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Refractories in the Industrial Production of Aluminium and its Alloys

THE AUTHOR

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ABSTRACT

The paper provides an overview of current refractory practice in the various processes which are involved in the production of primary and secondary aluminium.
A brief description of the types of refractories used in each part of the process is given as a guide for consideration by the reader.

KEYWORDS

bauxite, alumina, corundum, monolithic, refractory
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1 History

Whilst most metals date back thousands of years one of the commonest metals in use today, Aluminium, was only discovered just over two hundred years ago. In 1807 Sir Humphrey Davey became convinced from his studies that alumina Al_2O_3 had a metallic base but it was not until 1825 that Hans Christian Oersted, Professor of Physics at the University of Copenhagen managed to produce the fist few particles. It took another thirty years after Oersted's experiments for the process to be advanced enough to enable H. Sainte-Claire Deville to prepare a bar of the metal which was exhibited at the Paris Exhibition in 1885 and a further five to produce this new precious metal at the rate of about two metric tonnes per annum. Despite the fact that Alumina in various types and purities is available abundantly in the earths crust economical production was impossible for years because of the cost of Sodium metal and Aluminium Chloride and the complexity of the operations which were integral to the Deville process at the time. In 1885 Charles Martin Hall became interested in aluminium whilst a student at Oberlin College, Ohio (USA), and became convinced that electrolysis was the key to reducing the metal from is oxide. Early experiments were deemed failures however until Hall found that Cryolite (Na_3AlF_6, sodium hexafluoroaluminate) was the key and patented his process. This was exploited to produce commercial quantities of aluminium in Pittsburgh, Ohio (USA), in an operation that eventually developed into Alcoa which is still one of the largest aluminium companies in the world.

At roughly the same time a French researcher called Paul Heroult discovered much the same process in his Paris laboratory and so the Hall Heroult process was born. This involves the reduction of aluminium metal from a .relatively pure alumina in the presence of Cryolite in an electrolytic cell with a low DC current at high amperage.The immediate result was that the price of aluminium dropped sharply and the interest in its commercial use rose just as strongly in a very few years. Most aluminium derives from bauxite which is an ore containing mainly Al_2O_3 as well as varying quantities of iron and Titania TiO_2 and is sometimes in hydrated form (Fig. 1).

It is generally found close to the surface in areas which are currently tropical or were when the bauxite was formed geologically such as West Africa, Western Australia, Central and South America and even in Europe for example in Les Baux in France and to a much lesser extent in the South West of Scotland in Ayrshire (Table 1).

2 Production

Bauxite if relatively pure may be beneficiated and calcined in rotary kilns to produce refractory grade while if less pure as is usually the case it is usually digested with caustic soda before precipitation and filtered to remove most of the impurities such as iron. The hydrated alumina is then also calcined but to a lower temperature.

Rotary kilns for the production of bauxite and alumina have traditionally been lined with dense high alumina bricks which must withstand temperatures in excess of 1650 °C for bauxite and 1250 °C for alumina as well as severe mechanical stresses. As in refractory usage globally however the use of monolithics is slowly encroaching on the use of bricks in part of the kiln linings especially for alumina (Table 2).

This includes lifters in the inlet end to turn the product to increase heat transfer and dams at the exit end to retain the product in the kiln for longer to improve quality. Nose rings and dampers are also usually supplied in high strength precast shapes. These

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Table 1 • Typical compositions of different grades of bauxite as received before calcining

Composition / mass-%	Bauxite for refractories	Bauxite for aluminium	Bauxitic clay for refractories
Al_2O_3	60.2	58.3	48.3
SiO_2	4.i	2.0	48.1
TiO_2	2.6	2.7	2.0
Fe_2O_3	2,8	25.0	1.2
CaO/MgO	0.3	0.2	0.2
Alkalis	0.0	0.0	0.1
LoI	30.0	11.8	0.1

Table 2 • Mineral phases identified in high fired refractory grade bauxite

Phase	Composition / mass-%
Corundum	65–70
Mullite	>15
Siliceous glass	10–15

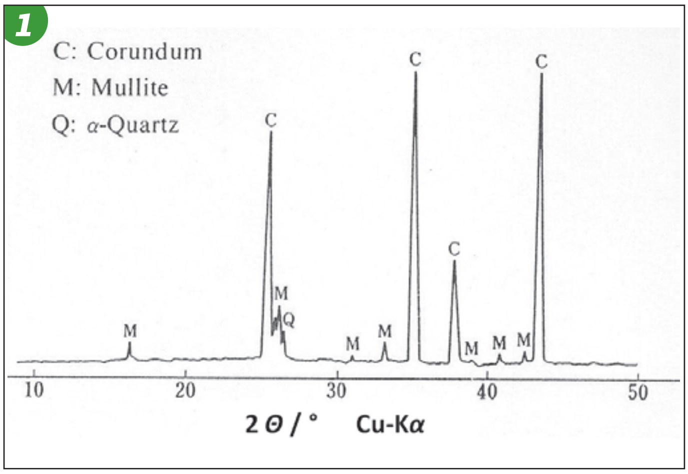

Fig. 1 • X-ray diffraction pattern of refractory bauxite

present no problems when properly designed manufactured and installed and can improve the life in these areas significantly often by a factor of more then four. The problem for monolithics mainly arises when larger installations must be carried out in the field. As previously noted most of the production sites are in tropical climates and it is extremely difficult to cast large sections at temperatures in excess of 25 °C ambient temperature. To overcome these difficulties it is often necessary to install at night when it is cooler and to use chemical inhibitors such as sodium citrate or lithium carbonate to slow the initial set but without affecting the strength of the installed monolithic to any significant degree.

Another development has been to ship the bauxite to more temperate climates such as the North West tip of Spain or the West of Ireland where large alumina calciners based on the fluidised bed process have been constructed and operated. These are largely lined with dense high strength castables and gun mixes backed by insulation.

When the alumina is delivered into the primary smelters it is added with cryolite to large high capacity electrolytic cells with prebaked graphite cathodes and anodes incorporated into the linings which are other wise mainly brick and insulation.

These cells which are rated at up to 300 KV can produce in a day about the same amount of molten aluminium metal that the original equipment could in a year and there are often up to a thousand of these in series in the potlines in major smelters.

3 Applications

3.1 Reduction cells

With the advent of extremely high quality cathodes and anodes and a target life of up to 5 years in operation the refractory load has shifted to the quality and performance of the side walls and to a lesser extent the subhearth. The subhearth may be installed with a monolithic dry barrier layer against the shell on top of which is placed high density high strength calcium silicate boards before laying high strength insulation firebrick and medium alumina firebrick as a base for the cathodes themselves. Sidewall construction in modern large cells is usually fired silicon nitride bonded silicon carbide tiles. These tiles must have high strength, high thermal conductivity and high resistance to both oxidation and chemical attack mainly from the cryolite.

It has been proven that if the oxidation can be slowed then this in turn slows the chemical attack and increases the sidewall life. Improved oxidation resistance derives from such factors as purer raw materials, high density pressing and lower porosity especially reducing the number and size of voids as chemical impurities are transported in the gaseous as well as the liquid phase during normal cell operation.

3.2 Carbon baking furnaces

Part of the success of cell operation comes from the supply of very high quality cathodes which can be very large, heavy and complex in section and are usually manufactured by specialist producers offsite in custom designed furnaces. Anodes however which are much smaller, not so complex and which are regarded as much more of a consumable item are very often manufactured on site at the smelter or at a central location which feeds groups of smelters economically from the same furnace. A carbon baking furnace is a large multicell unit with individual sections in which the cathodes are fired in reducing conditions. The hot gases are transferred forward to the cells in front to preheat them for added fuel efficiency. This however gives rise to other problems since the gases themselves and the emissions from the cathodes contain impurities such as low melting point compounds which affect the refractory life performance and life significantly in service.

Most baking furnaces are constructed from tongue and groove alumino silicate bricks in two main qualities but in many shapes. These are 65 % alumina and 45 % alumina qualities based on high purity raw materials pressed into dense shapes with minimum porosity and maximum strength in the form of creep resistance. It is important that as few impurities as possible penetrate the brick structure and those that do penetrate

Fig. 2 • **Precast hot metal transfer cruse**

Fig. 3 • **Precast big block sidewell melter**

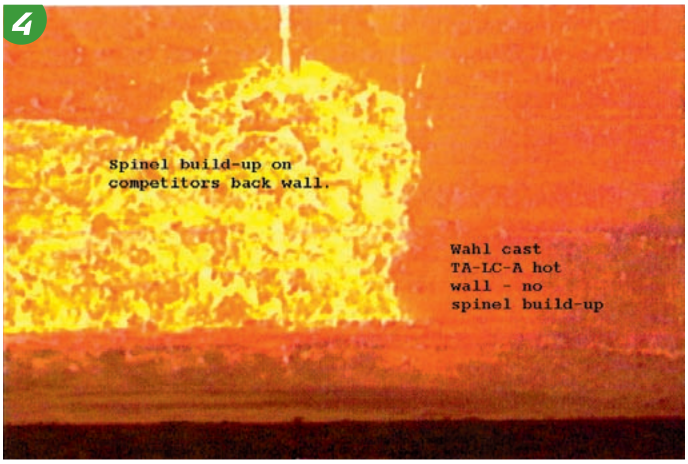

Fig. 4 • **Corundum growth**

Fig. 5 • **Aluminium furnace door with wear strip and heat shield**

do not prematurely adversely affect the stability of the wall and the baffles at repeated high temperature firings in strongly reducing atmospheres.

Around the periphery of these very large furnaces there is extensive use of insulation firebricks since these contribute greatly to lowering the thermal mass and the heat losses. There are also precast prefired flue covers which sit on top of the cell walls.

These are in some cases effectively burner blocks as some furnaces are top fired directly into the flues and are again in high strength high alumina grades similar to those in the walls.

3.3 Hot metal transfer cruses

When the liquid aluminium metal is siphoned out of the cell into the hot metal transfer cruse to be taken to the holding furnace then this is sometimes accompanied by a small quantity of flux from the crust on the bath.

The siphon tube itself is usually alloy steel although sometimes with a refractory tip where it is inserted through the crust into the bath. The cruses are refractory lined ladles with at least five metric tonne capacity and so transfer the contents of two or more cells during each cycle. Each cruse may be used up to about eight times per day once preheated and commissioned into service. The cruse linings have traditionally been relatively thin brick lings in the side wall with a thicker lining in the base. Typical brick lives might be 6 months whereas new designs of precast prefired monolithics can give up to twice or more cycles. The base tile which can be cast in one piece would normally be at least 120 mm thick and set on top of a levelling layer of castable and a thin layer of micro porous insulation against the base to retain heat during the Journey and to protect the floor. Sidewalls can be cast in place or better precast with 35 mm thick curved tiles with micro porous insulation paper behind them (Fig. 2).

3.4 Over the road ladles

Some units require transfer ladles to travel much greater distances sometimes over public roads or rail links which require refractory linings to be more secure and to retain more heat for longer using heavily insulated covered units with thicker linings.

3.5 Melting and holding furnaces

It is in the holding and melting furnaces that perhaps the greatest advances have been made over recent years. These furnaces were formerly relatively small brick lined units with arched roofs of either sprung arch or semi suspended design. The requirements have changed substantially however and now furnaces need to treat much greater quantities of molten aluminium and alloys more quickly and at significantly greater heat inputs in the case of melters. These furnaces are frequently also tilting furnaces rather than the old static design and this puts much higher metallurgical and mechanical load on the furnaces in operation. Modern furnaces need to be built more quickly and cheaply, to be commissioned more quickly and safely, to operate at higher loads and to last much longer between major repairs. To do this has required a complete rethink of basic furnace design and

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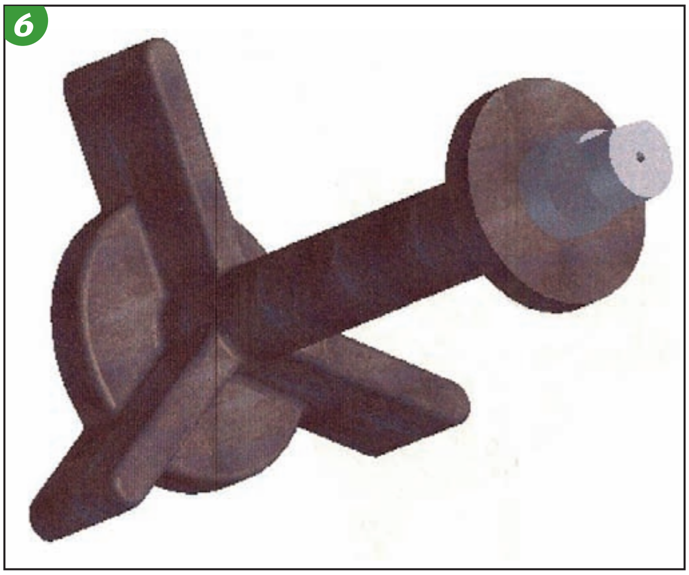

Fig. 6 • Precast refractory impeller for UBC process

construction. Today bricks are seldom still used in the larger furnaces which are not only monolithic but normally precast, prefired big block construction throughout (Fig. 3).

The hearth and lower side and end walls are thinner than previously because high quality precast blocks can out perform other materials such as bricks built on end. No matter how good the bricks and the standard of construction the mortar in the joints has always been an area of weakness which precast blocks easily overcome.

The working hearth is set onto a safety sub hearth and free flow castable of a similar composition to the blocks is used to complete the lining by infilling between them.

Rather than used bricks of fixed standard thickness it is now normal to calculate the total hearth and working layer thickness for the maximum performance and economy. By knowing the most detailed information on the refractory quality which is of a uniformly high standard due to precasting under controlled conditions the theoretical freeze plain of the metal can be adjusted to any desired position even amazingly to a point outside of the lining itself if for example furnace capacity is more important than energy savings or well within the working lining for maximum security.

3.6 Wear mechanisms

When metal and fluxes do eventually react with refractory it is important that the refractory itself contains a coherent dense high fired stable high alumina aggregate. Normally the metal and flux preferentially attack the silica in any alumino silicate refractory to produce more alumina and small quantities of silicon metal. At first sight this might not appear to be too much of a problem but unfortunately the alumina in the form of corundum has a higher volume than the original silica and it tends to form an accretion on the refractory surface. This is exceptionally difficult to remove with conventional cleaning tools. The reaction is not only a result of conditions below metal level but also significantly affected by the constitution of the furnace atmosphere above it (Fig. 4).

Above metal level the main criteria is for energy conservation rather than resistance to molten metal and the same thickness of wall can be constructed of different materials in different layers and thicknesses to the metal contact areas. Roof can also be precast in large panels onto anchor systems which match closely the steel roof beams of the main structure. The flat roof allows greater furnace volume and greater height between the bath and the roof itself which can be important when charging scrap. The door surrounds of jambs and lintels themselves tend to be precast prefired blocks to withstand high mechanical damage from scrap charging while the sill must deliver all this and withstand contact by molten metal also. Doors themselves have been redesigned away from heavy potentially dangerous water cooled systems to precast unitary arrangements which are safer and easier to operate as well as improving the door seal and increasing lives (Fig. 5).

3.7 UBC furnaces

The growth of recycling light scrap such as used beverage cans has resulted in the utilisation of sidewall melting designs where the scrap has to be melted quickly and efficiently without causing excessive dross formation. To assist this precast refractory impellers are used and have an enormous beneficial effect on the process (Fig. 6).

3.8 Receivers and launders

Discharge receivers and launders as well as the launder systems themselves as well as filters and degassers are now mainly lined with precast blocks which may range in quality from ceramic matrix composites to fused silica.

In hot metal contact materials the aim has been to increase the density and decrease the porosity of the refractory while increasing its hot strength. To this aim chemical modifiers are added to the mix not only to adjust its properties during manufacture but also to provide pore blockers in the remaining pores which not only provide a physical barrier to the molten aluminium but affect its surface tension.

3.9 Foundry furnaces

Other secondary process such as tower melters have also made great advances not only in design but also in the use of the types of materials deployed. In the tower itself slurry infiltrated fibre castable provide incredible impact resistance in key target areas. In the crossover channel and in the holder itself increased use of large precast blocks is now normal and door frames can be cast in one piece as can the door. Rotary drum furnaces can also utilise such high quality material in the lip.

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