Synthetic alumina raw materials – key elements for innovative refractories

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Synthetic alumina-based raw materials have enabled the development of new refractories for many applications in the steel industry, mainly for blast furnace linings, tapholes and main troughs, torpedo cars and transfer ladles, electric arc furnaces, steel ladles, tundishes, slide gate plates and nozzles. Some of the most important new developments are castable refractories with dispersing aluminas, the matrix advantage system for vibration and self-flowing castables and the InfilCast® technology for the placement of monolithic castables.

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Applications of synthetic alumina raw materials

Refractory aggregates like tabular alumina, magnesia aluminate spinels, and fine refractory matrix components like calcined and reactive aluminas, calcium aluminate cements, and dispersing aluminas, which are used in both shaped and unshaped refractories, have made significant contributions to the development of high performance refractories.

A comprehensive review of *production processes, properties and applications* of synthetic aluminas is given by Hart [1]. Kendal [2] and Keegan [3] describe the applications of synthetic aluminas in different industries.

Beside these applications, the main volume market for synthetic alumina raw materials is the refractory industry. 65–70% of refractories are used in the *iron and steel industry*. The continuous advancement of steelmaking technology and processes requires higher quality refractories, which has led to an increase in the use of synthetic alumina raw materials, despite an overall decrease in specific refractory consumption in steelmaking [2]. Key advantages of alumina in its main refractory applications are high thermomechanical strength, chemical stability, high thermal shock resistance, good abrasion resistance, and easy handling.

Applications in the iron and steel industry

Applications of alumina raw materials and refractories in steelmaking processes are given in **table 1**, which also includes the average specific refractory consumption for each process.

Blast furnace lining. Jeschke and Mörtl [4] describe the lining of large, modern blast furnaces. Besides fireclay (35–45% Al₂O₃) and high alumina bricks (60–75% Al₂O₃ based on andalusite or mullite), mullite-bonded corundum bricks (90–95% Al₂O₃) are sometimes used for the *stack*. Krebs [5] reports on monolithic linings of parts of the cooling box of the stack with self-flowing castables. For the lining of the *bottom and hearth* of modern blast furnaces, a ceramic cup, which comprises sintered mullite bricks at the bottom and large precast panels in front of the carbon wall, is used to protect the carbon bricks and extend their service-life. Today corundum-based castables are used instead of chrome-corundum for environmental reasons [6].

Blast furnace taphole. Since 20 years ago, the number of operating blast furnaces has been decreasing while the iron production has been kept nearly constant by higher outputs from larger furnaces [7]. An increase in tapping temperature from 1450 up to 1550 °C is observed [4]. Higher temperatures combined with prolonged tapping time and the requirements of constant flow, safety, and reduction in the specific refractory cost have led to the development of new taphole muds. Compared to conventional muds, the new muds contain increased amounts of alumina and silicon carbide, up to 50% and 15-20%, respectively, SiO2 decreased from about 60 down to < 10%, and about 15% carbon. The specific refractory consumption of the new muds is 0.5–0.8 kg/t hot metal [1, 4, 7]. Besides aluminosilicates, bauxite, and corundum, there is a potential for high purity aluminas because of severer working conditions expected for taphole muds in the future.

Table 1. Applications and specific refractory consumption of synthetic raw alumina materials for steelmaking refractories (references see text)

Process	Type of refractory			Alumina	a product		Refractory consumption	
	, ,	Tab	Spi	Calc.	React	Disp.	CAC	kg/t iron or stee
Blast furnace:							700	
Stack, ceramic cup	High alumina bricks							
	and castables	Х		Х	X	Х	Х	
Taphole mud	A-SiC-S-C masses	Х		Х	X			0.5-0.8
Main trough	A-SiC-C castables	Х	Х	x	X	X	X	0.3-0.6
Slag runner	A-SiC-C castables			×	X	Х	X	0.15-0.3
Iron runner	A-SiC-C castables			×	Х	Х	X	0.15-0.3
Tilting trough	A-SiC-C castables			X	х	Х	x	0.1
Hot metal transport:								
Torpedo ladle	High alumina							
,	bricks and castables,	X		Х	X	Х	х	0.4-0.5
	A-SiC-C bricks							
Transfer ladle	High alumina							
	bricks and castables	(x)		x	x	X	х	0.4-0.5
Electric arc furnace:	A-MA castables							
	and bricks	х	х	х	X	X	х	0.1-0.3
Steel ladle:								
Bottom, side wall	A-MA-M castables,							
	high alumina							
	and A-M-C bricks	Х	Х	×	х	X	x	1.5-4.0
Safety lining	High alumina castables	(x)	(x)	x	x	x	x	< 0.05
Secondary metallurgy:					T			***************************************
RH-snorkel	A-MA castables	х	х	×	Х	Х	X	0.1-0.2
Ladle covers	A-MA castables	Х	х	X	x	x	x	0.2
Precast shapes:								
Purging plugs,								
wellblocks, lances etc.	A-MA castables	x	x	X	x	x	x	0.15-0.25
Slide gate plates	A-S-C	x	(x)		х			0.05
Continuous casting:			14.00		Nisha(if	dalaw.	dalaini katan	
Tundish, permanent lining	High alumina							
	castables and bricks	(x)		X	_ X	X	X	0.05
Long nozzle,	A-S-C SiC isostatic							
monobloc stopper,	pressed							
subentry nozzle		X			to, kolud.	HULLINUS.	95 MATERIA (* - 1	0.2
*	$gO Al_2O_3$; $M = MgO$; $S = SiO_3$		arbon			is in bolishing.		0.2

Blast furnace main trough. Low cement and ultra-low cement castables with 60-85% Al₂O₃ and 5-25% SiC are used for the wear lining of the main trough [7, 8]. Replacement of ramming installation with vibration casting and self-flow casting has a strong impact on the improvement of working conditions in the casthouse [7]. In 1992 Nameishi [9] described the development of main trough materials in Japan from ramming mixes made of Roseki chamotte-SiC-C to vibration castables made of Al₂O₃-SiC-C. The bonding changed from clay + deflocculant to ultrafine silica powder + cement. Nameishi [9] expected that the future direction for the improvement of main trough castables would be a decrease in the silica content and the development of agents that can reduce the amount of water. Today, multimodal reactive aluminas are available as effective matrix components for those improvements that will be described later. Jeschke and Mörtl [4] reported in 1993 that free-flowing mixes have certain limitations; setting time, in particular, has to be adjusted according to the requirements on site. New developments for setting control like the dispersing aluminas will also be described later.

Consumption data are given by Jeschke [4] and Zhong [8]. Larger furnaces always have higher specific refractory consumption than smaller furnaces, mainly because of high-

er erosion. The flow speed of the iron in a trough is higher for larger furnaces, because the trough cross section is not increased in proportion to the tonnage of iron produced per minute [10]. A study of the corrosion wear of castables versus temperature shows a remarkable increase in wear, by 100% and 350% if temperature is increased from 1500 °C to 1550 °C and 1600 °C, respectively [11]. Avis [10] reports a special trough castable lining for a jumbo blast furnace with an average tapping temperature of 1520 °C. A corundum-based castable (30% SiC) caused problems which were attributed to high wear. Replacement of fused corundum with tabular alumina solved the problems, and despite higher raw material costs, the overall specific cost was reduced.

It is important to note that *tabular alumina* (3.55 g/cm³) has a bulk density that is 11% lower than that of brown fused corundum (3.95 g/cm³). Since about 60% of the mixes is coarse aggregates, tabular alumina reduces the material demand by 6–7% in weight, which lowers specific refractory consumption by about 0.02 kg/t iron. Lower bulk density of tabular alumina is due to small intracrystalline (closed) pores (< 1–10 μ m), which are not infiltrated by slag and considerably improve the thermal shock resistance of the aggregate [1]. Compared to brown fused corundum with an

impurity content of 4–5% (TiO_2 , SiO_2 , Fe_2O_3 , and alkalis), tabular alumina has a much higher chemical purity ($Al_2O_3 > 99.4\%$) which contributes to the improvement of the wear resistance of the trough castables.

The *slag corrosion resistance* of Al₂O₃–SiC–C castables is improved by adding spinel which forms less liquid phase with slag than pure alumina materials, despite accelerated decomposition of SiC when it coexists with spinel [12]. Alumina-rich spinel shows advantages over stoichiometric spinel, because of less oxidation of SiC [13].

Torpedo car and transfer ladle. For torpedo cars, various high alumina refractories are used, the required quality of which depends on the hot metal treatment. When no hot metal treatment is performed, fired bricks of andalusite and bauxite are the common linings [14], and the specific refractory consumption is 0.4-0.5 kg/t hot metal. When desulphurization, dephosphorization, and desiliconization are performed in the torpedo car, the specific consumption increases to 0.9 kg/t and Al₂O₃-C and Al₂O₃-SiC-C bricks of higher quality are used [4, 9, 15, 16]. These types of bricks are also used for the impact zone when no desulphurization is carried out in the torpedo car. Corrosion tests of Al₂O₃-SiC-C bricks have shown that the wear rate is 50-60% lower with synthetic alumina raw materials than with natural materials like and alusite and calcined aluminous shale [9]. Kataoka [16] anticipated in 1995 that monolithic refractories would play an increasingly important role for torpedo car linings in the future. The development of the shotcreting technology supports that prediction, because it removes the need for the construction and installation of a former, which is difficult to realize in a torpedo car. Trials with shotcreting technology will continue for new linings and repairs.

Transfer ladles (hot metal charging ladles) are commonly lined with alumina bricks, fired or chemically bonded. Sometimes carbon-bonded high alumina bricks are used in parts of the ladle, at the bottom, for example. The spout is often lined with monolithic high alumina materials by ramming, casting, or gunning. Reisinger et al. [17] report on monolithic bottom and side wall linings of a 120 t transfer ladle with a high alumina self-flowing castable.

Electric arc furnace. Special parts of electric arc furnaces, e.g., roof (delta section), charging and slagging doors, pouring spouts, and tapping systems, are lined with high alumina materials. In view of high temperatures and severe working conditions, these are very often precast shaped refractories based on tabular alumina and corundum. The lining life of those prefabricated blocks is approx. two or three times higher than that of installations on site [4]. The Infil-Cast® technology, a new installation method for monolithic refractories developed by Alcoa, has undergone successful trials in EAF cover heart sections as well as in steel ladle bottoms and wellblocks in several European countries. With this technology, the lining life of the EAF cover heart at a German steel plant was increased by about 50% compared to an alumina-spinel castable formulated with a conventional particle size distribution [18].

Steel ladle. The replacement of ingot casting by continuous casting and the increasing demand for steel cleanliness require a variety of metallurgical processes to be performed in the steel ladle. Their metallurgical aspects and demands

on refractories are discussed in detail by Bannenberg [19]. The development of ladle metallurgy (secondary metallurgy) has resulted in much severer working conditions for the ladle refractories because of increased tapping temperatures, extended residence time of the steel in the ladle, stirring, heating, and various aggressive slag compositions, e.g., for desulphurization [20]. The development of ladle lining refractories in response to such working conditions has been discussed by several authors [8, 9, 15, 16, 21-27]. Cheap acid materials like slinging sand or Roseki chamotte have been replaced by high alumina bricks (e.g. andalusite or bauxite) or zircon-containing materials. Today, basic bricks (magnesia-carbon or dolomite) or high alumina castables (tabular alumina, corundum, spinel, or spinel-forming) or alumina-magnesia-carbon bricks are standard lining materials for steel ladles. They are used either alone or in combination in various installation practices, e.g., aluminaspinel-castables at the bottom and in the side wall, and magnesia-carbon bricks in the slag line. Ladle lining practices can remarkably differ between regions and steel plants as the result of different metallurgical processes, working conditions, and refractory concepts.

With the introduction of high quality lining materials *specific refractory consumption* of steel ladle linings decreased significantly, e.g., from about 9 kg/t of steel with slinging sand down to below 1.5 kg/t with alumina-spinel castables combined with relining techniques [25, 26, 28, 29]. In a modern integrated steel plant the steel ladle lining accounts for about 25% of total refractory consumption both in tonnage and costs [20]. However, specific refractory consumption strongly depends on the metallurgical processes applied and can be as high as 10 kg/t when Vacuum Oxygen Degassing (VOD) or Ladle Furnace (LF) processes [30] are used.

A detailed laboratory investigation of *high alumina* castables based on natural and synthetic raw materials is given by Buhr [31] in order to provide users in the steel industry with a basis for assessment. Theoretical investigation and practical experiments show that the high purity of raw materials and the low silica content particularly in the castable matrix exert remarkable influences on the thermomechanical properties, especially at high temperatures [31, 32]. For the performance of monolithic ladle linings, proper workability of the castable is essential. The development of self-flowing mixes has eased casting practices and reduced failure attributable to improper densification of the castable installed with vibration.

Monolithic permanent and safety linings of steel ladles are based on natural high alumina materials or tabular alumina and spinel, and extend lining life to several years [17, 33].

Recent developments of *alumina-magnesia-carbon bricks* for steel ladles combine the advantages of high alumina with those of carbon-containing refractories. This type of resin-bonded brick contains 60–90% Al₂O₃ (tabular alumina, corundum, bauxite), 6–11% (sometimes up to 33%) MgO, 6–8% carbon, and optional antioxidants.

Precast shapes. The main applications of precast shapes are in *steel ladles and tundishes*. They include purging plugs and injection lances, wellblocks, nozzles, impact pads, precast ladle bottom elements, and tundish furniture for steel flow modification. These refractory products are not only part of the refractory lining but necessary for the performance of a required metallurgical treatment. Purging plugs at the ladle bottom, for example, are required to ex-

hibit reliable stirring performance and high wear resistance [20]. Temperatures as high as 1750 °C in steel ladles require refractories based on *synthetic aluminous materials* like tabular alumina or spinel, while lower temperatures in tundishes (about 1550 °C) permit the use of natural raw materials (bauxite, andalusite) as well as synthetic ones. An investigation of purging plugs made of alumina and alumina-spinel for steel ladles shows a favorable high hot crushing strength of 25 to 43 MPa at 1600 °C [34].

Slide gate plates. Slide gate plates were the first important and successful application of tabular alumina in the steel industry. High wear resistance combined with excellent thermal shock resistance is the key advantage of tabular alumina in comparison with fused corundum [1]. The development of slide gate plate refractories has been described by several authors [8, 9, 16, 24, 35-37]. Commonly used mullite-bonded alumina refractories (85-90% Al₂O₃) have been improved by reducing silica content and adding graphite and carbon bonding. Mullite improves the thermal shock resistance but its SiO₂ content decreases resistance against corrosion caused by calcium-treated steel, high manganese steel, and high oxygen steel. Slide gate plates with an addition of ZrO2 instead of SiO2 feature high corrosion and thermal shock resistance. Walker et al. [37] and Anderson et al. [36] report on the development of magnesia-spinel plates to improve thermal shock resistance.

Continuous casting. The most commonly used refractories for *permanent tundish linings* are high alumina castables based on andalusite or bauxite. Monolithic linings show better performance than bricks in terms of both lining life and economy [17, 38, 39]. Sufficient mechanical strength and high thermal shock resistance are key properties of high performance tundish castables [31].

With its excellent thermal shock resistance, fused silica was initially used as a principal material for submerged entry nozzles in continuous casting, but it suffers dramatic wear when used with manganese-containing steel. Isostatically pressed Al₂O₃-SiC-SiO₂-C (graphite) refractories are now used for the main body of long nozzles (ladle shrouds), monobloc stoppers, and submerged entry nozzles. Usually, the alumina content is 50-60% and the carbon content 20-30%. A ZrO₂-C material with extremely high wear resistance is used for the slag line of the submerged entry nozzle. MgO-C materials improve corrosion resistance of the cap of monobloc stoppers and the inlet of submerged entry nozzles for casting calcium-treated or high oxygen steels [24, 40–43]. Nomura et al. [44] report on spinel coatings to improve the corrosion resistance of submerged entry nozzles against high-oxygen steels.

Refractories consumption in the iron and steel industry

Specific refractory consumption in steelmaking strongly depends on the applied *steelmaking technologies*. In the western countries most open hearth furnaces were taken out of operation in the 1970s. During that time, in Germany, for example, refractory consumption decreased from 35 kg (1970) to 23.4 kg/t (1980) of crude steel [21]. The expansion of continuous casting to more than 90% of the steel cast in most of the developed countries further decreased the re-

fractory consumption to below 15 kg/t crude steel, e.g., 10.7 kg/t in Japan in 1997 [45].

The decrease in specific refractory consumption has been more intense for shaped refractories (bricks) than *unshaped refractories* (monolithics). As a result of this, the ratio of unshaped to total refractories in terms of specific consumption has been increasing. In Japan, the 1989 consumption of unshaped materials in steelmaking was for the first time higher than that of shaped materials [45]. Increasing consumption of unshaped refractories is also reported in Germany [20].

The increasing importance of *monolithic refractories* in steelmaking is related to the development and use of high performance low and ultra-low cement castables. Newly developed synthetic alumina raw materials have been the key elements for these innovations, and they are described in the following part of the article.

Synthetic alumina raw material innovations

Castable formulation principles. Before discussing the innovative synthetic alumina products, we will take a look at the *principles* of refractory castable formulation to show the idea behind and benefits from these new products. In general, a castable is made from several components that include refractory aggregates, e.g., tabular alumina and spinel of different grain size fractions up to 10 mm, a binder like calcium aluminate cement, and fine-grained materials like calcined aluminas, reactive aluminas, or microsilica which are essential for the formulation of low and ultra-low cement castables. The fine-grained fraction including the binder is called the matrix. Defined as the fraction below 45 μ m, the matrix accounts for approximately 25% of the total weight in the case of vibration castables and 35% in self-flowing castables.

The final performance of a castable not only depends on its refractoriness but also on physical properties like density, porosity, strength, etc. The former is determined by the chemical and mineralogical compositions. Microsilica addition, for example, significantly reduces the refractoriness of a tabular alumina castable bonded by a pure calcium aluminate cement; the theoretical temperature for the onset of melting is lowered from 1875 °C to 1512 °C [31]. Physical properties, on the other hand, are critically affected by the amount of water needed for the mixing and placement of a castable. Increasing the water addition by 1% results in an increase of about 3% in the open porosity in dried and fired castable installations and significantly reduces their slag resistance.

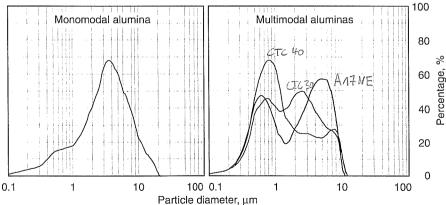
These simple examples show the importance of taking both chemical and physical aspects into consideration in the formulation of castables.

The key for minimizing the amount of water necessary for mixing a refractory castable and obtaining desired rheological behavior is to optimize *particle packing* especially in the matrix down to the submicron range. Successive particle sizes must be put together in such a way as to minimize the void, which is filled with water. Microsilica has particle sizes ranging down to below 1 μm and has been a key component in the development of low and ultra-low cement castables with low water demand. But it reduces the refractoriness of castables by forming low melting phase compositions with calcium aluminate cement.

Monomodal and multimodal reactive and calcined aluminas. In general, the composition of the matrix is especially important for the refractoriness of a castable, because the calcia originating from calcium aluminate cement is located in the matrix. The development of *superfine ground aluminas* allowed the replacement of microsilica in the finest part of the particle size distribution. Those aluminas were used first in ceramic applications and are called "reactive aluminas" because of their high sintering reactivity resulting from their high specific surface area and small primary crystal size. Reactive aluminas are a subgroup of calcined aluminas, their BET surface areas being as high as or above 1.5 m²/g and soda contents below 0.1%.

Innovation in reactive aluminas has led to the development of aluminas with a multimodal particle size distribution as shown in figure 1, which was measured with a laser optical instrument (Cilas HR 850). Aluminas whose particle size distribution exhibits only one peak are monomodal with a majority of particles within a tight particle size range. Aluminas with two or more peaks are called multimodal. In a castable formulation, monomodal alumina covers a small portion of the particle size range of the matrix, and has to be surrounded by other matching products for the desired rheological properties to be achieved. Multimodal aluminas cover a broad range of the particle size, which helps improve the rheological behavior of castables even with a reduced amount of water. A variety of such products are available to meet individual requirements in respect of sintering reactivity and volume stability as well as different placement technologies for vibration, self-flow, and gunning castables [46-50].

Calcium aluminate cements. For high performance castables, calcium aluminate cements (CAC) containing 70 and 80% Al₂O₃ are most commonly used. While 70% CAC's typically consist of pure clinker, 80% CAC's consist of clinker plus calcined alumina addition in order to bring the total alumina content up to 80%. In high quality cements, the total content of impurities like SiO_2 and Fe_2O_3 is below 0.5%.



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Product: Type:		CT 800 SG calcined	电电弧流流 化氯甲烷 化氯酚	CTC 30 reactive	CTC 40 reactive						
Chemical composition (typical)											
Al_2O_3	[%]	99.7	99.8	99.8	99.8						
Na ₂ O	[%]	0.12	0.06	0.09	0.08						
Physical properties (min-max)											
BET surface area	$[m^2/g]$	0.8-1.5	2.4 - 3.7	3.0-4.5	4.0-5.5						
d50 – Cilas	[μm]	3.3-4.3	2.0-3.0	1.4-2.0	0.9–1.3						
Reactivity → higher BET, lower d50											

Figure 1. Properties of monomodal and multimodal aluminas

For *low cement castables* (LCC, total CaO 1–2.5%) and ultra-low cement castables (ULCC, total CaO < 1%), 70% CAC is preferred. The innovative 70% ${\rm Al_2O_3}$ cement CA-270 is optimized specifically for low water demand; compared to conventional 70% CAC's, CA-270 is made from much denser clinker and exhibits a bimodal particle size distribution, which contributes to dense particle packing of castable matrix. The hydraulic bonding properties of cements depend primarily on their mineralogical phase compositions, not on chemical compositions. The mineralogy of CA-270 is optimized so that castables can achieve high strength even at a low cement content.

Being hydraulic binders, calcium aluminate cements develop heat during their *hydration* (exothermic reaction) with the mixing water. The amount of heat generated and its time frame depend on various factors such as CAC reactivity, ambient temperature, pH, and additives used to accelerate or retard setting. The heat evolution can be measured and recorded with thermocouples and a data logger and used to control the setting behavior of castables [47, 51]. Numerous tests have proved that the EXO start (first increase in temperature) correlates very well with the time for the end of the flow or working time which is usually determined by the vibration flow cone test. The EXO max corresponds with the time for maximum temperature development and correlates with the development of strength high enough for demolding.

Dispersing aluminas. To take full advantage of the castable matrix whose particle size distribution has been optimized for the lowest water demand and desired rheological behavior, it is essential that all the matrix components are homogeneously distributed during mixing with water. **Dispersing agents** are commonly used to de-agglomerate fine particles. Also used are **additives** that influence the hydraulic reaction of the cement and steer the setting time of castables. Homogeneous mixing of these agents and additives is difficult, since usual additive concentrations are in the range of 0.01–0.1% which corresponds to 0.1–1 kg/t of

castable mix. The homogeneous mixing of its components is inherently difficult.

The dispersive function of dispersing agents can be seen during the mixing of a high performance castable whose water demand is below 5%. With water added, the castable initially looks completely dry. After some mixing, matrix fines start dispersing, and first small crumbs and later larger lumps form. Further mixing results in gradual release of water from the void among particles as the dispersed reactive alumina replaces the water in the void, and final mix consistency is obtained after thorough mixing. The total mixing time usually takes 4–6 minutes

Setting behavior required of castables varies greatly according to their applications. For example, castables for blast furnace trough linings need a long setting time even at elevated temperatures, because about 100 t of

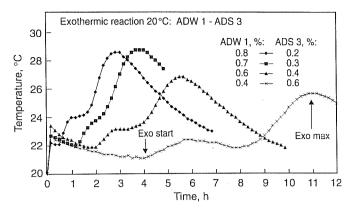


Figure 2. Dispersing alumina combinations and their influence on castable setting (exothermic reaction). (Exo start = end of flow; Exo max = demolding strength; ADS = dispersing alumina, retarding type; ADW = dispersing alumina, accelerating type

castable must be placed without lamination, which may occur if setting starts too early. On the other hand, producers of precast shapes, e.g., purging plugs for steel ladles, have a strong interest in a short demolding time, which corresponds to a short setting time so as to reduce the number of formers needed for their production.

Dispersing aluminas are innovative products with the function of dispersing matrix fines combined with the function of steering the setting behavior of castables. When dispersing aluminas are used, no other additive is needed to adjust the rheological and setting behavior of castables to individual requirements. Two types of dispersing aluminas, the retarding type (ADS 1 or ADS 3) and the accelerating type (ADW 1), are used together in a predetermined ratio for a desired setting time. The total amount of dispersing aluminas is recommended to be approx. 1% in weight of the castable. As long as the total amount is kept unchanged, the dispersing capability of dispersing aluminas remains stable no matter which type (S or W) or types are used. For castables containing microsilica, dispersing aluminas M-ADS 1 and M-ADW 1 have been developed according to the same principle as was applied for developing the original dispersing aluminas.

The advantages of dispersing aluminas in comparison to conventional additive packages are highly homogenized mixing, high reproducibility of well-defined setting times, and easy control of the setting time in a wide temperature range. Homogeneous mixing is easily achieved, because the amount

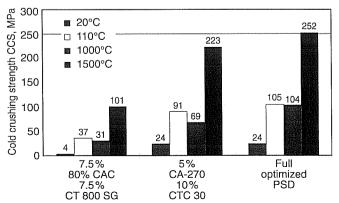


Figure 3. Cold crushing strength of castables with different matrix compositions (PSD = particle size distribution)

of dispersing aluminas added to one t of castable is as much as 10 kg. The *exothermic reaction* shown in **figure 2** clearly demonstrates the influence of different ratios of S-type to W-type dispersing aluminas on the setting behavior.

The Matrix Advantage System (MAS)

The MAS consists of matrix components based on *new alumina raw materials* that facilitate the design of matrices for vibration (VIB), self-flow (SF), and dry gunning (GUN) placement [46–48]. It is intended to offer user-friendly combinations of a small number of matrix components, which are individually optimized to deliver optimum performance in many types of placement.

The MAS *components* include:

- a single 70% Al₂O₃ cement CA-270 for vibration selfflow – dry gunning placement,
- reactive aluminas for vibration self flow dry gunning placement, and
- dispersing aluminas for vibration and self-flow placement.

To exemplify the *benefits of this system*, improvements made to a vibration castable based on tabular alumina are discussed below. In this case fines (cement and alumina) occupying 15% of the castable were replaced with MAS components [46].

The original formulation contained 80% CAC and a calcined alumina (CT800SG), 7.5% each, which were replaced with 70% CAC (CA-270) and a reactive alumina (CTC 30 or CTC 40), 5% and 10%, respectively. CaO and Al_2O_3 levels were identical in both formulations. Polycarbonic acid, an additive used in the original mix, was replaced with the dispersing aluminas ADS 1 and ADW 1 for optimum dispersion and setting control. Compared to the original mix, the new mix containing MAS components exhibited the following *improvements:*

- water demand decrease by 28% (from 6% to 4.3%),
- softer mix consistency,
- remarkable increase in cold crushing strength (CCS) at 20 °C from 3.8 MPa to 24.4 MPa (CTC 30) and 26.9 MPa (CTC 40), and
- remarkable increase in hot modulus of rupture (HMOR) at 1500 °C from 5.2 MPa to 16.9 MPa (CTC 30) and 18.1 MPa (CTC 40).

The increase in *hot strength* is due to the sintering reactivity of the aluminas used, CTC 40 being the most reactive. Further improvements in the mix properties were achieved by optimizing the packing density in the coarse and medium fractions of the castable. The use of closed sizes as well as finely ground tabular alumina T-60 0–0.020 mm led to a further reduction in the mixing water demand to as low as 3.6%, which still imparted soft consistency to the mix. This mix, whose particle size distribution was fully optimized in the whole particle size range, exhibited a higher density and a remarkably high CCS at 1000 °C, which closed the typical strength gap [46] as shown in **figure 3.** It is mentioned in passing that similar improvements have been made with MAS on self-flowing and gunning formulations.

InfilCast technology

InfilCast[®] is a completely *new monolithic placement technology* which takes advantage of large ball-shaped aggregates (converter discharge sieved 18–22 mm) or grains

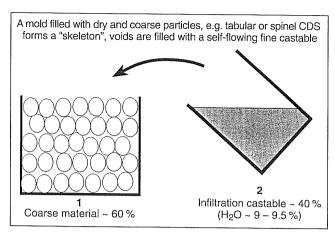


Figure 4. Principle of InfilCast technology (CDS = Converter discharge sieved)

of irregular shapes (6–12 mm) of tabular alumina or spinel [49]. This technology, which was patented by Alcoa, is based on those coarse grains and a fine slip. Dry coarse grains are introduced into a mold and subsequently fully infiltrated with a special slip, **figure 4.** This slip embodies all the experience gained through the development of high performance matrix products. Its components include special infiltrating ("AFL") aluminas, the new CA-270 cement, and the dispersing aluminas ADS and ADW.

Initial results, as mentioned before, clearly indicate that this new placement technique has several *advantages* over conventional castable technologies. The technology enables the use of high performance raw materials like tabular alumina and spinel in forms that can be produced at lower processing costs than with crushed and sieved grains. One interesting aspect of the InfilCast technology is the dry placement of coarse materials that occupy 60% of the whole body. This means that only fine matrix materials that occupy 40% of the body remain to be mixed.

References

- Hart, L. D. (ed); Lense, E.: Alumina Chemicals Science and Technology Handbook, 1990, American Ceramic Society, ISBN 0-916094-33-2.
- [2] Kendal, T.: Industrial Minerals April 1995, 23-43.
- [3] Keegan, N. (ed.): Raw Materials for the Refractories Industry, 4th edition, paper: Tabular & Calcined Aluminas Positive performance, Industrial Minerals Raw Material Survey 1998, p. 51/60.
- [4] Jeschke, P.; Mörtl, G.: Recent Trends in Refractories ... Unitecr Proc., São Paulo 1993, p. 17/67.
- [5] Krebs, R.: Experience with Advanced Monolithics ... Unitecr Proc. Vol. 3, New Orleans 1997, p. 1282/1292.
- [6] Habashi, F.: Handbook of Extractive Metallurgy Vol. 1 (1997). Wiley-VCH, Weinheim, Germany, p. 101/102.
- [7] Rüther, P.: Hochofenstichloch- und Rinnenmassen. VDEh-Seminar Feuerfesttechnologie Teil 1, Nov. 29–Dec. 2, 1999, Ahrweiler, Germany.
- [8] Zhong, X. C.: Refractories Developments ... UNITECR Proc. Vol. 1, Kyoto 1995, p. 75/85.
- [9] Nameishi, N.; Nagai, B.; Matsumura, T.: Taikabutsu Overseas Vol. 12 (1992) No. 2, p. 40/50.
- [10] Avis, R. N.: Customized Solutions ... Proc. of 3. India Intern. Refractories Congr. IIREFCON, Vol. 1, Kalkutta 1998, p. 39/44.
- [11] Clavaud, B.; Gondolf, M; Avis, R.: Development of a Wear Factors Modelisation ... Unitecr Proc. Vol. 1, Kyoto 1995, p. 144/150.
- [12] *Iida*, M.; *Toritani*, Y.; *Tanaka*, S.: Effect of Spinel and Silicon-Carbide ... United Proc. Vol. 1, Kyoto 1995, p. 151/158.
- [13] Samukawa, F.; Muroi, N.; Tanaka, S.: Taikabutsu Overseas Vol. 18 (1998) No. 4, p. 37/41.
- [14] Koltermann, M.: Taikabutsu Overseas Vol. 5 (1985) No. 2, p. 35/40.

- [15] Kasai, K.: Nippon Steel Techn. Report No. 61, April 1994, p. 83/89.
- [16] Kataoka, S.: Refractories for Steelmaking in Japan. Uniteer Proc. Vol. 1, Kyoto 1995, p. 1/27.
- [17] Reisinger, P.; Preβlinger, H.; Mayrhofer, H.; Fischer, N.: Monolithic Refractories ... Uniteer Proc. Vol. 1, New Orleans 1997, p. 255/264.
- [18] Personal communication H. Siek, Georgsmarienhütte, Germany.
- [19] Bannenberg, N.: Demands on Refractory Material for Clean Steel Production. United Proc. Vol. 1, Kyoto 1995, p. 36/52.
- [20] Bannenberg, N.; Buhr, A.: Stahl u. Eisen 118 (1998) No. 10, p. 83/87.
- [21] Koltermann, M.: Shinagawa Techn. Report Vol. 34 (1991), p. 1/8.
- [22] Nagai, B.; Matsumote, O.; Isobe, T.: Development of Monolithic Refractory Linings ... Uniteer Proc. Aachen 1991, p. 83/86.
- [23] Rasim, W.; Kessler, R.; Keller, K.; Teimann, H.: Monolithische Zustellung tonerdereicher Stahlgießpfannen ... Proc. 35. International Colloquium on Refractories, Aachen, 1992, p. 117/120.
- [24] Asano, S.: Progress of Steel Making Technology and Refractories Situation in Japan. Uniteer Proc., São Paulo 1993, p. 69/94.
- [25] Artelt, P.: Keramische Zeitschrift, 45. Jahrgang (1993) No. 9, p. 538/544.
- [26] Koch, E.; Reisinger, P.; Jungreithmeier, A.; Karhut, G.: Veitsch-Radex Rundschau 1-2/1994, p. 494/511.
- [27] Reisinger, P.; Koch, E.; Jungreithmeier, A.; Karhut, G.: Steel Technology Intern. 1995/96, p. 101/104.
- [28] Eitel, W.: Monolithische umweltbewußte Feuerfestzustellung ... 33. Intern. Coll. on Refractories, Aachen, 1990, p. 420/435.
- [29] Köster, V.; Klan, W.; Reuther, G.; Wethkamp, H.; Eitel, W.: Stahl und Eisen Special, October 1992, p. 103/108.
- [30] Whiteley, P. G.: Refractories the Next Decade, Industrial Minerals Sept. 1991, p. 27/43.
- [31] Buhr, A.: Stahl und Eisen 116 (1996) No. 9, p. 59/66.
- [32] Kriechbaum, G. W.; Gnauck, V.; Routschka, G.: The Influence of SiO₂ and Spinel ... Proc. 37. Intern. Coll. on Refractories, Aachen, 1994, p. 150/159.
- [33] Joint meeting of ATS-VDEh Refractory Committees, May 28–29, 1998, Paris.
- [34] Becker, J. U.; Berger, R.; Buhr, A.; Rasim, W. A.; Tiemann, H.: Purging Plugs for Steel Ladles ... Unitecr Proc. Vol. 1, New Orleans 1997, p. 143/152.
- [35] MacZura, G.: Production Processes, Properties and Applications ..., in Alumina Chemicals Science and Technology Handbook, 1990, American Ceramic Society, p. 109/170.
- [36] Anderson, D.; Taylor, D.; Cameron, I. V.: Development of Refractories ... United Proc. Vol. 3, New Orleans 1997, p. 1385/93.
- [37] Walker, B. L.; Allan, N.; Bailey, J. H.: The Development of Multi-life Magnesia ... Uniteer Proc. Vol. 3, New Orleans 1997, p. 1425/34.
- [38] Berger, R.; Köhler, K. U.; Schütt, H.: Stahl und Eisen 110 (1990) No. 11, p. 75/79.
- [39] Beelen, C. M.; Peeroboom, D. H.: Successful Use of Monolithics ... Proc. 35. Intern. Coll. on Refractories, Aachen, 1992, p. 75/80.
- [40] Buhr, H.; Oberbach, M.; Muschner, U.: High-Quality-Refractory ... 5th IISI – VDEh Technical Exchange Meeting on Refractories, April 9–10, 1992, Kyoto, Japan.
- [41] Ando, H.; Ozeki, H.; Muroi, T.; Oguri, K.: The application of Basic Materials for CC Refractories, Proc. Vol. 2 Uniteer 1995, Kyoto, p. 116/124
- [42] Poirier, J.; Guiban, M. A.; Tassot, P.; Hanse, E.; Thillou, B.; Benson, P.: Development of New Submerged Nozzles. Proc. Vol. 2 Unitecr 1995, Kyoto, p. 79/86.
- [43] Lee, S. J.; Pohl, S.: Composite Refractory Components ... Proc. 39. Intern. Coll. on Refractories, Aachen, 1996, p. 90/94.
- [44] Nomura, O.; Ushida, S.; Lin, W.: Development of a New SEN for High Oxygen Steel, Shinagawa Technical Report No. 42 (1999), p. 31/38.
- [45] Taikabutsu Overseas Statistics Vol. 18 (1998) No. 3, p. 59.
- [46] van Garsel, D.; Kriechbaum, G. W. et al.: Progress in Refractory Raw Materials for Monolithics, Kermetal, Kosice/Slovacia, 8.–9. 10. 1997.
- [47] van Garsel, D.; Kriechbaum, G. W., et al.: Developments for Improved Durability of Alumina Based Castables, IRE Colloquium, Johannesburg/South Africa 7, 8, 1997.
- [48] Kriechbaum, G. W.; Gnauck, V., et al.: The Matrix Advantage System ..., Proc. 39. Intern. Coll. on Refractories, Aachen, 1996, p. 211/218.
- [49] Kriechbaum, G. W.; Gnauck, V., et al.: New Developments of Tabular Alumina ... Proc. 40. Intern. Coll. on Refractories, Aachen, 1997, p. 143/150.
- [50] van Garsel, D.: High Alumina Cements & Chemical Binders, IRE Institute of Refractories Engineering, South Africa, 8. 3. 1996.
- [51] Alcoa Industrial Chemicals Europe, Olof-Palme-Str. 37, 60439 Frankfurt/Main, Germany: Calcium Aluminate Cements – Cement Test Methods brochure MSDS 993.