Fused-cast for glass

Glass refractories is becoming an increasingly commoditised sector with R&D efforts focusing on low cost materials utilisation, as Carlo Ratto reveals

Fused cast refractories are well known in all glass market segments; these refractories represent the major structural component of each glass smelting furnace in all glass contact and most superstructure areas. In spite of being among the most recently developed type of refractories (invented and introduced in USA and Europe in the first half of the 20th century), fused cast refractories have rapidly grown into a "forced choice", owing to indisputable technical advantages relevant to campaign length, furnace productivity and glass quality.

After less than a century since their initial development, fused cast refractories are still an unquestioned choice when designing a glass furnace and – until the next generational change – no alternatives exist. These refractory products have been introduced in applications other than glass but, so far, well over 90% continue to be used within the various segments of glass applications.

After more than 50 years of this market’s expansion, there has been a progressive growth slowdown owing to market saturation, reduced downstream applications and, as a consequence of improved furnace design and fusion technologies, a continuous reduction of the specific refractory usage (kg/tonne of glass produced).

For example, in 1950, 15kg of refractories were used per tonne of glass produced, and now this has declined to around 5kg/tonne (steel uses around 16kg/tonne – see IM October 2009: Into the fire).

The most recent decade saw a stagnation (in some areas a recession) in the refractory markets of the western world, and at present only Far East markets still manifest clear signs of growth: in general terms, there is a remarkable overcapacity at a global level and the profitability of this business has moved from ancient highs to the present lows, typical of commodities under pressure of low-cost manufacturers (yes, China!).

Nowadays, the fused cast sold market is estimated to total around 100,000 tpa, comprising: 80% alumina-zirconia-silica (AZS) type; 15% alumina products; and 5% of various specialties (chrome-alumina, zirconia, MA spinels).

AZS refractories

AZS refractories are produced under different chemistries, mostly ranging 32-41% ZrO₂, 11-15% SiO₂ content and 1-1.7% Na₂O. About 0.5% includes various minor components and the complement is Al₂O₃.

About 80,000 tonnes of AZS refractories are sold every year with an estimated average composition of 49% Al₂O₃, 36% ZrO₂, 13% SiO₂, and 1.5% Na₂O. We can easily infer the amount of mineral utilisation, based on the following considerations:

- Zirconia content comes almost exclusively from zircon sand (ZrSiO₄) directly as a batch component and indirectly through the utilisation of synthetic baddeleyite (monoclinic zirconia or FMZ). This is also a batch component, mostly produced via thermal dissociation of zircon sand in the presence of carbon in an electric arc furnace (EAF).
- The necessity of utilising a de-silicon form of zircon in AZS formulations comes from the fact that almost all AZS chemistries must have a ratio ZrO₂/SiO₂ well above 2.03, which represents the zircon stoichiometry. Natural baddeleyite was once utilised as a batch component, but the commercial availability of this mineral is now less practical and therefore almost all of the zirconia utilised in AZS fused cast refractories comes from zircon sands, for a global quantity a bit above 43,000 tpa.
- For alumina content the main sources are various types of Bayer alumina. Minor amounts come with zircon sand impurities and some is utilised as a fluxing agent in the preparation of de-silicon zircon (a kind of FMZ with variable amounts of residual silica) and comes into the batch with this component. In total, the amount of Bayer alumina utilised – directly and indirectly – is around 39,000 tpa.
- Na₂O is a minor component of fused cast refractories. It is added to the AZS composition as a minor component of alumina, but mostly as Na₂CO₃, with global tonnages reaching around 2,000 tpa.

Zircon characteristics

Zircon sand is essentially the only natural mineral, utilised in form of sand with relatively strict technical specifications. Years ago, when the AZS fused-cast sector was a very profitable speciality refractory market, the only quality of zircon sand utilised was “premium grade A”, with a very low content of iron and titanium dioxide, low alumina content, de-dusted and without sulphur contamination from fossil fuels.

This zircon is a speciality sand not normally utilised for foundry and most sinter refractories, representing a fraction of the overall zircon sand market and in the topmost price range. These sands were once mostly coming from the west coast of Australia and the USA (only for domestic AZS fused cast manufacturers).

Pricing cyclicity followed the major sands market relevant to other end user segments (such as ceramics), always floating on top of the standard grade price.
In the last couple of decades, with the progressive draining of the AZS fused-cast profitability margin, most major historical manufacturers have initiated a critical review of the real technical need of utilising “premium A” grade versus intermediate or “standard grade”.

The result is that, today, most western players are using a blend of premium and standard grade, where the alumina content is not a binding factor (alumina is indeed a major component that can be balanced), while the main limit in impurities is the sum “Fe₂O₃ + TiO₂”.

This sum should stay under 0.30% to prevent deterioration of some technological properties like the tendency of releasing defects (blistering) to the glass in contact and the discharge of a glassy exudate from the hot face at temperatures above 1,200°C, which is also cause of glass contamination.

The utilisation of these lower quality sands, obviously financially motivated, is possible when the process control is very effective and other sources of contamination (eg. reprocessed scrap crushing) are well controlled; this also means that “security margins” in the manufacturing are reduced and accidental out-of-spec episodes more possible.

Additional sources of zircon sands have become available in Australia (west and east coasts), South Africa, South America and, more recently, a number of different “exotic” sources have come online, while the suppliers’ market has undergone progressive consolidation.

Some historical mines, like in the USA, have been depleted, while others have been replaced by different sites and characteristics. This overall change in the sources’ configuration has increased the necessity to control other parameters like the content of radioactive materials, a peculiar characteristic of heavy sands, to be considered against different countries’ environmental and health regulations.

Overall, the content of uranium and thorium has been capped at a maximum of 500ppm. As a matter of fact, several zircon sand sources fail against this criterion.

Another point to check carefully, when considering a new source of zircon sand for this specific application, is the presence of very minor amounts of some contaminants (eg. copper, chrome), normally not taken into consideration but possible, in principle, of imparting discoloration to the refractory and to the glass in contact (which is the worst outcome) even when present at levels of a few ppm.

Though this problem must be a very rare occurrence for zircon sands it was, for example, a serious issue with natural baddeleyite from South Africa, which contained traces of copper (and phosphates) at levels sufficient to impart a light blue colour to the white glass in contact with refractories produced utilising that mineral.
Alumina properties
Bayer alumina, or alumina trihydrate, is a processed material and therefore, in general terms, more controllable than a natural mineral. Acting on numerous variables in the manufacturing process, alumina is commercially available in a wide range of grades including low-calcined, high-calcined, gamma or alpha, medium or low soda content, with variable reactivity, specific surface, ultimate crystal size and so forth.

The largest quantities are supplied to the metallurgical market for aluminium production, but a large range of speciality grades are dedicated to catalysts, fillers, abrasives, ceramics, refractories and fused cast refractories (see IM March 2011: ATH – a finely divided market).

Similarly to zircon sands, for the first half a century of fused-cast manufacturing the only alumina considered usable (particularly in Europe) was a kind of speciality grade, often produced in dedicated batches, under strict quality parameters and, obviously, offered by a few selected suppliers at a considerable price premium.

The commoditisation of AZS fused-cast manufacturers has pushed hard towards revaluing the possibility to utilise more standard alumina (up to the metallurgical type) or a blend of qualities, with the aim to reduce the batching cost and to secure multiple and reliable vendor configurations. The consolidation of the non-metallurgical alumina market, and the rationalisation of its manufacturing structure, has also led to the closure of minor speciality production capacity, forcing the R&D structure of users toward alternative sourcing.

Today, most fused-cast manufacturers utilise various types of Bayer alumina, though in the west the major source is still in the range of high-calcined alpha alumina, and some amount of reactive qualities.

Manufacturers have learned how to utilise cheaper materials, but this is only possible by rearranging some of the process parameters. An easy and uncontrolled replacement of one quality with another can still be the cause of expensive deteriorations in process yield; the effect of alumina’s physical properties on the process viability (and particularly on the development of cracking in the finished blocks) is still under investigation to understand more clearly the cause and effect relationship, but the evidence of such correlation is statistically proven.

The China factor
One major driver of the commoditisation of fused-cast raw materials has been the progressive introduction of low cost producers, mostly originating in China, which have developed their own technology and a basic know-how.

Low cost products penetrate the western market through hard price leveraging and an aggressive commercial approach, destroying the profitability of the business on a global basis and largely contributing to the aforementioned changes.

Since the major competitiveness factor for low cost material manufacturers is labour, the relative impact of energy and raw materials on the costing is enhanced. These manufacturers (which do not enjoy any advantage on raw materials and energy costs), therefore, are forced to buy zircon sand and alumina mostly based on price.

While major western manufacturers belong to large industrial groups and enjoy enough volume leverage to negotiate procurement of the main raw materials directly from primary producers, the low cost producers are extremely fragmented and usually buy zircon sand from traders and stock holders which (in addition to marking-up prices), can have problems guaranteeing a stable primary source and, therefore, quality level.

It is worth mentioning that these low cost fused-cast materials, under technically led procurement, could have marginal chance of penetration in the west, but nowadays most glassmakers (and particularly the large corporations) have definitely switched from technical to financially-driven procurement.

This is forcing organisations to buy refractories under a strong price drive, in spite of assuming some unknown level of risk; this is also part of the commoditisation process.

In conclusion, the transformation of AZS fused cast refractories from speciality to commodity products, and the emergence of low cost manufacturers, has brought along an evolution in the quality of industrial minerals utilised.

For traditional western manufacturers, as well for low-cost producers, the average quality of products has not improved. Most of the R&D activity, instead of being orientated towards newer and better products and services, has targeted the possibility of utilising lower quality raw materials; in some cases reducing the safety margin between the requested and offered technical performance of the refractories.

The more glassmakers enjoy getting short-term financial advantages, the less they will permit further development of products and services in the area of refractories; this will push towards the utilisation of cheaper commodities in the area of raw materials, in an overall downward spiral.

To see again development of better and different materials, on both ends of the supply chain (industrial minerals to refractories to glassmakers), we may have to wait for a new global renaissance, fuelled by an improved economy, a better balanced approach to business and a longer-term investment policy. It is hard to say when (and if) this will happen!

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