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Removing bubbles from molten glasses: A Critical Review

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Abstract*— during the melting process of batch materials, different types of gases from diverse sources are released, resulting in a huge amount of bubbles and gaseous inclusions in the glass melt. These bubbles have undesirable effects on the optical quality and mechanical properties of final products. Therefore, it is necessary to remove bubbles from the melt. This process is called refining. Behavior of bubbles inside the molten glass depends on factors including diameter, composition and position of bubbles which are functions of temperature. Bubbles can be eliminated from glass melts either by physically rising to the surface or by chemical dissolution of the gaseous species into the surrounding melt. Chemical agents are used to improve the fining process, but most of these common chemical agents are harmful. Although there are some alternative physical refining methods which can be used instead; in practice, bubbles can be eliminated by using combination of two methods simultaneously. In this study, the different methods of glass refining are reviewed.

Keywords: Bubbles, Chemical agent, molten glass, refining.

I. INTRODUCTION

During The investigation on glass industry in terms of raw materials and process optimization offers interesting perspective and understanding of how this industry has been progressively developed [1]. According to Figure 1, glass industry is being used for different functionalities in various environments, from mass production like glazing and containers to nanotechnology processing including hard disk drives, solar glass, amorphous semiconductors, optical fibers, coatings, cutting tools and displays. That is why different studies show that development and production of glass involve significant and interdisciplinary knowledge and expertise [2-15].

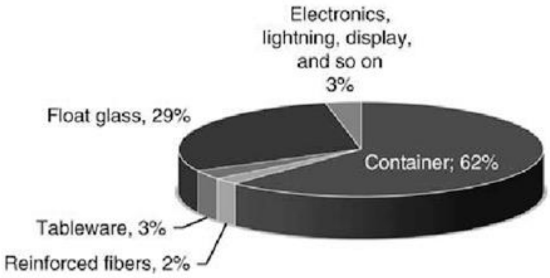

Figure 1: Market shares of major glass applications [1]

Glasses have lots of applications in dairy life and present several benefits as an industrial material [1-13] such as:

- Ability to recycle;
- Chemical inertness;
- Non-polluting nature on ultimate disposal;
- Ability to be manufactured from abundant raw materials;
- UV filtration (amber and green glass), optical and transparency qualities;
- Low gas permeability and
- High intrinsic strength.

More than 90 percent of glass industry products are sold to other industries such as building industry, car manufacturing and the food and beverage industry [12]. The most important principles behind industrial glass manufacture are as follows:

- Meltability;
- Workability;
- Refining and
- Economics.

The terms fining and refining refer to the removal of gaseous inclusions or bubbles, from the molten glass. Although the presence of bubbles in a glass sample is not necessarily detrimental for many scientific studies, bubbles are definitely undesirable in most commercial glasses. Bubbles in commercial products are almost always considered flaws and can create severe problems in practice [16-18]. Figures 2 and 3 show the trapped bubbles in the glass melt and a container, respectively[19].

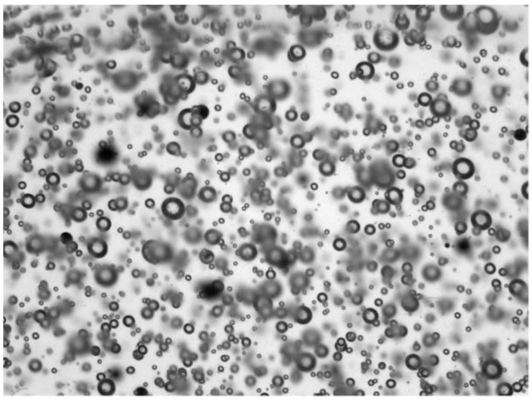

Figure 2: Glass just after batch melting [14]

Figure 3: Bubbles in the glass [19]

Bubbles can be completely removed from glass melt by chemical and physical methods. Physical methods including Buoyancy effect, ultrasonic and sound waves, applying a centrifugal force in the molten glass and employment an appropriate heat treatment procedure. Chemical methods contain dissolution of the gaseous species into the melt by using chemical refining agents (figure 3). In this study, the chemical and physical methods of refining molten glasses are reviewed.

II. PREVIOUS WORK

Ruud G. C. Beerkens [20] investigated on gas release during melting and refining stages. He proposed a method for gas evolution based on thermodynamic equilibrium condition, different significant parameters in practice, calculations and modeling. Ruud G. C. Beerkens [21] also showed several new innovative ideas related to the industrial glass melting. He analyzed effective parameters in melting process of glasses by using precise experimental data. Masataka Kawaguchi et al. [22] presented different solutions in order to improve refining process among preparation of uniformly mixed fine batch and acceleration of refining. In addition, he claimed helium atmosphere can reduce seeds in molten glasses. Kuji Fujita et al. [23] studied effects of refining agents and UV transmitting property of soda lime glass. They added a small amount of iron oxide in specific condition in order to improve the characteristics. Figure 4 illustrates comparison of the amount of bubbles in a glass sample by change in the percentage of Sb_2O_3 as a refining agent.

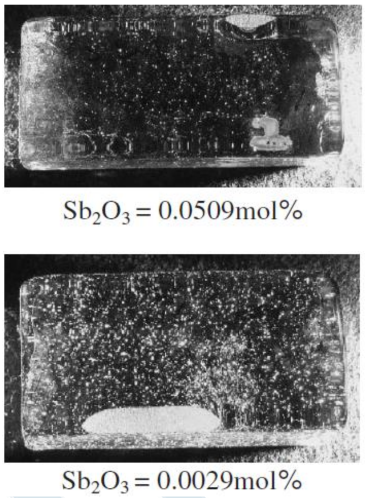

Figure 4: Photograph of bubbles in as-cast glass sample, their thickness are 20 mm [23]

Andrea Weiss Bookbinder et al. [24] illustrated new method for refining oxide glass by controlling the hydrogen permeation blistering within the vessel. Megan Aurora De Lamielleure et al. [25] proved a method of reducing gaseous inclusion in glass melting process in a patent. They designed an efficient heat treatment cycle in the correct condition for use in industrial glasses.

Jaehun Chun et al. [26] studied on melter feed viscosity during heating and correlated bubbles with the volume fractions of dissolving quartz particles and the gas phase. Also, they investigated the approaches to homogenize and equilibrate the glass melt. A group of researchers [27] demonstrates effect of additional carbon dioxide on bursting the bubble as an inclusion in molten glass. Michael Cable [28] investigated on refining of a soda-lime-silica glass with and without chemical agents. He designed a furnace based on new condition and distinct convection currents. In addition, he decreased the number of seeds at the beginning of refining process by using chemical agents and raising the temperature. Moreover, he presented two mechanisms for refining [29] as for theoretical expression and numerical calculations. Junjie Luo et al. [30] presented a series of studies to relate the periodicity of bubble formation to part scan speed, laser power and filament feed rate. Their experiments suggested that forming of bubbles has direct relation with laser power. According to Figure 5, bubbles have three different types in a glass sample as a substrate.

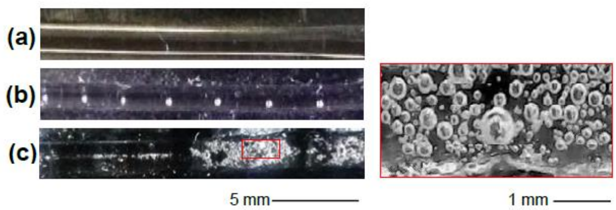

Figure 5: Dark field images of three types of bubbles (a) sporadic bubbles, (b) periodic bubble pattern, and (c) foam layers [30]

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III. PHYSICAL METHODS

- Removal of bubbles by Buoyancy effects

The principle of Buoyancy effect is based on Stoke's Law, which has relation to the velocity, V_s, of a solid sphere in a liquid with different density:

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

Where g is the gravitational acceleration, $\Delta\rho$ is the difference in density between the sphere and the liquid, r is the radius of the sphere, and η is the viscosity of the liquid. For special cases, it has been shown that:

$$V_b = \frac{3V_s}{2}$$

Where V_b is the rate of rise of the bubbles.

These two equations show that the rate of ascent of a bubble is inversely proportional to the viscosity of a melt and directly proportional to the density of the melt. In addition, these equations predict that the rate of removal of bubbles will be proportional to the square of the bubble radius. For instance, very fine seed cannot be impressively eliminated from a molten glass with low fluidity by simple bubble rise in the absence of any other processes. There are some solutions in order to solve this problem including upward fluid motion that can be obtained by mechanical stirring, design of a glass tank floor to produce upward currents, localized heating to produce a locally hotter and thus less dense region in the melt and finally bubbling with a gas introduced near the bottom of the melt.

However these predictions are generally dominant, there are some exceptions that these equations do not entirely predict the results of all experimental studies since the chemistry of molten glass can change this simple relationship.

Bubble radius plays a paramount role in velocity of the rate of ascent of a bubble that is function of surface tension. Both macroscopic and microscopic factors affecting the improvement of the surface tension include chemical composition of the melt, inclusions, thickness and pressure difference between the inside and outside of the bubble [16, 39].

- Removal of bubbles by ultrasonic and sound waves

Radiation of ultrasonic waves in the molten glass have a degassing effect. Of course the result of ultrasonic and sound waves on gaseous inclusion in a liquid is very complicated. Furthermore, in practice, installation of these types of devices in the refining process of an industrial tank will be very arduous [13]. For this reason, an alternative solution will be used to overcome this limitation. This process does not require addition of chemical agents or catalysts and therefore does not generate undesirable streams. In addition, this process does not have negative effect on environmental. In this method, O_2 and H_2 bubbles meet each other in molten glass and create reaction with shock waves that has a same effect as ultrasonic wave technique (figure 6) [40, 43].

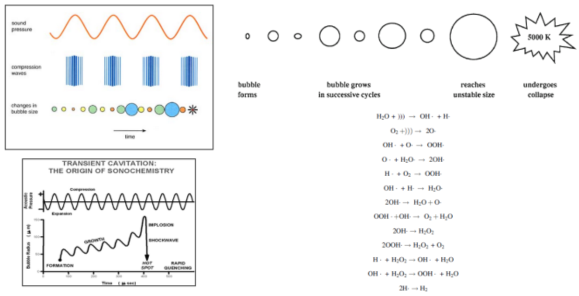

Figure 6. Bursting the bubbles through reaction O_2 with H_2 [42, 43]

- Employment an appropriate heat treatment procedure and optimum design

Preparing an approach to decrease gaseous inclusions and bubbles in a molten glass is very important. This method can include some steps, such as: (a) increasing the temperature of batch material to melting temperature T_M within a melting vessel in order to form molten glass which contains a multivalent oxide material; (b) decreasing the temperature of molten glass within a refractory tube to a cooling temperature T_C, to maintain the molten glass for a predetermined resident time; and (c) increasing the temperature of cooled molten glass within a refining vessel to a refining temperature T_R $>T_M$.

On the other hand, the content of bubbles in the melt is therefore decreased by melting under reduced pressure, exposing the melt to the pressure of an inert gas, etc [24, 33].

Furthermore, refining process may be improved by applying an additional force like a centrifugal force on bubble in the molten glass in a rotating discontinuous cylinder [44].

IV. CHEMICAL METHODS

- Removal of bubbles through common refining agents

Chemical refining agents added to molten glass can release large quantities of gases, which form large bubbles and gaseous inclusion through rising up to the surface of the melt. These large bubbles trend to carry smaller bubbles and seeds to the surface as well. In addition, some of these agents cause the absorption of oxygen atoms from the bubbles at lower temperatures, thus reducing the size of seed due to diffusion from the bubble into the melt. The seed eventually shrinks to below the critical radius, where the surface energy causes the complete disappearance of the bubble. Different agents exist due to the fact that the temperature should fit between the decay of the agents and a sufficient low viscosity of the melt. Therefore for melt with different composition, several types of agents do exist; whiles the fitting is not always optimal. Thus, for some melts a mixture of agents or additional agents could be a solution for improving the process.

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Arsenic and antimony oxides are known as the most efficient chemical refining agents, chiefly when they combined with alkali nitrates in the batch. These oxides are usually added to the batch in 0.1 to 1 wt% quantities. The refining action of arsenic and antimony oxides results from a series of chemical reactions which occurs at different stages of the melting process. During batch melting, these oxides react with nitrates to release nitrogen oxides and O_2, as, for example, in the reaction:

$$4KNO_3 + 2As_2O_3 \rightarrow 2K_2O + 2As_2O_5 + 4NO\uparrow + O_2\uparrow$$

These chemical reactions release abundant quantities of NO and O_2 gases, which form large bubbles and rapidly rise up to the surface of glass molten. When batch decomposition is completed, melts are usually heat up to higher temperatures and soaked until completely refined. As the dissolved oxygen is consumed, oxygen from nearby bubbles will diffuse into the melt. Therefore, the process leads to reducing their internal pressure and hence reducing their diameter of bubbles. Accelerated diffusion from the bubble into the melt will increase by high internal pressure, until the bubble is completely diminished. Surface energy of bubbles plays a paramount role in the recent case. The rate of ascent of bubbles increased along increasing in partial pressure difference between the inside and outside of the bubble. However, from an environmental point of view, it would be desirable to provide alternative methods for refining process without having to employ arsenic as a refining agent.

Also sodium sulfate uses as a source of considerable gas during batch decomposition, as well as supplying a portion of the sodium for soda-lime-silicate melts. Sulfate refining is strongly affected by the reactions with furnace gases or other sources of carbon. Nitrates can also act as a refining agent even in the absence of arsenic or antimony oxides. Decomposition of nitrates releases large quantities of nitrogen and oxygen gases. In addition, halides are the most useful refining agents through their efficiency in lowering the viscosity of molten glass. Oxides of a few multivalent cations can be used as chemical refining agents by acting as sources of O_2, in a manner similar to arsenic and antimony oxides. Cerium oxide is a good example for multivalent cations:

$$4CeO_2 \rightarrow 2Ce_2O_3 + O_2\uparrow$$

SnO_2, MnO_2, Fe_2O_3, Pb_3O_4, etc., are known as other oxides of multivalent cations which can also act as minor refining agents via similar reactions. Some of these oxides are added for reasons other than their refining action [16, 34, 37, 38, 39].

- Application of Helium gas to facilitate the refining process

As mentioned before, some of refining agents have undesirable effects on environment. Helium molecules can dissolve in the interstices of a molten glass, physically. Helium has the smallest molecule size among all gases so it is able to diffuse throughout the molten glass faster than other inert gases. Consequently, dissolved helium molecules in the molten glass rapidly penetrate into seeds to enlarge them without any destructive effect on environment. In addition, since the diffused helium in the fine bubbles decreases the partial pressures of pre-existing gases in them, more refining gases such as oxygen and sulfur dioxide can be extracted from the molten glass. As a conclusion, melting process under helium atmosphere inside the furnace can contribute to refining [22]. Figure 7, shows the comparison of a glass samples which fabricated in helium and air atmospheres.

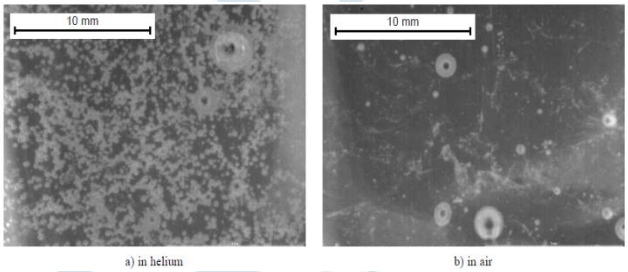

Figure 7: Seeds in Molten glass [22]

V. CONCLUSION

Using both chemical and physical methods together can improve the quality of production, kinetics of melting process and refining of glass melting in the industrial glasses. Assessment of chemical composition, refining agents and especially their level of addition is one of the most difficult stages in glass melt design, because there are few significant calculation rules. It is recommended that appropriate amount of refining agents and applying physical method has been developed through laboratory trials [16, 18]. Since, there are many variations on removing gaseous inclusions and refining process, it can be noted that, in practice, several methods whether physically or chemically, are simultaneously used to reduce this dilemma. This is why in glass industry, the procedures carried out experiments based on trial and error to achieve the optimum results. After finding the most appropriate solution, by using the modeling techniques [45] based on the best results of laboratory tests, the procedure is optimized. Herein after, the optimized procedure is implemented for industrialization.

REFERENCES

[1] Le Bourhis E (2008) Glass: mechanics and technology. John Wiley & Sons.

[2] Dorfeld WG, Lineman DM, inventors; Corning Incorporated, assignee (1998) Method of reducing bubbles at the vessel/glass interface in a glass manufacturing system. United States patent US 5,785,726.

[3] Wallenberger F, Bingham P (2010) Fiberglass and Glass Technology: energy-friendly compositions and applications.

[4] Moraes, Samira NS, Daniella L. Morgado, and Marcelo Nalin (2019) Application of Raman spectroscopy to industrial research: Determination of impurities in glass bottles.Vibrational Spectroscopy 100: 57-63.
[5] Schweizer T. Properties (1998) processing and applications of glass and rare-earth doped glasses for optical fibers. EMIS Data Review, Series.22:320.
[6] Fanderlik I, editor. (2013) Silica glass and its application. Elsevier.
[7] Luo, Junjie, et al. (2016) Bubble formation in additive manufacturing of glass." Advanced Optics for Defense Applications: UV through LWIR. International Society for Optics and Photonics, Vol. 9822.
[8] Uusitalo O. (2014) Float glass innovation in the flat glass industry. Springer.
[9] Hubert, Mathieu. (2019) Industrial glass processing and fabrication. Springer Handbook of Glass. Springer, Cham, 1195-1231.
[10] Persson R. (1969) Flat glass technology. London: Butterworths.
[11] Ma, Qianli, et al. (2019) A novel method for accelerating bubble rising in highly viscous molten quartz." International Journal of Heat and Mass Transfer 138:1359-1367.
[12] Wintour N. (2015) The glass industry: recent trends and changes in working conditions and employment relations. International Labour Organization.
[13] A Collection of Papers Presented at the 75th Conference on Glass Problems Greater Columbus Convention Center Columbus (2014), Ohio November 3–6,
[14] Clark, Terence J. Process and Apparatus for Refining Molten Glass. U.S. Patent Application No. 16/807,884.
[15] Hujova, Miroslava, and Miroslava Vernerova. (2017) Influence of fining agents on glass melting: A review, Part 1." Ceram.-Silik 61: 119-126.
[16] Cable M. (2005) Classical glass technology. Materials science and technology.
[17] Pleše, P., et al. (2019) Nucleation and growth of bubbles on plagioclase crystals during experimental decompression degassing of andesitic melts. Journal of Volcanology and Geothermal Research 388 106-179.
[18] Ding J, Hade AJ, Hess DR, inventors. (2008) Method for homogenizing a glass melt. United States patent application US 12/277,676.
[19] Hujova, Miroslava, and Miroslava Vernerova. (2017) Influence of Fining Agents on Glass Melting: A Review, Part 2. Ceramics–Silikáty 61.3: 202-208.
[20] Beerkens RG, Schaaf J. Gas. (2006) release and foam formation during melting and fining of glass. Journal of the American Ceramic Society. 89(1):24-35.
[21] Beerkens R. (2008) Analysis of elementary process steps in industrial glass melting tanks–some ideas on innovations in industrial glass melting. Ceramics–Silikaty.52(4):206-17.
[22] Kawaguchi M, Kato T, Imamura Y, Yoshida N, Aoki S. (2008) Challenge to improve glass melting and fining process. Ceram. Silikáty.;52(4):217-4.
[23] Fujita K, Takahara Y, Chikaura Y. (2008) Influence of refining agent in soda lime glass for ultraviolet ray transmittance. Materials transactions. 49(2):372-5.