

BONITE – A NEW RAW MATERIAL ALTERNATIVE FOR REFRACTORY INNOVATIONS

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ABSTRACT

In the current paper, *Bonite* is introduced as a new synthetic dense refractory aggregate based on the mineralogical phase calcium hexaluminate, CA6. The paper discusses chemical and physical properties of both, the new raw material and different test castables based on Bonite, tabular alumina and combinations thereof. Advanced tests like aluminium resistance, thermomechanical properties, thermal conductivity, resistance in carbon monoxide atmosphere and microporosity are discussed in respect of application areas for Bonite.

INTRODUCTION

Synthetic alumina based tabular alumina and AR 78 / AR 90 spinels are established dense raw materials aggregates for high performance alumina refractories. They are combined with fine matrix components like calcined and reactive aluminas, calcium aluminate cements (CAC) and dispersing aluminas to formulate refractory castables [1, 2]. At temperature $>1300\text{ }^{\circ}\text{C}$ CAC-bonded castables form the mineralogical phase calcium hexaluminate ($\text{CaO}\cdot 6\text{Al}_2\text{O}_3 = \text{CA}_6$), which strongly bonds to alumina or spinel grains. In cement bonded castables, however, the CA6 formation is limited to the fines in the refractory castable matrix. The calcium aluminate formation from the cement bond is accompanied by a volume increase of up to 14 %. The CA6 based microporous lightweight aggregate SLA-92 has been introduced in 1998 [3, 4] and is established in various applications [5, 6]. However, an industrial produced dense CA6 aggregate has not been available. In order to expand the properties of dense calcium hexaluminate from the matrix fines to the whole castable formulation, the new synthetic refractory aggregate *Bonite* has been developed.

Bonite is a pre-reacted aggregate and thus shows no volume increase due to the formation of new phases during heat-up. Calcium hexaluminate is described in the literature as a refractory material that exhibits:

- very high refractoriness (onset of melting $1830\text{ }^{\circ}\text{C}$),
- low solubility in iron containing slag
- high stability in reducing atmospheres, e.g. CO,
- high chemical resistance in alkaline environment, and
- low wettability by molten metals and slag (ferrous and non-ferrous)
- thermal expansion coefficient similar to corundum

The thermal expansion coefficient of CA6 ($8.0 \times 10^{-6}\text{ K}^{-1}$ from 20-1000 $^{\circ}\text{C}$ [7]) is similar to that of Al_2O_3 , which indicates a low thermal expansion mismatch between both materials.

This generally allows mixing of both raw materials, alumina and CA6, in any ratio as technically required.

Details can be reviewed in the literature [7, 8, 9, 10, 11].

Bonite combines the above described characteristics of CA6, resulting in advantages e.g. in the aluminium industry (low wettability by molten aluminium), the cement industry (high chemical resistance in alkaline environment), the steel industry (high refractoriness and low solubility in iron containing slag) and in the petrochemical industry (stability in reducing atmospheres).

The availability of Bonite as a high-quality dense synthetic calcium hexaluminate is a complement to the high alumina aggregates tabular alumina and spinel, which have been thoroughly described in various publications.

MELTING BEHAVIOUR OF CALCIUM HEXALUMINATE

Calcium hexaluminate is the most alumina-rich intermediate compound of the $\text{CaO} - \text{Al}_2\text{O}_3$ system with a high melting point at $1830\text{ }^{\circ}\text{C}$ (s. Figure 1)

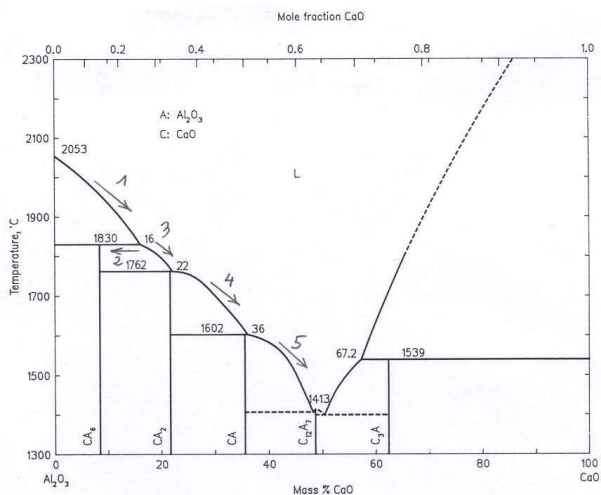


Fig. 1: Phase diagram of the $\text{CaO}-\text{Al}_2\text{O}_3$ system [20], see text

CA6 shows a peritectical melting behaviour. This is important for the production of a dense CA6 aggregate, because it excludes a melting process to achieve a homogeneous raw material with respect to phase composition. If a completely molten CA6 composition is cooled down, corundum is the first phase starting to crystallize at about $1980\text{ }^{\circ}\text{C}$.

By further cooling, and assuming conditions to achieve an equilibrium, at $1830\text{ }^{\circ}\text{C}$ this corundum (about 45 wt-%!) would completely react with the remaining liquid phase to form CA6 (s. arrow 2 in Figure 1).

However, such equilibrium conditions can never be achieved in industrial fusing processes, e.g. for fused alumina aggregate manufacturing. Instead, only a minor part of the crystallised corundum would react with the liquid to form CA6 but the remaining CaO rich liquid would crystallise in non-equilibrium to CA6 (arrow 3), CA2 (arrow 4) and, depending on the temperature gradient during cooling, even CA and C12A7 (arrow 5). Due to the temperature gradient within a fused block, this would result in a very inhomogeneous “CA6” product with only minor contents of the desired CA6 phase.

Therefore, a high temperature sintering process as for tabular alumina and spinels AR 78 and AR 90 is used for the manufacturing of the dense CA6 aggregate Bonite. With the sinter process, a situation much closer to equilibrium can be achieved by the appropriate feedstock and process conditions (e.g. temperature profile). The result of this process is a homogeneous product in respect of phase composition and physical properties as described below.

BONITE MATERIAL PROPERTIES

Bonite is composed of about 90 % calcium hexaluminate with only minor content of corundum, and traces of calcium dialuminate. Bonite has a CaO content of typically 8.5 %, less than 0.9 % SiO₂, and only traces of other impurities (s. Table 1).

It has a bulk density of more than 3.0 g/cm³, which is about 90 % of the theoretical density of calcium hexaluminate. Figure 2 shows the microstructure of Bonite, which is characterised by the platy shaped CA6 crystals and only very few micropores in between.

Bonite is available in various closed and open grain sizes. Closed sizes: 1-2 mm, 1-3 mm and 3-6 mm, open sizes: 0-1 mm, 0-0.045 mm, 0-0.020 mm. The available grain sizes and the corresponding particle size distribution are similar to the corresponding tabular alumina or spinel sizes, which allow easy substitution into similar castable formulations or mixtures of the different aggregates.

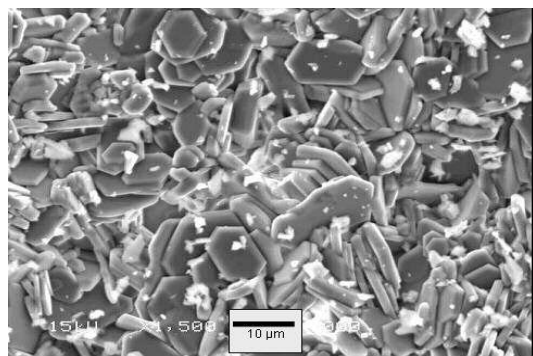


Fig. 2: Scanning electron micrograph (SEM) of Bonite grain 3-6mm (broken surface). CA6 platelets with only few micropores between the crystals.

BONITE REFRACTORY PROPERTIES

The properties of *Bonite* based refractories are demonstrated by three different silica free vibration castables and compared to a pure tabular alumina castable (TAB 1). The castables contain

Tab. 1: Typical data of Bonite in comparison to tabular alumina and spinels

Chemical Analyses		Bonite	Tabular T-60/T-64	Spinel AR 78	Spinel AR 90	Spinel MR 66
Al ₂ O ₃ ^(*)	%	90	> 99.4			
MgO	%			22.5	9.5	33
CaO	%	8.5		0.24	0.14	0.39
Na ₂ O	%			0.09	0.15	0.03
SiO ₂ ^(**)	%	0.9	< 0.09		0.05	0.09
Fe _{mag}	%	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Physical Properties						
BSG	g/cm ³	3.0	> 3.5	> 3.2	> 3.3	> 3.2
Apparent Porosity	%	8.5	< 5	< 2.6	< 3.0	< 2.9
Water Absorption	%	2.7	< 1.5	< 0.8	< 0.9	< 0.9

(*) By difference

(**) All sizes excluding 0-0.045 mm STD and 0-0.020 mm

Tab. 2: Composition of test castables

Component \ Type			Bonite	Bonite / Tabular		Tabular
			BON 1	BON 2	BON 3	TAB 1
Coarse Fraction (0.5-6mm)	Bonite	%	55		55	
	Tabular T-60/T-64	%		55		60
Fine Fraction (0-0.5 mm)	Bonite	%	15	15		
	Tabular T-60/T-64	%			15	15
	Bonite 0-0.045 mm	%	5	5		
	Bonite 0-0.020 mm	%	7	7		
	T-60/T-64 0-0.020 mm	%			12	7
Reactive Alumina	CTC 30	%	13	13	13	13
Cement	CA-270	%	5	5	5	5
Dispersing Aluminas	ADS 3	%	0.50	0.50	0.45	0.40
	ADW 1	%	0.50	0.50	0.55	0.60
Water		%	6.2	4.7	5.5	4.1

either Bonite in both, coarse and fine sizes (BON 1), only in the fines (BON 2), or only in the coarse sizes (BON 3). Details on the castable composition are given in Table 2.

The vibration flow of the castables was determined with a cone test (lower Ø 100 mm, upper Ø 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 EN 1402 “Unshaped refractory products”, Part 5 and Part 6. Hot properties (HMOR, RuL), thermal shock resistance, bulk density, open porosity and thermal conductivity were tested by DIFK, Bonn, Germany. Further details on sample preparation are described in previous papers [12]. Physical properties of the test castables are compiled in Table 3.

Due to the slightly higher porosity and lower porosity of Bonite, the water demand and the apparent porosity of the Bonite castables are higher than the tabular alumina castable. To reach a vibration flow of 200 mm 4.7-6.2 % water is required for Bonite castables, whereas approx. 4.0-4.1 % is sufficient for tabular alumina.

Tab. 3: Data of Bonite and Tabular vibration test castables

	Type	Bonite ^(*)	Bonite / Tabular		Tabular
	Pre-treatment	BON 1	BON 2	BON 3	TAB 1
VIB Flow [cm]	10 min	20.7	20.5	21.1	20.1
	30 min	20.2	20.0	21.6	20.1
	60 min	19.6	18.4	19.9	19.3
EXO	Start 1 / min	113	55	135	106
	Start 2 / h	3.6	2.0	4.2	2.8
	Exo Max / h	5.9	3.7	6.4	4.4
Bulk Density [g/cm ³]	110°C / 24h	2.88	3.10	2.97	3.22
	1000°C / 5h	2.85	3.07	2.93	3.19
	1500°C / 5h	2.78	3.06	2.86	3.15
Apparent Porosity [vol.-%]	110°C / 24h	17.6	13.2	15.2	12.6
	1000°C / 5h	22.3	16.3	21.1	14.8
	1500°C / 5h	25.7	18.1	24.1	15.6
CMoR [MPa]	20°C / 24h	5	5	5	6
	110°C / 24h	15	18	17	20
	400°C / 5h	11	17	15	14
	1000°C / 5h	10	13	12	18
	1500°C / 5h	57	64	55	61
CCS [MPa]	20°C / 24h	38	35	23	35
	110°C / 24h	101	122	100	115
	400°C / 5h	102	152	123	152
	1000°C / 5h	76	92	77	132
	1500°C / 5h	315	306	250	345
PLC [%]	110°C / 24h	± 0	± 0	± 0	± 0
	400°C / 5h	-0.09	-0.03	-0.06	+0.51
	1000°C / 5h	± 0	+0.08	+0.05	± 0
	1500°C / 5h	+0.59	+0.22	+0.87	+0.1
Thermal Shock Resistance [cycles]	950°C → RT (air)	>30	>30	>30	>30
HMoR [MPa]	1500°C / 5h	5	8	6	19
RuL (at 0.2 MPa) pre-fired at 1000 °C	D max	0.84 %	0.93 %	0.93 %	0.96 %
	T Dmax	1192 °C	1200 °C	1200 °C	1200 °C
	T 1	1578 °C	1616 °C	1602 °C	>1700 °C
	T 2	1630 °C	1689 °C	1653 °C	>1700 °C
Thermal Conductivity [W/mK] (Hot Wire Method)	300 °C	2.0	n.a.	n.a.	5.0 ^(**)
	600 °C	1.8	n.a.	n.a.	4.2 ^(**)
	1000 °C	1.7	n.a.	n.a.	3.6 ^(**)
CO resistance (ASTM) [class]	540 °C	A	n.a.	n.a.	n.a.
	1095 °C	B	n.a.	n.a.	n.a.

(*) sample was also tested after heating to 1400 °C

(**) for alumina castables at 3 g/cm³ acc. to Routschka [13]

However, all Bonite castables show a smooth vibration rheology, which could be easily changed at a similar water demand to self flow rheology by an increase of fines in the castable matrix composition. The EXO max, which is an indication for the time when the demoulding strength of the castable is achieved, is around 4-6 hours and can be easily adjusted within a wide range by changing the dispersing alumina ADS 3/ADW 1 ratio [12].

The test castables show technically sufficient strength in all temperature areas, e.g. CCS >75 MPa (1000 °C) and >250 MPa (1500 °C) or cold modulus of rupture (CMOR) is >10 MPa (1000 °C) and >55 MPa (1500 °C). The density at 1000 °C is between 2.85 g/cm³ (BON 1) and 3.19 g/cm³ (TAB 1) clearly reflecting the Bonite/tabular ratio in the corresponding castable. Bonite castables show only a slight permanent linear change at 1500 °C pre-firing.

The thermomechanical behaviour up to 1700 °C of the pure Bonite castable BON 1 (pre-fired 1000 °C) is shown in Figure 3. The maximum expansion is 0.84 % at 1192 °C and T1 is 1578 °C, and T2 1630 °C. The hot modulus of rupture (HMoR) is lower than for the tabular castable, but still 5 MPa for the pure Bonite castable. All Bonite test castables have a high thermal shock resistance of >30.

The thermal conductivity of the Bonite castable is shown in Figure 4. It is much lower compared to the corundum based castable with a bulk density of 3.0 g/cm³ and, in spite of the comparably high density of 2.85 g/cm³, even lower than the high alumina castable with only 2.5 g/cm³ bulk density. The low thermal conductivity of Bonite is of interest for applications, where a combination of wear resistance and insulating behaviour is desired or required, e.g. for the permanent lining in steel ladles or the lining of aluminium melting furnaces. A Bonite castable or brick would provide the wear resistance and the thickness of the insulating layers could be reduced.

Due to its chemical and mineralogical similarity, Bonite could also be mixed with the lightweight insulating material SLA-92 combining wear resistance with insulation properties, and providing refractory materials with a wide range of bulk density from 1.0 to 2.9 g/cm³.

As described in the literature, CA6 exhibits a low solubility in iron

containing slag and shows also a low wettability by molten ferrous and non-ferrous metals, which makes Bonite highly suitable e.g. for aluminium melting furnaces and aluminium runner linings. The high stability in reducing atmospheres, e.g. CO, and the high chemical resistance in alkaline environment makes Bonite also interesting for applications in the chemical, petrochemical or cement industries.

ALUMINIUM RESISTANCE OF BONITE

Classical refractories used so far in the aluminium industry are high alumina based on alumino-silicate or bauxite refractory aggregates. Often, anti-wetting additives like BaSO₄ or CaF₂ are added to reduce the penetration by molten metal or slag. Although the temperature of the liquid aluminium is below 900 °C, the roof temperature may be

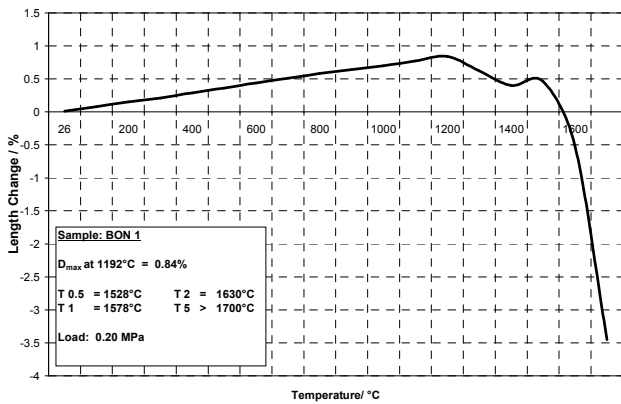


Fig. 3: Refractoriness under load (RuL) at 0.2 MPa of Bonite castable (BON 1)

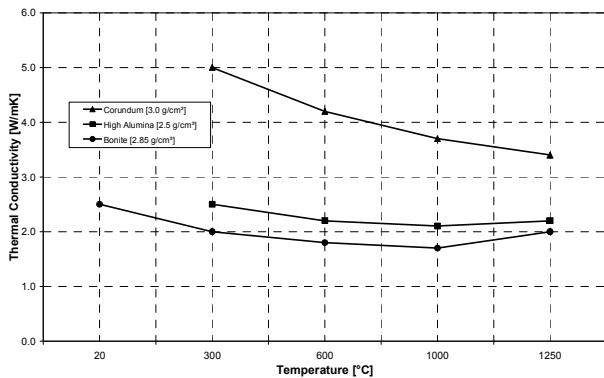


Fig. 4: Thermal conductivity of Bonite castable (BON 1) and other high alumina castables [13] (hot wire method DIN EN 993-15)

as high as 1200 °C with hot spots even above. These high temperatures are caused by higher production rates, which lead to more intense conditions like higher charging weights and higher temperatures in the melting furnace. Anti-wetting additives like BaSO₄ or CaF₂ loose their effect at temperatures above 900 – 1100 °C due to decomposition or reactions with the refractory oxides [14, 15].

Calcium hexaluminate exhibits a low wettability by molten aluminium even at temperatures clearly above 1200 °C. Bonite castables have been subjected to an enhanced aluminium resistance test at the Corus Research Center in Ijmuiden, The Netherlands, in which refractories are tested under more severe conditions than in an ordinary cup test [16, 17].

In the Corus test several cylindrical samples of 50 mm diameter and 50 mm height are simultaneously subjected to alloy 7075 enriched to 5.5 % Mg in a silicon carbide crucible with a volume of 15 litres. The samples are dried at 110 °C and pre-fired at 800 °C/12 h before being placed on top of 20 kg aluminium alloy in the crucible. The crucible is covered with a refractory lid and sealed with mortar. A corundum tube is inserted through a hole in the middle of the lid and argon gas supplied through the tube to the crucible. The crucible is heated 4 °C/min to 700 °C and the tube is lowered to 7 cm above the

bottom of the crucible and the argon flow is set to 50 l/h. The furnace is now set to 900 °C and the samples temperature dwell is set to 120 h. After the test, the furnace is allowed to cool down naturally to 700 °C. The crucible is opened and the samples are taken out of the molten metal.

Three Bonite based castables have been compared to two commercially available castables, which are commonly used as refractories in aluminium furnaces. The commercial castables are composed of bauxite, silica fume and BaSO₄ (BX 1) or bauxite, high purity reactive alumina and BaSO₄ (BX 2). Figure 5 a-d shows the samples before (left sample) and after (right sample) the aluminium resistance test. A pure Bonite based castable pre-fired at 800 °C shows no discoloration (BON 1); the test piece is almost as white as it was before the test (Figure 5 a). In contrary, the bauxite/silica fume castable pre-treated under the same conditions shows even with BaSO₄ as anti-wetting a discoloration (BX 1). Two infiltration zones can be observed: a thin black outer ring and a thoroughly grey discoloration to the centre of the test piece (Figure 5 b).



Fig. 5 a: Test pieces of pure Bonite castable (BON 1) before (left) and after (right) aluminium resistance test. Test piece fired at 800°C before test

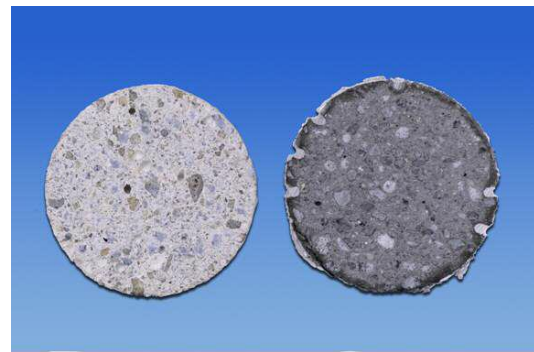


Fig. 5 b: Test pieces of commercially available Bauxite castable (BX 1) before (left) and after (right) aluminium resistance test. Test piece fired at 800°C before test

The pure Bonite sample (BON 1) and the bauxite/silica fume sample with BaSO₄ (BX 1) have been pre-fired at 1400 °C before subjecting to the aluminium resistance test to simulate intense temperature conditions in aluminium melting furnaces. The Bonite castable shows even after 1400 °C pre-firing only slight discoloration (Figure 5 c), whereas the bauxite sample shows dark discoloration (Figure 5 d). A yellow discoloration and the odour of sulphide have been observed which indicate the pyrolysis of the anti-wetting agent.

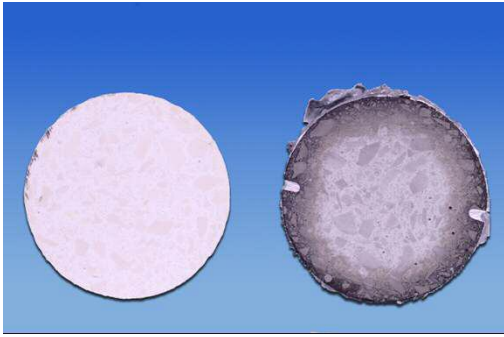


Fig. 5 c: Test pieces of pure Bonite castable (BON 1) before (left) and after (right) aluminium resistance test. Test piece fired at 1400°C before test.

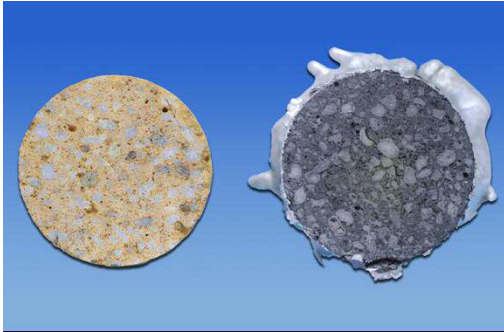


Fig. 5 d: Test pieces of commercially available bauxite castable (BX 1) before (left) and after (right) aluminium resistance test. Test piece fired at 1400°C before test.

An explanation for the enhanced Aluminium resistance of Bonite versus bauxite/silica fume/BaSO₄ under extreme conditions can be explained with the corresponding pore size distribution of the castable. Besides the low wettability of Bonite, the microporosity of the Bonite castable contributes to the high aluminium resistance.

As already mentioned in recent publications the microporosity of castables is important to reduce the aluminium penetration during use [15, 18, 19]. Gabis and Exner report about castables with very narrow pores, which behave in aluminium corrosion tests as well as those containing anti-wetting agents. With pore diameters below 1-2 μm, the penetration of liquid aluminium can be hampered. So microporosity of the castables is, in combination with the anti-wetting behaviour of Bonite, a better alternative to anti-wetting agents especially at high application temperatures.

The microporosity of selected test castables has been measured after pre-firing at 900 and 1400 °C. At 900 °C, all castables have a low average pore size diameter: BON 1 = 0.3 μm, BX 1 = 0.6 μm, and BX 2 = 1.2 μm. But at 1400 °C, the bauxite based castables with anti wetting agents show a remarkable increase of average pore size diameter towards 4.4 μm (BX1) resp. 16.0 μm (BX2), whereas the Bonite based castable is still below 1 μm (s. Figure 6). This demonstrates the stable micropore diameter of the high purity Bonite castable even at temperatures up to 1400 °C, which provides a wide safety buffer even for demanding applications.

The increase of pore size diameter for the bauxite castables is caused by two factors: the decomposition of the BaSO₄ and sintering

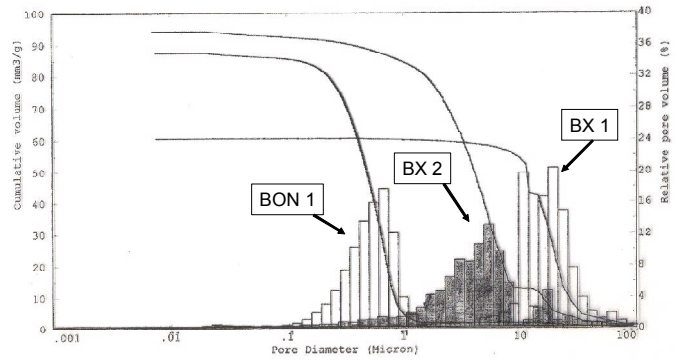


Fig. 6: Micropore size distribution (Hg intrusion method) of Bonite castable BON 1, bauxite/microsilica castable with BaSO₄ (BX 1) and bauxite/alumina castable with BaSO₄ (BX 2), all pre-fired for 5h at 1400°C

reactions including a liquid phase, which applies especially for the bauxite castable BX1, containing silica fume in the fines. BX2 with reactive aluminas instead of silica fume in the fines provides a higher refractoriness of the castable matrix, and therefore less liquid phase is formed during pre-firing at 1400 °C, and pore size growth is hampered.

Another advantage of Bonite for aluminium applications is the high chemical purity in comparison to e.g. bauxite based materials. As discussed in a previous paper [21], increasing demands on the purity, e.g. for thin foils, and many different alloys containing magnesium, require refractories with a high stability against molten aluminium or Al-alloy contact. Impurities in the refractories like SiO₂, Fe₂O₃, and TiO₂ can be reduced by the aluminium or alloy components to their metallic state. The alloy can be contaminated and layers of corundum (Al₂O₃) are built-up on the refractory lining which is a major problem of aluminium refractories. Due to the lack of impurities, refractory linings based on Bonite and high purity reactive aluminas will provide a much higher stability against reduction by molten aluminium or alloys.

STABILITY OF BONITE IN CARBON MONOXIDE ATMOSPHERE

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 SiO₂ can be reduced by the process gases to gaseous SiO, which afterwards condenses in heat exchangers (“fouling”) and reduces the efficiency of this aggregate. Due to the SiO₂ decomposition the strength of the refractory lining decreases and the porosity increases. The hydrogen attack is discussed in more detail by Tassot et al. [22].

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 phenomena is discussed in detail by Bartha and Köhne [23] and Tassot et al. [22], including calibrations of pressures build up by the Carbon deposition and dependency of the reaction on temperature and gas atmosphere composition and pressure.

CO resistance of a Bonite castable has been tested at the German refractory institute DIFK according to ASTM C288-87. A conventional castable with 80% Bonite sizes, 20% CA-14 M cement and 12% water demand has been used to achieve more severe test conditions due to the higher open porosity (31%) of that castable

after firing compared to a more advanced low cement castable like BON 1. Bars were treated for 5 hours under oxidizing conditions at 540 °C and 1095 °C, respectively. The test specimens were afterwards treated at 500 °C for 200 h in CO atmosphere (>95 %). The Bonite castable was rated Class A (= highest resistance class) after pre-firing at 540 °C resp. Class B after 1095 °C according to the ASTM norm.

CONCLUSIONS AND OUTLOOK

The mineral calcium hexaluminate is already well-known from the literature, but with the introduction of Bonite it is now available as a new dense synthetic refractory aggregate. The bulk density of Bonite is 3.0 g/cm³, which is about 90 % of the theoretical density of calcium hexaluminate (3.38 g/cm³).

Bonite based test castables show a hot modulus of rupture at 1500 °C of 5 MPa or higher, and a high refractoriness under load with a temperature T₁ of min. 1578 °C at load of 0.2 MPa. The high thermal shock resistance mentioned in the literature for Calcium Hexaluminate has been proved for Bonite based test castables. In spite of the high density of 2.85 g/cm³, the Bonite based test castable shows a very low thermal conductivity of only 1.7 W/mK at 1000 °C. This offers opportunities for combined wear and insulating linings, e.g. for steel ladles or aluminium melting furnaces.

The low wettability of Bonite based refractories is proved by the high aluminium resistance in the advanced laboratory test of Corus IJmuiden. Even after high pre-firing temperature of 1400 °C, where conventional Aluminium refractories show a high increase in pore size diameter and a reduced infiltration resistance, Bonite exhibits superior infiltration resistance behaviour. This provides a potential for major improvements of aluminium and other non ferrous metal applications.

Even a conventional, high porosity Bonite based castables achieved a class A/B rating in CO resistance acc. to ASTM C288-87, which makes Bonite suitable for petrochemical applications.

The high alkali resistance of calcium hexaluminate, which is known from the literature, is currently being tested for Bonite based refractories. This is of special interest e.g. for applications in the cement industry but also others.

With Bonite, a new innovative tool is introduced to improve refractories for various industrial applications. First industrial trials, e.g. in the aluminium industry, have already started.

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