THE EFFECT OF AMBIENT TEMPERATURE UPON THE PLACING PROPERTIES OF DEFLOCCULATED CASTABLES

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Abstract

The advent of new installation techniques such as shotcreting, has meant that the ability to control deflocculated (LCC type) refractory castable placing characteristics has become a pre-requisite. One of the major parameters which influence the placing properties is ambient temperature. It is clear that a greater understanding of the underlying mechanisms, which are influenced by ambient temperature, will aid the further development of more reliable deflocculated castable systems.

The effect of temperature on classical Calcium Aluminate based systems has been studied over a number of years. However, no basic studies are available for deflocculated systems based on high purity Calcium Aluminate cements. This paper examines the effect of ambient temperature conditions upon the placing properties of these deflocculated castable systems.

Differing deflocculated castable systems are investigated with different reactive fillers such as fume silica, alumina and magnesia. Different additive systems are also studied, ranging from simple sodium polyphosphate additions to multiple additive combinations. 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. The practical implications of the findings are discussed and guidelines given which aim to further develop the robustness of these systems.
1 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 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. Three distinct phases can be identified: dissolution, nucleation and precipitation.

The hydration process 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 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, 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 attained 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 ambient temperature significantly modifies the hydrates that result, due to the fact that their solubility changes with temperature. 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 (AFNOR) 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 $CAH_{10}$. The solubility of $CAH_{10}$ increases significantly with temperature thus making precipitation more difficult as the temperature increases.

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

Above 27-28°C the nucleation process is driven by $AH_3$ as it precipitates more readily at these temperatures than $CAH_{10}$ 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 so doing 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 when fine reactive powders (fillers) and additives are present as in the case of deflocculated 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.
2 Experimental

2.1 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

2.2 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, is inserted a conductivity probe along with a stirring device. 80g of distilled water are added to the beaker and the solution stirred continuously until a constant temperature is reached. 16g of solids are weighed (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. The data is captured via a data logger to a P.C. The investigation at different temperatures can easily be effected 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 » which is typically comprised of the reactive alumina, fume silica and additives. The conductivity curve that results is found to be unique for each specific combination and thus the hydration kinetics of these complex systems can be studied using conductivity analysis.

A generalised curve of an LCC binder phase system is shown in figure 2. The binder phase contain 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 phases 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 a 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 conductivity rises and this is the point at which the bulk dissolution of the CAC occurs. The rise in conductivity to a maximum is followed by a nucleation period leading to the massive precipitation of the hydrates at point B. The profile shown in figure 2 is significantly modified compared to pure cement systems7.

The initial dissolution is delayed compared with the cement only system and the dissolution occurs at a much slower rate with the LCC system. However, the precipitation occurs during a similar time period 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\(^6\) 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. This is believed\(^8\) to be due to surface reactions that result 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 analysed. 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, then they should only be used on a relative basis.

The results are often presented as the time to dissolution start (inflection point A on the curve) and the time to the precipitation reactions 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.

### 2.3 Results

The binder phases 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 silica 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.

<table>
<thead>
<tr>
<th>Additive used</th>
<th>Code</th>
<th>Addition based upon 100% castable dry mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Tri-polyphosphate</td>
<td>TPP</td>
<td>+0,03 to +0,15</td>
</tr>
<tr>
<td>Sodium Hexametaphosphate</td>
<td>HMP</td>
<td>+0,06</td>
</tr>
<tr>
<td>Sodium methacrylate</td>
<td>PA</td>
<td>+0,05</td>
</tr>
<tr>
<td>Boric acid</td>
<td>BA</td>
<td>+0,022</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>SC</td>
<td>+0,001</td>
</tr>
<tr>
<td>Lithium Carbonate</td>
<td>LC</td>
<td>+0,05</td>
</tr>
<tr>
<td>Secar 51</td>
<td>S50</td>
<td>+2</td>
</tr>
</tbody>
</table>

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### Table 1: LCC Binder phase composition

<table>
<thead>
<tr>
<th>Binder material</th>
<th>LCC-FS System</th>
<th>LCC-AA System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% in binder phase</td>
<td>% in castable</td>
</tr>
<tr>
<td>Alumina Pechiney AC34B5</td>
<td>33.3</td>
<td>5</td>
</tr>
<tr>
<td>Alumina Pechiney P152SB</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fume Silica Elkem 9971U</td>
<td>33.3</td>
<td>5</td>
</tr>
<tr>
<td>Cement Secar 71</td>
<td>33.3</td>
<td>5</td>
</tr>
<tr>
<td>Additives</td>
<td>+ Variable addition</td>
<td></td>
</tr>
</tbody>
</table>
2.4 LCC 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 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.

![Figure 3: The effect of TPP dose upon an LCC binder phase dissolution and precipitation times](image)

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 behaviour 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 (50%AC) 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%AC). That is to say the 70% AC addition was 4% and the 50%AC 2%. The effect of this latter addition is illustrated in figure 4. Lithium Carbonate (LC) was also added as an additional 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%AC 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%AC 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.
Figure 4: The effect of an addition of a 50% Calcium Aluminate Cement upon the Dissolution and Precipitation times

However at the higher TPP addition, which is the most sensitive at low temperature, the substitution of a 50% AC 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 optimised, low, TPP dose there is little or no effect. In practical terms, a low TPP addition would optimise the flow values whereas a higher addition TPP is often preferred to reduce sensitivity to ageing \(^{13}\). In this case a 50% AC would be beneficial for low temperature behaviour without penalising the working and hardening 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 optimised TPP addition.

1.5 LCC-AA system without fume silica

Two types of additive systems have been evaluated based upon previous studies of fume silica free additive systems \(^{14}\).

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

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 6.1. 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 linear behaviour 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 profitably to control low temperature placing characteristics. An example of this is shown in figure 6.2 Here, the compressive green strength is measured after 24 hours and before drying. The 24-hour C.C.S 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 6.2 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 cannot be directly compared with figure 6.1 as the conductimetry is performed in a dilute solution. Nevertheless the relative trends can be compared.

Figure 6.1: Precipitation times of an LCC-AA system

Figure 6.2: 24hour compressive strength of an LCC-AA system

3 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 Mono Calcium Aluminate 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 behaviour.

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 LC is particularly effective in reducing the ‘nucleation’ times where low TPP (0,03) doses are employed. However the mechanism of action is somewhat different in the two cases. The use of a 50%AC 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\textsubscript{3}. 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 a suitable flow decay and working time\textsuperscript{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 delay to the precipitation reactions.

![Figure 7: Comparison of ‘Nucleation time’ for an LCC-FS system with differing additives](image)

**4 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 explanation of actual castable placing properties.

For fume silica containing systems the temperature sensitivity can be effectively reduced through the use of an additional additives(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 is conditioned by the addition level of the dispersing phosphate. Where low TPP dose is employed a more effective option is to consider LC. Here, the
mechanism of action relies on reducing the nucleation times.
High purity systems which do not contain fume silica and which are based on a 70% AC 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.

5 Acknowledgments

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