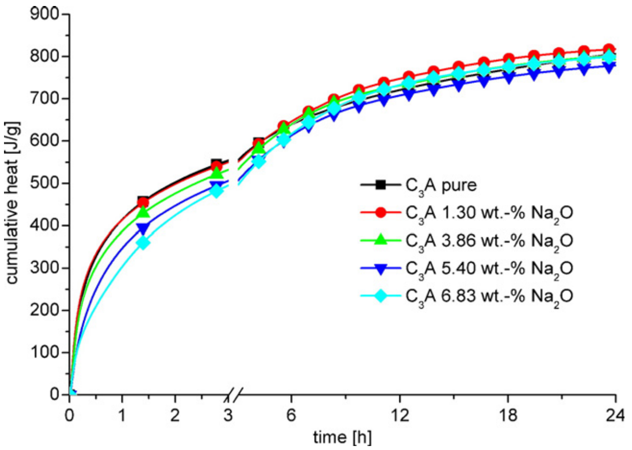

Fig. 16. Cumulative heat of hydration for C_3A solid solutions with Na_2O.

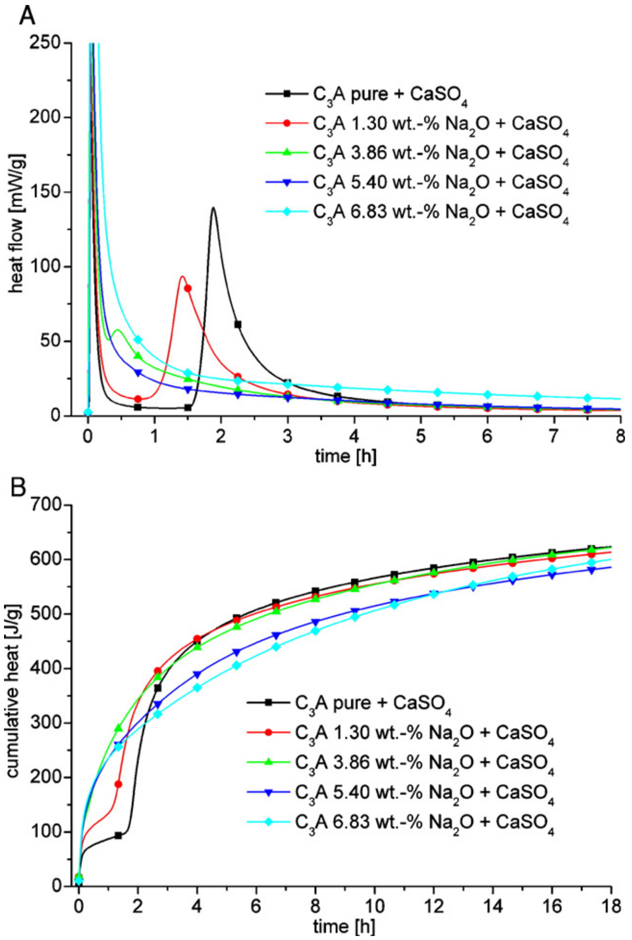

Fig. 17. A) Thermal heat and B) cumulative heat of hydration for pure C_3A solid solutions with Na_2O in the presence of $CaSO_4$.

4. MgO was only incorporated into the crystal structure up to 0.4 wt.%, the incorporation of K_2O into the crystal structure is doubtful. K_2O strongly accelerated the hydration of C_3A, the influence of MgO was not straight forward. For MgO and K_2O the effect on the hydration was most likely caused due to by-products formed during the synthesis.

All in all, the reactivity of C_3A is not directly correlated with the height of changes in the parameters of the crystal structure, but rather connected to the kind of doped metal oxide. In order to predict the reactivity of C_3A from the X-ray data, one has to determine the parameters of crystal structure and the kind of oxides that caused these changes.

Before this method can be applied to predict the reactivity of all clinker components from the X-ray diffraction, more work has to be done on the influence of combinations of different foreign oxides on the crystal structure and hydration activity.

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