THE IMPACT OF CASTABLE COMPOSITION AND CALCIUM ALUMINATE CEMENT TYPE ON THE RHEOLOGY AND MECHANICAL PROPERTIES OF LCC AT LOW AMBIENT TEMPERATURES

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ABSTRACT

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 that can be placed using a variety of techniques such as casting, gunning, self flow, pumping and shotcreting. The usage chain of monolithic refractories containing calcium aluminate cement contains several steps such as mixing, placing and consolidation, curing and dry out and finally use in service. Each of these steps within the castable placing chain is intimately linked to the hydration process of calcium aluminate cement (CAC).

The paper addresses the key issues that impact the reliability and predictability of placing properties in reduced cement systems. The effect of CAC type will be assessed through the impact on placing properties as well as placed properties of reduced cement castable systems and reference will be made to the underlying hydration and dehydration reactions.

The role of CAC depends to a great extent upon the system type. In the case of high cement conventional systems, the CAC acts as the fundamental binder dictating to a significant extent the placing and the placed properties. In the case of reduced cement or low cement castable (LCC) systems the situation is quite different. The (CAC) behaves in these systems, more as a chemical reactive than a fundamental binder system. Low cement castable rheology and setting characteristics can be difficult to predict in the field, especially when placing at low ambient temperatures such as is commonly encountered during the winter months. This difficulty can be magnified when changing the fume silica source or its characteristics. This paper will investigate different combinations and types of calcium aluminate cement, as well as fume silica and admixture packages on the placing properties and the mechanical properties of reduced cement castables. A parametric study is conducted into the effect of these different raw materials with the objective of optimising placing properties and identifying useful compositional zones for these key raw materials. An analysis of the underlying mechanisms will show the key characteristics that need to be identified for each raw material.

Conclusions will show that a necessary prerequisite of predictable placing properties is the use of high quality calcium aluminate cement.
1 Introduction

One of the variables that can create placement problems is the temperature of the environment during placement. The advent of new installation techniques such as shotcreting has meant that the ability to control deflocculated or LCC (Low or reduced cement type castables) refractory castable placing characteristics has become a prerequisite. One of the major parameters which influence LCC placing properties is ambient temperature. It has a profound effect upon the relationship between workability as a function of time and the time required to demould cast pieces. For example, at 20°C the trade off between achieving suitable placing properties in terms of fluidity and workable time and the strength development is relatively easy to manage. However, at 5°C there is often a severe increase in set and hardening times. This needs to be corrected to avoid to slow hardening and the cost impact of not being able to demould cast forms.

The relationship between workability and hardening is also impacted by the choice of formulation variables such as the source of raw materials and their intrinsic variability. An example of this trade off is shown in figure 1. Here two LCC castables are compared (see table 1 for details) with two different fume silica types. The acceptable target zone is shown in white in which a minimum 6 hours strength of 7MPa is sought whilst at the same time ensuring a minimum flow of 120% at 30 minutes. It can be clearly seen that in the case of FS92 the strength development is much slower and the flow lower than the corresponding model castable based upon FS94. At 5°C the differences are even more marked and no strength could be measured after 6 hours from casting in the case of FS92.

This paper investigates ways in which castable systems can be optimized in terms of their low temperature hardening characteristics by adjusting the addition ratio of calcium aluminate cement (CAC), fume silica (FS), Sodium tri polyphosphate (TPP).

![Figure 1: The trade off between workability and strength development at 6hours for FS92 and FS94 in a low cement model system](image-url)
The designing of a lab experiment that will optimize castable performance in the field is no easy task. Countless trials can be conducted that will still not cover all the variables encountered in actual working conditions and will usually not give any information about the robustness of the formula. The Box-Behnken method of experimental design is one of many that can minimize the number of results required for three factor experimental design. The results will lead to a surface showing the optimized parameters being sought by the experimenter. The work done for this paper uses the Box-Behnken method of design in two different experiments designed to optimize key performance properties of a model low cement castable (LCC) at simulated low ambient temperature placing conditions
Experiments were performed at 5°C using the variables of weight percent of calcium aluminate cement (CAC), weight percent of fume silica (FS) and weight percent of Sodium Tripolyphosphate (TPP).
Due to the low temperature, the second set of experiments later included the use of proposed hardening accelerators Lithium Carbonate, Lithium Hydroxide (LH) and Calcium Hydroxide (CH).
Finally the optimized values predicted by the model are compared with actual results for verification and conclusions drawn as to the optimum addition levels of CAC, TPP and FS.

2 Experimental

2.1 Model systems
The model castable systems that were used are displayed in table 1. The aggregate was based upon a white fused alumina (WFA) and the base system was also comprised of a mixture of two fine alumina types. The Fume silica type and addition level, CAC addition level and the sodium tri polyphosphate were the key variables studies. Two types of fume silica were used, FS92 with 91.03% Silica content and FS94 with 96.9% Silica. The balance being represented by the impurities Carbon, water, Fe₂O₃, MgO, S0₃ and the alkalis. The specific surface areas were similar at 18.2 and 17.6 m²/g respectively.

2.2 Experimental design model
An experimental design was constructed based on 3 factors 15 runs, with values from -1 to +1. The design chosen was the Box-Behnken designs as they are economical and therefore particularly useful when it is expensive to perform the necessary experimental runs. Statistica™ V6.0 was used to develop the experimental analysis and analyse the collected data. An initial series of runs were performed to establish base levels of the three key variables, FS, CAC and TPP. These levels were then varied from -1 to +1. The details of the 15 runs can be seen in the experimental design plan in table 2.
### Table 2: Experimental design plan

<table>
<thead>
<tr>
<th></th>
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<th>System</th>
<th>System 2</th>
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</thead>
<tbody>
<tr>
<td>White Fused Alumina</td>
<td>3-6 mm</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>White Fused Alumina</td>
<td>1-3 mm</td>
<td>20</td>
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<tr>
<td>White Fused Alumina</td>
<td>0-1 mm</td>
<td>20</td>
<td>20</td>
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<td>&lt;100 mesh</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Reactive alumina</td>
<td>&lt;200 mesh</td>
<td>8</td>
<td>8</td>
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<tr>
<td>C2S (BET 3.3m²/g)</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C2S (BET &lt;1m²/g)</td>
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<td>5</td>
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<tr>
<td>Fume silice 92</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Fume silice 94</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CAC 70%</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Sodium Tri polyphosphate (TPP)</td>
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<td>+0.05 – 0.2</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td></td>
<td>5.0</td>
<td>5.0</td>
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</tbody>
</table>

#### 2.3 Experimental procedure

Properties for each system were characterised through the water demand, flow profile, working time, exothermic profile and the mechanical resistance (transverse and compression). Industry standard test methods were used for evaluation of these parameters.

**Flow value**: The flow value has been determined using a cone with 100 mm base diameter, 50 mm high and 70 mm top diameter. Flow measurements on the resulting patty are carried out either after 20s of vibration or without vibration in the case of self flowing castables. The measured flow value is expressed as a % of the original diameter. The amplitude of the vibration table was 0.5 mm.

**Working time**: The time after mixing at which the initial cone will not flow at all under vibration is called the working time.

**Flow decay**: Flow values measured as a function of time and displayed as a curve. The slope shows at what speed an initial flow decays, or is maintained.

**Exothermic profiles**: The exothermic profiles are determined at 20°C with samples placed in insulated chambers. A thermocouple, imbedded in a cast sample, is linked to a data capture system and the temperature recorded as a function of time. The time taken to reach the maximum temperature is recorded (Pm) as well as the first peak associated with CAC dissolution (Pi).

**Cold Modulus of Rupture and Cold crushing strength**: MOR and C.C.S values were measured on 4x4x16 cm prisms cured or dried to 110°C for 24 hours.
# Results

For the WFA based model system, which varied the content of FS, CAC and TPP while testing at 5° C the following surfaces were generated from the test results. Only the most significant ones from the test results have been included in this paper. Figure 2 shows the response surface curves developed from the experimentally measured flow at 60 minutes for the 15 runs using both FS types at different addition ratios of FS, TPP and CAC. For each graph the effect of varying two variables (from low to high values) is shown. The third variable not shown (either CAC or FS depending upon the graph) is held at the constant median level corresponding to 5% by weight %. Figure 2 shows a very clear and visible dependence on the TPP addition rate on the flow at 60 minutes irrespective of the fume silica type. Lower TPP addition rates are required if the flow is to be optimized. The relationship between the flow and FS/CAC/TPP addition rates is somewhat more sensitive in the case of the FS92 based LCC system.

![Response surface curves](image)

Figure 2: Response surface curves for the impact of compositional variables (FS%, FS type, CAC % and TPP %) on LCC vibration flow at 60 minutes

A similar presentation of data is shown in figure 3 using the cold compressive strength as measured after 6 hours from casting as the dependant variable. The surfaces show that the acquisition of resistance at 6 hours from casting is not only dependant upon the addition rate but also the FS and TPP. Higher short term strengths linked to higher CAC additions can only be achieved at generally higher TPP additions. It is easier to achieve higher 6 hours strengths with FS92 than with FS94. Since adding more TPP to the system increases the strength at 6 hours, but decreases the flow (figure 2), a compromise must be made as both characteristics cannot be optimized simultaneously using TPP addition alone.
A summary of the results and the areas where a compromise must be defined are shown in figure 4. This figure shows the impact of varying TPP/FS and TPP/CAC on the necessary compromise between placing and hardening characteristics. A Low FS addition, irrespective of the TPP addition, tends to lead to low flow and poor hardening characteristics. At high FS additions LCC flow is improved.

Figure 4: Summary of the impact of compositional variables (TPP, CAC and FS %) on placing properties and strength development
The strength development performance depends upon the TPP addition level. At low TPP additions strength development is slow. A similar scenario is seen for relationships between TPP/CAC. Low CAC additions yield low strengths and generally low flows. High TPP additions coupled with high CAC additions favours strength development. Therefore an optimum must exist which achieves the best compromise between flow and strength development.

From this analysis, it is possible to use the data to define the optimum compositions necessary to achieve the best compromise in terms of maximizing the flow at 60 minutes and maximizing the strength at 6 hours. The best trade off at 5°C, irrespective of TPP dose would be achieved at 5% FS94 and 5% CAC respectively. For the FS92 a higher quantity of 6% FS92 and 6% CAC is proposed. The higher quality fume silica is more easily controlled and is able to ensure appropriate fluidity at a lower addition than in the case of FS92. The correlations (not shown) with the formulation variables and the resulting usage characteristics are significantly better with FS94 again suggesting a more predictable behaviour The full impact of variable TPP additions, as predicted by the model, are shown in figure 5.

The trade off between flow at 60 minutes and the strength development at 5°C after 6 hours can be seen for the two fume silica systems. For each type the optimum addition ratio of CAC/FS as predicted by the model has been used. The statistics from the model also predict that at this cold temperature of 5°C the variation of the 6 hour strengths is high. The 95% confidence limits for the 6 hr strength value are 0 – 10 MPa when the FS92 fume silica is used. In the case of the FS94, the confidence limits are much tighter at 8 to 11 MPa.

![Figure 5: Predicted LCC placing properties and strength development as a function of TPP addition (%) at optimum FS and CAC addition ratios](image-url)
The optimum TPP addition is around +0.18% in the case of the FS92 and +0.125% in the case of FS94. The data was verified experimentally and a close agreement coherent with the confidence limits of the model was found. For example, the measured strengths with the LCC based on FS94 at 6 hours was 9.1 MPa compared to a predicted 9.1 MPa. This was for a composition based upon 6% FS, 6% CAC and +0.125% TPP.

An additional approach to optimise low temperature hardening is to use accelerators and in so doing change the trade off between workability and hardening. Using the base model system from table 1 with 6% CAC, 6% FS94 and +0.125% TPP the effect of adding three different accelerators was evaluated. The flow results that were achieved along with the measured compressive strengths after 6 hours are shown in figure 6. These graphs show the impact of increasing accelerator dose. Upon increasing addition rate, all three of these accelerators will eventually reduce the flow value below the desired level. Calcium hydroxide is the most dramatic as a complete loss of flow is found at levels above +0.01%. With the Lithium salts the flow reduces as the dose increases but in the case of Lithium hydroxide it remains at an acceptable level.

LiOH is the only accelerator capable of boosting the 6 hr strength to a value well in excess of the reference case at 0% addition without significantly impacting negatively upon the 24 hour strengths and while staying in the range required to keep the flow values from reaching zero.

![Graphs showing the impact of different accelerator types and dosage rates on LCC castable hardening and strength development](image)

Figure 6: The impact of different accelerator types and dosage rates on LCC castable hardening and strength development
In summary, these experiments focused on a few important placing and hardening characteristics of LCC’s at 5° and was designed to reach a quick optimum of these properties. There are other performance criteria that must be validated with additional testing before LCC could be used in the field.

4 Conclusions

In conclusion, the use of experimental design models such as a full factorial design or the Box Behnken model can lead to a quicker result than the classical single variable analysis models. Creating surface plots of the results and running the statistics leads the experimenter to the closest values for all the requirements and also gives information about the robustness of the system.

Changing fume silica types can have a dramatic effect upon low cement castable properties especially in terms of robustness to low ambient temperature. It is much more difficult to optimise systems with low purity fume silica.

For each given FS type an optimum binder phase composition can be found which yields target placing characteristics. Generally it appears that a lower quality FS requires a higher TPP dose.

Optimum CAC/FS ratio can depend upon FS type. The lower the quality FS the higher the CAC and FS addition needs to be.

Lower purity fume silica has a smaller ‘target zone’ in terms of binder phase combinations.

The trade off between flow decay and strength development can be further optimised via the use of accelerators. For low to medium purity fume silica systems Lithium Hydroxide is the most effective.

Experimental design provides a quick and easy way to optimise compositions with the minimum number of experimental runs.

5 References

