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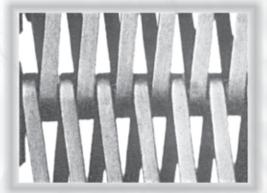
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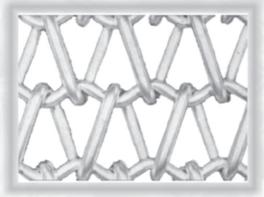
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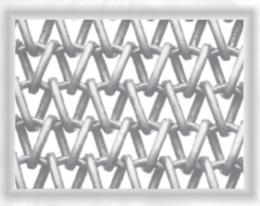
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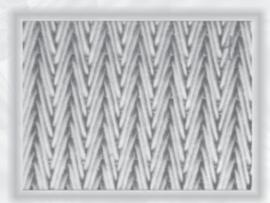
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GLASSPEXINDIA 2011 is being held in Bombay Exhibition Centre, Hall 6, Mumbai, India on 12-14 January, 2011 under the sponsorship of The All India Glass Manufacturers' Federation. Exhibition is being organized by **Messe Dusseldorf GmbH**, **Germany**, organizers of world famous Glasstec International trade fair, Düsseldorf Germany. International conference is being organized by the AIGMF. Latest technology in glass manufacturing will be showcased in the exhibition. Papers on 'Managing Sustainable Growth' will be presented in the conference. Shri PK Kheruka, Chairman organizing committee, International Conference has already written to members for nomination of delegates to the conference. AIGMF is extending full support to the event and wants to ensure its grand success. I request all those associated with the glass industry and interested in its speedy growth to participate in GLASSPEXINDIA 2011 by booking stalls in the Exhibition and sending delegates to the International Conference.

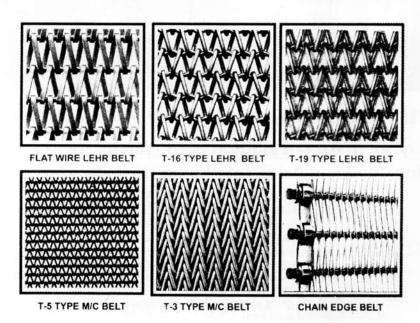
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Glass Melting Innovations Glass Melting Technology: A Technical and Economic Assessment

Part I - Fuel Fired Melting*

By

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(Glass Manufacturing Industry Council, 735, Ceramic Place, Wesrerville, OH 43086-6136)

Abstract

This is first part of a report prepared by the Glass Manufacturing Industry of USA under the US Department of energy-Industrial Technology Programme. It gives the background and future course of development in glass melting technology. In this part of the report Fuel fired funaces and Plasma melting Technology have been dealt with. In the second part to appear in the next issue Electric melting and batch preheating prospects will be dealt with.

Introduction

Many innovations in industrial glassmaking have been explored during the second half of the 20th century as glassmakers have sought to solve critical industry problems. Few of these innovations have been commercialized. Instead, the design of the ancient 1867 Siemens furnace has evolved steadily over some 136 years to meet basic requirements for glass manufacturing with minimal financial or technological risk. The need for advances in glass melting systems remains crucial to the future of glass manufacturing in the United States. In the course of investigating the technology developments proposed or considered over the past 30 years, Phil Ross accumulated all relevant patents on file that dealt with improvements in the glass melting process. Walt Scott, a retired PPG scientist, reviewed 325 patents to evaluate their relevance with regards to a series of 22 categories identifying the main concepts of importance to the glass manufacturing process. These patents are compiled in Appendix A* for their relevance to one or more of these 22 categories. Interested investigators will find these listings to be of great value in identifying technology developments that have been considered in each of these areas as they consider possible approaches to take in the future. To comply with increasingly stringent clean air laws and environmental requirements, combustion heated furnaces must be replaced, modified or re-equipped, as they are inherently air polluting. Improved techniques must be developed to recycle glass industry wastes and used glass products. Electric melting must be improved for longer furnace life, higher quality glass and fuel efficiency. Contemporary glass melting tanks, must be redesigned, adapted, or replaced with less expensive, more flexible melting technologies. Anti-NOx techniques may influence glass-melting technology perhaps more than cost or lack of tank furnace flexibility. The high initial capital cost of furnace construction or furnace rebuilds must be addressed either through design or materials

Each segment of the glass industry has unique interests and requirements. In deciding whether a technology is appropriate for an industry segment, the attributes of the technology must be evaluated.

- First, the quality requirements of the glass product's application must be satisfied. Any new technology must be capable of producing a melt with properties at least as good as those produced by conventional furnaces.
- Second, the cost of manufacturing a glass product must be low enough to compete in a competitive market, including competition with alternative materials.
- Third, a process must be compatible and reliable with the product forming process for a capital intense manufacturing process to be operated efficiently; some manufacturing requires flexibility of pull rate and for composition changes.

This historical review of selected innovations in glass melting technology provides a basis for further study of glass melting technology. Descriptions of the

Permission to publish this report from Executive Director, GMIC, is gratefully acknowledged. Copy right. GMIC, USA, 2004. List of patents and bibliography will be published in subsequent issues- Ed

technologies provide a basis for further research and analysis that could lead to new glass melting technologies for a new age. The list of innovative systems is by no means complete, nor is it intended to be. Many advanced glass technologies have not proved to be commercially successful, but in the light of advanced materials, state-of-the-art equipment, and advanced glass science and engineering they might suggest future directions for research and development.

1. Systems innovations

A number of glass melting technologies that have been developed and tested conduct both melting and refining by non-conventional means. The innovations in advanced glass melting reviewed here cover all aspects of the glass melting process, from batch preheating to emissions control. The continuous fossil fuel furnace has been improved continually with the development of new refractories, the substitution of fossil fuels for producer gas, and over a century of experience. To address some of their more critical problems, glass manufacturers have modified tank designs and developed flame technology and flue gas treatment to reduce emissions. Innovations in flame technologies, electric melters and complete melting and refining systems that developed over the last half of the 20th century have been documented by James Barton of Saint-Gobain, France, and his work provides the basis for much of the analysis to follow. (Barton 1993) Traditional glass melting has evolved and improved as advances have been devised in combustion technology; refractories have been improved; raw materials have been discovered as beneficial; and process controls have been developed for the glass-forming process. However, before a non-conventional idea can be accepted and introduced into glass manufacturing, the innovation must improve glass formation mechanisms by optimizing heat transfer, extending refractory life, and minimizing operation complexity.

1.1 Segmented melting

A segmented system in continuous tank furnaces can address the drawback caused by the recirculation flow in the melting tank, which results in a broad residence time distribution by limiting the maximum residence time of the molten glass in the furnace tank. Since the shortest residence time should be sufficient to complete fining and melting, the minimum residence time is a critical value that depends on the required glass quality and temperature level in the furnace. Many of the attempts to design an advanced glass melting process have applied a segmentation of the melting process in distinct steps, incorporating driven systems to increase dissolution of sand particles and initial gaseous evolution from raw

materials. Segmentation was considered in the design of Saint Gobain's FAR and FARE melting processes (the PPG P-10 melter, Section 2. and next issue), and the Owens-Illinois RAMAR melting technology (see next issue). These innovative processes have not been commercialized either because of high development costs or because of economic issues, glass quality issues, or intense refractory wear. (See next issue Appendix C.)

1.2 Segmented glass furnace design

In segmented glass furnace design, the residence time of the molten glass in the melter is limited. The recirculation of the molten glass results in a broad residence time distribution. The shortest residence time should always be sufficient for complete fining and melting, but required glass quality and temperature level in the furnace create a critical minimum residence time. Some glass scientists and industrialists believe that glassmaking could be optimized by segmenting the various stages of the process. Each step requires special conditions, each of which is different from the conditions of the process step before and after it.

Segmentation of the tank appears to be the most promising design for a melting process with a narrow residence time distribution and a minimum residence time greater than a critical residence time value. Optimum conditions for each process step could be controlled. The capacity of the melting process can be increased by methods of acceleration and/or removal of glass volumes that do not contribute to the primary objective of converting raw materials into refined, homogeneous glass. The process capacity can be increased by any process acceleration or dead volume decrease. Increasing the capacity of the entire melting process leads to energy savings or space miniaturization, as well as reduction of capital cost per ton of product produced.

The advantages of the segmented melting tank furnace design are:

- Residence time distribution can become much smaller.
- Average residence time and tank volume can be reduced.
- 3. Optimum conditions, such as temperature, residence time, and mixing can be controlled in a segment of the furnace almost independently of the operation of another section.
- 4. The most suitable heating source can be used for each section.
- 5. In a separate fining section, new fining techniques,

such as low-pressure fining, high temperatures, acoustic techniques or gas bubbling (stripping) techniques, can be applied. Residence time in the fining section can be limited to two to three hours.

- 6. Local repairs can be carried out more easily in a segmented melter.
- 7. Total volume of the melter can be reduced by a factor of 3 to 5 per ton of glass melt produced. Thermal losses through the furnace walls will also decrease from that of a conventional rectangular tank furnace. Only one small section, the fining section, will operate at high temperature.
- Segmented melting is flexible. A composition or color change will require less time in the new glassmelting concept than in the single-tank furnace.

2. PPG P-10 process (1987)

In one of the most revolutionary advances in glass melting in the past century, PPG developed the P-10 melting system with the intent to devise glassmaking technology that would reduce energy consumption; lower capital investment per ton of glass produced; allow greater flexibility in glass compositions; generate less solid waste from furnace rebuilds; and comply with increasingly stringent air emission standards for NOx, SOx and particulate. Each phase of the glassmaking process was optimized independently to achieve these

goals. The process that was developed addressed a number of key issues:

- to intensify the melting process to reduce the size of furnaces;
- to improve refining time to remove seeds and gaseous inclusions;
- to extend refractory life and reduce costs of lining rebuild:
- to incorporate air emission controls into the process;
- to minimize energy input and maximize return of waste heat into the melting process;
- to reduce the size of batch material particles for more effective melting and rapid color composition changes;
- to increase capability to produce specialized glass formulations that are difficult to produce in conventional melters.

The glass formation process is segmented into four distinct processing devices: batch preheater/calciner; glass melter (primary melter); glass dissolver (secondary melter), vacuum refiner. (Pecoraro et al., 1987) In the PPG system, raw materials are preheated, using waste heat from the melting phase and de-carbonated in two

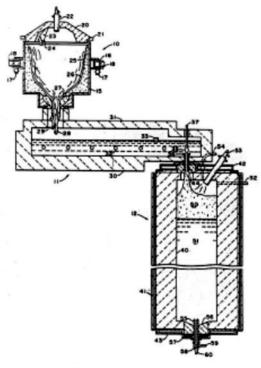


Fig 1. PPG P-10 Primary Melter, Secondary Melter, and Vacuum Refining

inclined rotary kilns, one in which lime and dolomite are calcined in four-fifths of the sand. In a longer kiln, sodium metasilicate is produced from the soda-ash and one-fifth of the sand. The calcined products and the sodium silicate are fed into a rotating melting pot and are maintained on the walls of the pot by centrifugal force. The batch on the wall virtually eliminates the need for a refractory lining on the pot. A central torch melts batch off the wall, which then flows out the bottom of the pot. The complete dissolution of batch is accomplished in a shallow heated canal equipped with electrodes or a series of compartments heated and agitated by submerged oxyhydrogen burners. Refining of the glass is achieved by reducing the pressure over the glass to 20-40 millitorr (only a few percent of atmospheric pressure). Under this low pressure, trapped or dissolved gases expand, forming bubbles and generating foam. Only small concentrations of fining agents (sulfates or water) are required. Burners in the low pressure space, rapid pressure changes and direct injection of water are used to break up the foam and limit its height. Before forming, the glass is stirred thoroughly, and frits may be added to color the melt at this stage. [Pecoraro, G.A., et al. USP 4 792 536 (1987). The total residence of the glass from entrance to exit is approximately half a day, which is very short compared to traditional glass melting approaches.

Air emission controls that anticipate more stringent regulations were incorporated into the P-10 system. Combustion of fossil fuels with air at high temperatures results in the formation of NOx emissions. This NOx can be minimized by using oxygen for heating in the primary melter and all other process areas. Minimally entrapped air nitrogen can enter the system because the combustion exhaust preheats the batch. Particulate emission is controlled by passing exhaust gases through a batch preheater and a conventional bag house that operates above the dew point. By converting to oxygenfuel combustion, eliminating use of sulfates, and filtering the system's exhaust gases through incoming prepared batch, all air emissions were reduced. In addition, by filtering the hot exhaust gases, heat can be recovered and used to promote more rapid melting. The ablative melter and vacuum refiner of the P-10 system demonstrated that reduced pressure can create the super saturation needed for good fining, and under proper conditions dissolved gases and bubble concentrations can be controlled. This method of vacuum refining used in the P-10 process requires no sulfates in the system, thus minimizing SOx emissions. The PPG P-10 process is non-polluting, has a short residence time and can produce glass with high ferrous iron contents free of amber coloration for antisolar automotive and architectural glazing. The P-10 melting system was installed at PPG facilities in Chehalis,

WA, and Perry, GA, and demonstrated that the technology met the original goals for which it was developed. When the project was started, energy required for a flat glass furnace was about 6 million BTU/ton. The developers of the technology thought theoretical energy consumption was 2.2 million and their tare for P-10 was 2.5 million. With the P-10 system, they reached 4.0 million with quality and believed that they would have reached 3.5 million. PPG discontinued use of the P-10 melting systems for glassmaking when the corporation was faced with excess manufacturing capacity. Moreover operating costs were not competitive with current energy and capital costs. Despite the technological accomplishments, the units experienced operating instability, cost of purchasing oxygen offset the low costs of natural gas, concerns remained around achieving low seed counts and production yields were lower than from conventional PPG glassmaking facilities. The PPG-10 process failed to achieve commercial scale-up and proliferation, primarily due to its failure to achieve desired cost benefits. PPG has since donated patent and preproprietary rights to the P-10 technology and equipment to Cleveland State University and is supporting efforts to market this technology to the industry.

During the production operation of these plants flat glass for automotive and architectural products was produced, which suggests that acceptable container glass could be produced in the system. Applications for the technology might be flat glass, fiberglass, container glass, sodium silicate and specialty glasses. The approach would be particularly attractive where rapid changeover in glass composition is needed and where additives and colorants are being used that are sensitive to the traditional elevated temperatures used in refining. Development barrier: The PPG P-10 melting system was patented but development was forestalled reportedly because of higher net cost of operation.

3.1 Glass Plasma Melter (Great Britain, 1994)

Plasma melting of glass was explored by the British glass industry in 1994 to compare the efficiencies of electrical plasma-arc and submerged electrode melting of soda-lime-silica glass. The project aimed to demonstrate the energy savings that would be possible from the inherently high melting efficiency combined with the flexibility to operate the furnace at high or low power. The furnace for the pre-competitive R&D project was built at British Glass by a team of furnace designers and operators from Pilkington, who operated a research furnace of similar size to the demonstration furnace, and Glass Furnace Technology Ltd. (GFT), who had considerable experience in the design and construction of commercial glass furnaces. The Research Group of British Glass and

the British Department of Trade and Industry initially funded the project. Subsequent government funding, obtained through the Future Practice Program of the United Kingdom Department of the Environment, was administered by the Energy Technology Support Unit (ETSU). The furnace built at British Glass incorporated a melting zone 0.6m2 in area and 400 mm deep. With conventional electrode heating and 100-150kg/h, using plasma in place of conventional electrical firing, the furnace had a throughput of 60 kg/h. Following the melting zone, a riser incorporated electrodes to boost and control the temperature of the glass in the sonic refining stage, which included sonic horns. The depth of glass at this point was 125 mm to allow for sonic treatment of the full depth of glass. The project successfully demonstrated high melting efficiency. Using the submerged electrodes, an average efficiency of 5 GJ/tonne (4.26 mmBtu/ton) was achieved (GJ/tonne x 0.852 = mmBtu/ton). The GJ/tonne from a fossil fuel-fired furnace of a similar size would be approximately 14.5-15.3 mm Btu/ton). Energy losses in the plasma melting due to the greater requirement for water cooling and the greater radiation losses indicated that efficiencies could not equal those of submerged electrodes.

The principal limitations at this time are torch materials and design. The commercial plasma torches used in this project were a less expensive version of the torches used in steelmaking. A cost-projection comparison between commercial plasma torches and conventional electric boosting confirmed that plasma would be significantly more expensive. Higher energy densities can be introduced with plasma arc melting (250 kVA) compared with submerged electrodes (100 kVA). Plasma melting is, therefore, more rapid than conventional electrical melting. In small tonnage, specialized applications that require intermittent production or rapid product changes, such as frit manufacture and in short-term runs of specialized glasses or glass components, plasma technology would provide a flexible melting system. (Dalton, D.A., "Plasma and electrical systems in glass manufacturing," IEE Colloquium [Digest], 229, p3/1-2 (1994)). Some barriers to further development have been materials for construction, insufficient funding, scale-up to commercial production, limited glass composition, and higher net cost.

3.2 Arc plasma melting (Johns Manville, 1980s and 1990s)

In the United States during the late 1980s and early 1990s, Johns Manville investigated arc plasma melting technology to melt E-glass batch as well as E-glass and insulation scrap glass. (U.S. patents 5,028,248 and 5,548,611, Johns Manville.) Melting rates up to 1200

lb/h were demonstrated, though glass quality and process control attributes were not addressed. For business and technical reasons, Johns Manville terminated the project in the mid-1990s, and it has not been commercialized.

3.3 High Intensity Plasma Glass Melting (Plasmelt Glass Technologies, LLC, 2004)

Recent efforts by Plasmelt Glass Technologies, LLC to build upon the considerable JM technology base have begun under DOE/OIT funding. A project -High Intensity Plasma Glass Melting-is being conducted by Plasmelt, a Colorado company formed to execute the research program. Cost share partners for these renewed efforts are Johns Manville and AGY. Although the initial work is being done on E-glass, a common fiberglass composition, the longer term work will be broader and aimed more generally at specialty glass applications. Plasmelt is soliciting interested glass companies to supply other non-fiberglass glass compositions that will be used in melting evaluations in the Boulder, Colorado Lab. These additional melting trials with additional companies are key components of demonstrating the broad generic applicability of plasma melting technologies to nonfiberglass compositions. This two-year program, which began in July 2003, has as its objective the production of high quality glass using DC transferred arc technology. The technology uses a small rotating skull melter. The melter has approximately 1.2 m² of melting area and is approximately 0.5 m in depth. With skull melting, glass batch becomes the refractory liner and no water jackets surround the glass melter, so heat losses will be significantly lower. All electrodes are above the glass, avoiding the issues of electrode-glass interactions. However, the transferred arc process forces some of the energy into the glass, making that portion of the heat transfer process nearly 100% efficient. An overall goal of greater than 50% energy efficiency is being pursued at a throughput of 500 pounds per hour. The work is being done on a full-scale melter so that scale up discontinuities do not apply when the 500 lb/hr pilot plant is installed at the first location. Although current efforts are focused on 500 lb/hr, throughputs of 1200 lb/ hr on E-glass batch have been demonstrated with this system. Even higher throughputs are possible on plasmabased scrap re-melting operations in this same melter. Glass quality has not yet been evaluated and the need for add-on refining downstream of the plasma melting unit will be proven or disproven with the work being conducted in this program. Although the research efforts are still in their infancy, it is quite clear that, similar to the British program, principle limitations are torch materials and design and the development of an overall stable and controlled operating process. The current research efforts are aimed at demonstrating the relationship between the

plasma based melting process and glass quality, energy efficiency, and environmental impact. Initial indications are that this melter would be ideally suited to smaller throughput specialty operations that require high degrees of flexibility in making compositional changes or that chose to run discontinuously. Since the technology is well suited to high temperature materials, additional high temperature materials evaluations will be performed during the program. Since the British and JM work was conducted over a decade ago, many improvements have evolved in high temperature materials, controls and sensing technologies. In addition, the current plasma project focuses all efforts on the development of a 500 lb/hr production operation. This focus narrows the range for the process research, increasing its probability of success.

4. Accelerated melting

In technology developed for accelerated melting, the batch is never allowed to float undisturbed on the surface of the molten glass. In five of the systems studied, the batch is fed into the burner with the combustion air. In the AGA Scrap Fiber Melter, the flame is tangentially directed into a vertical cylinder where the melting is completed in the thin film as it flows downward. The Vortex system uses a cyclone, which is horizontal. Others use a downward-flowing thin layer in melting. In the FAR process, preheated agglomerates are charged onto the top of an inclined plane, where they are melted by intensive burners. Refractory wear, which is known to be a problem in many thin-layer melters or cyclones, is avoided by mild air-cooling. In the Sechage, Prechauffage, et Enfournement Directe (SPEED) (Drying, Preheating and Direct charging) system devised at Saint-Gobain in 1982, the refractory is replaced by a sloped incline, the surface of which is renewed automatically as the partially melted material slides downward. In the Pilkington melter, the incline remains completely glazed while being fed from behind. The downward flow in the PPG centrifugal melter is controlled by the speed of rotation. Rapid heat exchange can also be obtained by driven systems that stir or otherwise agitate the melt. In the Brichard furnace, the agitation was brought about by immersed burners; the electrically heated melters used in the RAMAR and FARE systems have rotating impellers that produce very high melting capacities Patents for Ericsson (1988) and McNeill (1990) use infrasound to improve heat exchange between batch particles and the preheated air stream that carries them toward the melter. The advantage of agitated melters is that the melting rate is proportional to a volume rather than to a surface area, and production demands can be met with smaller furnace systems. (These will be discussed later in this chapter.)

4.1 Submerged Combustion Melting (SCM) (Glass Container Industry Research Corp. 1960-1970s)

In the 1960s and 1970s, an era when furnace development focused on increasing production rates in existing furnaces, three trials of SCM were conducted at container furnaces in North America. These trials were sponsored through the Glass Container Industry Research Corp. The combustion equipment was developed by Selas Corporation. SCM has been licensed by the Gas Technology Institute (GTI) in the United States and is being actively developed for a number of commercial applications. Difficulties in applying the SCM technology included burner noise and vibration; low temperatures realized in dissolving sand in premelters used to boost furnace output. If the technology were to be pursued in high-temperature operations, higher refractory wear rates would be anticipated. While electric generation of Joulian heat is a source of energy, it is costly. In Submerged Combustion Melting (SCM), fuel and oxidant are fired directly into the bath of molten material to produce mineral melts. In this advanced melting system, combustion gases bubble through the bath, providing high-heat transfer to the bath and turbulence to promote mixing and uniform product composition. By enhancing heat transfer into the glass melt and increasing mixing actions, the glass melting rates are increased. In SCM, molten materials are drained from a tap near the bottom of the bath, and raw material is fed to the top of the bath. The raw material requires little or no crushing. Two 75 ton/d submerged combustion melters are currently in operation for mineral wool production, one in the Ukraine and another in Belarus. These commercial melters use recuperators to preheat combustion air to 300°C. The melters operate with less than 10 percent excess air and produce NOx emissions of less than 100 vppm (corrected to 0% O₂) along with very low CO emissions. As combustion gases bubble through the bath, the rate of heat is transferred to the bath material to create turbulence in mixing, resulting in a uniform composition of the glass product. (Olabin, Valdimir M., et al., Ceramic Engineering and Science Proceedings, 17(2), 84-92 (1996). Development barriers include materials of construction, insufficient funding, scale-up, limited glass compositions, glass quality and safety.

4.2 GI-GTI Submerged Melter (1995)

The Glass Institute—Gas Technology Institute (GI-GTI) submerged melter employs oxy-firing, a deeper bed than the Selas melter, no moving parts in the bath of molten glass, and externally cooled panels instead of refractory walls. The melter is simple, inexpensive and reliable; can be started and stopped for glass composition changes; and has been proven (with other materials) as a high-temperature melter. The deep bed requires fewer

burners and better control of melting, compared with the Selas melter. High heat transfer rates and rapid mixing allow for a much smaller melter with glass surface area per ton of glass some eight times lower than a tank furnace. Externally cooled walls further reduce melter size and cost while eliminating 80 percent of the refractory needed. In the GI-GTI submerged melter, a layer of glass freezes on the inside surfaces of the melter, protecting the walls and enabling melting of any composition, including aggressive glasses. Any glass, including black glass and high melting temperature glasses, can be melted. Thermal efficiency is high in oxy-gas firing mode because the sensible heat method in heating nitrogen by eliminating air is avoided. Heat loss per square foot of wall area is higher than for refractory tank furnaces, but the large reduction in wall surface area leads to an overall reduction in wall heat loss per ton of glass pulled. The wall panel cooling system design can include a heat recovery step that will boost melting. Hot exhaust gas, as in tank melters, can be used to preheat raw material, natural gas or oxygen. In a 5.5 tonne/day pilot-scale SCM unit that was constructed and operated in GTI's combustion laboratories, the SCM technology is being extended from air gas to oxy-gas firing.

Four test series using oxy-gas burners have been conducted in the pilot-scale submerged combustion melter. Combustion was stable over a turndown ratio of more than 3:1, and the burners were easily started, shut down, and restarted as desired. The coarse feeder was used for all tests. The air-gas burners and the fines feeder have not yet been tested under high-temperature melting conditions. All tests were conducted in batch mode, feeding known quantities of raw material into the melt from the coarse feeder and then producing a bubbling melt in the melt chamber. Sodium silicate, rather than soda ash and silica, was tested to produce a viscous melt. More than 100 kg of sodium silicate was charged, and a product melt was collected. Several mineral wool compositions and cement kiln dust were also tested to demonstrate the wide range of stable operating capabilities of the SCM unit. This intensified the heat exchange between the products of combustion and the processed material while lowering the average combustion temperature. The intense mixing of the melt increases the speed of melting, promotes reactant contact and chemical reaction rates, and improves the homogeneity of the glass melt product. The melter can also handle a relatively nonhomogeneous batch material. The size, physical structure, and especially the homogeneity of the batch feed do not require strict control. Batch components can be charged either premixed or separately, continuously or in portions. Stable, controlled combustion of the fuel within the melt is critical. Simply supplying a combustible mixture of fuel and oxidant into the melt at a temperature exceeding the ignition temperature of the fuel does not sufficiently stabilize combustion. A physical model for the ignition of a combustible mixture within a melt, as well as its mathematical description, shows that for the majority of melt ignition of a combustible mixture injected into the melt as a stream starts at a significant distance from the injection point. This leads to the formation of cold channels of frozen melt and explosive combustion. To avoid this, GTI has designed several multiple nozzle burners to minimize the ignition distance in one of three ways: 1) by stabilization of the flame at the point of injection using special stabilizing devices; 2) by splitting the fuel oxidant mixture into smaller jets; or 3) by preheating the fuel/oxidant mixture. Commercial SCM applications could be extended from mineral wool to a range of commercial glass system, but solutions must be found for the problems of batch handling, integrated melting and fining, heat recovery, process sensors and control, scaling up from 75 tpd, and volatilization. SCM technology has recently been confirmed for use in the production of high-temperature mineral melts. Five 75tonne/day melters are in operation, two in Ukraine and three in Belarus. The Gas Institute (GI) of the National Academy of Sciences of Ukraine has developed SCM technology. The insulating materials produced to date in the commercial operations in the former Soviet Union were basalt mineral wool products. The chemistry of this product does not have alkali or borates. In the extension of this technology to alkali and borate glass compositions, researchers should anticipate refractory and air emission challenges not previously experienced. Development of the Submerged Combustion Melting concept has been hampered by materials of construction, insufficient funding, scale-up, limited glass composition, glass quality and safety issues.

5.1 Advanced Glass Melter (AGM) (Gas Research Institute, 1984)

In Advanced Glass Melter (AGM) technology, flue gases preheat the combustion air by means of a metallic recuperator. The process is based on rapid suspension heating of the batch material and thin-film glass fining using a high-intensity, gas-fired internal combustion burner. The AGM process is a radical departure from the batch melting and glass fining technology used in conventional glass furnaces. Initial engineering in development of the AGM technology was completed for a conceptual 50-tonne/day fiberglass melter. The performance goals of the AGM were to achieve energy input less than equivalent to 3.2 million Btu/ton, NOx less than equivalent to 4.0 lb/ton, SOx less than equivalent to 1.0 lb/ton, and particulates less than equivalent to 0.2 lb/ton. The system was developed to demonstrate enhanced

controllability and flexibility, as well as lower capital and operating costs of conventional fossil fuel and electric furnaces.

The primary steps of the AGM process are:

- rapid suspension heating of the batch components in a high-intensity gas-fired combustor;
- acceleration of the suspension of gas-solids in a converging nozzle that directs flow of the gassolids at the molten pool;
- impact and separation of the glass-forming ingredients in the molten pool, which is also the site for glass-forming reactions;
- initiation of glass homogenization and fining in the pool configuration.

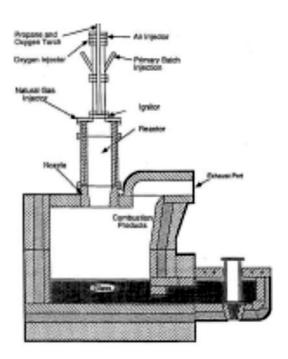


Fig. 2 GRI's Advanced Glass Melter

In the AGM melting process, mixed batch, preheated air and gas are injected into the internal combustion burner (combustor) from which the hot particles are projected downward onto the cap of a partially cooled conical refractory center body inside the glass separation chamber. The melt that forms on the cap refines as it flows down the sides of the cone in a thin layer and is collected. From the burner, hot particles and drops of liquid fall onto the cooled cap of a refractory center body inside the glass separation chamber. Melting is completed in the area of impingement and refining takes place in the thin layer

of melt as it flows down the sloping sides of the center body. Carbonates of the batch may be injected near the lower end of the burner cavity to avoid destabilizing the flame with carbon dioxide. (Barton, 1993; Glass Ind. 1988) (Westra, L.F., Donaldson et al. "How the advanced glass melter was developed," Glass Industry, 69[4] 14-17 (1988))

The objectives in developing the AGM were to conduct feasibility tests of short duration on laboratory scale on an in-flight, rapid glass melting furnace concept; establish a technical basis for an overall systems engineering design; and evaluate economic feasibility of the technology. (Westra, L.F., et al., Glass Industry 69[4] March 1988, 14-17, 40) The Gas Research Institute began development of AGM in 1984 with Avco Research Laboratory and Vortec Corporation, which originated the basic suspension-heating concept. Feasibility test results from melting a simple soda-lime glass in a 7 tpd AGM research unit verified that totally dissolved silica could be produced, indicating that glass might be produced that would be suitable for insulation fiberglass. In 1987, a laboratory-scale AGM was developed to produce insulation fiberglass. In this second phase of the program, operating performance was verified and quality levels and control capabilities were assessed for production of insulation fiberglass. In a 13 tpd pilot demonstration unit constructed at the Knauf fiberglass facility in Shelbyville, IN, five tons of commercial quality wool fiberglass were produced in a trial. The demonstration run was limited to less than 10 days and was shut down due to the challenges that arose:

- Variable feed rate into the combustor: bridging and plugging of batch material hampered temperature control in the AGM chamber;
- Combustor noise: combustor noise exceeded 95 db required workers near the unit to use hearing protection;
- Refractory wear: batch raw materials were deposited on the AGM superstructure; fusing reactions were significant and operating life was expected to be extremely short;
- Exhaust carryover: more than one percent of the batch feed was carried into the exhaust system; high dust in the flue gas could increase difficulty of operation and maintenance of waste heat recovery and emissions control.

Because the AGM furnace is several times smaller than a tank-type furnace of the same production capacity, the structural heat losses from the melter are reduced substantially. A major advantage of AGM technology is its ability to reduce fuel consumption by higher heat transfer to the batch components; rescue structural heat losses; and recover substantial amounts of heat from combustion off-gases. The furnace heat rate of an AGM system is projected to be a total of about 24 percent lower than for a conventional gas-fired furnace.

Glass quality is the greatest concern expressed for the AGM. Carryover difficulties may be serious for chemical homogeneity or refractory stone problems for a larger scale operation. Some manufacturing sectors question whether AGM can produce chemically homogeneous molten glass and be free of seeds and blisters. Another concern with AGM technology is the life of refractories. Most refractories experience chemical reactions at high temperatures when exposed to glassmaking materials, especially alkalis, borates and alkaline earths. The reactions erode the structure, creating contaminants that run down into the molten glass. Batch component carryover and high gas impact velocities in AGM operation are extreme.

This technology might be considered for insulation fiberglass and sodium silicate, glasses in which presence of seeds or other heterogeneity is less critical than other glasses. Once steady state conditions are established for a given pull rate, the reliability of batch feed rate and conditions within the combustor will influence the operation. Batch carryover in the melting chamber will be of concern for the refractory components. AGM could have operational flexibility for rapid composition or color changes as a result of reduced glass inventory, more rapid load change capability, and reduced startup time for the furnace mass.

Adoption of AGM technology is dependent on demonstration of the capability of melting standard rather than fine batch; dual-fuel capability; long-term continuous operation; product quality assurance; negligible volatilization of batch components; and proper interfacing with downstream operations. No plausible approaches have been proposed to address these issues. The AGM system failed to achieve commercial scale up and profitability.

5.2 Nuclear Waste Vitrification (Westinghouse, Savannah River Technologies; Southwest Research Institute; West Valley Demonstration Project; Battelle; 1970s)

Since the 1950s, research and development using glass to immobilize liquid radioactive wastes has been underway. Borosilicate glass, phosphate glass and nepheline-syenite are among the glasses investigated. Requirements for vitrification technology to produce an acceptable glass product are stringent and test the limits

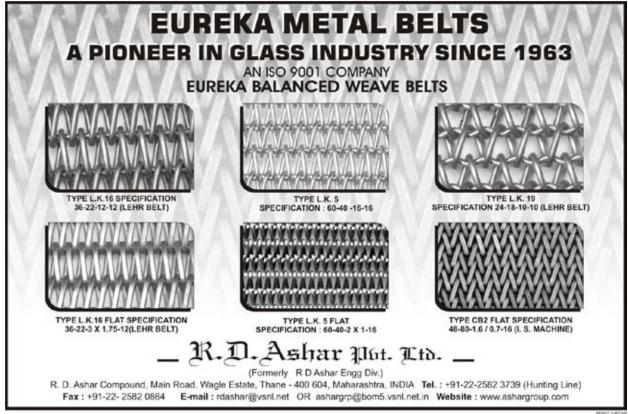
of glass melting processes. Processing constraints range from viscosity and melting and liquidus temperatures to electrical conductivity, redox condition of the melt, solubility of noble metals, and sulfur and phosphate concentrations. The chemical durability, crystallinity and glass transition temperature must meet stringent specifications. The most widely accepted and mature technologies for vitrfying high-level waste in borosilicate glass are joule-heated melter and induction melting technology. Facilities for melting high-level waste containing glass must be designed to operate remotely by robotic controls. Batch components are maintained in shielded walls to minimize exposure of workers to radiation. (Jain, V., "Glass Protects Environment-Contains Radioactive Waste Materials," the GlassResearcher: Bulletin of Glass Science and Engineering, Center for Glass Research: Alfred, NY, 12[1&2] 8-9 (2002-2003)) A ceramic, Joule-heated, slurry-fed melter is in operation at the Defense Waste Processing Facility (DWPF) at the Savannah River Site in Aiken, SC. The control bases for such a melter are unique and complex. The borosilicate hot glass must be able to accept a variety of waste compositions.

Melter controls are extremely sophisticated and must function precisely for melter temperature, glass composition, product durability, waste loading limits, glass redox control, and glass cooling requirements. Melting rates have been increased by the addition of reducing agents such as formic acid, sucrose and nitrates. The exothermic reactions that occur at critical stages in the vitrification process are responsible for the rate increases. Nitrates are balanced by reducing agents to avoid persistent foaming that would destabilize the melting process. Melter residence times are minimized to homogenize glass and assure the acceptable quality of the glass. Research at the Westinghouse Savannah River facility has determined that melters and waste-processing facilities can be reduced in size if mechanical agitation is used to minimize heat transfer requirements for effective melting. A new class of melters has been designed and tested. Melt rates have exceeded 155 kg. m⁻². h-1with dry feed (1.77 sq.ft. per ton per day). The melt rate is eight times greater than in conventional waste glass melters of the same size. [Bickford, D.F., et al., "Control of radioactive waste glass melters. I, preliminary general limits at Savannah River,"J. of the Am. Cer. Society, 73[10], 2896-2902 (Oct. 1990); Bickford, D.F., et al., "Control of radioactive waste glass melters. II, Residence time and melt rate limitations," J. of Am. Cer. Soc., 73(10), 2903-2915 (Oct. 1990).] Development barriers for broader, commercial application of this technology are materials of construction and insufficient funding.

(To be concluded in the next issue Ed.)

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Use of Sodium Sulphate in Glass Batch Part I- Melting Accelerator

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Abstract

A review of the use of sulphate in glass batch has been presented. Sodium sulphate alone or in combination with reducing agents serves many purposes starting from accelerating glass batch reactions, controlling redox of the melt, fining of the glass and production of amber colour. The reactions going on in the glass batch containing sulphate- reducing agent are varied and a large number of studies have been made in recent years to understand the reactions. In the first part of this article the acceleration of glass batch melting during batch heating has been discussed

Introduction

Sodium sulphate, also called salt cake has been used in glass melting since a long time. Its addition in flat glass is almost compulsory to remove the silica scum that is present at the surface of the glass bath. Sodium sulphate alone or in conjunction with other additives serves several purposes.

- 1. Molten sodium sulphate is a surfactant. It lowers the surface tension of the batch-melt interface of the charge which has started melting and helps in faster reaction and dispersal of the reaction products. The gas evolution during melting also brings about a vigorous stirring action. It also brings about a movement of the glass batch. Batch free time is reduced and longer time is available for glass homogeneisation and refining.
- 2. It has a high melting point and the compound is stable in the melted condition. Having a low density compared to the molten glass it floats on the surface of the glass as sulphate gall and any undissoved silica which has also a lower density than molten glass that may come up to the surface reacts with the sulphate and is thus removed. This is especially important for flat glass.
- 3. Sodium sulphate in conjunction with a reducing agent like carbon/coke or sulphides acts as refining agent at high temperature especially when the glass melting is above 1450°C.
- The combination of 3 above with Iron is also used to produce amber colour of various depth of colour.

 It is an oxidizing agent which supplies oxygen ad helps in removing organic materials that is introduced with the cullet. It is used to control the redox of the glass melt.

In what follows below we will discuss all the above functions based on knowledge available in literature. In this part the reaction with glass batch has been discussed.

Wey1¹ has presented a historical review of the work done since the nineteenth century on the use of sulphate in glass melting. More systematic work was done by Bruckner^{2,3,4} which started the understanding of its effects. Bruckner's observations were later confirmed by Conroy, Manring and Bauer^{5,6} and led to the understanding of the role of salt cake in glass melting. With large scale production of flat glass and with the restriction of SO, emission and the increased amount of foaming that occurs during oxy-fuel firing a large number of studies have been done during the last few years. Research work have been reported which deal with hot stage microscopy, analysis of reaction gases and redox chemistry of the sulphur containing batches along with a reducing agent. Refining of both container and flat glass mainly use sulphate carbon refining because of the elevated temperature of processing used at present. In this part of the article we will address only that part related the effect of sulphate or sulphate-carbon on the glass batch.

Physico-chemical Data

The physico-chemical date of Na₂SO₄ and other compounds are tabulated here and will be used for discussion later.

Table I- physico chemical data of some compounds

Compound	Melting point	Density g/cm ³	Std Free energy of formation
Na ₂ SO ₄	884°C	2.664 (anhydrous) 1.464 (decahydrate)	-1270 kJ/mol
CaSO ₄	1460°C	2.96 (anhydrous) 2.32 (dihydrate)	-1322.0 kJ/mol
BaSO ₄	1580°C	4.50	-1362.0
Na ₂ O	1132	2.27	-375.5
Na ₂ S	1176	1.85	-349.8
CaS	2525°C	2.59g/Cm ³	-477
CaO	1176°C	1.85 g/Cm ³	-603.3
BaO	1932	5.72	-520

Glass batch reaction In an intimately mixed glass batch of soda, calcium carbonate(calcite) and sand all -150 mesh the reaction of glass formation starts at 790°C at the melting of the eutectic between soda and calcium carbonate and CO_2 loss takes place rapidly⁷ (fig. 1). The reaction ends at 840°C. No free lime is found in a mixture

cooled rapidly from this temperature showing that all the flux had reacted with the quartz. The compound formed after quenching was found to be Na₂O.CaO.SiO₂ which means only part of the quartz equivalent to the compound had reacted. Unreacted quartz evidently remains in the first melt and gradually dissolves in the liquid which changes its composition with time and becomes more acidic. When Alumina is added a new endothermic dip is observed at 890°C indicating the reaction of the nascent sod-lime-melt with alumina. Alumina remainrd inert while the soda lime silica reaction was taking place. No further reaction was observed when the glass batch was heated to 1400°C. While this is true for intimately mixed fine powder the reaction may not be as rapid and complete when coarse materials as in normal glass batch is used.

The reaction between the eutectic and double carbonate of Na₂CO₃-CaCO₃ ends at 840°C when sodium sulphate is still solid and melts near the temperature where alumina reacts. The melting of the sodium sulphate with low surface tension permeates the unconverted batch and reaction product and accelerates further dissolution of silica with the already formed melt.

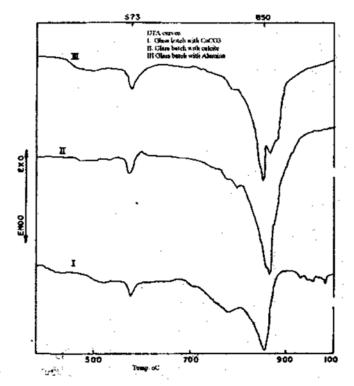


Fig. 1 Glass batch reaction with fine batch material. Glass composition in wt. % 72 SiO₂, 16.5 Na₂O₂, 11.5 CaO

- I. Na,CO, added as calcium carbonate
- II. With calcite
- III. With Alumina

Sulphate as a reaction accelerator

When sulphate is used in the batch it melts congruently at 884°C. Na₂SO₄ like NaCl is very stable and does not decompose even before 1400°C. Its boiling point when the SO₂ pressure reaches one atmosphere is 1429°C. If free silica is present as in coarse grain of batch slow reaction starts at 1100°C. Because of its low viscosity and surface tension of 194.8 dyne/Cm at 900°C and 184.7 dyne/Cm at 1100°C it spreads over the melt-unmelted material very rapidly. It allows rapid release of the CO₂ formed during the initial glass batch reaction. Na₂SO₄ dissolves in the silicate but is insoluble in higher silicate and comes out of the glass on the unmelted batch surface or as droplet or is present inside the bubbles and the following equilibrium exists

$$Na_2SO_4$$
 in Glass \leftrightarrow molten $Na_2SO_4 \leftrightarrow Na_2SO_4$ in Gas bubble (1)

At higher temperature in batches containing no reducing agent like carbon/coke, sulphate reacts only slowly at 1100°C to 1300°C according to the reaction

$$Na_{2}SO_{4} + n SiO_{2} = Na_{2}O.nSiO_{2} + SO_{2} + 1/2O_{2}$$
 (2)

When coarse grains of quartz are available the sulphate reacts up to high temperature nearing 1400°C by above reaction and gets depleted leaving little sulphate for refining action. Above 1300°C reaction with residual silica releases SO₂ and O₂ and create a convective motion as the gases pass through the sulphate gall and glass layer. The decomposed SO₂ containing bubble may travel through the batch and may pick up Na₂O and helps to build up droplets and gall layer. And the equilibrium in reaction 1 is shifted towards right. If it is a silica rich layer that the droplets meet the reaction will go towards the left. This also happens when the sulphate meets the silica scum. Sodium sulphate dissolves in the glass melt at higher temperature and at 1400°C, near its decomposition temperature, the sulphate breaks up as follows

$$Na_{2}SO_{4} = Na_{2}O (glass) + SO_{2} + 1/2 O_{2}$$
 (3)

The rapidity of this reaction depends on the water content and percentage of Na₂O in the glass. The insoluble gas bubbles rises and cleans the glass. At this temperature the glass has a low viscosity of around 20Pas. As decomposition takes place a vigorous stirring action occurs.

Whether the sulphate is added as $CaSO_4$ or $BaSO_4$ they will react with Na_2O of the glass or decomposed Na_2CO_3 by the reactions, where, ΔG° is the approximate standard free energy change of the reaction and is negative.

$$CaSO_4 + Na_2O = Na_2SO_4 + CaO \Delta G^{\circ} \sim -276KJ/mol$$
 (4)

$$BaSO_4 + Na_2O = Na_2SO_4 + BaO \Delta G^{\circ} \sim -37 \text{ KJ/mol}$$
 (5)

Addition of gypsum will form equivalent amount of Na₂SO₄ in the glass and the CaO will go into the glass. Therefore the CaO may be used as gypsum instead of salt cake

Bruckner equilibrated sodium sulphate melt over the molten glass and determined the SO₄ content at different depth in the glass and found that the sulphate had penetrated inside. Use of an indicator like Co to the surface showed that there was no colouration in the depth of glass that indicated that the sulphate layer did not move in the glass by convection as a whole. The sulphate ion and particularly the Na₂O had moved in. This movement of the species that are soluble in both layers reduces the interfacial tension and brings about a convection movement in the sulphate-glass layer. This is similar to surfactant action in detergents. A solute which can dissolve in both the phases of an immiscible two liquid combination brings about a sharp reduction of the surface tension and vigorous movement of the two surfaces relative to each other, in this case melt-solids under reaction.

The surface excess concentration relative to the bulk in the two phases is expressed as

$$C = -d\gamma/da2$$

Where C is the surface excess concentration a_2 is the activity of the solute in phase 2.

 γ is the surface tension

If the surface concentration of the solute is positive then change of surface tension with increase in the activity of the solute in the second phase is negative. There are three types of solute that changes the γ . One where the γ actually increases with increase of concentration of the solute. This is the case where the solute is strongly absorbed in one liquid. In another type of solute for example fatty acid on water the γ continuously decreases with the addition of solute. This is for example fatty acid on water where the polar end of the fatty acid is attached to the polar region of water. The third type is the sharp reduction of interfacial tension and leveling off with further addition of the solute. Examples are the sulphate salts, sodium salt of fatty acids on water.

A sulphate layer between the formed glass and the batch under reaction covers both the melt surface and the unmelted grain. The sodium side of the sulphate that is soluble in the just formed glass attaches itself to the glass and the sulphate side remains in the melt. Similarly it reacts with the residual silica the Na attaching and reacting with it. The $\mathrm{SO_4}$ part remains in the melt side and has to break up as $\mathrm{SO_2}$ and $\mathrm{O_2}$. They form bubbles

and leave the sulphate layer. The affinity of Na for both the phases sharply reduces the surface tension of both the glass-sulphate and unmelted batch - sulphate layer and brings about a vigorous movement of the glass sulphate –unmelted batch combination. This added to the release of gases brings about mixing and homogeneisation.

Hot stage microscope work reveals that when sulphate is present in the batch and the molten layer covers the unmelted particles the lime grain and the batch material virtually scoots around bringing convection in the batch. This scooting phenomenon starts when the sodium sulphate starts decomposing and the gas released escapes through the batch-sulphate layer. The gas bubbles either contain droplets of sodium sulphate or their wall is surrounded with a liquid of the salt. The presence of this liquid lubricates and helps in the movement of the bubbles towards the surface. The droplets are microscopic in size and are different from the gall present on the surface. Thus sodium sulphate brings about a homogeneistion in the batch by producing a convection current.

Optimum amount of sulphate

There is an optimum amount of sulphate which may be used. The alkali carbonates dissolve the sodium sulphate on melting and the reaction of the alkali carbonates with quartz when present alone is retarded. However the total action of sodium sulphate addition in small amount still helps in final melting and refining. There is an optimum sodium sulphate range that gives the least batch free time. If sodium sulphate in excess of the optimum amount is used the batch free time is retarded however it is still lower than the batch without sulphate. In container glass batch this amount was found to be around 7 part of sulphate per thousnad part of sand.

It may be noted that use of salt cake more than the optimum amount is still better than the batch without salt cake. In flat glass the amount of sulphate used is more than this amount.

Table II. Batch free time for addition of sulphate in a container glass batch (Ref.5)

Amonut of sulphate (Lbs/ton sand)	Batch free time (minutes)
Nil	32
7.0	28
15.0	23
30.0	18
40.0	18
50.0	28
100	28

Analysis of Gas evolution during melting

Gases evolved^{8,9} during melting of sulphate containing batch has been useful to follow the course of reaction in sulphate containing batches.

Carbon free batch. When no carbon is added along with Na₂SO₄ or there is no carbon as contamination in the batch material there is no solid-solid reaction between the sulphate and the batch material. When the sulphate melts and spreads over the batch it does not react with silica even up to 1100°C. Only when coarse silica grains are present that have not reacted with the other batch materials does the following reaction take place;

$$Na_2SO_4 + n SiO_7 = Na_2O.nSiO_7 + SO_7 + 1/2 O_7$$
 (6)

The sodium sulphate remaining may dissolve in acidic oxidizing silicate melt and decompose at temperatures of 1400°C to 1500 °C releasing fining gases like SO₂ and O₂ in the molar ration of 2:1

In an oxidizing batch i.e where no carbon or coke is added result of gas evolution is shown on fig 2. Evolution of a mixture of O_2 and SO_2 is observed at two temperatures between 1200°C and 1300°C and between 1400°C -1500°C. The reducing agents present in the raw batch probably reacts with the sulphate producing sodium sulphide. On further heating the sulphide-sulphate reaction takes place between them or with the sand releasing O_2 and SO_2 . After the initial formation and reaction of sulphide enough sulphate remains to react at higher temperature with sand or silicate melt and to decompose at 1400 °C.

Gas evolution studies up to 1300°C indicate the reaction sulphate undergoes is not with the silicate batch but with the reducing agent like carbon added to the batch or that which is present as a contaminant. At lower temperature the following reaction involving sulphate and Carbon occurs. CO_2 is released during decomposition of batch carbonates between 800-1000°C having its peak at 900°C . This volume of CO_2 is so high at this temperature that no oxygen from the atmosphere can come to the bath surface. The C reacts with the evolved CO_2 at temperatures of 700°C to 1000°C

$$CO_2 + C = 2CO \tag{7}$$

The gas analysis over sulphate containing batch does not show any SO₂ release below 850°C. After the sulphate melts at 884°C it may react with the carbon or the CO formed getting reduced by reactions

$$4C + Na_{2}SO_{4} = 4CO + Na_{2}S$$
 (8)

$$4CO + Na_{2}SO_{4} = 4CO_{2} + Na_{2}S$$
 (9)

The sodium sulphide may form an eutectic with sodium sulphate which has a melting point of 732°C or

may react with the decomposing CaCO₃ to form CaS. The sulphate -sulphide mixture is stable up to 1200°C but in the presence of sand and with the rise of temperature may help in dissolution of the sand by the sulphate -sulphide reaction in the molar ration of 3:1

$$3Na_2SO_4 + Na_2S + n SiO_2 = 4 Na_2O. nSiO_2 + 4 SO_2$$
 (10)

If large amount of carbon is available in the batch all the sulphate may be reduced to sulphide in the temperature range $740-900^{\circ}\text{C}$ and go in solution in the melting batch and may later produce amber colouration during cooling of the final melted glass. It may be noted that the reduction of sulphate may occur in stages with the initial formation of sulphite

$$2 \text{ Na}_{2}\text{SO}_{4} + C = 2\text{Na}_{2}\text{SO}_{3} + \text{CO}_{2}$$
 (11)

The course of the reactions are clearly brought about by recent studies on evolved gas analysis (EVA) during glass batch reaction. Figure 2 shows the gas evolution of a float glass batch where 0.05 wt. percent of batch of Coke and 0.5 wt. percent of SO₃ as Na₂SO₄ were added to the batch. The evolution of CO₂ by batch decomposition is followed by evolution of CO as shown by reaction (7). The release of SO₂ which peaks at around 1250°C is due to sulphate sulphide reaction (10). The reaction with cullet is similar

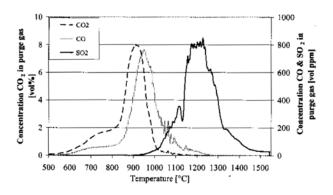


Fig. 2 Release of gases in a slightly reducing batch containing .05 wt percent of batch of Carbon and 0.5% salt cake. (Ref.8)

This low temperature SO_2 evolution is not seen when only 0.5 wt % of SO_3 is used as salt cake without any reducing agent as shown in the figure 3. The CO_2 release is at its usual place but little evolution of CO because of absence of reducing agent and the SO_2 evolution is delayed to 1450°C with small evolution at lower temperature and also the release of O_2 .

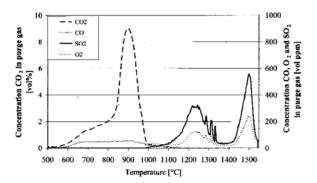


Fig 3. Gas release from batch when no reducing agent is present (ref. 8)

The role of carbon - sulphate ratio on glass melting: The C: SO, has a role to play on glass batch reaction and the time of melting. When the carbon sulphate molar ratio is zero which means only sulphate is used (Fig 3) the sulphate remains in the batch and brings about the fining at 1400°C. The melting time is given by the sum of sand dissolution time and fining time When the molar ratio is less than or equal to 1 the sand dissolution is accelerated due to bubble formation and foaming that occurs at lower temperature (1300°C). The second generation of bubbles appear at 1450°C due to decomposition of sulphate and the total melting time is the sand dissolution time added to the time required for fining by the low temperature bubble formation. If the ratio is greater than 1 sand dissolution rate is increased and foaming occurs and the heating rate may be low due to foam, The fining is also slow as little sulphate is left at the fining temperature. The melting time will be given by fining time of bubble nucleation at medium temperature.

Conclusion: In this article the effect of salt cake on the glass batch reaction has been summarized from available literature data. The surfactant action of salt cake brings about a movement due to lowering of interfacial tension. The release of SO, and O, brings further stirring in the glass batch resulting in mixing and homogeneisation. Phenomena of sulphate reaction with reducing agents, evolved gases due to the first reactions and later with nmelted batch are many and should be properly understood to use salt cake effectively in glass batch. Improper use may lead to frothing, deceleration of founding time, or formation of amber colour. Recent direct studies on gas evolution during reaction of batches containing salt cake and reducing agents have helped to understand the reactions, the temperature at which they occur and the reactions leading to batch melting.

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THE GLASS INDUSTRY IN INDIA – AN ANALYSIS

The Indian glass industry is more than hundred years old. Today, the glass industry is estimated to be more than US \$2.5 billion. The growth of the Indian economy has given a fillip to the growth of glass industry in India. India has been able to maintain stable GDP growth rate despite global downturn. Some of the factors which have contributed to such growth are:

- Huge geographic & demographic spread
- Rising middle class population
- Increasing disposable income especially in the rural–agri sector
- Increasing employment opportunities specially in Service sector
- Easier availability of finance
- Booming Infrastructure & reality sector, especially through PPP route

Glass being chemically inert and pure, and thus safer to be used, has resulted in increased popularity and demand among consumers. Some of the key properties such as transparency and recyclability make glass the most suitable medium of packaging of liquor, pharmaceutical/life saving drugs and food items. The perception of glass as having a high quality or premium image compared to plastic and metal is also facilitating its growth. Majority of raw materials required by the industry are available indigenously, providing excellent scope for growth and development.

In the recent years, the demand for float glass has outpaced real GDP growth during the last few years. This is the result of growing Indian economy, where demand is boosted by the booming automotive and construction sectors. Innovations have extended the range of uses for glass and allowed it to play a greater role in the world in which we live. In a country like India where temperatures vary from 0° centigrade to over 45° centigrade, in many cities, usage of laminated and glazed glass play an important role in conserving energy.

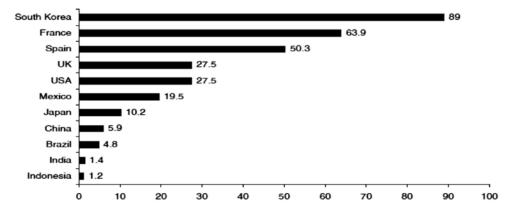
In addition to, factors like increasing demand from emerging markets of India and China, rising cosmetic sales, changing lifestyle, increasing per capita income are also driving the growth of glass industry.

Container Glass Industry

The container glass industry in India is quite old and has remained a cottage industry for a long time. In recent years, the industry has transformed and developed from rudimentary mouth blown and hand working processes to a fully automated production on a large scale. The container glass industry in India is approximately US \$0.87 billion. The installed capacity of both small and large players of the Indian glass container industry is over 7000 MT per day. There are 10 medium and large container glass manufacturers. Besides, there are several small manufacturers in the semi/unorganized sector with smaller furnaces having melting capacity of less than 500-600 MT per day. This segment of the glass industry enjoys its growing market share with its advantages of being healthy, hygienic, pure, eco-friendly and many more.

The major consumer industries for container glass are liquor, beer, pharmaceuticals, soft drinks, food and other (non-CSD beverages) segments. Export has a 10 per cent share of the total container glass industry off takes. The Alcobev segment uses more than 60 per cent of India's glass container production, followed by food at

Per Capita Glass Consumption



15 per cent, pharmaceuticals at 12 per cent, carbonated beverages segment contribute between 3-4 per cent of the total demand and rest by others.

The major growth driver for the container glass industry is the low per capita consumption of 1.4 kg in India as compared to 27.5 kg. in US and 10.2 kg. in Japan and strong economic drivers for end-user segments (liquor and beer, pharmaceuticals, food, cosmetics, etc.).

Float Glass Industry

This segment of the glass industry is still at the nascent stage with just 8 float glass lines compared to China having 196 lines. India's total installed capacity for float glass is around 4700 tons per day with worth around US \$0.75 billion. There has been an increase in demand for float glass as a result of increased investment from the construction and automotive sectors. Float glass manufacturers are gearing up to meet this demand and are planning to increase their installed capacities. It has been growing with a CAGR of 13% over the last five years. The major source of revenue comes from Architectural – 85 per cent, Automotive – 10 per cent and Others – 5 percent.

The float glass market of India has huge growth potential. It is seen that general awareness about glass as a building material is increasing. The construction and automobile sectors which are the largest users of float glass are expected to grow with a CAGR of 20% and 15% respectively. Once the legislation for the usage of right type of glass for windows etc. is legislated by the government, the usage of float glass will get a further boost. Low per capita consumption of glass of India, which is 0.88 kg only, compared with other developing countries such as China -12 kgs, Thailand 9 Kgs, Malaysia 13 kgs, Indonesia 4 kgs, is a clear indicator of huge potential for growth of this industry.

Tableware

During the last decade tableware segment of glass industry has made strong efforts to improve quality of glass tableware manufactured in India. It is heartening to note that by adoption of latest technology they are now producing international quality glass tableware including those of opal and crystal glass. However, tableware segment of the industry is facing tough competition from imports from China and other countries. Price difference at which imported glass tableware are being sold in the Indian market suggests not only dumping the goods in the Indian market but also evasion of customs duty. Urgent steps therefore need to be taken for checking this unhealthy competition. Indian industry has made concerted efforts to increase exports. During the last few

years the exports have increased many fold and presently export from India are around to Rs. 35 Crores.

Other segments

Some of the other segments in glass industry which have been growing in recent years on the basis of strong export growth are glass fibre & wool, ophthalmic glass, glass lampware, bangles, table/ kitchenware, mirrors, glass beads and false pearls.

Indian glass industry is at the early stage of maturity, but demand for glass is growing steadily. Aggressive and organized efforts on the part of manufacturers and processors are expected to achieve higher levels of awareness among glass specifies and users. In the next five years, the Indian float glass market will move to higher maturity levels. Further, constant technical innovations by manufacturers are keeping customers constantly interested in glass and glass products.

The growth of organized retail, infrastructural growth moving in tandem with the growth in the Indian economy has acted as catalyst for glass industry. It has increased the growth rate of packaging industry as well as the requirement of infrastructural materials. Glass being chemically inert, impermeable, FDA approved and environment friendly has distinct advantages over other forms of material. Also due to the constant lifestyle changes and the growing consumer consciousness about health, hygiene and eco-friendly products, glass is expected to grow at a higher rate in coming years.

The glass industry is still estimated to grow at a healthy rate largely driven by rapid Indian economic growth of 7-8% per annum, growing export potential to Europe, America and rest of the world (Increasing demand of superior packaging standards for the international market) and improved technologies being adopted by the glass manufacturing companies who are investing in innovative and state of the art technology for world class products.

Coming of Age

Glass industry is one of the oldest in the world. Glass Industry in India remained in the form of a cottage industry till the beginning of 20th century. The industry has made laudable strides moving from the traditional mouth blown process to automatic light weight container manufacturing technology and is also manufacturing of Float Glass as well as opal & crystal ware.

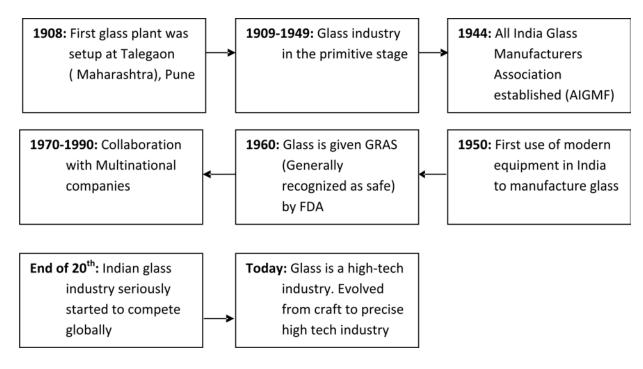
Glass industry remained in the primitive stage till 1950; glass melting took place in pot furnaces and small tank furnaces were fuelled by either coal or gas--although some furnaces at the coastal cities used furnace oil. It

was towards the end of the decade when Indian glass industry seriously started competing globally by using modern equipments for melting and production of glass. Improved furnaces were installed to conserve energy and reduce the cost of production. Easy availability of raw material further improved the cost efficiency and flat glass industry upgraded to float process. Glass found its use in various industries such as beads, glass fibre & wool, tableware, ophthalmic/optic fibre for cable. The industry is progressing steadily and will hopefully reach global standards in the weaker sectors as well as in those that are currently strong.

Today, glass is a High-Tech Industry. It has evolved from a craft to a fully high-tech industry. Modern glass plants are capable of making millions of glass containers per day (about 700 bottles per minute), which are used for products from wines and spirits, to foods and juices as also cosmetics and pharmaceuticals. Innovative glass packaging continues to give longer shelf life and valuable shelf appeal to products packed there in and is good for the earth because it is made from virtually inexhaustible

raw materials, is 100% recyclable, refillable, and reusable. Consumers choose glass to preserve the taste and purity of foods & beverages.

In the last 10 years, demand for float glass and its consumption has increased manifold because of its usage for architectural purposes. There has been a great demand for using flat glass in structural glazing and curtain walls, which has resulted in a phenomenal increase in the availability of flat glass in terms of type, composition and characteristics. Indian architecture in recent years has evolved progressively toward the use of green building materials with an increasing number of projects now applying for green building certifications. Glass usage has thus increased as per the requirements of green buildings. Furthermore, developers have become more demanding in terms of glass performance and processing quality. This has led to an increase in the use of highperformance glass in contrast to the ordinary reflective glass that formerly dominated the landscape in India. Thus the emphasis on proper processing infrastructure to process such glass has assumed greater significance.



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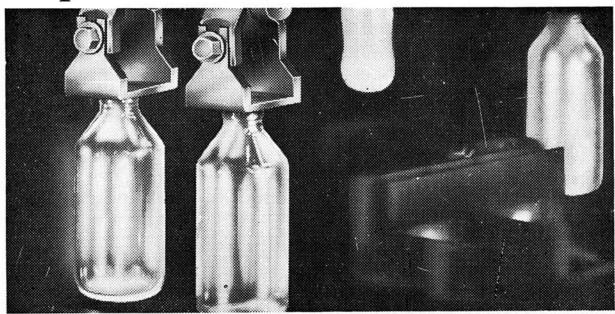
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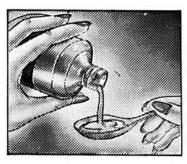
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GLASSPEXINDIA 2011 Exhibition & Conference

The All India Glass Manufacturers' Federation has been endeavoring to keep the members updated about technological advancements in glass industry, in different parts of the globe. With this in view the federation has been organizing International Exhibitions and Conferences since 1995. In continuation of the same AIGMF is now sponsoring GLASSPEXINDIA 2011 – International Exhibition and Conference. The Exhibition is being organized by **Messe Dusseldorf GmbH, Germany**, at Bombay Exhibition Centre, Mumbai from 12-14 January, 2011. Concurrent with GLASSPEXINDIA 2011 exhibition an international conference is being organized by the AIGMF on January 12-13, 2011. In order to give time to delegates to visit stalls in the exhibition conference timings are being kept from 2:30 pm to 5:00 pm on both days.

Theme of the conference has been selected as 'Managing Sustainable Growth'

Latest technological developments will be on show in the exhibition and a wide range of papers pertaining to various aspects of the theme will be presented in the International Conference. We hope that delegates will enrich their knowledge by participating in the conference and seeking clarifications during question answer time.

Details regarding papers to be read at the Conference along with dates and timings will be circulated separately. Registration of delegates has commenced. The fee structure is as under:

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Delegates to the conference will be given:

- (i) Conference Kit which will include a complimentary copy of the special issue of KANCH containing papers to be presented at the Conference. Kindly note that supply of kits to delegates, registering after 10th, December, 2010 will depend on availability.
- (ii) Complimentary lunch on days of the conference viz., January 12-13, 2011
- (iii) Cultural evening and Cocktail/Dinner on 14th January, 2011. Delegates are welcome to bring their spouse/guests for Cocktails/Dinner (subject to a maximum of two) at an additional charge of Rs.1000.00 per person (Indian delegates) and USD 50.00 per person (foreign delegates).

Those interested in attending the Conference are requested to complete the enclosed Registration Form and send it along with Cheque/Demand Draft for the appropriate amount payable to "The All India Glass Manufacturers' Federation" at New Delhi. For payments in US Dollars, the Cheque/Demand Draft may please be made in the name of "The All India Glass Manufacturers' Federation" payable at New York. The amount can also be remitted through Bank of Baroda, New York, SWIFT BIC BARBUSS 33, FEDWIRE/ROUTING NUMBER 026 005 322, giving full particulars of recipients as given below:

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With regards and best wishes,

Yours sincerely,

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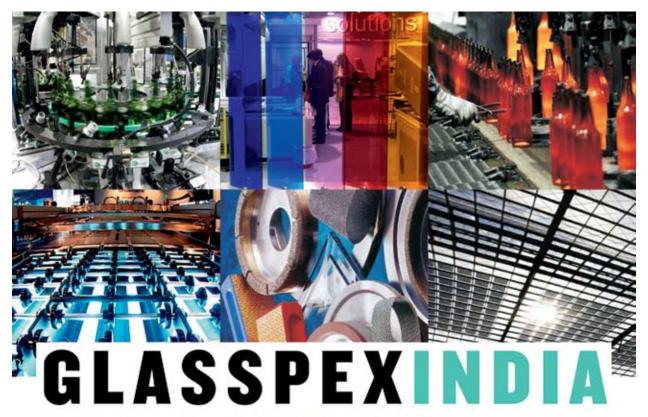
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 - > Hot Water generation for process heating

Superior Features:

- Ensures an unaffected operating pressure of the furnace
- Engineered to prevent Cold End Corrosion.
- Online installation of the WHR system
- Depreciation upto 80% can be claimed within first year
- □ Payback period 2 yrs. to 5 yrs.
- □ Earns Carbon Credits.

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