

---

# Glass Melting

---

---

COPYRIGHTED MATERIAL



## RAPID REFINING OF SUBMERGED COMBUSTION MELTER PRODUCT GLASS

David Rue, Walter Kunc, and John Wagner  
Gas Technology Institute

Bruno Purnode  
Owens Corning

Aaron Huber  
Johns Manville

Segmented glass melting processes require special attention to glass refining before glass is delivered to the forming process. Refining levels vary based on product requirements, allowing this step to be designed as needed, but most commercial glasses require refining. Submerged combustion melting (SCM) produces a homogeneous molten glass that contains a large number of bubbles ranging all the way up to 2 cm. in diameter. Efforts to rapidly refine SCM glass have led to an understanding of methods that hold promise and those that are ineffective for this glass. A crucial factor involves the number and distribution of bubbles and how they move within the viscous glass. A two-stage refining approach holds promise. This approach enables attainment of glass for fiber quality in the first stage and glass for higher quality applications (container, float, etc.) in a second stage. This paper describes efforts to develop and study batch and continuous refining of SCM product glass. A wide range of refining approaches have been proposed and explored in the past, and the current work is reviewed in the context of this body of earlier work.

### CONVENTIONAL MELTING AND SUBMERGED COMBUSTION MELTING

The great majority of glass made industrially is produced in refractory melters. While these furnaces vary significantly in size, temperature, residence time, and refractory composition based on the glass composition and fining quality required, the overall approach of using a single large tank with a long residence time is the same. Glass batch and cullet (if included) is charged at the back of the furnace, and fined glass ready for a final conditioning step, a forehearth, or a forming process is discharged at a controlled rate from a throat on the front wall of the furnace. Usually heat is supplied by air-gas or oxygen-gas burners above the melt surface. In some furnaces electrodes below the melt surface provide a portion or even all of the heat needed for batch heating and glass forming reactions, and to hold temperature for homogenization and glass fining.

Submerged combustion melting provides a different path to a homogeneous molten glass. In SCM<sup>1</sup>, batch and cullet (if used) is also charged at the back of the furnace and molten, homogeneous glass is discharged at a controlled rate from a throat or opening on the front wall. The means of heating in SCM is a carefully arranged group of oxygen-gas burners firing directly up into the melt pool. This provides excellent heat transfer and mixing along with a much shorter average residence time of one to four hours. With a residence time of 10 to 20 percent of conventional

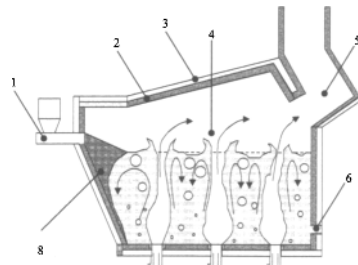


Figure 1. 1 Feeder, 2 Refractory, 3 Cooled walls, 4 Melt, 5 Vent, 6 Tap, 7 Burners, 8 Feed pocket

melting and with the refractory walls replaced with water-cooled panels, an SCM has a much smaller footprint and lower capital cost than a conventional tank.

SCM product glass needs fining, thus the need for a segmented production process. Glass leaving the SCM has been measured to contain up to 35% voids by volume. These voids are predominantly carbon dioxide from the combustion process, with lower levels of oxygen and argon, and trace amounts of CO and NO<sub>x</sub>. Combustion is carried out, as in conventional melters, slightly fuel-lean, so the oxygen in the bubbles is unused oxygen. Because of the differences between glass melted in conventional melters and SCM, the approach to refining could be different.

### GLASS FINING APPROACHES

One reason for the large size of conventional melters is to allow time for bubbles and seeds to rise to the glass surface. Buoyancy in the viscous melt can be enhanced by one or more methods that take advantage of the relationships described by Stokes Law as modified for viscous liquids<sup>2</sup>.

$$V_b = \frac{3}{2} V_s = \frac{g \Delta \rho r^2}{9 \eta}$$

Stokes Law states that the bubble velocity ( $V_b$ ) is proportional to the gravitational constant ( $g$ ), the difference in density of the gas and liquid ( $\Delta\rho$ ), and the square of the bubble radius ( $r$ ), and is inversely proportional to the melt viscosity ( $\eta$ ). Industrially practiced methods include the use of bubblers and bubble curtains to combine smaller bubbles into faster rising larger bubbles, the use of fining agents (As<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>SO<sub>4</sub>, other sulfates, and sometimes other oxides (such as CeO) to add additional gases to increase bubble size, and the use of refining to allow the tiniest seeds to dissolve fully into the glass.

The physics of bubble buoyancy behavior is the same for SCM. Process dynamics, however, dictate which approaches can be considered for rapid fining of SCM glass. SCM glass is homogeneous with large numbers of bubbles that range from tiny up to 2 cm. in diameter. The large number of inclusions eliminates any possible benefits of bubblers, bubble curtains, and chemical fining agents that are used industrially. Also, SCM fining should be rapid or the benefits of a small, intense melting process are lost. A number of other fining methods have been proposed and sometimes employed over the years<sup>3</sup>. These have been studied and evaluated with reference to SCM glass fining requirements.

The most common of the alternate fining approaches is the use of a thin layer zone or fining shelf. By creating a zone with a shallow depth, bubbles have less distance to travel, and fining time is reduced<sup>4</sup>. This approach is commonly applied with electric melters and specially designed furnaces such as the Sorg LoNOx melter. Thin layer refining can accelerate refining, but the method can require large surface areas for glasses that are slow to refine. A second alternative approach is to extract bubbles under reduced pressure or vacuum. The method was demonstrated at industrial scale by PPG in the P-10 process<sup>5</sup> and has been applied in a different way by Asahi. Reduced pressure can accelerate fining but drawbacks include the mechanical complexity, sealing concerns, and the need for foam control.

A third means to speed refining is to use mechanical methods to either screen out bubbles or to gently stir glass to bring bubbles to the surface more quickly<sup>6</sup>. Care must be taken to devise approaches that do not add new bubbles to the glass. Even when well executed, issues remain regarding mechanical wear of stirrers. Also, stirring alone is likely to help refining but not lead to complete refining. A fourth proposed fining method is the application of heat in precise locations to lower glass viscosity and increase bubble velocity. Microwaves have been proposed as one way to

accomplish this<sup>7</sup> since silicate melts are susceptible to microwave heating. The approach is energy-intensive and the means to carry out this approach industrially are not yet demonstrated.

Two related approaches to fining are the injection of steam<sup>8</sup> and the injection of helium<sup>9</sup> to replace or supplement some or all of the fining agents normally used. Steam, particularly in conjunction with sulfates, can accelerate refining. Helium has the virtue of very low density and is expected to very effectively combine with other gas inclusions and increase bubble buoyancy rates. Steam can be understood as a practical way to reduce sulfate requirements, but high temperature steam must be generated and injected uniformly into the melt. Helium refining is promising, but care must be taken to use only a small amount of helium, to distribute helium uniformly in the glass, and to capture and recycle helium if possible.

Centrifugal refining holds promise as a very fast fining approach<sup>10</sup>. Spinning the molten glass at up to 1500 rpm has been shown in lab testing to reduce fining time to minutes. Complexities in scaling to industrial capacities and concerns over high speed rotational equipment have prevented adoption of this approach. A final proposed fining method, acoustic or ultrasonic refining, relies on bubble exclusion rather than Stokes Law<sup>11</sup>. In this approach bubbles are prevented by the acoustic field from passing out of the melter. This promising approach has not been demonstrated at large scale and the materials required for long service life have not been identified.

### SCM RAPID FINING TESTING

The selection of the first rapid refining approach to evaluate with SCM glass was made in the following manner. Helium refining and acoustic refining were considered immature and would require research programs of their own to test. Steam refining and mechanical stirring were considered inapplicable to SCM glass because large numbers of bubbles and high water levels are already present in the glass. Rapid refining by application of precise heating using microwaves or other methods was determined to be too energy intensive and to not be easily adapted to the SCM process. Reduced pressure refining has been proven at industrial scale, but foam control is challenging. The large number of small to large bubbles in SCM glass may be manageable during vacuum refining, but the development of the process would be complex and likely beyond the available development resources. Centrifugal refining also would appear compatible with SCM glass, but the development of the process equipment would require resources beyond those available. Both vacuum refining and centrifugal refining have not been adopted by the glass industry, despite demonstrated successes, therefore these methods were set aside temporarily but kept in mind as possible matches to the SCM process.

Short residence time refining, or holding SCM glass at constant temperature for precise time periods in a chamber with relatively shallow depth, was deemed promising. Because SCM glass is already homogeneous, no further mixing is required. The large number of bubbles, with many of the bubbles having a large enough size that they should quickly rise to the surface, and the high oxygen and steam content in the SCM glass, were supportive of the potential to refine the glass in a reasonable residence time of no more than several hours.

To quickly assess the potential for refining SCM glass with short residence times, an SCM test was conducted with a commercial non-boron E glass composition. Fully melted glass was collected in mullite crucibles that were placed in an electric oven held at 1250°, 1350°, and 1450°C for 0, 20, 60, and 120 min. The crucibles were then placed in a second electric oven held at 800°C overnight to anneal the glass. Once cooled, the crucibles were cut in half as shown in Figure 2 so the refining potential could be determined. Quantitative void fractions were not measured, but visual observation showed that residence times as short as 20 min. led to significant clarification of the glass at the bottom of the crucible, and residence times of 120 min. produced a much more clarified glass.

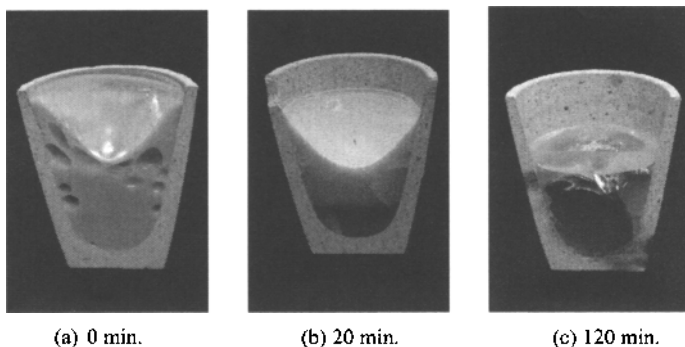


Figure 2. Static Clarification of SCM E Glass at 1350°C, (a) no refining, (b) clearing at bottom, (c) clearing throughout

Promising results from the static crucible refining tests led to preparation of equipment for continuous SCM-short residence time refining tests. An electrically-heated refractory conditioning channel was designed and built. The channel allows steady flow of glass at constant temperature with no stirring. Glass depth can be varied from 7 to 18 cm, and temperature can be as high as 1450°C. Glass flow rates can be 150 to 750 kg/h, giving residence times up to several hours as desired. The channel was close-couple to the SCM with a heated refractory chute. An oxy-gas torch was placed at the exit from the channel to prevent heat losses and to provide a combustion gas environment over the surface of the glass in the channel that simulates expected industrial conditions.

Two continuous steady-state tests were conducted with SCM glass produced from the same borosilicate E glass batch and then sent into and through the conditioning channel. In Test SCM-R-1 two SCM steady state temperature periods were maintained (1370° and 1425°C). SCM discharge rates were varied over a small range between 400 and 550 kg/h giving a similarly small range, and fairly short, residence time range.

The second combined SCM-refining test was conducted under similar operating conditions but with improved process control and more detailed analyses. After the first test, a slide gate was devised for the discharge end of the SCM tap. This electrically-driven and externally heated ceramic plate allowed control of melt flow in test SCM-R-2 over a much wider range from 175 to 450 kg/h. This allowed the refining residence time to be set and varied by nearly a 3:1 ratio. To collect more detailed data than in the first test, the SCM temperature during constant batch charging and glass discharge was held steady at 1425°C,  $\pm 10^\circ\text{C}$ , throughout the second test. The chute connecting the SCM and the conditioning channel was better insulated with improved heating to prevent loss of glass temperature. The conditioning channel was held at 1355°C, as measured by an optical pyrometer at the channel discharge. Limited analyses were conducted with SCM and refined glass from the first test, but care was taken in the second test to collect more samples using a graphite mold, to anneal samples at 800°C, and to conduct more extensive analyses of the collected samples from the melter and the conditioning channel.

## RESULTS

Assessment of the short residence time refining of SCM glass has been made with samples collected from similar operating conditions of tests SCM-R-1 and SCM-R-2. The SCM was maintained under continuous steady state operation at 1425°C using the same borosilicate E glass pre-mixed batch. Samples weighing approximately 0.5 kg were collected from the SCM tap and from the conditioning channel discharge in graphite molds. Samples were allowed to cool, with some samples annealed at 800°C. Chemical analyses found the glass samples from the conditioning channel were fully melted and homogeneous, with uniform compositions across both tests. The collected glass samples were split in half, and chemists at GTI and Johns Manville independently measured void fractions of the samples.

Void fraction analyses from test SCM-R-2 tap and refiner samples are presented in Figure 3. Analyses show the void fraction of the tap samples was similar throughout the day of operation. Voids were measured between 25 and 33%. The test was conducted with melt flow rate decreasing (and refiner residence time increasing) as the day continued. Results show that as residence time increases, a large decrease in void fraction is obtained. Average void fraction of samples after the conditioning channel decreased from 16 to as low as 0.3%, equivalent to a decrease in void fraction from 45 to 99% relative to the voids in the SCM product glass. Refining with short residence time was able to convert the foamy SCM glass to a solid glass with remaining bubbles by removing 99% of the gaseous inclusions.

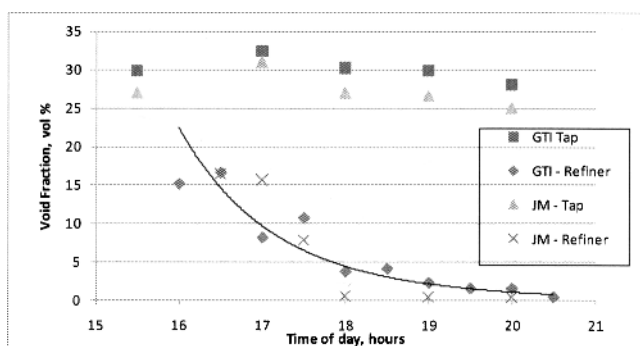


Figure 3. Test SCM-R-2 Tap Glass and Refiner Glass Void Fractions, SCM at 1425°C, Refiner at 1355°C, Pull Rate 175-450 kg/h (Samples Measured Independently by GTI and JM)

The relationship between void fraction in refined glass and residence time in the conditioning channel is shown in Figure 4 for samples collected during both tests. Residence times were shorter in the first test and were longer, covering a wider residence time range, in the second test. All samples were measured for void fraction independently by GTI and Johns Manville chemists. Glass samples from the two tests present the same pattern of reduced void fraction with increased residence time. A short relative residence time period produced a reduction in void fraction to 16%, a removal of inclusions of around 45%. By increasing the residence time, the void fraction decreased. A relative residence time of 3.5 times the initial short residence time produced glass with gaseous inclusions reduced to as low as 0.3%, a removal equivalent to 99% of the SCM glass voids.

Rapid Refining of Submerged Combustion Melter Product Glass

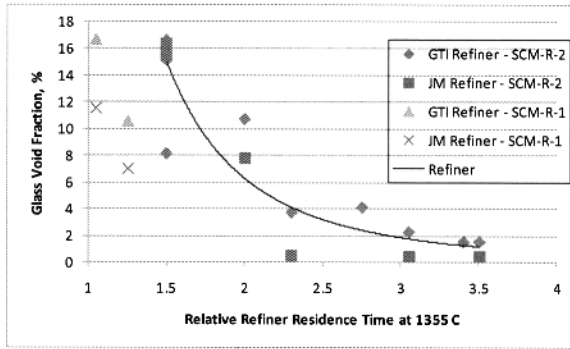


Figure 4. Refiner Glass Void Fractions From Two Tests, Samples With SCM at 1425°C, Refiner at 1355°C, Pull Rate 175-600 kg/h (Samples Measured Independently by GTI and JM)

Inclusions in SCM glass have been found to range from microns to as large as 2 cm. Centimeter sized bubbles are not common, but many bubbles are in the range of 10 mm. to 1 cm. Figure 5(a) provides a close-up view of SCM glass with no refining. The bubbles are uniformly dispersed throughout the glass, and relatively large bubbles can be easily identified.

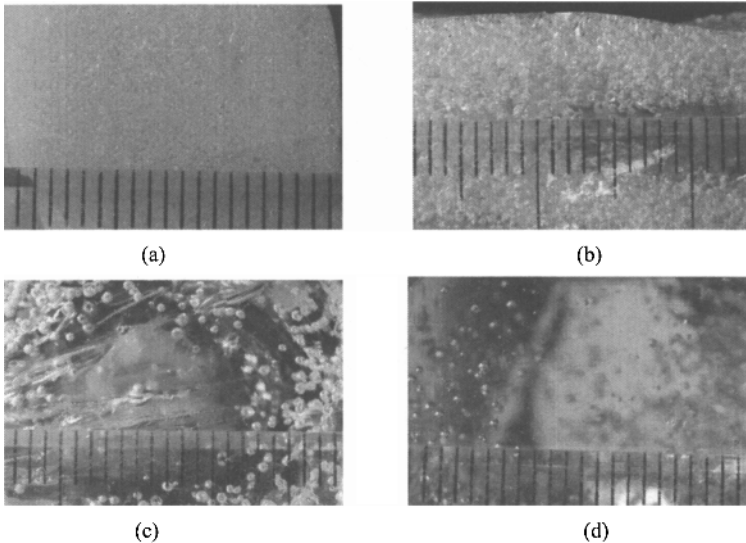


Figure 5. SCM-R-2 Glass (a) SCM Tap (29% voids) and With Relative Refining Residence Times of (b) 1.5 (16% voids), (c) 2 (11% voids), and (d) 3 (<1% voids) – 1 mm Line Spacing

The other photographs in Figure 5 show examples of the level of refining achieved with various refining time periods. With extended refining times the number of inclusions clearly decreased. The longest relative refining time of 3.5 produced isolated bubbles in the glass matrix. Viewing the photographs as a set shows that the average bubble size increases with additional refining time. This is speculated to be the result of bubble coalescence as larger bubbles rise the fastest and merge with smaller bubbles. An advantage of this process is that bubbles will rise more quickly as they merge and become larger, therefore reducing overall refining time.

As higher levels of refining are reached in future tests, different means will be needed to collect samples. Hand sampling with graphite molds will add bubbles to the molten glass. At high refining levels, this will impact the quality of the product glass.

### SUMMARY

The short residence time refining step has proven capable of removing 99% of the bubbles in SCM glass. This level of refining may be sufficient for certain market segments such as wool insulation and large diameter continuous fibers. However, most glass applications require much higher quality. Glass ready for forming into fine continuous fibers, containers, tableware, flat glass, and other items requires gaseous inclusion levels from a thousand to a million times better than has been achieved to date. Short residence time refining is anticipated to be able to achieve at least a further ten-fold improvement in quality with careful control, but higher quality levels will require a different or supplemental refining approach.

Future work with the SCM technology will focus on more detailed study and testing of short residence time refining. Variables to be explored include melt depth, refiner residence time, temperature, and conditioning channel introduction and removal methods. Other work will consider further refining of SCM glass by new methods. These methods may be on the list of those described above or may be wholly new to the glass industry but well adapted to SCM glass.

### REFERENCES

1. Rue, D., Wagner, J., Aronchik, A., "Recent Developments in Submerged Combustion Melting", 67<sup>th</sup> Glass Problems Conference, Oct. 2006.
2. Shelby J., *Introduction to Glass Science and Technology*, 2<sup>nd</sup> ed., p. 42. Roy. Socy., of Chem., 2005.
3. Ross, C.P., Tincher, G., *Glass Melting Technology: A Technical and Economic Assessment*, GMIC, at [www.gmic.org](http://www.gmic.org), Oct. 2004.
4. Beerkens, R., "Analysis of Elementary Process Steps in Glass Melting Tanks", *Ceramics – Silikaty*, 52(4), 2008, p. 206-17.
5. Pecoraro, G., Shelestak, L., Cooper, J., "Vacuum Refining of Glassy Materials With Selected Water Content", U.S. Pat. 4,919,700, 1989.
6. Demarest, H., "Method of and Apparatus for Removal of Gas Inclusions From a Molten Glass Pool", U.S. Pat. 4,406,683, 1983.
7. Berson, X., Vivet, A., Bertrand, E., "Microwave Refining and Melting Furnace", U.S. Pat. 5,597,504, 1997.
8. Kobayashi, H., Beerkens, R., "Water Enhanced Fining Process A Method to Reduce Toxic Emissions From Glass Melting Furnaces", U.S. Pat. 5,922,097, 1999.
9. Buehl, W., "Method of Fining Glass", U.S. Pat. 3,622,296, 1971.
10. Richards, R., "Glass Melting Method", U.S. Pat. 5,573,564, 1996.
11. Spinosa, E., Ensminger, D., "Removing Inclusions", U.S. Pat. 4,316,734, 1982.

