

Alkali- and CO-resistance of dense calcium hexaluminate Bonite

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Abstract

Calcium hexaluminate Bonite was introduced as a new synthetic dense refractory aggregate in 2004. Key material properties are high chemical purity, high refractoriness, high thermal shock resistance, and high resistance to corrosion by molten aluminium.

For the current paper further tests with Bonite based castables have been performed, such as alkali-resistance, CO-resistance, and thermal conductivity focusing especially on applications in cement-, glass-, and petrochemical industries.

Introduction

Synthetic alumina based materials are established aggregates for high performance refractories. Tabular alumina (T60/T64) has been used for decades and also sintered alumina rich spinels (AR78/AR90) are known for many years [1, 2]. In combination with fine matrix components like calcined and reactive aluminas, calcium aluminate cements, and dispersing aluminas high performance refractory castables can be formulated. Recently, Bonite has been introduced as a new synthetic aggregate based on calcium hexaluminate [3]. It is described as a high purity dense aggregate with high temperature- and thermo shock resistance, and low thermal conductivity. In the meantime, the advantage of Bonite is already proved in various applications in the aluminium industry. The potential of Bonite based refractories in the aluminium, cement and petrochemical industries will be discussed in the following.

Aluminium Industry

The bottom of electrolytic reduction cells is lined with carbon blocks, which act as cathode for electrolytic reduction. To maintain the heat balance of the pot, castables or brick blocks that have low thermal conductivity are used as back-up of the cathode carbon. These materials should also protect the steel shell from penetration of aluminium and liquid cryolite and should have high chemical resistance to fluoride attack, thermal stability, and mechanical strength. Also the refractory materials in transfer ladles should preserve energy during operation, protect the underlying insulation materials from infiltration by molten metal and protect the steel casting from high temperatures and molten metal. Bonite could potentially be used as a combined safety – and insulating lining as it exhibits low thermal conductivity and high wear resistance.

Melting furnaces are used to melt scrap or recycled aluminium which requires a high heat input. Thus, the roof temperature can exceed 1100 °C. Alkali salts, such as chlorides and fluorides of Na and K may also be added as fluxes. These fluxes are used to remove oxide layer and impurities from the scrap and to protect the aluminium alloy from further oxidation. The refractory lining should resist increased chemical attack of these components and also oil coming from recycling of aluminium scraps. During charging of the melting furnaces, high mechanical strength of the lining is required as well as high thermal shock resistance. Holding furnaces receive molten metal either from primary production potlines or from melting furnaces and therefore operate at lower temperatures around 900 °C.

Refractory linings in aluminium furnaces generally require high chemical purity raw materials, since impurities like SiO₂, Fe₂O₃ or TiO₂ can be reduced by molten aluminium or alloy elements to their metallic state and contaminate the alloy. During the reaction, tremendous tension and subsequent cracking in the lining appear due to the change in molecular volume [4, 5]. In addition, layers of corundum (Al₂O₃) are built upon refractory lining of melting or holding furnaces, which is a major problem of aluminium furnaces.

The advantage of Bonite based refractories over conventional high alumina refractories containing anti wetting agents like BaSO₄ has already been demonstrated in an enhanced aluminium resistance test [3]. With focus on application in aluminium melting furnaces and transport ladles it was also shown that the low wettability of Bonite remains at elevated temperatures up to 1400 °C, while conventional bauxite/BaSO₄ refractories may lose their anti-wetting properties under these conditions. Further test of Bonite refractories with respect to alkaline resistance in the aluminium industry will be described and discussed in this paper.

Cement Industry

In a recent publication, Klischat reviews different lining concepts for cement rotary kilns [6]. He states, that for the lining of cement rotary kilns fireclay, high alumina products, or basic materials are used as bricks or unshaped monolithics, depending on the prevailing operating conditions. Fireclay products with 10–45% Al₂O₃ and 50–80% SiO₂ have low refractoriness but high alkali resistance. Alkali resistance is important due to the increasing use of so-called

secondary or alternative fuels. Reviewing publications of various cement producers, secondary fuels could be wood, paper, textile fibre, but also used tyres, sewage sludge or used oil. Klischat states that high alumina products with 45–55% Al_2O_3 , in contrary, have a higher refractoriness but a lower alkaline resistance. High alumina products based on bauxite or mullite (> 70% Al_2O_3) are only used in areas with high abrasive load.

Depending on the alkali and temperature load, alumina enriched fireclay bricks are used in the safety zone often containing additives like silicon carbide for increased alkaline resistance. The kiln outlet is lined with bauxite bricks showing a high abrasion resistance and a high hot strength. In case of increased thermal and abrasion loads high alumina castable of approx 95% Al_2O_3 are recommended. Due to the required abrasion resistance, also the kiln hood and the burner pipe are lined with high alumina linings based on alumina enriched fireclay or andalusite. The alkali resistance of high alumina refractories can be improved by addition of silicon carbide to the refractory formulation. Now the new Bonite aggregate is available as a potential alternative with a high alkali resistance and high refractoriness.

Basic materials based on magnesia and dolomites are able to withstand high thermal and chemical loads. Magnesia containing bricks are compatible to the clinker compound formed during raw meal firing. However, disadvantages of basic linings are high thermal expansion (TE), low thermal shock resistance (TSR), and high thermal conductivity (TC) which results in a limited application area. To overcome these disadvantages, magnesium aluminate (MA) spinels or the new Bonite can be used. Combined with spinel, thermal shock resistance and coating ability are improved and thermal expansion is reduced. These materials are used in the upper transition, the sintering, and the lower transition zone.

The application of Bonite in cement linings is of high interest, since it combines important properties like alkaline resistance with high thermal shock resistance, high abrasion resistance and low thermal conductivity. Bonite is currently tested in several zones, e.g. kiln outlet and burner lances and is already tested in basic brick as an exchange for MA-spinel [7].

Petrochemical Industry

Petrochemical applications with direct contact of the refractory lining to the process atmosphere are hydrogen reformers and gasifiers, which are operating with reducing gases containing hydrogen and carbon monoxide. Process conditions are pressures around 25 bar and temperatures in the range of 950–1100 °C. Additionally, catalyst crackers (fluid catalytic cracking units = “cat crackers”), ethylene furnaces, pressurized fluid bed boilers, and transfer lines can be listed as demanding refractory applications [8].

Important requirements of petrochemical applications are the stability of the refractory oxides against reduction, resistance against CO attack, and abrasion resistance due to the high velocities of catalyst bearing gas streams in the vessels. Oxides with lower stability like SiO_2 can be reduced by the process gases to gaseous SiO, which afterwards condenses in heat exchangers (“fouling”) and reduces the efficiency of this unit. Due to the SiO_2 decomposition the strength of the refractory lining decreases and the porosity increases. Hydrogen attack on refractories is discussed in more detail by Tassot et al. [8].

According to the Boudouard equilibrium $2\text{CO} = \text{CO}_2 + \text{C}$, carbon monoxide can disintegrate in the temperature range around 500 °C and lead to a carbon build up within the refractory structure, destroying it from the inside. Free iron or iron oxide impurities in the refractory material are necessary as catalysts for the reaction. This

Tab. 1. Typical data of Bonite

Chemical Analysis		Bonite
Al_2O_3 (*)	%	90
CaO	%	8.5
Fe_2O_3	%	0.09
SiO_2	%	0.9
Fe_{met}	%	0.01
Physical Properties		
Bulk Density	g/cm^3	3.0
Apparent Porosity	%	8.5
Water Absorption	%	2.7

(*) By difference

phenomena is discussed in detail by Bartha and Köhne [9] and Tassot et al. [8], including calibrations of pressures build up by the carbon deposition and dependency of the reaction on temperature and gas atmosphere composition and pressure. The CO resistance of refractories is currently under investigation by DIFK, Bonn, with several industry partners.

To achieve the desired hydrogen and carbon monoxide resistance, appropriate refractory materials must be selected. Low content of SiO_2 and metallic iron from crushing results in a high resistance against CO attack [10, 11]. Bonite, for example, is suitable for applications in petrochemical industry since it has a high chemical purity and contains only low amounts of SiO_2 (0.9%) and iron from crushing (typically 10–50 ppm, max. 200 ppm). Bonite based refractories have also a high strength over the entire temperature range: cold crushing strength (CCS): 89 MPa (110 °C) and 233 MPa (1500 °C); cold modulus of rupture (CMoR): 15 MPa (110 °C) and 47 MPa (1500 °C) and they have a high thermal shock resistance [3].

Bonite material properties

Bonite is a synthetic dense aggregate produced in a sinter process. It is composed of about 90% calcium hexaluminate (CA_6) and only minor content of corundum, and traces of calcium dialuminate (CA_2). Bonite contains around 90% Al_2O_3 , 8.5% CaO, less than 0.9% SiO_2 , and only traces of other impurities like metallic iron (<0.02%) (see Table 1). It has a bulk density of 3.0 g/cm^3 (around 90% of the theoretical density of CA_6), a low apparent porosity (8.5%) and allow water absorption (2.7%). The thermal expansion coefficient of CA_6 ($8.0 \times 10^{-6} \text{ K}^{-1}$ from 20–1000 °C) is similar to that of Al_2O_3 [12]. Bonite material properties and the low wettability of Bonite by molten aluminium have been discussed in detail in a previous paper [3].

Bonite refractory properties

Properties of Bonite based refractories are demonstrated by a vibration castable (BON) and compared to either a conventional tabular vibration castable (TAB) and an andalusite vibration castable (AND). Castable details are given in Table 2.

The vibration flow of the castables was determined with a cone test (lower \varnothing 100 mm, upper \varnothing 70 mm, height 50 mm; vibration time: 30 s with amplitude of 0.5 mm). From all castables test pieces have been prepared and tested according to the European standard ENV 1402 “Unshaped refractory products”, Part 5 and Part 6. The hot modulus of rupture (HMoR), bulk density, open porosity and thermal conductivity were tested by DIFK, Bonn, Germany. Further details on sample preparation are described in a previous paper [13].

The Bonite and tabular test castables have been set up to achieve a comparable open porosity level for the alkali resistance tests (see Table 3). The andalusite low cement test castable has a lower water

Tab. 2. Castable composition

Component \ Type			Bonite	Tabular	Andalusite
			BON	TAB	AND
Coarse Fraction (0.5–6 mm)	Bonite	%	55		
	Tabular T60/T64	%		56	
Fine Fraction (0–0.5 mm)	Andalusite	%			58
	Bonite	%	15		
	Tabular T60/T64	%		17	
	Bonite -45 MY	%	5		
	Bonite -20 MY	%	7		
T60/T64 -45 MY	%		7		
Andalusite	%			17	
Kerphalite (0–0.16 mm)	%			7	
Reactive Alumina	CL 370	%	13		13
Cement	CA-14 M	%	5		5
	CA-25 C	%		20	
Dispersing Aluminas	ADS 3	%	0.75	–	0.75
	ADW 1	%	0.25	–	0.25
Water		%	7.0–7.5	7.5	5.4–5.6

Tab. 3. Castable data

Type		Bonite BON	Tabular TAB	Andalusite AND
VIB Flow [cm]	10 min	20.5	20.8	17.8
	30 min	20.6	20.0	17.8
	60 min	20.5	18.8	17.6
Bulk Density [g/cm ³]	110 °C / 24h	2.87	2.95	2.67
	1000 °C / 5h	2.82	2.82	2.65
	1500 °C / 5h	2.74	2.80	2.58
Apparent Porosity [vol.-%]	1000 °C / 5h	21.5	23.7	18.7
CMOR [MPa]	110 °C / 24h	15	11	6
	400 °C / 5h	10	13	5
	1000 °C / 5h	9	13	2
	1500 °C / 5h	47	18	16
CCS [MPa]	110 °C / 24h	89	70	24
	400 °C / 5h	103	78	35
	1000 °C / 5h	55	73	24
	1500 °C / 5h	233	58	126
PLC [%]	110 °C / 24h	– 0.02	± 0	± 0
	400 °C / 5h	– 0.02	+ 0.10	+0.06
	1000 °C / 5h	– 0.03	– 0.02	+0.25
	1500 °C / 5h	+ 0.82	– 0.10	+1.00
HMoR [MPa]	800 °C	9	n.d.	n.d.
	1200 °C	6	n.d.	n.d.

demand and therefore has a lower open porosity after pre-firing at 1000 °C. The EXO start of Bonite castable, which is an indication for the working time, was set to around 2 hours and can be easily adjusted within a wide range by changing the dispersing alumina ADS 3/ADW 1 ratio [13].

The mechanical strength of the Bonite test castable is considered to be sufficient over the entire temperature range, e.g. at 1000 °C: CCS 55 MPa and CMoR 9 MPa. The density at 1000 °C is 2.82 g/cm³ and the apparent porosity is 21.5%. Bonite castables show only a slight permanent linear change at 1500 °C pre-firing. The refractoriness under load (0.2 MPa) of the Bonite castable (pre-fired 1000 °C) shows a maximum expansion of 0.84% at 1192 °C, a T1 of 1578 °C, and a T2 of 1630 °C, for details see [3]. Physical properties of the test castables are compiled in **Table 3**.

Alkaline resistance test

Alkaline resistance of Bonite was tested in established industry tests with two different salt compositions.

Focus aluminium industry

In aluminium melting furnaces or transport ladles, alkaline salts such as chlorides or fluorides of Na and K interact with the refractory lining. To simulate these conditions, a crucible of 80 × 80 × 80 mm with a cover from test material is pre-fired at 1000 °C. The hole (Ø 54 mm, 45 mm deep) is filled with an aluminium alloy AZ8GU (Mg/Zn containing) which is covered with a mixed salt composed of 45% NaCl, 45% KCl and 10% NaF. The test crucible is treated at 950 °C for 72 hours.

Bonite shows neither infiltration nor reaction with aluminium, and also no visible

reaction with the salt mix (**Figure 1**). Although some alkali infiltration can be detected (**Figure 2**), this infiltration leads neither to the formation of cracks nor to damage of the test crucible. This test confirms the high aluminium resistance of previous investigations [3] and demonstrates a high resistance also against alkali salts in aluminium production.

Focus cement industry

The refractory lining in cement kilns is exposed to high chemical attack by alkalies and, depending of the lining area, to temperature and abrasion attack. So far lining concepts were a compromise of alkaline resistance (basic materials), refractoriness, and abrasion re-



Fig. 1. Bonite test crucible after aluminium plus alkali salt resistance test (aluminium alloy AZ8GU, 45% KCl, 45% NaCl, 10% NaF)

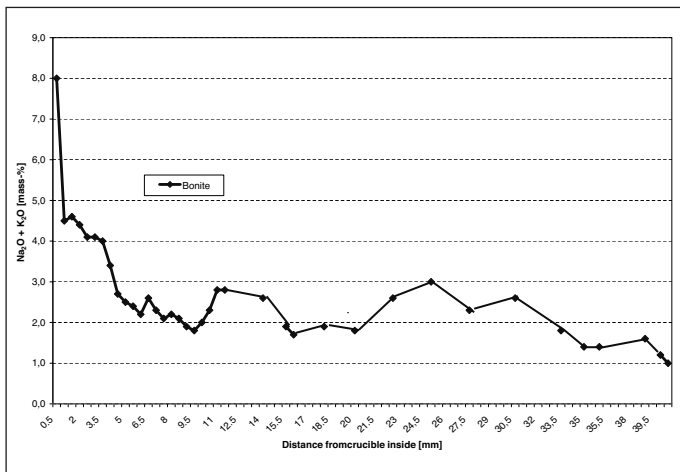


Fig. 2. Alkali infiltration in Bonite test crucible after aluminium alloy (AZ8GU) plus mixed salt (45% KCl, 45% NaCl, 10% NaF) resistance test (by energy dispersive x-ray, EDX)

sistance (corundum based materials). To test Bonite with focus application in cement kilns, three castables based on Bonite (BON), tabular (TAB), and andalusite (AND) have been compared. A crucible of 70 × 70 × 70 mm with a cover from test material is pre-fired at 1000 °C. The hole (Ø 50 mm, 45 mm deep) is filled with K₂CO₃, and the test crucible is treated for 5 hours at 1100 °C.

Figure 3 a-c shows the test crucible after exposing to K₂CO₃. The tabular test crucible is cracked and about 11–12 mm infiltrated by the salt, and the andalusite test crucible is fully infiltrated (>20 mm) and destroyed. The Bonite test crucible shows almost no visible infiltration (4–5 mm) which indicates its alkaline resistance. The alkaline infiltration has been monitored by semi-quantitative SEM-EDX (see Figure 4). The tabular test sample showed up to a depth of 11–12 mm a K₂O content of about 20% and afterwards a steep decrease to < 1%. The andalusite test piece was totally infiltrated by the salt indicated by a K₂O concentration which drops only at above 20 mm from almost 50% to 3%. The Bonite test sample, shows already at 4.5 mm a drop of K₂O from around 50% to < 1%.

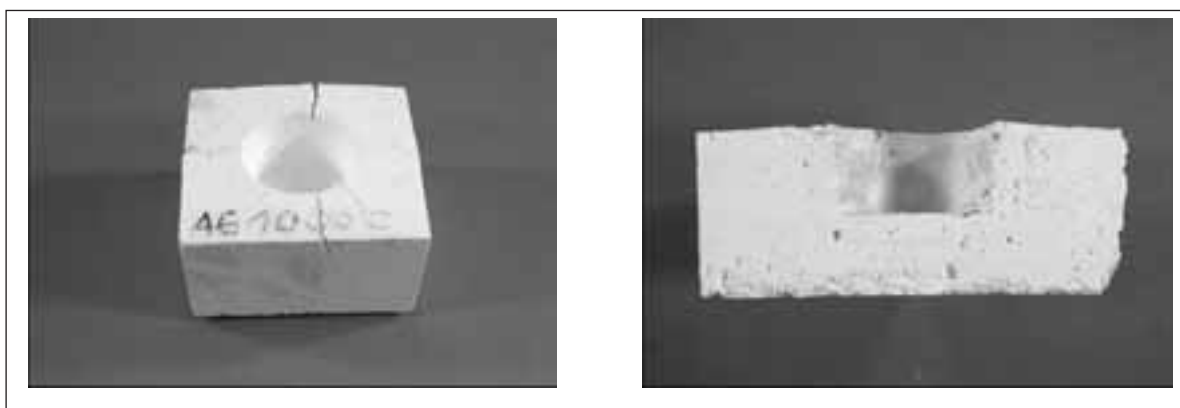


Fig. 3a. Tabular crucible after K₂CO₃ resistance test

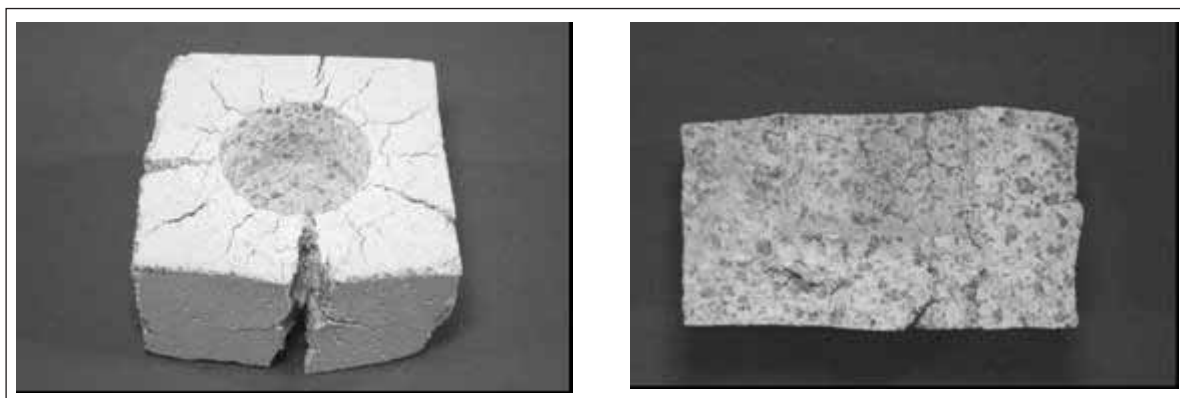


Fig. 3b. Andalusite crucible after K₂CO₃ resistance test

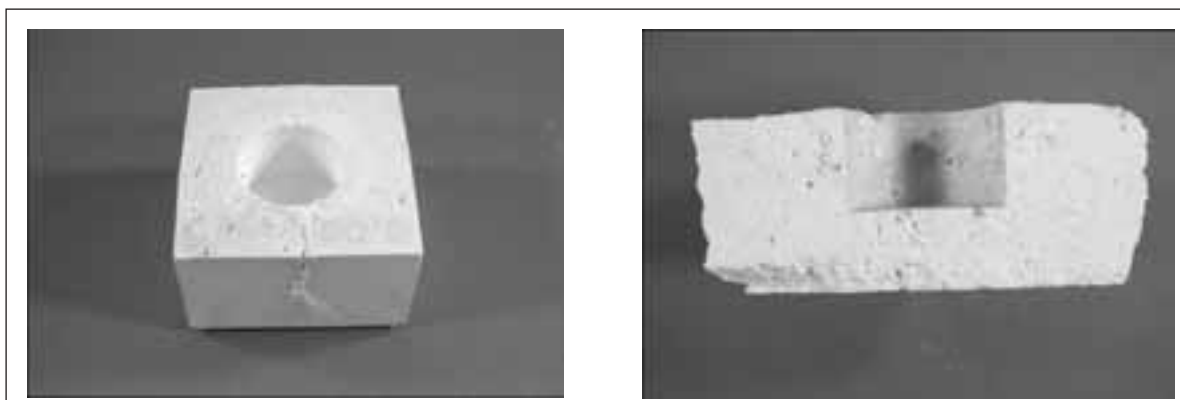


Fig. 3c. Bonite crucible after K₂CO₃ resistance test

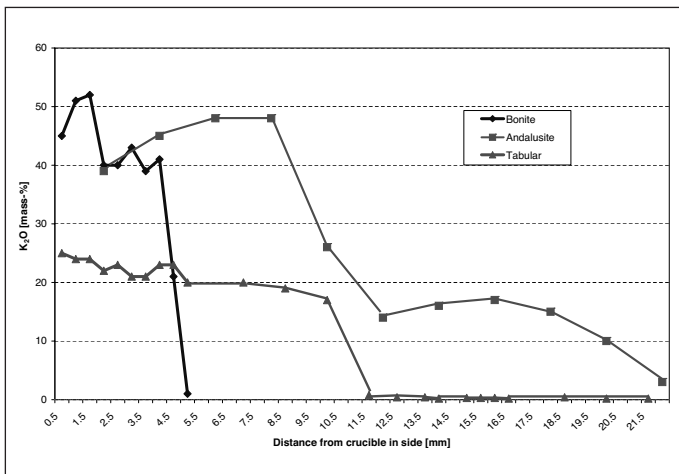


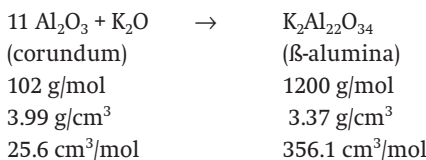
Fig. 4. Infiltration of K₂O from K₂CO₃ into refractory material

The phase compositions of the infiltrated areas have been analyzed by x-ray diffraction. The following main phases were formed by reaction of potassium-oxide with the corresponding refractory material:

- Tabular: “β-alumina” (K₂Al₂₂O₃₄ = KA₁₁), and KAlO₂ = KA,
- Andalusite: kalsilite (KAlSiO₄) and corundum
- Bonite: “β-alumina” (K₂Al₂₂O₃₄ = KA₁₁).

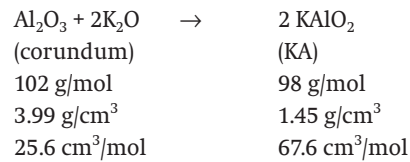
The density of the reaction products is lower compared to the original phases in the refractories which lead to remarkable volume expansions. These expansions can destroy refractories and alkali resistant materials show only minor expansions. The theoretical volume increase of the alkali reactions observed in this investigation has been calculated.

The formation of “β-alumina” KA₁₁ takes place according to



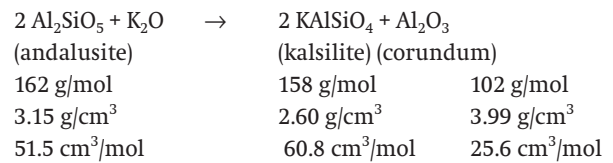
With $\Delta V = 1/11 V_{\beta\text{-alumina}} - V_{\text{corundum}}$ a volume increase of +26.4% is calculated [14] which could lead to crack formation by reaction of tabular based refractories with alkali.

The formation of KAlO₂ (= KA) is accompanied by a tremendous volume increase:



With $\Delta V = 2 V_{\text{KA}} - V_{\text{corundum}}$ a volume expansion of +428% is calculated.

Andalusite based refractories form kalsilite and corundum:



With $\Delta V = 2 V_{\text{kalsilite}} + V_{\text{corundum}} - 2 V_{\text{andalusite}}$ a volume expansion of +85.8% is calculated.

In Bonite refractories, the formation of KA₁₁ and NA₁₁ does not lead to a new crystal structure, since CA₆ has the same structure. Since the specific density of CA₆ (3.38 g/cm³) is similar to KA₁₁ (3.37 g/cm³) and NA₁₁ (3.25 g/cm³) no low density phases are formed and therefore only little expansion takes place. This results in a much lower expansion and crack formation of Bonite refractories. The infiltration of alkalis into the test pieces is also accompanied in a densification with decrease of apparent porosity (see Table 4).

The high infiltration resistance of Bonite to alkalis is caused by the mineralogical structure of CA₆. Calcium hexaluminate has a crystal structure similar to “β-alumina” (KA₁₁ or NA₁₁). Between the planar alumina layers (spinel structure type with vacant positions) large cations Ca²⁺ are incorporated and in these layers also alkalis (Na⁺, K⁺) can be incorporated without volume change. Therefore, Bonite based refractories show much higher volume stability under alkali attack compared to other high alumina refractories. Corundum, in contrary, forms by reaction with alkalis “β-alumina” (KA₁₁ or NA₁₁) which is associated with an expansion of 26.4% for KA₁₁ and 29.6% for NA₁₁. Andalusite and also mullite form low density alkali silicate phases like kalsilite or nepheline (NaAlSiO₄) with remarkable volume expansions.

Table 4. Data of the infiltrated zone (K₂CO₃ resistance test)

Focus Cement (K ₂ CO ₃)	Sample	Bonite BON	Tabular TAB	Andalusite AND
Density [g/cm ³]	Infiltrated	2.69	2.74	2.21
	Not-infiltrated	2.64	2.74	2.54
Apparent porosity [vol.-%]	Infiltrated	10.7	13.7	16.4
	Not-infiltrated	21.5	20.3	18.7
Water absorption [mass.-%]	Infiltrated	4.06	4.99	7.42
	Not-infiltrated	8.00	7.43	7.37
Phase analyses	Infiltrated	Major: hibonite (CA ₆) Minor: KA ₁₁ corundum	Major: corundum Minor: KA ₁₁ KAlO ₂	Major: andalusite Minor: quartz kalsilite KAlSiO ₄ corundum
Infiltration depth [mm]		4-5	11-12	> 20

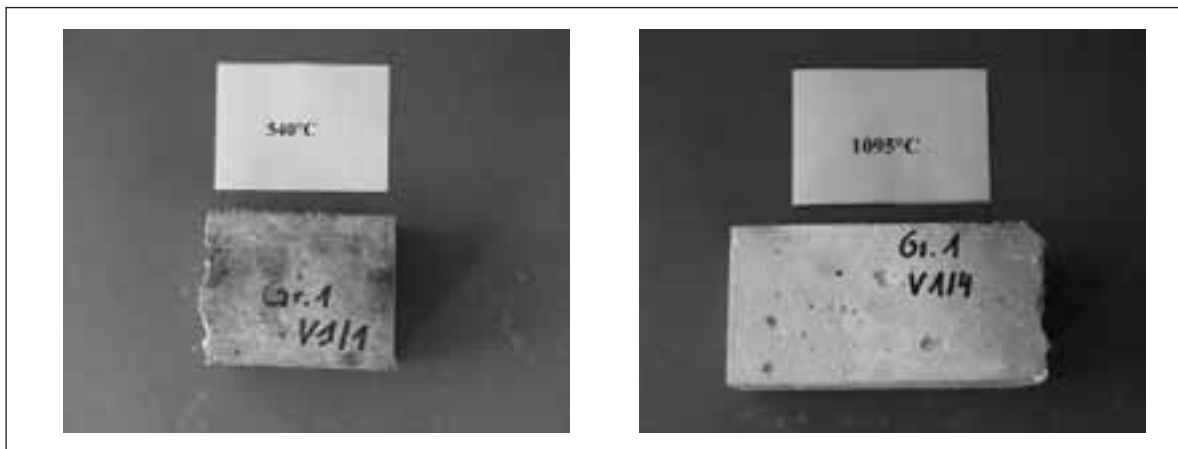


Fig. 5. Bonite test pieces after CO resistance test pre-fired at 540 °C (left) and 1095 °C (right), ASTM C288-87

CO resistance of Bonite

The CO resistance of a Bonite castable was tested at the German Refractory Institute (DIFK)/Bonn according to ASTM C288-87. In contrary to the test described before, a conventional Bonite castable (20% CA-14 M, water demand 12%) with 32% apparent porosity after firing was tested to achieve more severe conditions by the high apparent porosity (32%) of the refractory material. Bars were pre-fired under oxidising conditions for 5 hours at 540 °C and 1095 °C, respectively. The CO treatment was performed in CO atmosphere (>95% CO) at 500 °C/200 hours. Despite of the desired high porosity of 32% at 1095 °C, the Bonite test piece was rated class A (highest resistance class) after pre-firing at 540 °C and class B after pre-firing at 1095 °C (see **Figure 5**). The lower classification of Bonite at 1095 °C pre-heating compared to 540 °C is questionable and the test shall be repeated. As demonstrated in the test, Bonite proves a high CO resistance, which is important especially for petrochemical applications and also for safety and insulating lining applications in general. Here, the critical conditions of CO attack at a temperature range around 500 °C can occur. For petrochemical applications, also the very low silica content is important to withstand hydrogen containing reduction atmospheres as discussed above.

Thermal conductivity

Figure 6 shows the thermal conductivity of high alumina refractories. In spite of the high density, Bonite has a very low thermal conductivity compared to other high alumina refractory materials, even aluminosilicate materials. The thermal conductivity at 1000 °C of Bonite (density 2.85 g/cm³) is only 1.7 W/mK compared to

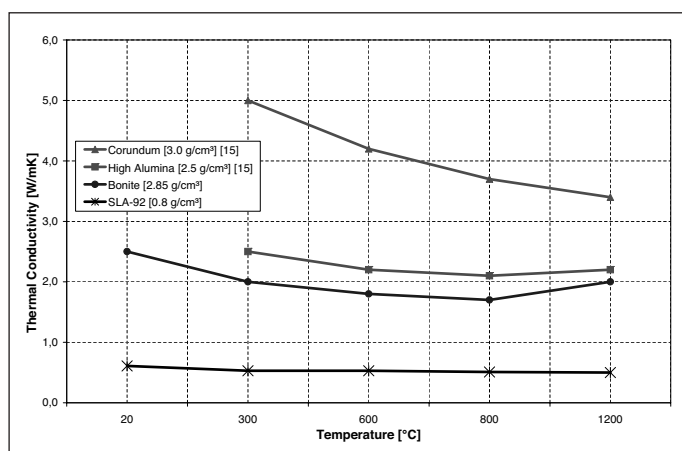


Fig. 6. Thermal conductivity of high alumina refractories (DIFK Bonn, hot wire method, DIN EN 993-15)

aluminosilicate (2.5 g/cm³) at 2.1 W/mK. Of course, the thermal conductivity of the lightweight aggregate SLA-92 is much lower. SLA-92 is already successfully used in aluminium-, petrochemical-, and steel applications [16]. Bonite and SLA-92 have the same chemical and mineralogical composition and can be combined to achieve refractory formulations with intermediate bulk densities and thermal conductivities.

Summary and outlook

Bonite shows high alkali resistance under different conditions, as demonstrated in an aluminium resistance test with alkali salt (45% KCl, 45% NaCl, 10% NaF) and a cement test with K₂CO₃. The Bonite crystal structure can incorporate alkali without forming low density phases. This avoids expansion and the formation of cracks. Bonite enables the formulation of new high alumina refractories which combine refractoriness with high alkali resistance.

The high CO resistance and chemical purity of Bonite is of special interest for petrochemical applications. This applies also for safety and insulating linings in general. The low thermal conductivity and the potential to combine Bonite with the lightweight aggregate SLA-92 could result in a combination of wear resistance with insulation properties, providing refractory materials with a wide range of bulk density from 1.0 to 2.9 g/cm³.

Successful industrial scale applications in the aluminium industry already show the potential of Bonite based new innovative refractories. Tests in other industries like the cement industry are ongoing, and are under consideration for other non ferrous metal applications and for the petrochemical industry. (F 55)

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Resistance of chrome ores to carbon thermal reduction as an index of operational strength of refractories

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Summary

In this paper are presented main results of investigation of thermal behavior of chrome ores from different deposits in oxidizing and reduction media. Interrelation of the speed of reduction with the degree of oxidation of natural chrome ores was established. It was found that South African chrome ore is preferable for production of refractories which are simultaneously resistant to chemical and mechanical influence of the burned material and gaseous media under high temperatures.

Introduction

Solving the task of service life increase of the heating units linings working in aggressive media (for example such as glass making furnaces, transitional zones of rotary kilns for cement clinker burning, incinerators etc.) demands application of materials resistant either to chemical and mechanical influence of the burned material and to the gaseous atmosphere under high temperatures.

Spinel present the most practical interest in this respect as they possess the highest chemical resistance in presence of magnesium, calcium, strontium and barium ortosilicates and the highest fusion temperatures [1]. Chrome spinels [2] are conspicuous for their considerable chemical resistance to acid silicate melts but their main drawback is the fact that they are easily reduced under heating.

From a number of magnesia spinels ($MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$) alumomagnesian spinel is conspicuous for its resistance to reduction but resistance of bricks made of this compound towards silicate melts is considerably lower than with chrome spinels.

Thus at first glance to increase operational characteristics of refractories it seems rather helpful to use chrome ores with increased content of alumina. But is it really correct? We can obtain reply to

this question only after analysis of chemical composition of chrome ores from different deposits and investigation of their thermal behavior in oxidizing and reducing medias.

Analysis of chemical composition

The general formula of natural chrome spinels is the following: $(Mg, Fe^{+2})O \cdot (Cr, Al, Fe^{+3})_2O_3$. Their main component is chromite which is either a $FeCr_2O_4$ compound or $FeO \cdot Cr_2O_3$ compound. Theoretical FeO and Cr_2O_3 ratio is in it 32:68. But chrome ores with such oxides ratio rarely occur in nature. FeO is often substituted for MgO and Cr_2O_3 – for Al_2O_3 . Chrome ores of various deposits possess different degree of change.

We studied chrome ores from three deposits: Turkey, Republic of South Africa and Philippines which are similar in Al_2O_3 content and different in mass fraction of Cr_2O_3 and FeO. Chemical composition of the materials is given in the **Table 1**, oxides ratio – in **Table 2**.

From the three investigated varieties of natural chrome spinels chrome ore from South Africa belongs to weakly oxidized ores which are the richest in content of the main component – chromite with predominant substitution along the line of $Cr_2O_3-Al_2O_3$. $FeO:Cr_2O_3$ ratio in the chrome ore from Philippines is close to theoretical. Its content in the general mass is not great and calculations confirm that substitution has homogeneously taken place along the both lines ($FeO-MgO$ and $Cr_2O_3-Al_2O_3$). As for the iron oxidation degree it belongs (the same as the Turkish ore) to the strongly oxidized ores. But in the latter in contrast to the above differences substitution of FeO for MgO prevails. But in spite of the increased Cr_2O_3 content Turkish chrome ore occupies intermediary position between South African and Philippines as for the chromite content.