Is there a Mr. Hyde inside the ‘Dr. Jekyll fused cast’?

P. Carlo Ratto* discusses the dark side of fused cast refractories.

Fused cast refractories have been highlighted for decades for their superiority in application, particularly in the glass melting furnace. Nevertheless, fused cast refractories, particularly AZS materials, are far from perfect, and the outstanding success in the glassmaking application stems essentially from one huge advantage over previous materials: corrosion resistance against molten glass contact.

However, if we were to describe a material ideally suited to glass contact and superstructure in the melting tank, the profile obtained would only minimally fit electrofused AZS materials for glass applications.

What, then, are the dark sides of these materials, so highly performing for what it is the corrosion resistance, to almost make neglected every unfavourable aspect?

The 'electrofused' are different from all other refractories

The ‘electrofused’ are different from all other refractories due to their manufacturing technology which, consists of a high temperature melting in an Electric Arc Furnace (EAF) of refractory oxides, their casting as a liquid in moulds, followed by a controlled cooling during which a partial crystallisation occurs with a consequent release of some of the mechanical tensions resulting from the rapid cooling.

Since, to a varying extent and composition dependent (and contrary to what happens for ice-water) the liquid refractory has a density lower than the solid, the process of cooling-solidification-crystallization inevitably leads to the formation of a shrinkage cavity, which is localised in the block zone correspondent to the final liquid location. This cavity, if you do not implement particular casting and machining techniques, remains largely within the block (the so-called regular cavity blocks, widely used in the superstructure application).

Immediately after casting in the moulds, the process of solidification-crystallization takes place starting from the ‘skin’ in contact with the mould, and proceeds towards the heart of the block in an oriented thermal field and in the presence of gravity; this means that the chemical composition (particularly in the case of AZS types with the precipitation of crystalline species of extremely different composition and density) is significantly different between different isothermal surfaces during the cooling process.

The crystallisation process inherent in the nature of fused cast refractories and the technology that manages the process, therefore, can only generate a solid that is heterogeneous in chemical and crystallographic composition, as well as with large variations in the morphology and size of the crystalline component.

All electrofused refractories containing variable amounts of Baddeleyite (typically the AZS), must contain a residual glassy phase which can ‘manage’ the monoclinic-tetragonal phase transition of zirconia and the corresponding strong volumetric change. It must be remembered that in a typical AZS this amorphous or glassy phase typically constitutes around 25% by volume of the refractory body. It is distributed among the crystalline species and, above its glass transition, constitutes a ‘soft buffer’ capable of absorbing the abrupt volumetric change of the phase transition of the zircon oxide crystals.

In summary, therefore, fused cast refractories, and particularly the most widely used in glass melting furnaces, are constituted by:

- A shrinkage cavity which may be predominantly, partially or minimally within the refractory body, depending on the production technology.
- A body chemically and physically heterogeneous.
- An amorphous phase (glass) represented by a silicate glass with variable composition, inhomogeneously distributed between crystals.

From these three fundamental points come facts that differentiate typical fused cast refractory to those formed with other technologies (pressed, vibro-
pressed and vibro-cast, iso-pressed, extruded, cast).

- As a result of the presence, in varying amounts, of a shrinkage cavity, the effective working volume (usable for containment function) is much smaller than the apparent physical size of the initial blocks. For the same reason, the thermal conductivity of the single block is heterogeneous due to the ‘insulation’ effect of the cavity that is sometimes partially filled with a mortar or other sealing medium.

The presence of a shrinkage cavity is thus a negative element in many respects. The dangers arising must be carefully managed through accurate knowledge of the different risk factors.

- The heterogeneous chemical and physical composition of the block results in an uneven corrosion resistance at glass contact. Since the cortical and sub-cortical structure of the block is much more resistant than the structure and composition of the heart it follows that the speed of corrosion is not linear in time, as a consequence of the moving of corrosion profile.

To complicate the situation, it must be remembered that the corrosion rate is exponential to the temperature, and that the temperature of the refractory hot face (working face) depends on its residual thickness and thermal conductivity, as well as the cooling configuration of the cold face.

The heterogeneous composition of a fused cast block makes it complex to predict the performance in glass contact, if not on the basis of ‘typical’ empirical values from previous experiences. Any unforeseen change in the block structure, e.g. as a result of badly controlled variables of the production process (as may sometimes occur in some low-cost factory), can lead to abrupt performance degradation, resulting in serious accidents, such as an unexpected glass leak.

The heterogeneous nature of a fused cast refractory body has an element of risk if and when the actual situation differs significantly from the typical performance condition with which the standards were evaluated during the phase of project engineering.

An understanding of the particular supplier process is an essential element for the success of the installation. In this regard it is worth remembering that a problem in a single sidewall block (or in a single tile of the sole) can result in a problem for the entire furnace.

From these observations comes the absolute need to inspect all electrofused items (blocks) components of a furnace, instead of testing materials based on a statistically correct sampling plan, as normally prescribed for sintered items (e.g. bricks), manufactured with other forming technologies.

- The electrofused materials, and particularly the AZS types, necessarily contain an amorphous phase (glass) in a quantity and quality different from most sinter refractories. This siliceous glassy phase, with a transition to the plastic state under 750°C, represents the only possibility of absorbing the volumetric changes related to the reversible phase transition of zirconium oxide (at a higher temperature) in an extremely dense body.

However, at temperatures under 500°C, the extreme rigidity of the structure makes it difficult for the release of thermal expansion stress, given the minimal presence of porosity. This structure peculiarity makes the process of preheating furnaces lined with electrofused in the lower temperature segments critical. The general opinion that the preheating of fused cast should be particularly accurate in corresponding to the phase transition of zirconium oxide (1150-1200°C) often overlooks the fact that most of the cracks are triggered by thermo shock at temperatures well below 500°C (they then propagate at

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This cavity has an element of risk in that it normally collects water during the phases of mechanical processing of the block. If this moisture remains trapped in the shrinkage cavity, particularly as a result of an inappropriate procedure of scar sealing, events of varying severity may occur during the preheating of the furnace, including triggering an explosion of superstructure sections, as occurred recently in Europe.

In other cases, for example when blocks with regular cavity are installed as channel sections (typically for the production of glass containers), there can be infilations of the glass in the cavity as a result of thermal fracturing of the channel block bottom during preheating. Such glass infilating the cavity, as a result of the presence of impurities, easily generates pressurised gas that, in turn, is released in the glass flow within the channel, producing macro defects in the items produced.
higher temperatures), when the control (and the homogeneity) of preheating is technically more problematic.

This same glassy phase, at temperatures higher than that of zirconia transition, when the material resumes a trend of almost linear thermal expansion, becomes responsible for a particular phenomenon, typical of AZS fused cast, known by the term ‘exudation’. This well-known phenomenon has been studied for decades to try and understand its root causes and minimise it, but it is still very much present in a modern AZS fused cast. It depends on a number of variables related to the macro- and micro-chemistry, on crystal structure and conditions of service.

Almost all of the defects introduced to the glass by the refractory (in contact and superstructure), typically zirconia-enriched (stones, nodules, cords, bubbles), are directly dependent on the presence of exudate, which is visually evident in the superstructure (appearance of a reflective shiny/liquid veil) under operational conditions. It is less obvious but equally present at the glass contact, where the exudate push causes the detachment of the passivation layer responsible for the high corrosion resistance of electrofused AZS.

The great deal of product and process knowledge that allows you to manage the quantity and quality of exudate is part of the body of know-how which, for decades, has differentiated primary producers like most Western players from several Eastern low-cost manufacturers. While product know-how becomes available on a global basis, the knowledge fallout in form of technological innovation of the production process is still a matter of distinction between acceptable and not acceptable producers in the context of emerging players.

And they really have a dark side!

Notwithstanding the fact that the outstanding corrosion resistance of fused cast refractories at glass contact (and particularly referring to the AZS) will ensure the predominance in application for side-walls and pavings of the glass melting tank for many years to come, we must be aware of the fact that the same characteristics responsible for this prominent performance are also the origin of a number of facts constituting what we might call the ‘dark side’ of electrofused.

This circumstance makes the decisions relevant to fused cast applications much more critical than when installing, for other applications than glass, refractories formed with other techniques. The evaluation of the technical and technological production process of a particular refractory manufacturer is, in many cases, necessary to ensure that the products procured are consistent with the performance standards used in the design phase of the furnace.

In the superstructure application, however, in recent years, there is the increasing trend to adopt new types of refractory which, while guaranteeing in application a durability comparable to the AZS fused cast, are not suffering from the negative consequences related to the presence of cavities and chemical-physical inhomogeneity, and even do not present the phenomenon of exudation, thereby eliminating almost all of the zircon-bearing defects due to dripping of exudate in the glass produced.

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