## Synthesis of Pure Cementitious Phases by Sol-Gel Process as Precursor

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Abstract. Calcium silicates and aluminates are the main constituents of ordinary Portland cement (OPC) and calcium aluminate cements (CAC) and therefore the pure phases are of great importance for the investigation of interactions between binder and additives or admixtures. Additionally, investigations on clinker phases doped with foreign ions enable the improvement of the performance of cements. For this purpose great amounts of pure phases are needed. These phases are hard to synthesize via a solid state reaction of solid educts. Thus there is a need for a new, more efficient route to synthesize these phases. The sol-gel process as precursor provides an alternative to the conventional method. In this paper experimental evidence is presented for an improved synthesis of calcium silicates and aluminates via sol-gel processes, the characterisation of these clinker phases and their hydration behaviour.

**Keywords:** Sol-gel processes; Calcium silicates, Calcium aluminates; Gels; Solid-state chemistry

### Synthese reiner Klinkerphasen über Sol-Gel Prozesse als Vorstufen

Inhaltsübersicht. Calciumsilicate und -aluminate sind die Hauptbestandteile von Portlandzement (OPC) und Tonerdezement (CAC). Die reinen Phasen sind von großer Bedeutung für die Untersuchung von Wechselwirkungen des Bindemittels mit Zusatzstoffen und -mitteln. Darüber hinaus ermöglicht die Untersuchung von mit Fremdionen dotierten Klinkerphasen die Leistungsfähigkeit von Zementen zu steigern. Für diese Untersuchungen werden große Mengen der reinen Phasen benötigt, die sich jedoch nur unter hohem Aufwand über Festköperreaktionen aus den festen Edukten

### 1 Introduction

Portland cement has been known now for more than 100 years and with a world production of  $1647 \cdot 10^6$  tons in 2001 [1] it is the chemical product, that is produced in the highest amount by far. This is due to the outstanding chemical and mechanical properties for building purposes. In ordinary Portland cement clinker (OPC) tricalcium silicate  $(Ca_3(SiO_4)O)$ , dicalcium silicate  $(Ca_2(SiO_4))$ , tricalcium aluminate (Ca<sub>9</sub>(Al<sub>6</sub>O<sub>18</sub>)) and tetracalcium aluminate ferrite  $(Ca_2(Al,Fe^{3+})_2O_5)$  are the main constituents. In the multiple phase system of OPC clinker, these four phases always contain minor and trace elements in different concentrations and the terms alite, belite, aluminate and ferrite are used for the doped versions of the pure phases. In calcium aluminate cements (CAC) monocalcium aluminate  $(CaAl_2O_4)$  is the most important phase. CAC can also contain other phases such as monocalcium dialuminate (grosssynthetisieren lassen. Deshalb war es notwendig einen neuen, effizienteren Syntheseweg zu finden, mit dem diese Phasen leicht zugänglich sind. Der Sol-Gel Prozess als Vorstufe für den Brennprozess stellt eine Alternative zur konventionellen Methode dar. In diesem Artikel werden experimentelle Daten zur optimierten Herstellung reiner Calciumsilicate und -aluminate, die Charakterisierung dieser Klinkerphasen sowie deren Hydratationsverhalten beschrieben.

ite,  $CaAl_4O_7$ ), mayenite ((CaO)<sub>12</sub>( $Al_2O_3$ )<sub>7</sub>), belite and ferrite.

Very high temperatures are needed to produce OPC and CAC clinker and even at 1450 °C only some of the components melt. The partial melting is necessary for the rapid reaction of the constituents to OPC and CAC clinker in industrial processes. This production process is the reason, why CAC and OPC contain different clinker phases, even though not all of them contribute to the strength development of the cement. Because of the appearance of a mixture of multiple binary and ternary phases, the OPC and CAC clinker systems are quite complex and therefore the use of pure doped or undoped clinker phases for fundamental research in cement chemistry is of great importance. They can for example be used for investigations on the hydration processes of one well defined clinker phase with various additives or admixtures or for the prediction of the influence of minor elements on the reactivity of cement. Normally these pure phases are synthesized by a solid-state reaction of the carbonates or oxides at high temperatures. For the most essential phases this process takes several hours up to days with several intermediate grindings [2-4]. The formation of the clinker phases can be accelerated by packing the different constituents very close. This is done by forming pellets from the raw material at very high pressure [5, 6].

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Via this well established method it is possible to produce pure phases, but the amount of clinker phases produced is too small for extensive studies. Hence fundamental research is often done without pure clinker phases, but with the complex multi phase system of the cement, which makes interpretation of the data difficult and sometimes impossible.

In order to provide a more efficient way for the synthesis of pure phases, the sol-gel process was introduced and optimized. This process has already been established for the synthesis of very homogenous types of glass and ceramics at lower temperatures than normally used and there have also been made some efforts to produce pure clinker phases. In all those cases the synthesis was done with sols of SiO<sub>2</sub> or  $Al_2O_3$  and  $Ca(NO_3)_2$  was used as a source for CaO in the later product. Goktas et al. [7] and Kerns et al. [8] synthesized amorphous calcium aluminates of different nominal composition via a sol-gel process, where they used aluminium sec-butylate  $(Al(OC_4H_9)_3)$  to produce the colloidal Al<sub>2</sub>O<sub>3</sub> as a starting material. Calcium silicate glasses were prepared by Saravanapavan et al. [9] and Laudisio et al. [10, 11]. They prepared in a first step colloidal SiO<sub>2</sub> as a starting material from tetraethoxy-silicate (TEOS). Yoshizawa et al. [12] used TEOS and  $Ca(NO_3)_2$  as starting material in a sol-gel process to synthesize Ca<sub>2</sub>(SiO<sub>4</sub>) at a temperature of 700 °C. Nettleship et al. [13] and Hong et al. [14] used the Peshini-resin process to synthesize  $Ca_2(SiO_4)$ . Roy et al. [15] were the first to synthesize clinker phases via a sol-gel process using a commercially available silica sol. A detailed kinetic study of Ca<sub>3</sub>(SiO<sub>4</sub>)O formation from sol-gel precursors was published by Wang et al. [16].

In this paper the synthesis of some of the most important clinker phases from commercially available colloidal SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> using a sol-gel process as precursor is described. The aim was to synthesize  $Ca_2(SiO_4)$ ,  $Ca_3(SiO_4)O$ ,  $Ca_9(Al_6O_{18})$ ,  $CaAl_2O_4$  and  $CaAl_4O_7$  in a more efficient way and without stabilising foreign ions. The main phases of OPC  $Ca_3(SiO_4)O$  and  $Ca_2(SiO_4)$  as well as the main phase of CAC  $CaAl_2O_4$  were investigated in detail.

### 2 Results and Discussion

The synthesis of pure clinker phases via a sol-gel process as precursor is a series of different steps. Figure 1 shows the schematic steps from a sol to the final product. The Understanding of every single step is of importance to optimize the synthesis. In the following chapters of this paper experimental evidence is presented that gives a better understanding of the synthesis and finally leads to an optimized procedure for synthesis.

# 2.1 Change in zeta potential and rheological behaviour of sols with pH

For the stability of most electrostatic stabilized inorganic sols, the zeta potential plays a major role. In Figure 2 the change in zeta potential of  $Al_2O_3$  and  $SiO_2$  with the pH is shown. The highest zeta potential of the sols is found at the



Figure 1 Schematic steps for the synthesis of cementitious phases via a sol-gel process. Colloidal silica or alumina is mixed with  $Ca(NO_3)_2$  and the pH is adjusted to a proper value. During gelation a network is formed. When the sample is heated, in a first step water evaporates to form a xerogel and  $Ca(NO_3)_2$  precipitates onto the surface of the network. In a second step  $Ca(NO_3)_2$  decomposes to CaO and reacts with the network to form the cementitious phase.



**Figure 2** Change in zeta potential for silica and alumina sol with the pH. At a low pH some of the hydroxyl groups on the oxidic surface are protonated and therefore the zeta potential is positive. At higher pH values some of the hydroxyl groups are deprotonated and the zeta potential becomes negative.

pH of the original solution. The iso electric point (i.e.p.) of  $SiO_2$  was found at pH 1.4 and for  $Al_2O_3$  it was 9.8. The measured values are very close to the ones of *Agrawal* et al. [17] (1.6 for  $SiO_2$ ) and *Healy* et al. [18] (8.9 for  $Al_2O_3$ ). In the case of  $Al_2O_3$  this is essential for the conditions of gelation, because the gelation takes place fastest near the i.e.p.. The coagulation of the particles can also be monitored by testing the viscosity of the sample. The change in viscosity of  $Al_2O_3$  in water at different pH. confirms the result of measured zeta potential (Fig. 3).



Figure 3 Change in viscosity and zeta potential for colloidal alumina in water at different pH. With lower values of the zeta potential the repulsive coulomb forces between particles decrease and the attractive van der Waals interaction of the particles get more important. At the i.e.p. the zeta potential of  $Al_2O_3$  becomes zero resulting in the strongest attraction of the particles and therefore the highest viscosity. For alumina the gelation is fasted near the i.e.p.

#### 2.2 Optimizing conditions for gelation

There are several ways to form a gel from a stable sol. One is to coagulate the sol at the i.e.p. (change in pH), the other is to coagulate the sol by adding an electrolyte. Additional to the pH and the electrolyte concentration, the gelation is influenced by the concentration of the sol and the temperature. Iler has shown, that the optimum pH for the shortest gelation time of a sol can vary according to the concentration of soluble ions [19]. Therefore the time of gelation of an alumina sol in a solution of Ca(NO<sub>3</sub>)<sub>2</sub> was measured at different pH values. As can bee seen from the change in viscosity with pH for  $Al_2O_3$  in pure water and in  $Ca(NO_3)_2$ solution, that is presented in Figure 4, addition of  $Ca(NO_3)_2$  enhances the viscosity of the alumina sol, because the potential drop of the particles is enhanced by the addition of electrolyte and thus the zeta potential is lowered. The maximum of the viscosity is shifted from pH 9.5 in pure water to 6.5 in a 0.95 mol/L solution of  $Ca(NO_3)_2$ .

In the case of the used silica sol, an instant change in viscosity for different values of pH could not be observed. The reason for this is the high stability of the silica sol. This made it necessary to monitor the change in viscosity for the process of gelation over several hours. The results are reported in Figure 5 and an examination of the data reveals, that the optimum pH for the gelation of silica in the presence of a 4 mol/L solution of  $Ca(NO_3)_2$  is at pH 5.5. The process of gelation can also be accelerated by increasing the temperature. 70 °C proved to be a good compromise between short gelation time and easy handling of the sample. The conditions for the synthesis of gels by sol-gel processes for different cementitious phases are outlined in Table 1.



**Figure 4** Change in viscosity for colloidal alumina in pure water and in a 0,95 mol/L solution of  $Ca(NO_3)_2$ . The high ionic strength in the solution result in a steeper drop of the potential and therefore in lower repulsive forces that gives higher viscosity. The adsorption of ions on the surface also changes the pH for the i.e.p. and therefore shifts the position of maximum viscosity.



**Figure 5** Gelation for colloidal silica in a 4 mol/L solution of  $Ca(NO_3)_2$  at different pH. Colloidal silica is very stable and the i.e.p. is not the point where the gelation is fasted. Therefore the test for the dependence of the gelation time on pH had to be performed over a longer period of time.

#### 2.3 Degree of gelation

While a sol is converted to a gel, the growing agglomerates have the same concentration of silica and water as the surrounding solution. These aggregates, the so called "gel phase" do not sediment and are not visible, because the density and the refractive index are the same as that of the remaining sol. For the same reason only a slow increase in viscosity can be measured before the sol converts into a gel. There are also only little changes in other properties up to a point, where the viscosity begins to increase rapidly (see Figure 6) and the gelation occurs at the "gel point" [19].

The degree of gelation was measured by using the method described by *Iler* [19]: A sample of a sol in the process of gelation was diluted threefold using a solution of

Table 1 Conditions	for	the	sol-gel	process
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	Ca <sub>3</sub> (SiO <sub>4</sub> )O	Ca <sub>2</sub> (SiO <sub>4</sub> )	C <sub>9</sub> (Al <sub>6</sub> O <sub>18</sub> )	CaAl <sub>2</sub> O <sub>4</sub>	CaAl <sub>4</sub> O <sub>7</sub>
$Ca(NO_3)_2 / (mol/L)$	4	4	1.89	1.89	1.89
$SiO_2 / (mol/L)$	4	4	_	—	-
$Al_2 \tilde{O}_3 / (mol/L)$	_	_	1.89	1.89	1.89
pH	5.5	5.5	8.0	6.5	8.0
approx. time for gelation / h	11	8	8	4	2



**Figure 6** Correlation between degree of gelation and viscosity. At the gel point a marginal improve in the degree of gelation gives an intense rise in viscosity.

 $Ca(NO_3)_2$  of the same concentration and pH as used in the sol-gel process. Thereby the solution stays stable during centrifugation. The mixture was centrifugated under a gravity insufficient to settle single colloidal particles (approx. 10000 g), but during the centrifugation the already gelled part of the sol settles because of its higher density in comparison to the non-gelled part of the sol, which is dissolved in the added electrolyte solution. The degree of gelation is calculated from the weighted gelled part of the silica sol after discarding the supernatant. This test could not be done with the  $Al_2O_3$  sol, because it stays not stable during the centrifugation.

# 2.4 Phase composition and reactivity of the synthesized cementitious phases

During the burning of the cementitious clinker phases different intermediates can occur, depending on the chemical and stoichiometric composition. The crystalline products can be analysed by XRD and for some phases it is also possible to find different modifications. For some phase mixtures a semi-quantitative analysis was done, but especially in the case of calcium silicates the results were not very reliable. Here the amount of Ca<sub>2</sub>(SiO<sub>4</sub>) and Ca<sub>3</sub>(SiO<sub>4</sub>)O was quantified according to the content of free lime detected by the Franke method [20] (sensitivity  $\pm$ 0.05 %, detection limit 0.1 %).

T / °C	1140	1230	1500/1230
CaO <sub>free</sub> / wt%	2.2	1.3	—
γ-Ca <sub>2</sub> (SiO <sub>4</sub> ) / wt%	0	0	40
β-Ca <sub>2</sub> (SiO <sub>4</sub> ) / wt%	95	90	60
Density / (g/cm <sup>3</sup> )	3.30	3.36	3.12



Figure 7 Polymorphic transformation of Ca<sub>2</sub>(SiO<sub>4</sub>). Only fine particles can form the hydraulic active metastable  $\beta_L$ -modification of Ca<sub>2</sub>(SiO<sub>4</sub>), that is of interest for hydraulic binders. If the coarser  $\beta_H$ -Ca<sub>2</sub>(SiO<sub>4</sub>) is formed during the synthesis, this is irreversibly transformed to the non-hydraulic  $\gamma$ -modification during cooling.

#### 2.4.1 Dicalcium silicate

Dicalcium silicate was synthesized using different temperature programs with a maximum temperature of 1140, 1230 or 1500 °C respectively. All samples were burned for 18 h with one intermediate grinding. The sample reacted at 1500 °C was additionally tempered at 1230 °C for several hours to decompose the Ca<sub>3</sub>(SiO<sub>4</sub>)O. After the burning the semi-quantitative composition of the three samples was analysed and showed clear differences that can be seen from the data presented in Table 2.

Figure 7 shows the polymorphic transformation of Ca<sub>2</sub>-(SiO<sub>4</sub>). All transformations are reversible, except for the one from  $\gamma$ - to  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>).  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) is the thermodynamically stable modification at ambient temperature, but it is barely hydraulic and thus is of no interest for hydraulic binder.

The hydraulic active  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) normally transforms to  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) during cooling and  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) is only stable at ambient temperature if foreign ions are incorporated into the crystal lattice. The transformation of Ca<sub>2</sub>(SiO<sub>4</sub>) without

foreign ions can be inhibited if the Ca<sub>2</sub>(SiO<sub>4</sub>) is quenched [21] or if fine  $\alpha'_L$ -Ca<sub>2</sub>(SiO<sub>4</sub>) is produced, which transfers to stable  $\beta_L$ -Ca<sub>2</sub>(SiO<sub>4</sub>) [22]. Therefore the particles have to be very small. *Locher* [23] reports, that the critical crystal size must be below 5-10 µm. The results of the own study show, that it is possible to produce pure  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) by the solgel process, if the right temperature is used for the synthesis.

In the samples synthesized at a temperature up to 1230 °C, no  $\gamma$ -modification of Ca<sub>2</sub>(SiO<sub>4</sub>) was found. Only if the temperature during the burning process was as high as 1500 °C,  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) was detected in the product. This is most likely, because at high temperatures small crystals can grow together to form coarse  $\alpha'_{L}$ -Ca<sub>2</sub>(SiO<sub>4</sub>) that transforms into  $\beta_{\rm H}$ -Ca<sub>2</sub>(SiO<sub>4</sub>) and finally to  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) during cooling. In contrast to that Nettleship et al. [13] and Hong et al. [14] and Lee et al. [24] who used other methods to synthesize  $Ca_2(SiO_4)$ , also found  $\beta$ - $Ca_2(SiO_4)$  as the main phase up to a reaction temperature of 1200 °C, but above that temperature  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) was the main phase and at 1400 °C it was the only existing phase. This shows, that crystals formed during the sol-gel process are much finer than the ones formed by other routes of synthesis. If that was not the case, all Ca<sub>2</sub>(SiO<sub>4</sub>) should have been transformed into the  $\gamma$ -modification.

The samples containing different concentrations of the two modifications of  $Ca_2(SiO_4)$  could also be differentiated by density ( $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) = 3.33 g/cm<sup>3</sup>.  $\gamma$ -Ca<sub>2</sub>(SiO<sub>4</sub>) = 2.97 g/cm<sup>3</sup>) and isothermic thermocalorimetry. The heat evolution of samples only containing the  $\beta$ -modification is distinctly higher than that of the samples containing both modifications. In overall the hydraulic activity of Ca<sub>2</sub>(SiO<sub>4</sub>) is much lower than the one of Ca<sub>3</sub>(SiO<sub>4</sub>)O.

#### 2.4.2 Tricalcium silicate

In the binary system CaO-SiO<sub>2</sub> the phases Ca<sub>3</sub>(SiO<sub>4</sub>)O, Ca<sub>2</sub>(SiO<sub>4</sub>) and CaO can occur under the used conditions. In the absence of foreign ions the triclinic I modification of Ca<sub>3</sub>(SiO<sub>4</sub>)O is the only one that exists as a metastable form at ambient temperature [21]. A series of samples was synthesized at different temperatures for different times. The resulting semi-quantitative phase composition is shown in Table 3. In the temperature range between 800 and 1250 °C  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) and free lime were the only crystalline phases that could be detected by XRD. The amount of free lime measured by the Franke method [20] was always below the theoretical value of 24.5 wt.-%. The reason for this is, that Ca<sub>2</sub>(SiO<sub>4</sub>) can intercalate excess CaO into its crystal structure [25]. At temperatures above 1250 °C free lime was bound by Ca<sub>2</sub>(SiO<sub>4</sub>) to form Ca<sub>3</sub>(SiO<sub>4</sub>)O.

After firing the samples for 14 hours at 1500 °C a free lime content between 3.5 to 6.0 wt.-% was found. After grinding the samples for 10 min in a planetary ball mill and burning them for another 14 h at 1500 °C, the content of free lime was between < 0.05 to 0.5 wt.-%. All the samples that had been fired three times had less than 0.05 wt.-% of free lime. In order to synthesize pure Ca<sub>3</sub>(SiO<sub>4</sub>)O via a conventional method, the mixture had to be fired at 1500 °C for at least 48 hours with four to five intermediate grindings.

All samples of Ca<sub>3</sub>(SiO<sub>4</sub>)O synthesized via a sol-gel process were fine powders ( $d_{50} \approx 16 \mu m$ ) and could be hydrated without previous grinding. Short additional grinding gave even finer particles, which were much more reactive. This shows a major difference between the sol-gel samples and the conventional ones, which were hard and compact after the synthesis and needed time and energy consuming grinding. The medium particle size  $d_{50}$  of a sol-gel Ca<sub>3</sub>(SiO<sub>4</sub>)O ground for 2 min in a planetary ball mill was about 6.5  $\mu m$ , whereas an extensively ground conventional Ca<sub>3</sub>(SiO<sub>4</sub>)O sample (12 min) had an particle size of 8.4  $\mu m$ .

The differences in reactivity between the sol-gel and the conventional  $Ca_3(SiO_4)O$  can best be shown through the differences in the heat of hydration and the degree of hydration (see Figures 8 and 9). The reactivity of the conventional sample is higher during the first period of hydration (with an extra peak after about 2 h caused by a small amount of free lime), whereas after an increased dormant period with a moderate rate of heat evolution for seven hours, the sol-gel sample then shows a very high reactivity and after 15 hours the heat of hydration of the sol-gel sample is higher than the one of the conventional sample. The differences in reactivity could also be monitored by the degree of hydration  $\alpha$ , which was measured by the loss of ignition at 950 °C. The sol-gel sample hydrated for 28 days showed no unhydrated  $Ca_3(SiO_4)O$  in the XRD analysis and therefore this sample was taken as reference for the degree of hydration ( $\alpha = 1$ ). In the case of the conventional  $Ca_3(SiO_4)O \alpha$  was 0.7 after 28 days of hydration and this again indicates that the sol-gel sample is more reactive compared to the conventionally produced  $Ca_3(SiO_4)O$ .

# 2.4.3 Tricalcium aluminate, monocalcium aluminate and monocalcium dialuminate

Cubic tricalcium aluminate was produced by firing the samples from the sol-gel process two to three times for 14 hours at 1260 °C with intermediate grindings. Table 4 shows the sample composition. Only mayenite and free lime were detected as by-products. After three firings the content of free lime was between < 0.05 and 0.5 wt.-%. After grinding the final product, no differences could be found in the particle size distribution compared to conventionally produced  $Ca_9(Al_6O_{18})$ . Furthermore the hydration activity of both the sol-gel and the conventional  $Ca_9(Al_6O_{18})$  was the same. This is due to the fact that the by-product mayenite melts partially and thereby the product loses the fine structure of the gel-network.

The composition of a  $CaAl_2O_4$  sample which was fired at different temperatures for different times is shown in Table 5. To produce pure  $CaAl_2O_4$ , a firing time of no more than 28 hours with just one intermediate grinding was necessary. Free lime could only be detected up to a firing temperature of 1000 °C. After 28 hours of firing at 1500 °C

Table 3 Sample composition of	the $3CaO + SiO_2$	system; $SiO_2$ from colle	loidal silica can not be	detected by XRD
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T / °C	600	700	800	900	1200	1300	1400	1500	1500	1500
t	30 min	30 min	30 min	14 h	28 h <sup>b)</sup>					
CaO <sub>free</sub> / wt-%	11.7	22.4	22.6	22.8	22.7	20.9	16.5	4.1	3.7	< 0.01
Ca <sub>3</sub> (SiO <sub>4</sub> )O (TI) <sup>a)</sup> / wt%	_	-	-	-	-	13.8	31.9	83.1	84.7	> 99
$Ca_2(SiO_4) (\alpha + \beta) / wt\%$	—	75.4	75.4	75.4	75.4	65.3	51.6	12.8	11.6	—
$Ca_3(SiO_4)O(11)^{a}$ / wt% $Ca_2(SiO_4)(\alpha+\beta)$ / wt%	_					13.8 65.3	31.9 51.6	83.1 12.8	84.7 11.6	>

a) Ca2(SiO4) can intercalate CaO into its crystal lattice

<sup>b)</sup> The sample was ground after 14 h



Figure 8 Overall heat of hydration for conventional and sol-gel  $Ca_3(SiO_4)O$  for one week. Up to 14 h the heat of hydration is higher for the conventional  $Ca_3(SiO_4)O$ .



**Figure 9** Heat of hydration for conventional and sol-gel  $Ca_3(SiO_4)O$  during three days. For the sol-gel  $Ca_3(SiO_4)O$  the induction period is longer, but the maximum heat evolution is very high.

Table 4 Sample composition of the 3CaO +  $Al_2O_3$  system at different reaction times at 1260  $^{\circ}C$ 

t / h	14	28	42
CaO <sub>free</sub> / wt%	2.5	1.2	0.4
$Ca_{9}(Al_{6}O_{18}) / wt\%$	81.5	86.8	97.3
(CaO) <sub>12</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>7</sub> / wt%	16.0	12.0	2.3

Table 5 Sample Composition of the $CaO + Al_2O_3$ system at differ-
ent temperatures and reaction times; Al2O3 from colloidal alumina
can not be detected by XRD

T / °C	800	1000	1200	1400	1500	1500
t	30 min	30 min	30 min	30 min	14 h	28 h <sup>a)</sup>
CaO <sub>free</sub> / wt%	5.4	1.4	-	-	-	_
(CaO) <sub>12</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>7</sub> / wt%	94.6	19.0	25.2	20.5	11.5	-
CaAl <sub>2</sub> O <sub>4</sub> / wt%	-	40.5	57.3	64.2	73.3	> 99
CaAl <sub>4</sub> O <sub>7</sub> / wt%	-	39.1	17.5	15.3	11.5	-
Density / (g/cm <sup>3</sup> )	-	-	-	-	2.92	2.98

<sup>a)</sup> The sample was ground after 14 h

**Table 6** Sample composition of the CaO +  $2Al_2O_3$  system for different reaction times at 1500 °C; amount of  $Al_2O_3$  was calculated from the overall composition

t / h	14	26	35	48	61
CaAl <sub>2</sub> O <sub>4</sub> / wt%	17.9	4.4	1.7	0.7	-
CaAl <sub>4</sub> O <sub>7</sub> / wt%	70.4	92.7	97.2	98.8	100
Al <sub>2</sub> O <sub>3</sub> / wt%	11.7	2.9	1.1	0.5	-
Density / (g/cm <sup>3</sup> )	3.04	3.00	2.97	2.95	2.92

the by-products  $CaAl_4O_7$  and  $(CaO)_{12}(Al_2O_3)_7$  combined to form pure  $CaAl_2O_4$ . As in the case of  $Ca_9(Al_6O_{18})$ , the ground products of the conventional and the sol-gel method did not show any significant differences in particle size distribution or hydraulic activity. This, again, was a result of the partial melting of the mayenite during the synthesis.

For the synthesis of CaAl<sub>4</sub>O<sub>7</sub> the longest firing time and the highest number of intermediate grindings were necessary. The results are given in Table 6. Because Al<sub>2</sub>O<sub>3</sub> from colloidal alumina can not be detected by XRD, the stated amount of Al<sub>2</sub>O<sub>3</sub> in Table 6 was calculated from the overall composition. After 61 hours at 1500 °C and four intermediate grindings pure CaAl<sub>4</sub>O<sub>7</sub> could be synthesized which showed hardly any hydraulic activity.

#### **Experimental Part**

Ludox TM50 (Grace Davison) was used as colloidal silica source and Aerodisp W630 (Degussa Aerosil) as colloidal alumina source. The calcium nitrate was prepared by dissolving CaCO<sub>3</sub> (p.a.) with a stoichiometric amount of HNO<sub>3</sub> (65 %, p.a.).

The particle size of the silica sol was measured using acoustic attenuation spectroscopy. The zeta potential of the silica and alumina sol was calculated from the colloidal vibration current. An acoustic sound wave is applied to the sample and a resulting electric field or current, the so called "colloidal vibration current" (CVI) is measured. Both methods were performed by using a DT 1200 from Dispersion Technology and are described in detail by *Dukhin* et al. [26, 27]. The particle size distribution of the synthesized phases was measured by laser diffraction using the laser particle analyser CILAS 1064 from Cilas. XRD was done on a Philips PW 1710 series automated powder diffractometer with Cu-K<sub> $\alpha$ </sub> radiation. The semi-quantitative composition of the clinker phases was calculated by using the Full Pattern quantification software ADM V6 from Wassermann. The heat of hydration was measured with an isothermic DSC (TAM Air, Thermometrics) and the amount of unbound CaO (free lime) was quantified by using the Franke method [20].

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