SILICEOUS DEFECTS IN FLOAT GLASS PRODUCTION

Akif Özcan, Bülent Arman and Esref Aydin
SISECAM Research Center, Turkey

Abstract

As in other glass furnaces, silica defects form a good proportion of the overall defects in float glass furnaces. A good deal of experience has been gained through the years by applying a systematic approach of defect investigation in float glass production. The experience has been fortified by follow-up post-mortems of crown silica refractories during cold repairs, the effect of change of raw materials, and change from fuel oil firing to natural gas. Based on this experience, an attempt will be made to classify silica defects.

Silica defects encapsulated in alumina-zirconia glassy-phase (knot) are assumed to be the fingerprints of carryover occurring around the doghouse. This phenomenon accelerates the corrosion of superstructure refractories.

In furnaces fired with natural gas, the formation of some species of silica defects are frequently encountered on the crown and bridge wall silica refractories in the flame free area. The waist crown and entrance of conditioning zone are also prone to this type of defect formation. The surface of refractories appear to be dry and the nature of material seems to be loose and friable.

Conglomeratic plate-like tridymite crystals with a minor amount of glassy phases have been observed. The loose and friable silica defects popularly known as "frost" are highly sensitive to furnace operational parameters and silica brick quality. Very often, they fall on the glass and have no chance of dissolution thus ending up as defects in the glass.

1. Introduction

Silica defects, are in the form of quartz, tridymite and cristobalite, which arise from so many different factors during glass melting. By employing the concept of systematic defect analyses over 15 years, thousands of defects have been examined. Experience shows that the siliceous defects make up about 10 percent of the total defects. However at any time, they may became the most predominant defects, since the main ingredient of the batch is sand and very large areas of the superstructure are constructed with silica materials. In these cases rapid and correct determination of the origin of such defects will reduce the losses.

Identification of silica stones are carried out by microscopic techniques and analytical instruments such as electron microprobe (EMP) and x-ray diffraction (XRD). In order to determine the origin of stones, it is necessary to know some information such as the
general distribution of the defects, furnace parameters, any other defects showing parallel increase with silica defects and to check the furnace operations. Although numerous silica defects have the same composition as silicon dioxide, more than 90% of these defects can easily be identified by a simple binocular microscope after a certain period of experience. The form of defect and it's components, crystal type and its dimensions, the character of the borders with base glass, distribution and density on the ribbon gives several clues about the origin of defects. In addition to this, some chemical analyses by electron microprobe, especially some trace elements within the glassy phase of the defects helps for determination.

Besides the systematic defect analyses, observation of used materials during the cold repair of furnaces is an important source of knowledge. Corrosion points and extent, crystal types and forms of different zones, absorption of volatile elements, condensation regions and localities of flows give important information about the causes of corrosion.

2. Descriptions of Used Silica Refractories

As it is known, large areas of superstructure and all of the crown are covered by silica refractories and mortars. When the old melting furnaces are observed during cold repair, some parts of the superstructure and crown are observed to be intensively corroded. The areas which are critical for corrosion occur in the right and left sides of the crown around hot point, expansion joints 1/2, 3/4, back wall over the doghouse, front wall at the melting end. High temperature and carryover, alkali penetration and condensations are the main parameters that act directly on corrosion of silica materials. The superstructure of the refining area seems to be of darker colours towards the colder parts. Oxides of vanadium and nickel in fuel-oil, are absorbed in the glassy phases of superstructure materials and increase at lower temperature zones. The appearance of refractories in refining areas of the furnaces heated by natural gas seem to be dry, irregular and flake.

![Figure 1 Petrographic structures of three samples](image-url)
Detail studies were accomplished\(^1\) on used silica refractories taken from some parts of the melting tank during cold repair (Fig. 1). 10 mm slices were cut from hot surface to the cold end for each sample and analysed by XRF, to obtain the element distribution profiles of each sample along the depth.

The following conclusions are summarized.

- Two kinds of mechanisms are affected on the element distribution along the depth. One is the diffusion of Na\(_2\)O and MgO from furnace atmosphere through the surface of the silica bricks. The second factor is the movement, towards the cold end, of CaO and other oxides such as Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), K\(_2\)O and TiO\(_2\) which are homogeneously distributed in the original bricks. The oxides move towards the colder depth of the bricks by temperature gradient, diffusion and vapor pressure of the furnace atmosphere.

- From hot surface to the temperature gradient of 1470°C, the bricks are composed of fish-scale cristobalite and some glassy phases.

- The amount of glassy phases increases towards the colder parts.

- The second zone is composed of plate or lath-like tridymites oriented vertically, because of compression and gravity.

- Na\(_2\)O and MgO contents of glassy phases decrease in depth but CaO and other oxides increase.

- Below the temperature point of 1200°C, pseudowollastonite crystals appear.

- In the zone, which has abundant pseudowollastonite crystals, the other elements oxides are at maximum concentration.

- Some part of CaO and all the other oxides like Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), K\(_2\)O and TiO\(_2\) are placed in the residual glassy phase after pseudowollastonite crystallization. This zone is between the temperatures of 1200 - 900 °C.

- After the last zone, the refractory structure does not show any change.

An example of chemical composition of pseudowollastonite and the adjacent glassy phase is given in the following table:

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Pseudowollastonite</th>
<th>Glassy-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>49.99</td>
<td>70.30</td>
</tr>
<tr>
<td>CaO</td>
<td>50.53</td>
<td>7.20</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td></td>
<td>4.50</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>K(_2)O</td>
<td></td>
<td>1.31</td>
</tr>
<tr>
<td>FeO</td>
<td></td>
<td>10.75</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td></td>
<td>4.66</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td></td>
<td>0.31</td>
</tr>
</tbody>
</table>
3. General Classification of Silica Stone Defects

The silica stones can be classified with respect to their origin:

Batch Stone
- inefficient melting Cristobalite
- segregation of batch
- corrosion of superstructure and crown
- carryover

Tridymite
- corrosion
- devitrification

Quartz
- coarse grained sand and clay contamination
- fragments from cold parts of the furnace

The schematic representations of silica transformations and probable sources of defects is shown in the following figure.

4. Silica Stones Arising from Corrosion of Furnace Refractories

Silica defects can be categorized into two main groups. The first group can be named as "drop-like" defects, arising mainly from increasing temperature, affected by fluxing agents and carryover, condensation of volatiles; the second group is "fragmental defects" originating from superstructure and crown by mechanical actions, slidings, sudden pressure differences, and repair activities.

4.1. Drop-like Defects

Crown drips: Drips are typically composed of secondary cristobalite /tridymite dentrites randomly distributed in a glassy phase having high silica content. Their forms are commonly apparent from the very smooth taper and the irregular shape of the larger end of the defect where they had broken away the parent drippage.
**Drippage from expansion joints and silica mortars:** They have the same form and crystalline characteristics as in crown drips, except the glassy-phase contains more iron, vanadium and nickel content, because of temperature drop within expansion joints and porous structure of mortar. Sometimes primary silica fragments can be seen besides secondary dentrites.

**Superstructure run-down:** Stones are largely secondary dentritic cristobalite in a certain orientation surrounded by glassy phase drove from fused AZS blocks. The defect have sometimes dentritic zirconia besides cristobalites. The principal source of stone is the crown or superstructure and they run-down over AZS fused cast breast walls, which pick up some zirconia dentrites or glassy phases including AZS components.

**Breast wall run-down, arising from carryover:** If the grain size of any batch component like sand, feldspar, dolomite and soda become finer, and the batch moisture content is low, improper firing and charging conditions can cause carryover. Dusty materials can be accumulated on the wet breast wall around doghouse and dissolve in time and run down to the melt. The petrographic features are the same as superstructure run-down, arising from crown. The only difference is rather fine and radial orientation of cristobalite dentrites starting from point sources.

### 4.2. Fragmental Defects

**Silica fragments & spallings:** Probable origin of such stones are the colder parts of the melter and refiner. Their common features show angular form, recent primary structure, mostly plate or lath-like tridymite crystals with no solution sac.

**Siliceous scales (frost):** Siliceous scale, known as "frost" which is formed on the surface of the silica bricks of the crown and side wall around melting end in the flame free zone of the float furnace heated by natural gas. When these siliceous scales drop on the surface of the melt in cooler part of the melter, being drawn up before it is completely dissolved into molten glass, causing serious production losses. Frost is composed of conglomeratic plate-like tridymite crystals with a minor amount of glassy phase. Experiences show that the atmospheric conditions of the melter and the quality of the silica bricks are the effective parameters on the mechanism of frost formation. This problem can be solved by permitting excess oxygen into the refining area.

During a frost problem, two different kinds of silica bricks of super-duty quality manufactured by different suppliers were placed together in the peep hole at the critical region at refining zone for 6 months. Later the bricks were removed and detail petrographic identifications and EMP analyses were carried out. The first brick was used in furnace having frost problem which had a CaO content of 2.9% and a flux factor of 0.32. The second brick had a CaO contents of 2.6% and a flux factor (Al$_2$O$_3$+ K$_2$O) of 0.39.

From the detail studies, the following points are summarized.

- Grain size distribution of two original bricks were different before testing.
- After 6 months of testing, the hot surfaces of both silica bricks were covered with tabular tridymite crystals with small amount of glassy phase.
- Thickness of tridymite zone of first brick was 35 mm and the second brick was 27 mm. Tridymite formation of the first brick was loose, friable with finger nail and oriented in a
certain direction; but the tridymite formation of the second brick was interlocking to each other and was not friable in spite of a knife. The results of the surface differences of the two bricks under testing in the same place and atmospheric condition were rather interesting.

-Pseudowollastonite crystals were formed in a depth of 27 mm for the first brick, and 20 mm for the second brick. That is to say the first brick was more permeable in such atmospheric conditions.

-Both original silica bricks were submerged into the Na$_2$SO$_4$ melt in 1100°C and later they were kept for 5 hours at a temperature of 1450°C. After the testing, the first brick was completely disintegrated.

It is believed that, the silica brick quality is important but not the single factor for frost formation. As a matter of fact, the problem was solved in spite of those bricks.

5. Silica Stones Arising from Batch Materials

These kind of defects may, from time to time, become the most predominant defect group. Their distribution is homogeneous along the ribbon and usually the defect density is suddenly increased. They originated from two principal factors. The first one is the batch feeding problems and contamination of batch materials (including coarse grain sand), the second one is the furnace operating conditions.

The following examples are given for such kinds of defects originated from batch materials.

**Batch stone drifting along the flux-line:** When the stones are drifted along the corroded side blocks at flux-line, because of shadow effect they are not dissolved but partly transformed to cristobalite within a glassy-phase belonging to AZS refractories or some primary or secondary zirconia with them. They are identified from breast wall run downs arising from carryover by their partial transformation.

**Batch stone originated from incomplete melting:** Small bubbles resulting from insufficient refining conditions are increased with such silica stones of batch origin. These kinds of defects show radial cristobalites started from a source points with a small amount of solution suc. Some small bubbles are commonly present within this kind of defect. Complete or partial cristobalite transformation is characteristic.

**Scum** is originated from alkali volatilization from surface of the molten glass at high temperatures and it is characteristic for tabular cristobalite crystals showing New-York pattern.

**Silica segregation** may arise from segregation of batch materials during storage, mixing or transportation. Nonconformity of grain size distribution of soda and sand may cause such silica defect also. This kind of defect is exactly the same with batch stones. The only difference is its lower density and no bubble defects beside it. It may not cause any severe production losses.

**Conglomerated sand** is the result of clay contamination of sand where clay materials envelope the sand grains to prevent dissolving.

**Silica stones within aluminous matrix or silica with nepheline or mullite crystals** are also the result of clay contamination of sand.
Silica defects arising from coarse sand grains identified by their massive structure, partial transformations and the absence of pore (no bubbles) within them.

6. Devitrification

The main sources of devitrification of the glass into tridymite are the water boxes and mixers in the furnace. The order of devitrification of components on such coolers is; devitrite, tridymite, diopside/wollastonite from cold to hot end. Therefore these devitrification components may be released from time to time by glass currents, temperature differences or mechanical actions. Such tridymite crystals are single or as crystal piles in glass with no solution sac. Rarely some broken refractories under the flux line or bottom can cause such devitrification problems.

7. Conclusion

Siliceous defects make up about 10 % of defects seen in glass production. They may originate from different sources like batch, corrosion of refractories and devitrification. These defects are all structural modifications of SiO\textsubscript{2} occurring as quartz, trydimite and cristobalite. A certain uncertainty still remains during identification, but by a built up of experience the origin of defects, interrelated with operational parameters, can be delineated.

The quality of refractories used play an important role for some of the silica defects. Frost is of this types. However, the application of suitable operational parameters may take care of the problem.

It is deemed to be important during the identification process to notice all details of textural differences of the minerals so that a sound correlation can be made.