GLASS MELTING FURNACE REFRACTORIES
AND REFRACTORY RELATED DEFECTS

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ABSTRACT

In glass industry the different types of products need different furnace design. The furnace can be a recuperative, a regenerative or an oxy fuel one in terms of the combustion system used. There are ten refractory types which are commonly used in the glass furnaces. The refractories used in glass furnaces are in contact with the glass, the superstructure, the crown and the regenerator materials and which is why they are constrained to chemical, physical, as well as thermal effects. Glass defects occur in many different forms while the defect sources exhibit a considerable diversity.

Keywords: glass furnace, refractories, defects.

INTRODUCTION

The glass furnace refractories have to endure severe environmental conditions throughout the campaign. Their selection is vital for the quality of the glass and the length of campaign. Thermal shock, physical wear, high temperature and corrosive chemicals are parameters affecting the refractory and hence the furnace performance. They are materials that can resist high temperatures and are expected to maintain their physical properties through the furnace life.

Glass Furnaces

In glass industry the different types of products need different furnace designs. The latter major differences refer to the combustion system type and the forming technique. Fig. 1 illustrates different furnace designs.

The furnace can be a recuperative, a regenerative or an oxy fuel one in terms of the combustion system used. The regenerative furnaces are more widely used. They are backfired or cross fired in accordance with the location of the burners.

Generally three main regenerative furnace types as seen in Fig. 1 are used in conventional industrial glass production.

Glass Furnace Refractories

There are ten refractory types which are commonly used in the glass furnaces. Their major mineral phases are shown in Table 1. Silicium dioxide (SiO$_2$) is the most common oxide participating in each step of the glass production as a raw material, a refractory and a coating compound in some cases.

Silica is present as refractory material in the super duty silica bricks of the crown. It is there in a superstructure also in fused silica form. Aluminum oxide (Al$_2$O$_3$) is used as corundum or alpha-beta alumina form in furnaces. Alumino-silicate refractories are used in the form of sillimanite, mullite or fireclay. Zirconia is present as zircon, dense zirconia, sinter or fused cast AZS form. Magnesium oxide is used in the form of periclase or spinel with alumina compound.

The most commonly used refractory materials contain four oxides: MgO, ZrO$_2$, Al$_2$O$_3$ and SiO$_2$.

Fig. 2 shows a ternary phase diagram referring to a glass furnace refractory. The refractory materials usually contain either a single or a combination of two or three oxides. For example aluminoxide, ircona and silica form a AZS refractory.

Generally speaking refractories are acidic, basic or neutral depending on the oxide species. Silica and alu-
minosilicate are considered acidic, refractories which are composed of MgO are basic, whereas alumina, zircon and chromium are neutral.

These terms are used to describe the slag character developed during the high temperature reactions with no reference to pH. It is a bad industrial practice to place acid and basic bricks together in direct contact. There is a potential risk of a reaction proceeding with their participation.

**Refactories, reactions and possible source of defects**

The refractories used in glass furnaces are in contact with the glass, the superstructure, the crown and the regenerator materials and which is why they are constrained to chemical, physical, as well as thermal effects. The latter affect each other and hence lead to refractory corrosion as illustrated in Fig. 3.

The refractory problems can cause glass defects dur-

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**Table 1. Major refractory types and mineral phases contained.**

<table>
<thead>
<tr>
<th>Oxide (s)</th>
<th>Refractory Type</th>
<th>Major mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Silica</td>
<td>Cristobalite, Tridymite, Quartz</td>
</tr>
<tr>
<td></td>
<td>Fused silica</td>
<td>Quartz, Glass</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Alumina</td>
<td>Corundum, α, β - alumina</td>
</tr>
<tr>
<td>SiO₂Al₂O₃</td>
<td>Mullite</td>
<td>Corundum, mullite</td>
</tr>
<tr>
<td></td>
<td>Silimanit, Fireclay</td>
<td>Silimanite</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zircon</td>
<td>Zircon (ZrO₂, SiO₂)</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
<td>Zirconia (ZrO₂, CaO)</td>
</tr>
<tr>
<td></td>
<td>Fused AZS</td>
<td>Corundum, zirconia, glass</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesia</td>
<td>Periclase, Spinel</td>
</tr>
</tbody>
</table>
ing the campaign. The defects which are determined by the refractory type and their location in furnace listed in Table 3. A troubleshooter should know the furnace operation parameters and the locations of all refractories used. To solve a problem this data has to be considered on the ground of additional knowledge on the plant operation and perhaps extra laboratory results.

According to the refractory producers more than 50 % of total inglass defects due to refractories. The other sources refer to the raw materials used, the melting process, the forming, annealing, etc. We focus on refractory related glass defects only in this work. The glassmakers expect to exclude glass defects and furnace wearout during the campaign through refractories introduction. In fact the main sources of glass defects refer to:

- Unsuitable raw materials;
- Refractory corrosion;
- Operation faults.

We tried to outline in the Fig. 4 the relations between the raw materials, the refractory and the glass which affect the quality obtained.

The raw materials, the refractory preference and the operational factors interact with each other. As shown in the Fig. 4 the raw materials are the most important

<table>
<thead>
<tr>
<th>Refractory Type</th>
<th>Location in Furnace</th>
<th>Defect Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>Melter and working end Crown, Melter refining and working end Superstructure</td>
<td>Silica refractory stone, Silica rundown/drip, Frost</td>
</tr>
<tr>
<td>Alumina</td>
<td>Melter superstructure (float), Awall (float), Waist crown (float), Forehearth canal/superstructure (containers, tableware)</td>
<td>Aluminous stone, cord</td>
</tr>
<tr>
<td>Mulite</td>
<td>Regenerator walls, waist crown</td>
<td>Aluminous stone</td>
</tr>
<tr>
<td>Silimanite</td>
<td>F/H cover block</td>
<td>Aluminous stone/cord</td>
</tr>
<tr>
<td>Zircon</td>
<td>Isolation between alumina/silica mortar, Monolithics</td>
<td>Zircon stones</td>
</tr>
<tr>
<td>Fused cast AZS</td>
<td>Melter sideblocks, Melter tuckstones, Melter pavings, Melter superstructure</td>
<td>AZS stone (AZS1, AZS2), AZS knots, cords</td>
</tr>
<tr>
<td>Magnesia</td>
<td>Regenerator walls, crowns, checkers</td>
<td>Spinel</td>
</tr>
</tbody>
</table>

Table 2. Refractory types based on the oxide species contained.

<table>
<thead>
<tr>
<th>Acidic</th>
<th>Basic</th>
<th>Inert or neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>Magnesite</td>
<td>Chrome</td>
</tr>
<tr>
<td>Zircon</td>
<td>Chrome-magnesite</td>
<td>Alumina</td>
</tr>
<tr>
<td>Mullite</td>
<td>Magnesite</td>
<td>Zircon</td>
</tr>
<tr>
<td>Silimanite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Firebrick</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Refractory types, location in furnace and defect potential.
factor which affects the glass directly or indirectly via the refractories used.

**Characterization**
Various analytical tools are used in problem solving sequence that lead to a fast and powerful diagnosis of these defects. The basic analytical methods are:
- Stereo and optical microscopy techniques with polarized light and thin section observation;
- SEM-EDS techniques like point analysis, mapping, linescan;
- If needed XRD can be used;
- Lately XRF mapping technique is used to analyze the micro area chemical composition aiming defect determination.

Sure, there are a lot of additional analytical techniques that can be used to define the defects character, but those mentioned above are fast and in fact the most powerful one.

**Refractory related glass defects**
Glass defects occur in many different forms while the defect sources exhibit a considerable diversity. For instance, two defects may have the same structure and character but an origin which comes from different sources and driven by different mechanisms. The glass technologist who investigates glass defects should be able to appreciate these differences aiming a successful trouble shooting. The refractories used are the most frequent source of stones. They affect the mineralogical properties and the formation conditions.

When we focus on silica, there are different types of silica defects. It is hard to outline the source because it is the major raw material used and besides a large amount of silica refractories are introduced to the melting furnaces. Micro analytical observation is required to define the source. Silica drip is a very common float glass defect which is in a trydimite form. Silica frost or trydimite scale comes also as a defect from float production. The crown or the superstructure silica refractories in the melter are affected by the alkaline vapor. That eutectic phase formed melts and recrystallizes on the refractory surface. These small crystals drop in the glass when the furnace atmosphere or temperature fluctuates. The glass producers use “frost burners” at the refiner area to dilute the alkaline atmosphere and prevent alkaline vapor from attacking the silica refractories.

Some photographs from the observation of a post mortem study on a float furnace are given below. Silica runs downs in a flow like fingers on the curtain wall of the melter. These silica formations may cause silica drip defects.

Fig. 6 illustrates frost formation on a silica refractory. Those tiny trydimite crystals cause silica frost defect when fall down on the glass.
The aluminous defects are other common refractory related defects. They can contain high amount of aluminum oxide and aluminosilicate phases.

Aluminosilicate refractories are used in all parts of the glass furnace and therefore stones of different Al$_2$O$_3$ concentration may arise from any location. Most of these defects look like each other. Analytical technics should be used to define the source of the fault. Trace elements like iron or titanium are the components determined by the observation.

Aluminous refractories not only generate crystalline stones. In most of the cases the latter are surrounded by a glassy phase as aluminous particulates tend to dissolve in the course of melting. Cords and knots can also occur, very often in case of containers or tableware production. In fact they result from the aluminous refractory
corrosion. These problems can be avoided by corrosion products dissolution in the glass melt. This required to improve the glass flows melting, the temperature distribution, and the waist pipe operations or to use stirrers.

Refractory related defects are connected to different parameters as raw material selection, batch moisture or other furnace parameters accelerating the refractory corrosion. Decrepitation is a very critical property which affects the refractories. It refers to the content of limestone and dolomite in the batch. Decrapitation can be described as “a rapid explosion of individual particles at the stage of CO\textsubscript{2} emission”.

Refractory dissolution is an unavoidable chemical and physical phenomenon. It is connected with the corrosion products homogenization within the glass melt. Fig. 8 shows a result of refractory corrosion. All rundowns, refractories dissolved and refractory volume loss lead finally to glass fusion.

AZS refractories are widely used in glass furnaces. They generally cause three types of faults:

- Primary AZS stones;
- Secondary AZS stones, or Secondary zirconia stones;
- AZS bearing knots and cords which are in fact most frequently seen.

The corrosion rate of a superstructure refractory is a function of many variables including the continuous attack by high temperatures, unsuitable vapors and particulates. The weak point of the electrocast AZS refractories is the glassy phase behavior, and the glass defects observed.

We wanted to correlate the AZS refractories used as a superstructure and a glass contact with the glassy defects located in glass during the cold repair observations and post-mortem investigations as they provide some valuable evidence about defects which may have occurred during the life time of furnace (campaign).

We analyzed samples taken from the superstructure. We found that the alumina to zirconia ratio was quite high. We analyzed also samples taken from interface between the glass contact AZS refractories and the glass. The ratio determined was ca 1.

Fig. 10. Post mortem samples and analysis results of AZS refractories.

Fig. 11. Spinel crystals inclusions in an aluminous knot.
In accordance with our experience $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ratio gives a clue about the source of the defect. We consider that if the ratio is high, the defect comes from the superstructure, while if the ratio is ca 1 the source of the defect comes from sideblocks.

Perfectly crystalline precursor spinel crystals are frequently observed embedded in aluminous knots during green glass production. They show up during the flint to green transition and also persist through the campaign. The occurrence of these crystals seems to be triggered off due to a higher temperature. However, it was decided to carry out some experimental work aiming to elucidate the mechanism of the formation and the conditions of existence.

The formation of spinel, $\text{MgO}\cdot\text{Al}_2\text{O}_4$, initially necessitates the presence of essential oxides, i.e. $\text{MgO}$ and $\text{Al}_2\text{O}_3$. These oxides may be contributed by dolomite ($\text{CaCO}_3\cdot\text{MgCO}_3$), feldspar ($\text{NaAlSi}_3\text{O}_8$) from the batch components, and from the magnesite bricks of the regenerator refractories. $\text{Al}_2\text{O}_3$ in the form corundum is of bonded or electrocast type. A temperature of 1453°C is essential for spinel formation.

Taking into account the suspicious source materials the following scenarios of the formation of spinel crystals as glass defects are advanced:

- Dolomite carry over gives rise to $\text{MgO}$ which consequently reacts with $\text{Al}_2\text{O}_3$ in bonded AZS or in the glassy phase of electrocast AZS. Under suitable temperature and fluxing conditions spinel may form in an aluminous knot which subsequently runs down into the glass.
- $\text{Al}_2\text{O}_3$ may be derived from feldspar of the batch carried to the regenerator where it reacts with $\text{MgO}$ of the basic refractory. It then finds its way back to the furnace by gas reversal.
- Basic refractories ($\text{MgO}$) coming into contact with fragments of spalling from $\text{Al}_2\text{O}_3$ checker works may form spinel crystals which find their way in the furnace.

Based on the analytical results consideration it was attempted to set up some experiments aimed to explain the formation of spinel crystals.

**CONCLUSIONS**

Better quality refractory materials increase production yield which is additionally affected by energy consumption, man power, investment cost and production losses. The choice of high quality refractories is not enough. The raw material properties and the operation parameters are also very important in avoiding defects. It is safe to use high quality refractories and raw materials.

Some experience, analytical observation and process information is required to understand the phenomena determining defects appearance. Objectively, every activity in glass production is vital but there is no doubt that furnace operation information is critical for solving a problem. Furnace operation parameters and all other plant data must be combined with laboratory results to determine the origin of defects.

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