Advantages of Calcium Hexaluminate in a Corrosive Environment

M. Schnabel, A. Buhr, G. Büchel, R. Kockegey-Lorenz, J. Dutton

A growing world population is demanding that all industries become smarter about how they use and reuse raw materials and energy. It also demands that they recycle their waste material to help preserve the environment. New technologies to increase the performance of processes or alternative designs are being pushed forward vigorously. Projects to reduce energy losses and therefore CO_2-emissions by better thermal insulation have high priority throughout all industries. In refractory applications, longer life of units will reduce material consumption in the linings. This in turn will save raw materials, some of which already face shortages around the world. More innovative new concepts and product solutions will be required to achieve these set targets.

Tab. 1 Properties of SLA 92 and Bonite

	SLA 92	Bonite
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	7,6
Fe_{mag}		0,01
Impurities	0,5	1,3
Physical properties		
Bulk density [g/cm³]		3,0
Lose bulk density [kg/l]	0,5 – 0,6	
Apparent porosity [vol.-%]	70 – 75	9,8

1 Introduction

About a decade ago new synthetic raw materials, based on calcium hexaluminate (CA6), a highly refractory mineral, were launched by *Almatis*. These have proved advantageous in various applications such as steel (in reheating furnaces and burner cover linings), in the petrochemical and chemical industry, in ceramic kilns (lining and kiln cars), and in the glass industry. This paper presents a brief overview of the special characteristics of calcium hexaluminate in various corrosive environments and should help drive the developer to new innovative refractory solutions.

2 Properties of CA6 aggregates

Almatis offers two aggregates, SLA 92 and Bonite, both available in a range of sizes. The major difference between the two products is their density and therefore their insulating properties (Tab. 1).

They are composed of about 90 % CA_6 with a small corundum content and traces of calcium dialuminate (CA_2). Both aggregates show the typical hexagonal plate-like crystal structure, which is assumed to be the reason for the low thermal conductivity of calcium hexaluminate when compared to other minerals of similar densities.

The dense Bonite is produced by the same process used to produce tabular alumina. Because of the controlled sintering process and the subsequent processing steps it is possible to produce a homogeneous, non-hydraulic CA6 aggregate with only traces of other impurities such as metallic iron (< 200 ppm).

SLA 92 is a super lightweight raw material for insulation applications. It results from a multi-step process with final calcination temperatures > 1550 °C. Bonite and SLA 92 were discussed in depth in previous papers. [1–6]

Because of their identical chemical and mineralogical composition, both calcium hexaluminate aggregates can be used singularly or in combination. This allows for the formulation of "tailor made" solutions taking into account density, strength and thermal insulation.

2.1 Reaction with other refractory raw materials

Calcium hexaluminate is the most alumina-rich intermediate compound of the CaO-Al_2O_3 system. It is therefore thermochemically stable with corundum. The thermal expansion coefficient of CA_6 ($8,0 \cdot 10^{-6}$ K^{-1} from 20 – 1000 °C) [7] is similar to that of Al_2O_3 indicating a low thermal mismatch between both materials. This allows mixing of both materials in any ratio technically required. For calcium hexaluminate based mixes with micro silica addition in the matrix, the stable phase composition is mullite-anorthite-cristobalite with first melt formation at 1345 °C [6]. This has to be taken into consideration when designing recipes for applications where a high thermal stability

*Marion Schnabel, Andreas Buhr,
Gunter Büchel, Rainer Kockegey-Lorenz,
Jerry Dutton*
Almatis GmbH
60 528 Frankfurt
Germany

Corresponding author: *M. Schnabel*
E-mail: Marion.Schnabel@almatis.com

Keywords: calcium hexaluminate, corrosion, insulation

Tab. 2 Typical synthesis gas composition

Pressure	Temperature	Gas composition [vol.-%]				
[hPa]	[°C]	H_2	CH_4	CO	CO_2	H_2O_{steam}
30 500	700 – 800	36,52	6,24	4,86	6,18	46,10

> 1350 °C is required. However, the fact that CA6 creates liquid phases at lower temperatures can also be used to formulate refractory products with a self-coating effect that reduces further penetration of corrosive media or to increase the elasto-plastic behaviour of a high alumina formulation.

3 Specific advantages of CA6 in selected application areas

3.1 Stability in H_2 / CO atmosphere

Various industrial processes operate under atmospheres that require special attention when selecting the right refractory lining material for a particular plant. In parts of the chemical and hydrocarbon processing industry, for example, steam reformers which are used to produce the required process gases from natural gas, the refractory material is in direct contact with the synthesis gases at high temperatures up to 1400 °C under extreme hydrogen and carbon monoxide conditions [8].

Also industrial furnaces, used for the treatment of metals or the sintering of metals and ceramics, are increasingly operating under inert gas atmospheres (H_2/N_2) demanding optimised refractory linings [9]. Reducing atmospheres can also be found in combustion processes for heat generation e.g. boilers with circulating fluidised beds (CFBs) [10].

3.1.1 Hydrogen attack

At temperatures > 1200 °C oxides with lower stability such as SiO_2, either as tridymite, cristobalite or in silicate form, react with hydrogen according to the following reaction:

$$SiO_{2\,(s)} + H_{2\,(g)} \longleftrightarrow SiO_{(g)} + H_2O_{(g)} \qquad [11]$$
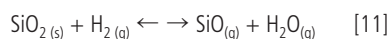
The extraction of silica weakens the refractory materials by reducing their strength and may cause premature lining failures. Furthermore the gaseous SiO can be carried downstream in the process where it will condense in areas of lower temperature leading to potential fouling in heat exchangers or contamination of the product. [12]

3.1.2 CO-resistance

Recent studies carried out at the *Research Association for Refractories (FGF)* in Bonn/DE describe the catalytic carbon deposition in refractory materials under a CO atmosphere. Metallic iron, hematite or magnetite act as catalytic reactive particles leading to carbon deposits in the lining following the Boudouard balance reaction $2\,CO \longleftrightarrow CO_2 + C$.

The catalytic reaction follows a vapour-liquid-solid mechanism where the carbon is absorbed in a liquid iron droplet until saturation. Thereafter the carbon is segregated on the surface of the droplet in at least two different types of structures: So called "bucky onions" decreasing the total growing rate and carbon nanotubes, which encourages further carbon deposition [13]. The destructive effect of these carbon structures depends on the predominant carbon modification with nanotubes being the much more critical form. Although the detailed wear mechanism of carbon disintegration is still under discussion a selection of appropriate refractory materials, especially with regard to low iron content will result in a high resistance in CO-bearing atmosphere. Because of the requirement for low silica and low iron content, only high purity refractory raw materials such as tabular alumina or premium grade white fused alumina are suitable aggregates for the formulation of dense castables or bricks. Insulating materials contain either bubble alumina or calcined alumina in the case of high purity firebricks.

Calcium hexaluminate is an interesting alternative due to its purity combined with its low thermal conductivity when compared with typically used raw materials.

In the frame of a German public sponsored development project [14], extensive calculations of the thermochemical stability of calcium hexaluminate were performed considering an atmosphere typical for petrochemical applications (Tab. 2).

It was concluded, that under a reducing atmosphere, calcium aluminate phases are stable over the entire temperature range. In the presence of water vapour and with increasing pressure the stability ranges of the CA phases do not change above 700 °C. Below 700 °C, only slight phase transformations result in equilibrium conditions [15]. In another project, the CO-resistance acc. ASTM C288-87 of a medium weight castable, (32 vol.-% porosity) based on dense calcium hexaluminate was tested and rated class A (highest resistance class) after pre-firing at 540 °C [3].

SLA 92 as an aggregate for insulating materials is of special interest because of its very low thermal conductivity in these mixes when compared to bubble alumina containing castables (Fig.1).
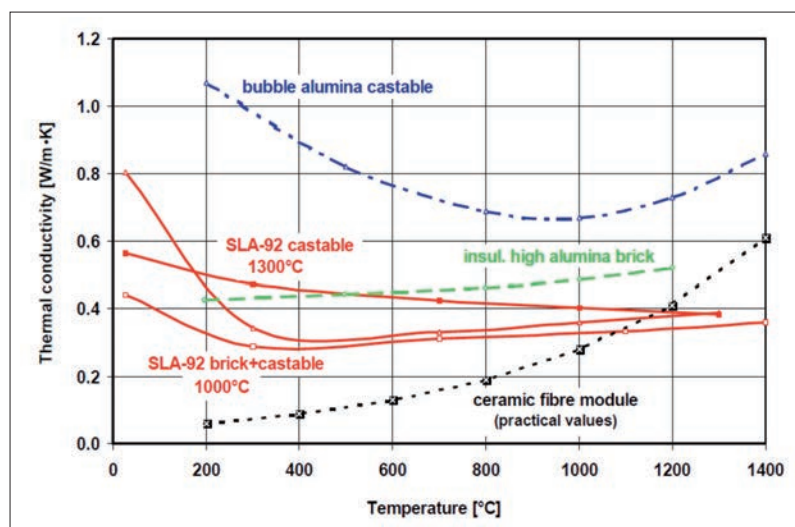

Fig. 1 Thermal conductivity of high temperature insulating materials

The improved insulation behaviour is pronounced at elevated temperatures where the thermal conductivity is dominated by radiation. Here, the micro porosity of SLA 92 shows a clear benefit compared to the big pores in bubble alumina grains. Furthermore the SLA 92 based castables are easier to handle and gunning mixes show significantly lower rebound due to the better embedding of the SLA 92 grains in the matrix.

3. 2 Resistance against alkali attack

Many high temperature applications such as cement kilns, incinerators, blast furnaces, gasifiers and glass furnaces face corrosion by alkalis. These can be in either vapour form or the corrosion can occur by direct contact with alkali rich melts or slags.

Although in literature it is often referred to as alkali corrosion in general, in reality the situation is more complex, since the corrosive compounds and the process temperatures vary depending on the application. Alkali sulphates are the typical salts found in cement plants, whereas carbonates are more prominent in CFBs and gasifiers. The burning of municipal waste, either in incinerators or its use as a secondary fuel in cement kilns leads to increased emission of chlorides and heavy metals such as zinc or lead. This further increases the corrosive potential due to formation of eutectic compounds with very low melting points (Tab. 3).

Dependent upon the alkali compounds and temperature in a given application, the destructive corrosion progresses with varying speeds but follows a similar mechanism.

At a temperature near the boiling point of the salt mixtures, the alkalis will be vapours.

Tab. 3 Melting and boiling points of typical corrosive compounds [16, 30]

	Melting point (MP) [°C]	Boiling point [°C]
NaCl	801	1461
KCl	772	1500
$CaCl_2$ (H_2O free)	782	>1600
Na_2SO_4	888	Decomposition at MP
K_2SO_4	1069	1689
$CaSO_4$	700	Decomposition at MP
K_2CO_3	891	Decomposition at MP
Na_2CO_3	851	Decomposition at MP
$ZnSO_4$	>680	Decomposition at MP
$FeCl_2$ (H_2O free)	674	1026

Melting point of typical salt mixtures [°C]	
Na_2SO_4 + Zn_2SO_4 (eutectic)	472
NaCl + $CaCl_2$ (49 % : 51 %)	500
NaCl + $FeCl_2$ (25 %: 75 %)	156

Initially the gaseous compounds diffuse into the refractory lining at a rate determined by the porosity and permeability of the material. In lining areas with lower temperatures the salts condense and recrystallize, densifying the porous structure of the refractory. Differences in the E-modulus of the original and densified material will lead to structural spalling when the temperature changes (Fig. 2).

The often quoted mechanism of "alkali bursting" is related to the reaction of the alkali compounds with the refractory material. New mineral phases within the $Na_2O/K_2O-Al_2O_3-SiO_2$ system are formed. The density of the reaction products is lower than the original phases in the refractories. This leads to considerable volume expansion. Corundum reacts with alkalis to form "ß-alumina" ($K_2O\cdot11\,Al_2O_3$ or $Na_2O\cdot11\,Al_2O_3$) giving expansions of 26,4 % for KA11 and 29,6 % for NA11. Andalusite and mullite form low density alkali silicate phases such as kalsilite or nepheline ($NaAlSiO_4$). The stresses induced by the expansion of the refractory material ultimately lead to cracking and spalling of the lining. The mechanism of alkali bursting is discussed more in detail by [17] and [3]. In areas where the refractory lining material is in direct contact with an alkali rich melt the solubility of the refractory compound in the melt is the most important criteria. In practice all corrosion mechanisms are often present in different zones of a unit or throughout the thickness of the refractory lining. The

Fig. 2 Spalling of incinerator lining due to alkali corrosion [16]
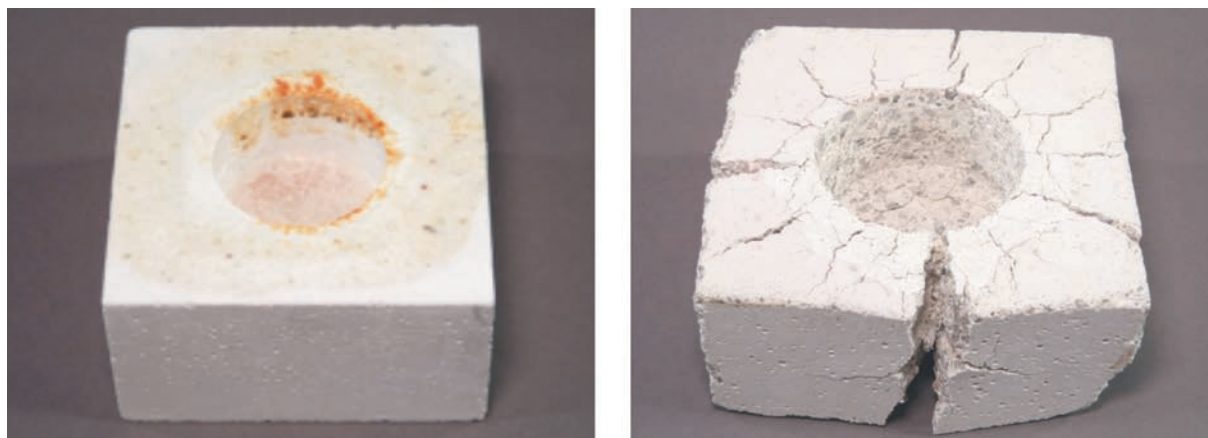
Fig. 3 Test cups after corrosion test with K_2CO_3 (left: Bonite, right: andalusite)

knowledge of the prevailing corrosion mechanism in a given application will define the concept used by the refractory materials developer to improve the alkali resistance.

For dense high alumina refractories the alkali resistance can be improved by addition of silicon carbide to the refractory formulation. The protective mechanism is described by *Poirier et al.* as a protective silica layer formed by the oxidation of SiC limiting the diffusion of gaseous compounds [18]. However, in practice, controlling the SiC oxidation to the right level is difficult. Unfavourable conditions such as increased temperatures, thermal cycling, water vapour or inconsistency of the corrosive compositions could accelerate the SiC oxidation leading to too much melt formation, resulting in damage to the lining. It could also lead to increased sticking of fly ash or clinker to the lining. The high thermal conductivity of SiC mixes is another potential drawback. This is an advantage in boilers or incinerators with power generation. However, in other applications, e.g. cement plants, the higher conductivity leads to increased energy loss when compared to pure alumina linings if no counteraction is taken. Bonite and SLA 92 are available as potential alternatives with high alkali resistance together with low thermal conductivity. The resistance of calcium hexaluminate to alkalis originates from the mineralogical structure of CA_6. Calcium hexaluminate has a crystal structure similar to "ß-alumina" (KA11 or NA11). Large cations Ca^{2+} are incorporated between the planar alumina layers (spinel structure type with vacant positions). In these layers alkalis (Na^+, K^+) can be incorporated without significant change of volume. Therefore, calcium hexaluminate

based refractories show much higher volume stability when under alkali attack compared to other high alumina refractories (Fig. 3). Thermochemical calculations have shown that in high alkali conditions and with increasing temperature, hibonite may form ß-alumina. This was shown by a corrosion test of microporous CA_6 (SLA 92) conducted at 1250 °C with K_2CO_3. It was confirmed that small amounts of hibonite decomposed and ß-alumina and CA_2 were formed, but with little crack formation in the cups. [3]. This was explained by the fact that in calcium hexaluminate refractories, the formation of KA11 and NA11 does not lead to a new crystal structure, as CA_6 belongs to the same family of crystal structures. [4].

At a project undertaken at the *Oak Ridge National Laboratory,* corrosion studies of various refractories were carried out to select the best suited material for back linings in black liquor gasifiers. The corrosive media cannot be fully blocked by the wear lining refractories. Therefore an alkali resistant back lining material is required to guarantee stability of the whole lining. The test materials were suspended in a molten mixture of sodium sulphide, sodium sulphate, and sodium carbonate at 1000 °C for 50 or 100 h. It was concluded that an alternative refractory material based on calcium hexaluminate (CA_6) was found to be highly resistant to penetration by the molten mixture and showed minimal expansion [19]. A similar situation can be found in the crown of glass furnaces. Insulating mixes based on alkali tolerant calcium hexaluminate were proposed by *Windle et al.* as the insulation layer, especially under oxy-fuel conditions when interfacial temperatures are increasing [20].

3.3 Resistance against metal and metal slag

The containment, handling, and processing of liquid metal are key parts of several metallurgical processes. These include the melting and casting of aluminium alloys.

Although the process temperatures in the aluminium industry are low when compared to iron or steel the requirements of refractory materials for direct contact with aluminium and aluminium alloys are many and various.

The refractory materials in transfer ladles should preserve energy during transport, protect the underlying insulation materials from infiltration by molten metal and protect the steel casing. The chosen lining concept has to guarantee the operating safety, especially for transportation on public roads. In melting furnaces, used to re-melt aluminium alloys or scrap, the refractory materials in the upper structure have to withstand temperatures that can easily exceed 1100 °C. With the use of oxy-fuel burners to increase the melting efficiency the temperatures can even be higher. Alkali salts, such as chlorides and fluorides of sodium and potassium may also be added to reduce oxidation of aluminium by the atmosphere. The refractory lining should resist increased chemical attack by these components. One of the most critical areas in aluminium furnaces is the belly-band area. Refractory materials installed in this zone are exposed to the high temperatures in the upper furnace, having contact to liquid aluminium and salts. Mechanical resistance is also required to withstand charging and cleaning procedures. Because of the low viscosity of aluminum alloys, furnace builders and refractory producers pay special

attention to the design of the furnace linings. By the selection of a multi-layer design with dense, medium-dense and insulating materials the solidification point of the alloy will occur in the wear or safety layer to avoid metal break through.

Refractory linings in contact with aluminium generally require high chemical purity raw materials. Because of its high oxidation potential, molten aluminium will reduce impurities like SiO_2, Fe_2O_3 and TiO_2 to their metallic state. The most common of such reactions is the reduction of silica by aluminium with a very high negative free energy change (Fig. 4). Alumino-silicates such as kyanite and mullite also lead to the formation of corundum, which is the major contributor to refractory damage.

Corundum formation is a major problem in aluminium furnaces and occurs by two commonly accepted processes.

External corundum growth occurs at the triple point junction of the aluminium, refractories and atmosphere. The outward corundum growth is explained by *Allaire*
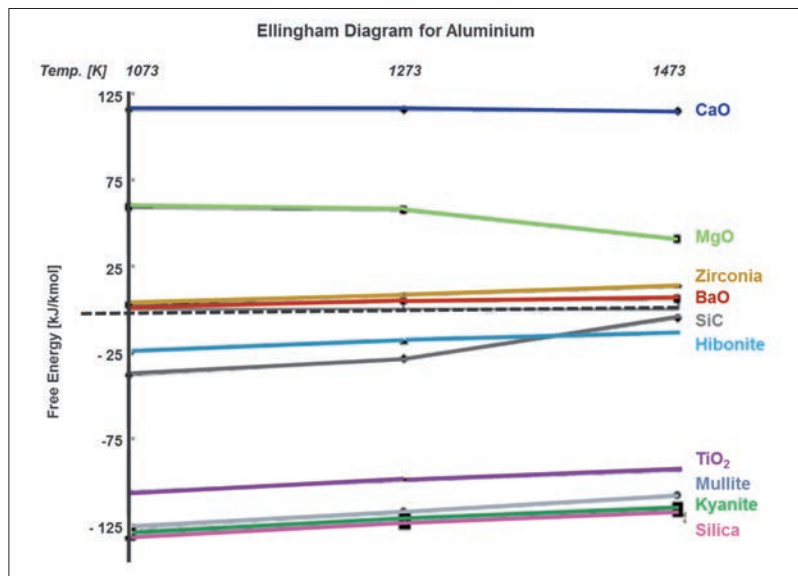
Fig. 4 Free energy of typical minerals used in refractory lining materials for aluminium and aluminium alloys [25]

[21] as direct metal oxidation. Some aluminium penetrates the refractory and moves up into the refractory by capillary action. The penetrated metal is then exposed to an open atmosphere, where it oxidizes to form more corundum. If magnesium is present, the "mushroom" growth is accelerated. Presence of fluxing agents and salts also en-

hances corundum growth. This corundum build-up reduces the furnace capacity causing frequent downtime of production lines, and severely reduces energy efficiency.

The internal corundum growth process is explained as an oxido-reduction mechanism. The corrosion of the refractory first leads to the formation of an Al_2O_3/Al composite. The formation of this composite is favoured at higher temperatures and lower oxygen partial pressure. At low temperatures, silica reduction is considered to be the rate-controlling process and is more favoured in the presence of magnesium. At high temperatures metal penetration is considered to be the rate-controlling process [21].

Internal corundum growth causes extreme damage to the refractory wall over time. This is due to stresses created by the alumina surface concretion and creation of porosity inside the castable structure. There is also a corresponding difference in thermal expansion behaviour, which leads to mechanical damage during thermal cycling. Furthermore, the thermal efficiency of the lining is reduced leading to greater heat losses and less heat retained in the process.

Classical refractories used so far in the aluminium industry are high alumina materials based on alumino-silicate or bauxite refractory aggregates. Often, additives like $BaSO_4$, CaF_2, SiC or phosphate are added to improve the resistance against molten metal or slag.

The function of the non-wetting additives is still not fully understood. *Aguilar-Santillan* [22] concluded that the non-wetting theory for the improvement of aluminium refractories by $BaSO_4$ additions does not appear to be the correct explanation. *Afshar et al.* postulated that the efficiency of non-wetting additives is in their potential role in converting silica to some alumino-silicate based crystalline phases that are more resistant to aluminium attack [23].

Whatever the mechanism, the practical experience has proven the function of these additives for temperature ranges below 1000 °C. At higher temperatures their efficiency is reduced and corundum formation will appear. But sometimes even at low temperatures corundum formation can be observed. A possible explanation is given by *Richter et al.* [24]. According to their tests the coarse refractory aggregates do not benefit from non-wetting additives and some corrode in contact with aluminium, even enhancing the corrosion of the matrix. As a consequence the development of an optimum non-wetting matrix is only part of the solution to improve the corrosion resistance of refractory materials to molten aluminium. With aggregates based on calcium hexaluminate it is possible to use aluminium resistant fractions throughout the whole product. The high resistance of calcium aluminates against metal and metal slags was already described in the literature [7]. In contact

with aluminium, calcium hexaluminate exhibits a high stability with a significantly lower Gibbs energy for the reaction compared to silica and mullite (Fig. 4).

The advantage of dense calcium hexaluminate based refractories over conventional high alumina refractories containing anti wetting agents such as $BaSO_4$, has already been described in detail in by *Buhr et. al.* In an enhanced aluminium resistance test at the *Corus Research Centre* in Ijmuiden/NL it was demonstrated that the superior resistance of calcium hexaluminate remains at elevated temperatures up to 1400 °C, while conventional bauxite/$BaSO_4$ refractories lose their protective properties [1, 2].

In the frame of a project supported by the *U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy* [26], calcium hexaluminate was tested together with other raw materials such as mullite and SiC as new potential lining material for aluminium furnaces. It was concluded that high-alumina based materials, in particular calcium hexaluminate (Bonite), are superior to traditional bauxite type materials. No metal penetration was observed (Fig. 5).

Another advantage of calcium hexaluminate that was emphasised in this work was the fact that calcium hexaluminate (Bonite), due to its inherent low thermal conductivity, increases the thermal efficiency of a furnace with the same lining thickness when compared to traditional refractory materials.
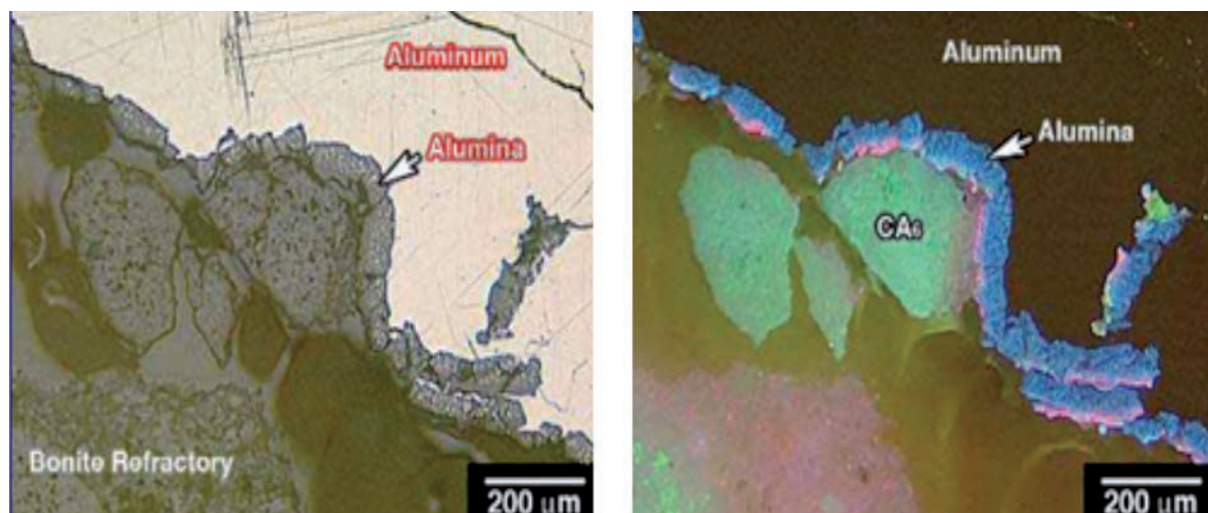
Fig. 5 RL/CL micrographs showing no metal penetration and minimal metal-refractory reaction. (Blue alumina layer is due to oxidation of aluminium, not due to refractory reduction) [25]

This effect could be further optimized by the use of the super lightweight aggregate SLA 92 or combinations of Bonite with SLA 92.

The advantage of the low thermal conductivity of calcium hexaluminate based aggregates in combination with their high resistance against CA-rich steel ladle slags was presented in detail in a previous paper [6].

4 Summary and outlook

Synthetic, calcium hexaluminate based raw materials exhibit various advantages when compared to traditionally used refractory aggregates in a given application:

- high refractoriness
- low thermal conductivity
- stability in H_2/CO atmosphere
- resistance against alkali attack
- resistance against metal and metal slag attack
- fibre free, therefore environmentally friendly.

But, it is the combination of the presented properties that makes calcium hexaluminate aggregates unique as refractory raw materials. The availability of two commercially available products, Bonite as a dense aggregate and SLA 92 as a super lightweight material, allows the developer to create "tailor-made" solutions taking into account density, strength and thermal insulation.

Successful industrial scale applications in the aluminium, glass and cement industry have already shown the potential of dense, calcium hexaluminate based Bonite in new innovative refractories. The light-weight aggregate SLA 92 has been successfully used in steel reheating furnaces significantly improving the energy performance of the units. It has also been used in petrochemical applications. Ceramic kiln linings have also been installed with this insulating material [27–29].

Both aggregates, SLA 92 and Bonite are produced by *Almatis* in Ludwigshafen/DE, which guarantees state-of-the art production processes, high quality and secure supply.

References

[1] Buhr, A.; Büchel, G.; Aroni, J.M.;. Racher, R.P: BONITE – A new raw material alternative for refractory innovations
47. International Colloquium on Refractories, Aachen, Germany (2004) 205–210

[2] Büchel, G; Buhr, A.; Gierisch, D.; Racher, R.P: Alkali- and CO-resistance of dense calcium hexaluminate Bonite
48. International Colloquium on Refractories, Aachen, Germany (2005) 208–214

[3] Kockegey-Lorenz, R.; Buhr, A.; Racher, R.P: Industrial application experience with microporous calcium hexaluminate insulating material SLA-92. 48. International Colloquium on Refractories, Aachen, Germany (2005) 66–70

[4] Garsel D.v.; Gnauck, V.; Kriechbaum,G.W.; Stinneßen, I.; Swansinger, G.; Routschka, G.: New insulating raw material for high temperature Applications
41. International Colloquium on Refractories, Aachen, Germany, 1998, Stahl und Eisen Special, 122–128

[5] Garsel, D.v.; Buhr, A.; Gnauck, V.; Routschka, G.: Long term high temperature stability of microporous calcium hexaluminate based Insulating materials. UNITECR 99, Dresden, Germany, 181–186

[6] Schnabel, M.; Buhr, A.; Garsel, D.v.; Schmidtmeier, D.; Zacherl, D.: Advantages of dense calcium hexaluminate aggregate for back lining in steel ladles. UNITECR 09, San Salvador; Brasil

[7] Criado, E.; de Aza, S.: Calcium hexaluminate as refractory material. UNITECR 91, Aachen, Germany, 403–407

[8] RHI Dinaris GmbH: Brochure "Chemical and hydrocarbon processing"

[9] Rank, J; Melzer, D.; Ullrich, B.; Anneziris, C.: High-temperature heat-insulating in hydrogenous atmospheres, cfi/Ber.DKG 86 (2008) [10] E50–53

[10] DGFS: Technische Unterlagen, 4. Auflage Mai 2011

[11] Hrab,Z. et. al: Einfluss der Zusammensetzung der Ofenatmosphäre auf die Eigenschaftsänderungen von Wärmedämmerzeugnissen Stavivo 64 (1986) [4] 158–160

[12] Crowley, M. S.; Fisher, R. E.: Petroleum and petrochemical applications for refractories alumina chemicals, Science and technology handbook, 471–488

[13] Krause, O.; Pötschke, J.: The predictability of CO resistance of refractory materials by state-of-the-art test methods, Interceram (2008) [3] 176–180

[14] Project No. 0327258 funded by Germany's Federal Ministry of Economics and Labour; BMWA

[15] Overhoff; A.; Buhr; A.; Grass J.; Wuthnow, H.: New microporous material for use in modern firing plants, cfi/Ber.DKG 82 (2005) [8] E29–32

[16] Schnabel, M.; Nielson, C.: Innovative refractory monolithic solutions for incinerators, 48. Inter-

national Colloquium on Refractories, Aachen 2005

[17] Schlegel, E.: Auswertung von Phasendiagrammen hinsichtlich der Alkalikorrosionsbeständigkeit feuerfester Baustoffe Teil 1. Keramische Zeitschrift (2009) [2-3] 94–97

[18] Poirier, J.; Colombel, L.; Prigent, P.: The corrosion mechanism of SiC refractory linings in waste incineration plants and in reactors of biomass gasification; 52. International Colloquium on Refractories, Aachen, Germany (2009) 49–52

[19] Keiser, J.R.; Hemrick G.J.; Gorog, P.; Leary, R.: Final Technical Report "Improved materials for high-temperature black liquor gasification; Oak Ridge National Laboratory; June 2006

[20] Windle, C.J.; Bentley, V.K.: Rebonded magnesia-alumina spinel products for oxy-fuel and alkali saturated atmospheres. UNITECR 99, Berlin, Germany 219–225

[21] Allaire, C: Mechanism of corundum growth in refractories exposed to Al-Mg alloys. Aluminium Transactions (2000) [3] 106–120

[22] Aquilar-Santillan, J.: Wetting of Al_2O_3 by Molten aluminium: The influence of $BaSO_4$ additions. Journal of Nanomaterials (2008) ID 629185

[23] Afshar, S.; Allaire, C.: Protection of alumina silicate aggregates against the corrosion by molten aluminium. 43rd Annual Conference of Metallurgists 2004, Hamilton, Ohio, 279–290

[24] Richter, T.; Vezza, T.; Allaire, C.; Afshar, S.: Castable with improved corrosion resistance against aluminium. 41. International Colloquium on Refractories, Aachen, Germany (1998) 86–90

[25] Karakus, M.; Headrick, W.; Shukla, D.; Bright, M.: Characterization of submerged and metal contact refractory materials for aluminum melting/handling processes. Conference "Materials Science & Technology", 2006, Cincinnati, OH, USA

[26] Multifunctional metallic and refractory materials for energy-efficient handling of molten metals. Award No: DE-FC36-04GO14038

[27] Wuthnow, H.; Pötschke, J.; Buhr, A.; Boßelmann, D.; Gerharz, N.; Golder, P.; Grass, J.: Experiences with microporous calcium hexaluminate insulating materials in steel reheating furnaces at Hoesch Hohenlimburg and Thyssen Krupp Stahl AG Bochum. 47. International Colloquium on Refractories, Aachen, Germany (2004) 198–204

[28] De Wit, T.; Lorenz, W.; Pörzgen, D.; Specht, M.; Buhr, A.: Innovative ceramic fiber free steel ladle preheaters at Corus Steelworks IJmuiden, 44. International Colloquium on Refractories, Aachen, Germany (2001) 108–112

[29] Pörzgen, D.; Heide, W.; Buhr, A.: Innovative refractorysolutions using a new microporous material for kiln cars in the ceramic industry. CN Ceramic News, Special Refractories 7 (2000) [2] 68–70.

[30] GESTIS – Stoffdatenbank ; IFA