

Influence of Foreign Oxides on Lattice Parameters and Reactivity of Pure Clinker Phases of OPC

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All OPC clinker phases contain foreign oxides in different composition and concentration which alter crystal structure and reactivity. A great variety of multiple doped C₃S containing MgO, Al₂O₃ and Fe₂O₃ as well as C₃A containing Fe₂O₃, SiO₂ and Na₂O was synthesized. The influence of foreign oxides on the properties of unhydrated samples was characterized by XRD combined with Rietveld calculations, ²⁹Si NMR and other techniques. The hydration characteristic was analyzed by isothermal conduction calorimetry and the hydration products were investigated by different techniques. From the data it can be concluded that some foreign oxides have a mutual effect on crystal structure and reactivity of C₃S and C₃A. The change in reactivity by doping with foreign oxides is not directly linked with the intensity of changes in lattice parameters but more a function of the kind and concentration of doped foreign oxide.

1 Introduction

With about 52-85 wt.-% the solid solution of tricalcium silicate (3CaO·SiO₂= C₃S) with MgO, Al₂O₃ and Fe₂O₃ is on the quantity basis the most important constituent of ordinary Portland cement (OPC) clinker. The solid solution is called alite and the hydration products are responsible for the high strength of hydrated OPC. Concerning the reactivity tricalcium aluminate (3CaO·Al₂O₃= C₃A) with incorporated foreign oxides like Fe₂O₃, SiO₂ or Na₂O is the other important constituent of OPC clinker. The solid solution is called aluminate, its reactivity is significantly higher than that of other clinker phases and it is responsible for the stiffening and setting of OPC. Moreover it is the clinker phase that shows the most distinct interactions with chemical admixtures like superplasticizers [1-6].

In former studies [7-9] it was shown that single doping with foreign oxides not only can affect the crystal structure of C₃S and C₃A but also its hydration characteristic. The hydration characteristic of the individual clinker phases is essential for the performance of OPC and therefore it would be of great interest for cement manufacturers and consumers to have a fast and easy method to analyze the kind and content of foreign oxides incorporated into clinker phases and to conclude from this on the hydration activity of cement. In addition to former studies with single doping, the main focus of this study was the influence of multiple doping of C₃S and C₃A and possible interactions of the doped oxides.

2 Experimental

The pure clinker phases were prepared using a sol-gel process prior to the high temperature synthesis [10]. Silica or alumina sol were mixed with a stoichiometric amount of a $\text{Ca}(\text{NO}_3)_2$ -solution. For doped samples solutions of $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, NaNO_3 , $\text{Al}(\text{NO}_3)_3$ or colloidal silica were substituted for Si or Ca in C_3S and Al or Ca in C_3A respectively, depending on the type of substitution. The mixture was heated to $\sim 70^\circ\text{C}$ under subsequent steering and kept at this temperature for several hours. During gelation some of the water evaporated and the gel was transferred into platinum crucibles. The samples were slowly heated to the synthesis temperature and further treated according to the parameters in **Table 1**.

	C_3S	C_3A
$\text{Ca}(\text{NO}_3)_2$ / (mol/l)	4	1.89
SiO_2 / (mol/l)	4	-
Al_2O_3 / (mol/l)	-	1.89
gel time / h	11	8
synthesis temperature / $^\circ\text{C}$	1500	1350
synthesis time	3-6 h	3-3 h

Table 1: Synthesis parameters for pure clinker phases

The synthesized set of C_3S and C_3A samples were ground in a planetary ball mill to the same fineness according to laser light scattering (d_{50} C_3S : 5.3 ± 0.5 ; d_{50} C_3A : 10.7 ± 2.9) and then characterized by XRD (Bruker D8 Advance) combined with Rietveld analysis (Topas 3.0). The hydration activity was monitored by isothermal conduction calorimetry (TAM air, Thermometrics) and the hydration products were characterized using different techniques.

For lack of space we only give a review over the influence of some foreign oxides on the crystal structure and hydration behavior of C_3S and C_3A . Detailed results will be published in a series of articles, soon.

3 Tricalcium silicate

A series of 48 samples was prepared. The abbreviations for C_3S doped with the most important foreign oxides MgO , Al_2O_3 and Fe_2O_3 are:

Foreign oxide	Concentration of foreign oxide in wt.-% (abbreviation)
MgO	0 (M0), 0.33 (M1), 0.66 (M2), 1.33 (M3), 2.00 (M4)
Al_2O_3	0 (A0), 0.50 (A1), 1.00 (A2)
Fe_2O_3	0 (F0), 0.37 (F1), 0.73 (F2), 1.10 (F3)
Reference	0 (R= M0A0F0)

3.1 Properties of unhydrated tricalcium silicate

A first hint concerning interactions between doped foreign oxides was the coloring. MgO or Al_2O_3 alone had no effect on the color C_3S , with Fe_2O_3

the color changed to brown. The combined doping of $\text{Fe}_2\text{O}_3 + \text{MgO}$ had no effect on the color whereas Al_2O_3 changed the color from brown to ochre. The grinding time necessary to achieve a comparable fineness was different, depending the kind and concentration of doped foreign oxides and can be summarized as followed:

- MgO has nearly no influence on grindability
- Fe_2O_3 distinctively extends the grinding time for the samples
- Al_2O_3 prolonged the grinding time strongly

In the case of combined doping, the influence of foreign oxides is not added up, but is dominated by the foreign oxide with the worst grindability.

Woermann et al. [11-15] and Bigaré et al. [16] published in the 1960es and 1970es detailed studies about the polymorphism of C_3S solid solutions. They determined solubility limits, type of substitution and modification of C_3S by means of different analytical methods. From X-ray diffraction the authors only published the diffraction angle of the reflex maxima in the region 32.0 to $32.8^\circ 2\Theta$ and 51.5 to $52.0^\circ 2\Theta$ together with the kind of polymorph, because at that time is was impossible to calculate lattice parameters of a complex structure like C_3S for so many samples. Nowadays powerful computers and Rietveld refinement enables to calculate lattice parameters from the whole powder diffraction, within a short time. This makes it possible to use the dataset of only a few lattice parameters to characterise structural changes between different samples instead to compare the XRD pattern itself.

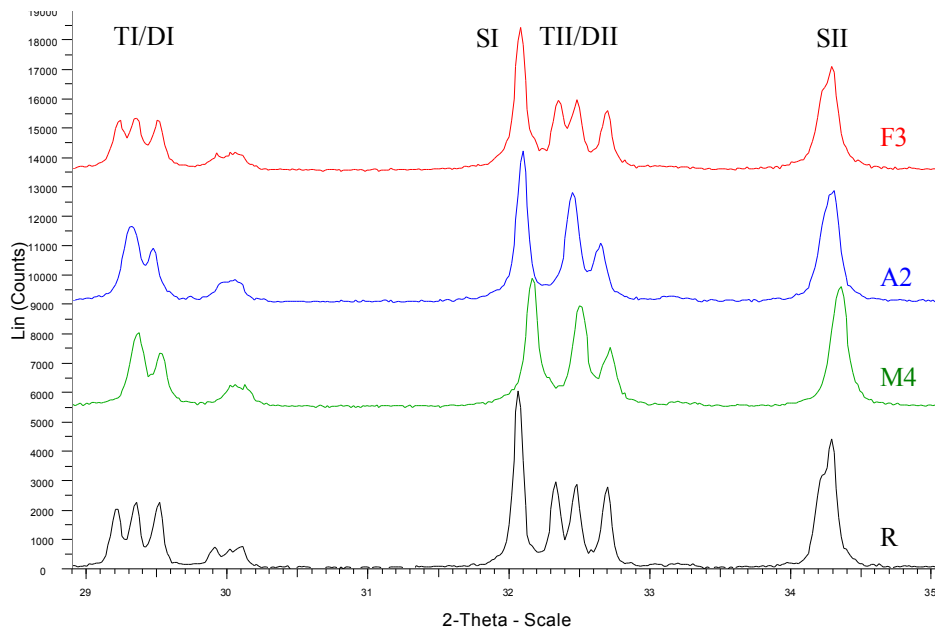


Figure 1: XRD of undoped C_3S (R) and with 2 wt.-% MgO (M4), 1 wt.-% Al_2O_3 (A2) or 1.1 wt.-% Fe_2O_3 (F3)

Table 2: Lattice parameter of C₃S samples

sample	a [Å]	b [Å]	c [Å]	a [°]	b [°]	g [°]
M0A0F0	11.6346	14.2131	13.6871	105.32	94.56	89.84
MgO						
M1A0F0	11.6292	14.2018	13.6774	105.29	94.56	89.87
M2A0F0	11.6264	14.1734	13.6460	105.12	94.66	89.91
M3A0F0	11.6147	14.1551	13.6344	105.14	94.67	89.92
M4A0F0	33.0887	7.0347	18.5084		94.16	
Al₂O₃						
M0A1F0	11.6380	14.2040	13.6812	105.24	94.59	89.87
M0A2F0	11.6462	14.1851	13.6655	105.10	94.67	89.88
Fe₂O₃						
M0A0F1	11.6343	14.2115	13.6858	105.30	94.56	89.85
M0A0F2	11.6333	14.2082	13.6836	105.29	94.57	89.86
M0A0F3	11.6351	14.2067	13.6835	105.27	94.59	89.86
MgO+Al₂O₃						
M1A1F0	11.6371	14.1795	13.6557	105.10	94.68	89.88
M1A2F0	11.6509	14.1709	13.6565	105.06	94.73	89.92
M2A1F0	11.6297	14.1750	13.6499	105.13	94.64	89.87
M2A2F0	11.6423	14.1356	13.6474	105.24	94.86	89.95
M3A1F0	33.0926	7.0376	18.5205		94.16	
M3A2F0	33.0885	7.0359	18.5243		94.17	
M4A1F0	33.1053	7.0388	18.5240		94.16	
M4A2F0	33.0919	7.0416	18.5302		94.19	
MgO+Fe₂O₃						
M1A0F1	11.6334	14.1795	13.6533	105.12	94.67	89.90
M1A0F2	11.6341	14.1802	13.6536	105.11	94.67	89.90
M1A0F3	11.6348	14.1797	13.6540	105.11	94.68	89.90
M2A0F1	11.6257	14.1722	13.6455	105.11	94.67	89.91
M2A0F2	11.6263	14.1717	13.6457	105.11	94.68	89.91
M2A0F3	11.6299	14.1710	13.6480	105.11	94.68	89.91
M3A0F1	11.6161	14.1589	13.6363	105.11	94.69	89.93
M3A0F2	11.6239	14.1211	13.6332	105.29	94.92	89.90
M3A0F3	11.6242	14.1218	13.6245	105.28	94.92	89.89
M4A0F1	33.1560	7.0440	18.5584		94.25	
M4A0F2	33.1413	7.0419	18.5570		94.25	
M4A0F3	33.1233	7.0408	18.5316		94.20	
Al₂O₃+Fe₂O₃						
M0A1F1	11.6399	14.1880	13.6640	105.13	94.67	89.88
M0A1F2	11.6402	14.1870	13.6610	105.12	94.68	89.87
M0A1F3	11.6399	14.1847	13.6603	105.12	94.67	89.88
M0A2F1	11.6484	14.1830	13.6648	105.09	94.69	89.90
M0A2F2	11.6636	14.1772	13.6607	105.01	94.74	90.05
M0A2F3	11.6616	14.1777	13.6590	105.01	94.72	90.06
0.66 %MgO+ Al₂O₃+Fe₂O₃						
M2A1F1	33.1400	7.0504	18.5543		94.22	
M2A1F2	33.1261	7.0484	18.5476		94.19	
M2A1F3	33.1297	7.0469	18.5420		94.19	
M2A2F1	33.1238	7.0485	18.5455		94.19	
M2A2F2	33.1166	7.0499	18.5484		94.20	
M2A2F3	33.1200	7.0483	18.5414		94.19	
2.0 %MgO+ Al₂O₃+Fe₂O₃						
M4A1F1	33.1033	7.0407	18.5255		94.15	
M4A1F2	33.0953	7.0402	18.5247		94.15	
M4A1F3	33.0969	7.0416	18.5274		94.15	
M4A2F1	33.0971	7.0397	18.5277		94.16	
M4A2F2	33.0969	7.0439	18.5304		94.17	
M4A2F3	33.0771	7.0335	18.5181		94.15	

The Rietveld refinement was based on structural data of triclinic [17] and monoclinic [18] C_3S . The lattice parameters of all investigated samples are summarized in **Table 1**. Like shown in **Figure 1**, shifts in the lattice of C_3S can qualitatively be observed in the X-ray diffraction, but transformations in the modification can only be obtained by Rietveld refinement.

Both elements, Mg and Al give distinct changes in lattice parameters and lead to the transformation of the triplet T1 and TII to doublets DI and DII (**Figure 1**). On first sight, the obtained changes are similar, but with the aid of Rietveld refinement it was demonstrated that only the highest doping with MgO (M4) lead to the transformation from triclinic to monoclinic C_3S . For all doped elements, Fe had the smallest effect on the crystal structure.

If the doping with MgO and Al_2O_3 were combined, the influence on the lattice parameters was summed up and the monoclinic C_3S already forms with 1.33 wt.-% MgO. It has to be mentioned that at high concentrations of foreign oxides, there is a kind of saturation below the limit of solubility of the individual foreign oxide. This is for example observable in the series of MgO doped samples with and without Al_2O_3 . The change in the diffraction pattern and lattice parameters is much lower if the concentration of Al_2O_3 is high. If only Fe_2O_3 is doped, lattice changes are very small, but significantly increase, if additionally MgO or more dominated Al_2O_3 are present in the case of combined doping.

With the doping of three foreign oxides, the influence is again dominated by MgO and Al_2O_3 but the combined doping also intensifies the influence of Fe_2O_3 on the changes in the crystal structure and with the addition of Fe_2O_3 and Al_2O_3 the monoclinic structure of C_3S is already reached with 0.66 wt.-% of MgO. The changes in XRD pattern and lattice parameters that are induced by Fe_2O_3 decrease with the total amount of doped foreign ions. If several foreign oxides are doped in high concentrations, the solubility limit of the individual oxides is exceeded and the samples have higher contents of free lime and several new peaks in the XRD pattern are visible, indicating the formation of a new phase that could not be identified yet.

In **Figure 2** the ^{29}Si MAS NMRs of undoped and doped C_3S are compared. Overlapping ^{29}Si resonances give broad signals with complex line shapes for doped samples. The line broadening not only occurs for monoclinic C_3S but is a result of the incorporation of foreign oxides. From the line broadening of doped C_3S it can be presumed, that the doped elements perturb the environment of SiO_4 -tetrahedra. The sample high in MgO is the only monoclinic one and this is also visible in a distinct peak-shift.

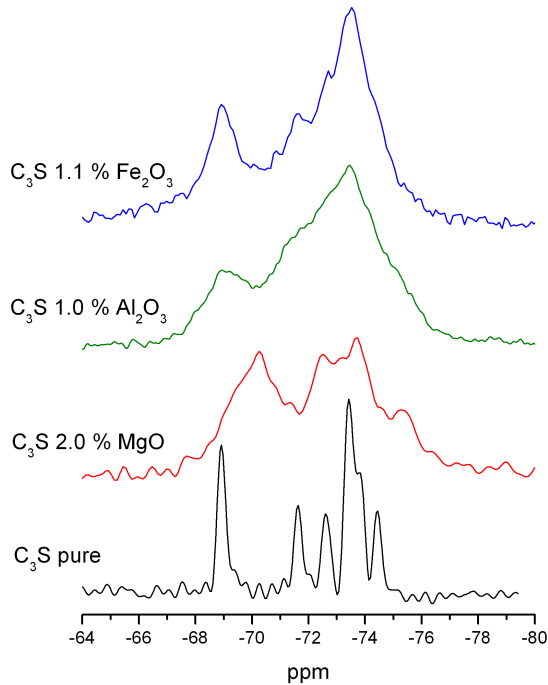


Figure 2: ^{29}Si MAS NMR of undoped C_3S (~ 170 scans) and C_3S with MgO , Al_2O_3 or Fe_2O_3 (~ 1000 scans)

3.2 Hydration of tricalcium silicate

The doping of C_3S with MgO does nearly not affect the hydration at any concentration. In contrast, the doping with higher amounts of Al_2O_3 intensifies the initial reaction and up to 15 h the heat of hydration is higher than for pure C_3S . Also Fe_2O_3 does significantly change the hydration characteristic. In the medium period of hydration, the heat evolution is lower than for other samples, but the long-term hydration is more intensive, because the heat of hydration is continuing on a medium level for a long time. After one week the heat of hydration was for all single doped samples higher than for pure C_3S (see **Figure 3**).

If two or three foreign oxides are combined, in most instances the effect is added up, but with some combinations there is also a mutual interaction of the doped elements. In all instances interactions with MgO are small, and the hydration is controlled by the doping with Al_2O_3 or Fe_2O_3 . In contrast to that the combined doping with Al_2O_3 and Fe_2O_3 yields in mutual interactions. High concentrations of Fe_2O_3 have the property to compensate the strong initial reaction caused by Al_2O_3 , whereas high concentrations of Al_2O_3 not only lower the maximum thermal power of the main hydration period, but also retard the hydration (**Figure 3**). Reasons for strong interactions between Al/Fe might be a similar substitution mechanism. All in all it has to be summarized that some dopings might retard the short- and medium-term hydration, but the long-term hydration is intensified in almost all cases.

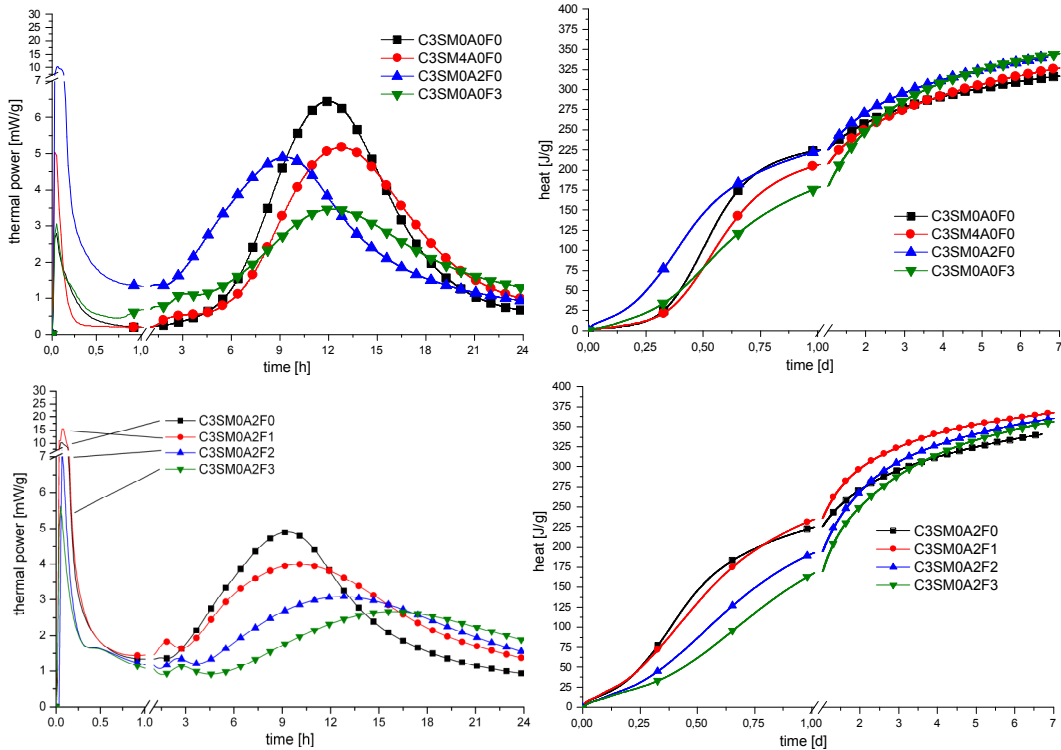


Figure 3: Hydration of pure C_3S with different dopings:
 above: 2 % MgO (M4), 1 % Al_2O_3 (A2) or 1.1 % Fe_2O_3 (F3)
 below: Al_2O_3 combined with Fe_2O_3 (F1-F3)

The investigation of the hydration products (XRD, TG/DSC and ^{29}Si NMR) revealed that after three month the hydration was completed for > 90 %. The doped elements did not form crystalline hydration products detectable by XRD. Some of the incorporated MgO formed amorphous $Mg(OH)_2$ that could be detected by TG/DSC but not by XRD.

4 Tricalcium aluminate

Four concentrations of foreign oxides were chosen according to the solubility limit, but the Na_2O concentration was chosen to stay < 2.4 wt.-%, when cubic C_3A is converted to orthorhombic C_3A . Additionally, a series of combined doping with Na_2O+SiO_2 in stoichiometric relations was prepared, because the incorporation of SiO_2 is favored in the presence of Na_2O [19, 20]. The abbreviations for the doping of C_3A with SiO_2 , Na_2O and Fe_2O_3 are:

Foreign oxide Concentration of foreign oxide in wt.-% (abbreviation)

Fe_2O_3	0 (Fe0), 1 (Fe1), 2 (Fe2), 3 (Fe4), 4 (Fe5)
SiO_2	0 (Si0), 1 (Si1), 2 (Si2), 3 (Si3), 4 (Si4)
Na_2O	0 (Na0), 0.52 (Na1), 1.03 (Na2), 1.55 (Na3), 2.06 (Na4)
SiO_2+Na_2O	0+0 (Si+Na0), 1+0.52 (Si+Na1), 2+1.03 (Si+Na2), 3+1.55 (Si+Na 3), 4+2.06 (Si+Na4)
Reference	0 (R = FOS0N0)

4.1 Properties of unhydrated tricalcium aluminate

The lattice parameters of pure and doped C_3A were refined by the Rietveld method using the structural data for cubic C_3A from Mondal et al. [21]. The results for lattice parameter a are summarized in **Figure 4**.

Doping with SiO_2 or Na_2O result in continuous shrinkage of the lattice, whereas the incorporation of much bigger iron ions leads to an expansion. In principle, the effect of the different foreign oxides is added up: the lattice parameter a for samples containing Na+Si is in most cases smaller than for samples only incorporating one of these oxides, but the intensity of changes is not directly added up. If samples are doped with Fe_2O_3 , the expansion of the lattice that is caused by Fe_2O_3 is nearly compensated by the incorporation of SiO_2 or Na_2O . It can be summarized that C_3A solid solutions with a certain range of lattice parameters exist, but since the change of lattice parameters moves into opposite direction for different metal oxides, some combinations can not be distinguished via XRD.

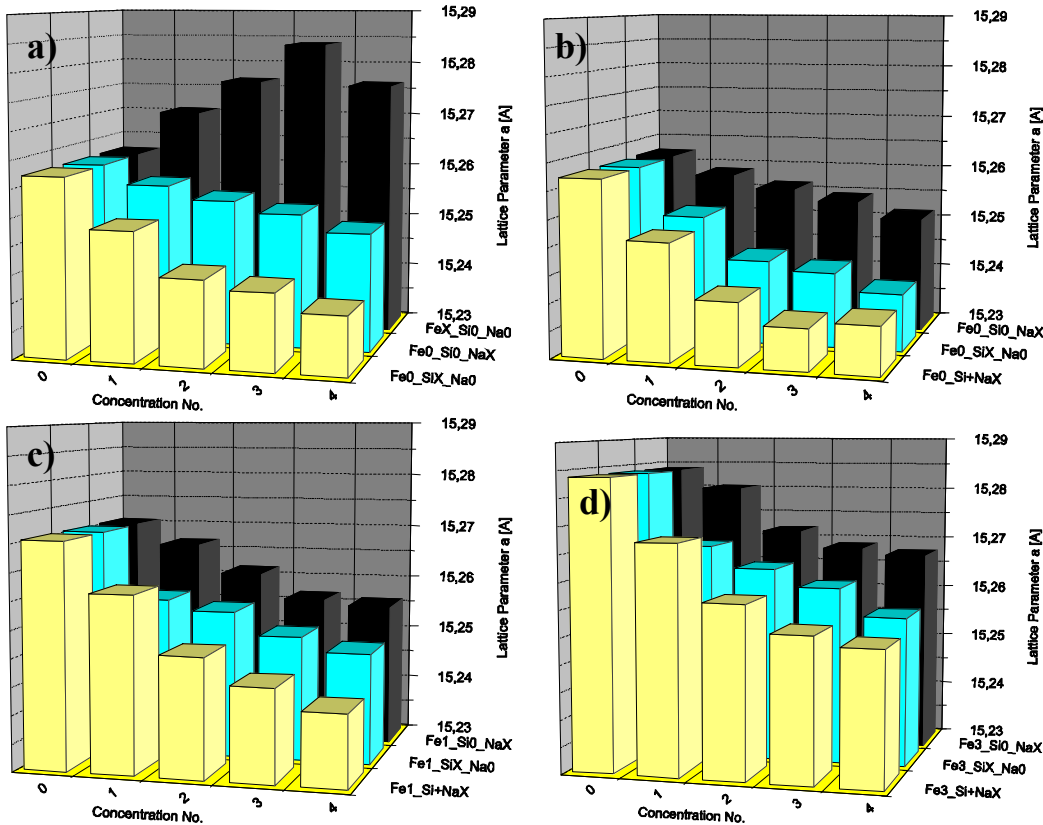


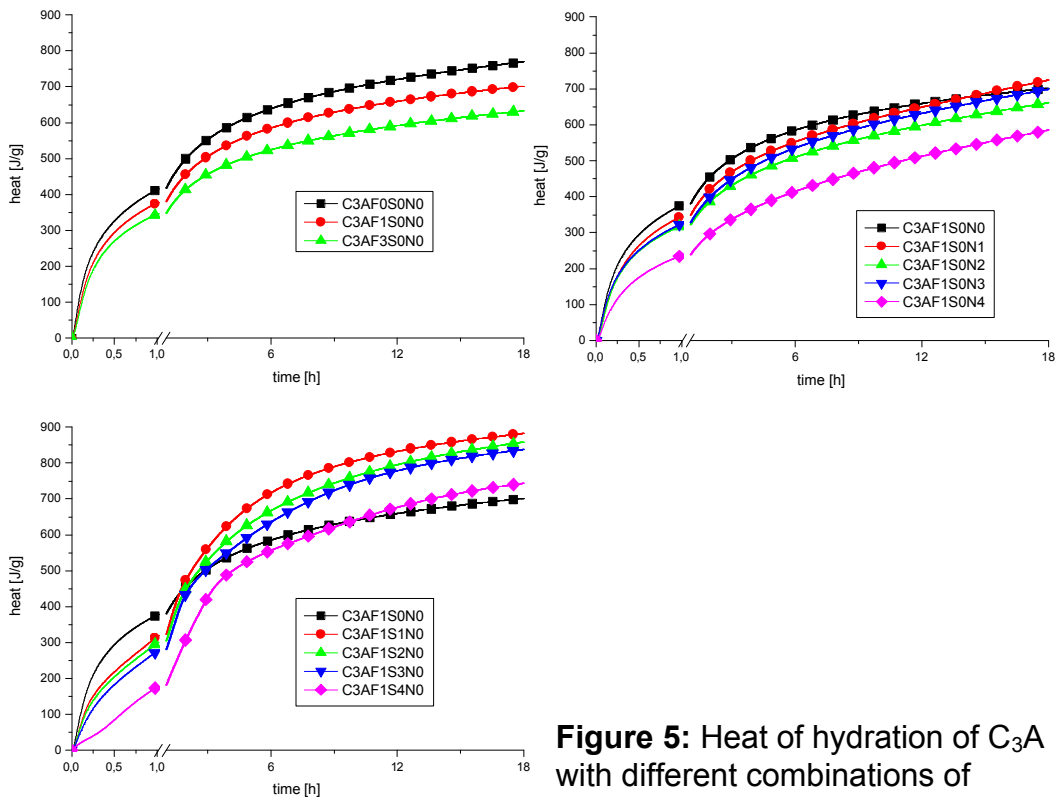
Figure 4: Lattice parameter a [\AA] of C_3A with:

- Fe_2O_3 , SiO_2 and Na_2O
- Na_2O , SiO_2 and combination SiO_2/Na_2O
- 1 wt.-% Fe_2O_3 + Na_2O , SiO_2 or combination SiO_2/Na_2O
- 3 wt.-% Fe_2O_3 + Na_2O , SiO_2 or combination SiO_2/Na_2O .

4.2 Hydration of tricalcium aluminate

The reaction of C_3A with water is very fast. In hydrating OPC the hydration of C_3A is controlled by adding $CaSO_4 \cdot xH_2O$ in order to retard the reaction and prevent false setting. The reactions that take place during hydration of a mixture of C_3A , $CaSO_4 \cdot xH_2O$ and water are very complex and depend on many constraints. Despite the fundamental relevance for cement hydration, these reactions are not fully understood yet. The reproducibility of the complex reaction is quite bad and for this project therefore the much simpler reaction of C_3A with water was taken to characterize the change in reactivity of C_3A by the incorporation of foreign oxides.

Figure 5 shows some examples on the influence of different foreign oxides on the kinetic of C_3A hydration. Na_2O slightly retards the hydration of C_3A in the short- and medium-term, but this effect is compensated when the hydration proceeds. This result confirms the findings of Boikova et al. [22] who interpreted that the retardation is most likely because the centre of the otherwise empty $Al_6O_{18}^{18-}$ -rings are occupied by additional Na-atoms and therefore the dissolution of the denser C_3A is retarded. The retardation caused by Na_2O is even amplified by the combined doping with Fe_2O_3 .



The single doping of C_3A with Fe_2O_3 gives a continuous decrease in reactivity that was found in the same way by Kemethmüller et al. [23].

Together with SiO_2 the reaction is even further retarded during the initial 1 to 2 hours, but later on the retardation is at least partially compensated by the influence of SiO_2 . Also the additional incorporation of Na_2O gives further retardation during the first several hours.

The influence of SiO_2 on the hydration of C_3A is not straight forward. During the first hour of hydration SiO_2 has a tendency to retard the hydration. Rising concentrations of Fe_2O_3 even support this tendency. If the hydration proceeds, the retarding effect is gradually compensated and inverted into acceleration. It is interesting to mention, that the acceleration is strongest with 1 wt.-% SiO_2 and is then steadily decreasing.

All hydration products were analyzed by XRD and in all cases nearly pure C_3AH_6 (katoite) was formed. The lattice parameter of katoite were refined by the Rietveld method. From the results in **Figure 6** it can be seen that Si is incorporated into the structure of katoite and this produces a decrease in lattice parameter a . Fe is also incorporated into C_3AH_6 and like in the case of C_3A the replacement of Al^{3+} by the larger Fe^{3+} causes an increase in a and a slight rise in the distortion of the lattice (strain). From the unchanged lattice parameter of the hydrated samples containing Na it can be concluded that sodium is not incorporated into katoite.

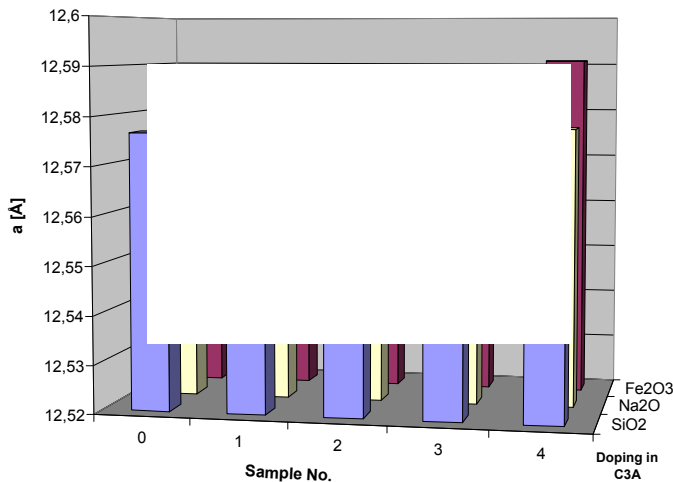


Figure 6: Refined lattice parameter a of C_3AH_6 prepared by hydration of undoped and doped C_3A

5 Conclusion

The work has shown that the incorporation of foreign oxides into C_3S and C_3A has an influence on different properties like color, grindability, lattice parameters and kinetic of hydration. Some combinations of foreign oxides have a mutual effect on the lattice parameters or hydration.

The lattice parameters of triclinic and monoclinic C_3S with different concentration of MgO , Al_2O_3 and Fe_2O_3 are quite unique for every combination of these doped elements. Therefore it is possible to conclude from the lattice parameters of alite on the kind and amount of incorporated foreign oxides. Due to the fact that the reactivity of C_3S depends on the

composition of alite, this information is of great value to predict the reactivity of alite of an unknown cement or to predict changes in reactivity during quality control.

For C_3A the knowledge of the lattice parameters of multiple doped samples can help to interpret the lattice parameter of the aluminate phase in OPC, but since the change of the lattice parameter of cubic tricalcium aluminate moves into the opposite direction for different doped metal oxides, some combinations of doped oxides can not be distinguished.

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