

Postmortem analyses of salvaged conventional silica bricks from glass production furnaces

Andrew Wereszczak¹⁾ and Hsin Wang

High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN (USA)

Musa Karakus

Department of Ceramic Engineering, University of Missouri, Rolla, MO (USA)

Warren Curtis

PPG Industries, Inc., Pittsburgh, PA (USA)

Victor Aume and Dennis VerDow

Thomson Consumer Electronics, Circleville, OH (USA)

The microstructure, phase content, and thermal conductivity of salvaged conventional silica bricks from float glass and TV-panel glass production furnaces were examined as a function of position through the brick, and compared with the original, unaltered brick materials. The silica brick from the float glass furnace was in service for approximately 10 years while that for the TV-panel glass furnace was for approximately 6½ years. The microstructure and phase content in both salvaged bricks showed gradients, from tridymite at the bricks' cold-face ends, to cristobalite at their hot-face end even though both bricks were an initial mixture of tridymite and cristobalite to begin with. The thermal conductivity of both bricks had increased as a consequence of these phase and microstructural changes. A thermal analysis model predicted that such changes would result in an increase in the bricks' cold-face temperature and heat content during service. The initially-produced temperature gradients and environment caused microstructural changes in the silica brick; however, the cause-and-effect relationship between temperature/environment and microstructural changes in the brick likely became mutually reversible once the microstructural changes initiated and the thermal conductivity of the brick started to change as a consequence.

Postmortem-Analysen von aus Glasschmelzwannen wiedergewonnenen konventionellen Silikasteinen

Das Gefüge, die Phasenzusammensetzung und die thermische Leitfähigkeit von konventionellen Silikasteinen, die aus Glasschmelzwannen zur Herstellung von Floatglas und Fernseh Bildschirmen stammen, wurden an mehreren Stellen innerhalb des Steins untersucht und mit dem ursprünglichen, neuwertigen Steinmaterial verglichen. Der Silikastein aus einer Floatglaswanne war ungefähr 10 Jahre im Einsatz, während der Stein aus der Fernsehschirmglaswanne etwa 6½ Jahre benutzt wurde. In beiden wiedergewonnenen Steinen zeigten sich Veränderungen im Gefüge und in der Phasenzusammensetzung, wobei Tridymit an der kalten Seite des Steins vorherrschte und Cristobalit an der heißen Seite des Steins, obwohl beide Steine zu Beginn ihres Einsatzes aus einer Mischung aus Tridymit und Cristobalit bestanden. Die thermische Leitfähigkeit beider Steine erhöhte sich als Folge der Änderungen im Gefüge und in der Phasenzusammensetzung. Ein Modell zur thermischen Analyse sagt aus, daß solche Änderungen zu einem Anstieg der Temperatur an der kalten Seite des Steins und des Wärmeinhalts während des Einsatzes führen. Das Temperaturgefälle zu Beginn des Einsatzes des Steins und die Umgebungsbedingungen verursachen mikrostrukturelle Veränderungen im Silikastein; die Ursache-Wirkung-Beziehung zwischen Temperatur/Umgebungsbedingungen und Gefügeänderungen im Stein beeinflussen sich jedoch gegenseitig, sobald die mikrostrukturellen Änderungen initiiert werden und die thermische Leitfähigkeit des Steins sich daher verändert.

1. Introduction

Many chemical and microstructural changes occur in silica refractories during their service in glass production

furnaces. For example, it has been recognized for several decades that gradients in porosity, chemical species, and phases occur in silica refractories through-their-thickness [1]. Many geometrical and operational parameters such as thickness of the refractory, refractory hot- and cold-face temperatures, vapor species in the furnace, and length of service, and initial material parameters such as

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¹⁾ Now with: US Army Research Laboratory, Aberdeen Proving Ground, MD (USA).

porosity and secondary phase constituents can affect the severity of the aforementioned created gradients. Furthermore, some of these independent parameters may become coupled over time; for example, changes or gradients in porosity can affect the thermal conductivity in the refractory which in turn will further alter thermal gradients and corrosion rates in the refractory.

It is important for furnace engineers to recognize the effects of these independent parameters on ultimate refractory performance in order to promote and prolong furnace life. Silica refractories remain the choice for superstructure applications for gas/air glass production furnaces. However, their corrosion resistance is a potential life limiter especially if oxygen boosting or hybrid designs are employed. The silica brick is typically corroded in two ways; a gradual loss of material over its hot-face surface and "ratholing" (large conical corrosion pockets) that occurs at a joint due to localized alkali condensation. The time-dependent changes in the silica brick microstructure (and near its hot-face), along with how temperature gradients in the brick change as a consequence, can affect these two corrosion histories. Thus, the understanding of their mechanisms would greatly benefit attempts to promote more efficient and prolonged furnace life.

The intent behind the present study was to postmortem silica brick salvaged from glass production furnaces and to compare those results with the original or unused material. To examine what effect the identified microstructural changes could have on heat transfer in the brick, thermal conductivity of the salvaged brick was also measured and compared to that of the silica's original state. The intent of the thermal conductivity analysis was to examine its coupled effects with that of microstructural changes.

2. Brick histories and characterization procedures

2.1 Service histories of the two salvaged silica bricks

The silica bricks used in the production furnaces for float and TV-panel glass had some similarities and differences in their original state. Both silicas¹⁾²⁾ were reported by their manufacturers to be Type A³⁾ silica brick [2]. Both contained a mixture of cristobalite and tridymite, although the silica used in the float glass furnace had a higher cristobalite to tridymite ratio (2.1:1) than that for the silica used in the TV-panel brick (0.75:1) [3]. Both had a calcium silicate as a secondary phase

¹⁾ Vega H, Harbison-Walker Refractories Company, Pittsburgh, PA (USA).

²⁾ Gen-Sil, A. P. Green Refractories, Mexico, MO.

³⁾ Flux factor (alumina plus twice the percent of alkalis) is less than 0.5 % for Type A silica.

[3]. Both silicas have been shown to have excellent creep resistance and have dimensional stability through 1650 °C (3000 °F) [3]. Lastly, the apparent density of the silica used in the float glass furnace was slightly higher (1.87 g/cm³) than that for the silica used in the TV-panel furnace (1.78 g/cm³) [3].

The silica brick salvaged from the soda–lime–silica float glass furnace had been in service for approximately 10 years. The brick's original dimensions were (7.6 × 15.2 × 45.7) cm³ ((3 × 6 × 18) in³) with the largest dimension being the hot-face to cold-face thickness. The brick was subjected to a hot-face temperature of approximately 1595 to 1615 °C (2900 to 2940 °F) and an estimated cold-face temperature of approximately 1195 to 1210 °C (2180 to 2210 °F).

The other examined silica brick was salvaged from a TV-panel glass furnace and had been in service for approximately 6½ years. The brick's original dimensions were (7.6 × 22.9 × 38.1) cm³ ((3 × 9 × 15) in³) with the largest dimension being the hot- to cold-face thickness. The brick was subjected to a hot-face temperature of approximately 1600 °C (2910 °F) and a calculated cold-face temperature of approximately 775 °C (1430 °F).

2.2 Characterization and analysis procedures

Sample preparation was different for each of the microstructural, phase content, and the thermal conductivity analyses; however, the common denominator among them was that specimens were sectioned or sampled from the interior of the salvaged bricks as a function of position along each salvaged brick's length. Cross-sections of the two salvaged bricks and the locations where the analyses were performed are shown in figure 1. Any microstructural, phase changes, or thermal con-

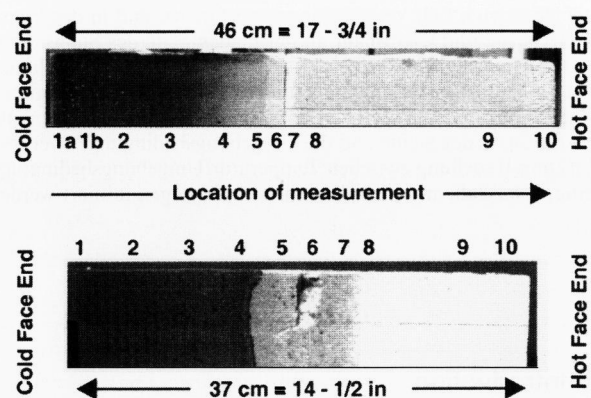


Figure 1. Cross-section of the salvaged conventional silica bricks removed from the float (top) and TV-panel (bottom) glass furnace. The numbered locations identify regions where phase, microstructural, and thermal conductivity measurements were made. Location 1 is each brick's cold-face end while location 10 is the bricks' hot-face ends.

ductivity changes were only considered in a direction perpendicular to the hot-face surface; it was assumed in this study that such changes occurred uniformly in planes parallel to the hot-face surface.

2.2.1 Microstructural imaging

Polished sections from the locations indicated in figure 1 were prepared for reflected light optical microscopy (RLOM). Samples were cut from the salvaged bricks, cleaned, dried, and then impregnated with a low viscosity Spurr Resin⁴⁾ to fill the pores. Cured sections were first ground with a diamond-impregnated grinding wheel down to 600 grit, and then polished with diamond paste and lapping oil. A cold-cathode cathodoluminescence (CL) microscopy system, CITL model Mk4 (Cambridge Image Technology Ltd., Cambridge (UK)) mounted on a standard Nikon petrographic microscope (Labophot2-Pol model with a Nikon UFX-DX photomicrographic system) was used for the RLOM imaging. This imaging instrumentation has been described in detail elsewhere by Karakus and Moore [4].

2.2.2 X-ray diffractometry

In preparation for x-ray diffraction (XRD), material was taken from both salvaged bricks at the locations shown in figure 1 and ground to less than 325 mesh ($<44 \mu\text{m}$) with an agate mortar and pestle. The room temperature phase content for each location was then identified using an automated Scintag 2000 x-ray diffractometer system. The scans were run using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at a step size of $0.03^\circ/\text{s}$ between $10^\circ \leq 2\theta \leq 45^\circ$. A nickel filter was used to suppress β -diffraction lines of the silica phases. The dependence of the phase content on the sample's location was compared with the phase content of the original silica identified in another study [3].

2.2.3 Measurement of thermal conductivity

The room temperature thermal conductivity (TC) of each sample cut from the locations shown in figure 1 was measured with a Hot Disk Thermal Constants Analyzer (HDTCA)⁵⁾. The HDTCA is based on the transient plane source method [5 to 7]. The combination heater/sensor consists of a nickel double-spiral pattern that is sandwiched between two thin layers of kapton. The temperature coefficient of resistance of nickel is used by the instrument's software in its analysis of thermal conduc-

tivity. A metered source provides electrical heating under constant power during the test (e.g., 1 W for 10 to 20 s) while the temperature increase of the sample is recorded by the heater/sensor. The thermal conductivity of the sample is then calculated from the time-temperature history. The determination of the thermal conductivity is based on an assumption that the sensor is located in an infinite medium, which may be approximated by a specimen with radius and thickness equal to or greater than the radius of the heater/sensor. Consequently, the TC measurements with this technique are more accurate the larger the test sample.

The HDTCA's heater/sensor was sandwiched between a piece of styrofoam insulation and a cut sample (HDTCA-single-side method). The thermal conductivity of each sample could be measured knowing the thermal conductivity and thermal diffusivity of the styrofoam. Thermal conductivity was measured as a function of location using a heater/sensor with a radius of 6.35 mm. Three measurements were taken at each location and about 20 min of thermal relaxation time was used between measurements. This technique was chosen for its ability to make non-destructive, localized thermal conductivity measurements. Other TC-measuring techniques [8 and 9] require more involved specimen preparation and average over a much larger area, making the TC mapping of the bricks impractical.

3. Results and discussion

The results from the microstructural, phase, thermal conductivity characterizations and the analysis of their effects on the change in cold-face temperature are presented for each salvaged brick and are compared to that of their original state. Any time dependence of the identified changes was obviously not examined because only characterizations of the final state of the silica bricks were made. The characterizations of the silica bricks from the float glass furnace are presented first followed by those for the TV-panel glass furnace.

3.1 Silica brick from float glass furnace

The original microstructure of the conventional silica used in the float glass furnace is shown in figure 2. It consisted of cristobalite (PDF# 39-1425), tridymite (PDF# 18-1170), and a small amount of calcium silicate (as identified by energy-dispersive spectroscopy/scanning electron microscopy = EDS/SEM). The original microstructure consisted of "fish-scale" cristobalite islands bonded with prismatic tridymite crystals enclosed in a calcium silicate matrix. Tridymite prisms farther away from the cristobalite islands were larger in crystal size (10 to 20 μm width and 20 to 80 μm length). Isolated cristobalite islands were very large, ranging from about

⁴⁾ Polysciences, Inc., Warrington, PA (USA).

⁵⁾ Hot Disk, Inc., Göteborg, (Sweden).

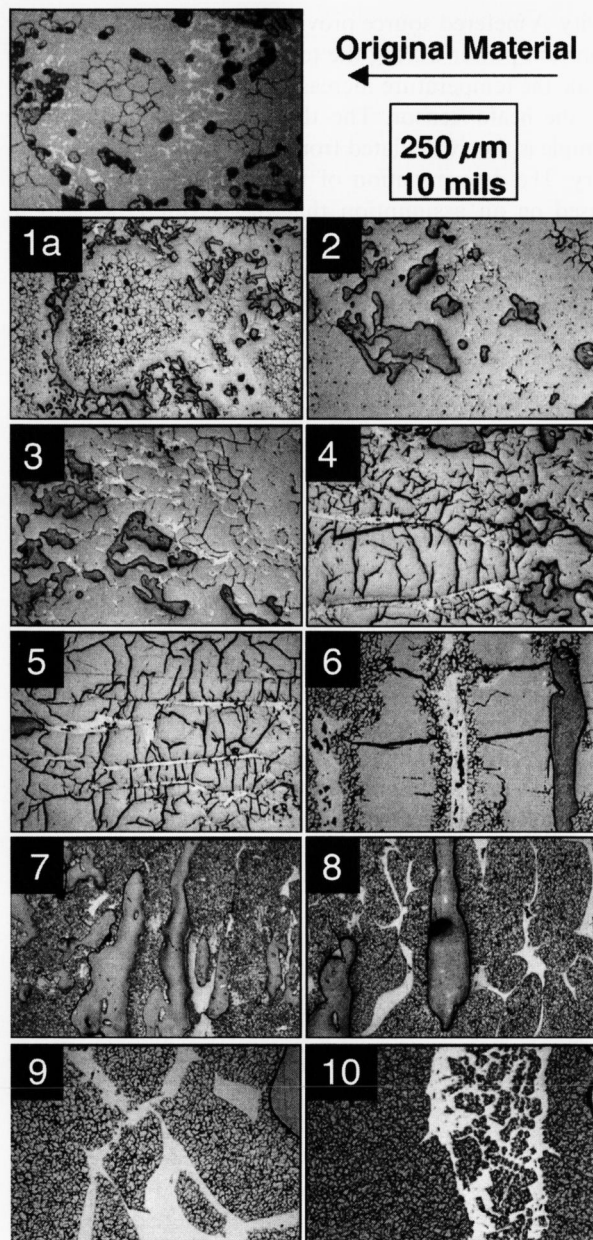


Figure 2. Reflected light optical microscopy images of the salvaged conventional silica brick removed from the float glass furnace. Original material microstructure is compared with microstructures of the salvaged silica brick as a function of position. Numbers correlate with locations labeled in figure 1.

200 μm to more than 2 mm. Examination of the calcium silicate phase by EDS/SEM analysis revealed two distinct phases; one was a pure calcium silicate phase with a composition (in mol%) of about 62 CaO and 38 SiO_2 (close to the stoichiometry of $2\text{CaO} \cdot \text{SiO}_2$) while the second phase was entirely amorphous and contained FeO, K_2O , Al_2O_3 , MgO, and TiO_2 .

The microstructures of the salvaged silica brick changed from its cold- to its hot-face end as shown by the RLOM micrographs in figure 2, and their trends

were consistent with those identified in other silicas from soda–lime–silicate glass furnaces [1]. The microstructures at the cold-face end (location 1a) consisted of “fish-scale” cristobalite islands bonded with prismatic tridymite crystals and calcium silicate matrix. Locations 2 to 5 contained tridymite grains that grew to large sizes and were characterized by both intense fissuring and a columnar habit. At location 6, fish-scale cristobalite starts to form around, or at, edges of the fissured tridymite. Here at location 6, the shape of the pores were found to be also larger and more elongated. A crack in the brick had formed between locations 6 and 7 during service and it appears to have been associated with a change in microstructure and phase content between these locations. The microstructures at locations 7 and 8 were very similar in that first, the cristobalite formed dominant fish-scale textures, and second, the shape of the pre-existing, large tridymite grains was preserved in the formation of the cristobalite. The shape of the pores also remained elongated in locations 7 and 8. The silica microstructures at locations 8 to 10 contained no tridymite. The microstructure consisted of cristobalite islands in a matrix of an amorphous phase. At location 10, skeletal crystals of cristobalite in a glassy phase were observed; this suggests that cristobalite skeletal crystals had crystallized or developed from the enclosed glass. The secondary phase in locations 8 to 10 was a single amorphous glassy phase and was very different from the secondary silicate phases at the cold-face end of the salvaged brick.

The change in phase content as a function of position in the salvaged silica brick is illustrated in figure 3, and is also compared with the phase content of its original state. The original silica consisted of a mixture of cristobalite and tridymite. The observed phase changes

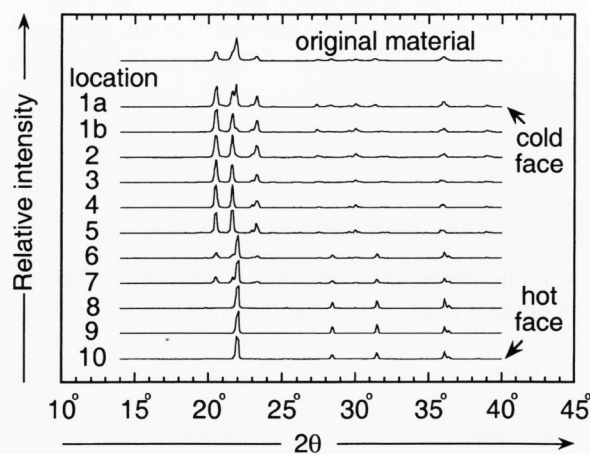


Figure 3. X-ray diffraction spectra of the salvaged conventional silica brick removed from the float glass furnace. Original material is compared with phase content as a function of position in the salvaged silica brick. Cristobalite's primary peak is located at $\approx 22^\circ$ while tridymite's primary peaks are located at $\approx 20.5^\circ$ and 21.6° .

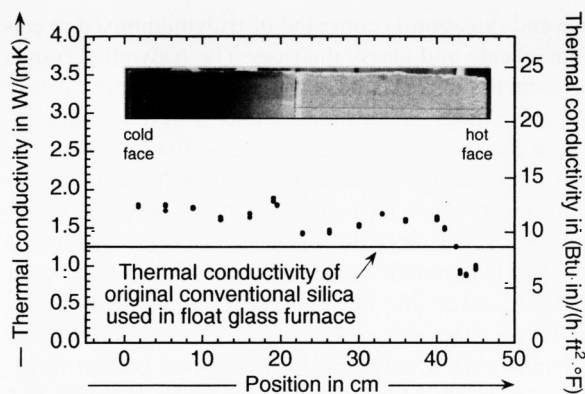


Figure 4. Room temperature thermal conductivity of the salvaged conventional silica brick removed from the float glass furnace. Original material thermal conductivity is compared with cross-section microstructures as a function of position.

from the XRD were consistent to the microstructural changes shown in figure 2. Location 1a (thin lightly-shaded portion located at immediate cold-face end of the salvaged brick) too was comprised of cristobalite and tridymite. Locations 1b to 5 were brownish-tan in color and were almost entirely comprised of tridymite, which is different than both the original state of the material and that at location 1a of the salvaged brick. Locations 6 and 7 were in a transition zone that was light tan to yellowish-white in color and contained both tridymite and cristobalite. Locations 8 to 10 were comprised entirely of cristobalite.

The changes in microstructure and phase content as a function of position in the salvaged brick resulted in a positional dependence of the room temperature TC. The TC ranged from approximately 1.7 to 1.9 W/(m K) (12 to 13 (Btu · in)/(h · ft² · °F)) between locations 1 to 5 which is where the microstructure primarily consisted of tridymite. The TC reduced to approximately 1.4 to 1.7 W/(m K) (10 to 12 (Btu · in)/(h · ft² · °F)) between locations 7 to 9 where cristobalite comprised the microstructure. Lastly, the TC reduced further to approximately 0.9 W/(m K) (6 (Btu · in)/(h · ft² · °F)) at location 10 (hot-face end) where the microstructure was comprised of cristobalite and a substantial amount of porosity. The measured TC of the original silica was 1.24 W/(m K) (8.61 (Btu · in)/(h · ft² · °F)) and shows that the TC of most of the salvaged brick had increased while the TC at the hot-face end had reduced.

Two thermal steady-state finite element models⁶⁾ were analyzed to qualitatively examine what effect the change in the silica's TC would have on its cold-face temperature. A two-dimensional model was constructed by considering the (45.7 × 15.2) cm² ((18 × 6)in²) face of this silica brick (used for both analyses). The first analysis considered a constant TC of 1.24 W/(m K)

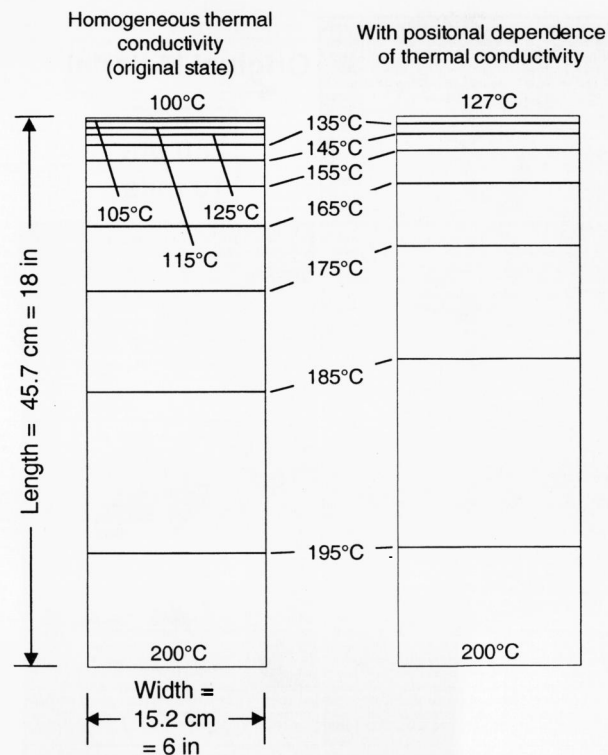


Figure 5. Two-dimensional example illustrating the effect of thermal conductivity changes on the cold-face temperature of the salvaged conventional silica brick removed from the float glass furnace. A steady-state cooling rate that produces a cold-face temperature of 100°C in an original silica block produces a higher cold-face temperature of 127°C when the thermal conductivities shown in figure 4 are considered.

(8.61 (Btu · in)/(h · ft² · °F)) for the whole brick (i.e., that which may have existed initially during the brick's service). A constant hot-face temperature of 200°C and a constant (arbitrary) cooling rate was applied at the cold-face end to produce a steady-state cold-face temperature of 100°C (see generated gradient in left-hand side of figure 5). A second analysis was performed using the TC values indicated in figure 4 with the same boundary conditions as the first analysis. The resulting temperature gradient is shown in the right-hand schematic in figure 5. The steady-state cold-face temperature had increased to 127 from 100°C as a consequence of the changes in the salvaged brick's TC and a greater volume of the brick is also at a higher temperature. Service temperature TCs are likely larger than those measured at room temperature; however, this analysis qualitatively illustrates that the cold-face temperature probably had increased as a consequence of the microstructural changes that had occurred in this silica during float glass furnace operation.

3.2 Silica brick from TV-panel glass furnace

The original microstructure of the conventional silica used in the TV-panel glass furnace is shown in figure 6

⁶⁾ COSMOS/M, Structural Research and Analysis Corporation, Los Angeles, CA (USA).

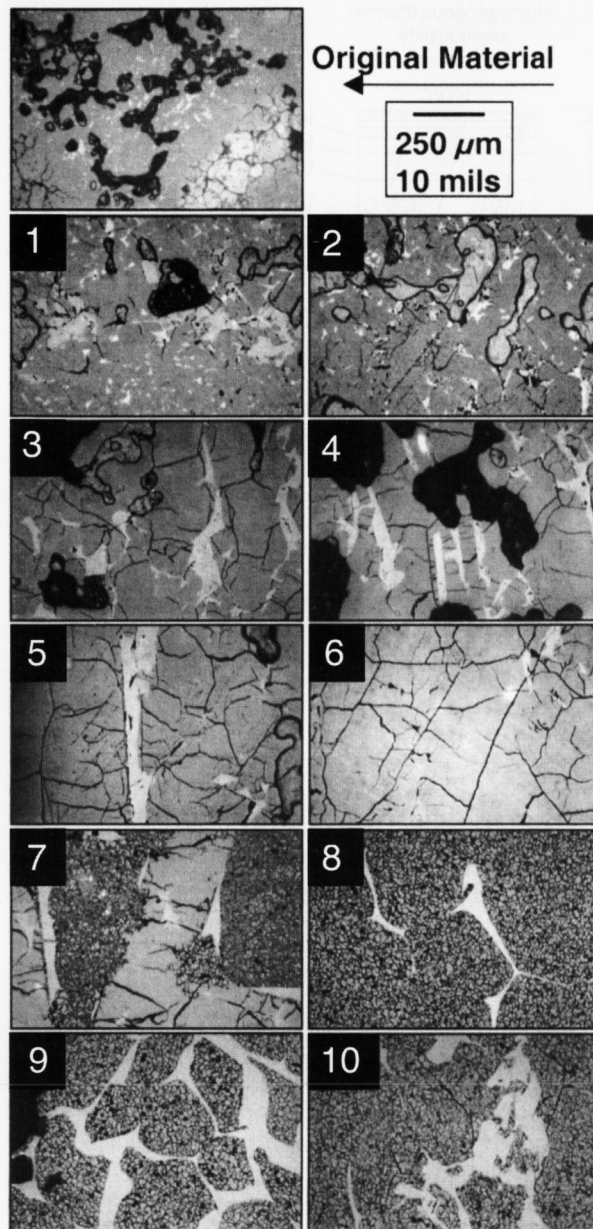


Figure 6. Reflected light optical microscopy images of the salvaged conventional silica brick removed from the TV-panel glass furnace. Original material microstructure is compared with microstructures of the salvaged silica brick as a function of position. Numbers correlate with locations labeled in figure 1.

and was quite similar to that of the original silica used in the float glass furnace. This silica also consisted of fish-scale cristobalite, prismatic tridymite, and a small amount of calcium silicate. Cristobalite islands in the microstructure were very large and tridymite prisms farther away from the islands increased in size as well.

The microstructures of the salvaged silica brick from the TV-panel glass furnace also changed from the cold- to the hot-face end as shown in the RLOM micrographs in figure 6, and also were consistent with results from Konopicky et al. [1]. The microstructures at the cold-

face end (location 1) consisted of tridymite mixed in calcium silicate and glassy matrices. The tridymite crystals were small and prismatic shaped. The microstructure and mineralogy at locations 2 and 3 were identical to that at location 1; however, large and fissured tridymite with a columnar structure started to be present. A calcium silicate phase formed between tridymite grains and had very small skeletal crystals. Location 4 was at the interface between the bricks' brownish-tan and yellowish zones; however, the morphology of the tridymite was similar on either side of this interface. Large and fissured tridymite with a columnar structure was present at locations 5 and 6. At location 7, most of the tridymite had been converted into "fish-scale" cristobalite. The microstructures at locations 8 to 10 were similar in that all the tridymite had converted to cristobalite, and the originally existing "skeletal" calcium silicate and glass matrix had become one single amorphous phase. There was a relatively low amount of porosity at the hot-face end (location 10) of this salvaged silica brick compared to that for the brick salvaged from the float glass furnace.

The change in phase content as a function of position in the salvaged silica brick is illustrated in the XRD patterns in figure 7, and is also compared with the phase content of the original state of this silica. Consistent with the RLOM in figure 6, the original silica consisted of a mixture of cristobalite and tridymite. Locations 1 to 6 were comprised of tridymite, location 7 consisted of both cristobalite and tridymite, while locations 8 to 10 were entirely comprised of cristobalite.

Similar to the salvaged silica from the float glass furnace, the changes in microstructure as a function of position in this salvaged brick resulted in a positional dependence of the room temperature TC (figure 8). The TC was approximately 1.9 W/(m K) (13 (Btu · in)/

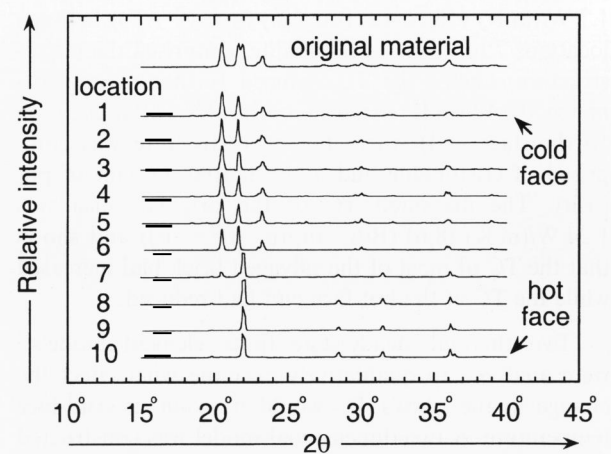


Figure 7. X-ray diffraction spectra of the salvaged conventional silica brick removed from the TV-panel glass furnace. Original material is compared with phase content as a function of position in the salvaged silica brick. Cristobalite's primary peak is located at $\approx 22^\circ$ while tridymite's primary peaks are located at $\approx 20.5^\circ$ and 21.6° .

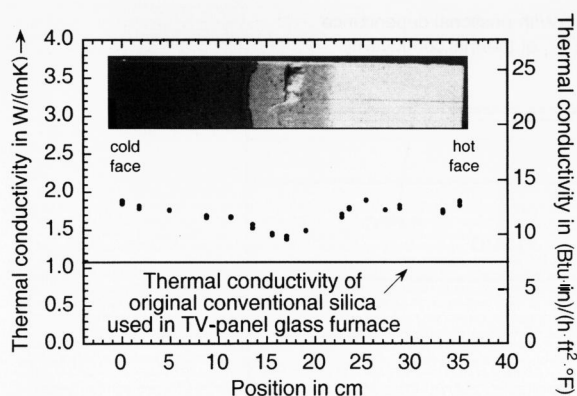


Figure 8. Room temperature thermal conductivity of the salvaged conventional silica brick removed from the TV-panel glass furnace. Original material thermal conductivity is compared with microstructures as a function of position.

($\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F}$) at location 1, decreasing to a minimum of approximately $1.4 \text{ W}/(\text{m K})$ ($9.7 \text{ (Btu} \cdot \text{in)} / (\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F})$) at location 5, and then increasing back up to approximately $1.9 \text{ W}/(\text{m K})$ ($13 \text{ (Btu} \cdot \text{in)} / (\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F})$) at location 8. The TC then remained relatively constant up to the brick's hot-face end (location 10). There were no obvious microstructural and phase change differences between locations 4 to 6 that could account for the observed TC minima. The measured TC of the original conventional silica was $1.18 \text{ W}/(\text{m K})$ ($8.19 \text{ (Btu} \cdot \text{in)} / (\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F})$) which shows that the TC of the whole salvaged brick had increased as a consequence of its 6 1/2 years of service.

Like the TC analysis conducted with the salvaged brick from the float glass furnace, two thermal steady-state finite element models were qualitatively analyzed to examine what effect the change in TC would have on the brick's cold-face temperature. The two-dimensional model considered the (38.1×22.9) cm^2 ((15×9) in^2) face of the silica brick. The first analysis considered a constant TC of $1.18 \text{ W}/(\text{m K})$ ($8.19 \text{ (Btu} \cdot \text{in)} / (\text{h} \cdot \text{ft}^2 \cdot ^\circ\text{F})$) for the whole brick (i.e., that which may have existed initially during the brick's service). A constant hot-face temperature of 200°C and a constant cooling rate (not equal to the cooling rate used in the analysis shown in figure 5) was applied to the cold-face end to produce a steady-state cold-face temperature of 100°C . The generated temperature gradient is illustrated in the left-hand side of figure 9. A second analysis was performed using the measured TC values shown in figure 8 with the same boundary conditions, and the resulting temperature gradient is shown in the right-hand side of figure 9. The steady-state cold-face temperature increased to 133 from 100°C as a consequence of the TC changes in the salvaged brick and a greater volume of the brick is also at a higher temperature. Like that for the silica from the float glass furnace, this analysis with the TV-panel glass furnace silica qualitatively illustrates that the cold-face

temperature probably had increased as a consequence of the microstructural changes that had occurred in this silica during its operation.

3.3 Common issues

A depth of 20 (8) and 15 cm (6 in), from the hot-face end of the salvaged float glass and TV-panel brick, respectively, was entirely converted to cristobalite. In these volumes, any originally present tridymite had dissolved and precipitated out as cristobalite during service [10]. Exposure of these conventional silicas to ambient air at 1550°C (2820°F) for no more than 250 h promotes such a total conversion [3]; therefore, the temperatures in this volume could have been as high as 1550°C during their service.

Paskocimas, et al. [11] observed similar phase gradients in the postmortem analysis of a silica brick and attributed it to the operating temperature gradient in their brick; namely, tridymite being stable between 870 and 1470°C , and cristobalite being stable above 1470°C . An explanation for the greater depth of cristobalite formation (from the hot-face end) in the float glass furnace brick was that a larger volume of it was above 1470°C . Even though their hot-face temperatures were believed to be the same, the relatively low thermal conductivity at the hot-face end of the float glass furnace brick (due to the greater amount of porosity formation) could have resulted in a relatively larger amount of it being subjected to relatively high temperatures. Furthermore, this process had $\approx 50\%$ longer time to occur in the float glass furnace brick (10 years) than for the TV-panel glass furnace ($6\frac{1}{2}$ years). Additionally, how the cold-face end of each brick was insulated could have affected the amount of brick subjected to temperatures greater than 1470°C . The cold-face temperature was reported to be higher for the float glass furnace than for the TV-panel glass furnace, so this could have also contributed to the silica from the float glass furnace having more of its volume converted to cristobalite.

The overall furnace heat losses increase with the age of the silica brick and the conversion in grain structure that occurs within it. Initially, the produced temperature gradients and environment cause microstructural changes in the silica brick; however, once these changes start to occur, the thermal conductivity of the brick is altered and the cause-and-effect relationships between temperature/environment and microstructural changes become dependent on one another.

Further complicating the understanding of these dependencies are the chemical effects. Those that have examined chemical diffusion into silica brick [1, 11 and 12] reported that alkali and alkaline earth vapors act as mineralizers and fluxing agents as they diffuse to the interior of silica brick. The formation of cristobalite from tridymite above 1470°C and the formation of tridy-

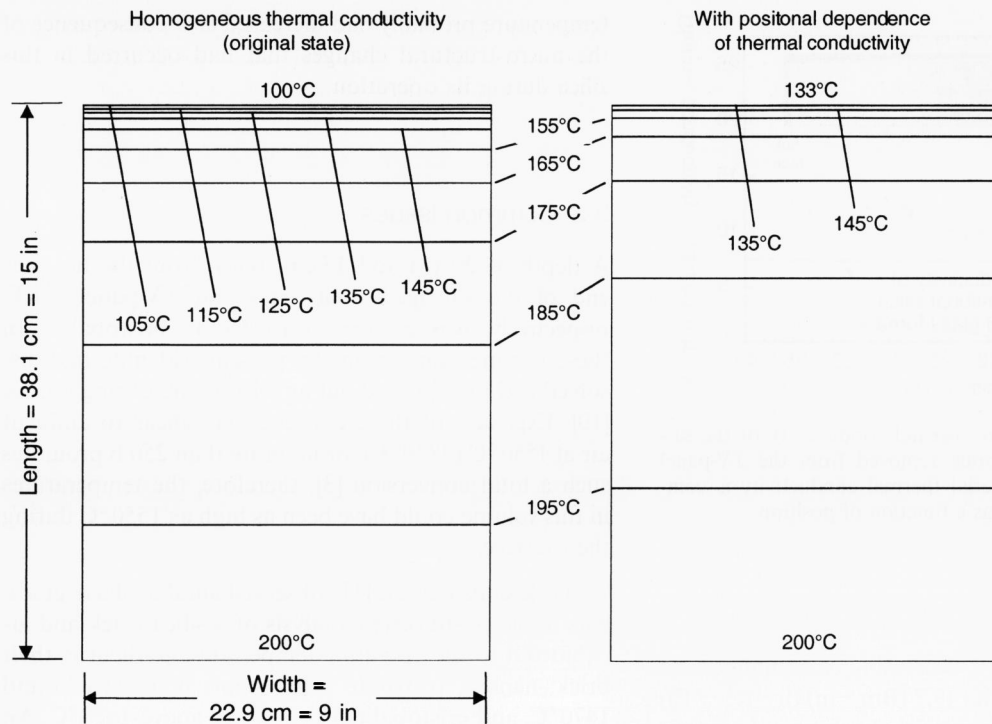


Figure 9. Two-dimensional example illustrating the effect of thermal conductivity changes on the cold-face temperature of the salvaged conventional silica brick removed from the TV-panel glass furnace. A steady-state cooling rate that produces a cold-face temperature of 100°C in an original silica block produces a higher cold-face temperature of 133°C when the thermal conductivities shown in figure 8 are considered.

mite from cristobalite below 1470°C are sluggish; the interior-diffusing alkali and alkaline earth species can promote these transformations though by their presence. The lower alkali vapor concentration in air/gas glass furnaces compared to oxy-fuel glass furnaces is the primary reason why silica brick remains a viable candidate for use in the former but less so in the latter [12 to 14].

Besides the near-surface volume of the silica salvaged from the float glass furnace, the room temperature TC of the majority of both silica bricks had increased (≈ 20 to 50%) during service from that of their original state. When the thermal conductivity of the continuous phase (k_c) is much greater than the thermal conductivity of a dispersed or porous (k_p) phase, then the thermal conductivity of the composite material (k_m) may be related to the volume fraction (v_p) of the dispersed or porous phase according to [15]

$$k_m \approx k_c \left[\frac{1 - v_p}{1 + v_p} \right]. \quad (1)$$

The suppliers of these two conventional silicas reported apparent porosities of approximately 20% for both. Considering a simple case where k_c is constant, then the apparent porosity of the salvaged silica bricks would have had to decrease to approximately 11% and 0% in the salvaged bricks in order to produce k_m increases of

20 and 50%. The porosity content did not decrease to these amounts judging from the RLOM imaging, so it can be concluded that porosity decreases could not alone have accounted for the increased TC of the salvaged silica bricks.

The authors are unable to fully explain why the TC of the salvaged bricks had increased; however, factors such as greater immigration of liquid phases from the hot-face end and more intimate grain-to-grain bonding due to improved secondary phase wetting of the grains may have resulted in improved heat transfer through the grains and ultimately through the silica brick (i.e., a larger-valued k_c in equation (1)). Alkalis and alkaline earth species in the furnace atmosphere can act as a mineralizer and fluxing agent and diffuse to the interior of the refractory [11]. Additionally, much, if not all, of each salvaged brick's volume was at temperatures in excess of the secondary phase's softening temperature, so a sintering effect such as this may have occurred. Sintering, or at least recrystallization, likely also occurred in the bricks' volume toward their cold-face end because the original cristobalite in the original materials was absent from large sections of each salvaged brick; namely the volume spanned by locations 1b to 5 in the silica brick from the float glass furnace (see figure 3) and the volume spanned by locations 1 to 6 in the silica brick from the TV-panel glass furnace (see figure 7). A consequence of these sin-

tering and dissolution effects may be relatively higher densities locally, better grain-to-grain contact, and subsequent improved heat transfer and higher TC values. It may be speculated that this effect may have been relatively severe at locations 7 and 8 in the float glass furnace's salvaged brick resulting in the observed minima of the TC in this volume of the brick.

The thermal conductivity of silica is expected to increase as temperature is increased [16]. The manufacturer of the silica used in the TV-panel glass furnace reported TC values for temperatures between 200 and 1315°C. These data were regressed by the authors against an exponential function which was then used to extrapolate the TC values to 1600°C. The extrapolated TC value at 1600°C was found to be approximately double the room temperature TC value that was measured with the HDTCA. Additional thermal steady-state finite element models were then analyzed to qualitatively determine how these larger TC values (at high temperature) would affect the cold-face temperature in each silica when a gradient in the TC was considered and compared with a constant TC. For this analysis for silica used in the float glass furnace: all the TC values in figures 4 and 8 were doubled; a hot-face temperature of 1600°C was used, and the previously used cooling rate that produced a cold-face temperature of 1200°C (and $TC = 2.48 \text{ W/(m K)} = 17.2 \text{ (Btu} \cdot \text{in)/(h} \cdot \text{ft}^2 \cdot \text{°F)}$) was considered. A cold-face temperature of 1300°C resulted from this analysis. A 35% increase in the cooling flux would have been required to produce a cold-face temperature of 1200°C. Likewise, a hot-face temperature of 1600°C was considered for the silica used in the TV-panel furnace and a cooling rate at the cold-face end that produced a cold-face temperature of 775°C produced a higher cold-face temperature of 1050°C when all the TC values in figure 8 were doubled. A 49% increase in the cooling flux would have been required to produce a cold-face temperature of 775°C. These increased cold-face temperatures in these analyses are a worst case scenario because the TC increases are less than 100% at temperatures less than 1600°C; however, they too suggest that the cold-face temperature of the salvaged bricks probably increased with service time.

4. Summary

The microstructure, phase content, and thermal conductivity changes in salvaged conventional silica bricks from a float glass and TV-panel glass production furnace were examined as a function of position through the thickness. The analyses of the microstructure and phase content in both salvaged bricks showed the presence of gradients from tridymite at the bricks' cold-face ends to cristobalite at their hot-face end even though both bricks were a mixture of tridymite and cristobalite prior to their service. The thermal conductivity of both bricks had changed as a consequence of the identified phase

content and microstructure changes, and a thermal analysis model indicated that their changes likely had caused an increase in the bricks' cold-face temperature and heat content during their service. A plausible future study would involve the examination of the time dependence of the observed microstructure, phase content, and thermal conductivity changes.

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Addresses of the authors:

A. Wereszczak
US Army Research Laboratory
Weapons and Materials Research Directorate
ATTN: AMSRL-WM-MC
Aberdeen Proving Ground, MD 210005 (USA)

H. Wang
Oak Ridge National Laboratory
PO Box 2008, BLDG 4515, MS 6069
Oak Ridge, TN 37831 (USA)

M. Karakus
Dept. of Ceramic Engineering, University of Missouri-Rolla
222 McNutt Hall
Rolla, MO 65401 (USA)

W. Curtis
PPG Industries, Inc., Glass Technology Center
PO Box 11472
Harmerville, PA 15238 (USA)

V. Aume and D. VerDow
Thomson Consumer Electronics
24200 US 23 South
Circleville, OH 43130 (USA)