THE IMPACT OF CALCIUM ALUMINATE CEMENT HYDRATION UPON THE PROPERTIES OF REFRACTORY CASTABLES

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1 Introduction

Monolithic refractory castables, bonded with calcium aluminate cements, have a rich history of over 80 years. They have evolved from high cement conventional formulations to the era of reduced cement castable systems[1] that can be placed using a variety of techniques such as casting, gunning, self flow, pumping and shotcreting. These developments have been made possible by the versatility of the calcium aluminate cements which play a major role in determining the properties of such monolithic refractories.

The usage chain of monolithics containing calcium aluminate cement contains several steps such as mixing, placing and consolidation, commissioning and dry out and finally use in service. Each of these steps within the castable placing chain are intimately linked to the hydration process of calcium aluminate cement (CAC). In order to understand the role of calcium aluminate cement (CAC), it is first necessary to consider the reactions that take place within CAC during the hydration process and then to link these reactions to the physical aspects of the castable properties. Their cementitious properties enable the refractory to be cast in place and to set and harden under ambient conditions. As the refractory is heated to high temperature, the water needed for placing and the formation of hydration products is driven off and the hot strength is provided by sintering and ceramic bonding. This process of first heating or “dry out” must be carefully managed to avoid undesirable strength loss, spalling or explosion.

This review will investigate in detail the hydration and dehydration reactions that occur from the point that water is added at the beginning of mixing through to the point that the installed refractory lining is put into service. The effect of these reactions on the physical properties of the castables will be shown in a variety of systems. The impact of parameters such as temperature, mineralogy and other formulation components will be also reviewed.

2 Calcium aluminate phases

The phases present in a given calcium aluminate cement (CAC) depend upon a number of parameters of which the chemistry is the most important. The anhydrous CAC phases present in a range of commercial products are shown in table 1.

Table 1: chemical composition and mineralogy of three different calcium aluminate cements

Cement chemistry abbreviations: C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3, M = MgO, T = TiO_2, H = H_2O

	40% alumina CAC	50% alumina CAC	70% Alumina CAC
Al_2O_3	37,5 – 41,5	50,8 – 54,2	68,7 – 70,5
CaO	36,5 – 39,5	35,9 – 38,9	28,5 – 30,5
SiO_2	42, - 5,0	4,0 – 5,5	0,2 – 0,6
$FeO+Fe_2O_3$	14,0-18,0	1,0 – 2,2	<0,4
$Ti0_2$	<4,0	<4,0	<0,5
CA	47-57	64 - 74	54 – 64
CA_2			+++
A			+
$C_{12}A_7$	1-5%	Trace	Trace
C_2AS	++	++	
C_4AF	++		
C_2S	Trace		
CT		+	

The mineralogy shown in table 1 is determined by quantitative methods using the Rietveld approach[2]. The dominant phase in all cases is CA, calcium monoaluminate. The reactions of calcium aluminates and their kinetics will be influenced by the composition of the mineralogical phases present in a given cement. A general comparison of the reactivity of the anhydrous phases is shown in table 2 taken from George[3]. It can be seen that as the phases become more lime rich, i.e. as the C/A ratio increases, then so does their reactivity.

Table 2: The reactivity of the various calcium aluminate phases

	C_3A	$C_{12}A_7$	CA	CA_2	CA_6
C/A	3	1,7	1	0,5	0,2
Reactivity at 20°C	Very rapid	Fast	Slow	Very slow	None

Table 3 taken from reference 1 lists some useful properties of the phases found in CAC. Monocalcium aluminate ($CaO.Al_2O_3$ or CA) is the most important component of CAC's and has a relatively high melting point (1600°C), and develops the highest strength among the phases listed during the relatively short time available for hydrating refractory concretes. It takes some time to start setting, but hardens rapidly after the initial set. Calcium dialuminate (CA_2) is a secondary phase in CAC's and is more refractory than CA but takes a long time to set due to its low hydraulic activity although accelerated as temperature increases[4]. While hydration of CA is known to be accelerated by the presence of CA_2, the opposite does not hold true. The hydration of CA_2 may actually be hindered by the presence of CA[5]. The strength of CA_2 after three days hydration is comparable to that of the pure CA. $C_{12}A_7$ hydrates rapidly and has a relatively low melting point. C_2S and C_4AF are common in Portland cement, but can also occur in the high-silica and iron-rich low-purity CAC's, respectively. C_4AF forms hydrates of calcium aluminate and calcium ferrite or solid solutions of the two hydrates. C_2AS (gehlenite) shows little tendency to hydrate and is an undesirable component of alumina cement which limits refractoriness and hot-strength properties[6].

Table 3: Properties of CAC Mineral Constituents

Mineral	Chemical Composition (wt %)				T_m	Density	Crystal
	C	A	F	S	°C	g/cm^3	
C	99.8				2570	3.32	Cubic
$C_{12}A_7$	48.6	51.4			1495	2.69	Cubic
CA	35.4	64.6			1600	2.98	Mon.
CA_2	21.7	78.3			1765	2.91	Mon.
C_2S	65.1			34.9	2066	3.27	Mon.
C_4AF	46.2	20.9	32.9		1415	3.77	Orth.
C_2AS	40.9	37.2		21.9	1590	3.04	Tet.
CA_6	8.4	91.6			1830	3.38	Hex.
$\tilde{\alpha}A$		99.8			2051	3.98	Rhomb

CA_6 is the only non-hydrating phase in the pure calcium aluminate system and is often a reaction product in alumina castables bonded with high-purity aluminate cement. It is believed that CA_6 is most readily formed in alumina castables when using CA_2 as a precursor[7]. Alumina (A) is sometimes present as an addition and this is especially true in the case of 80% alumina calcium aluminate cements.

3 Calcium aluminate cement hydration

In contrast to Portland cements where the hydrates formed remain broadly similar[8] with time and temperature the hydration of CAC is strongly dependant upon temperature. The ambient temperature significantly modifies the hydrates that result. The associated hydration reactions are shown in table 4.

Table 4: Hydration scheme for mono calcium aluminate.

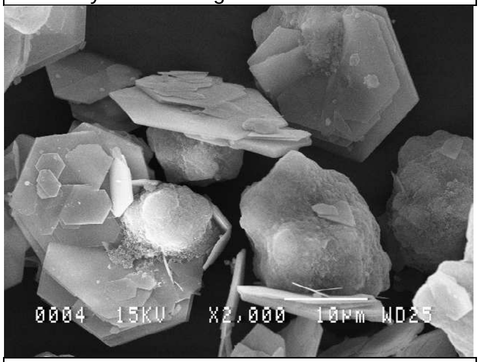
Temperature	Hydration	Reaction
< 10°C	CA + 10H	→ CAH_{10}
10 – 27°C	2CA + 11H	→ $C_2AH_8 + AH_3$
	CA + 10H	→ CAH_{10}
>27°C	3CA + 12H	→ $C_3AH_6 + 2AH_3$
F(t°C + time)	$2CAH_{10}$	→ $C_2AH_8 + AH_3 + 9H$
	$3C_2AH_8$	→ $2C_3AH_6 + AH_3 + 9H$

Below 10°C it is the formation of CAH_{10} that dominates and this continues up to around 27°C. Between 10 and 27°C CAH_{10} and C_2AH_8 are formed together. At higher temperatures above 27°C C_3AH_6 formation occurs early in the hydration process. It is believed that the formation of C_3AH_6 often passes through a transient C_2AH_8 phase[8]. The other two important reactions are the conversion of the metastable hydrates, CAH_{10} and C_2AH_8 to the stable C_3AH_6

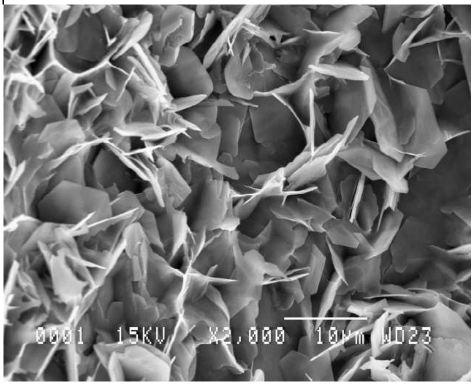
hydrates. In addition to the C-A-H hydrates, Alumina tri hydrate (AH_3) is also formed as part of the hydration reactions. All these reactions are time, temperature and humidity dependant.The morphology of the AH_3 that is formed also changes with temperature. At lower temperatures it exists as a gel form and becomes increasingly crystalline as the temperature increases. Analogous hydration reactions can be written for CA_2 as well as for $C_{12}A_7$. Other hydrates have also been reported[10,11] and are known to exist, for example the hydrates C_4AH_{13} and $C_4A_3H_3$. The later existing mainly under hydrothermal conditions (such as exists in refractory concrete during the dry out phase). The morphology and some key properties of each of the main hydrates are shown in Fig. 1.

Fig. 1: Key properties and Micrographs of the calcium aluminate hydrates

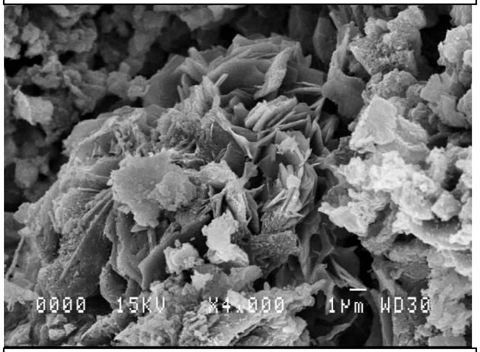
CAH_{10}
Density = 1720 Kg/m^3
Cubic system : Hexagonal



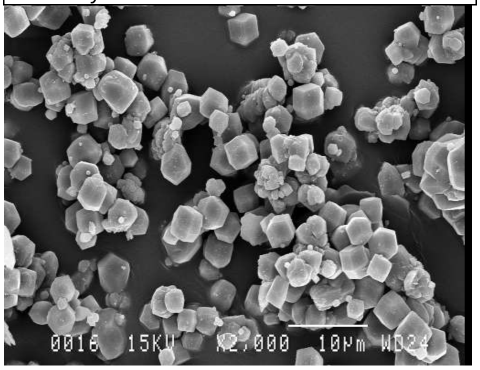
C_4AH_{13}
Density = 2046 Kg/m^3
Cubic system : Hexagonal



C_2AH_8
Density = 1950 Kg/m^3
Cubic system : Hexagonal



C_3AH_6
Density = 2520 Kg/m^3
Cubic system : Cubic



4 Mechanisms

The mechanism of hydration of calcium aluminate is via solution, where an anhydrous phase dissolves and is followed by the precipitation of the hydrates from solution[3]. Three distinct phases can be identified; dissolution, nucleation and precipitation. The hydration process[10] is initiated by the hydroxylation of the cement surface followed by dissolution of cement in water and the liberation of calcium and aluminium ions. A small amount of gel like hydrates will form at this point if the solution concentration rises over the super saturation limit level of the hydrates C_2AH_8 and AH_3. The dissolution will continue, with a consequent increase in the concentration of calcium and aluminium ions until a saturation point is reached.

This is the point which is the equilibrium solubility of the anhydrous phases with the hydroxylated surface layers. After the dissolution phase there follows an induction period during which nuclei attain a critical size and quantity.

Once this is achieved the nucleation phase is followed by a rapid and massive precipitation of the hydrates, leading to a drop in solution concentration. This is a dynamic process which continues to consume anhydrous cement. In a physical sense, it is the growth of these hydrates which interlock and bind together to provide mechanical resistance. The driving force of the hydration reactions is the lower solubility of the hydrates compared to the anhydrous species. The ambient temperature significantly modifies the hydrates that result due to the fact that their solubility changes with temperature[12].

As has been explained, hydration is a process that involves the passage of ions into solution. This can be followed experimentally[13] using conductimetry and is shown schematically in Fig. 2. In this technique a quantity of cement is put into solution in a cell and the change in conductivity with time is continuously monitored. The water is maintained at constant temperature which is normally 20°C. The conductivity of a solution is directly linked to the number of ions in solution. The measured conductivity will increase as the quantity of ions in solution increases. The resulting data is collected electronically and presented in the form of a curve (fig. 2). Three distinct zones can be identified.

- The first zone **(I)** is characterised by a rapid increase in conductivity. This corresponds to the dissolution of the anhydrous cement. Calcium aluminate cement forms ions in the presence of water and these ions correspond to Ca^{2+} and $Al(OH)_4^-$. This phase is exothermic and heat is generated. There is a slow precipitation of gel like hydrates[14] These primary hydrates form both in solution and as small colloidal particles surrounding the anhydrous grains.

- The second zone **(II)** is the plateau with a stable conductivity; this corresponds to the induction period where nuclei or germs are formed preceding precipitation. This is also referred to as the saturation stage where saturation, in terms of ionic concentration, is being reached. There is no change in ionic concentration during this period where there is slow growth of gel like hydrates which equals their dissolution rate.

- The third zone **(III)** is characterised by a rapid decrease in conductivity. This corresponds to the formation of hydrates (~ setting) as the solution concentration is oversaturated with respect to the hydrates. The massive precipitation causes a decrease in conductivity. The precipitation of the hydrates is responsible for the flocculation of the calcium Aluminates due to two mechanisms. Firstly, hydrate formation consumes water and thus workability decreases and secondly, hydrates have a negative surface charge which is attracted to the positive surface charge on the anhydrous particles. This step is exothermic and the heat liberated can be followed as a means of following the hydration process. This step will only occur when over saturation (with respect to the hydrates) is achieved and when a sufficient number of structured nuclei are present. In the case of pure CA this may require a considerable time.

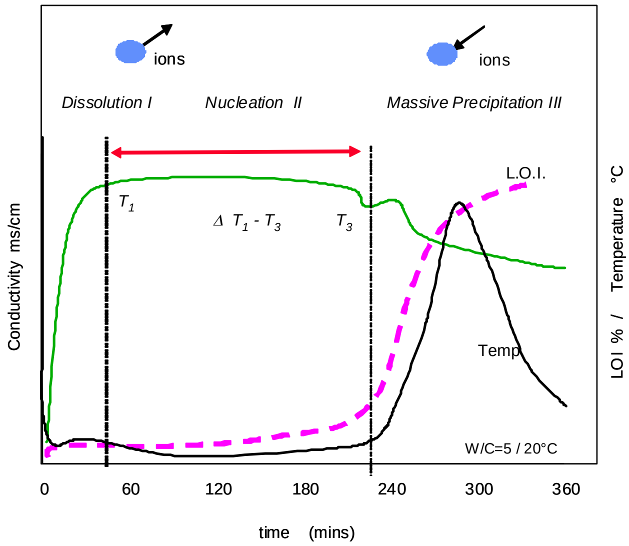


Fig. 2: Conductimetry curves for Secar® 71

Also shown in fig. 2 are the comparison curves for the increase in loss in ignition. It is clear that the decrease in conductivity is coherent with hydrate formation as evidenced by the increase in LOI of the cement material. Similarly the evolution of conductivity follows the determined concentrations of $[Ca^{2+}]$ ions in solution.

5 Relationship of hydration reactions to castable proprties

The impact on castable properties due to these hydration reactions can be measured through a variety of physical techniques. Two castable properties are of specific interest, as they govern the time scheduling of castable installations; the workable time that a castable can be placed before becoming unworkable or stiff and the time when the cast structure has sufficient strength that the formwork and moulds can be stripped.

Fig. 3 shows the link between these aspects of castable properties, workability and hardening time and the hydration process as followed by conductimetry and exothermic profiles[14]. The period of workability is linked to the formation of gel like hydrates. These can not be measured by classical techniques and their detection necessitates techniques such as AFM and X ray transmission microscopy[15]

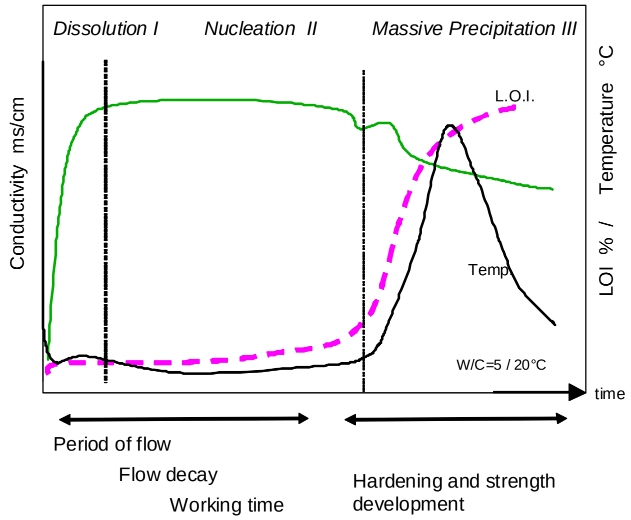


Fig. 3: The link between hydration steps and castable properties

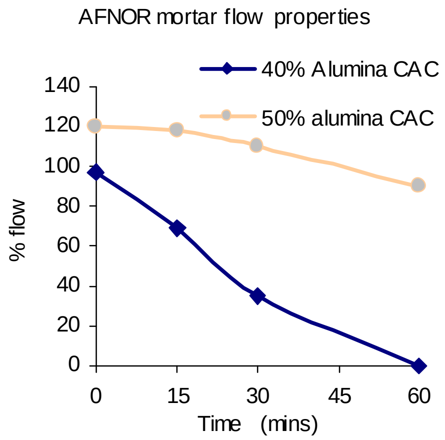
These particles are of nanometric size and lead to a progressive structuring of the material as they develop in size and quantity.

The working time occurs when there is sufficient flocculation and stiffening so that the castable will not move under vibration and thus cannot be properly consolidated anymore. The hardening generally starts to occur as the massive precipitation occurs as can be seen by the increase in temperature (exo profiles) and decrease in ionic activity (conductimetry) in Fig.3. Thus, a quicker time to the massive precipitation will result in a reduced time to attain a given strength. The optimisation of castable properties often aims at modifying these antagonistic properties i.e. prolonging the working time and reducing the hardening time. Clearly, this can only be achieved if an understanding of the underlying hydration reaction kinetics is achieved. The hydration mechanisms and kinetics such as those described above can be significantly modified[16,17] when fine reactive powders (fillers) and additives are present as in the case of deflocculated castables. The nature of these reactions depends to a large extent upon each unique combination of CAC, fillers and additives. It is possible in these systems to distinguish short-term hydration reaction effects, related to castable placing characteristics, from longer-term hydration mechanisms that are linked to castable hardening. The reactions are complex and occur at all stages through the castable processing chain. The identified chemical reactions occur via solution and are based upon ionic dissolution, complexing mechanisms and precipitation reactions. The effect of the surface must also be considered. The impact of these components as well as the base mineralogy on CAC hydration and the link to several key castable properties will be discussed in the next section.

6 Factors affecting CAC hydration and castable properties

6.1 Mineralogy

CAC mineralogy has a large impact on both the placing properties and castable workability as well as the hardening. As shown in table 2 the higher the C/A ratio the greater the reactivity of the CAC.



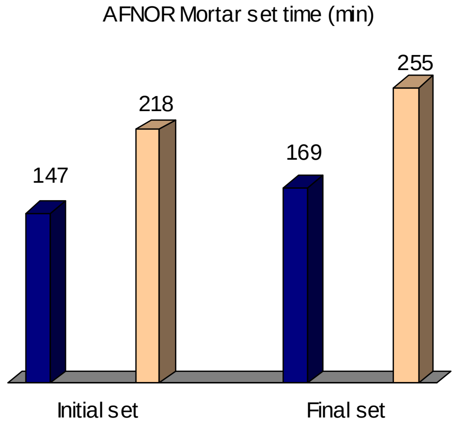
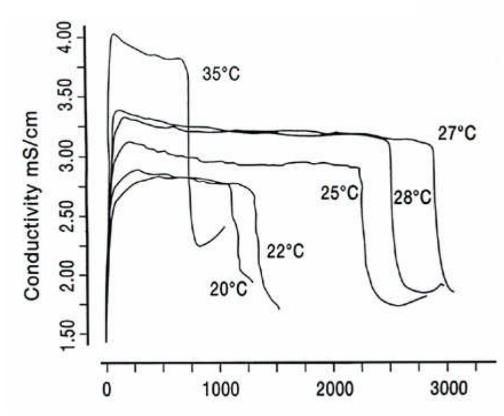


Fig. 4: Placing and set properties of two Calcium aluminate cement

However, all commercial products are comprised of a multi phase assemblages and when considered together the effect of each phase is not linear. This is illustrated in Fig. 4 which shows the basic placing properties of 2 different CAC cements the properties of which are shown in table 1. As can be seen the CAC with a higher $C_{12}A_7$ contents has more rapid flow decay along with a quicker set.

An explanation for this difference in behaviour can be found by studying the hydration reactions of the different pure calcium aluminate phases. $C_{12}A_7$ has a higher C/A ratio (1,7/1) than CA (ratio = 1) and this gives a higher calcium ion concentration in solution than in the case of CA. This brings the solution into a rapid over saturation with respect to C_2AH_8 and it is this phase that precipitates rapidly. These hydrates are formed at an early stage in the hydration process. These hydrates serve to reduce the flow via a flocculation and decrease the nucleation time leading to a rapid massive precipitation i.e. shorter set. This is illustrated in Fig. 5 which shows the conductimetry curves for the $C_{12}A_7$ phase at different temperatures. If the curves at 20°C are compared it can be seen that the $C_{12}A_7$ containing cement displays a very rapid dissolution followed by a rapid precipitation with a very short nucleation period. The massive precipitation occurs at a much shorter time interval than the A phase. The CA phase shows the classical dissolution, nucleation and precipitation periods. Fig. 5 taken from reference 12 also shows the impact of temperature upon hydration as measured by conductimetry with clear differences between CA and $C_{12}A_7$ phases being evident. In the case of $C_{12}A_7$, the precipitation of C_2AH_8 phase[8] accelerates continuously as temperature is increased. By contrast, the anomalous setting of CA can be seen around 28°C where the precipitation takes place later as the temperature increases from around 20 to 28°C. The explanation for this anomalous behaviour is linked to the increasing difficulty of nucleating CAH_{10} as the temperature increases. This arises as the solubility of CAH_{10} increases with increasing temperature making it more difficult to nucleate. At the same time the nucleation of AH_3 becomes quicker as temperature increases. Up to 27°C the nucleation speed is controlled by the formation of CAH_{10} (increasing precipitation time with temperature). Above this temperature the nucleation of AH_3 is more rapid than CAH_{10} and this controls the hydration and precipitation times which now decrease with increasing temperature.

Conductimetry curves for CA



Conductimetry curves for $C_{12}A_7$

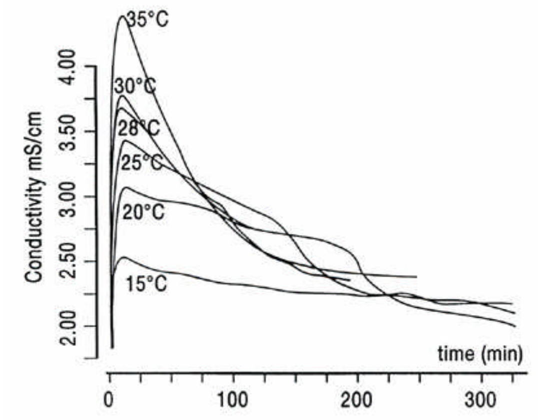


Fig. 5: Conductimetry curves for two different calcium aluminate cement phases

This is seen in real cement systems as a lengthening of set around 27°C. Fig. 6 shows this effect as measured by the exothermic profiles of an AFNOR sand mortar system and a 70% alumina cement at different temperatures.

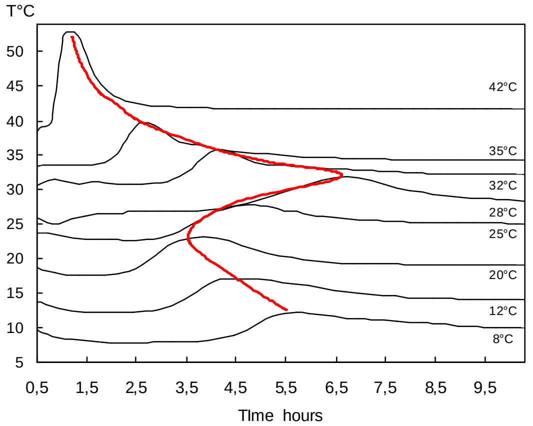


Fig. 6. Exothermic profiles at different temperatures for a 70% alumina cement.

The anomalous set around 28°C can be seen by the longer time taken (around 8 hours) to reach the exothermic peak temperature.

6.2 Additives

Chemical additives or admixtures can be used to modify the placing properties of refractory castables. This is achieved via two basic mechanisms, which can be active either as unique mechanisms or as a combination of both types:

- Modification of CAC reactivity via chemical interactions with the hydration reactions and kinetics
- Modification via a physical effect such as steric dispersion or viscosity modification via water retention.

The nature of chemical interactions of additives on calcium aluminate cements is shown in Fig. 7. Depending upon the specific additive the dissolution, nucleation and precipitation reactions of the CAC can be modified[18,19,20,21,22] The specific nature of interaction is also dependant to some extent on the starting mineralogy as well as the other components of a castable system.

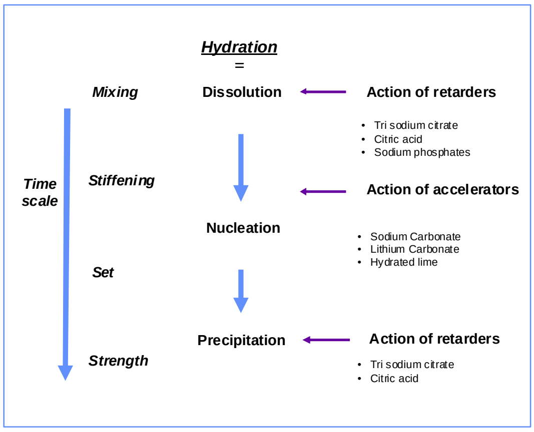


Fig. 7: The mode of action of generic additives on CAC hydration.

Two specific examples of two classical additives, lithium carbonate (LC) and tri-sodium citrate (TSC), upon the hydration of a 70% alumina cement are shown in Fig.8.1 and 8.2 These well-known additives are used to accelerate hydration in the case of LC and retard hydration in the case of TSC. Conductivity analysis shows the mechanism of action for each of these additives. With increasing dosage of LC, the massive precipitation time is reduced significantly while the dissolution time remains constant. In fact, the nucleation period decreases. The inverse is true for TSC, where the nucleation time increases as the dose increases.

The actual mechanism can often be deduced by withdrawing samples of the suspension at specific intervals and « stopping » the reaction by washing the sample with alcohol, followed by subsequent (ICP, XRD) analysis of the solution. The shortening of the massive precipitation time in the case of LC has been found to be due to an increased nucleation rate of alumina trihydrate (AH_3).

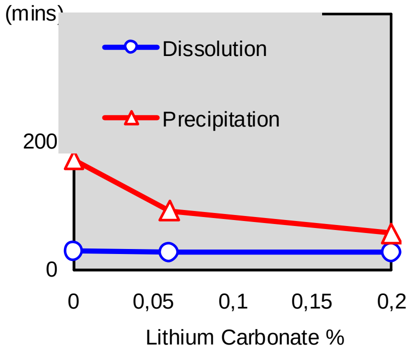


Fig. 8.1 : The effect of lithium carbonate on the hydration of a 70% alumina cement

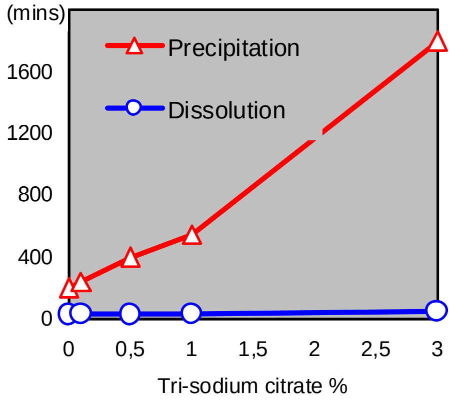


Fig. 8.2: The effect of trisodium citrate on the hydration of a 70% alumina cement

The retardation of the massive precipitation seen with TSC is due to a lengthening of the induction period. This is believed to be due, from solution chemistry analysis, to the formation of a gel containing citrate, calcium and aluminium ions. The downside is that this gel can perturb castable rheology and decrease the flow. These interesting results show that the action of these additives upon the three stages of CAC hydration is specific. This opens the possibility to envisage the use of multiple additives to optimise castable systems, each acting upon a specific phase of the hydration process. Thus, the combination of these two additives in a castable would give a castable with a long working time followed by a rapid hardening.

6. 3 Reactive fillers

The two most commonly used fine fillers are fume silica and reactive alumina. Each of these fillers provokes different interactions with CAC and its hydration. The specific properties of reactive alumina (BET, Soluble sodium) and their impact upon CAC hydration have been reported[23,24] in the context of reduced cement castable systems. The accelerating effect of both the surface and the soluble sodium content on the dissolution and precipitation reactions was demonstrated. This is in contrast to fume silica which tends to have a retarding effect upon the CAC dissolution.

The hydration mechanism of a 70% alumina cement is significantly modified in LCC systems containing fume silica. This is particularly noticeable when a dispersing additive (in this case sodium tri-polyphosphate – TPP) is present.

The initial dissolution is delayed (Fig. 9) compared with the cement only system as shown in figure 3. Also, the dissolution occurs at a much slower rate with the LCC system. However, the precipitation occurs during a similar time period for both the dispersed system and the cement alone. The precipitation time corresponds well with the onset of hardening and the acquisition of mechanical resistance in castables. The initial level of conductivity is derived from the TPP additive which is added directly into solution. This also offers a possibility of using conductivity as a means to control the TPP dose in castables. The initial conductivity is strongly correlated with the TPP dose.

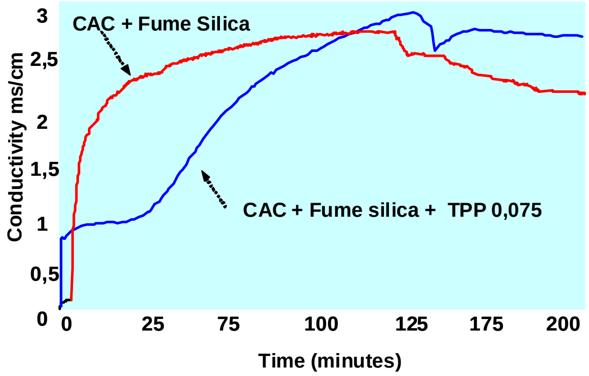


Fig. 9. Conductimetry curves for different combinations of CAC, fume silica and TPP

The delay in CAC dissolution is the mechanism[25] which provides the castable with sufficient working time. The longer the delay in dissolution, the longer the working time becomes. This retarding effect on CAC dissolution is not seen when binary combinations of phosphate and CAC or fume silica and CAC are analysed. It is presumed, therefore, that the surface of the fume silica in the presence of phosphates also plays a key role. It can be considered that the length of the working time of low cement castables results from a series of interactions between the additives and the fine fillers, together with the CAC. The working time is not simply dependent upon the cement alone as in the case of classical or conventional castables with a high cement dose. Thus, by studying the duration of this delayed dissolution through conductimetry, a method exists by which castable working times can be measured and optimised more precisely than through classical methods.

The practical implications of this are that in a reduced cement castable system when only alumina is used as the fine filler then provision must be made for a retarding mechanism otherwise the flow decay will be extremely rapid. This is further illustrated in the example below.

A study of numerous low cement binder phase systems (variations of both fillers and additives) has highlighted[16] significant differences in the exothermic profiles measured by calorimetry. Two exothermic peaks can be identified. The two peaks have been generically labelled as Pi and Pm. The points Pi and Pm are taken as the points of maximum heat flow and the time taken to reach these peaks is recorded. The peak Pm is believed to correspond to the massive precipitation of the hydrates, whereas Pi is associated with the dissolution phase of the cement. In terms of castable placing characteristics, Pi is associated with the loss of workability and castable flow decay. Pm corresponds to the onset of strength development during castable hardening. There exists a relationship between working time of the full castable and the apparition of this peak, but the relationship depends upon the composition of each specific binder phase composition (fumed silica, alumina etc). Fig. 10 illustrates this effect. The curves represent the peak Pi for two different systems of reactive fillers. The first graph shows a system containing 25% of a 70% alumina cement, 50% of a reactive alumina (CT3000SG) and 25% of fumed silica (Elkem 971U). The additive system is a binary system (sodium polymethacrylate and citric acid) added at 0,5% by weight of the total castable binder phase. The system in the second graph is identical except for a substitution of the fumed silica by the reactive alumina (i.e. CAC=25% and reactive alumina = 75%). The dotted line in both graphs shows the measured working time of each castable which corresponds to the apparition of Pi in both cases. The graphs provide some explanation of the well known effect that removing fumed silica from the system results in a much shorter working time of the castable.

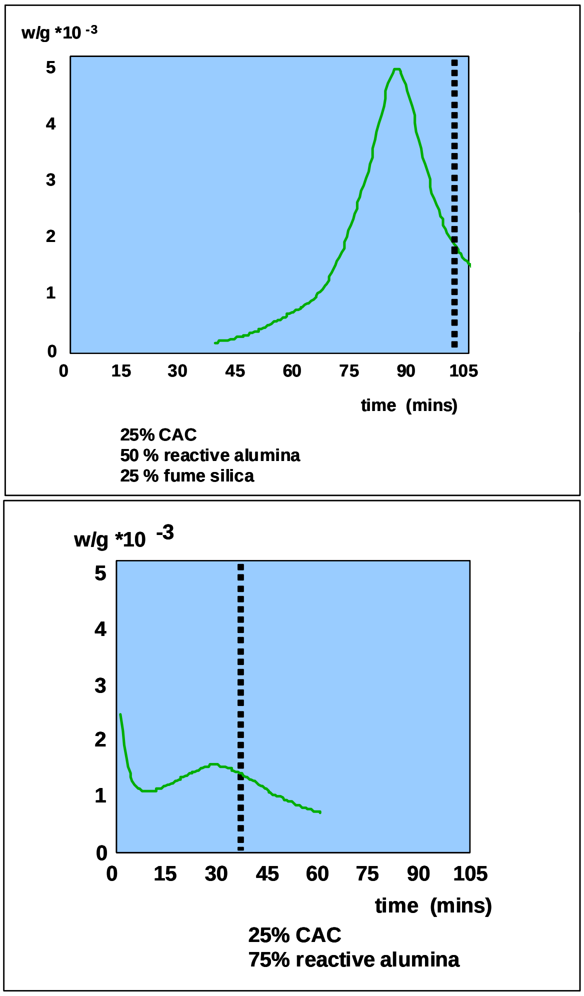


Fig. 10: The impact of different filler systems upon the first calorimetric peak.

The heat flow data clearly shows that there is a chemical reaction related to the fillers and that, although they are not hydraulic binders, they act in a chemical sense within low cement castable systems. In effect, the fume silica provides a strong retarding effect upon the cement dissolution, which gives a usable working time to the castable. By contrast, the system without fume silica does not have this retarding effect upon cement dissolution. As a consequence, a short working time and rapid flow is expected. In the case of an actual castable, this would need to be corrected through a modification of the additive system, for example, by using a fluidifier which also retards the CAC or via the incorporation of a specific retarder. This applies specifically to systems that are controlled by ionic interactions. Another alternative exists and that is to use a dispersion system that relies on steric effects[26] to overcome the impact of an intrinsic accelerating effect of reactive alumina.

Table 5: The effect of fume silica properties on CAC and castable characteristics

Element/ Property % increasing	**Effect on CAC hydration**	**Impact on LC castable properties and characteristics**
Na_2O, K_2O, MgO, SO_3	Provoke creation of gels and flocculation	Reduced flow and rapid flow decay
SO_3	Retards hydration kinetics	Increased hardening time
pH	Accelerates precipitation	Decreased hardening time
BET	Accelerates precipitation.	Reduced flow and rapid flow decay
LOI /moisture content	Retards dissolution via hydroxylation of the surface of the cement grains	Increases ageing and shelf life of dry mix
	Promotes presence of early hydrates which affect rheology	Reduces flow
Carbon	Delays precipitation reactions	Reduces mechanical strengths

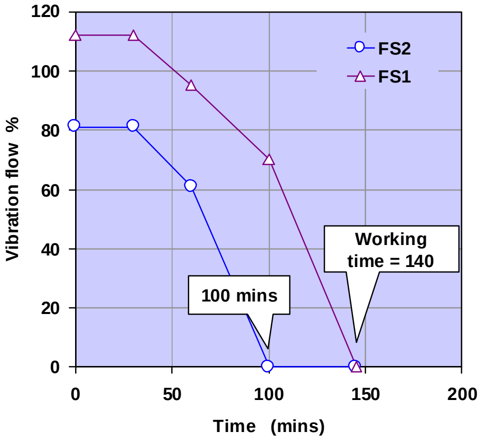
Fume silica displays a natural retarding effect on the CAC dissolution when used in combination with additives such as phosphates that rely on electrostatic dispersion and so the management of working time is more straightforward. However, the variable nature of impurities in fume silica can perturb the hydration reactions and lead to variable working and hardening times in reduced cement castables. The impurities present in fume silica as well as the basic physical properties can have a marked effect on castable properties via interactions with the hydration process. The main effects are summarised in table 5:

The following example illustrates the differences in castable properties that result as a consequence of fume silica type. Two fume silica types have been evaluated in low cement castable based upon sintered alumina with 5% fume silica and 5% of a 70% alumina CAC. Sodium Tripolyphosphate was used as the dispersant at 0,03% (dry wt. basis). The analysis of the fume silica is shown in table 6.

Table 6: Analysis of two fume silica types

		FS1	FS2
BET (m2/g)		20	17.6
% C (free)		0.27	0.81
H_2O	%	0.789	1.982
SiO_2	%	97.64	94.71
Fe_2O_3	%	0.07	0.1
MgO	%	0.22	0.56
SO_3	%	0.08	0.14
K_2O	%	0.28	1.28
Na_2O	%	0.09	0.13
pH		6.3	7.9

FS1 contains fewer impurities in terms of alkalis, free carbon and has a more acidic pH and lower sulphate content. Based on the above discussion it would be expected that this fume silica yields better placing properties in terms of flow, flow decay and castable working time.



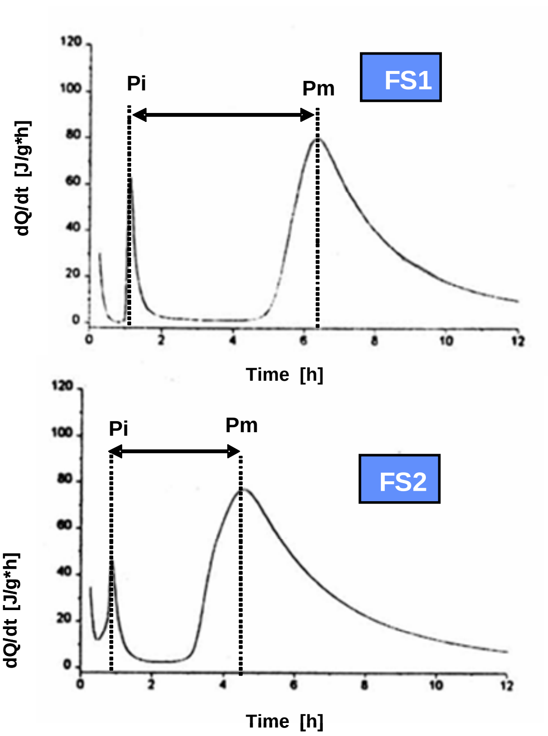


Fig. 11: The effect of two fume silica types on castable placing properties and CAC hydration

Fig. 11 shows the experimental data which confirms this hypothesis. In addition a study of a simplified binder system (CAC + FS) shows using calorimetry reveals the effect upon CAC hydration. The intermediate peak Pi occurs later with FS1 and the induction period (difference between Pi and Pm) is also longer.

The exact mechanism of interaction around this intermediate peak is unclear but an explanation has been proposed[27] whereby a primary layer of CASH develops on the surface of the cement grain this then converts into an alumina poor CASH or CSH type layer. In so doing a large quantity of $[Al(OH)_4]^-$ is liberated into the solution. This renders the solution oversaturated and metastable with a likelihood of AH_3 precipitation and flocculation i.e. the end of castable working time. A clearer understanding of these mechanisms that describe the various observations is still needed and is of importance if the complete control of such systems is to be ensured.

7 Initial drying and the impact on CAC hydrates

Once the installed castable is hard, and the moulds removed drying can commence. During heating the microstructure of the bond phase undergoes various transformations.

A marked difference in mechanical properties exists between the as cast state and after drying at 110°C depending upon the starting mineralogy of the CAC. Figure 12 demonstrates this.

- In the case of the 50% alumina cement, on heating from ambient temperature to 100°C, the cement hydrates that are initially formed are converted to the stables hydrates AH_3, and C_3AH_6, with a release of free water, increase in density of the hydrates, increased porosity and a reduction in the measured mechanical strength

- In the case of the 70% alumina cement which contains appreciable quantities of CA_2 an increase in strength is observed after drying. As in the example above initial heating leads to conversion and the release of free water. In addition, the excess water used for casting is also liberated as steam. Some of the water released by the conversion of metastable to stable hydrates leads to further hydration of the CA_2 and there is an increase in strength, as discussed in a previous study[28]

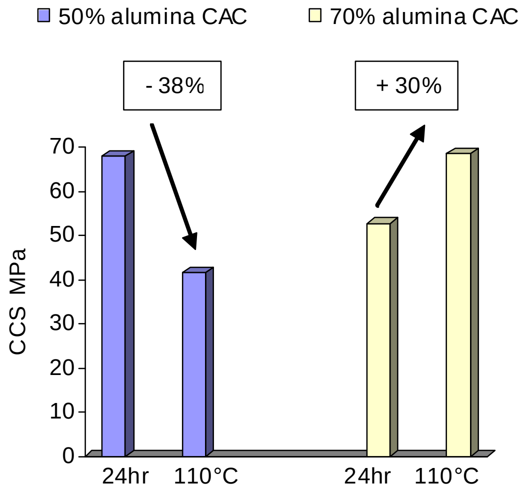


Fig. 12 Comparison of as cast and dried strengths of two different CAC types

8 Calcium aluminate cement de-hydration

The de-hydration phase is illustrated using a high purity castable with 30% of an 80% CAC and 70% of a sintered alumina with a maximum particle of 7mm and with a water addition of 8,5%. During the heating, the bond phase undergoes various transformations which can be followed either by an analysis of the phase composition or indirectly via the mechanical and physical properties. These are shown in Figs. 13 and 14. The example serves to illustrate the intimate link between CAC dehydration reactions, themselves a consequence of the initial hydration, and the installed castable properties:

- Up to 24 hours after casting, there is incomplete hydration which continues after drying at 110°C; the residual CA as well as a large part of the CA_2 is hydrated during drying at 110°C. At this point the strength is at a maximum reflecting the degree of hydrate development. AH_3 appears as a crystalline phase gibbsite

- Between 100 and 400°C: AH_3 and C_3AH_6 gradually decompose to give amorphous anhydrous relics and water vapour. This water vapour has to escape from the concrete. The porosity increases from 13 to 17% and consequently the mechanical strengths decrease. This two stage release of water is an advantage of CAC based systems as it helps to reduce build-up in vapour pressure compared to other bond systems which tend to release water over a narrow temperature range.

- 400-900°C: During this subsequent dehydration phase the previously stable hydrates C_3AH_6 continue to dehydrate progressively to $C_{12}A_7H$ and at the same time Gibbsite (AH_3) is transformed to Alumina hydrate relics. The measurable mineralogy does not change significantly during this period. Porosity continues to increase to around 23% and strengths decline relative to the strengths at 110°C

- Above 800-1100°C, the relics of the cement phases and elements of the bonding phase re-crystallize first to $C_{12}A_7$ then CA and from 950°C CA_2 starts to form progressively. Porosity reaches a maximum of around 25% and the strengths tend to a minima

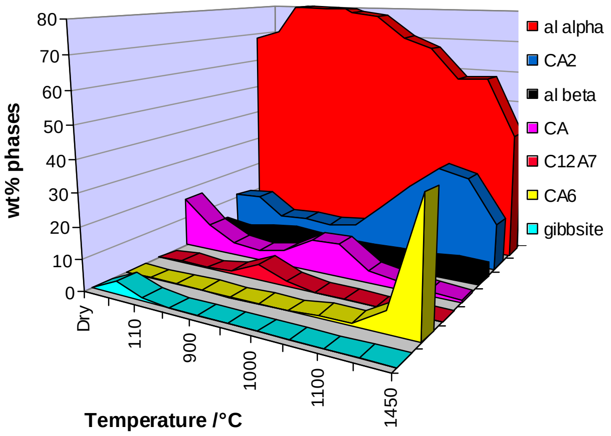


Fig. 13 The change in phase composition as a function of temperature for a high purity alumina castable

- 1100 – 1300C° CA_2 reaches a maximum of about 30% at about 1100°C. Alumina decreases as it is consumed in the reaction $CA + A \rightarrow CA_2$

- Above 1300°C the reaction continues towards thermodynamic equilibrium, with CA_6 formed from CA_2 and Al_2O_3. The final content of CA_6 reaches about 40% at 1450°C. The porosity decreases as evidence of the sintering reactions taking place and the strengths increase in parallel with the development of the ceramic bonding.

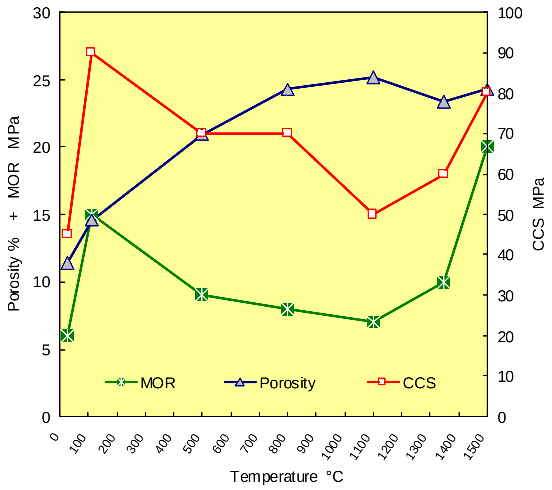


Fig. 14 Change in Mechanical properties and porosity of a high purity castable as a function of firing temperature.

9 Summary and conclusions

This review paper has shown the intimate link between CAC hydration and castable properties. Improvements in castable technology can only be successfully achieved via a greater understanding of this link.

This is especially true in the case of reduced cement systems where the CAC and its hydration are affected by the presence of fine fillers and additives. Hence, the notion exists that the binder system in reduced cement castable systems is comprised of an interdependent system between three key components, CAC, fillers and additives. It is the versatility of the CAC in terms of the possibility to modify the hydration reactions that has made the development of such castable systems possible.

It is likely that the future generations of castables will become increasingly sophisticated as installation techniques and performance constraints become more demanding. The development of these castables will only be successful if they are derived from an understanding of the underlying mechanisms and interactions. Thus, the continued development of techniques able to study these complex interactions is forecast to be a key success factor in the future.

10 References

1) W.E. Lee, W. Vieira, S. Zhang, K. Ghanbari-Ahari, H. Sarppoolaky, C. Parr, “Castable refractory concretes”, Intl. Mat. Reviews, Vol 46, No.3, 2001, 145- 167

2) T. Füllman, G. Walenta, T. Bier, B. Espinosa, K.L. Scrivener, “Quantative Rietveld analysis of calcium aluminatec cements”, World Cement Research, June 1999, 91 -96

3) C.M. George, “Aspects of Calcium Aluminate Cement (CAC),” Hydration Proceedings of the Refractories Symposium, American Ceramic Society, St. Louis Section, St. Louis, 1994.

4) M. Ohta, T. Kimma and H. Yanagida, “The early stage hydration of $CaO.2Al_2O_3$,” J. Ceram. Soc. Jap. Int. 96, 36-40 (1988)

5) A.Capmas S. Möhmel, W. Geβner, D. Müller, “The Behaviour of CA/CA_2 Cements During Hydration and Thermal Treatment”, Proc. UNITECR’ 97 (New Orleans, USA, 1997) 1273-1282.

6) Th. Bier, N.E. Bunt, C. Parr, “Calcium Aluminate Bonded Castables – Their Advantages and Applications”, Alafar

proceedings, Bariloche, Argentina, Vol. 2, 1996, pp. 73-84.

7) E. Criado, D. A. Estrada, and S. De Aza, “Dilatometric Study of the Formation of CA_2 and CA_6 in Cements and Refractory Concretes”, Bull. Sp. Ceram. Glass Soc. 15 [5] 319-21 (1976).

8) K. L Scrivener and A. Capmas, Calcium Aluminate Cements”; Chapter 13 in Lea’s Chemistry of Cement and Concrete, 4th ed. Edited by Peter C. Hewlett, John Wiley and Sons New York, 1998.

9) S. Rashid, P. Barnes, X. Turrillas, “The rapid conversion of calcium aluminate cement hydrates as revealed by synchrotron energy diffraction,” Adv. Cem. Res 4 [14] 61-7 (1991)

10) F. Sorrentino, D. Sorrentino, C.M. George, “Mechanisms of Hydration of Calcium Aluminate Cements,” in Scalny J.P. ed. Materials Science of Concrete, vol IV. Amercian Ceramic Society 1995; 41-90.

11) A.J. Majumdar, R. Roy, “ The system $CaO-Al_2O_3 – H_2O$,” J. Am Ceram Soc. Vol 39, nb. 12, 1956, 434-442

12) A.Capmas, D. Ménétrier-Sorrentino, D. Damidot, “Effect of Temperature on Setting Time of Calcium Aluminate Cements”, in Calcium Aluminate Cements, ed. R.J. Mangabhai, Chapman and Hall, 1990.

13) Th. A. Bier, A. Mathieu, B. Espinosa and J. P. Bayoux, "The Use of Conductimetry to Characterise the Reactivity of Calcium Aluminate Cements", UNITECR, Sao Paulo, Brazil, 1993, pp.705-716.

14) C. Fentiman, C. M. George, R. Montgomery, “The Heat Evolution Test for Setting Time of Cements and Castables”, Advances in Ceramics, Amercian Ceramic Society, 13; 1985.

15) V.H.R Lamour, P.J.M. Monteiro, “Microscopic studies of the early hydration of calcium aluminate cements”, Proc. Intl. Conf. On Calcium Aluminate Cements, R.J. Mangabhai,ed, F.P. Glasser, ed, IOM communications, Edinburgh, 2001, pp169-180

16) H. Fryda, K. Scrivener, Th. Bier, B. Espinosa, “Relation Between Setting Properties of Low Cement Castables and Interactions Within the Binder System (CAC-Fillers-Additives-Water)”, Vol. 3 UNITECR 97 Proceedings, USA, 1997, pp.1315-1323.

17) J.P. Bayoux, J.P. Letourneux, C. M. George, “Fumed Silica and Cement Interactions Parts 1-3”, UNITECR 89, Anaheim, USA, 1989.

18) Chappuis et Al., "Admixture for calcium aluminates cements in refractory concretes" Presented at the American Society meeting, Indianapolis, April 1989.

19) S.A. Rodger, D.D. Double, “The chemistry of hydration of high Alumina cement in the presence of accelerating and retarding admixtures”, Cement and Concrete Research, Vol.14, 1984, pp 73-82

20) D. Sorrentino, J.P. Bayoux,R. Montgomery,A. Mathieu, A. Capmas, “The Effect of Sodium Gluconate and Lithium Carbonate on the Properties of Calcium Aluminate Cements”, UNITECR 91, Germany 1991, pp. 530-533.

21) Th. A. Bier, A. Mathieu, B. Espinosa and C. Marcelon ; "Admixtures and Their Interactions with High Range Calcium Aluminate Cement." ; UNITECR Proceedings, Kyoto, Japan, Vol. 1,1995, pp. 357-364.

22) Th. A. Bier, Ch. Parr ; "Admixtures with Calcium Aluminate Cements and CAC Based Castables" presented at the 28th Annual SA Ceramic Society Symposium at Johannesburg, RSA 1996.

23) A. Mathieu, A. Capmas, J.P. Bayoux and D. Richon; “Calcium aluminate cement and reactive alumina”; UNITECR ’93, Brazil, 1993

24) C. Parr, C; Wöhrmeyer, B. Valdelièvre, A. Namba, “Effect of formulation parameters upon the strength development of calcium aluminate cement containing castables,” J. Tec. Assoc. refractories Japan, 23 [4] 231 – 238 (2003)

25) A. Mathieu, B. Espinosa, “Electrical Conductimetry to Control LCC’s”, Proceedings of Alafar Conference, Mexico, 1994, pp. 139-156.

26) C. Parr, B. Valdelièvre, A. Namba, “The effect of ambient temperature conditions on the placing properties of deflocculated refractory castables”, Taikabutsu Overseas, 21,[3], 148-154, (2000)

27) S. Moehmel, W. Gessner, Th. Bier, C. Parr, “The influence of microsilica on the course of hydration of monocalcium aluminate”, Proc. Intl. Conf. On Calcium Aluminate Cements, R.J. Mangabhai, ed, F.P. Glasser, ed, IOM communications, Edinburgh, 2001, pp 319-329

28) E. Nonnet, N. Lequeux, P. Boch, “Elastic properties of high alumina cement castables from room temperature to 1600°C” Journal of the European Ceramic Society, 19, (1999) p1575-158