Cement and Concrete Research 39 (2009) 973–980

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Synthesis of pure Portland cement phases

A. Wesselsky [a,b], O.M. Jensen [b,*]

[a] Lafarge Research Center, St. Quentin Fallavier, France
[b] Department of Civil Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

ARTICLE INFO

Article history:
Received 14 March 2009
Accepted 16 July 2009

Keywords:
Portland cement (D)
Cement manufacture (E)
Ca_3SiO_5 (D)
Ca_2SiO_4 (D)
$Ca_3Al_2O_6$ (D)

ABSTRACT

Pure clinker phases are often used to test cement hydration behavior in simplified experimental conditions. These phases are in general structurally identical to, but chemically much simpler than their heavily substituted counterparts found in technical clinkers. The synthesis of the pure phases is covered in this paper, starting with a description of phase relations and possible polymorphs of the four main phases in Portland cement, i.e. tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium alumino ferrite. Details of the process of solid state synthesis are described including practical advice on equipment and techniques. In addition, mix compositions that have been successfully used are given.

1. Introduction

Portland cement contains five main components. In their pure form, these so-called phases are tricalcium silicate (Ca_3SiO_5 or in cement notation shorthand [1] p.3–4: C_3S), dicalcium silicate (Ca_2SiO_4 or C_2S), tricalcium aluminate ($Ca_3Al_2O_6$ or C_3A), a tetracalcium alumino ferrite (often given as $Ca_4Al_2Fe_2O_{10}$ or C_4AF) and a sulfate phase (often gypsum, $CaSO_4 \cdot 2H_2O$ or $C\$H_2$).

The study of cement hydration is complicated by the complex composition of this material. In order to simplify experiments or to evaluate the specific contribution of a cement component, pure and separated cement components may be used. As commercially available Portland cements are a homogenous mix of all components, it is practically impossible to separate specific components. Therefore a need exists to produce these phases in a pure state in a lab environment.

Theoretical background on the relevant phases is compiled in this paper from published sources with special focus on parts useful in relation to solid state synthesis. Where applicable, some references to other preparation techniques beside the solid state approach are given. This theoretical section is combined with suggestions on how to perform a solid state synthesis as well as suggestions for sample mix compositions.

2. Chemical background

2.1. C_3S

The phase relations in the system CaO–SiO_2 were described in an early paper by Day, Shepherd and Wright in 1906 [2] and later revised by other authors [3–6].

The diagram (Fig. 1) shows the possibility of C_3S formation at temperatures in the range 1250–2150 °C. Typically it will form by combination of C_2S and CaO when the temperature rises above 1250 °C. In a pure system at room temperature, C_3S is metastable and has a triclinic structure. At rising temperature polymorphs show first a monoclinic and later rhombohedral structure. Accurate determination of the transition temperatures is difficult, with different methods like X-ray diffraction and optical microscopy yielding slightly different results ([7] p. 111). Commonly agreed data on transition temperatures are given in Table 1.

The phases dealt with in this paper are the triclinic and the monoclinic polymorphs. The latter is normally encountered in technical clinkers due to the stabilizing effect of both foreign ions and quenching, although small quantities of triclinic C_3S may also be present in some cases. The suggested sintering temperature for pure C_3S phases, is 1600 °C. This temperature is considerably higher than the 1450 °C reached in an industrial kiln [1] p. 55. This is to compensate for the absence of melt in the pure system, since in the technical process the melt facilitates the sintering at the lower temperatures. At 1600 °C, the stable phase is the rhombohedral polymorph.

When a pure, stoichiometric C_3S sample is quenched from the sintering temperature, it undergoes all the transformations shown in Table 1, and finally yields the triclinic form T_1 ([1] p. 29). The

---

* Corresponding author.
E-mail address: omj@byg.dtu.dk (O.M. Jensen).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.07.013

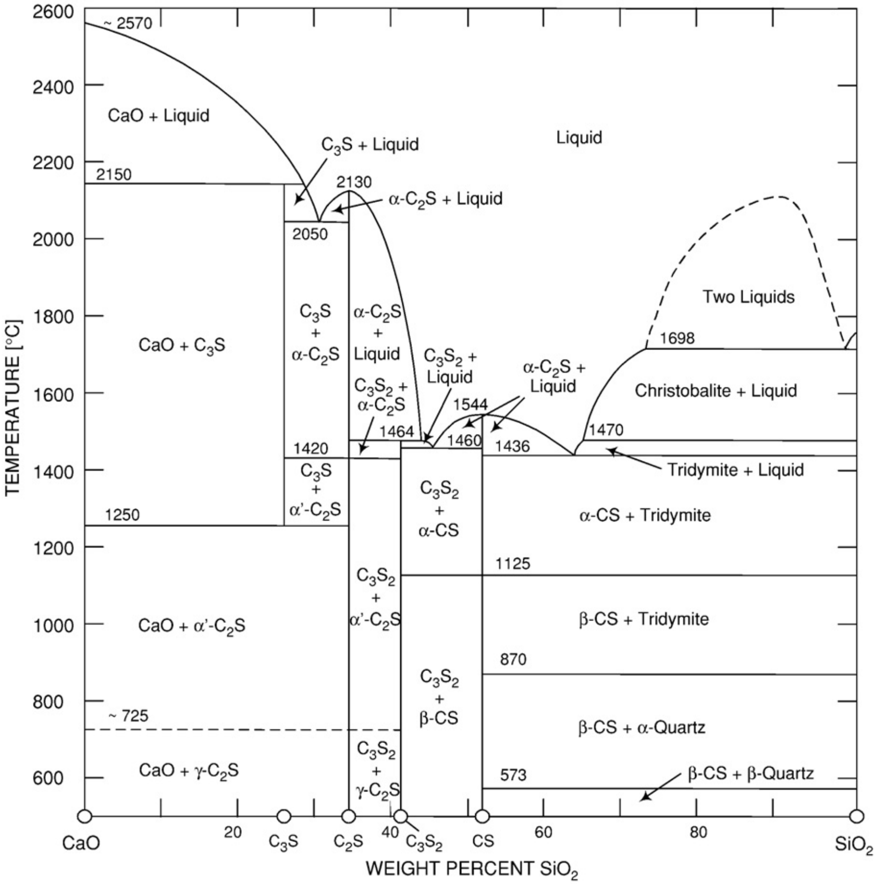

Fig. 1. Phase diagram of the binary system CaO–SiO_2 after [1] p. 30. This diagram shows the composition, possible secondary phases and transition and melting temperatures for both C_2S and C_3S.

quenching itself is necessary to make sure the C_3S does not dissociate back into C_2S and CaO, since C_3S is only metastable at temperatures below 1250 °C, cf. Fig. 1. C_3S dissociation, however, is a very slow process and can be avoided by rapid cooling.

To produce a monoclinic form of C_3S stable at room temperature, foreign ions have to be incorporated. A wide range of substituting ions has been identified in industrial clinkers, such as Al^{3+}, Mg^{2+} and Fe^{3+} ([1] p. 7), and also Mn^{3+} and P^{5+}[8]. The amount of foreign ion encountered in these clinkers is typically 3–4 wt.% ([1] p. 7). These ions are readily incorporated into the C_3S structure [9,10]. The stabilizing agent will influence the properties of the clinker phases including their reactivity [11]. A composition resembling the substituted C_3S found in industrial clinker has been published in [12]. Also the stabilizer may influence subsequent analysis as is the case for Fe^{3+} in relation to NMR [13].

The different polymorphs of C_3S can be identified conveniently and accurately with X-ray powder diffraction techniques. A database with patterns used for identification of phases in an X-ray powder diffraction scan is available from [14]. As a starting point for analysis, Table 2 gives a selection of reference codes from this PDF2 database for the phases described in this paper. The patterns were selected for good matching with the observed features and their quality assessment in the database. Only patterns that were either rated high quality or ones calculated from existing structures were included. Patterns with a connection to a known structure described in the "Inorganic Crystal Structure Database" ICSD [15] were preferred. This is a starting point for subsequent quantitative analysis with the Rietveld method [16,17].

C_3S can be produced easily with the solid state sintering process described further on in this paper. Alternative ways of production include microwave sintering [28] and a sol-gel process [29].

2.2. C_2S

C_2S is a stable phase from room temperature up to its melting point at 2130 °C, see Fig. 1. It undergoes several polymorphic phase

Table 1
Transition temperatures for C_3S ([7] p. 111, [1] p. 5). T = triclinic, M = monoclinic and R = rhombohedral.

Transition step	T1 ⇆ T2	T2 ⇆ T3	T3 ⇆ M1a	M1a ⇆ M2a	M2a ⇆ M2b	M2b ⇆ R
Temperature [°C]	620	920	980	990	1060	1070

Table 2
XRD identification patterns for commonly used phases and their modifications.

Phase	Crystal system	PDF2 database reference code	ICSD collection code	Reference
C_3S stoichiometric	Triclinic	00-031-0301	Not available	[18]
C_3S — "alite"	Monoclinic	01-085-1378	064759	[19]
		01-086-0402	081100	[20]
γ-C_2S	Orthorhombic	01-080-0941	068753	[21]
β-C_2S — "belite"	Monoclinic	01-070-0388	000963	[22]
α'-C_2S	Orthorhombic	a'_H: 00-031-0298 a'_L: 00-031-0299 a'_L: 00-049-1672	Not available	[23] [24]
C_3A stoichiometric	Cubic	00-038-1429	Not available	[25]
C_3A stabilized	Orthorhombic	00-032-0150	Not available	[26]
C_4AF	Orthorhombic	01-070-1498	002841	[27]

transitions in this temperature range. Fig. 2 gives information about the reversibility and the temperatures at which these changes occur.

The modification encountered in industrial clinkers is typically β-C_2S. The modification present during sintering is either α or α', but these high temperature polymorphs normally transform into the β phase upon cooling and are not seen in the final product. A most unwanted transformation is β-C_2S into γ-C_2S, since γ-C_2S is almost non-reactive with water. In addition the β–γ transformation destroys the clinker nodule integrity by volume expansion due to the low density of the γ-phase. The phases discussed in this paper are the common β-modification as well as α'-C_2S, which is more reactive than β-C_2S and still reasonably easy to stabilize [30]. Although α'-C_2S is not normally present in Portland cements, its increased reactivity makes it interesting especially for manufacturers of so-called "Belite cement" [31]. Being the high temperature polymorph, in the technical process α-C_2S is never stable enough to be found in the clinker after cooling down to room temperature. It is therefore not considered further on in this paper.

In an industrial clinker C_2S can incorporate up to 4–6 wt.% foreign ions. The main substituents are Al^{3+} and Fe^{3+}, with S^{6+}, Mg^{2+} and K^+ also being common ([1] p. 18). There is also good miscibility with both P_2O_5 and B_2O_3, and both systems have been studied extensively (e.g. [32,2] for P_2O_5 and [33–35] for B_2O_3). Especially boron has proven a very successful stabilizer [36].

The identification of β-C_2S by XRD with the pattern given in Table 2 poses no problems. To find a good match for the α'-C_2S is much more difficult, as there is no single pattern that covers all encountered peaks. It is therefore necessary to exclude all other possible phases and modifications by trying to match with their corresponding patterns: β-C_2S, C_3S and CaO, and potentially also γ- and α-C_2S.

Apart from the solid state sintering process, successful synthesis can be done by a sol-gel method, using calcium nitrate and silicon oxide as starting materials. It is based on chelation in a solution of suitable oxides or salts with the aid of an alpha-hydroxycarboxylic acid, the so-called liquid mix or Pechini process [37].

2.3. C_3A

The binary system CaO–Al_2O_3 in Fig. 3 shows C_3A melting incongruently at 1542 °C. In industrial clinkers C_3A can incorporate up to 2% of SiO_2 and 3–4% of Fe_2O_3 [38]. However, the most critical substituent is Na^+, since it induces changes in the crystal structure as detailed in Table 3.

The cubic C_3A can be easily sintered without any need for stabilization. The orthorhombic form can be stabilized by Na_2O as seen from Table 3. K_2O has been tested as alternative stabilization agent, but without success [39,40]. The cubic form is normally encountered in technical clinkers, but if sodium concentrations in the clinker are high enough, it is not uncommon to have part of the C_3A in the orthorhombic modification.

XRD identification of C_3A is generally easy, as the observed peaks are normally well defined and clearly match the reference pattern. Because the pattern of the cubic and orthorhombic form overlap completely but for a few extra peaks for the orthorhombic form, it is, however, difficult by the XRD technique to rule out the existence of a few percent of cubic C_3A in a sample made up from the supposedly orthorhombic form.

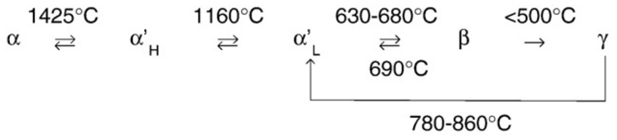

Fig. 2. Transition temperatures of C_2S polymorphs after [1] p. 14. All phase transitions are reversible except the one of β to γ. When heated, the γ polymorph does not transform into the β-form but instead converts directly into the α'$_L$-form upon reaching a temperature between 780 and 860 °C.

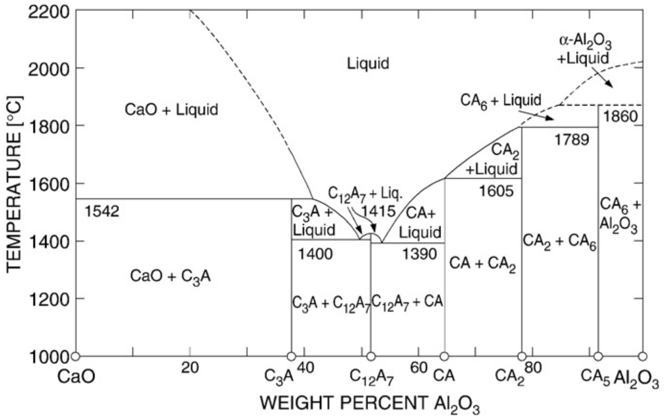

Fig. 3. Binary system CaO–Al_2O_3 after [1] p. 31. Possible secondary phases for C_3A can be found in this diagram as well as its (incongruent) melting temperature.

2.4. C_4AF

The ferrite phase is found in the ternary system CaO–Al_2O_3–Fe_2O_3. There exists a broad range of possible compositions due to the extended solid solution series between the end members C_2F and $Ca_2(Al_{0.7}Fe_{0.3})_2O_5$, see Fig. 4. In equilibrium with iron substituted C_3A, the C_4AF composition can be in the range $x = 0.48$ to 0.7 for $Ca_2(Al_xFe_{1-x})_2O_5$. The idealized composition C_4AF lies at the lower end of this range ($x = 0.5$). Possible foreign ions in the structure include Mg^{2+} and Si^{4+} [42], Mn^{3+} [43], Ti^{4+} [44] and small amounts of SO_3 [45,46].

A small amount of Fe^{3+} may be reduced to Fe^{2+} when sintering phases in the range $0.48 < x < 0.7$ in air [47]. This leads to the formation of additional phases, impeding the goal of a pure phase synthesis.

The ferrite phase found in technical clinkers is much more complex due to a great degree of substitution of Fe^{3+} (and in some cases also Al^{3+}) with foreign ions like Mg^{2+}, Si^{4+} and Ti^{4+} or Mn^{3+}. The composition can vary significantly in the same clinker batch or even on the micro level for a single clinker grain. Taylor gives as an approximated composition $Ca_2AlFe_{0.6}Mg_{0.2}Si_{0.15}Ti_{0.05}O_5$ ([1] p. 26).

XRD identification is complicated by the chemical variability of the phase, so there is seldom a reference pattern exactly reflecting the chemical composition. But the match is normally close enough to allow for an identification based on several reference patterns of different composition and by observing general trends of peak shifts between these. The sample should also be checked for the presence of monocalcium aluminate CA and calcium aluminate sulfate phases like Yeelimite $Ca_4Al_6O_{12}(SO_4)$. The latter might form if there is sulfur introduced into the system by impurities in the iron oxide raw material.

3. Compositions and synthesis conditions

The following procedures and mixtures are based on the experiences of the authors. They are not the only possible route to a

Table 3
Influence of Na_2O content on C_3A crystal structure from [1] p.20 after [41].

Weight-% Na_2O (approx.)	Compositional range (x) for $Na_{2x}Ca_{3-x}Al_2O_6$	Designation	Crystal system
0.0–1.0	0.00–0.04	C_I	Cubic
1.0–2.4	0.04–0.10	C_{II}	Cubic
2.4–3.7	0.10–0.16	C_{II} + O	–
3.7–4.6	0.16–0.20	O	Orthorhombic
4.6–5.7	0.20–0.25	M	Monoclinic

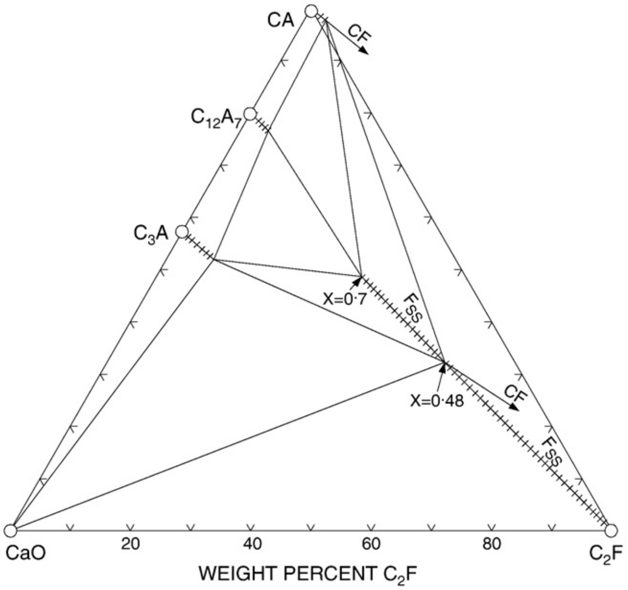

Fig. 4. Part of the larger system $CaO–Al_2O_3–Fe_2O_3$. This ternary phase diagram shows the sub-solidus phase relations in the $CaO–C_2F–CA$ sub-system. Hatched lines denote solid solution series. [1] p. 37.

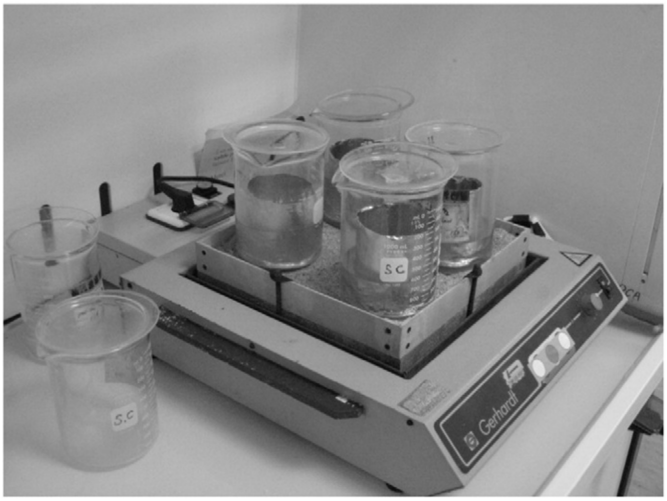

Fig. 5. Crucible cleaning setup with HCl in a heated sand bed. Petri dishes covering the glass beakers reduce the evaporation rate of the acid, but the apparatus still needs to be placed under a fume hood.

successful synthesis. For most steps of the sintering process there are several alternatives which will be mentioned, but the focus will be on the method preferred by the authors. Differences in available equipment or raw materials may make it necessary to choose a different route of synthesis or modify the one described in the paper. The procedures detailed below may thus be considered a starting point for solid state synthesis.

3.1. Sample synthesis

3.1.1. Equipment

Necessary lab equipment includes a mixing device, platinum crucibles, a high temperature furnace and a grinder.

Different types of mixing device can be used. For dry mixing a tumble mixer with a sealed receptacle or a vibratory disc grinder may work well. Wet mixing can be done using a standard 5-l epicyclical lab mixer (often referred to as “Hobart mixer”) or even a kitchen blender.

The material of the crucibles should preferably be a platinum alloy containing 10% rhodium, since pure platinum will not withstand well the high temperatures used especially for C_3S and C_2S synthesis. As the incorporation of iron atoms into the material makes platinum brittle, it would be prudent to use, if available, some older crucibles when doing the synthesis of C_4AF phase. Cleaning of the crucibles can be done by soaking for several hours in hot 1:1 diluted hydrochloric acid (a possible setup is shown in Fig. 5) or hot 1:10 diluted nitric acid. Afterwards, the crucibles may be gently rubbed with beach sand to remove all residues. Finally, they should be rinsed thoroughly with deionized water to remove any trace of the acid. In cases of severe contamination with silicate material, hydrofluoric acid can be used instead of hydrochloric acid. For removing persistent aluminate material residue, concentrated hydrochloric acid may be useful. Note that in order to handle in particular hot hydrofluoric acid, special laboratory precautions are needed.

The furnace should be electrically heated, able to hold a temperature of 1600 °C for several hours and allow for rapid unloading of the crucibles to facilitate quenching. For the synthesis discussed in this paper there is no need for maintaining controlled atmosphere conditions — all experiments are performed at ambient pressure in atmospheric air. Muffle furnaces are common lab equipment and fulfill all requirements. The only drawback is the high thermal stress exerted on the refractory lining when the furnace is opened repeatedly at high temperatures for quenching purposes. Therefore the sample unloading should be done as quickly as possible. Vertical tube furnaces sometimes allow dropping the sample from inside the heating tube without thermal shock to the furnace, but the size of these samples is often quite limited. Another advantage of vertical tube furnaces is the superior temperature accuracy and stability compared to muffle furnaces. The latter often have an accuracy of only ±50 °C with a significant temperature gradient throughout the sample cavity. This is due to their bigger size and the different position of heating elements and the thermal sensor. Especially when handling samples close to the melting point, this uncertainty should be observed in order to avoid accidental melting.

The grinder should have an agate or tungsten carbide liner, since steel, for example, may potentially contaminate the samples. Most types of grinder available for lab use will produce acceptable results, but a vibratory disc mill may be preferred, because it is easy to clean and produce good results even from coarsely crushed hard materials.

In addition to the above mentioned equipment it may be helpful to use a molding press to compact the powdered precursor. To assure the purity of the produced substances, an X-ray powder diffraction device is recommended. Other methods to follow the progress of synthesis include the wet chemical determination of free lime content by glycerol–ethanol [48] or ethylene glycol extraction [49,50] or a DTA/TG analysis [51].

3.1.2. Raw materials

The starting point of each synthesis is commercially available lab chemicals in powder form. The purity should exceed 99% whenever possible. Typically encountered impurities below 1% will not severely influence the phase synthesis. On the other hand, attention should be paid to the fact that even small amounts of impurities might lead to an, possibly unwanted, stabilization of certain phases through substitution, cf. Section 3 above. For example, most iron oxide Fe_2O_3 commercially available in bigger batch sizes will have a purity in the 97–98% range, containing a notable amount of sulfur. This impurity will lead to the formation of a calcium aluminate sulfate phase, e.g. Yeelimite $Ca_4Al_6O_{12}(SO_4)$, when trying to synthesize pure C_4AF.

The main constituents used for the syntheses discussed in this paper are SiO_2 (e.g. as ground quartz), Al_2O_3 (corundum), $CaCO_3$ (calcite), Fe_2O_3 (hematite) and $CaSO_4 \cdot 2H_2O$ (gypsum). The used stabilizers are MgO, Al_2O_3 (corundum), H_3BO_3 (orthoboric acid), $Na_2B_4O_7 \cdot 10H_2O$ (borax) and $NaNO_3$.

The materials should be dry, but determination of the loss on ignition (LOI) for each substance is necessary nonetheless. The applied temperature is selected according to the analyzed material. For oxides like SiO_2 or Al_2O_3 a temperature of 1050 °C is suitable. $CaCO_3$ will decompose to CaO at this temperature, giving a conversion factor. Often CaO is used as component in the calculation of mix designs, so this factor is needed anyway for weighing in the raw materials. Another possibility for $CaCO_3$ is to carry out the "LOI" at 105 °C, i.e. below its calcination temperature. In this case the theoretical loss on ignition of 43.97 wt.% derived from the stoichiometric formula is used to determine the mass of $CaCO_3$ necessary to yield a certain amount of CaO in the final product. Materials containing water or hydroxide groups in their formula units, like $CaSO_4 \cdot 2H_2O$, NaOH and especially the boron compounds H_3BO_3 and $Na_2B_4O_7 \cdot 10H_2O$, are difficult to treat. They often decompose at temperatures below the 105 °C normally used to assure the removal of all residual moisture. A thermo-gravimetric analysis of these materials may be the best way to determine any moisture in the material.

The particle size should preferably correspond to a fine powder, i.e. passing a 63 μm sieve. Standard, commercially available chemicals should already have the desired fineness. The fineness of the raw materials determines both how well compacted the powder will be during sintering and the reactive surface area. Especially for SiO_2 it is beneficial to use a very small particle size. Further, amorphous SiO_2 should be preferred since this also increases reactivity during sintering. As a drawback very fine powders pose problems during weighing and homogenization, as they stick easily to tools or get carried away by air drafts. Several manufactures offer fine amorphous SiO_2, e.g. Aerosil from Degussa.

3.1.3. Sintering procedure

The suggested basic procedure for a solid state synthesis is identical for all phases. Using the LOI as a correction factor, the materials are weighed and homogenized according to the desired mix design.

This homogenization is best performed in a tumble mixer or other dedicated closed mixing device. A tightly closing small grinder might also be appropriate. Another possibility is to add for example water or acetone to the powdered chemicals and mix the resulting slurry in a standard 5-l epicyclical lab mixer or kitchen blender. For any method it should be assured that all parts of the mix get homogenized by manually scraping the walls and removing possible build-up on the mixing blade itself.

The dry, homogenized powder mix can be poured directly into the platinum crucibles. The slurry from the wet homogenization has first to be dried completely at 80 °C–105 °C. The resulting "cake" is broken into small pieces and placed into the crucible. At this stage, no compaction of the material in the crucibles is necessary. The top quarter of the crucible volume should be left empty, or, alternatively, a loosely fitting lid that does not hinder gas exchange with the surroundings may be placed on top of the crucibles to avoid possible projection of material.

An initial calcination is performed to remove the carbon dioxide bound in the calcium carbonate that is predominant in all mixtures. This is necessary to avoid the violent CO_2-gas evolution that would occur if the $CaCO_3$ were exposed directly to e.g. 1600 °C. The calcination is normally performed by placing the filled crucibles into the cold furnace, heating up to 1000 °C at 16 °C/min (i.e. roughly 1 hour to reach 1000 °C). This temperature is held for 1 h. From here two further courses are possible: either 1) cool down the furnace and remove the sample to perform a compaction of the calcined powder before proceeding or 2) increase the temperature and perform a first sintering right away. Case 1 gives a better material contact due to the compaction and should therefore initially improve the sintering progress.

However, for the total procedure it is typically more effective to skip the compaction step after the calcination and proceed directly with the first sintering. In this case, a quenching will be performed at the end of the sintering interval, i.e. the crucible is removed from the furnace at sintering temperature and the material poured directly from the crucible into a bigger receptacle made from refractory or even better steel (Fig. 6). This helps to disseminate the heat quickly and freezes the sample in the desired modification state. The cooling may be further promoted by an air stream. When air cooling is used, the flow of air should be low enough to not carry away particles.

The resulting materials subsequently need to be ground. Depending on the amount of material and the available grinder, the material may have to be crushed first. This can be done manually using a mallet or a small scale jaw crusher. A thoroughly clean device should be used to avoid contamination. Manual crushing is more time consuming but may be preferred due to its lower risk of contamination for small batch sizes. The subsequent grinding should be done to a fineness that allows the powder to become "sticky" and facilitates the compaction of the material. Powder that passes a 63 μm sieve is usually fine enough. In order to follow the synthesis progress, a small amount of this powder should be analyzed, e.g. by X-ray powder diffraction.

After this, the sintering process is repeated. To facilitate the reaction in the solid state, a good compaction of the material is an advantage. The compaction can be done in several ways. The simplest approach is to pour the powder into the platinum crucible and then compact it by pressing down on it with an appropriately shaped tool. Another way is to produce pressed pellets in a molding press, which gives a much higher compaction. Best results are achieved when the treated material is slightly wet. As the cement phases react with water, it is advisable to use an organic liquid like ethanol or isopropanol. The preparation of pressed pellets is time consuming, so for larger quantities of material the use of some form of nodulizer is advisable. The compacted material should be thoroughly dried before

Fig. 6. Sample during quenching — the sintered material has just been poured from a platinum crucible into a big steel receptacle to enhance cooling.

proceeding, especially if organic liquids have been used (dry over night at 80–100 °C).

With the compacted material in the crucible, the furnace should be heated up to the specific sintering temperature and maintained at this temperature for a specific time. Quenching should be performed straight after the sintering as described above. Sometimes the material may stick to the crucible, especially for the phases C_3A and C_4AF. In this case, the cooling of the sample can be promoted by placing the crucible on a steel surface and blowing compressed air onto the outside of the crucible with. Blowing air directly on the sample should be avoided in this case, as it may result in cracking of sintered nodules and spalling of material clinging to the crucible surface and thereby projection of hot material out of the crucible.

After cooling to room temperature, the material is crushed and ground as mentioned above. Should the X-ray diffraction analysis show no other phases than those desired, the synthesis is finished. In general, two to five sintering cycles are needed to achieve a sample with phase purity above 99 wt.%.

3.1.4. Grinding and storage

After satisfactorily achieving purity it may be necessary to grind the sample to a desired fineness. Special attention should be paid to this, as it will influence the reactivity of the product.

In the cement industry, the specific surface area is usually determined by Blaine's method [52]. This is relatively rapid, so during grinding, intermittent samples can be taken and analyzed and the grinding process can be stopped as soon as the desired fineness has been reached. The resulting powders may be cross-checked by other methods like BET [53], but laser granulometry [54] is preferable as it can give the full particle size distribution rather than just an average value.

For calcium aluminate phases, the final grinding is also a possibility for intimate mixing with a sulfate carrier like gypsum. The co-grinding of both phases resembles the actual industrial process [1] p.84, and the particle size as well as the homogeneity of the resulting powder plays an important role in the reactivity of the C_3A-sulphate system.

The amount of sulfate to be added to the calcium aluminate should be decided based on the intended use of the mix. To allow complete conversion to monosulfate requires an addition of 63.7 wt.%. For full conversion of the calcium aluminate to ettringite, addition of 191.2 wt.% of gypsum to the C_3A is necessary.

In general, all cement phases react with moisture and should be stored in a dry atmosphere. Normally this is achieved by storage in a desiccator over silica gel. If gypsum is already mixed with cement phases, this may be an additional problem. Using thermodynamic data from [56], the relative humidity of air in equilibrium with gypsum is calculated [57] as being 27%. Experimental data from [58] show that practically no hydration of pure phases will occur at levels of relative humidity below 60%, so based on these data no hydration effects of an addition of gypsum to pure phases is to be expected even during storage for several months. However, gypsum mixed with clinker is known to provide enough moisture to alter samples ([6] p.84, [55]), probably by a small part of gypsum converting to the hemihydrate form in presence of a strongly hygroscopic phase like C_3A, thereby releasing some water.

Sealed storage can for example be established by placing the sample into evacuated, hot sealed, aluminized polyethylene bags. The sealed bags should be checked periodically for repressurization. In this case, repacking is necessary. Additionally, the storage of the sealed bags over silica gel could minimize the effects of failing vacuum.

3.1.5. Material analysis

The method of choice to quickly follow the progress of synthesis is X-ray powder diffraction (XRD) analysis. It directly shows impurities and residual raw materials in the product and is therefore more versatile in determining the progress of sintering as compared to another popular method in cement industry, the free lime analysis. XRD makes it easy to check e.g. if the correct polymorph of the desired phase is produced, if additional, non-wanted phases are being formed or if there are unreacted raw materials left in the sample (Fig. 7). With modern equipment, XRD analysis is a very fast and simple method, able to produce results in 20–30 min.

As a drawback, the detection limit for each phase can be relatively high compared to other methods. Depending on the sample it can range between 1 and 2 wt.% in the case of non-overlapping peaks [59]. If the peaks of a low-quantity phase are severely overlapped by those of a phase of higher quantity, the detection limit can rise significantly. In order to reliably detect and quantify e.g. a small CaO impurity below a few weight percent in a pure phase sample, the use of another method of quantification, e.g. wet chemical ethylene glycol extraction, should be considered.

Nuclear Magnetic Resonance (NMR) is another possible technique to characterize the final synthesis products [60]. Whereas X-ray diffraction is based on the ordered position of atoms repeated throughout the whole material, solid state nuclear magnetic resonance (NMR) is based on the interaction of certain nuclei (^{27}Al, ^{29}Si) with high frequency electromagnetic pulses in a constant magnetic field. The interaction allows to distinguish different chemical neighborhoods (i.e. coordination) for the nucleus under investigation and to quantify its occurrence in the different coordination states, but due to its more complex experimental setup it cannot be considered an ad-hoc method. However, especially in the investigation of hydration processes, the NMR method plays an important role [61]. A difficulty of the NMR method is its liability to interference from iron atoms [13], which are always present in a Portland cement. Also, only some types of atoms (like Al and Si) are more easily measurable because their predominantly occurring isotopes can be detected by the NMR technique.

3.2. C_3S

Both triclinic and monoclinic forms are sintered in the same conditions, they only differ in the composition of the raw material mix. In both cases the stoichiometric ratio of CaO to SiO_2 is 3:1, but for the monoclinic form, the raw material mix also contains small amounts of MgO and Al_2O_3 to stabilize this crystalline structure (see Table 4). The magnesium atoms substitute for calcium in the structure, whereas the aluminum replaces both calcium and silicon atoms in equal proportions. The influence of these ions on the structure is discussed in detail in [62].

The sintering protocol for both phases is identical: 2 h of heating ramp to 1600 °C, then holding there for 2 h. Subsequently the sample is quenched.

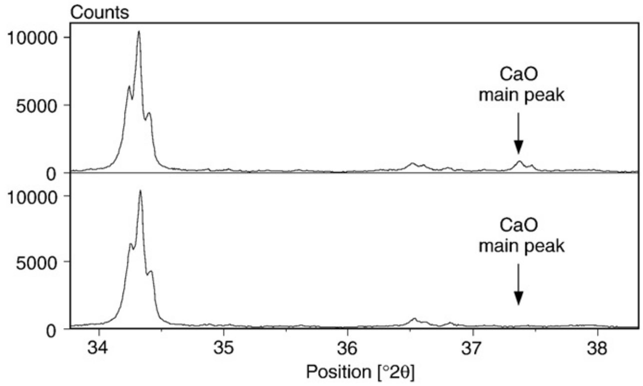

Fig. 7. Progress of sintering of triclinic C_3S as seen by XRD. Top: After the first sintering cycle. C_3S-content of the material is estimated as in the 90% range, since there is a small amount of CaO detectable in the XRD diagram. The arrow marks the CaO main peak, all other visible peaks belong to triclinic C_3S. Bottom: The same sample as above after a second sintering cycle. The main peak of CaO has vanished; all visible peaks belong to triclinic C_3S. The purity can be assumed to be 98–99%.

Table 4
Suggested mix composition in g for 100 g of final C_3S product and the resulting atomic ratios.

	$CaCO_3$	SiO_2	Al_2O_3	MgO
C_3S triclinic	131.506 Ca/Si = 3.000	26.316	0	0
C_3S monoclinic	127.614 Ca/Si = 2.964	25.843	0.701 Al/Si = 0.032	1.177 Mg/Si = 0.068

In the case of monoclinic C_3S the amounts given correspond to: 98.2 wt.% of stoichiometric mix of CaO and SiO_2, 1.1 wt.% of MgO and 0.7 wt.% of Al_2O_3.

3.3. C_2S

Both the α'- and β-modifications of C_2S are sintered in the same conditions, but their composition differ in the amount and type of stabilizer used. Both mixtures are based on the stoichiometric mix of 2 mol CaO and 1 mol SiO_2, but the β-form is stabilized with B_2O_3 (added in the form of H_3BO_3 to the stoichiometric mix).

The α'-form is stabilized by B_2O_3 and Na_2O in the form of $Na_2B_4O_7 \cdot 10H_2O$ added to the stoichiometric mix (see Table 5). The resulting phase is believed to be the α'-form based on X-ray diffraction results, because several patterns for α'-structures fit most of the peaks. But as no available pattern produced a perfect match, some uncertainty about the actual structure produced by this mix remains.

In order to reduce the amount of foreign ions in the final product, H_3BO_3 was used as stabilizer instead of the more potent $Na_2B_4O_7 \cdot 10H_2O$ for the stabilization of β-C_2S. The effectiveness of B_3O_2 with no Na_2O as a stabilizer for the α'-form remains to be evaluated by further research.

The sintering protocol is 1 h 45 min heating ramp to 1450 °C, then holding for 4 h. Subsequently the sample is quenched.

3.4. C_3A

The stoichiometric mix of 3 mol CaO and 1 mol Al_2O_3 yields the cubic modification of C_3A. Stabilization with sodium (added in the form of sodium nitrate) is necessary to acquire the orthorhombic form. The content of Na_2O in the raw mix for orthorhombic C_3A specified in Table 6 is equal to 10.57 wt.% — well above the 3.7–4.6 wt.% Na_2O given in Table 3 for the stabilization of the orthorhombic form. This is due to the relative high volatility of sodium at high temperatures and the resulting loss during sintering. As this loss can be influenced by differences in experimental conditions (size of crucible, size and ventilation of furnace, etc.), it might be necessary to adjust the amount of $NaNO_3$ in the mix to suit the different evaporation rates. If cubic C_3A is detected, the amount should be increased slightly for further experiments. The presence of monoclinic C_3A on the other hand requires a slight reduction in sodium content.

The substitution reaction works by Na^+ replacing Ca^{2+} and another Na^+-ion occupying an otherwise vacant site in the centre of rings formed by Al_6O_{18} [63]. According to [64], this gives a solid solution with the general formula $Na_{2x}Ca_{3-x}Al_2O_6$.

The sintering protocol is 1 h 45 min heating to reach 1450 °C, then holding for 3 h. Subsequently the sample is quenched. For the samples containing sodium nitrate a cover should be used to reduce the evaporation of sodium.

Table 5
Suggested mix composition in g for 100 g of final C_2S product and the resulting atomic ratios.

	$CaCO_3$	SiO_2	H_3BO_3	$Na_2B_4O_7 \cdot 10H_2O$
β-C_2S	115.752 Ca/Si = 2.000	34.745	0.354 B/Si = 0.010	0
α'-C_2S	111.851 Ca/Si = 2.000	33.574	0 B/Si = 0.133	7.108 Na/Si = 0.067

In the final product the amounts given correspond to: 0.40 wt.% of B_2O_3 for β-C_2S and for α'-C_2S 2.60 wt.% B_2O_3 and 1.16 wt.% Na_2O.

Table 6
Suggested mix composition in g for 100 g of final C_3A product and the resulting atomic ratios.

	$CaCO_3$	Al_2O_3	$NaNO_3$
C_3A cubic	111.124 Ca/Al = 1.500	37.736	0
C_3A orthorhombic	98.059 Ca/Al = 1.448	34.487	14.496 Na/Al = 0.252

Table 7
Suggested mix composition in g for 100 g of final C_4AF product and the resulting atomic ratios.

	$CaCO_3$	Al_2O_3	Fe_2O_3
C_4AF idealized	82.380 Ca/Al = 2.000	20.982	32.861 Fe/Al = 1.000
$C_4A_{0.5}F_{1.5}$ iron rich	77.762 Ca/Al = 4.000	9.903	46.527 Fe/Al = 3.000

3.5. C_4AF

The so-called ferrite phase can have a wide composition range in real clinkers. As examples, both the stoichiometric, idealized compound C_4AF (Brownmillerite) is given here as well as an iron rich variety. The idealized mix contains 4 mol of CaO, 1 mol of Al_2O_3 and 1 mol of Fe_2O_3. The iron rich mix has 4 mol of CaO, 0.5 mol of Al_2O_3 and 1.5 mol of Fe_2O_3. See Table 7.

The sintering protocol is 1 h 30 min heating to reach 1300 °C, then holding for 2 h. If the sample shows severe melting or sticks to the surface of the crucible, sintering at 1250 °C for 3.5 h should be tried. Subsequently the sample is quenched.

Acknowledgements

The exact origin of the sintering procedure described in this paper is unknown to the authors. It is based on procedures generally used for solid state phases synthesis. Though the contents of this paper are entirely the responsibility of the authors, several comments on the procedure were given by F.P. Glasser during the post-doc stay at the University of Aberdeen of the second author in the mid 1990s. This is gratefully acknowledged.

We would also like to thank the members of the Lafarge Research Lab for their help and expertise in preparing and testing the pure phase samples.

References

[1] H.F.W. Taylor, Cement Chemistry, 2nd ed.Thomas Telford, London, 1997.
[2] A.L. Day, E.S. Shepherd, The lime-silica series of minerals, Am. J. Sci. 22 (4th series) (1906) 265–302.
[3] W. Gutt, Manufacture of Portland cement from phosphate raw materials, Building Research Station Paper CP90/68, HMSO, London, 1968, p. 5.
[4] Y.I. Ol'shanskii, Equilibrium of two immiscible liquids in silicate systems of alkali-earth metals, Doklady Akad. Nauk SSSR 76 (1) (1951) 93–96.
[5] G.A. Rankin, F.E. Wright, The ternary system CaO–Al_2O_3–SiO_2, Am. J. Sci. 39 (4th series) (1915) 1–79.
[6] J.H. Welch, W. Gutt, Tricalcium silicate and its stability within the system CaO–SiO_2, J. Am. Ceram. Soc. 42 (1959) 11–15.
[7] M. Regourd, Chrystal chemistry of Portland cement phases (Chapter 3), in: P. Barnes (Ed.), Structure and Performance of Cements, Applied Science, Barking (UK), 1984, pp. 109–138.
[8] A. Diouri, A. Boukhari, J. Aride, F. Puertas, T. Vazquez, Stable Ca_3SiO_5 solid solution containing manganese and phosphorus, Cem. Concr. Res. 27 (8) (1997) 1203–1212.

[9] T. Hahn, W. Eysel, E. Woermann, The crystal chemistry of tricalcium silicate solid solutions, 5th ISCC, vol. 1, 1969, pp. 61–73.

[10] K. Mohan, F.P. Glasser, Thermal-decomposition of Ca$_3$SiO— at temperatures below 1250 degrees — 2. Influence of Mg, Fe, Al and Na oxides on decomposition, Cem. Concr. Res. 7 (3) (1977) 269–276.

[11] R.W. Nurse, The effect of some minor components on cement setting and hardening, 7th conference on the Silicate Industry, Budapest, 1963.

[12] U. Ludwig, A. Wolter, Formation and stability of C$_3$S and alites, 9th Intern. congress on the chemistry of cement, New Delhi, Vol. 2, 1992, pp. 99–103.

[13] J. Skibsted, H.J. Jakobsen, C. Hall, Quantitative aspects of Al-27 MAS NMR of calcium aluminoferrites, Adv. Cem. Based Mater. 7 (2) (1998) 57–59.

[14] JCPDS, Powder Diffraction File™ (PDF), JCPDS — International Centre for Diffraction Data, Newtown Square (USA), 2007.

[15] FIZ, Inorganic crystal structures database (ICSD), FIZ Karlsruhe, Karlsruhe (Germany), 2007.

[16] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (2) (1969) 65–71.

[17] R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1995.

[18] M. Regourd, Determination of the lattices of microscopic crystals. Application to the different forms of tricalcium silicate, Bull. Soc. Fr. Mineral. Cristallogr. 87 (2) (1964) 241–272.

[19] F. Nishi, Y. Takeuchi, I. Maki, Tricalcium silicate Ca$_3$O[SiO$_4$]: the monoclinic superstructure, Z. Kristallogr. 172 (1985) 297–314.

[20] W.G. Mumme, Crystal-structure of tricalcium silicate from a Portland-cement clinker and its application to quantitative XRD analysis, Neues Jahrb. Mineral. Monatsh. 4 (1995) 145–160.

[21] A. Della Giusta, G. Ottonello, L. Secco, Precision estimates of interatomic distances using site occupancies, ionization potentials and polarizability in Pbnm silicate olivines, Acta Crystallogr. B: Struct. Sci. 46 (1990) 160–165.

[22] K.H. Jost, B. Ziemer, R. Seydel, Redetermination of the structure of ß-dicalcium silicate, Acta Crystallogr. B: Struct. Sci. 33 (1977) 1696–1700.

[23] M. Regourd, M. Bigaré, J. Forest, A. Guinier, 5th ISCC, vol. 1, 1969, p. 44.

[24] Reference [14], in: Smith (Ed.), ICDD Grant-in-Aid, Penn State University, University Park (USA), 1973.

[25] Reference [14], in: W. Wong-Ng, H. McMurdie, B. Paretzkin, C. Hubbard, A. Dragoo (Eds.), ICDD Grant-in-Aid, NBS, (USA), 1987.

[26] F.C. Lee, F.P. Glasser, Powder diffraction data for compounds in the series Na$_x$(Ca$_{3\pm x}$Na$_x$) Al$_2$O$_6$, J. Appl. Crystallogr. 12 (1979) 407–410.

[27] A.A. Colville, S. Geller, Cystal-structures of Ca$_2$Fe$_{1.43}$Al$_{0.57}$O$_5$ and Ca$_2$Fe$_{1.28}$Al$_{0.72}$O$_5$, Acta Crystallogr. B: Struct. Sci. 28 (1972) 3196–3260.

[28] H. Li, D.K. Agrawal, J. Cheng, M.R. Silsbee, Formation and hydration of C$_3$S prepared by microwave and conventional sintering, Cem. Concr. Res. 29 (1999) 1611–1617.

[29] D. Stephan, P. Wilhelm, Synthesis of pure cementitious phases by sol-gel process as precursor, Z. Anorg. Allg. Chem. 630 (2004) 1477–1483.

[30] M.Y. Benarchid, A. Diouri, A. Boukhari, J. Aride, I. Elkhadiri, Hydration of iron-phosphorus doped dicalcium silicate phase, Mater. Chem. Phys. 94 (2005) 190–194.

[31] W.-H. Chae, D.-C. Park, S.-H. Choi, Early hydration of modified belite cement prepared by adding borax, Korean J. Ceram. 2 (3) (1996) 147–151.

[32] R.W. Nurse, J.H. Welch, W. Gutt, High temperature phase equilibria in the system dicalcium silicate–tricalcium phosphate, J. Chem. Soc. 220 (1959) 1077–1083.

[33] E.P. Flint and L.S. Wells, The system lime-boric oxide-silica, in : N.B.o.S. US Department of Commerce (Ed.), Journal of Research of the National Bureau of Standards, 1936, p. 727.

[34] J.G. Fletcher, F.P. Glasser, Phase relations in the system CaO-B$_2$O$_3$-SiO$_2$, J. Mater. Sci. 28 (1993) 2677–2686.

[35] K. Suzuki, I. Hira, Study on the system of 2CaO*SiO2-3CaO*B$_2$O$_3$, Yogyo-Kyokai-Shi 78 (6) (1970) 17–22.

[36] C.-K. Park, Phase transformation and hydration of dicalcium silicate containing stabilizers, J. Ceram. Soc. Jpn. 109 (5) (2001) 380–385.

[37] S.-H. Hong, J.F. Young, Hydration kinetics and phase stability of dicalcium silicate synthesized by the Pechini process, J. Am. Ceram. Soc. 82 (7) (1999) 1681–1686.

[38] F.C. Lee, H.M. Banda, F.P. Glasser, Substitution of Na, Fe and Si in tricalcium aluminate and the polymorphism of solid solutions, Cem. Concr. Res. 12 (2) (1982) 237–246.

[39] H.W.W. Pollitt, A.W. Brown, 5th ISCC, vol. 1, 1969, p. 322.

[40] I. Maki, Nature of the prismatic dark interstitial phase in Portland cement clinker, Cem. Concr. Res. 3 (1973) 295–313.

[41] Y. Takeuchi, F. Nishi, I. Maki, Crystal-chemical characterization of the 3CaO–Al$_2$O$_3$–Na$_2$O solid-solution series, Zeit. Krist 152 (3–4) (1980) 259–307.

[42] J. Neubauer, W. Mayerhofer, Solid solution series of ferrate and aluminate phases in OPC: Part I. The ferrate phase, 22nd International Conference on Cement Microscopy, Montreal (Canada), 2000.

[43] R.-I. Kondo, S. Goto, M. Fukuhara, in: Review of the 32nd General Meeting, Cement Association of Japan, Tokio, 1978, p. 38.

[44] M.B. Marinho, F.P. Glasser, Polymorphism and phase-changes in the ferrite phase of cements induced by titanium substitution, Cem. Concr. Res. 14 (3) (1984) 360–368.

[45] T.B. Bergstrom, C. Hall, K.L. Scrivener, Interstitial material in oil-well cements: Evidence from X-ray microanalysis, Adv. Cem. Res. 4 (1991) 141–147.

[46] C. Hall, K.L. Scrivener, Oilwell cement clinkers — X-ray microanalysis and phase composition, Adv. Cem. Based Mater. 7 (1) (1998) 28–38.

[47] A.J. Majumdar, The ferrite phase in cements, Trans. Br. Ceram. Soc. 64 (1965) 105–109.

[48] ASTM standard C114-07 : Standard Test Methods for Chemical Analysis of Hydraulic Cement, ASTM International, West Conshohocken (USA), 2007.

[49] M.P. Javellana, I. Jawed, Extraction of free lime in Portland cement and clinker by ethylene glycol, in: R.F. Gebhardt (Ed.), Rapid Methods for Chemical Analysis of Hydraulic Cement, ASTM International, West Conshohocken (USA), 1988.

[50] Lafarge chemical method no. 42: Free CaO, in: R.F. Gebhardt (Ed.), Rapid Methods for Chemical Analysis of Hydraulic Cement, ASTM International, West Conshohocken (USA), 1988.

[51] V.S. Ramachandran, J.J. Beaudoin (Eds.), Handbook of Analytical Techniques in Concrete Science and Technology: Principles, Techniques, and Applications, Noyes Publications, Norwich (USA), 2001.

[52] T.P. Lees, Surface area measurements of cements by air permeability methods, World Cement 13 (1982) 350.

[53] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (2) (1938) 309–319.

[54] E.L. Weiss, H.N. Frock, Rapid analysis of particle size distributions by laser light scattering, Powder Technol. 14 (2) (1976) 287–293.

[55] F.W. Locher, Influence of burning condition on clinker characteristics, World Cem. Technol. 11 (2) (1980) 67–73.

[56] V.I. Babushkin, G.M. Matveyev, O.P. Mchedlov-Petrossyan, Thermodynamics of Silicates, 4th ed.Springer-Verlag, Berlin, 1985.

[57] O.M. Jensen, Thermodynamic limitation of self desiccation, Cem. Concr. Res. 25 (1) (1995) 157–164.

[58] O.M. Jensen, P.F. Hansen, E.E. Lachowski, F.P. Glasser, Clinker mineral hydration at reduced relative humidities, Cem. Concr. Res. 29 (9) (1999) 1505–1512.

[59] H.P. Klug, L.E. Alexander, X-ray diffraction procedures, 2nd ed.John Wiley and Sons, New York, 1959.

[60] J. Skibsted, H.J. Jakobsen, C. Hall, Quantification of calcium silicate phases in Portland cements by Si-29 MAS NMR spectroscopy, J. Chem. Soc.-Faraday Trans. 91 (24) (1995) 4423–4430.

[61] M.D. Andersen, H.J. Jakobsen, J. Skibsted, Incorporation of aluminum in the calcium silicate hydrate (C–S–H) of hydrated Portland cements: a high-field $_{27}$Al and $_{29}$Si MAS NMR investigation, Inorg. Chem. 42 (7) (2003) 2280–2287.

[62] Á.G. De la Torre, R.N. De Vera, A.J.M. Cuberos, M.A.G. Aranda, Crystal structure of low magnesium-content alite: application to Rietveld quantitative phase analysis, Cem. Concr. Res. 38 (11) (2008) 1261–1269.

[63] F. Nishi, Y. Takeuchi, The A1$_6$O$_{18}$ rings of tetrahedra in the structure of Ca$_{8.5}$NaAl$_6$O$_{18}$, Acta Crystallogr. B 31 (4) (1975) 1169–1173.

[64] D. Stephan, S. Wistuba, Crystal structure refinement and hydration behaviour of doped tricalcium aluminate, Cem. Concr. Res. 36 (11) (2006) 2011–2020.