# MATERIAL DESIGN FOR NEW INSULATING LINING CONCEPTS

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## INTRODUCTION

Synthetic raw materials based on calcium hexaluminate ($CA_6$) are commercially available as dense aggregate "Bonite" and super lightweight aggregate "SLA-92". Both are used successfully in various applications. The key properties of $CA_6$ such as high chemical purity, high refractoriness and high thermal shock resistance are well known in the industry. Particularly outstanding is the low thermal conductivity of SLA-92 in the high temperature range above 1200°C. This is also the case with the dense Bonite when compared to other minerals with a similar density. In recent years energy saving concepts and environmentally friendly solutions have increasingly become the focus of attention as the industry has to cope with increasing energy costs and ever changing environmental regulations, e.g. limitation of $CO_2$ emissions. Therefore innovative concepts and material solutions are required in order to optimise the performance of the processes. The combination of dense and lightweight $CA_6$ enables the development of tailor-made solutions which take into account density, strength and thermal insulation without changing the chemical-mineralogical composition of the refractory. New insulating castable concepts will be presented and discussed in this paper.

## PROPERTIES OF $CA_6$ MATERIALS

Both SLA-92 and Bonite are composed of about 90% $CA_6$, with only a minor content of corundum and traces of calcium dialuminate ($CA_2$). The $CA_6$ aggregates show the typical hexagonal plate-like crystal structure (Fig. 1 and 2). Whereas SLA-92 is a super lightweight raw material with a porosity of typically 70 – 75%, Bonite is the dense sintered counterpart with a much lower porosity. The properties of SLA-92 and Bonite are summarised in table 1 and have been discussed in detail in previous papers. [1-7].

## EXPERIMENTAL

The properties of $CA_6$ based castables are demonstrated in two pure SLA-92 based vibration castables and a Bonite based one

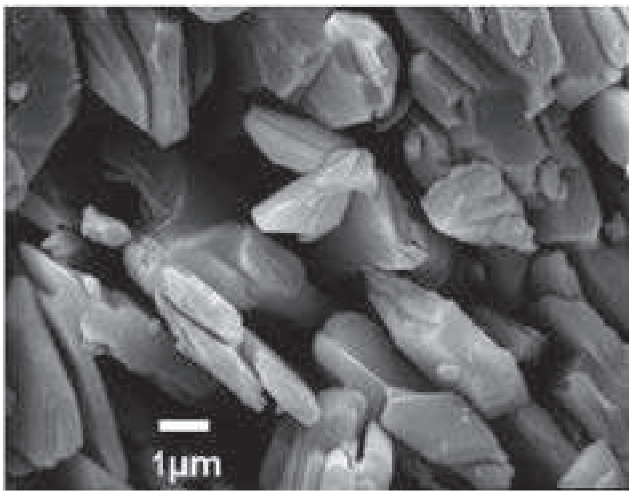


*Fig. 1: Microstructure of lightweight $CA_6$ SLA-92*

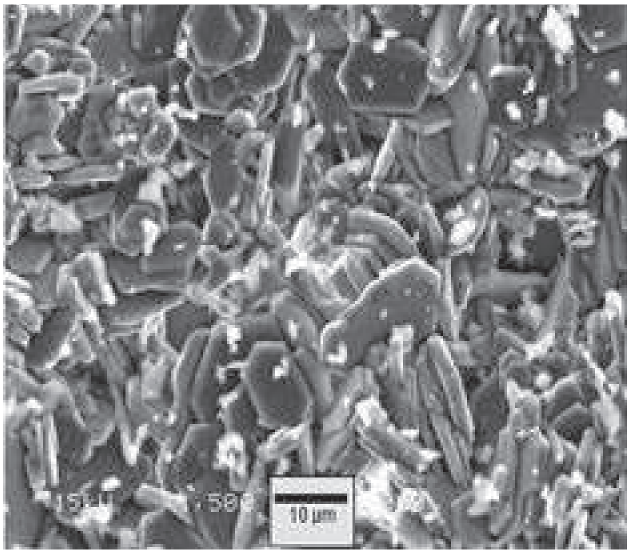


*Fig. 2: Microstructure of dense $CA_6$ Bonite (different scale to be considered compared to figure 1)*

representing the low and the high density range respectively. In addition two castable formulations with intermediate densities were developed as examples to demonstrate the combined use of SLA-92 and Bonite (table 2). These castables are named accord-

Tab. 1: Properties of SLA-92 and Bonite

| | SLA-92 | Bonite (LD) |
|---|---|---|
| **Mineralogical composition** | | |
| Main phase | $CA_6$ (~ 90%) | $CA_6$ (~ 90%) |
| Minor phase | Corundum | Corundum |
| **Chemical analysis** [mass-%] | | |
| $Al_2O_3$ | 91 | 91 |
| CaO | 8.5 | 7.7 |
| $Fe_2O_3$ | 0.04 | 0.08 |
| $SiO_2$ | 0.07 | 0.5 |
| $Na_2O$ | 0.4 | |
| $Fe_{mag}$ | | 0.01 |
| **Physical properties** | | |
| Bulk density [g/cm³] | 0.8 | 2.8 |
| Lose bulk density [kg/l] | 0.5 | |
| Apparent porosity [vol.-%] | 70 - 75 | 23 |
| **Available sizes** | | |
| 3 - 6 mm | x | x |
| 1 - 3 mm | x | x |
| 0.5 - 1 mm | | x |
| 0 - 1 mm | x | x |
| 0 - 0.5 mm | | x |
| - 45 MY | | x |
| - 20 MY | | x |

ing to their fired density, for example mix "VIB 1.1" has a fired density of 1.1 g/cm³. Two SLA-92 based patch mixes are also included in this investigation to show the multiple range of applications for $CA_6$ materials (table 3).

Tab. 2: Vibration castable formulations based on SLA-92 and Bonite

| | | | VIB 1.1 | VIB 1.3 | VIB 2.2 | VIB 2.4 | VIB 2.6 |
|---|---|---|---|---|---|---|---|
| **Component** | | | | | | | |
| SLA-92 | 3 - 6 mm | % | 25 | 15 | | | |
| | 1 - 3 mm | % | 20 | 27 | | | |
| | 0 - 1 mm | % | 25 | 21 | 30 | 15 | |
| Bonite | 3 - 6 mm | % | | | 25 | 25 | 20 |
| | 1 - 3 mm | % | | | 15 | 15 | 20 |
| | 0.5 - 1 mm | % | | | 7 | 7 | 15 |
| | 0 - 0.5 mm | % | | | | 10 | 15 |
| | -45 MY | % | | | | 6 | 5 |
| | -20 MY | % | | | | | 7 |
| T60/T64 | -20 MY | % | | 7 | | | |
| Reactive Alumina | CL 370 | % | | 4 | 10 | 12 | 13 |
| | CT 10 SG | % | | 6 | 3 | | |
| Cement | CA-25 R | % | 30 | | | | |
| | CA-14 M | % | | | | | 5 |
| | CA-270 | % | | 20 | 10 | 10 | |
| Additives | ADS/W | % | | 1.5 | 1 | 1 | 1 |
| | Carboxymethyl-cellulose | % | 0,06 | 0,04 | | | |
| **$H_2O$** | | **%** | **60** | **43** | **16.5** | **12.5** | **9.8** |
| **Castable properties** | | | | | | | |
| C MoR | 20°C / 24h | MPa | 1 | 1 | 2 | 3 | 2 |
| | 110°C / 24h | MPa | 1 | 3 | 5 | 8 | 10 |
| | 1000°C / 5h | MPa | 1 | 2 | 4 | 5 | 7 |
| | 1500°C / 5h | MPa | 3 | 6 | 14 | 21 | 38 |
| CCS | 20°C / 24h | MPa | 4 | 6 | 10 | 16 | 18 |
| | 110°C / 24h | MPa | 5 | 15 | 27 | 59 | 60 |
| | 1000°C / 5h | MPa | 5 | 12 | 23 | 42 | 55 |
| | 1500°C / 5h | MPa | 6 | 23 | 62 | 116 | 202 |
| Bulk density | 110°C / 24h | g/cm³ | 1.17 | 1.39 | 2.31 | 2.51 | 2.67 |
| | 1000°C / 5h | g/cm³ | 1.11 | 1.28 | 2.23 | 2.44 | 2.60 |
| | 1500°C / 5h | g/cm³ | 1.11 | 1.27 | 2.18 | 2.39 | 2.58 |
| PLC | 110°C / 24h | % | - 0.11 | - 0.06 | - 0.07 | - 0.04 | - 0.06 |
| | 1000°C / 5h | % | - 0.08 | - 0.11 | - 0.10 | - 0.07 | - 0.05 |
| | 1500°C / 5h | % | - 0.72 | - 0.19 | + 0.66 | + 0.45 | + 0.07 |
| Thermal conductivity (prefired 1000°C/5h) | 20°C | W/mK | 0.46 | | 1.50 | | |
| | 300°C | W/mK | 0.33 | | 1.29 | | 1.50 |
| | 600°C | W/mK | 0.27 | | 1.18 | | 1.30 |
| | 1000°C | W/mK | 0.29 | | 1.07 | | 1.30 |
| | 1200°C | W/mK | 0.38 | | 1.19 | | 1.50 |

Test bars and bricks from all castables were prepared and tested according to the European standard EN 1402 "Unshaped refractory products", parts 5 and 6. The dry castable components were mixed in a Hobart mixer type A 200 for one minute and another four minutes after the addition of water. The ready mixed castables were cast into the moulds under vibration. The amplitude was varied during the casting and densification process within the range from 0.2 to 0.5 mm depending on the specimen size and the densification behaviour of the castable. A special focus was given to the stability against separation of the different $CA_6$ aggregates due to the difference in density. Observations made are discussed below.

Thermal conductivity testing up to 1200°C was performed by DIFK, Bonn, Germany according to the hot wire method (parallel wire) DIN EN 993-15 using standard sized bricks pre-fired at 1000°C/5h.

Wynn et al. [8] highlighted the importance of microstructure for the thermal conductivity. In their study insulating firebricks produced by casting provided the lowest thermal conductivity when compared to bricks of similar chemical composition which were produced by the slinger or the extrusion process. The cast material is said to be advantageous because of the micro-porous structure.

Tab. 3: Patch mix formulations based on SLA-92

| | | | PATCH SLA 1 | PATCH SLA 2 |
|---|---|---|---|---|
| **Component** | | | | |
| SLA-92 | 0 - 1 mm | % | 90 | 50 |
| Reactive Alumina | CL 370 | % | | 20 |
| Cement | CA-14 M | % | | 30 |
| | CA-270 | % | 10 | |
| Additives | Bentonite | % | 0.5 | |
| | Carboxymethyl-cellulose | % | 0.5 | 0,04 |
| **$H_2O$** | | **%** | **63** | **41** |
| **Castable properties** | | | | |
| Bulk density | 110°C / 24h | g/cm³ | 1.01 | 1.65 |
| | 1000°C / 5h | g/cm³ | 0.91 | 1.40 |
| | 1500°C / 5h | g/cm³ | 0.92 | 1.47 |
| thermal conductivity (prefired 1000°C/5h) | 20°C | W/mK | 0.29 | 0.79 |
| | 300°C | W/mK | 0.27 | 0.50 |
| | 600°C | W/mK | 0.26 | 0.44 |
| | 1000°C | W/mK | 0.26 | 0.43 |
| | 1200°C | W/mK | 0.30 | 0.51 |

## CASTABLE DEVELOPMENT

The target for the development of the $CA_6$ test castables was a homogeneous blend of lightweight SLA-92 and dense Bonite in different ratios in order to adjust the bulk density in the range from 1.1 to 2.6 g/cm³. In addition, different strength and insulating properties should be achieved.

A low castable density of 1.1 or 1.3 g/cm³ is represented by pure SLA-92 castables which require high water addition because of the high porosity of SLA-92. For these castables small amounts of Carboxymethyl-cellulose (CMC) were added to the mix to improve the homogeneity and avoid bleeding of the mix. The CMC was either added as a powder to the dry mixed castable or together with the mixing water as Blanose sol. Because of the high water demand, these castables require a smooth vibration during casting. In order to reduce the water demand of VIB 1.1 and to improve the strength properties, the castable matrix was optimised by adding calcined and reactive aluminas as partial replacement of the cement and also by adding dispersing aluminas. This resulted in VIB 1.3.

The castables containing both SLA-92 and Bonite achieve densities of 2.2 and 2.4 g/cm³. SLA-92 is used as size 0 – 1 mm only to ensure a better and more homogeneous distribution of the lightweight aggregate in the castable mixture. The cement content in the intermediate density formulations was lowered to 10 %, being partly substituted by reactive alumina CL 370. Water demand for these mixes is in the range of 12 to 17 %.

Castable compositions which contain SLA-92 in the coarse fraction, have also been tested. All these tests resulted in separation of SLA-92 and Bonite as well as separation of water after a certain period of time. The use of commercially available stabilisers only slightly improved that behaviour but resulted in higher plasticity of the castable, which hampered the flow properties. This approach was therefore disregarded.

The final mix in the test series is VIB 2.6, a low cement castable based on Bonite which requires 9.8 % water addition to achieve vibration flow consistency.

In addition to the vibration castables, two SLA-92 based patch mixes have also been developed. The formulations shown in table 3, for example, can be used as spray coating for submerged nozzle insulation (PATCH SLA 1) or as plastic filler (PATCH SLA 2). Both recipes contain a considerable amount of SLA-92 0 – 1 mm. In PATCH SLA 1 cement is the binder and Bentonite works as a plasticiser. The SLA-92 content in PATCH SLA 2 is lower and the formulation contains a higher amount of cement CA-270 and reactive alumina CL 370. An addition of clay here is not required. CMC is added in both mixes to improve the stickiness and plastic consistency. PATCH SLA 2 provides a good deal of flexibility with regard to the castable composition. The SLA-92 content can be increased up to 80% and consequently the content of CL 370 and CA-270 can be decreased. The consistency of both mixes can be adjusted in a wide range by varying the water addition, and can therefore be adjusted to specific requirements of the application.

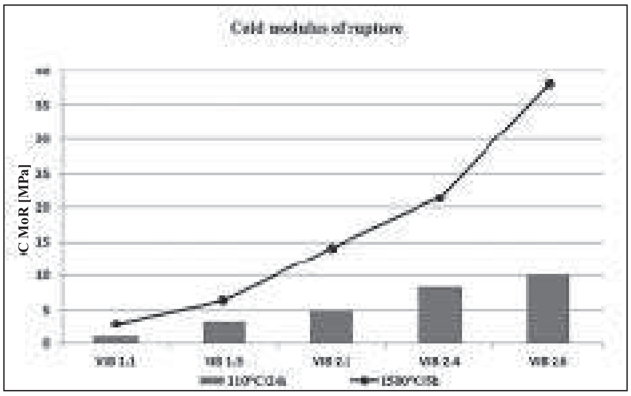


*Fig. 4: Cold modulus of rupture of $CA_6$ based vibration castables*

**RESULTS AND DISCUSSION**

The chemical compositions of the test castables are listed in table 4. All castables show a constant composition of about 89% $Al_2O_3$ and 10% CaO independent of which aggregate is used. The impurity level for all mixes is very low: $Fe_2O_3$ below 0.1% and $SiO_2$ below 0.5%.

Tab. 4: Chemical composition of $CA_6$ based castables

| | | VIB 1.1 | VIB 1.3 | VIB 2.2 | VIB 2.4 | VIB 2.6 | PATCH SLA 1 | PATCH SLA 2 |
|---|---|---|---|---|---|---|---|---|
| **Chemical composition** | | | | | | | | |
| $Al_2O_3$ | % | 88 | 89 | 90 | 90 | 91 | 89 | 87 |
| CaO | % | 11 | 11 | 9 | 9 | 8 | 10 | 13 |
| $Fe_2O_3$ | % | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| $SiO_2$ | % | < 0.1 | < 0.1 | 0.3 | 0.3 | 0.4 | 0.4 | < 0.1 |

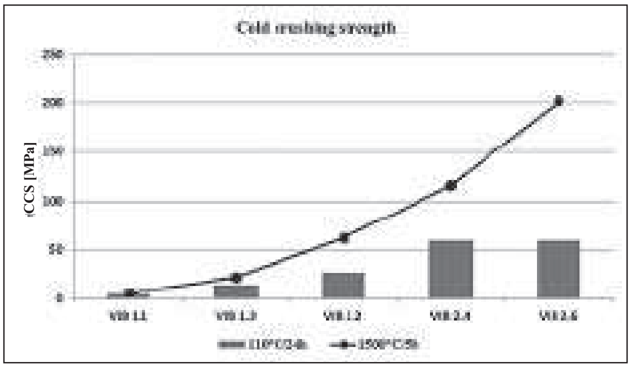


*Fig. 5: Cold crushing strength of $CA_6$ based vibration castables*

The fired density of the different vibration castables was adjusted within the range from 1.1 to 2.6 g/cm³ (figure 3). The higher the density, the higher the Bonite content in the mix and the lower the SLA-92 content. A castable formulation representing the density range of 1.8 – 2.0 g/cm³ was excluded from the investigation due to the segregation. This formulation required coarse SLA-92 in combination with different Bonite sizes and the coarse SLA-92 tended to segregate.

The strength properties shown in figures 4 and 5 correlate with the fired densities. When comparing the pure SLA-92 containing castables VIB 1.1 and VIB 1.3, the cold modulus of rupture is improved by a factor of two and the cold crushing strength by almost a factor of three for VIB 1.3. This is due to the matrix optimisation by using tabular alumina fines, calcined and reactive alumina and dispersing aluminas as additives. The water demand is reduced from 60% for VIB 1.1 to 43% for VIB 1.3.

The strength properties are further improved by partial substitution of Bonite instead of SLA-92. The higher strength of the dense Bonite grains when compared to the porous SLA-92 grains provides a stronger framework which results in higher dried and fired strengths.

The different castable concepts cover the range of 1 – 10 MPa for cold modulus of rupture at 110°C/24h and 3 – 38 MPa at 1500°C/5h. The cold crushing strength at 110°C/24h can be adjusted between 5 and 60 MPa and between 5 and 200 MPa after firing at 1500°C/5h. The highest strength values are achieved by the pure Bonite based castable VIB 2.6.

Apart from density, the thermal conductivity is also a focal point in insulating lining concepts. The thermal conductivity was tested in three of the five vibration castables (figure 6) and in the patch mixes (figure 7). In general the thermal conductivity for all mixes is low. The higher the content of SLA-92 in the formulation, and the lower the density, the lower the thermal conductivity which is measured. The same applies for the patch mixes. Because of the 90% content of SLA-92 in PATCH SLA 1 the thermal conductivity is = 0.3 W/m·K up to 1200°C. The thermal conductivity of CA6 based castables can be adjusted in the range from approximately 0.25 to 1.7 W/mK (figure 8) by blending the two aggregates SLA-92 and Bonite, and by modification of the castable matrix.

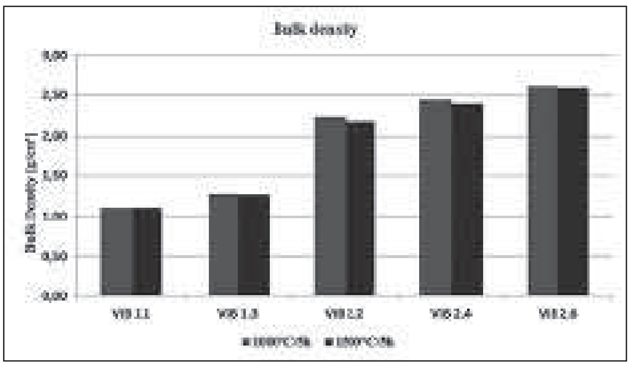


*Fig. 3: Fired bulk density of $CA_6$ based vibration castables*

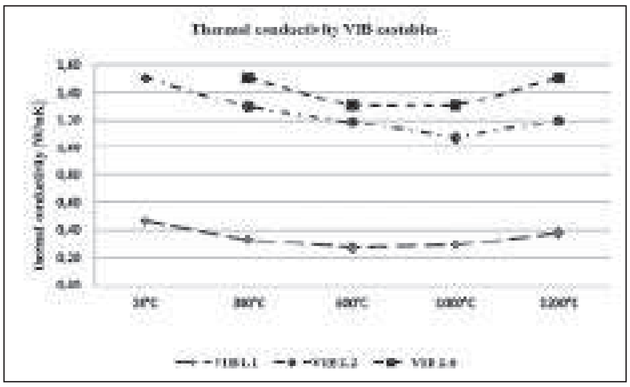


*Fig. 6: Thermal conductivity of $CA_6$ based vibration castables prefired at 1000°C/5h*

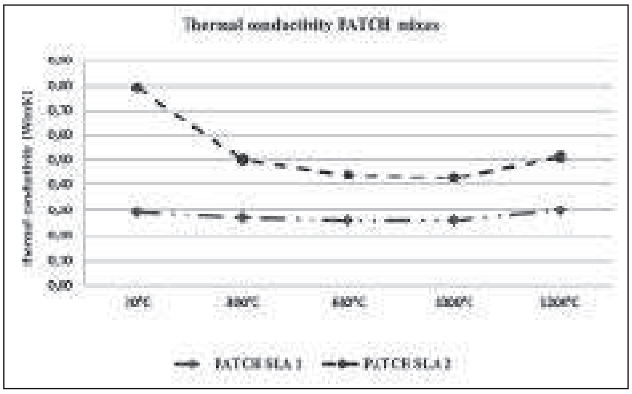


*Fig. 7: Thermal conductivity of SLA-92 based patch mixes pre-fired at 1000°C/5h*

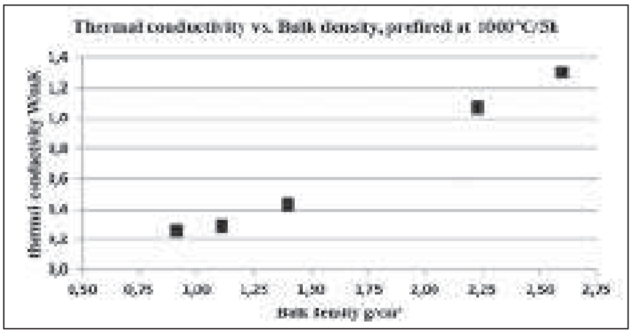


*Fig. 8: Thermal conductivity at 1000°C vs. bulk density of $CA_6$ based castables pre-fired at 1000°C/5h*

A comparison of the raw material costs for the different castable concepts is shown in figure 9. Instead of cost per tonne, the cost per cubic metre of lining was calculated. This approach is more common for insulating refractory applications. Although the price level of the pure SLA-92 based castable is higher when compared to the SLA/Bonite and Bonite based ones the castable costs in relation to the material requirements are lowest.

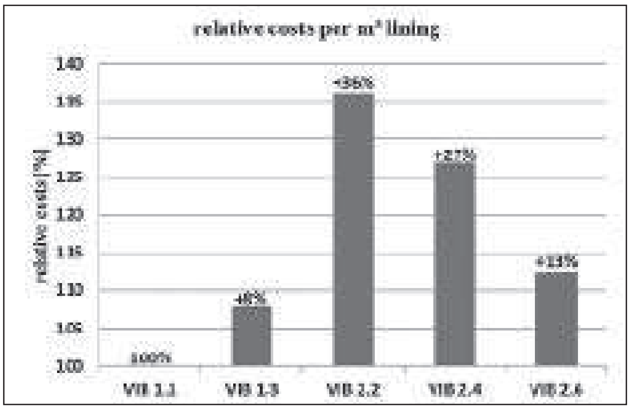


*Fig. 9: Relative cost comparison of the different castable concepts*

**CONCLUSION**

The castable concepts based on different ratios of lightweight SLA-92 and dense Bonite demonstrate the flexibility with regard to castable design. The bulk density can be adjusted in a range from 1.1 to 2.6 g/cm³. The same applies for the strength which can be increased if required for a specific application. This can be important, for example, in areas where the mechanical wear is higher or in areas which are only exposed to lower temperatures and consequently strength development through sintering is hampered. The use of $CA_6$ aggregates in patch mixes allows the use of alternative lining techniques, e.g. coating or spraying. The thermal conductivity for all castable concepts is low and therefore is beneficial when considering the overall energy efficiency of the equipment.

In addition to the properties discussed in the paper, synthetic calcium hexaluminate based materials exhibit a high alkali resistance, both in a test with alkali salt and with $K_2CO_3$ [2; 7]. The high chemical purity and the absence of Silica results in a high stability in a $H_2$/CO atmosphere [9]. In the CO-resistance test according to ASTM C288-87 $CA_6$ based test pieces were rated class A and B even with the high porosity in the case of SLA-92 [2,6]. The thermal shock resistance is important for various applications, and is excellent for refractories based on both SLA-92 [5] and Bonite [1]. The thermal shock resistance for the castable concepts presented in this paper was also tested but results were not available in time for publication. 7

It is the combination of all properties that makes calcium hexaluminate unique as a refractory material. Once the concept of using calcium hexaluminate has proven suitable for an application in general, properties such as density, strength and thermal insulating behaviour can be adjusted to the requirements of the particular application. Furthermore the option of castable tailoring may enable the switch from a multilayer to a monolayer lining by taking advantage of the combined use of SLA-92 and Bonite.

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