

Merits of using andalusite-based refractories compared to bauxite-based refractories

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Synopsis

Historically bauxite-based refractories have been used in applications where and alusite-based refractories could work. Bauxite-based refractories were chosen over andalusite-based refractories mainly because of the availability of low-cost Chinese bauxite and also because many furnaces were designed by international companies that cannot easily access high-quality products. Currently, the availability of low-cost bauxite is under threat as a result of high export duties and tariffs as well as restrictions on the amount of material that China allows to be exported. South Africa is a major producer of andalusite, and this guarantees stability with respect to both availability and price. Refractories based on andalusite have an added economic advantage over bauxite-based refractories in that unlike bauxite, which requires high-temperature calcination before use, and alusite is used in its raw state. This paper constitutes a literature study of the merits, both technical and economic, of using refractories based on andalusite compared to bauxite-based refractories.

bauxite, andalusite, refractory, furnaces, calcination.

Introduction

The refractory industry in recent years has witnessed a dramatic increase in the cost of virgin raw materials. This has been largely due to increasing development in the Asian market, particularly India and China, where owing to domestic demand materials such as bauxite and magnesia are no longer readily available for export (Buhr and Spreij, 2009; Industrial Minerals; Hutton, Yates, and Green, 2009; Buhr et al., 2006; Schmidt-Whitely, 2008; Feytis, 2010; Tran, 2007; Wanecq, 2010; O'Driscoll, 2003; Saxby, 2012). In the 1990s low-priced Chinese bauxite replaced other alumina-bearing materials such as andalusite, mullite, and in some instances even chamotte. At that time it was easy for refractory suppliers to provide their customers with new refractories having higher alumina contents (Buhr and Spreij, 2009). The general perception was that a higher alumina content meant superior performance. For this reason, bauxite-based refractories became a preferred option where a higher alumina content was

required. With raw materials being the major cost driver in the refractories business, many refractory producers outside China are facing an uncertain future. Escalating costs and falling quality of imported Chinese raw materials put local manufacturers at significant disadvantage compared to Chinese refractory producers, who can export to South Africa at zero rate import duties (Buhr and Spreij, 2009; Feytis, 2010; Saxby, 2012). The situation has since changed in the past years, especially since 2007 (Buhr and Spreij, 2009). This is illustrated in Figure 1.

The objective of this paper is to show that the usage of andalusite refractories could be revived in applications where they have been replaced by bauxite. This is driven by both technical and economic factors.

Availability of raw materials

Andalusite

Andalusite supply is fairly tight, with commercial sources limited to South Africa, which is the major producer, and France (Feytis, 2009; Xiong, 2010). Damrec, through its subsidiary Samrec, has four andalusite mines in South Africa producing more than 200 000 t/a. Andalusite Resources, an alternative supplier, operates close to the Thabazimbi andalusite facility of Imerys, owned by Damrec (Feytis, 2010). China produces andalusite on a smaller scale, mainly for domestic uses. The typical composition of South African andalusite deposits is given in Table I.

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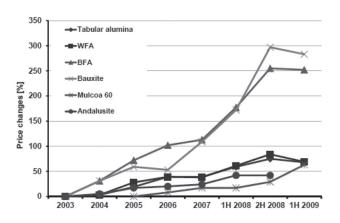


Figure 1—Price development of high-alumina refractory raw materials 2003–2009 (Industrial Minerals)

Bauxite

The typical chemical analysis for refractory grade bauxite is given in Table II.

The refractories industry is in general dependent on China for raw materials, for example 95% of refractory bauxite production is controlled by China (Buhr and Spreij, 2009; Hutton, Yates, and Green, 2009; Schmidt-Whitely, 2008; Wanecq, 2010; O'Driscoll, 2003). China is also a major supplier of refractories (Buhr and Spreij, 2009). In China the introduction of environmental regulations and energy efficiency policies resulted in the closure of highly polluting shaft and round kilns (Hutton, Yates, and Green, 2009). Although welcomed environmentally, this move led to shortages in raw materials and increased costs. On the other hand, China changed its policy, and now discourages the export of raw materials (Buhr and Spreij, 2009; Hutton, Yates, and Green, 2009; O'Driscoll, 2003). This has been brought about by limiting the volume of material by imposing a system of export licenses, fees, and taxes. Exports of raw materials such as dead-burned magnesite, graphite, and bauxite, for example, are restricted and heavily taxed (Buhr et al., 2005; Tran, 2007; Wanecq, 2010):

- ➤ The export tax on bauxite is 15%
- ➤ Export licenses are auctioned to selected domestic bidders only

- ➤ The export license cost far exceeds the issue price
- ➤ An output VAT of 17% is raised (from 2006).

None of these costs are borne by Chinese domestic producers, and exports of finished products made from these raw materials are not taxed (Buhr and Spreij, 2009). The result of these measures has been a steep rise in price in the global market. It is important to note that refractory product exports are not subject to such limitations. Due to the licensing and taxation of exported raw materials, Chinese domestic producers of refractories enjoy a cost advantage in export markets (Buhr and Spreij, 2009; Tran, 2007; Wanecq, 2010).

The net result of these measures by China is that international demand for raw materials exceeds supply, and the resulting increase in costs is often passed on to the user. With China being a player in the refractories business as well, this strategy is not always an advantage. To remain profitable/viable, refractory users have to turn to alternative materials that can serve the same purpose. One such example is the use of andalusite refractories in applications where bauxite is currently being used (Buhr and Spreij, 2009). Being a locally produced raw material, South African andalusite is not subject to export restrictions. South Africa is the major producer of andalusite, and this guarantees stability with respect to both availability and price. A stable supply of andalusite as an alternative to bauxite ensures that the local refractory manufacturing industry is protected. The local user industry is also guaranteed a consistent supply of a high-quality product that is not subject to foreign exchange fluctuations. Compared to bauxite as a refractory raw material, and alusite offers the following advantages:

An andalusite crystal remains stable with a small increase in volume after firing, and hence the internal porosity does not change. Andalusite does not, therefore, require any preparatory firing before use (Dubreuil and Sobolev, 1999; Hubert, 2001). Bauxite suitable for use as a refractory aggregate is produced by calcining the ore at 1600-1650°C (Bradely and Hutton, 2011. Calcination is done to drive off chemically combined water, to sinter the material at sufficiently high temperature for it to shrink to a higher density and low porosity, and to convert all the alumina and silica into corundum and mullite so that there is no

| Table I | | | | | | | | | | | | | |
|--|--------------------------------|----------------------|--------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|--|--|--|--|
| Typical chemical composition of South African andalusite deposits (Hubert, 2001) | | | | | | | | | | | | | |
| Concentrate | Al ₂ O ₃ | SiO ₂ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | Na ₂ O | K ₂ O | LOI | | | | |
| Randalusite Purusite Krugerite K57P | 59.5 58.9 57.6 | 38.7 38.5 40.3 | 0.65 0.80 0.80 | 0.15 0.15 0.25 | 0.10 0.20 0.10 | 0.10 0.10 0.15 | 0.10 0,10 0.10 | 0.20 0.35 0.20 | 0.50 0.90 0.50 | | | | |

| Table II | | | | | | | | | | | | |
|---|--------------------------------|------------------|--------------------------------|------------------|----------|--------------------------------------|--|--|--|--|--|--|
| Typical chemical composition of refractory grade bauxite, % (Buhr and Spreij, 2009) | | | | | | | | | | | | |
| Concentrate | Al ₂ O ₃ | SiO ₂ | Fe ₂ O ₃ | TiO ₂ | CaO+ MgO | K ₂ O + Na ₂ O | | | | | | |
| Bauxite | 85–90 | 5–10 | 1–2 | 3–4 | 0.4-0.8 | 0.20-0.80 | | | | | | |

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free silica. Since andalusite does not require calcining it offers significant economies in that it saves energy, an advantage that is certain to be of importance in the light of increased energy costs (Overbeek, 1989, Ihlen)

- Andalusite offers better scope for control of dimensional tolerances and warpage, especially in the manufacture of complex shapes
- Andalusite is one of the minerals that can be used at its natural grain size as an aggregate in the manufacture of refractory bricks
- Andalusite has a higher chemical purity than other refractory raw materials, particularly bauxite and chamotte (Hubert, 2001). Furthermore, the grain size is consistent up to a few millimetres, each grain being a single monolithic crystal with a very low open porosity. The low content of impurities (Figure 2) such as Na₂O, K₂O, MgO, CaO, Fe₂O₃, TiO₂ results in a small amount of glass phase at high temperatures, and as a result provides a high resistance to thermal shocks, a high deformation temperature, and a good creep resistance (Xiong, 2010; Hubert, 2001; Dubreuil, Filari, and Sobolev, 1999). These parameters are much higher than those of corresponding alumina-containing refractories based on bauxite, mixtures of fireclay and bauxite, or mixtures of bauxite and alumina.

The refractory characteristics of andalusite are related to its ability to form the refractory mullite phase, which combines high strength with resistance to physical and chemical corrosion at elevated temperatures (Dubreuil and Sobolev, 1999; Overbeek, 1989; Ihlen, 2000; Hubert, 2001; Dubreuil, Filari, and Sobolev, 1999). These properties are desirable at high temperatures and in chemically corrosive environments. In the fired state a refractory based on andalusite is composed of predominantly mullite as the major phase, together with glass, whereas a bauxite-based material is composed of corundum as the major phase with minor quantities of mullite and glass (Overbeek, 1989).

Advantages of andalusite-based refractories over bauxite-based refractories

High refractoriness under load

Refractoriness under load refers to the ability of a material to withstand specific conditions of load, temperature, and time (Baxendale, 2004). It is dependent on the softening point and

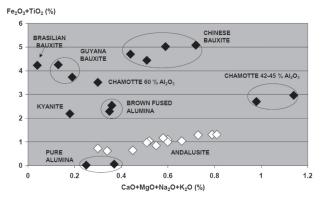


Figure 2-Chemical impurities in alumina aggregates (Hubert, 2001)

the amount of glassy phase within the refractory system. Andalusite-based refractories are associated with a high refractoriness under load (Xiong, 2010; Hubert, 2001). This is due to the low volume and high viscosity of the liquid phase formed and the very rigid structure of the mullitized microstructure.

High creep resistance

Creep in compression is described as plastic deformation of a refractory under a specific stress over time. As with refractoriness under load, the ability of a refractory to withstand creep under compression depends on the softening point and the amount of glass phase in the refractory system (Baxendale, 2004). Andalusite-based bricks show extreme resistance to creep during thermal cycling between 1000°C and 1500°C (Xiong, 2010; Hubert, 2001). Because of impurities (Figure 2) in bauxite, especially alkalis, a molten phase forms at temperatures as low as 1100°C (Buhr and Spreij, 2009). The presence of a molten phase decreases the creep resistance despite the overall higher alumina content of bauxite.

Good resistance to chemical attack and penetration by slag and metal

Andalusite-based refractories offer excellent resistance to penetration and attack by slag and metal. This is due to the dense, homogenous single-crystal structure, in which there are virtually no channels of weakness along which slag can permeate and travel (Buhr and Spreij, 2009; Dubreuil and Sobolev, 1999). As a result, and alusite-based refractories are superior to refractories based on chamotte, bauxite, and

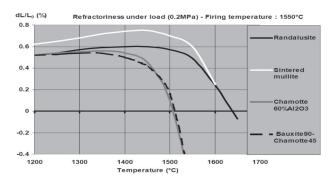


Figure 3-Refractoriness under load of various alumina bricks (Hubert, 2001)

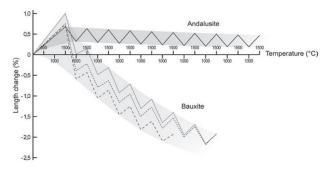


Figure 4-Creep resistance of andalusite and bauxite bricks (Hubert, 2001)

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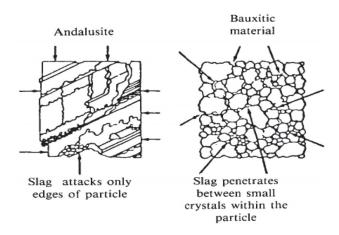


Figure 5-Effect of slag penetration (Overbeek, 1989)

bauxitic clays, in which even the smallest piece of material is still a composite of minerals between which the slag can penetrate.

Thermal shock resistance

Refractories based on andalusite exhibit high resistance to thermal shock. This is attributable to their typical network microstructure (Buhr and Spreij, 2009; Xiong, 2010; Dubreuil and Sobolev, 1999; Overbeek, 1989; Ihlen, 2000; Hubert, 2001; Dubreuil, Filari, and Sobolev, 1999). The liquid glassy phase that is entrapped in the mullite crystal acts as a shock absorber that prevents crack initiation during thermal cycling.

Material requirements

The density difference between andalusite and bauxite refractories is typically 8–10% (Buhr and Spreij, 2009). Bauxite-based linings therefore have a higher material demand compared to andalusite-based linings, a factor that needs to be considered in economic comparisons of lining concepts.

Conclusion

Andalusite-based refractories possess superior critical refractory properties over bauxite based-refractories and can thus be used in applications where bauxite-based refractories are currently used. Andalusite-based refractories often confer better thermomechanical properties such as hot strength, refractoriness under load, creep resistance, and thermal shock resistance. South Africa, being the single biggest producer of high-quality refractory-grade andalusite, guarantees stability with respect to price and availability, whereas bauxite, which is an imported product, is subject to export restrictions and foreign exchange fluctuations.

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