Technical Papers

High-Alumina Secondary Raw Materials from Aluminium Melting

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Abstract

During aluminium melting slags with high content of metal and oxides are formed on the surface of the melt. By processing these slags (dross and salt cake) to recycle the metallic aluminium, the oxides remain as a residual high-alumina concentrate. Due to the increasing amounts of aluminium slags, more than 100,000 t/a of such high-alumina secondary raw materials are presently recovered in Germany. The available information given here on generation and processing of aluminium slags as well as on properties and possible applications of the produced high-alumina secondary raw materials ought to encourage new users in the ceramic and refractories industry to test these materials. Producers of Portland cement have already taken benefit of these materials as a cost-effective alumina source.

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1 Availability of Raw Materials

High alumina raw materials are the basis of ceramic products with high thermal resistance, high mechanical strength, high electrical resistivity and high chemical resistance, i.e. refractory materials, abrasives, insulators and wear-resistant ceramics. The term "alumina" is commonly used for the chemical combination of aluminium and oxygen as well as for calcined, sintered and fused material of Al_2O_3 in the form of powders, grains or ceramics.

High-alumina natural raw materials (bauxite, sillimanite, kyanite and andalusite) as well as high-alumina synthetic raw materials (calcined alumina, corundum, mullite and spinel), are available world-wide in sufficient quantity, good quality and at increasing prices. High-alumina secondary raw materials from the processing of dross and salt cake from the aluminium smelters industry can be an additional and especially cost-effective alternative.

There are approximately 30 aluminium smelting facilities in Germany. These facilities produced 575,000 t primary aluminium and 418,000 t secondary aluminium in 1995 [1]. Each ton of secondary aluminium alloy results in 0.5 to 0.7 t of salt cake [2]. Each ton of salt cake contains 0.4 t of oxidic aluminium compounds which can be separated when processed as a high-alumina material.

Presently, the availability of these high-alumina secondary raw materials from the processing of dross and salt slag in Germany exceeds the annual figure of 100,000 t and is expected to grow according to the increasing rate of consumption and recycling of aluminium metal.

For the central processing of salt cakes in Germany the company B.U.S Berzelius Umwelt-Service AG, Duisburg, Germany operates two plants:

- SEGL GmbH, Lünen, and
- HANSE GmbH, Hannover (both Germany).

This central processing guarantees constant quality as well as long-term availability of a high-alumina secondary raw material called Oxiton.

2 Generation and Processing

Aluminium has a very high affinity to oxygen. As difficult as it is to reduce aluminium oxide to metal by aluminium electrolysis with high expense of electrical energy, it is easy to reform aluminium to alumina when it comes in contact with the oxygen in the air :

$$4Al + 3O_2 \rightarrow 2Al_2O_3.$$

This process already takes place at ambient temperature, whereby a freshly treated metal surface is coated by a thin layer of oxide of some nanometers thickness. By melting and pouring aluminium in air at temperatures above 800 °C the metal oxidation is of course even much more stronger. The dross thereby formed is a mixture of fine-grained particles of oxide and metal. This dross can coat the surface of the melt to a thickness of up to some centimetres. *I. Alfaro* [3] showed the detailed steps in the generation of aluminium dross and described the dimension of the formed oxide particles to be approximately 0.3 mm.

For remelting recycled aluminium scrap and dross rotary kilns are mainly used in Germany. To prevent oxidation by air, the molten metal in these kilns is usually covered by a layer of salt consisting of approximately 70 mass-% NaCl, 28 mass-% KCl and 2 mass-% CaF_2. During the melting process these melting salts are combined with a considerable amount of metallic aluminium to form a mixture called salt slag. When this salt slag is processed the aim of the foundries is only to get back the metal and the salt. For the high-alumina residual oxides other applications must therefore be found.

The essential steps in the treatment of salt slag by the Oxiton-generating B.U.S process are [2]:

- dry crushing, milling and separation of metal by screening
- leaching of salts by water

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- separation of water insoluble oxides by thickening and filtration
- crystallisation and dewatering of the recycled salt
- cleaning of the off-gases and recovery of NH_3 as ammonium sulphate.

The processing of drosses and slags from aluminium production is also usual procedure in the USA and Canada. In these countries, however, a dry treatment of dross is preferred. This is done by burning it with a plasma flame. In this way the metal recovery is reported to be higher than that from a rotary kiln [4]. The oxidic residues are called

- Noval in Canada [4] and
- NMP (Nonmetallic Product) in the USA [5].

Table 1: Chemical composition of high-alumina secondary raw materials			
	Oxiton Germany [6] [mass-%]	NMP USA [5] [mass-%]	Noval Canada [4] [mass-%]
Al_2O_3	59-66	60-70	53-65
AlN	1-2	1-10	9-18
Al (Metal)	1-5		5-10
MgO	6-9	13-17.5	
$MgO \cdot Al_2O_3$			5-12
SiO_2	6-9	4-9	1-2
CaO	3	1-1.5	3
F	1-2		
CaF_2			0.5-1.5
Na_2O	1	2.0	
Na_3AlF_6			0-4
NaCl			0-3
Cl	<0.4	<1.0	
K_2O	0.5	1.5	0.4
Fe_2O_3	1.4	1-1.9	0.5-2
MnO			0-1
L.o.I. (800 °C)	8-10		

Table 2: Sintering properties of Oxiton (dry pressed at 50 N/mm²)			
Temperature [°C]	Thermal Expansion [%]	Bulk Density [g/cm³]	Open Porosity [%]
110		1.66	43.7
200	+0.1		
300	+0		
400	-0.1		
500	+0.1		
600	+0.3		
700	+0.9		
800	+1.3		
900	+1.5		
1000	+1.7		
1100	+1.9	1.47	55.8
1200	+2.0		
1300	-0.7		
1400	-8.7	2.42	26.7

3 Properties of the Oxides

The chemical compositions of Oxiton [6], NMP and Noval are principally very similar (Table 1). The chemical composition of these high-alumina secondary raw materials depends essentially on the composition of the aluminium metal. Virtually all used metallic alloys are optimised in physical, chemical and workability properties. Typical components of aluminium alloys are mainly magnesium und silicon.

During the melting of aluminium in air the metal does not only combine with oxygen. It also reacts – to a lesser degree – with the nitrogen of the ambient atmosphere, forming aluminium nitride:

$$2Al + N_2 \rightarrow 2AlN.$$

In the chemical composition of dross and salt slag, AlN must also be taken into account. If these residues are processed with water, the aluminium nitride decomposes to aluminium hydroxide by releasing ammonia gas:

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3.$$

With the dry processed products of the USA and Canada the AlN content comes up to 18 mass-%. In the very intensive wet treatment of the Oxiton-generating German process, the aluminium nitride is decomposed to a great extent. Thereby, the ammonia is captured and converted into ammonium sulphate fertiliser. A residual amount of aluminium nitride remains in the Oxiton. Therefore, the filter humide Oxiton smells slightly of ammonia. After drying Oxiton there is no longer any noticeable smell.

The main mineralogical components of high-alumina secondary raw materials such as Oxiton are corundum and spinel. The cause is the intensive exothermic oxidation of aluminium metal with such high local temperatures, that the alumina transforms into the high-temperature modification corundum. Magnesium reacts even easier and more exothermal with oxygen than aluminium. Therefore, the magnesium oxide formed in the oxide layer immediately transforms with alumina to spinel $MgO \cdot Al_2O_3$ [7].

Some other physical properties of Oxiton are [5]:

- The true specific density is 2.95 g/cm³.
- The particle size is less than 200 µm, with a medium particle size of about 10–20 µm and ultimate particles <5 µm.
- The melting point is higher than 1600 °C.

The sintering properties of Oxiton are shown in Table 2. Sintering begins in the range of 1200–1300 °C. This corresponds to sintering results with alumina residues from the treatment of aluminium salt slags in Spain [8].

4 Possible Applications

Judging from several application tests and the composition of high-alumina secondary raw materials from processing aluminium salt slags, the following applications are proposed: refractories, fused grains, cement and glass, mineral wool, ceramic fibres, foundry and steel mixes and abrasives [2, 4, 5, 8]. In the USA the refractory lightweight aggregate Plasmal is produced by plasma fusion [9]. German research results further demonstrate the possibility of manufacturing high-porous sintered grains for lightweight concrete and bricks using Oxiton [10].

By reason of some content of calcium fluoride in Oxiton, fluoride can be emitted in the production of fired ceramics. This should not be a technical problem, as common clays also have a certain content of fluoride and therefore, the separation of fluorides from the off-gases is already state-of-the-art in ceramic plants. The rate of fluoride emission depends on the composition of the burned material, the sintering temperature and time. CaF_2 melts at 1360 °C. In the main actual application of Oxiton, as an alumina component for burning clinkers of Portland cement at 1450 °C, there is no remarkable emission of fluoride, because the fluoride is incorporated in the mineral $11CaO \cdot 7Al_2O_3 \cdot CaF_2$. This mineralic phase favours the early strength of cement. The addition of Oxiton to the cement raw mix reduces the sintering temperature and therefore saves energy.

Trials with Oxiton in refractory mixes and bricks for the lining of aluminium melting kilns showed that Oxiton is not attacked by molten aluminium. This is not surprising, as the oxidic particles of Oxiton are formed when they come in contact with molten aluminium. The content of fluorspar CaF_2, known as a non-wetting additive in refractories for contact with liquid aluminium, is in this case an advantage of Oxiton [11].

Regarding refractory mixes and concretes with a binder of calcium aluminate cement, it is of interest that Oxiton, by its very fine particle size, can replace up to 25 % of the substantially more expensive cement as a filler (Table 3).

Table 3: Refactory mortar and concrete mixes with Oxiton

Mortar Mixes		1	2	3
Aluminate Cement 'Secar 51'	[mass-%]	100	75	50
Oxiton	[mass-%]	0	25	50
Water Addition	[mass-%]	23	31	44
Initial Setting Time	[h]	2:40	2:30	3:20
Final Setting Time	[h]	4:00	4:10	5:30
Cold Crushing Strength	[N/mm²]	90	90	45
Concrete Mixes		1	2	3
Aluminate Cement 'Secar 51'	[mass-%]	20	15	10
Oxiton	[mass-%]	0	5	10
Tabular Alumina				
0.0-0.5 mm	[mass-%]	44	44	4
0.5-1.5 mm	[mass-%]	36	36	36
Water Addition	[mass-%]	11	11	10
Cold Crushing Strength	[N/mm²]	40	40	20

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Kurzfassung/Résumé/Resumen

Hoch Al_2O_3-haltige Sekundärrohstoffe aus der Aluminiumverhüttung

Während der Aluminiumverhüttung bilden sich Schlacken mit einem hohen Gehalt Al_2O_3 auf der Oberfläche der Schmelze. Diese Schlacken werden wiederaufbereitet, um weiteres Aluminium zu gewinnen. Die verbleibenden Oxide führen zu einem hoch Al_2O_3-haltigen Konzentrat. Aufgrund der sich vergrößernden Menge von Aluminiumschlacken, werden zur Zeit in Deutschland mehr als 100000 t/a dieser hoch Al_2O_3-haltigen Sekundärrohstoffe gewonnen. Die im folgenden gegebenen Informationen über die Erzeugung, Verarbeitung, Eigenschaften und mögliche Anwendungen dieser Schlacken, soll Fachleute der keramischen Industrie dazu ermutigen, diese einzusetzen. Produzenten von Portlandzement profitieren bereits von dieser kostengünstigen Al_2O_3-Quelle.

Matières premières recyclées à haute teneur en alumine provenant de la fusion de l'aluminium

Au cours de la fusion de l'aluminium, il se forme en surface du liquide des scories à haute teneur en métal et en oxydes. Le retraitement de ces scories (en rebut et gâteau de sel) pour recycler l'aluminium laisse les oxydes sous forme d'un concentré à haute teneur en alumine. L'accroissement des quantités de scories d'aluminium fait que l'Allemagne dispose de plus de 100000 t/an de ces matières premières recyclées à haute teneur en alumine. Les informations disponsibles sur la production et le retraitement des scrories d'aluminium, comme les propriétés et les possibilités d'application des matières premières recyclées, devraient inciter de nouveaux utilisateurs parmi les industries céramiques et réfractaires à tester ces matériaux. Les producteurs de ciment Portland ont déjà tiré parti de ces matériaux comme source d'alumine bon marché.

Materias primas de alto eontenido de alúmina provenientes de la fundición de aluminio

Durante la fundición de aluminio, se forman escorias de alto contenido de metal y óxido en la superficie. Estas ecorias se preparan a efectos de obtener un mayor rendimiento en aluminio. Los óxidos restantes conducen a un conentrado de alto contenido de Al_2O_3. Debido al volumen de escorias en aumento, hoy en día se obtienen en Alemania más de 100000 t/a de estas materias primas secundarias de alto contenido de Al_2O_3. Las informaciones presentadas sobre la obtención, preparación, propiedades y posibles aplicaciones de estas ecorias pretenden animar a la industria cerámica a la aplicación de estos productos. La industria del cemento portland ya hace uso de esta fuente económica de Al_2O_3.