53.rd International Colloquium on Refractories, Aachen, 8-9. September 2010

TECHNICAL AND ECONOMIC REVIEW OF HIGH ALUMINA RAW MATERIALS FOR STEEL REFRACTORIES

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ABSTRACT

This paper discusses technical and economic trends in high alumina raw materials and refractories in the past 20 years. The typical data of various high alumina materials are presented and discussed for selected steel applications. This also provides a basis for the consideration of raw material substitutions in other applications.

INTRODUCTION

High alumina refractories in the iron and steel industry were thoroughly discussed in 1990 by authors from Europe, Japan, and America [1-3]. Many changes have taken place over the past 20 years for technical and economic reasons.

Technically, the ongoing development of steel producing technology required improved high alumina refractory materials e.g. in steel ladle linings but it is not solely limited to this application. The trend towards higher purity materials has already been discussed by the authors in 1990 and the development in the past 20 years has proved them to be right. In general, for many refractories this trend is still ongoing. New high alumina raw materials and refractories have been developed and become standards in the industry, e.g. alumina-rich synthetic spinel containing purging plugs for steel ladles. The standard lining materials for steel ladles since 1990 have been replaced by new and better performing materials which are suitable for the more demanding application conditions of today.

However, the economic reasons for change in this period have been almost as important as the technical reasons, especially when considering the availability and pricing of the Chinese high alumina raw materials, bauxite and brown fused alumina over the past 2/3 years (figure 1).

In the 1990s, low priced bauxite from China replaced other alumina materials in some applications, e.g. andalusite, mullite, and in some cases even chamotte based materials. It was then relatively easy for the refractory suppliers to sell new refractories with higher alumina content to their customers, because the general perception was that higher alumina content automatically meant higher performance. In that time the global refractory industry became very dependent from Chinese bauxite and brown fused alumina. The situation has changed dramatically in the past few years and especially since 2007 (figure 1). This is due to the overall development in China. The tremendous growth of steel production in China significantly increased the internal demand for refractories and raw materials. The Chinese policy has changed from supporting raw material export to discouraging it [5]. Bauxite and brown fused alumina exports from China have been limited in volume by export licenses and are now subject to taxes and fees. This has resulted in steep price increases in the world market. Conversely refractory product exports from China are not subject to such limitations [6].

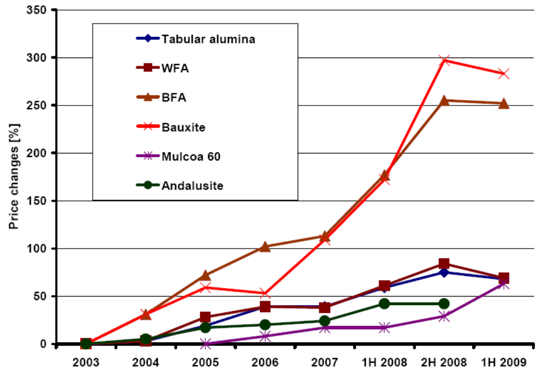

Fig. 1: Price development of high alumina refractory raw materials 2003 - 2009 [4]

The global refractory industry is now challenged to establish alternatives both from availability and also from a strategic point of view. The world economic crisis in 2009 has eased the situation only temporarily. The general challenge is expected to remain as discussions during the UNITECR conference in October´09 in Brazil and the recent development in 2010 clearly proved.

Alternative alumino-silicate high alumina materials could face a revival in applications where previously they had been partly replaced by bauxite. Because of the steep price rises of brown fused alumina and bauxite, synthetic alumina based raw materials are now much more competitive in applications using these raw materials.

It is important to be aware of the inherent differences between the various high alumina raw materials when considering a substitution in a particular application. The overall alumina content of a refractory product is one aspect but this alone is not sufficient to assess the performance under various application conditions. Such questions have for example been discussed recently in the refractory committee of the German Steel Institute VDEh.

This paper reviews the use of high alumina refractories in selected steel applications taking into account technical changes over the past 20 years. The applications and material data discussed will also provide a basis for the consideration of raw material substitution in other applications.

HIGH ALUMINA RAW MATERIALS

Typical data of high alumina raw materials are given in table 1.

Andalusite (Al_2SiO_5) is one of the few minerals which can be used in refractories without pre-firing. It transforms to mullite and cristobalite in the temperature range from 1200 to 1500 °C, accompanied by a volume increase of between 3 and 6 % (theoretically 3.7 %).

The other two minerals from the Sillimanite group, Kyanite and Sillimanite, also transform but show a higher volume increase. Therefore they need to be pre-fired

Tab. 1: Typical data of high alumina raw materials for refractories

		Andalusite	Mulcoa 60	Mulcoa 70	Bauxite	Brown Fused Alumina	White Fused Alumina	Tabular Alumina	Sinter Spinels AR78/AR90	Bonite (dense CA6)
Al_2O_3	%	56-59	60	70	85 - 90	94 - 97	99.5	99.6	> 99 (Al_2O_3+MgO)	90
SiO_2	%	38-40	35.8	25.6	5 - 10	0.8 - 1.5	0.02	0.01	0.08	0.9
TiO_2	%	0.2-0.5	2.4	3	3 - 4	1.5 - 2.5	0.01	0	0	0
Fe_2O_3	%	0.8-1.5	1.2	1.2	1 - 2	0.15 - 0.5	0.08	0.04	0.1	0.1
Alkaline Earths	%	0.1-0.3	0.2	0.2	0.4 - 0.8	0.4 - 0.6	0.03	0.02	0.2 (CaO)	9.0
Alkalies	%	0.2-0.8	0.2	0.15	0.2 - 0.8	0.2 - 0.4	0.3	0.33	0.12	0.15
Bulk Density	g/cm³	3.1	2.78	2.89	3.1 - 3.4	3.8 - 3.9	3.5-3.9	3.55	3.3/3.4	3.0
Apparent Porosity	%		5.7	6.2	10-15%	1.5	0 - 9	1.5	1.8	8.5
Water Absorption	%				3-5%	0.4	0 - 3	0.5	0.5	2.7

before being used as an aggregate in refractories. Andalusite has a low impurity level but high silica content of 38-40 %. The grains are Andalusite crystals and have practically no open porosity. Andalusite is mined in South Africa (245,000 tpa), France (65,000 tpa), and China (small domestic use). New mining projects are ongoing in Peru (plan 60,000 tpa [7]) and Mongolia. The global Andalusite market shrunk from about 500,000 mt in the early 1990s to about 250,000 mt over the past 15 years due to replacement by low price bauxite from China [8]. Now, andalusite capacity expansion projects are ongoing in South Africa (+40 % to 350,000 mt) [9]. A new Sillimanite source of 50,000 tpa in India is reported recently [10].

Mulcoa 60 and 70 are fired products from Georgia, USA. They are based on kaolinitic clays which contain bauxite with alumina added. The overall Mulcoa capacity including lower alumina grades is 625,000 tpa, and a new kiln with a capacity to produce 75,000 tpa was added in 2009 [11]. High alumina chamotte (60 and 70 % Al_2O_3) are also produced in China. Synthetic alumina based mullite products play only a niche role in refractories for steel production.

Refractory grade bauxite is calcined bauxite and it accounts for only 1-2 % of the globally mined bauxite because of the requirement for max. 2 % Fe_2O_3. Corundum is the main phase after calcination. The main resources are located in China and Guyana. Guyana has been in Chinese ownership since 2007 giving total Chinese ownership of global refractory grade bauxite resources of about 95 % [12]. A Brazilian source established in the 1990s has been consumed.

Chinese and Guyanese bauxite have comparable alumina, titania, and iron oxide contents but differ in their content of alkalies and alkaline earths and therefore in their mullite content. Chinese bauxite typically has a higher amount of glassy phase and less mullite. This influences the hardness at lower temperature and also the thermo-mechanical behaviour. Guyana capacity is about 300,000 tpa, a planned expansion of a 150,000mt is currently on hold [13,14].

Global demand for Chinese bauxite in 2008 was about 1.2 million tonnes but exports were limited to 940,000mt [5,6]. Apart form limited availability, declining quality with regard to alumina content and density has worried refractory producers worldwide.

Brown fused alumina (BFA) is produced from low iron calcined bauxite by fusion in an electric arc furnace at temperatures above 2000 °C. Coke and iron borings are added as reducing agents to lower the amount of impurities (SiO_2, TiO_2, Fe_2O_3). Ferro silicon is obtained as a by-product [15]. BFA has a higher density and a lower amount of impurities when compared to bauxite. The quality of BFA is also determined by proper selection of material after cooling and crushing.

The total world market is reported to be about 1 million tonnes per year [16], but maybe as much as 1.2 – 1.5 million tonnes [6]. This is split between abrasive and refractory applications. China accounts for about half of global BFA supply [12]. Prices for BFA have been about half of that for synthetic alumina based aggregates like tabular alumina and white fused alumina (WFA) for some years but due to the price surge since 2007, they have now moved much closer. Tabular alumina and WFA are considered as alternatives [17]. As is in the case of bauxite, the quality of BFA ex China has somewhat deteriorated over the past few years.

WFA is based upon synthetic alumina and as with BFA it is produced by fusion at temperatures above 2000 °C. The density of the product depends upon the cooling conditions and can vary considerably (table 1) between different processes. A high density can only be achieved by slow cooling, fast cooling results in high open porosity. Due to different cooling conditions throughout the fused block, the homogeneity of the final product also depends on proper selection of material after crushing. The total world market is reported to be about 500,000 mt, split between abrasives and refractory [16].

Tabular alumina is a refractory aggregate produced by sintering at temperatures up to 1900 °C. The production process could be described as a ceramic process which involves fine milling of a calcined alumina feedstock, ball forming, drying, and sintering [18]. It leads to a very homogeneous product with a characteristic microstructure: tabular alumina has large tablet shaped crystals with small internal closed pores. Because of these pores, the bulk density is lower than BFA or WFA products, but the open porosity is only 1.5 %. The global market for tabular alumina is about 450,000 tpa, and Almatis provides globally standardised specifications in all regions [19].

Alumina rich spinels based upon synthetic alumina and high purity magnesia feedstock were introduced in the early 1990s specifically for alumina based refractories for steel applications [20,21]. Magnesia rich spinels which were already being used in basic cement kiln bricks could not provide the desired performance in these applications. Spinel is produced either by sintering or fusing. The sinter process provides advantages for such non-stoichiometric compositions due to the homogeneous process conditions when compared to fusing (heterogeneous cooling) [22].

Bauxite based fused spinels have a higher amount of impurities. This impacts the performance in demanding applications. The global spinel market is estimated at 70,000mt. This figures includes magnesia rich spinels, sintered, and fused products.

A new dense high alumina aggregate based on calcium hexaluminate was introduced in 2004 [23]. The product is sintered using the same process as tabular alumina. It provides the same positive properties as the calcium hexaluminate phase which is formed at high temperatures in cement bonded high purity castables, but as a pre-reacted aggregate it shows volume stability over a wide temperature range. The combination of high refractoriness and low thermal conductivity provides a new alternative for back linings in steel applications [24].

BLAST FURNACE RUNNERS

Low cement and ultra low cement castables with 60-85 % Al_2O_3 and 5-25 % SiC are used for the wear lining in the main trough. The specific refractory consumption is between 0.3 and 0.6 kg/t hot metal. BFA is the most common aggregate for these castables although tabular alumina is also used in some cases.

The modern larger blast furnaces always have a higher specific refractory consumption when compared to smaller furnaces. This is mainly due to higher erosion. They have higher tapping temperatures and the dimension of the runner´s cross section is not increased in proportion to the tonnage of iron produced per minute. Tabular alumina has been reported to provide advantages under such demanding conditions [25].

The BFA price increases and quality issues have lead to an increased interest in tabular alumina for this application and industrial tests are ongoing. Table 2 shows a comparison between a tabular and a BFA based ultra low cement vibration castable. Here, the matrix composition has been kept constant, and only the aggregate has been exchanged. Both castables show comparable strength data. The higher density of the BFA aggregate (3.8 g/cm³) when compared to tabular (3.55 g/cm³) shows in a 5-6 % higher density of the castable. The material demand for a lining is therefore 5-6 % lower when tabular is used as the aggregate. This should also be considered when an economic comparison is made between both concepts.

Figure 2 shows the test bars after firing at 1500 °C in air. No differences can be found in oxidation of the castables. The BFA test bar shows molten spots at the surface due to local impurity peaks. The cut surfaces show some larger cracks in the BFA test bar but not in the tabular bar.

Blast furnace runner castables are complex products often containing up to 20 constituents. The consistent properties of sintered aggregates provide an alternative to BFA giving predictable and reliable performance.

Tab. 2: Data of test castables for BF runner – BFA and tabular basis.
* Data critical due to melting phase formation at surface of test bars (Fig 2)

			VIB	VIB
			TAB	**BFA**
Coarse fraction (up to 10 mm)	Tabular T60/T64	%	50	
	BFA	%		50
Fine fraction	T60/T64 0 - 1 mm	%	7	
	BFA 0 - 1 mm	%		7
	SiC up to 1 mm	%	20	20
Reactive Alumina	E-SY 1000	%	15.2	15.2
Cement	CA-270	%	2	2
Silica fume	Elkem U971	%	1	1
Additives	Carbon	%	2.5	2.5
	Antioxidants	%	2.3	2.3
	Dispersion + set control	%	0.1115	0.1115
Water		%	4.5	4.5
CMoR	20°C / 24h	MPa	2	2
	110°C / 24h	MPa	9	8
	1000°C / 5h	MPa	6	5
	1500°C / 5h	MPa	11	5
CCS	20°C / 24h	MPa	15	16
	110°C / 24h	MPa	56	54
	1000°C / 5h	MPa	55	44
	1500°C / 5h	MPa	63	77
Density	110°C / 24h	g/cm³	**2.92**	**3.07**
	1000°C / 5h	g/cm³	**2.8**	**2.91**
	1500°C / 5h	g/cm³	**2.8**	**2.89**
PLC	110°C / 24h	%	± 0	± 0
	1000°C / 5h	%	-0.01	-0.25
	1500°C / 5h	%	+0.8 *	+1.2 *

Fig. 2: BF runner test castable bars after firing at 1500°C in air. Test bar surface (Tabular left up, BFA left down) and cut surface. Locally occurring melting due to impurities in BFA, no difference in oxidation resistance

Tab. 3: Typical data of high alumina bricks [26]

Type	Fired bricks				Carbon-bonded bricks					
Chemical analysis [weight %]	Andalusite	Bauxite	Corundum	Spinel	Andalusite Carbon	Alumina SiC Carbon	Alumina Carbon	Alumag-carbon Alumina +Bauxite	Alumag-carbon Alumina	Alumag-carbon Alumina
SiO_2	37	11	4	0.1 - 1.0	36	9-11	< 1	2 - 4	0.4	0.4
Al_2O_3	61	82	95	93	62	65	97	80 - 87	91	65
TiO_2	0.3	3.6	< 0.1	0.1	0.3	2.5	< 0.1	1 - 2	< 0.1	< 0.1
Fe_2O_3	1.0	1.6	0.3	0.1	1.0	1.5	0.1	0.5 - 1.0	0.2	0.2
CaO	0.2	0.3	0.1	0.1	0.3	< 0.2	< 0.1	< 0.3	< 0.2	< 0.5
MgO	< 0.1	0.3	0.1	5.0	0.2	0.2	0.2	6 - 10	6 - 7	33
Na_2O	< 0.1	0.1	0.3	0.1	0.1	0.2	0.3	< 0.2	< 0.4	< 0.3
K_2O	0.3	0.4	0.1	0.1	0.4	10-12	< 0.1	< 0.4	< 0.1	< 0.1
SiC	-	-	-	-	-	5-10				
Res. C*[1]	-	-	-	-	5	5	5	6 - 8	6 - 8	6 - 8
X-ray*[2]	Andalusite Mullite Cristobal. Quartz	Corundum minor: Mullite Tialite	Corundum Mullite	Corundum Spinel	Andalusit minor: Quartz Corundum Graphite	Corundum Graphite SiC minor: Mullite Tialite	Corundum Graphite minor: ß-Alumina	Corundum Periclase Graphite minor: Mullite Tialite	Corundum Periclase Graphite minor: ß-Alumina	Corundum Periclase Graphite minor: ß-Alumina
Bulk density [g/cm^3]	2.5	2.7	3.2	3.1 - 3.2	2.7	2.8 - 3.2	3.1	3.0 - 3.1	3.1 - 3.2	3.1
Open porosity [%]	16	22	18	17 - 19	7 - 9	7 - 10	7 - 10	6 - 8	5 - 6	7
Cold crushing strength [MPa]	65	> 40	>50	75	75	90 - 110	80	40 - 80	40 - 80	40 - 80
HotCS [MPa] (Temp. ℃)	11 (1500)	5 (1500)	23 (1600)	n.d.	10 (1500)	n.d.	5 (1500)	n.d.	n.d.	10 (1500)
Thermal cond. [W/mK] 300 ℃ 600 ℃ 1000 ℃	 1.9 1.8 1.7	 2.2 2.3 2.4	 4.5 4.0 3.5	 4.0 3.5 3.0	 2.4 2.3 2.2	 3 - 5 2.5 – 4.5 2 - 4	 5.0 4.0 3.5	 6 5 4	 6 5 4	 7 6 5

*[1]Carbon additionally to 100 % sum of oxides; *[2]X-ray: Corundum=α-Al_2O_3, ß-Alumina=$Na_2O \cdot 11Al_2O_3$, Spinel=$MgAl_2O_4$, Mullite=$3Al_2O_3 \cdot 2SiO_2$, Andalusite=Al_2SiO_5, Tialite=Al_2TiO_5, Anorthite=$CaAlSi_2O_8$, Cristobalit=SiO_2, Quartz=SiO_2, Periclase=MgO, Graphite=C

Tab. 4: Data of high alumina castables [26,23]

Type	Castables*[1]						
Chemical analysis [weight %]	Andalusite	Bauxite	Alumina	Alumina Spinel	Alumina Spinel forming	Alumina Spinel Spinel forming	Bonite (dense CA_6)
SiO_2	36 - 38	8.5	0.1	0.1	1.0	< 1.0	0.75
Al_2O_3	58 - 61	85	98	92	93	90	91
TiO_2	< 0.2	3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Fe_2O_3	0.6 – 1	1.5	0.1	0.1	0.1	0.1	< 0.1
CaO	1 - 2	1.0	1.4	1.5	< 1.0	< 1.0	8.2
MgO	0.2	0.2	< 0.1	5.0	4.0	6.0	0.1
Na_2O	0.1	0.1	0.3	0.3	0.3	0.1	0.1
K_2O	0.2	0.2					
X-ray*[2]	Andalusite minor: Quartz, Anorthite, Corundum, Cristobal.	Corundum minor: Mullite, Tialite Anorthite, Cristobal.	Corundum minor: ß-Alumina	Corundum Spinel minor: ß-Alumina	Corundum Periclase minor: ß-Alumina	Corundum Spinel minor: ß-Alumina, Periclase	Hibonite minor: Corundum, CA_2
Bulk density [g/cm^3]	2.5 – 2.7	2.8 - 2.9	3.0	2.9	2.95	3.1	2.85
Open porosity [%]	14 - 18	17 - 22	18	19	20	17	17
Cold crushing strength [MPa]	50 - 100	80	60	60	40	60	50
HotCS [MPa] (Temp. ℃)	2 – 14 (1400)	1 (1400)	n.d.	28 (1600)	5 (1600)	7 (1600)	n.d.
Thermal cond. [W/mK] 300 ℃ 600 ℃ 1000 ℃	 2.6 2.3 2.2	 4.0 3.5 3.0	 5.0 4.5 3.5	 5.0 4.5 3.5	 5.0 4.5 3.5	 5.0 4.5 3.5	 2.0 1.8 1.7

*[1]Data of castables prefired 1000 ℃, 12 hrs; *[2]X-ray: Corundum=α-Al_2O_3, Hibonite CA_6=$CaAl_{12}O_{19}$, CA_2=$CaAl_4O_7$, ß-Alumina=$Na_2O \cdot 11Al_2O_3$, Spinel=$MgAl_2O_4$, Mullite=$3Al_2O_3 \cdot 2SiO_2$, Andalusite=Al_2SiO_5, Tialite=Al_2TiO_5, Anorthite=$CaAlSi_2O_8$, Cristobalite=SiO_2, Quartz=SiO_2, Periclase=MgO

TORPEDO CARS AND HOT METAL TRANSPORT

Various high alumina refractories are used for torpedo cars. The required quality of which depends on the hot metal treatment. When no hot metal treatment is carried out, fired bricks of andalusite and bauxite are the common linings, and the specific refractory consumption is 0.4-0.5 kg/t hot metal.

When desulphurisation, dephosphorisation, and desiliconisation are carried out in the torpedo car, the specific consumption increases to 0.9 kg/t h and carbon bonded Al_2O_3-C (AC) and Al_2O_3-SiC-C (ASC) bricks of higher quality are used. These types of bricks are also often used in the impact zone and slag line when no hot metal treatment is carried out in the ladle. Complete AC/ASC linings can achieve a specific refractory consumption below 0.2 kg/t and lining lifes of 3 years when no hot metal treatment is applied. The higher price of the carbon bonded bricks and their higher thermal conductivity needs to be taken into consideration for a full economic evaluation.

The torpedo car application provides a good example for the discussion of general differences between andalusite and bauxite refractories. This might be helpful for consideration of other applications as well. Table 3 shows data of typical high alumina bricks. Bauxite materials have higher alumina and lower silica contents but also higher impurities when compared to andalusite. The lower silica content is an advantage for the slag resistance when slag basicity $CaO:SiO_2$ is higher than 0.9 (fig 3), and also if the slag contains higher amounts of MnO. Alumina-silicate refractories form low melting Manganese silicate phases at 1100 to 1200 °C [28] when the MnO content in the slag is above 6 % [27]. Manganese can accumulate in the slag and reach contents even higher than in the steel from where it originates.

The thermo-mechanical properties show a different picture. Andalusite shows much better creep resistance (fig. 4) when compared to bauxite. Because of the impurities in bauxite, especially alkalies, a molten phase is formed at temperatures as low as 1100 °C [29]. This molten phase decreases the creep resistance despite of on overall higher alumina content of bauxite. The different thermo-mechanical behaviour also applies for low and ultra low cement castables as shown in extended investigations [30]. As a general rule it can be stated that a high creep resistance becomes even more important when the residence time of iron or steel in a vessel increases.

Andalusite is well known for its high thermal shock resistance which is an advantage for use in vessels not in continuous use. For example hot metal ladles lined with Andalusite can afford an intermediate cooling period without requiring additional heating in between. A recent study has discussed the thermal shock resistance of andalusite in detail [31].

When andalusite castables are used or andalusite bricks fired only at temperatures between 1200 and 1400 °C, the formation of mullite is not complete and the material will exhibit a volume increase during use at higher temperatures. This can be helpful to close joints in a lining or keep them tight. For other applications, e.g. hot blast stoves, where dimensional stability is mandatory, this effect must be avoided. Mulcoa 60 and 70 based materials do not show this behaviour. They also often provide better thermo-mechanical properties when compared to bauxite.

The density difference between andalusite and bauxite refractories is typically 8-10 %. Therefore the higher material demand for bauxite based linings needs to be taken into consideration in economic comparisons of lining concepts.

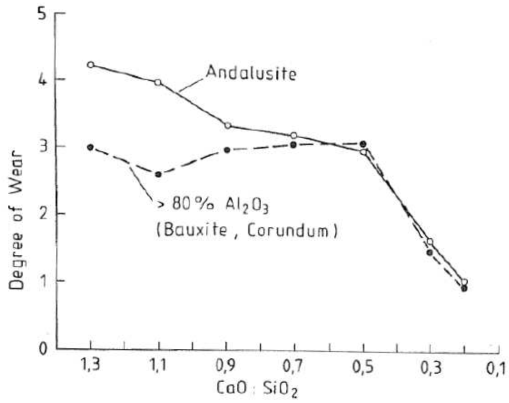

Fig. 3: Resistance of andalusite and bauxite / corundum bricks against slag with different $CaO:SiO_2$ ratio at 1520 °C / 4 h [27]

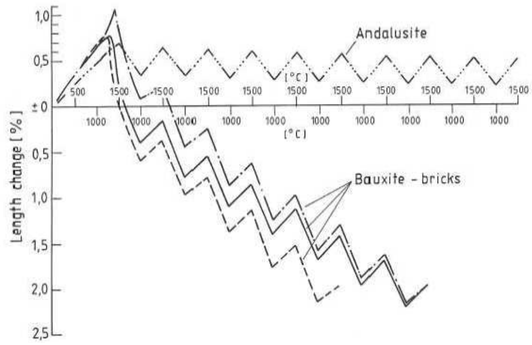

Fig. 4: Creep of andalusite and bauxite bricks tested under torpedo car application conditions; load 0.2 MPa, temperature change between 1000 and 1500 °C [27]

STEEL LADLES AND PRE-CAST SHAPES

The steel ladle is the most dynamic area with regard to the development of steel producing technology, "secondary metallurgy". Process modifications for the production of new and improved steel qualities constantly change the requirements of the steel ladle lining. Therefore the steel ladle linings must be adjusted to these new requirements [26].

The steel academy, an institution of the German Steel Institute VDEh, is regularly organising international symposiums on steel ladle linings in Europe, where 10 – 12 European steel works present their ladle linings and new developments [31]. The number of ladles with bauxite or andalusite based refractories in the wear lining has declined from eight to zero in the period 2000 to 2008.

Why has that happened? In the 1990s, bauxite and andalusite based linings were very common in addition to basic materials. In 1995, trials with low cement castables (tab. 4) in the Dortmund steel works, Germany have shown that andalusite is no longer a suitable material when

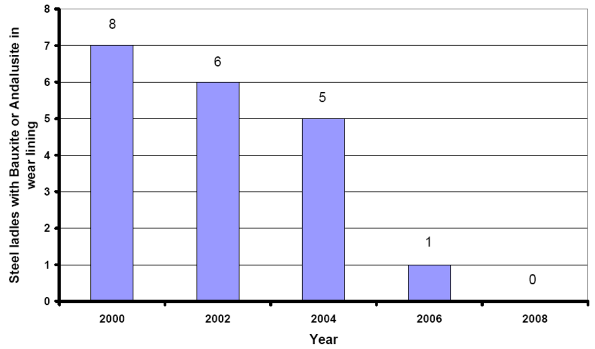

Fig. 5: Number of steel ladles with bauxite or andalusite based wear linings presented in international seminar on steel ladle lining in Europe 2000 – 2008 [32]

the calcium aluminate steel ladle slag contains more than 30 % CaO. The average CaO:Al_2O_3 (C/A) ratio increased from 0.6 in 1993 to about 1 in 1995 for metallurgical and process reasons. The high silica content of andalusite led to a strong reaction with the basic slag and considerably increased the wear. Andalusite containing castables only achieved about 50 heats when compared to about 130 heats with bauxite castables at that time [33].

The steelworks in IJmuiden, The Netherlands reported in 2001 the substitution of andalusite bricks by MgO/C bricks and subsequently by fired spinel bricks [34,32]. This was driven by the introduction of the direct strip plant (DSP). This new process required a calcium treatment of the steel and a change in slag composition towards a higher C/A ratio. The estimated lifetime of the andalusite brick decreased by up to 70 % with 20 % DSP heats treated in the ladle and 90 – 95 % with 100 % DSP heats. This would have meant a lining life of only 4-8 heats!

Figure 6 shows an induction furnace slag test performed with materials used in steel ladle back linings. The test conditions are summarised in table 5. The andalusite brick was almost completely worn after 2 hours and has a wear rate of 12 mm/h. The bauxite brick has a lower wear rate of 4.6 mm/h but shows a deep infiltration of the calcium alumina slag (C/A ratio 1.08).

Meanwhile, bauxite materials have reached their limit in wear linings in steel ladles because of the following factors: increase of tapping temperatures and residence time of steel in the ladle, more aggressive slag compositions and steel treatment conditions, higher demands on steel cleanliness and thermo-dynamic stability of the refractory lining (avoid a re-oxidation of steel). Bauxite materials show increased slag penetration and wear, and due to their silica and glassy phase contents, they are susceptible to reaction with e.g. aluminium killed steel grades.

Today, andalusite and bauxite materials are mainly used as a back lining but not as a wear lining. The recently developed dense calcium hexaluminate, bonite, provides an interesting alternative for back lining applications. The thermal conductivity is lower when compared to an andalusite brick (1.7 vs. 2.0 W/mK at 1000 °C). The slag resistance is better when compared to a bauxite brick (fig. 6, wear rate 3.2 mm/h) [24]. The creep resistance at 1500 °C is also better when compared to bauxite (fig. 7).

Tab. 5: Induction furnace slag tests at DIFK, Bonn, Germany; test conditions for wear lining (AluMagCarbon bricks and spinel castables) and back up lining materials (Fired bricks and dense calcium hexaluminate castable)

	AMC bricks	**Spinel castables**	**Fired bricks & Bonite castable**
°C / h	1650 / 3	1650 / 2	1600 / 2
Steel	15 kg ST 52	18 kg ST 37	15 kg ST 52
Slag	1 kg	1 kg	0.75 kg
C/A ratio	1.08	1.08	1.08
wt %			
CaO	40	40	41.5
Al_2O_3	37	37	38.5
SiO_2	5	5	5
MgO	5	5	5
FeO	3	3	6
MnO	4	4	4
CaF_2	6	6	

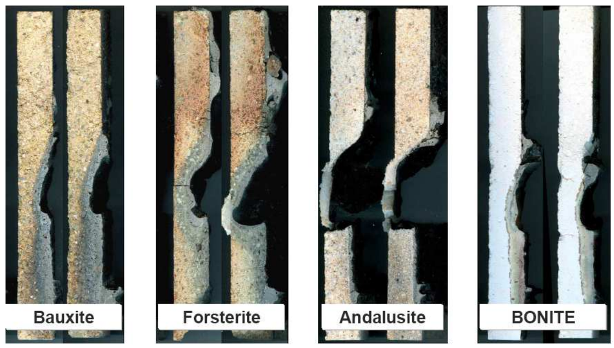

Fig. 6: Induction furnace slag test at 1600 °C / 2 h and CaO:Al_2O_3 ratio = 1.08. Bricks of Andalusite, Bauxite, Forsterite vs. Bonite (dense CA_6) castable [24]

A reduction of back lining thickness is often desired to increase the steel capacity of the ladle. Still, the safety and thermal insulation features of the back lining must be maintained.

The standard materials for wear linings to meet the demands of modern steel making are synthetic alumina based castables (tab. 4) or bricks, alumina-magnesia-carbon (AMC) bricks (tab. 3), or basic bricks (magnesia-carbon, or doloma) which are also the standard for slag lines. Ladle lining concepts are discussed in detail in a previous paper [26].

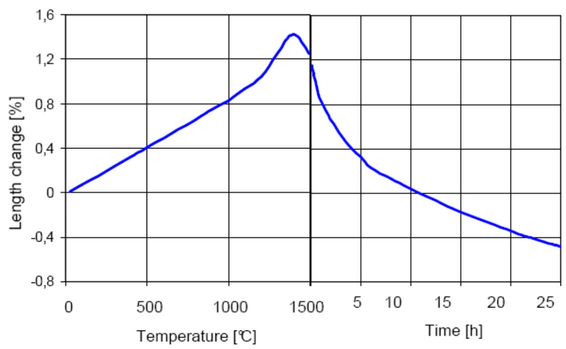

Fig. 7: Creep resistance of dense calcium hexaluminate, Bonite, based castable after pre-firing at 1500 °C / 5 h

With the development of high performance low- and ultra-low cement castables, monolithic ladle linings have become increasingly important in steel ladles. The use of synthetic alumina based castables combined with a relining technique is a widespread technology today.
Voest Alpine Stahl Linz, Austria and Ruukki Rahe, Finland, reported very low specific refractory consumptions of 0.43 kg/t and 0.73 kg/t resp. for the bottom and side wall of steel ladle when applying this technology [32]. The castables are spinel containing, either by addition of pre-reacted spinel or magnesia for spinel formation in situ or a combination of the two.
Figure 8 shows the induction furnace slag test of different spinel castables:

- spinel containing low cement castable (SP LCC),
- spinel containing plus spinel forming ultra low cement castable (SP-SF ULCC),
- spinel containing plus spinel forming no cement castable (SP-SF NCC),
- spinel forming castable (SF ULCC).

The test conditions are given in table 5. Here calcium fluoride (CaF_2) was added to the calcium aluminate slag to give more severe test conditions. The wear rate of all castables tested was between 6.9 and 8.5 mm/h and at the same level as for AMC bricks, with a comparable magnesia content of about 5 to 6 %, tested under the same conditions (fig 9). Castables with spinel formation showed a slightly lower wear rate but higher infiltration depth. The NCC castable shows the highest wear rate but lowest infiltration depth. The overall best slag resistance was achieved with a combination of spinel and spinel forming (SP-SF ULCC).

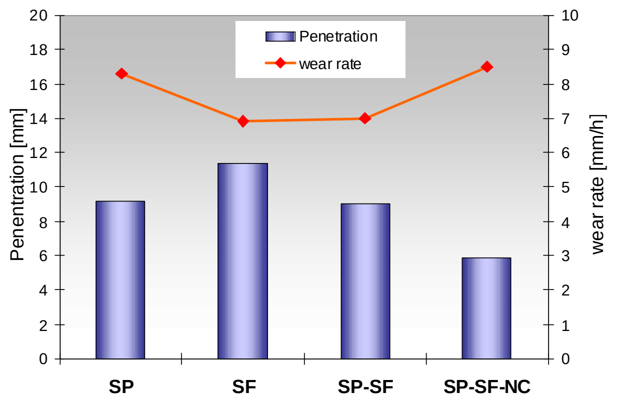

Fig. 8: Induction furnace slag test at 1650 °C / 2 h and $CaO:Al_2O_3$ ratio = 1.08 (+ CaF_2). Spinel (SP) and Spinel forming (SF) castables and combinations thereof; MgO contents between 4.5 and 6.3 %, open porosity at 1500 °C between 15.3 and 17.7 % [35]

All castables with spinel formation contain minor amounts of silica fume which is required to achieve the desired working time during installation and to overcome excessive volume expansion during the formation of spinel in situ. A small amount of silica fume has a considerable impact on the thermomechanical properties of the castable as shown in figure 10. The hot modulus of rupture (HMoR) of a tabular alumina based castable at 1500 °C is increased from 17 MPa to 23 MPa when 25 % alumina rich spinel AR 78 is added to the fine fraction. The castable does not show a compression up to 1700 °C. If a part of the spinel is replaced by magnesia and alumina to form spinel in situ and silica fume is added, the material shows strong compression in RuL, and the HMoR decreases to 1-2 MPa.

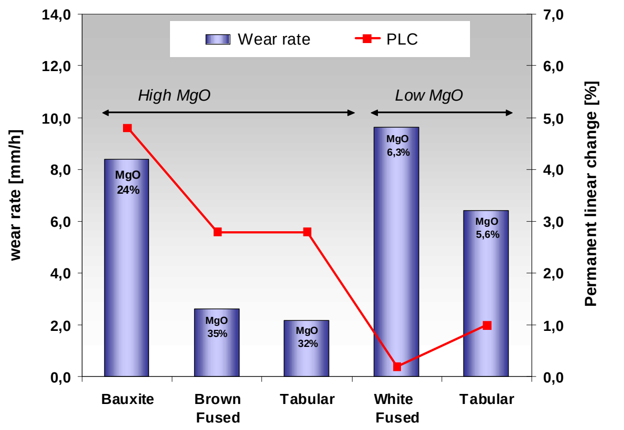

Fig. 9: Induction furnace slag test at 1650 °C / 2 h and $CaO:Al_2O_3$ ratio = 1.08 (+ CaF_2). Resin bonded AluMagCarbon bricks with high and low MgO content. Permanent linear change is considerable higher with high MgO content

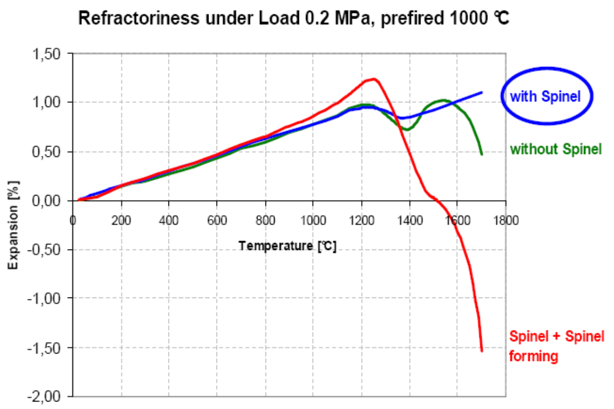

Fig. 10: Refractoriness under load (RuL) of tabular and spinel self flowing castables (samples pre-fired 1000 °C / 5 h)

This is in line with the theory. The $CaO-MgO-Al_2O_3-SiO_2$ phase diagram evaluation shows that the temperature of onset of melting decreases from above 1820 °C for SiO_2 free formulations to below 1400 °C for SiO_2 containing formulations [30].
However, which concept is the best depends upon the application. In steel ladle bottoms and especially for purging plugs and well blocks, the volumetric stability under high temperature and pressure is most important. High erosion resistance is also important. Spinel containing castables have become the standard for this application and provide the best performance [36].
The requirements in steel ladle side walls are different. Every steel ladle shell shows some deformation between transport, residence, and treatment - the “water bucket” effect. Here it is an advantage if the lining is not absolutely rigid but shows the ability for stress relaxation to avoid stress peaks which may lead to cracking.

The volume expansion due to the in situ spinel formation can close joints at the surface, practically the same effect as with andalusite materials in other applications. Therefore castables with spinel formation provide advantages in ladle side walls, and the combination of spinel containing and forming can be considered the best solution here.

The situation is different with fired spinel bricks in the ladle side wall. The steelworks in IJmuiden, The Netherlands reported that a fired spinel brick with 1 % SiO_2 achieved only 40 % of the life achieved with a brick with 0.1 % SiO_2 [34]. This also shows that fired bricks behave totally differently to monolithic linings which develop their properties during use depending upon the temperature profile in the lining.

AluMagCarbon (AMC) bricks combine the advantages of alumina and spinel with those of carbon containing refractories. Carbon reduces the wettability of refractories and therefore the infiltration of slag and metal. The high thermal shock resistance of high-alumina refractories when compared to basic refractories is further improved by carbon due to its inherent high thermal conductivity.

AMC bricks contain free magnesia which forms spinel at the hot surface of the bricks where carbon is burned out. The volume increase due to the spinel formation closes joints at the surface and reduces the slag infiltration. The magnesia content can range from 5 – 6 % up to 35 % but the high contents result in a very high volume increase during use (permanent linear change 3 % and more, fig. 9). This creates very high stress in a lining. Therefore bricks with lower magnesia content have become the standard. Figure 9 shows the induction furnace slag test under the same conditions used for the spinel castables. The tabular alumina based bricks show the best slag resistance.

In ladle side walls, BFA based AMC bricks are normally used, sometimes with addition of bauxite. Higher amounts of bauxite reduce the performance of the bricks. This has been reported by Arcelor-Mittal Steel Gent, Belgium [32]. These bricks are also often used in the bottom impact area. Here, tabular alumina provides better performance when compared to BFA. Corus Steel IJmuiden, The Netherlands reported a lining life reduction of 50 % when tabular alumina was replaced by BFA [32]. Tabular alumina provides the most consistent rate of spinel formation in AMC bricks during thermal cycling and a higher creep resistance. The better performance of tabular alumina based AMC bricks with regard to spinel formation and slag resistance was also reported by Bose [37].

TUNDISHES

High alumina materials are used for the permanent lining of tundishes, and a basic wear lining is applied at the front. These tundishes are cooled down to exchange the wear lining after each use. In hot cycle tundishes alumina materials are used as the wear lining. Andalusite and bauxite materials in the permanent lining are most common for tundishes with basic wear lining and tabular or WFA materials for tundishes with alumina wear lining.

Andalusite provides advantages due to the high thermal shock resistance. The slag resistance is less important unless the basic wear lining gets damaged and a carry over slag from the steel ladle can get in contact.

Monolithic permanent linings were successfully introduced in the 1990s [38,39] and have become the standard. Initially vibration castables were used for the introduction of the monolithic technology. Subsequently self flowing castables have proved advantageous with regard to easy and failure free installations. Self flowing castables contain a higher amount of matrix fines and therefore also matrix aluminas to achieve the desired rheology. The addition of matrix aluminas also has an effect on the hot properties of the castables. Figure 11 shows the position of two andalusite castables in the phase diagram CaO-Al_2O_3-SiO_2. The composition of the castables is in the triangle Mullite-Anorthite-Cristobalite. Accordingly the theoretical onset of melting is at 1345 °C. The low hot crushing strength (HCS) of 1 MPa at 1500 °C of castable 1 (without matrix aluminas) is in line with the theory.

However, castable 2 with matrix aluminas shows a HCS of 11 MPa at that temperature. This can be explained by the change in the composition of the total matrix fines due to the addition of matrix aluminas. When only the matrix fines below 0.12 mm are considered, the matrix of castable 1 still remains in the same triangle. However, the matrix composition of castable 2 moves to another triangle (Mullite-Anorthite-Corundum), which has a higher temperature of onset of melting (1512 °C). The effect can also be seen clearly in the creep resistance in figure 12 [30].

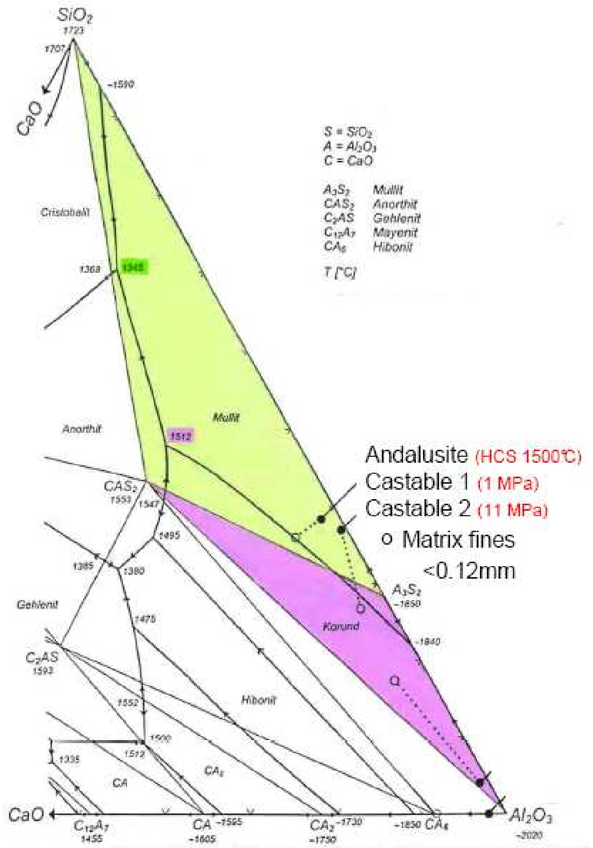

Fig. 11: Matrix composition of Andalusite based low cement castables with and without addition of fine matrix aluminas in the phase diagram CaO-Al_2O_3-SiO_2 [40]. Castable 2 with matrix aluminas, castable 1 without. HCS = hot crushing strength

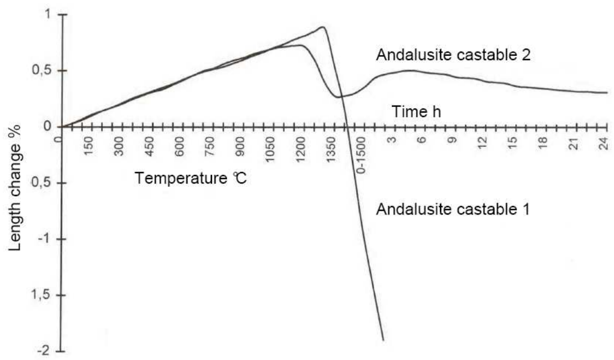

Fig. 12: Creep resistance of Andalusite based low cement castables at 1500 °C. Castable 2 with matrix aluminas (HCS at 1500 °C: 11 MPa), castable 1 without (HCS 1 MPa) [30]

The previous example shows how important the composition of the refractory matrix can be for the overall behaviour of the material. The development of various reactive aluminas, including spinel containing grades, has enabled significant performance improvements for both castable and brick applications. When considering a substitution of a higher alumina aggregate (BFA, bauxite) with lower alumina aggregates (andalusite, Mulcoa, chamotte), special attention should be given to the matrix fines. In many cases, the new material may provide even better properties than the original one.

CONCLUSION

Alumino-silicate materials, andalusite and Mulcoa 60/70, can replace bauxite in applications where slag basicity is not too high (C/S ratio below 0.9 or C/A ratio below 0.6), and Manganese content of the slag is below 6 %. They often provide better thermo-mechanical properties such as hot strength, refractoriness under load, creep resistance, and thermal shock resistance. Bauxite and alumino-silicate materials have reached their technical limit as wear linings in steel ladles in Europe. It can be expected that they will also be replaced in other regions by either synthetic alumina based materials or basic refractories.

Synthetic alumina refractories such as those based upon tabular alumina have become even more competitive against BFA because of the steep price increases from China. They have proved their performance by very low specific refractory consumption and lower cost in steel ladle applications for more than 15 years. They provide an economic alternative to BFA in runner castables, AMC bricks, and foundry applications. The global refractory industry needs alternatives to Chinese sourced raw materials and new developments of high alumina aggregates are being considered. An example is discussed by Schönwelski [41].

Spinel containing alumina refractories have become a standard material over the past 20 years. Depending upon the application, either pre-formed or in situ forming spinel can be preferable. A combination of both concepts provides the best slag resistance in steel ladle side wall applications. Functional refractories such as purging plugs show the best performance with pre-formed alumina rich spinel.

When considering the substitution of high alumina aggregates in refractory product formulations, density differences between the aggregates must be taken into account. The ratio of aggregate to matrix fines changes, as does the material demand for filling a defined volume. This is also technically important for all pressed products. A simple focus on the particle size distribution of the aggregate sizes alone is not sufficient. Lower density aggregates provide an economic advantage by lower material consumption, unless the lower density is accompanied by high open porosity.

The technical development in steel making is continuously ongoing and drives the growing demand for better performing and more cost effective alumina refractories. High purity synthetic alumina based raw materials provide the potential for these future demands. This not only applies for applications in wear linings, but also to back linings as shown by the new development of dense calcium hexaluminate, Bonite.

The matrix fines play an important role in the performance of refractories. Matrix aluminas and especially new reactive aluminas have an important share in the development of new high performance refractories over the past 20 years. The development focus in matrix aluminas has been widened recently from pure particle packing aspects and low water demand in castables, to also include workability aspects as well. Easy mixing and easy placement are very important to avoid on site installation failure. New products such as the E-SY aluminas provide that desired behaviour.

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