CALCIUM ALUMINATE AGGREGATES FOR USE IN REFRACTORY CASTABLES

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1 Introduction

Refractory concrete found in and around furnaces of the aluminium industry are generally exposed to temperatures below 1000°C. For this reason, when the choice of bonding systems for such refractory concrete is to be made, the development of mechanical strength - even without sintering - has to be considered. Concretes currently used may include the addition of a flux, which can partially impede the penetration of aluminium and enable sintering at lower temperatures. However, if overheating of the furnace occurs, these fluxes can lead to excessive wear through precipitation of the flux.

When the choice of a binder combination for refractory concrete has to be made, Calcium Aluminate Cements (CAC) play an important role. For example: high alumina refractory concrete with a pure Calcium Aluminate Cement bonding system have been successfully used in aluminium melting furnaces. This paper explains reactions within the concrete binder during installation, drying and firing, the possible uses of Calcium Aluminate Cement (CAC) bonded concrete and specifically the applicability of calcium aluminate aggregates for refractory castables to be used in the aluminium industry. Until now, such concrete systems have only been used surrounding the furnace in the floor areas. Here they have offered considerable enhancement of durability as compared to other civil concretes.

2 Survey of the CAC

The Calcium Aluminate Cement (CAC) used in refractory concrete can be divided into two groups. The first of these are those that are manufactured by the melting process and are typically made from bauxite and limestone (Table I). The final chemical composition of this type of cement ranges to 40-52% Al₂O₃ and will have ferric oxide contents ranging from about 16% for CFL and to less than 3% for Secar® 51. Those that are manufactured by the sintering process are typically made from more pure sources of alumina and therefore have a higher Al₂O₃ content of about 70 % for Secar® 71 and 80% for Secar® 80. These high alumina cements contain almost no secondary components such as Si-, Fe- and Ti-oxides. Therefore, the low alumina fused calcium aluminate cements are especially suited for applications with temperatures up to about 1500°C, whereas the high alumina cements manufactured according to the sintering process are - depending on their type and aggregate – usable up to approximately 1800°C.

| Table I. Chemical analysis of Calcium Aluminate Cements in mass (%) |
|-----------------|-------|-------|-------|-------|
|                 | CFL   | S51   | S71   | S80   |
| Al₂O₃           | 39.5  | 52    | 71    | 81    |
| CaO             | 38    | 38    | 28    | 17    |
| SiO₂            | 4.0   | 5     | <0.8  | <0.4  |
| FeO+Fe₂O₃       | 16    | <3.0  | <0.4  | <0.3  |
| MgO             | <1.5  | <1.0  | <0.5  | <0.5  |
| TiO₂            | <4.0  | <4.0  | <0.4  | <0.3  |

3 CAC in refractory concrete for aluminium melting furnaces

Choice of CAC-type

In most of the furnaces used for the manufacture of aluminium, temperatures of 1600°C are not achieved. Therefore the use of high alumina CAC is typical and most advantageous. The high degree of purity and the composition of the mineral phases impede any reactions between the liquid metal and the CAC.

Choice of bonding-system

In furnaces used for the manufacture of aluminium metal, temperatures of less than 1000°C are typically observed. Because of this service temperature, refractory concrete will not reach high strength through the classic sintering or ceramic bonding reactions normally observed in high temperature refractory usage. Instead, the...
concrete matrix requires a bonding system that will promote high strength at temperatures of about 500-1000°C. It is in this temperature range that calcium aluminate based bonding systems have been very successful.

Table II shows some examples of binder systems that can be used for aluminium resistant refractory concrete. Bonding-systems based on 10-20% Secar® 80 are essentially SiO₂ free. In the presence of low alkali aluminium-alloys, low cement bonding systems (LCC, ULCC) based on Secar® 71 have also been very successful. With Secar® 71, it is possible to formulate a binder with a cement content of approximately 1-5 %, often in combination with micro fine silica and/or reactive, very fine alumina. In particular, the combination of micro silica and Secar® 71 can achieve very high strengths at temperatures between 500 and 1000°C.

Alkali rich aluminium alloys require a bond system that has a low amount of free alumina as well as free silica. In these applications a binder based on approximately 10-20% Secar® 71 and a minimal amount of free silica is preferred.

Alkalis in aluminium alloys are a potential reactant with the refractory material (Figure 1). Corundum build-up, silica gas development or β-alumina reactions with a subsequent volume expansion can all disrupt the melting process.

Table II. Examples of the bond systems in a typical refractory concrete used for molten aluminium metal contact (mass % relative to total mix)

<table>
<thead>
<tr>
<th></th>
<th>Low alkali aluminium alloy</th>
<th>Alkali rich aluminium alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secar® 80</td>
<td>10-15 15-20</td>
<td></td>
</tr>
<tr>
<td>Secar® 71</td>
<td>1-5 10-15 15-20</td>
<td></td>
</tr>
<tr>
<td>Microsilica</td>
<td>2-8 0-2 0-2</td>
<td></td>
</tr>
<tr>
<td>Additive</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Reactive Al₂O₃</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Infiltration Inhibitor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Max. service temperature (°C)</td>
<td>1200 1800 1200 1200 1800</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Examples of possible reactions between molten aluminium, dross and refractory lining

Because Secar® 71 contains virtually no free alumina, it can be used to formulate alkali resistant bonding systems. Secar® 71 is composed principally of mono calcium aluminate (CaAl₂O₄) and calcium di-aluminate (CaAl₄O₇).

The alkali resistance of calcium aluminate is well known in other applications[1]. The sodium within the aluminium alloy does not react with the silica-free and reactive alumina-free Secar® 71 containing bond system. In fact, with a bond system comprised exclusively of Secar® 71, the aluminium cannot reduce the components of the matrix and sediments formed on the wall by corundum are minimised or eliminated.

Therefore, in many cases of CAC-rich bonds, the addition of an infiltration reducing anti-wetting additive such as calcium fluoride or barium sulphate can be eliminated. This is due to the development of a low porosity structure with high penetration resistance.

Consequently, incidents of furnace overheating at temperatures greater than 1200°C do not represent any danger for the integrity of the refractory concrete assuming that suitable refractory aggregates are used.
Phase formation during relining, drying and heating of refractory concrete in Non Ferrous-metal furnaces

The reactions in the cementitious matrix of a concrete, play an important role in determining the strength development of a refractory concrete to be used within an application range of 500-1000°C. Figure 2 shows the reactions of cement hydration. The mono Calcium Aluminates (CA), which is primarily responsible for the green strength, reacts with the added water to form calcium aluminates hydrates. The hydrates which are then formed will depend on the environment, temperature and the size of the construction (mass effect of heat generation) and will include CAH_{10}, C_{2}AH_{6} + AH_{3} or C_{3}AH_{6} + 2AH_{3}. As these hydrates form, the concrete will harden\(^{[2]}\). When very reactive SiO\(_2\) (micro-silica) is present, calcium aluminates silicate hydrates of zeolitic structure can be formed\(^{[3]}\). During the drying and heating of the refractory concrete, the following reactions - according to the type of bond system – will result depending upon the specific combination of bond system and matrix composition.

In SiO\(_2\)-free mixes using Secar\(^{8}\) 80 and Secar\(^{7,1}\), the reactions are first characterised by dehydration of the hydrate phases. This dehydration invokes a decrease in strength. In order to overcome this decrease in strength a sufficient amount of cement needs to be used. After dehydration of the hydrates, recrystallisation of the calcium aluminates phases occurs with the formation of C\(_{2}\)A\(_{7}\) and corundum, and at higher temperatures then CA and CA\(_2\) are found. In case of the Secar\(^{8}\) 80, the very fine alumina produces additionally a very close combination of matrix components and aggregates. Dehydration of the calcium aluminate hydrate phases starts at temperatures as down as 150°C and is completed at approximately 550°C.

In the case of large construction pieces, additional drying and dehydration time are required to allow the water to diffuse from the center to the surface of the concrete.

Micro silica containing bonding systems, which can contain zeolitic calcium aluminate silicate hydrates, begins dehydration at temperatures above 550°C and then develop gehlenite and/or anorthite. Additionally, the pores filled with fine SiO\(_2\) and possibly the precipitation of the partially suspended silica\(^{[4]}\) contribute to strength development in the temperature range of 500-1000°C.

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**Hydration Reactions in Refractory Concrete**

$\text{CA} + \text{H} \rightarrow [\text{CAH}_{10}]$

$\text{C}_{2}\text{AH}_{6} + \text{AH}_{3}$

$\text{C}_{3}\text{AH}_{6} + 2\text{AH}_{3}$

$\text{CA} + \text{H} + \text{S} \rightarrow [\text{CAH}_{10} + \text{CAS}_{2}\text{H}_{6} + \text{S}]$

$\text{C}_{2}\text{AH}_{6} + \text{AH}_{3} + \text{CAS}_{2}\text{H}_{6} + \text{S}$

$\text{C}_{3}\text{AH}_{6} + 2\text{AH}_{3} + \text{CAS}_{2}\text{H}_{6} + \text{S}$

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**Reactions during drying and firing in Refractory Concrete**

**without microsilica**

$\text{CAH}_{10}$

$\text{C}_{2}\text{AH}_{6} + \text{AH}_{3}$

$\text{C}_{3}\text{AH}_{6} + 2\text{AH}_{3}$

$\text{CA} + \text{A} + \text{Ca}$

**with microsilica**

$\text{CAH}_{10} + \text{CAS}_{2}\text{H}_{6} + \text{S}$

$\text{C}_{2}\text{AH}_{6} + \text{AH}_{3} + \text{CAS}_{2}\text{H}_{6} + \text{S}$

$\text{C}_{3}\text{AH}_{6} + 2\text{AH}_{3} + \text{CAS}_{2}\text{H}_{6} + \text{S}$

$\text{C}_{2}\text{A}_{7} + 5\text{A}$

$\text{12 CA}$

$\text{12 CA}$

$\text{C}_{2}\text{A}_{7} + \text{S}$

$\text{CAS}_{2}$

$\text{CA} + \text{A}$

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Figure 2. Chemical reactions of calcium aluminate cement within refractory concrete (non stoichiometric presentation for clarity)
Calcium Aluminates aggregates for concrete floors in non ferrous metal production plants

As described in Chapter 2, a distinction between calcium aluminate manufactured by melting and those manufactured by sintering needs to be made. The calcium aluminate clinker manufactured by fusion has the characteristic of almost no porosity. Aggregates made out of this clinker (ALAG) and the concretes which incorporate them, ALAG-concrete (Table III and IV), withstand extremely high abrasion environments (Table V), without the need of any complicated bond systems.

### Table III. Chemical Analysis of Calcium Aluminate aggregates (mass %)

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃+FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALAG</td>
<td>41</td>
<td>37</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>R-50</td>
<td>52</td>
<td>39</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

This effect is due to the high density of the aggregate and also the chemical and mineralogical compatibility of the calcium aluminate aggregate and the calcium aluminate cement. This affinity between binder and aggregate creates a unique binding “bridge” which leads to an extremely strong integration of the aggregate into the cementitious matrix.

This type of strong integration is not possible with inert aggregates as ordinarily the grain does not participate in the reaction with the cementitious binder. This is why concrete formulated with ALAG aggregate has advantages when compared to conventional concrete produced with calcium aluminate cement and inert aggregates. In addition to the high abrasion resistance, concretes of this type are also known for shock resistance.

ALAG concrete has been subjected to an impact test according to the French CNR method that drops a 1 kg steel ball from a height of 1 meter 2700 times on to the sample within 3 hours (Figure 3). Table V shows results of this test.

### Table IV. Composition and mechanical strength of Alag concrete

<table>
<thead>
<tr>
<th>Composition of Alag concrete</th>
<th>CFL</th>
<th>ALAG-line 0-2.5 mm</th>
<th>ALAG-coarse 2.5-12.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>20</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Mass in kg for m² of concrete</td>
<td>515</td>
<td>1030</td>
<td>1030</td>
</tr>
</tbody>
</table>

**Mechanical strength of Alag concrete**

<table>
<thead>
<tr>
<th>Green strength development at 20°C (N/mm²)</th>
<th>1 day</th>
<th>7 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
<td>70</td>
<td>90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dried and fired strengths (N/mm²)</th>
<th>MOR</th>
<th>CCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>9.0</td>
<td>95</td>
</tr>
<tr>
<td>800°C</td>
<td>6.5</td>
<td>72</td>
</tr>
<tr>
<td>1100°C</td>
<td>4.0</td>
<td>45</td>
</tr>
</tbody>
</table>
Table V. Abrasion and impact resistance of Alag concrete

<table>
<thead>
<tr>
<th>Abrasion resistance per ASTM C 704</th>
<th>Sample preparation</th>
<th>Volume lost (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C, 24 h</td>
<td></td>
<td>5.4</td>
</tr>
<tr>
<td>815°C, 5 h</td>
<td></td>
<td>9.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Impact resistance of Alag Concrete and OPC construction concrete per CNR-Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample preparation</td>
</tr>
<tr>
<td>ALAG-concrete, 20°C, 7 days</td>
</tr>
<tr>
<td>ALAG-concrete, 20°C, 28 days</td>
</tr>
<tr>
<td>OPC-concrete, 20°C, 28 days</td>
</tr>
</tbody>
</table>

The compressive strength of ALAG-concrete, even after a thermal shock treatment, is - compared to concrete with inert aggregates such as basalt - about twice as high (Figure 4). Other values of physical characteristics are exhibited in Table VI.

Figure 4. Compressive strength after thermal shock for different types of concrete (cycles of 24 h at 21°C, 23 h at 105°C, 6 h at 500°C)

Table VI. Thermal and physical properties of Alag concrete

<table>
<thead>
<tr>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
</tr>
<tr>
<td>1000°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Creep at temperature (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1180°C</td>
</tr>
<tr>
<td>1280°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Shrinkage (%) at 20°C and 50% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
</tr>
<tr>
<td>28 d</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Permanent Linear Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100°C</td>
</tr>
</tbody>
</table>

Installation of an ALAG-Concrete

The relining of a floor in a furnace bay is typically installed using checkered slabs of approximately 2 x 2 m² (Figure 5).

Figure 5. Installation of industrial floor in checker pattern

**a) Casting**

(1) The casting method of a concrete depends on the type of mould

**b) Casting with removable moulds**

i) Moist wood

ii) Metal mould

iii) Joints out of PVC (not for temperature related applications)

**c) Casting with Dry Joints**
Installations of 10-25 cm thickness can be placed on solid ground. If working to repair a damaged floor, the damaged zone should be removed before the CFL-ALAG concrete can be installed (Figure 6).

After 6 hours, the compressive strength reaches 35-45 N/mm$^2$ and after 24h the concrete is strong enough to be put back into service (Figure 7).

Here the advantage of a bond system comprised of calcium aluminate cement as compared to Portland cement (OPC) is shown very clearly. Figure 8 shows the strength development of sand mortars made with OPC and CFL. This comparison exhibits why concrete made out of CFL-ALAG has at 24 hours double the strength of normal OPC concrete.

**Application examples**
Currently ALAG-concrete is often used for floors in front of non-ferrous metal furnaces as a substitute for Portland cement concrete made out of sand and gravel (OPC-concrete). This is a harsh environment for OPC-concrete as hot parts are placed on the cold floor, splashes of melt originate from the furnace and especially because of the very strong abrasion and shock requirements as heavy charging bins for the furnace are put down and moved backward and forward. Also, the handling of the aluminium dross can create an environment of abrasion and shock (Figures 9 and 10).

Compared to OPC-concrete, CFL-ALAG concretes offer considerable improvements related to durability. An example is available from a German aluminium plant where the floor in front of the melting-furnace was covered with ALAG-concrete. In comparison to the original Portland

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**Figure 6. Repair of existing floor with Ciment Fondu® / Alag® concrete**

**Figure 7. Installation schedule for industrial floor from placement to usage.**

**Figure 8. Compressive strength development of a sand mortar in OPC, Ciment Fondu® and lithium carbonate accelerated Ciment Fondu®**
cement concrete, there was an increase of durability of about 100%. The OPC-concrete had to be replaced after 4 years while the ALAG-concrete is still in service after 8 years.

Similar results have been attained in many other aluminium plants around the world.

![Figure 9. Installation of Alag concrete in pot lines and cast house](image)

![Figure 10. Installation of Alag concrete in area of ladle stand and aluminium dross storage area](image)

In these examples, not only is the longevity of the concrete of great importance but also the reduced total repair downtime due to the rapid hardening of the ALAG-concrete. While there is no major difference between the initial set of the OPC and of the ALAG-concrete - which enables a relining of the floor without any problems - the ALAG-concrete hardens more quickly than the OPC-concrete (Figure 8).

Consequently floor repairs can be done in a short period of time - for example, during a weekend shutdown. The regular melting and cast operations of the plant are not significantly affected by the short repair time. After approximately 8 hours from installation of the concrete, the floor can be placed back into service. Comparatively, an OPC-concrete needs a considerably longer amount of time before being put back into service. Because of all this, OPC-concrete repairs are not only more frequent, but the downtimes during repair are considerably longer. All these issues lead to cost reductions when ALAG-concrete is specified.
Another example of CFL-ALAG concrete floors is the installation underneath copper converters. In this example, the adherence of copper and slag to the CFL-ALAG concrete is minimal, adding to the already enhanced temperature and shock resistance.

5 CAC aggregates for refractory concrete

A new product is now available that provides the ability to create a concrete with the strength properties of ALAG while exhibiting more refractory properties. This aggregate, R-50 is also based upon a fused calcium aluminate. It is known that an aggregate made completely out of calcium aluminate exhibits excellent alkali resistance\(^1\). As already described in section 4, the calcium aluminate aggregate binds extremely well in a chemical-mineralogical way with the calcium aluminate cement. This leads to a close contact between the matrix and aggregate. The cracks often appearing around the grains of an inert aggregate can be avoided through the use of R-50.

Table VIII shows the results. The highest fired strength is attained with the LC-binder system. Up to a pre-fire temperature of about 1200°C the concretes are largely volume stable. At a pre-fire-temperature of 1400°C, expansion occurs because of the feldspar and/or the development of mullite.

Laboratory tests have been conducted with various concretes formulated using R-50 (Table VII). Typical refractory concrete particle size fractions were used and combined with different bond-systems. Comparisons have been made between a LC-binder made out of micro-silica (5%) and Secar\(^®\) 71 (5%) and a pure binder made out of Secar\(^®\) 71 (15%) as well as with pure binders made out of Secar\(^®\) 51, Secar\(^®\) 71 and Secar\(^®\) 80 (20% each). The 15% Secar\(^®\) 71 mix with R-50 was compared with a similar mixture of tabular alumina acting as the aggregate.

![Table VIII. Properties of concrete formulas tested](image)

The very close association of CAC and R-50 becomes evident when comparing the R-50 to tabular alumina (Formula 2 vs. 3).
The strength at pre-fire-temperatures up to 800°C is much higher in the case of R-50 concrete despite the fact that the water demand is a little bit higher. In comparison to the pure CAC-binders with R-50 aggregate (Formulas 4 - 6) it appears that Secar© 71 promotes the highest cold compression strengths after a pre-fire up to 800°C.

The highest cold flexural strengths appear with the Secar© 51 formula at 800°C. With the Secar© 80, sufficiently high cold compression strengths and cold flexural strengths in the whole range of tested temperatures are reached. Secar® 80 has the lowest water demand and provides good flow behaviour.

The high chemical stability of the calcium aluminate linked to the distinctive physio-chemical binding power between CAC and R-50 enable the use of these refractory concretes under particularly difficult conditions which contain materials that are extremely aggressive to refractory concretes.

**Severe Alkali-attack**

A castable composed of R50 and Secar© 71 consists almost completely of calcium aluminate. This confers a high chemical resistance against alkalies. A test simulating alkali attack has been used to evaluate R50 based concretes. In this method a test bar is covered on the upper surface with a mixture of Na₂CO₃ and K₂CO₃-mixture. The covered sample is then fired to 1250°C. Reference samples without the alkali coating are also fired at the same time. After firing the samples are measured and the resulting difference in linear dimensional change between the two samples (coated and non-coated) evaluated. Samples are also tested for cold MOR. The results of the systems investigated are shown in Figure 11 and Figure 12 respectively.

![Figure 11](image1.png)

*Figure 11. The effect of alkali attack upon permanent Linear change after heating to 1250°C*

![Figure 12](image2.png)

*Figure 12. The effect of alkali attack upon cold Modulus of Rupture after heating to 1250°C*

The refractory castable with the silica containing LC-bonding shows less than ideal behaviour. The pronounced permanent linear expansion probably is a result of alkali bursting that will normally lead to destruction of the concrete. Only a small alteration in dimension due to alkali attack is found with R50 and a bond system comprised of 20% S71 or 20% Secar© 80 (samples 5 and 6 respectively). When sintered-alumina is used, a large expansion is seen due to the formation of beta-alumina.

The destruction of the bonding system through the alkali burden with the LC system is also shown by the drastic decrease of the cold flexural resistance (MOR). Comparing samples 4, 5 and 6, the advantage of the high-grade cements Secar© 71 and Secar® 80 is obvious.
Abrasion resistance
Samples were evaluated for abrasion resistance using the ASTM C704 method after drying at 110°C and after firing at 800°C. In order to assess high temperature behaviour and likely abrasion resistance, samples were subjected to hot modulus of rupture tests and refractoriness under load tests.

The results are shown in Figure 13.

![Figure 13. Abrasion resistance (ASTM C704)](image)

It is clear from these results that when abrasion resistance is the key wear mechanism then sample 1, R50 with an LC bond system, shows the highest abrasion resistance (lowest volume loss). The sample with R50 and 20% Secar® 80 (sample 6) is the next best and also shows good abrasion resistance. In spite of their significantly lower bulk density than the sample 2 based upon sintered alumina, both these samples displayed a greater abrasion resistance. Samples 2, 4 and 5 had somewhat higher volume loss and consequently lower abrasion resistance. This is probably due to their finer grain structure.

We can observe a similar picture with regard to the hot bending strength (HMOR) where sample 1 with the LC-bond and the R50 aggregate as well as sample 6 with 20% Secar® 80 shows by far the highest values (Figure 14). The hot bending strength in case of the sintered alumina (sample 3) is very low at 800°C and only reaches a comparable value with sample 2, containing R50, at 1200°C.

![Figure 14. Hot Modulus of Rupture](image)

As would be expected, considerably higher values for sample 3 with sintered alumina can be observed at the higher temperature of 1400°C.

The refractoriness under load tests (Figure 15) of the R50 containing samples confirms that the maximum operating temperatures stays around 1350°C and 1400°C.

![Figure 15. Refractoriness under load at 0,2N/mm² loading](image)

Resistance to molten Aluminium
Figure 16 shows the crucible ‘cup’ type static corrosion tests. Cast samples are produced into which cores are drilled. These cores are filled with aluminium-alloy AZ8GU at 800°C and held at this temperature for 72 hours. At the end of the test the ‘cups’ are emptied, cooled and sectioned.
Figure 16. Corrosion test with aluminum alloy, after 72 hr at 800°C

As shown in these figures there is very little adherence of aluminium to the refractory samples containing the R50 aggregates, and where it does exists only extremely thin layers are seen. Corundum formation is low and infiltration cannot be identified. This is in contrast to sample 3 with sintered alumina where a considerable adherence of aluminium combined with formation of corundum can be observed as along with a clearly recognisable infiltration into the microstructure.

These observations correlate perfectly with the open porosity of the samples (Figure 17). Compared to sample 3 with sintered alumina, all R50 containing samples, in spite of the low bulk-density, have a small open porosity.

Figure 17. Apparent Porosity after thermal treatment

Thus, the combination of a calcium aluminate aggregate coupled with an extremely low porosity seems to be particularly effective in limiting aluminium ingress and therefore they have an interesting potential in Aluminium contact applications.
6 Summary

Calcium Aluminate Cements with an Al$_2$O$_3$ content between 40 and 80% can be used in nearly all types refractory concrete applications.

Typical service temperatures in the non-ferrous metal industry, for example the aluminium melting furnace, are usually less than 1000°C. The high range CAC with 70 or 80% Al$_2$O$_3$ have succeeded because of their mineralogical composition and their stability against attacking melts.

Beyond this, CA-aggregates are used in special niche applications of these industries. For example, the concrete floor in front of an aluminium melting furnace or under a copper converter is seriously stressed by mechanical loads, abrasion, temperature changes and splashes of the melt. Here the lifetime of concrete constructed of CA-aggregates and CAC is almost 100% higher than the lifetime of ordinary building concrete. An ALAG concrete can be put into service much faster when compared to a normal OPC-concrete.

The newest type of calcium aluminate aggregate R50 has also shown interesting properties and can be considered for use in applications where aggressive environments are far more severe. Based on the results shown, potential applications could include areas of high alkali attack, applications requiring a high degree of abrasion resistance at intermediate temperatures as well as metal contact applications where metal infiltration is the decisive wear mechanism.

The unique properties of this aggregate including its chemical composition, mineralogy and almost pore free structure mean that metal contact applications within the non-ferrous industries, such as aluminium, are possible. Not only that the infiltration is limited by physical effects but the calcium aluminate mineralogy is also resistant to attack by aluminium.

The traditional advantages, as found with ALAG concrete, such as the integration of the bonding system between aggregate and cement are also conserved for this new R50 aggregate. Furthermore this should also confer a high degree of resistance to infiltration by Aluminium metal due to the elimination of cracks which are traditionally found between the aggregate and the CAC bond.

Depending upon the dominant wear mechanism of each given application the formulation of R50 containing castables can be engineered to give optimum results.

The new R50 aggregate offers interesting possibilities to reduce refractory wear and optimise the cost/performance of refractory installations.

7 References