

## Feature Article. . .

# THE EFFECT OF ENVIRONMENTAL TEMPERATURE CONDITIONS ON THE RHEOLOGY OF DEFLOCCULATED REFRACTORY CASTABLE

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## ABSTRACT

Deflocculated, high technology castables are known to be problematic during placement at the job site and in some pre-cast shops. One of the variables that can create placement problems is the temperature of the environment during placement. This paper will address the effect of temperature on conventional and deflocculated castable systems and will also discuss the implications of the findings and how they can be used to make the system more robust.

Results will be generated utilizing formulations of both pure calcium aluminate cement as well as formulated cements with 80% alumina. The formulations are based upon sintered alumina and have different reactive fillers such as fume silica, magnesia and alumina. Different additive systems are also studied, ranging from simple sodium polyphosphate additions to multiple additive combinations based upon both electrostatic and electrosteric dispersion including inorganic and organic polymer products.

Chemical and physical techniques are used to investigate and explain the practical results. Mechanisms are proposed which can explain the practical results and conclusions drawn as to how this understanding can be used to reduce the sensitivity of deflocculated castable systems to ambient temperatures.

## INTRODUCTION

In order to understand the effect of ambient temperature on castable placing properties it is necessary to first consider the hydration process of Calcium Aluminate Cement (CAC). The hydration mechanism of Calcium Aluminate is via solution, where an anhydrous phase dissolves and is fol-

lowed by the precipitation of the hydrates from solution [1]. Three distinct reactions can be identified within the hydration reaction: dissolution, nucleation and precipitation.

When the anhydrous cement grain is exposed to water, the hydration process [2] is initiated by the hydroxylation of the cement surface. This is followed by the dissolution of the cement into water, which liberates calcium and aluminum ions. A small amount of hydrates will form at this point if the solution concentration rises over the super saturation limit level of the hydrates C<sub>2</sub>AH<sub>8</sub> and AH<sub>3</sub> (usually in a localized area). The dissolution will continue with a consequent increase in the concentration of Calcium and Aluminum ions until a saturation point is reached, which is the equilibrium solubility of the anhydrous phases with the hydroxylated surface layers. After the dissolution reaction, there follows an induction period during which nuclei are formed and grow to a critical size and quantity. When this critical size and quantity is achieved, a rapid precipitation of the hydrates occurs. This causes a drop in solution concentration where more anhydrous cement can now be dissolved. 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 ambient temperature significantly modifies the hydrates [1] that result, due to the fact that their solubility changes with temperature [3]. This change in solubility will change the precipitation kinetics as a function of temperature and result in differing setting times according to temperature.

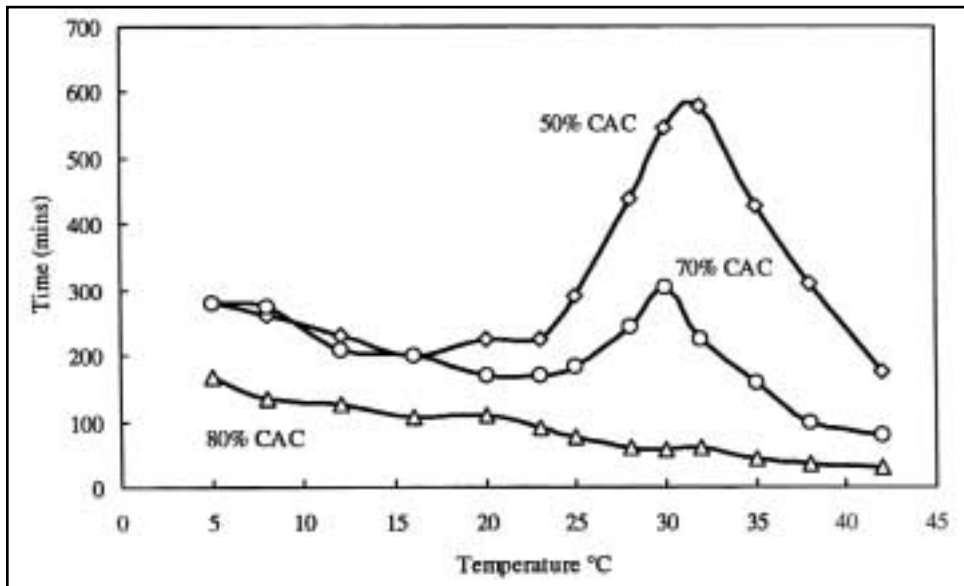
The practical implications of this can be seen in Figure 1, which shows the

setting time as a function of temperature for three Calcium Aluminate Cements. The tests are done in a sand mortar (ISO 679) and the initial setting time is measured using a Vicat apparatus. The effect of temperature is quite marked depending upon the CAC type, with the 50% Alumina Cement showing the biggest changes and the 80% the lowest. The anomalous setting at 27-28°C can clearly be seen. This lengthening of set as the temperature increases to 27°C has been attributed to an increased nucleation time with CAH10. The solubility of CAH10 increases significantly with temperature thus making precipitation more difficult as the temperature increases.

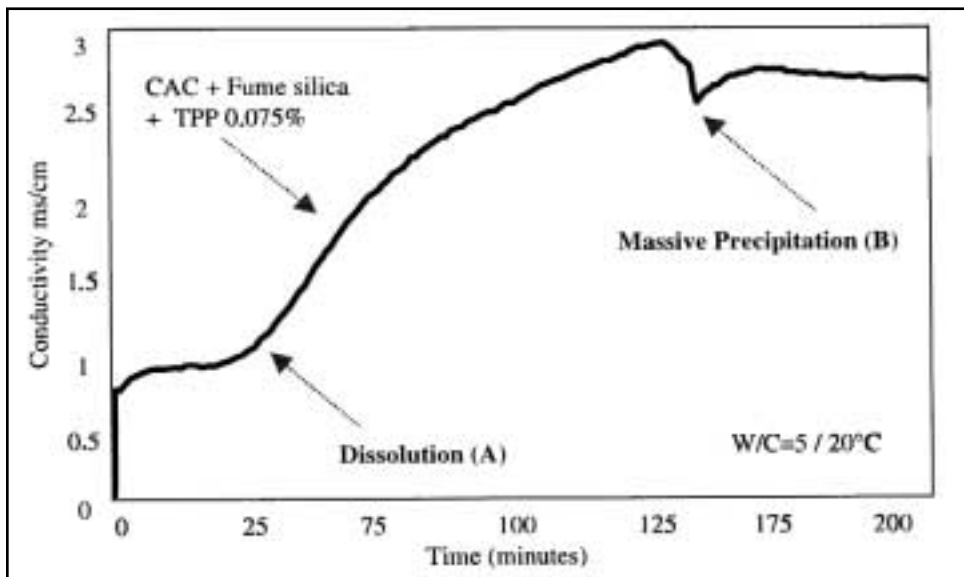
## CEMENTS

Above 27-28°C the nucleation process is driven by AH<sub>3</sub> as it precipitates more readily at these temperatures than CAH10 and so the set time decreases. The differences seen between the 50% and 70% Alumina Cement can be attributed to the different mineralogical compositions. The 80% Alumina Cement is interesting as it shows the lowest temperature dependence. The unique combination of alumina, cement clinker and additives present in this class of cement modifies the hydration process and in doing so reduces the temperature sensitivity. The anomalous setting seen with the other cements is also removed. This latter fact provides an insight into possible effects when fine reactive fillers and additives are present.

The hydration mechanisms and kinetics of the different CAC types such as those described above can be significantly modified [4] when fine reactive powders (fillers) and additives are present as in the case of deflocculated



**Figure 1: The effect of temperature upon the setting of three different Calcium Aluminate cements**



**Figure 2: LCC binder phase conductimetry curve**

castables. Thus the effect of ambient temperature may well be significantly different in these deflocculated castable systems. The following investigation uses conductivity measurements to follow the hydration process in these systems at different ambient temperature conditions.

## EXPERIMENTAL Conductimetry

The conductivity of a dilute cement suspension is measured as a function of time and this allows the complete hydration process to be followed. This technique has been applied equally to

classical refractory systems as well as deflocculated castables [5] [6].

## EXPERIMENTAL PROCEDURE

The conductimetric cell is comprised of a double walled beaker, which is connected to a water bath to maintain a constant temperature. Into this, a conductivity probe is inserted along with a stirring device. 80g of distilled water is then added to the beaker and the solution stirred continuously until a constant temperature is reached. 16g of powder is then placed (plus any additives) into the cell and the measurement started. The probe measures the conductivity continuously in milli-siemens/second for a period of 1440 minutes (24 hours).

The data is captured via a data logger to a P.C. This equipment enables the researcher to investigate different temperatures easily by changing the water bath temperature. Results on identical samples yield reproducible results with coefficients of variation around 1-2%. Furthermore the results can be reproduced with the same system over significant time intervals. The measurement is performed on the matrix part of deflocculated castables. Normally, this constitutes the binder phase and typically comprises the reactive alumina, fume silica and additives. The conductivity curve that results is found to be unique for each specific combination and thus hydration kinetics of these complex systems can be studied using conductivity analysis.

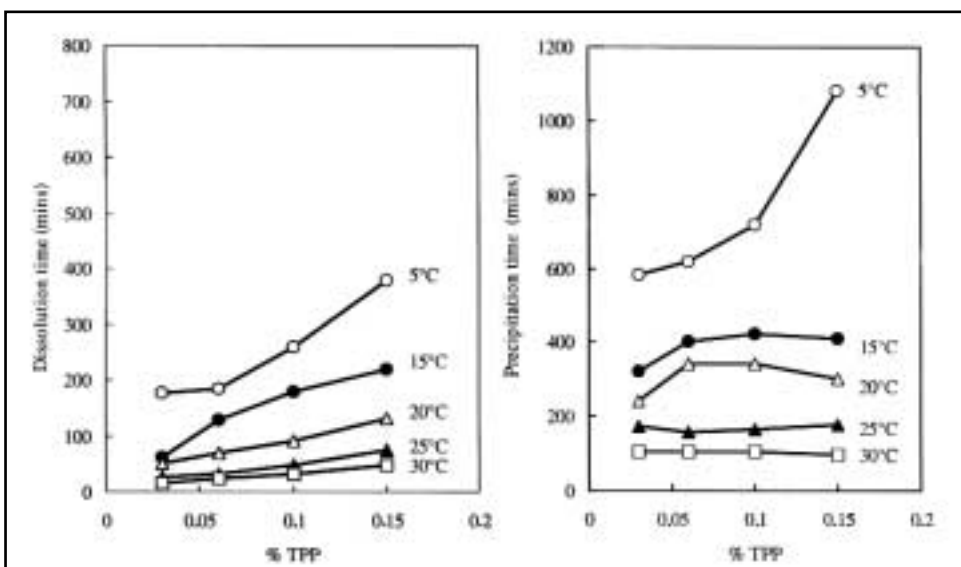
A generalized curve of a LCC binder phase system is shown in Figure 2. The binder phase contains equal proportions of a 70% Alumina Cement and fume silica. Sodium Tri- polyphosphate (TPP) is used as the dispersing additive. The TPP dose is based upon the cement dose and not the total binder phase.

The different reactions of the hydration process can be clearly distinguished. The initial conductivity value, at time zero, is determined by the additives present. In this example, the Sodium Tri-polyphosphate (TPP) additive is added directly into solution. This also offers the possibility to use conductivity as a means to control the TPP dose in castables. The initial conductivity level has been found to be strongly correlated with the TPP dose. This is followed by a plateau during which the value stays relatively constant. At point A, the measured conductivity begins to rise corresponding to the bulk dissolution of the CAC. The rise in conductivity to a maximum is followed by a nucleation period, which leads to the massive precipitation of the hydrates at point B. The profile shown in Figure 2 is significantly modified compared to pure cement systems [7].

In comparison between cement only and LCC systems, we see that the initial dissolution is delayed in the LCC as compared to the cement only system and also, the dissolution occurs at a much slower rate with the LCC system.

Binder material	LCC-FS System		LCC-AA System	
	% binder phase	% in castable	% binder phase	% in castable
Alumina: Pechiney AC34B5	33.3	5	-	-
Alumina: Pechiney P152SB	-	-	65	11
Fume Silica: Elkem 971 U	33.3	5	-	-
Cement: Secar 71	33.3	5	35	6
Additives	+ Variable addition			

Additive used	Code	Addition based upon 100% castable dry mass
Sodium Tri-polyphosphate	TPP	+0.03 to +0.15
Sodium Hexa-metaphosphate	HMP	+0.06
Sodium methacrylate	PA	+0.05
Boric acid	BA	+0.022
Sodium Carbonate	SC	+0.001
Lithium Carbonate	LC	+0.05
Secar 51	S50	+2



**Figure 3: The effect of TPP dose upon an LCC binder phase dissolution and precipitation times**

However, the precipitation occurs at a similar time for both the deflocculated system and the cement alone. The precipitation time corresponds well with the onset of hardening and the acquisition of mechanical resistance in castables.

The delay in CAC dissolution has been shown to be the mechanism which provides the castable with sufficient working time. The longer the delay in bulk dissolution, then the longer the working time becomes. It is believed that the delay in dissolution is due to a reaction on the cement grain surface that results in the formation of calcium phosphate precipitates, which tend to block CAC dissolution. This retarding effect on CAC dissolution is not seen when binary combinations of

phosphate and CAC or fume silica and CAC are analyzed. Therefore it is presumed that the surface of the fume silica in the presence of phosphates also plays a key role. Maeda [9,10] proposes a mechanism whereby the fume silica interacts with the surface of the cement grain and a diffusion layer is created which controls the dissolution. 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 is the case of classical or conventional castables with a high cement dose. Thus, by studying the duration of this delayed dissolution through conductimetry, a rapid method

exists by which castable working times can be measured. As the measurements are in a dilute medium, they should only be used on a relative basis.

Conductimetry results are often presented as the time to dissolution start (inflection point A on the curve) and the time to the precipitation reaction and hydrate formation i.e. the first minimum on the curve at point B. As the measurement is performed in a dilute suspension the final value does not descend to zero but tends towards a constant value. This represents an equilibrium between the anhydrous and hydrated phases in solution.

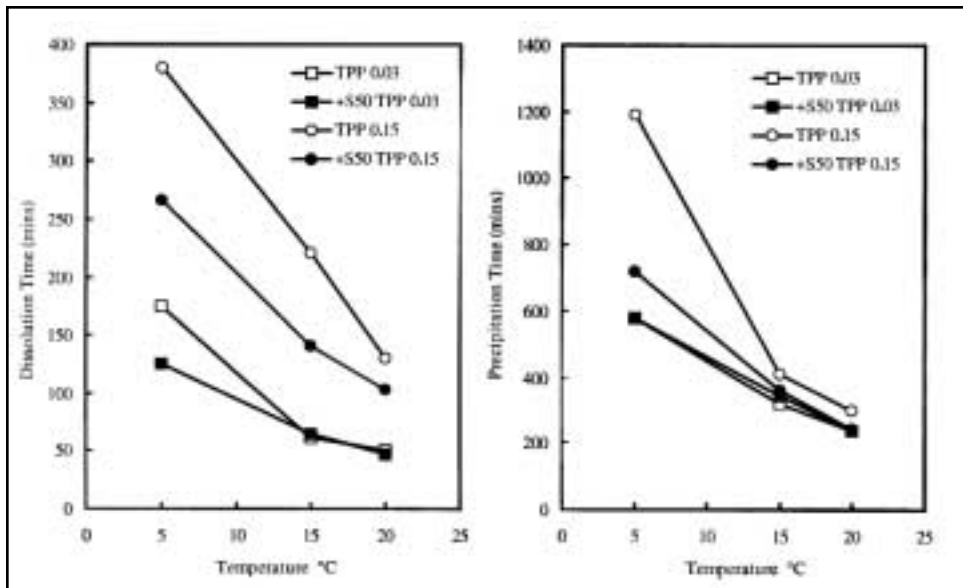
## RESULTS

The binder components in Table 1 were used to study the effect of ambient temperature on LCC castable systems. Two basic systems were explored. The LCC-FS system is derived from a fume silica containing LCC whereas the LCC-AA system is without fume and uses only alumina as the fine filler. This is typical of a binder phase used for high purity low cement castables which contain Alumina-Magnesia spinel additions. The differing additives that were used are found in Table 2.

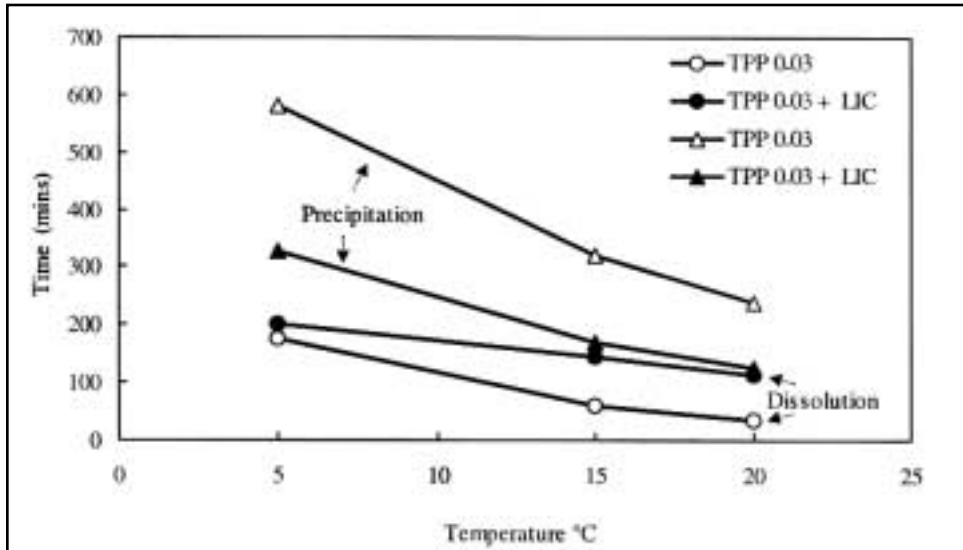
The additive doses are expressed as a percentage of the total castable (including aggregates to give 100%) dry mass and are in effect additions to the 100% dry mass on a weight basis. The additive doses are based on previous experience gained during the study of model castables [11]. The choice of fine fillers [12] has a marked impact upon the castable flow properties and for this reason retarders are normally added to systems without fume silica.

### LCC-FS (SYSTEM WITH FUME SILICA)

The effect of differing TPP dose upon the dissolution and precipitation reactions within the LCC-FS binder phase was measured at temperatures between 30°C and 5°C. The time to maximum dissolution and the first precipitation minima were recorded. The results are shown in Figure 3 with the graph on the left representing the dissolution times and the graph on the right representing the precipitation times. The temperature dependence of



**Figure 4: The effect of an addition of a 50% Calcium Aluminate Cement upon the Dissolution and Precipitation times**



**Figure 5: The effect of Lithium Carbonate upon an LCC FS binder phase**

the system is extremely marked at low ambient temperatures (5°C) with an extension of both the dissolution time and the time to massive precipitation. As the temperature increases towards 30°C there is a convergence of both dissolution and precipitation times irrespective of TPP dose. The sensitivity to low temperature becomes noticeably more marked at higher TPP doses. At doses of +0.15% TPP (weight basis - total dry weight) the dissolution and precipitation times increase by almost three fold.

These results suggest that lower TPP dose rates will result in a more robust castable system at 5°C. The practical implications of these conductivity

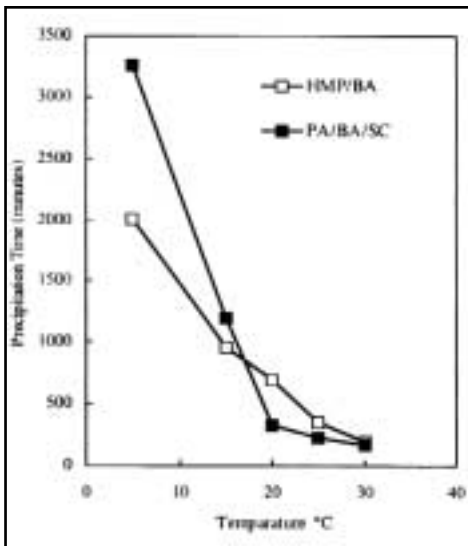
results would be a long working time and also hardening time at 5°C especially in the case of higher TPP dose rates. The results show that LCC systems can display a large variation in placing property behavior according to the ambient temperature. This variation is due not only to the CAC but also to the nature of interactions between the CAC, the fine fillers and the phosphate. The dosage level of the additives needs to be carefully controlled to avoid extreme prolongation of castable working and hardening times. Conductivity provides a useful insight into the mechanisms that control the CAC hydration and consequent effects upon castable placing characteristics.

Compared to conventional castable systems (Figure 1) it can be seen that there is no anomalous setting around 27°C and that at low temperatures (5°C) there is a marked lengthening of both the dissolution time and precipitation time.

In order to try and reduce this sensitivity at low temperature, different additives were used to try and reduce both the dissolution and precipitation times. A 50% Alumina Cement (S50) was added to the binder phase systems containing 0.03% TPP and 0.15% TPP. A 2% addition was partially substituted for the 70% Alumina Cement (70% CAC). That is to say the 70% CAC addition was 4% and the 50% CAC 2%. The effect of this latter addition is illustrated in Figure 4. Lithium Carbonate (LC) was also added as an extra additive.

It is clear that the use of two cements modifies the dissolution and precipitation times but that the modification is dependent upon both the TPP addition and the temperature. At normal ambient temperatures of 20°C the substitution of a 50% CAC has little or no effect upon the dissolution and the precipitation times irrespective, of whether a high (0.15%) or low (0.03%) addition of TPP is used. At low temperatures there is a visible difference in the dissolution and precipitation times for the 50% CAC substituted binder phase. At low TPP additions there is only a small modification of the dissolution time and almost no effect upon the precipitation time.

However at the higher TPP addition, which is the most sensitive at low temperature, the substitution of a 50% CAC is effective in reducing the dissolution and precipitation times. This addition could be an effective way of reducing low temperature sensitivity where higher doses of TPP are employed. With an optimized, low, TPP dose there is little or no effect. In practical terms, a low TPP addition would optimize the flow values whereas a higher addition TPP is often preferred to reduce sensitivity to aging [13]. In this case a 50% CAC would be beneficial for low temperature behavior without penalizing the working and harden-



**Figure 6a. Precipitation times of an LCC-AA system**

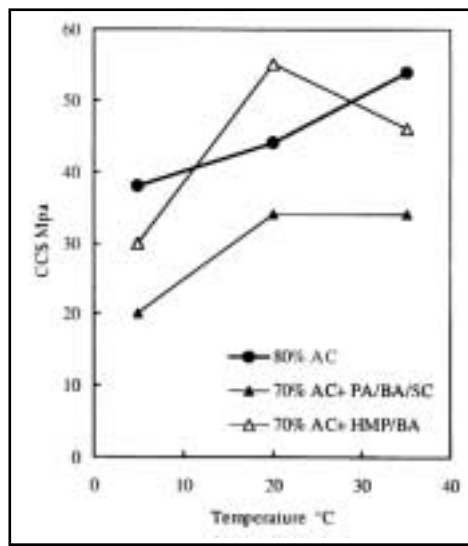
ing times at normal ambient (20°C) temperature conditions.

The effect of a Lithium Carbonate addition is exhibited in Figure 5. The dissolution time can actually be seen to lengthen slightly but the relationship with temperature becomes more stable. By contrast the precipitation times are almost halved. Thus the addition of LC can be an effective way to reduce the temperature sensitivity even at a low and optimized TPP addition.

### LCC-AA (SYSTEM WITHOUT FUME SILICA)

Two types of additive systems have been evaluated based upon previous studies of fume silica free additive systems [14].

A largely ionic system based upon a phosphate (HMP) with a retarder BA is compared with a polyacrylate (PA) system. This latter system relies upon an electrosteric dispersion mechanism and is used together with a retarder (BA) and a pH stabiliser (SC). The effect of temperature upon the precipitation times is shown in Figure 6a. A comparison with the systems containing fume silica is also included. The ternary system PA/BA/SC shows an extreme sensitivity at low temperatures with the precipitation time being in excess of 3000 minutes at low temperatures. A radical reduction in precipitation time occurs between 15 and 20°C. The binary system of HMP/BA is somewhat less sensitive and shows a more



**Figure 6b. 24 hour compressive strength of an LCC-AA system**

linear behavior than the ternary system. Both systems, however, are significantly more sensitive than the fume silica based binder phases.

In order to correct this low temperature sensitivity the use of further correcting additives could be considered. This would result in a fairly complex additive system, which might not be practical from an industrial perspective. For temperatures above 15°C it is evident that either the standard binary or ternary systems offer satisfactory performance. A more interesting solution for these high purity systems without fume silica, at low temperature, lies in the example shown in Figure 1. The use of an 80% Alumina cement that already incorporates a sophisticated additive system can be used to control low temperature placing characteristics. An example of this is shown in Figure 6b. Here, the compressive green strength is measured after 24 hours. The 24-hour CCS is a useful indicator of hardening. The results are based on an Alumina-Spinel castable derived from the LCC A-A binder phase system in Table 2. As shown in Figure 6b the 80% Alumina cement used shows a stable development of green strength whereas the other systems show a significant variation. It should be noted that the results could not be directly compared with Figure 6a as the conductimetry is performed in a dilute solution. Nevertheless the relative trends can be compared.

## DISCUSSION

The differences seen, as a function of TPP dose and temperature, with the fume silica containing systems can probably be attributed to solubility effects. For example, the solubility of calcium ions from the Mono Calcium Aluminate phase is seen to decrease with decreasing temperature [3] whilst TPP has a solubility which remains unchanged in the temperature range 10-25°C [15]. The delay in CAC dissolution has been attributed to the formation of Calcium Phosphate species [8]. Thus it is clear that the actual reactions are complex and are also likely to be linked to surface implications. The fact that the time to the dissolution phase can be reduced, at low temperature, through the addition of a 50% CAC suggests that the dissolution kinetics of calcium ions play a significant role in determining low temperature behavior.

Figure 7 shows a summary of the effects seen with the LCC-FS system. The 'nucleation' time is derived from the difference between the dissolution and the precipitation times. The term 'nucleation' is used advisedly in the sense that the estimation here makes reference to the period from flocculation and loss of working time to the apparition of the massive precipitation. It may well be that the actual nucleation occurs within this time frame and not through its entirety. At high TPP (0.15) doses then a mixture of cement types is effective in reducing the temperature sensitivity.

The use of lithium carbonate (LC) is particularly effective in reducing the 'nucleation' times where low TPP (0.03) doses are employed. However the mechanism is somewhat different in the two cases. The use of a 50% CAC reduces the dissolution times as well as the precipitation times. In the case of an addition of LC, the 'nucleation' time is reduced as the precipitation is significantly shortened. This has been seen to be due to the enhancement of the nucleation of AH<sub>3</sub> [16]. The fact that the solubility of LC increases as the temperature decreases probably assists this shortening of the nucleation time. This could mean that the castables using this system would both maintain working time and hardening

times irrespective of ambient temperature. This, however, remains to be validated experimentally.

The system without fume silica shows clearly the type of compromises which face a refractory formulator. These systems are inherently more difficult to control in terms of establishing suitable flow decay and working time [4]. It is possible that the very additives used to control flow decay could also delay the precipitation reaction and consequent hardening at low temperature. Evidence of this is seen by the fact that the dissolution period occurs over a long period of time, which consequently delays the precipitation times. Germination times can also be significantly affected. The slower release of Calcium ions at low temperature would tend to exaggerate this effect and would partially account for the extremely long delay to the precipitation reactions.

## CONCLUSIONS

Conductimetry is a useful technique to study the effects of castable binder phases at different ambient temperature conditions. It is clear that the impact of temperature upon the dissolution and precipitation times is specific to each binder phase composition. The nature of all the interactions between the cement, the fine reactive fillers and the additives needs to be considered to establish an explication of actual castable placing properties.

For fume silica containing systems the temperature sensitivity can be effectively reduced through the use of an additional additive(s). A relatively simple option is to consider the use of two CAC types (50% and 70% alumina) to adjust the "reactivity" in terms of calcium ion dissolution. This will ensure more stable working and hardening times at low temperature. However, the effectiveness of this mechanism can be affected by the addition level of the dispersing phosphate. Where low TPP doses are employed, the more effective option is to consider LC. This relies on reducing the nucleation times. High purity systems which do not contain fume silica and which are based on a 70% CAC can show a high sensitivity to low temperature conditions. To avoid a complex additive combination the use of an 80% AC appears to be attractive as a simple but effective way to control hardening times at low temperatures.

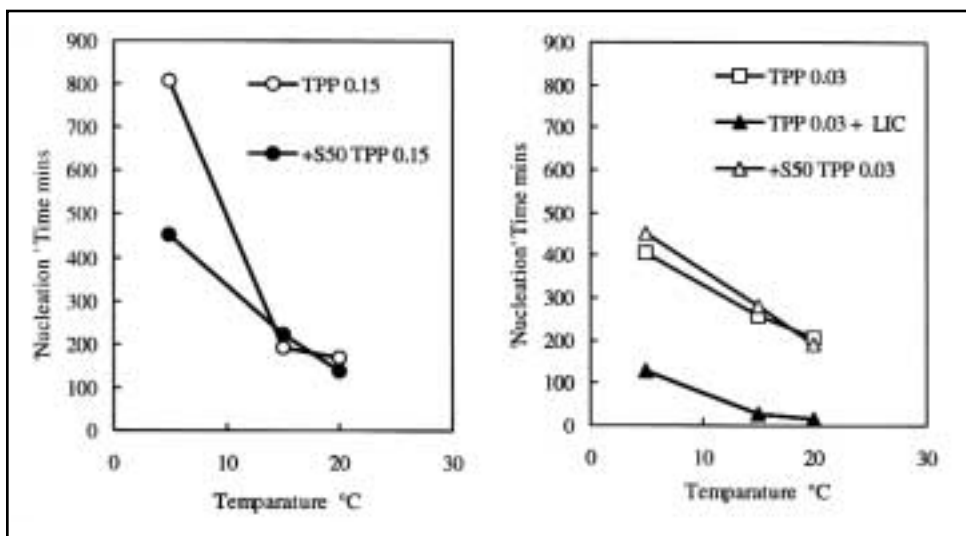
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## REFERENCES

1. K. L. Scrivener, A. Capmas, "Calcium Aluminate Cements"; Chapter 13 in *Lea's Chemistry of Cement and Concrete*, 4th ed. Edited by P. C. Hewlett. John Wiley & Sons, New York, NY, 1998.

2. D. Sorrentino, F. Sorrentino, C. M. George, "Mechanisms of Hydration of Calcium Aluminate Cements"; pp. 41-90 in *Materials Science of Concrete*, Vol. IV. Edited by J. P. Scalny. The American Ceramic Society, Westerville, OH, 1995.
3. A. Capmas, D. Menetrier-Sorrentino, D. Damidot, "Effect of Temperature on Setting Time of Calcium Aluminate Cements"; in *Calcium Aluminate Cements*, edited by R. J. Mangabhai. Chapman & Hall, 1990.
4. 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)", pp.1315-1323 in *Proc. UNITECR'97*, Vol. 3. The American Ceramic Society, Westerville OH, 1997.
5. Th. A. Bier, A. Mathieu, B. Espinosa and J. P. Bayoux, "The Use of Conductimetry to Characterize the Reactivity of Calcium Aluminate Cements"; in *Proc. UNITECR'93*. The American Ceramic Society, Westerville, OH, 1993.
6. A. Mathieu, B. Espinosa, "Electrical Conductimetry to Control LCC's"; in *Proc. ALAFAR 1994*.
7. Th. Bier, Ch. Parr, "Admixtures with Calcium Aluminate Cements and CAC Base Castables"; in *Proc. 28th Annual Symposium of South Africa Ceramic Society*, 1996.
8. J. P. Bayoux, J. P. Letournex, C. M. George, "Fume Silica and Cement Interactions"; in *Proc. UNITECR'89*. The American Ceramic Society, Westerville, OH, 1989.
9. K. Jono, E. Maeda, K. Sorimochi, "Reaction between Alumina Cement and Phosphate," *Taikabutsu*, **50**[4] (1998).
10. E. Maeda, K. Jono, "Adsorption of Silica onto the Cement Particle Surface in Castables," *Taikabutsu*, **52**[3] (2000).



**Figure 7: Comparison of 'Nucleation time' for an LCC-FS system with differing additives**

11. C. Parr, Th. Bier, "The Design Fundamentals of High Technology Castables – An Understanding for Steel Makers"; in Proc. ISS Conference, Chicago, 1999.
12. Th. Bier, C. Parr, C. Revais, "The Roles of Fine Silica and Reactive Alumina and the Interactions with Calcium Aluminate in Refractory Castables," *Taikabutsu*, **51**[1] (1999).
13. C. Parr, C. Revais, D. Jones, M. Bennet, "Ageing of a Low Cement Castable"; in Proc. UNITECR'97. The American Ceramic Society, Westerville, OH, 1997.
14. J. F. Cousin, C. Parr, C. Aevais, Th. Bier, "Formulation of Spinel Castables and the Impact of Additives and Alumina on their Rheology"; Proc. Irefcon, India, 1998.
15. Technical Data Sheets for Sodium Tri-Polyphosphate, FMC Corporation, USA, 1995.
16. C. Parr, C Revais, H. Fryda, II "The Nature of Chemical Reactions that Occur During Castable Installation and Analytical Techniques Used to Follow these Reactions", *Am. Ceram. Soc. Bull.*, 1999. 

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