THE ADVANTAGES OF CALCIUM ALUMINATE CEMENT AS A CASTABLE BONDING SYSTEM

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ABSTRACT

The paper compares castables based on calcium aluminate cement bonding systems with alternative bonding systems. Each aspect of the usage chain is investigated from placing through dry out to the in service aspects such as high temperature mechanical properties and corrosion resistance. From the observed data, important physical, chemical and structural changes in the castables can be seen to occur throughout the placing chain depending upon the specific choice of bond system fine fillers and additives. The impact of these formulation parameters upon final durability is also assessed. Mechanisms are proposed to account for the different characteristics of each specific system. Conclusions are drawn as to the merits of each type of system and the specific advantages that CAC based systems possess with respect to both placing and in service properties.
Introduction

References indicate that the first "refractory concretes" can be traced as far back as 1856 when H.S.C. Deville prepared a refractory crucible using alumina aggregate and alumina cement\(^1\). Calcium aluminate cement and its industrial production were patented by Lafarge in 1908\(^2\). The first industrial production of calcium aluminate cement was by Lafarge in 1913. It was not until the 1920's that the heat resistance properties of calcium aluminates were exploited.

The first references of a commercial refractory concrete can be found around 1922-4 where work in both France and the USA led to the development of Bauxite/Ciment Fondu\(^a\) based compositions\(^3\),\(^4\). During the early days of refractory concretes, the main aggregates available for use were calcined clays and crushed fired refractory bricks. Tabular alumina, although available in the 1940’s, was not then widely used in monolithic refractories, presumably due to its relatively high cost. The concretes were crudely made and even more crudely applied. Mixing was commonly done by hand in a mortar box or wheelbarrow, and casting, slap-trowelling, and hand-forming were the most common early forms of installation, although some gunning was also done\(^5\),\(^6\). During the 1930’s there was great expansion everywhere in the use of refractory and refractory insulating concretes in a variety of applications. By the outbreak of World War II refractory concrete was well established in many industries that used furnaces and ovens\(^3\).

By the 1960’s, castables based on high-purity CAC and high purity aggregates were common\(^7\). These were relatively simple compositions and comprising of refractory aggregates and cement with cement contents typically greater than 15%. They were becoming increasingly sophisticated in terms of particle size management and adapted to specific conditions and installation techniques.

More and more products were being manufactured as proprietary mixes in house rather than on site field mixes. Despite the tremendous advantages of ease of placing and monolithic construction, these conventional or regular concretes did not always possess, depending upon the specific application, the required installed characteristics.

Conventional castables are placed with water, usually 8 to 20%. This water content is required to ensure placement by casting. The combination of the water and cement to form calcium aluminate hydrates results in the hardening of the castable ensuring sufficient strength at low and intermediate temperatures. A small portion of the water is absorbed by the aggregate and does not contribute to the hydraulic bond. The majority of water is concentrated in the matrix between the fine particles and reacts with the cement to form the hydraulic bond. Upon heating, the hydraulic bond dehydrates, re-crystallises above 900°C and new mineral phases are formed via ceramic reactions. It is during this change that open porosity increases\(^8\). This porosity is dependent on cement content and type. The amount of water for mixing and the quantity of porosity at temperature are dependent on one another. Therefore, if water quantities can be reduced a lowering of porosity is also possible. With the careful selection of calcium aluminate cement optimized in mineralogical content, conventional castables can be formulated and placed at low water additions. These castables exhibit stable rheological properties for successful placement which in turn ensures good mechanical properties. At service temperature (1200°C) low melting phases CAS2 and C2AS are formed due to the presence of this liquid phase which restrains the thermo mechanical performance and reduces the maximum temperature resistance or refractoriness.
The 1970’s saw the first era of the low cement castable (LCC) with the landmark patent by Prost9. In the LCC system, the CAC cement is part of a complex binder system. This system can be viewed as an interdependent triangle. In this triangle the CAC, fine sub micron fillers such as silica fume and the additives all play a role in the binding system. The particle packing is optimised via the even dispersion of the ultra fine particles in the matrix. This allows a reduction in water for placement which in turn yields a decrease in porosity and an increase in mechanical strengths. The reduced lime content and the fine oxide powders which favour the formation of a fired bonding matrix results in improved hot strength, higher thermal shock resistance, lower porosity, and increased corrosion resistance in comparison to conventional castables. This evolution continued in the 1980’s when concretes were produced with very low cement contents down to 2% or less and are now known as ultra low cement castables10,11. Ultimate performance with these products is enhanced via increased refactoriness (with lime contents as low as 0.2%). The presence of silica and alumina in ultra low cement formulations react with one another and precipitate mullite at temperatures above 1300°C. This mullite formation increases hot strength considerably. If the lime content is too high, mullite formation will be suppressed. The late 1980’s and 1990’s can be characterised by the development of new installation technologies. The first of these was low cement refractory castables that could be placed by pumping and or self flowing techniques12. This was followed by the era of wet gunning or shotcreting13. The first references to this type of installation technology being found in Japan in the early 1980’s. The quest for lime free castable binder systems can be traced back to the 1950’s with the arrival of the first phosphate bonded systems15,16. This was followed in the 1980’s by the development of Alumina bonded systems using Rho alumina17, which was first reported in Japan in the early 1980’s. Other systems have been developed based upon resins, clay minerals and silicate bonding systems5. More recently silicate bonding has developed via the use of Silica sols. Once again the literature reveals that this was first reported in Japan18,19,20 in the 1980’s with a similar concept being promoted in the USA in the 1990’s. This evolution is largely driven by the quest to eliminate lime as a route to enhance corrosion resistance in molten metal, liquid and gas contact applications. Better corrosion resistance is reported21 for cement free systems but physical and mechanical properties remain superior with cementitious systems. There is also a necessary trade off between the ease of placing of higher cement systems, their installed properties and the low, ultra low cement and cement free systems which offer a greater installed performance but at the expense of less robust installations21. Current refractory technology covers a huge range of castables that can be applied by a wide range of installation technologies and are suitable for an ever increasing range of applications. Today, as was the case over 80 years ago CAC remains the dominant bond system for refractory concretes. This is clearly illustrated by the growth in CAC demand over the last 20 years linked to both a growth in the volume of monolithic castables and growth in the downstream consuming industries23. This paper investigates some of the factors that account for the dominance of the CAC bonded castables through a comparison of different castable types using a variety of bond systems. The merits of each type of system are assessed and the specific advantages that CAC based systems possess with respect to both placing and in service properties are evaluated.
Definition of different castable systems

Three model CAC based castable types and two generic cement free castables are compared. A primary definition of the different castable types can be made on the basis of the bond system employed. One such method of classifying refractory castables is in relation to the overall lime content. For example, the ASTM C 401-91, Standard Classification of Alumina and Alumina Silicate Castable Refractories, uses the following classification based upon chemistry and lime content:

<table>
<thead>
<tr>
<th>Castable Classification</th>
<th>Lime Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Castable Refractory</td>
<td>CaO &gt; 2.5%</td>
</tr>
<tr>
<td>Low Cement Castable Refractory</td>
<td>1.0% &lt; CaO &lt; 2.5%</td>
</tr>
<tr>
<td>Ultra Low Cement Castable Refractory</td>
<td>0.2% &lt; CaO &lt; 1.0%</td>
</tr>
<tr>
<td>No Cement Castable Refractory</td>
<td>CaO &lt; 0.2%</td>
</tr>
</tbody>
</table>

However, this is somewhat inadequate as it doesn’t describe the field of medium and high cement concretes that conform to a dense logic that use CAC in combination with additives and fine fillers. The type of filler system, alumina, magnesia, silica or other ultra fine powder will strongly condition the castable properties. Clearly the definition above doesn’t take this into account and therefore caution is needed when making comparisons between different castable types purely on the basis of CaO content. Nor does this definition properly describe the field of castable systems using other bond systems. The advantage of this basic classification system is that it does reveal the wide variety of castable formulation types that can be defined based upon the use of CAC as the primary bonding system. As such it is retained as a basis of defining different castable types used in this comparison. Five different castable systems are compared according to the following matrix composition logics:

<table>
<thead>
<tr>
<th>Castable</th>
<th>Formulation Logic</th>
<th>CAC%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCC FS</td>
<td>Alumina, Silica Fume, CAC, Additives</td>
<td>1.45%</td>
</tr>
<tr>
<td>ULCC</td>
<td>Alumina, Silica Fume, CAC, Additives</td>
<td>0.58%</td>
</tr>
<tr>
<td>LCC - A</td>
<td>Alumina, CAC, Additives</td>
<td>1.7%</td>
</tr>
<tr>
<td>HAB</td>
<td>Alumina, Silica Fume, Hydratable Alumina, Additives</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>CSS</td>
<td>Alumina, Silica Fume, Silica sol + hardener</td>
<td>&lt;0.1%</td>
</tr>
</tbody>
</table>

CAC based castables

Table 1 shows the model formulation logics used for the Calcium aluminate bonded castable types. Two low cement castables are considered, LCC FS, uses silica fume as the ultra fine filler and the other LCC-A is based on a matrix containing only Alumina and CAC. In addition a ULCC based on the same logic as the LCC FS systems is compared. The additive system is held constant for the LCC FS and the ULCC system and is based on a quaternary system using two dispersing additives, a polyphosphate and a polyacrylate, citric acid as a retarder and sodium bicarbonate as a pH buffer. The LCC A system uses the same polyacrylate as a dispersant with citric acid and sodium carbonate as retarders. The different additive systems are required due to the different characteristics of the ultra fine fillers. Fume silica provides a retarding effect on rate of dissolution of the CAC into solution and this helps to maintain a suitable castable working time. In the case of the LCC A system there is no such intrinsic retarding mechanism and this needs to be created through the use of retarders.
Table 1: Model CAC containing formulations: %

<table>
<thead>
<tr>
<th></th>
<th>LCC- FS</th>
<th>ULCC- FS</th>
<th>LCC-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tabular Alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-10 mesh</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>8-14 mesh</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>14-28 mesh</td>
<td>19</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>-48 mesh</td>
<td>29</td>
<td>29</td>
<td>12</td>
</tr>
<tr>
<td>-60 mesh</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>-325 mesh</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>Elkem 971</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Reactive Alumina</td>
<td>P152 SB</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Reactive Alumina</td>
<td>CT3000SG</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>Cement</td>
<td>Secar® 71</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Additives</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Darvan 7S</td>
<td>0,03</td>
<td>0,03</td>
<td>0,05</td>
</tr>
<tr>
<td>Sed. Tripolyphosphate</td>
<td>0,02</td>
<td>0,02</td>
<td></td>
</tr>
<tr>
<td>Sodium bi carbonate</td>
<td>0,002</td>
<td>0,002</td>
<td>0,02</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>0,0015</td>
<td>0,0015</td>
<td>0,008</td>
</tr>
</tbody>
</table>

Pure 70% alumina cement has been chosen as it offers the greatest flexibility to develop the comparative systems such as those shown in figure 1.

The CAC used is commercially available 70% Alumina cement. It should be noted that although the product itself has been available for many years, a continuous improvement programme has meant that it is far removed from the cement of 15/20 years ago. The improvements have been made in response to the evolution of castable technology. With the development of each new castable product type, whether it is a change in the formulation logic or installation technology, extra demands are made upon the cement. For example, the reduction in cement content between LCC and ULCC systems has made the castables intrinsically more sensitive. Small changes in CAC reactivity can manifest themselves as large changes in placing properties of the castable. This is due to the nature of interactions between the CAC, the additives and the fine fillers and the role of the CAC changing to be more of a chemical reactive (in terms of reaction kinetics and the impact on placing properties). Logically, improvements targeted a reduction in variability of the 70% alumina cement as a primary objective. During the last decade a significant reduction in standard deviations of the basic cement properties of flow and set have been achieved. This is represented schematically in figures 1 and 2. In addition to this, the specific reactivity profile of the 70% alumina cement has been tailored and adapted to one that gives a stable platform on which to construct all types of sophisticated castables. Furthermore, advances in process and manufacturing technology have allowed a global product to be created that is produced in multiple sites with the same usage characteristics across the globe. Thus, significant advances in this 70% alumina cement have been achieved through the management of its intrinsic reactivity. This delivers stable castable placing properties when used in reduced cement castable systems. This is illustrated in figure 2. Without these advances, the ability to produce castables on an industrial scale that can be pumped, cast or gunned under a variety of environmental conditions would be severely compromised. The historical advances in CAC technology have been in parallel with the development of new castable types. The current trend is moving towards simultaneous development of both the CAC and the castable system in order to further advance castable technology.
Figure 1: Continuous improvement to reduce variation in reduced cement castable properties

Figure 2: The impact of CAC type and regularity on the stability of placing properties in a self flow LCC
Alternative bond systems: Hydratable Alumina

As a consequence of the ultra fine pore structure, that results from hydratable alumina, lower porosities are achieved which has improved corrosion resistance to liquids and gases. The "close" bonding matrix and low liquid formation at high temperatures as previously mentioned yields increased hot strengths with volume stability and limited crack formation. Higher thermal conductivities and densities generated yield limitations as well.

Hydratable alumina or ρ-alumina (rho alumina) is a transition alumina with a specific crystallinity. The product is over 90% alumina with a LOI of 6-9% and low sodium levels. In the presence of water, rho alumina will form AH₃ gel and AH₁₂ gel. Upon heating the gels dehydrate and eventually form ceramic bonds.

By combining hydratable alumina with silica fume to promote the formation of the highly refractory mullite, hydratable aluminas are being used to provide improved hot strengths and excellent thermal shock resistance. Like all bonding systems, HAB's have their advantages and disadvantages. Curing for HAB's must commence at temperatures above 18°C (65°F) or strength development is impeded. When used as a substitute for CAC the HAB's are often combined with Silica fume to promote the formation of mullite at high temperature. 26 In addition, it has been found helpful to add a minute amount of CAC as a means of controlling the cold set 27, 28.

As with all binding systems there are specific trade offs and in the case of HAB’s the advantages with respect to a calcia free system are mitigated by their tendency to explode during dry out. For silica fume containing mixes very low permeability values have been obtained and caution regarding firing schedules is necessary as typical dry out schedules for cements are not suitable for hydratable alumina. Explosive spalls are possible if careful attention is not paid to heat up at 204° - 276°C (400 - 500°F). Therefore their widespread application remains limited to areas where the removal of CaO can add value and also where dry out can be tightly controlled (for example precast).

The following model system was used for the comparative tests. The aggregate composition was kept the same as for the CAC containing systems. To this 5% of an alumina binder, Actibond 2005 was added along with 3% 971 fume silica from Elkem and 10% of a reactive alumina with a D50 <0.5 microns and a surface area between 4-5 m²/g. 0.05% sodium hex meta phosphate was used as a dispersing agent.

Alternative bond systems: Silica sol

A colloid or sol is a stable dispersion of particles in water. Particles are small enough that gravity doesn’t cause them to settle. Particle sizes range typically from 1 to 100 nanometres 30. For comparison, the primary silica fume agglomerates can range up to 500 nanometres with individual particles around 100 nanometres. Particle size can also be expressed in terms of specific surface area, i.e. the higher the specific surface area, the smaller the particle size. The particle size also affects the maximum possible SiO₂ content. That is, small particles can only be stable in more dilute silica sols. The pure silica sols are anionic and are typically sodium- or ammonium-stabilized to a pH of 9-11. Through modification using sodium aluminate, however, the sols are stable down to a pH of 3-4. One of the common myths is that silica sols do not contain water but it is evident from the above that water is the liquid carrier in which the silica particles are dispersed. Silica sols have different silica contents ranging from 15 to 50% with the balance being water. Clearly when silica sols are used as binders,
water is indirectly added to the castable. If for example 10% of colloidal silica is added to a castable then the actual percentage of water added could be in the range of 5 to 8.5% based upon the castable dry weight.

The bonding mechanism of silica sol occurs via a gelling phase. When combined with other solid particles, the colloidal silica particles can be linked together in branched chains. The branched chains can be generated by pH changes, Salt, Oxide or Solvent additions to provoke gelling. The gelling can also be induced by water removal (e.g. drying). The hydroxyl groups (Si-OH) generate siloxane bonds Si-O-Si resulting in a three dimensional network via the expulsion of water. Removing H from the SiOH groups favours the gelation process. A cold setting mechanism can be induced via the destabilisation of the sol through the addition of either CaO or MgO cations. The Calcium can be present in the form of a minor addition of CAC. MgO favours the anionic reaction by the formation of Mg(OH)2 and removal of Hydrogen from the Si-OH groups. This promotes Si-O-Si formation and enhances the gelation rate. Patented compositions use this approach to ensure hardening in the cold state

An additional disadvantage of the colloidal silica is the need to add a special liquid binder on site. This increases costs (water is indirectly transported inside the sol) and requires special on site organisation to feed/dose the correct addition at the mixer. The risk of an incorrect addition has a potentially serious effect on the installed properties. Unlike the other castable systems where water is added, the addition of the colloidal silica actually changes the final castable composition in terms of silica content. Furthermore specific storage conditions are required to avoid settling and coagulation of the sol thus rendering it useless. Manufacturers’ recommendations vary but typically the sol must be stored at temperatures greater than 5°C and room temperature is preferred. There is the risk of the colloidal silica settling and coagulating and prior to use. Clearly, this could be pose organisational difficulties on site during winter applications.

The use of colloidal silica bond systems means that silica is always going to be present in the final product and this would exclude their application in numerous steel plant applications where the presence of silica is not desirable. Clearly there are some applications where this could be an advantage and perhaps the most obvious is in the area of acid resistant Refractories.

As a model colloidal silica bonded system a castable dry mix was used which contained 2% fume silica, 971 grade from Elkem, and 7.5% reactive alumina with similar properties to that used in the HAB system. 0.1% Magnesia (sea water C/S 1:1), with a 150 micron maximum particle size was added as a hardening aid. A 40% colloidal silica sol (Bindzil) was used and added to the castable at a rate of 8%. This gave an effective water addition of 4.7% and an additional Silica addition of 3.2%. This amount was chosen to give a comparable water addition to the CAC and HAB bonded castables.

### 3 Experimental procedure

Properties for each system were characterised through the water demand, flow profile, working time, exothermic profile, conductivity, calorimetry and the mechanical resistance (transverse and compression). In addition the ultrasonic profiles were monitored during the hardening phase.

**Flow value**: The flow value has been determined using a ASTM C230 flow cone with 100 mm base diameter, 50 mm high and 70 mm top diameter. Flow measurements on
the resulting patty are carried after 20s of vibration. The measured flow value is expressed as a % of the original diameter or as mm (% flow = mm - 100).

**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.

**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.

**Hot properties**: The hot state properties have been evaluated by the following measures:

- After firing to 1200°C and 1500°C with 5 hours soak time: density, porosity, volume change.
- At temperature after soak: hot modulus of rupture,

- Refractoriness under load is determined according to DIN EN 993-8 and DIN EN 1402-6 with samples pre-fired to 1100°C. The sample is tested under a load of 0,2MPa.

### 4 Experimental Results

**Placing properties**

The flow properties and associated water additions are shown in figure 3. The flow properties were initially targeted around 200mm (or 100%). However, with the colloidal silica system (CSS) the water added was kept in a similar range to the other castables in order that a good comparison of installed properties could be made. For this reason the 200mm flow could not be achieved in this system. As can be seen from figure 3 the LCC A system shows the largest flow decay. The silica fume containing systems maintained a similar flow profile over time. The colloidal silica system maintained a stable flow, albeit at a lower level than the other castables.

![Figure 3: Water addition and flow properties of the compared castable systems](image-url)
The working times are similar except for the HAB system which showed a long working time and a somewhat slower strength development as a consequence. Figure 5 shows the as cast compressive strengths after 24 hours. As can be seen from the graph, the as cast strengths of the cement free systems are extremely low with marginal values being recorded after 24 hours at 20°C. For comparison some data is shown where the cure conditions were maintained at 10°C and 30°C. Even at lower and higher curing temperatures satisfactory strengths are recorded for the LCC/ULCC systems. The Colloidal silica system was left for a longer time with the result that the strength did increase but only after a total of 48 hours cure did it reach 15MPa almost 50% lower than the LCC A system. One of the advantages of CAC based systems, even with ultra low cement additions of only 2%, is their ability to harden under a variety of conditions and even under low temperature conditions.
The effect of water addition variation (figure 6) on the CSS is somewhat difficult to assess. As more sol is added to increase the water addition more effective binder is added and the silica content increases which could be detrimental in certain applications. The as cast 24 hours strengths show a strong dependence upon the colloidal silica addition. The HAB system remains low irrespective of water variation. The CAC bonded castables show an increase in strength as the water addition is lowered and a slight decrease as the addition is increased. Although given the amount of cement added the dependence is not as great as expected. At very low water additions the strength tends to drop off. Presumably this is due to a too dry mass which is not properly consolidated under vibration.

Moisture loss

Literature\textsuperscript{36} refers to the fact that colloidal silica bonded castables release water at lower temperatures than calcium aluminate bonded systems as the water is not chemically bonded. More than 90\% of the total water being released after only 110°C. A DTA analysis of commercial colloidal silica shows the water removal in two stages with an initial peak at 80 to 100°C and a second peak at 660°C. No information is given in the literature as to the specific CAC type and castable used in the comparison.

The amount of water contained within the hydrates of CAC bonded castables depends upon a number of parameters including the degree of hydration, starting mineralogy of the cement, the castable system and most particularly the water to cement ratio. Table 2 shows the results of model calculations for different castable types. The underlying hypotheses are a total hydration rate of +75\%, a starting mineralogy in the system CA/CA\textsubscript{2} for a 70\% alumina cement and hydration at different temperatures. Conversion is only assumed to occur at temperatures above 35°C. The model estimates the quantity of total water (expressed as a \% of the total water added). For example, in the case of the conventional castable at 20°C, 45\% of the initial 9\% water that is added is combined via hydrates. 55\% of the water remains as free water.

As can be seen from the model the amount of combined water depends to a large degree on the castable type. A ULCC system, at 20°C, has only 14\% of the initial water combined via hydrates. This means that 3,3\% of the 3,8\% that is added remains as “free” water that can be liberated on drying at 110°C.
Table 2: Model calculation of the amount of added water combined in calcium aluminate hydrates as a function of castable type.

<table>
<thead>
<tr>
<th></th>
<th>Main hydrate</th>
<th>CC</th>
<th>LCC FS</th>
<th>ULCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement content</td>
<td>15%</td>
<td>5%</td>
<td>2%</td>
<td></td>
</tr>
<tr>
<td>Water addition</td>
<td>9%</td>
<td>4.2%</td>
<td>3.8%</td>
<td></td>
</tr>
<tr>
<td>W/C</td>
<td>0.6</td>
<td>0.84</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Quantity of the initial water combined via hydrates (as cast): %</td>
<td>CAH10</td>
<td>83</td>
<td>59</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>C2AH8/AH3</td>
<td>45</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>&lt;&lt;20°C</td>
<td>C2AH8/AH3</td>
<td>33</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td>&gt;35°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Therefore it is extremely important to consider the specific castable type when making such comparisons. Experimental measurements were made to determine the moisture loss of the different castable systems as a function of temperature when heated to constant mass. This would serve as a comparison relative to the model calculations. The results can be seen in figure 7. The figure demonstrates that the ULCC system and the CSS system show similar water loss as a function of drying temperature. Clearly the conventional concrete contains a higher quantity of combined water. However, this would be compensated by a higher permeability.

Figure 7: Measured moisture loss as a function of temperature for the different castable systems
Permeability and dry out

A comparison of permeability data is shown in figure 8. This is a summary sourced from the literature\textsuperscript{37,38,39,40} supplemented by internal measurements. As can be seen the intrinsic permeability of the colloid silica system is somewhat higher than the calcium aluminate containing systems. The use of organic fibres is able to bring the permeabilitys much closer.

In the examples shown the polypropylene fibre addition ranges from 0.05% to 0.08%. It is clear that their addition changes fundamentally the measured permeabilitys as does the actual matrix composition of the castable\textsuperscript{39}. This implies that permeabilitys can only be considered and compared in the context of very specifically defined castable systems.

![Figure 8: Typical permeability measurements of different castable systems](image)

Given that, from the literature, organic fibres appear to be widely used today it is most useful to compare castable permeabilitys in fibre containing systems. In such situations the differences in permeability between the different bond systems is somewhat reduced. Current product trends are towards calcium aluminate cement bonded castables with large fibre doses that can be dried out as rapidly and as safely as other monolithic castable bond systems and types. The HAB system shows the lowest permeability values as cast. Although permeability is a key parameter\textsuperscript{41}, the successful dry out of installed concretes depends on a number of other parameters.

Amongst the other first order parameters is the tensile strength as discussed by Yamamoto which was one of the first attempts to model castable dry out\textsuperscript{42,43}. Although this model has been superseded, as it doesn’t consider the effect of the dehydration, it is none the less useful as an illustration of the critical parameters that affect explosive spalling. In this model explosive spalling occurs if the internal pressure surpasses the tensile strength of the structure.

An approximation to the explosive spall resistance can be estimated by the model which calculates the product between the tensile strength and a derived coefficient ‘A’.
‘A’ is derived from the permeability divided by the product of the density and moisture addition. Thus, the product of the permeability and the tensile strength has some relevance to the final explosive spalling resistance. If this estimated for the systems under review the cementitious systems score generally higher than the colloidal silica. This is by virtue of their greater strengths which are better able to resist the vapour pressure generated during the water removal process.

Another example of the potential optimisation of the dry out cycle is shown in figure 9 and is taken from reference 40. Here the dry out of a high purity LCC A type castable with an alumina spinel addition is modelled. Different dry out schedules are shown along with their impact on the estimated maximum vapour pressure. The measured permeabilities are in the order of $10^3$ nano perms. Through the modification of the dry out curve an optimised heat up to over 1000°C can be achieved in less than 30 hours. This ensures a low maximum vapour pressure (estimated at 1.1 MPa). Alternatively, if organic fibres were included then the schedule can be reduced to almost 20 hours. This compares favourably with quoted dry out schedules for cement free systems.

![Alumina Spinel Castable: open back face/200mm](image)

Figure 9: optimisation of a dry out curve for a high alumina castable (after reference 40)

**Installed properties**

Figures 10 and 11 show the porosity and mechanical strengths of the different castable types after firing at temperatures up to 1100°C. Porosity increases for both the LCC and CSS bonded castables as a function of temperature. This is to be expected as water is removed during the initial heat up. As a direct consequence of the low as cast strengths the dried strengths of the cement free systems remain lower than the cement containing systems. However, the CSS system picks up significant strength during the dry out process.
Due to the nature of the bonding system water is expelled and the 3 dimensional Si-O-Si network is formed. This confirms the notion that the cold hardening properties of such bond systems are not as good as calcium aluminate bonded systems.

The measurement of hot strengths is probably the most abused method of characterisation of castable systems. By virtue of the method itself the results for refractory concretes can be significantly modified. For example, if pre firing of the samples is performed at high temperature then the amounts of mullite, CA₆ and other high temperature phases present in the concrete prior to the test can be controlled and predetermined. Similarly unless the matrix system of each castable type is clearly defined then the results and comparisons can also be misleading.
Discussion and conclusions

Figure 12 shows a comparison of the hot modulus of rupture (pre firing only to 1100°C) at 1200°C and 1500°C of the different castable types. The data shows that reducing CaO% in the formulation to zero does not necessarily give better hot strengths.

The type of filler system and matrix chemistry needs to be considered. At medium temperatures the LCC-FS show by far the best properties and as is well known as the temperature increases to 1500°C the hot strength decreases due to the presence of gehlinite and anorthite (CAS$_2$ and C$_2$AS). However, the quantities are limited in this example due to the alumina enriched matrix.

For applications up to these temperatures the LCC FS system would offer exceptional abrasion resistance. The HAB system showed surprisingly low hot strengths given that the castable composition. Reducing CaO% in the formulation to zero does not necessarily give better hot strengths. High hot strengths can be achieved with calcium containing systems through the elimination of silica and the presence of CA$_6$ as the high temperature bonding phase.

The refractoriness under load reveals a similar trend. The cement free CSS system shows similar data to the LCC FS castable and the LCC A system yields by far the highest RUL values. This is shown in table 3.

Table 3: Refractoriness under load of different castable systems

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>LCC A</th>
<th>LCC FS</th>
<th>CSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of max. thermal expansion °C</td>
<td>0.6%</td>
<td>1052°C</td>
<td></td>
</tr>
<tr>
<td>% expansion</td>
<td>1052°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>1350-1650</td>
<td>1314</td>
<td>1314</td>
</tr>
<tr>
<td>T 0% - 0,1%</td>
<td>1314</td>
<td>1314</td>
<td></td>
</tr>
<tr>
<td>T 0,5%</td>
<td>1652</td>
<td>1409</td>
<td>1498</td>
</tr>
<tr>
<td>T 1,0%</td>
<td>Not achieved</td>
<td>N/D</td>
<td>1500</td>
</tr>
</tbody>
</table>

Conventional castables have long been associated with ease of placement. At the first introduction of low cement and ultra low cement castables, installation sensitivity was a drawback which discouraged many refractory installers and consumers. The current generation of LCC and ULCC products have significantly improved placement characteristics in comparison to the first generation products. Additionally, refractory installers have learned the techniques and sensitivities required for the use of these products. Today, precautions are still necessary in the placement of formulations with reduced cement levels. Ease of installation has greatly improved with castables containing lower cement contents. Improvements may be attributed to the increased knowledge of the mechanisms in the interdependence of the cement, fillers and additives. This knowledge has motivated the development of improved cements and fillers which meet the exacting demands and requirements for reduced cement formulations. Despite this knowledge, ULCC and no cement castables still tend to be more sensitive to installation parameters than conventional castables. Each castable type has its own specific characteristics which result in a unique trade off of between robustness and final performance. In the same context each castable type and each bond system have inherent characteristics that mean they do not all work equally well in all applications. A choice needs to be made application by application and it is dangerous to generalise.

The choice of calcium aluminate bonded castables by refractory manufacturers has grown significantly in the past few years. Today, castables are selected both for ultimate performance and ease of installation coupled with reduced risk of installation failure.
The single biggest advance of CAC for castables lies in its flexibility that allows a multitude of castable types and installation technologies to be developed. The basic properties of cold as well as hot cohesion can easily be achieved with calcium aluminate cement bonded systems. This is coupled with a choice of installation robustness versus installed characteristics and performance. No other bond system is able to offer such options. This is summarised in figure 14.

![Figure 14: The trade off between installation robustness and installed properties/performance](image)

The selection of calcium aluminate cement must be considered carefully in the quest to optimise performance and installation success. There must be a continuing evolution in the quality of the CAC characteristics to meet the exacting demands of the refractory formulations. For further progress to be made simultaneous development of the castable and the bond system is needed. These developments will surely fuel the growth of castables and their potential replacement for other types of refractories.
References


32. US patent 5147839, Composition and Method for manufacturing steel containment equipment


