CHALLENGE TO IMPROVE GLASS MELTING AND FINING PROCESS

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In this paper, two fundamental factors, such as preparation of uniformly mixed fine batch and acceleration of fining, are addressed and will be discussed. The glass melting furnace can be considered as a physically and chemically mixing reactor at an elevated temperature, typically higher than 1500°C. To enable glass manufacturing process at lower temperatures, a better preparation of glass batch close to a physically uniform condition is required. Therefore, it has been investigated whether a glass forming raw material batch pulverized with a ball mill could improve the melting behavior. Analysis of the gases released during the batch reactions and evaluation of the residual silica with XRD analysis have shown that the pulverization facilitates the batch reaction and lowers the vitrifying or fusion reaction temperature. These results suggest that the pulverization of batch could improve the melting and fining behavior and decrease the melting temperature. The application of helium gas may enhance the fining process during a glass melting process. The fining effect by diffusion of helium through the surface of the glass melt into this glass melt by application of a helium atmosphere has been investigated both by a laboratory experiment and in a pilot scale test. These results have indicated that helium dissolution in glass melt is very effective to eliminate seeds. However, this diffusion method of helium entering through the glass melt surface from a helium atmosphere is considered only suitable to a small scale production in which the glass melts can be in direct contact with the helium atmosphere for a long time. To increase helium dissolution into glass melt, helium bubbling in glass melt is considered effective as a pre-conditioning step, especially in tank furnaces with large throughputs. A laboratory experiment on helium bubbling through the molten glass has indicated that this helium bubbling in the glass melt has both merit and demerit. The merit is that a large amount of helium could be dissolved in the glass melt, resulting in expansion of seeds. The demerit is that a lot of new blisters could be introduced into the melts and a certain amount of fining gas could be lost from the glass melt by the helium stripping effect. Therefore, a optimum design of the bubbling process by helium gas should be developed.

INTRODUCTION

Glass melting processes consume large amounts of fuel oils and fuel gases, resulting in combustion gas emissions that contribute to the greenhouse effect on the global climate. Therefore, the development of an environmentally benign glass melting technology is desired. An investigation of important performance factors for glass melting has been carried out by our laboratories. In this report, two fundamental factors for improving melting performance are addressed, such as the preparation of uniformly-mixed fine raw material batch and the acceleration of glass melt fining, using helium gas.

APPLICATION OF UNIFORMLY-MIXED FINE BATCH TO FACILITATE THE MELTING PROCESS

Most of the energy in the whole glass manufacturing process is consumed in the melting and fining processes taking place in glass furnaces. Therefore, melting efficiency improvement in these furnaces could be an excellent solution to reduce energy consumption. In advance of glass melting, glass forming raw material batch can be prepared in an appropriate way to improve its melting efficiency. A uniformly-mixed finer batch is considered to provide a larger contact area of the constituent raw materials which facilitates batch reaction. The effect of the uniformly-mixed fine batch on the melting process will be described in the following [1].

A uniformly-mixed fine batch is prepared by mixing the complete batch without cullet and applying ball milling. An example of alumino-borosilicate glass forming raw material batch milling is shown in Table 1. The average particle size after the mixing with ball milling for five hours was 30 μm while that after the standard mixing for 0.5 hours was 100 μm. The CO_2 emission during heating the complete batch of the uniformly-mixed fine batch and the standard batch was measured by evolved gas analysis under atmospheric pressure, using a prescribed heating schedule. The results are shown in Figure 1. The CO_2 emission starts from 450°C and a small peak is observed at 480°C in

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the reaction of the uniformly-mixed fine batch, while the CO_2 emission starts from 570°C in the standard batch. This result indicates that the uniformly-mixed fine batch starts the batch reaction at a lower temperature than the standard batch. Above 600°C, for the uniformly-mixed fine batch, more CO_2 is emitted, the peak of CO_2 emission rate is higher, and CO_2 emission ends at a temperature 100°C lower than for standard batch. So, in the comparison for alumino-borosilicate glass melting starting from raw material batches, CO_2 emissions during heating of the batch indicate that uniformly-mixed fine batches can make the batch reactions take place more rapidly at lower temperature.

Secondly, the dissolution characteristic of difficult to solve materials, such as silica sand was observed. Another alumino-borosilicate glass forming raw material batch or corresponding uniformly-mixed fine batch in a long platinum boat was melted in an electric tube furnace applying a temperature gradient in the furnace and boat. After three hours, the boat was taken out from the furnace and annealed. Figure 2 shows the images of the top surface of the glass samples. The white part in the images corresponds to residual silica grains or seeds. Clearly, fewer silica grains and fewer seeds were observed using the uniformly-mixed fine batch than for the case of the standard batch. Also the results of XRD analysis demonstrated there were fewer silica grains, using the uniformly-mixed fine batch.

In addition, the effect of the uniformly-mixed fine batch on the glass homogeneity was investigated as follows. The standard alumino-borosilicate glass forming batch or corresponding uniformly-mixed fine batch in a platinum crucible was melted in an electric furnace at the temperature, which was 200°C higher than the reference temperature as shown in Figure 2. After 30 minutes the glass was taken out and annealed. Figure 3 shows the images of the prepared cross sections of the glass samples. Clearly, weaker cords and fewer seeds were observed using the uniformly-mixed fine batch than the standard batch.

The results described above indicate that the uniformly-mixed fine batches can facilitate and enhance timely batch reactions, effectively dissolve silica grains and efficiently homogenize the molten glasses. In other words, the uniformly-mixed fine batch can be an effective measure to achieve a high melting efficiency.

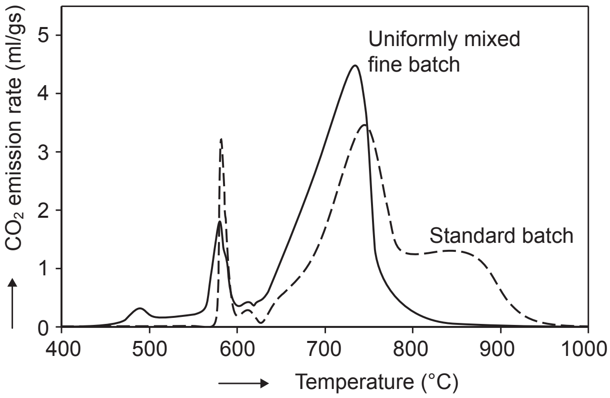


Figure 1. CO_2 emission during batch reaction.

Table 1. Preparation of a uniformly-mixed fine batch.

Glass system	SiO_2-Al_2O_3-B_2O_3-$(R_2+R)O$	
Mixing	Mixing with ball milling	Standard mixing (without ball milling)
Mixing time	5 hours	0.5 hours
Average particle size	30 µm	100 µm

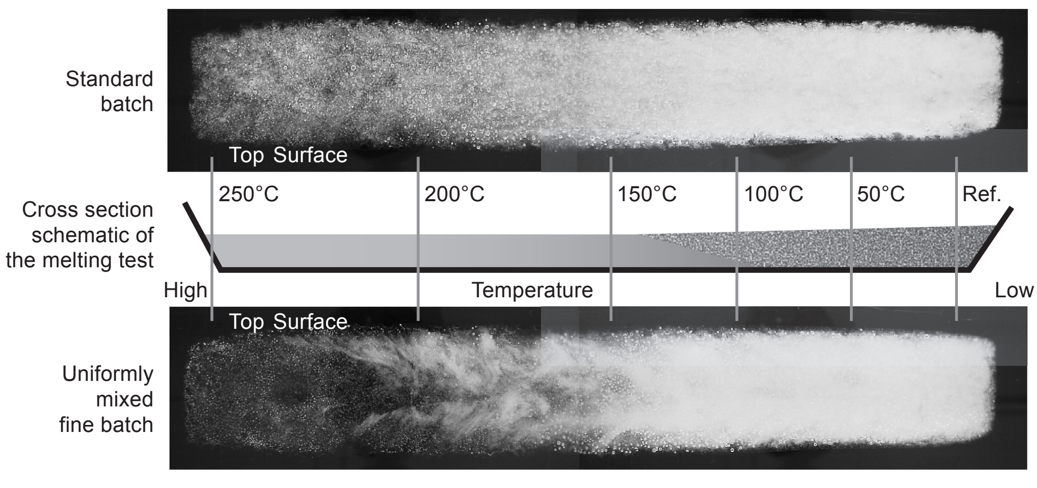
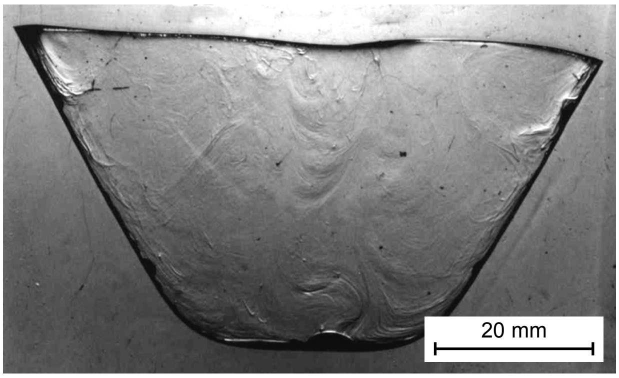
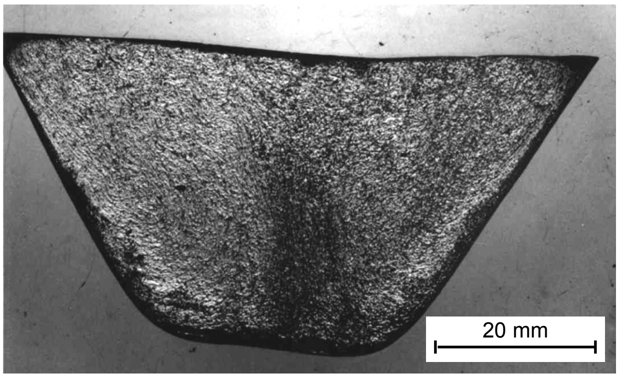


Figure 2. Glass samples melted in an electric furnace having a temperature gradient.



a) Glass made from uniformly-mixed fine batch



b) Glass made from standard batch

Figure 3. Comparison of glass homogeneity influenced from batch preparation.

APPLICATION OF HELIUM GAS TO FACILITATE THE FINING PROCESS

Effect of helium

Helium gas may enhance the removal of gas bubbles and seeds from the molten glass during a glass melting process. This fact was discovered more than thirty years ago [2]. Recently, the fining effect of helium gas has been reported on again [3,4]. Helium physically dissolve in the structural interstices of a molten glass. Helium has the smallest molecule size of all gases and is able to diffuse throughout the molten glass faster than other inert gases, which also physically dissolve in molten glass as shown in Figure 4 [5,6]. Consequently, dissolved helium in the molten glass quickly diffuses into seeds to enlarge them. In addition, as the diffused helium in the seeds reduces the partial pressures of pre-existing gases in the seed, to get an imbalance of partial pressures between the molten glass and the seed. Then, more fining gases such as oxygen and sulfur dioxide can be extracted from the molten glass. As a result, growth rates of the seeds in the molten glass containing helium will increase, and fining comdition of the molten glass is improved. Since the mass transfer between the melt and the seeds depends on the concentration levels and concentration gradients of gases in the molten glass surrounding the bubbles, we thought that as much helium as possible should be dissolved in the melt to supply a large flux of helium to the seeds during their early development.

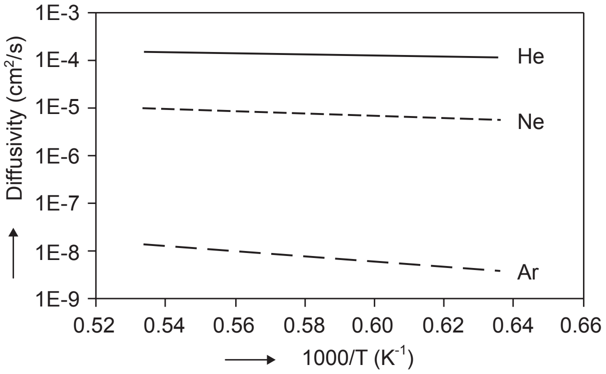


Figure 4. Difussion coefficient of noble gases, helium in an alkali-free glass, neon and argon in vitreous silica.

Helium atmosphere

The following experiment was carried out to confirm the fining effect in molten glasses by helium. An alumino-borosilicate glass was melted from a batch under several kinds of test condition applying different fining agents in an electric furnace at 1550°C. In some tests, the atmosphere inside of the electric furnace was changed to helium after melting of glass for two hours. After a period of melting procedure for six hours, the molten glass was taken out from the electric furnace and was cast in a graphite mold and annealed. Then, the number of seeds in the obtained glass samples was counted. The result is shown in Table 2. Clearly, the number of seeds in the glass samples decreased in case of a helium atmosphere. The result has been reported also previously [6].

In another investigation, the expansion of the seeds in a helium atmosphere was visually observed. E-glass cullets were melted at elevated temperature in a transparent vitreous silica crucible in helium and air atmosphere. The cullet melting process was observed with a CCD camera and the chaptered images were processed with an image analyzing software. Figure 5 shows some of the obtained images of the molten E-glass at 1350°C. The in-situ observation reveals that the seeds certainly grow larger in a helium atmosphere at this temperature. The effect of a helium atmosphere was also investigated in a pilot scale test. An alumino-borosilicate glass was continuously melted in a platinum pot having a volume of 5000 cm[3] and a controllable atmosphere. Cullet was continuously filled in from a top opening of the pot, and the molten glass was drawn out through a nozzle at a bottom of the pot at the rate of 1 kg/h. The number of seeds was counted and the helium contents were measured by evolved gas analysis in the drawn glasses. The helium concentration was calculated as the measured helium content divided by the helium solubility of the alumino-borosilicate glass at an atmospheric pressure at the melting temperature. The change of the number of seeds, the helium concentration and the melting temperatures are shown in Figure 6. When the atmosphere was changed to helium, the number of seeds decreased rapidly. Finally, no seed was found at a certain temperature when the helium concentration in the melt was about 30% of the saturation value. Although the atmospheric change back to air increased the number of seeds abruptly, elevation of temperature of 30°C reduced the number of seeds again. The pilot scale test condition results indicate that the fining effect of 30% of the helium saturation can be estimated to correspond with the fining temperature decrease by 30°C.

As shown in this section, the use of a helium atmosphere is a very effective measure to decrease seeds in molten glasses. However, this method is thought to be limited to the very small production quantities (relatively shallow glass melt depths) in which the molten glasses can be in contact with the helium atmosphere for a long time. In other words, the key to the successful application of helium to fining glass is to design the glass-making process in such a way that the molten glass is in contact with the helium atmosphere as long and effectively as possible.

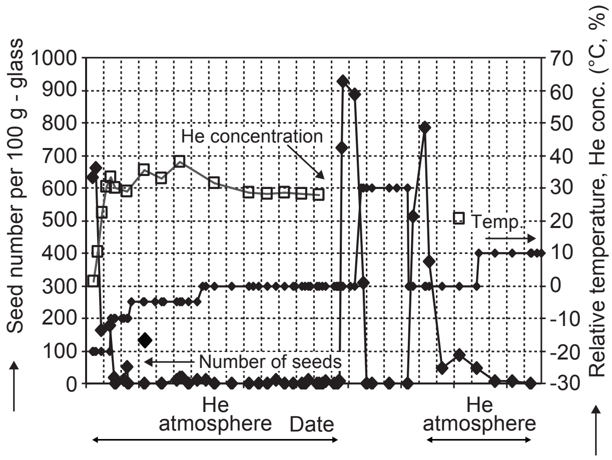
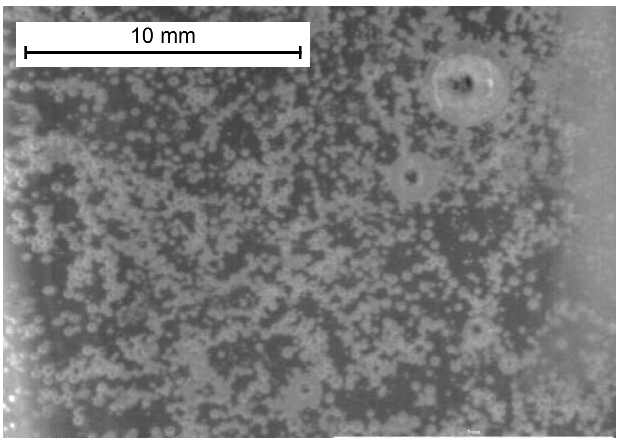


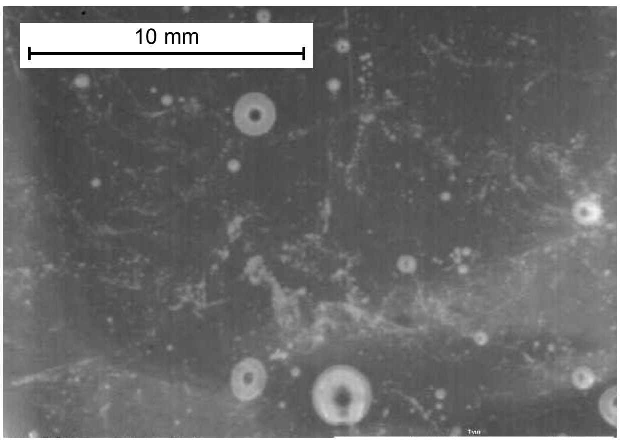
Figure 6. Change of number of seeds and helium concentration in the drawn glass, and melting temperature, in the pilot scale test.

Table 2. Number of seeds in the glass melted in helium and air.

Fining agent added to the batch (wt%)				Atmosphere	Number of seed (pieces/100g-glass)
SnO_2	As_2O_3	SO_3	Cl (as $BaCl_2$)		
1.0	0	0	0	Helium	10
0	1.0	0	0	Helium	10
0	0	0.4	1.0	Helium	160
1.0	0	0	0	Air	460
0	1.0	0	0	Air	1590
0	0	0.4	1.0	Air	2630



a) in helium



b) in air

Figure 5. Seeds in molten E-glass at 1350°C.

Helium bubbling

Rongen et. al. [6] have shown that the pre-conditioning of a molten glass by helium gas may enhance the fining process. To increase helium dissolution into a molten glass, helium bubbling in the molten glass is considered effective [7] as a pre-conditioning step, especially in tank furnaces with large throughputs. Figure 7 shows the helium content in the glass after helium bubbling in 1500 g of a molten E-glass at 1300°C [8]. The dissolved helium content increased with increased bubbling period and reached to 80% of the saturation level at that temperature using a bubbling rate of 30 ml/minute for two hours. In this condition, the average diameter of the helium bubbles was 2 cm. This result indicates that the bubbling could be an effective method to dissolve helium into molten glasses. Sufficient helium can be effectively dissolved into the molten glass if the bubbling conditions are optimized, for example the number of bubbling nozzles, the helium flow rate, bubble sizes and the bubbling temperature. Optimum condition variables would depend on the glass composition and the throughputs.

However, it should be noted that there are two disadvantages to helium bubbling. One is that bubbling might introduce new undesirable blisters into molten glasses. Figure 8 shows the number of blisters and the average blister's size in an alumino-borosilicate molten glass after bubbling for two hours with a gas flow rate of 50 ml/min at 1550°C. Clearly, the number of blisters increased with the bubbling. However, this phenomenon is independent of the kind of bubbling gas used. Accordingly, control of the bubbling conditions is very important in order to avoid the generation of new undesirable blisters. Concerning figure 8, it should be noticed that the average blister size is larger with helium bubbling than with nitrogen bubbling. It is believed that other dissolved gases in the melt have been pulled out from the melt into the introduced blisters and gives additional bubble growth due to a helium effect, which is so-called "stripping effect". The stripping effect is essentially the helium fining effect itself. However, the stripping effect could be a disadvantage during bubbling, because fining gases, such as oxygen and sulfur dioxide, may be released in an early stage by helium bubbling before the main fining process takes place. As a result, evolution of these fining gases might prove to be insufficient during the subsequent fining process of a molten glass.

Figure 9 shows the ratio of Sn^{2+} ions to the total Sn in an alumino-borosilicate glass containing SnO_2 and melted with or without helium bubbling. Obviously, the Sn^{2+} ratio was increased by helium bubbling. The Sn^{2+} increase means that extra oxygen gas was lost due to the reaction, "$SnO_2 \rightarrow SnO + 1/2O_2$". However, it is thought

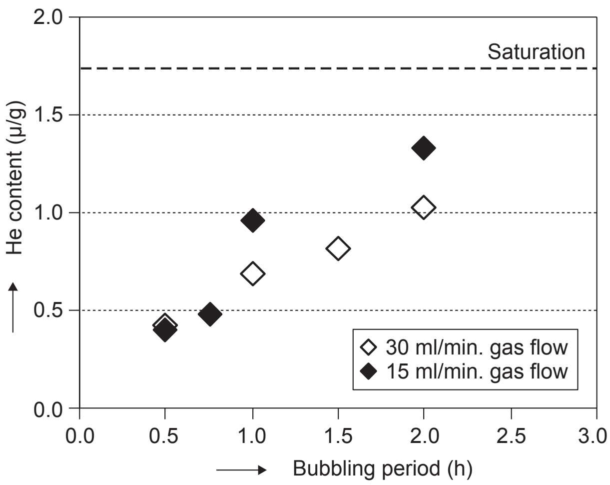


Figure 7. Helium content in an E-glass after bubbling at 1300?, measured by evolved gas analysis.

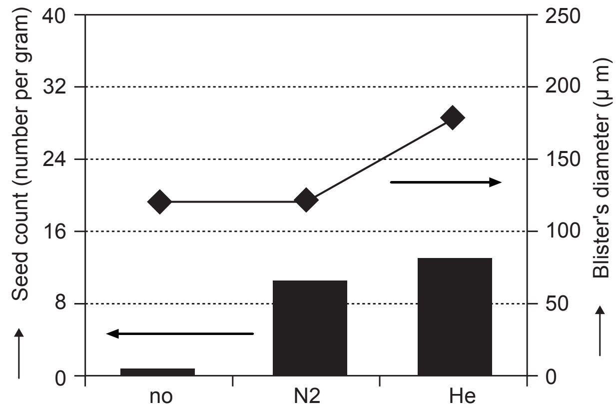


Figure 8. Number of blisters and the average blister's size in alumino-borosilicate molten glasses after bubbling for two hours at 1550°C.

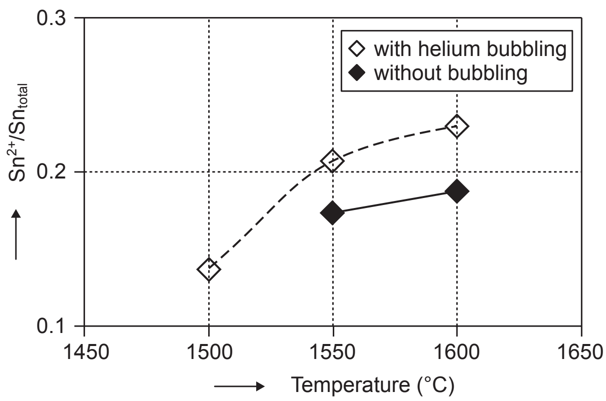


Figure 9. Sn^{2+} ratio to the total Sn in an aluminoborosilicate molten glass with or without helium bubbling.

that the loss of oxygen could be reduced by performing helium bubbling at as low temperature as possible, as shown in Figure 9.

As shown in this section, the application of helium bubbling is very effective measure to dissolve a large amount of helium into molten glasses as a pre-conditioning step. At the same time, this method has two disadvantages, which are undesirable induced blisters and loss of fining gases. In order to overcome these disadvantages, it is important to control the bubbling conditions, such as the bubble size and the time interval between the formation of each bubble, depending on viscosity and temperature.

CONCLUSION

Applications of uniformly-mixed fine batch to facilitate and enhance the melting-in process and helium gas to facilitate the fining process have been investigated. The applications could lower the melting and fining temperature and reduce the energy consumption and CO_2 emission in the melting and fining processes.
In comparison with the standard batch, the uniformly-mixed fine batch could reduce melting temperature, seeds and cord in their primary melts.

There are two methods to apply helium gas to molten glasses, a helium atmosphere above the molten glass and helium bubbling. A helium atmosphere can reduce seeds in molten glasses, although the application is thought to be limited to the very small production quantities, in which the molten glass can be in contact with the helium atmosphere for a long time.

Helium bubbling is effective measure for dissolving substantial amounts of helium into the molten glasses as a pre-conditioning step. Although there are two disadvantages, undesirable introduced blisters and loss of fining gases, they can be overcome if the bubbling conditions are well controlled.

In both applications of helium atmosphere and helium bubbling, the optimization of the conditions is very important.

For the optimization of industrial glass melting performance (melting-kinetics, fining, homogenization), Computational Fluid Dynamics modeling and modeling of fining processes: bubble growth and bubble ascension are thought to be effective tools to find optimum furnace designs and process settings.

Meanwhile, at the moment, it cannot be stated that the quality of glass articles is sufficient and there are no glass defects caused by glass melting process. In fact, there would be room for large reduction in energy consumption and CO_2 emissions during glass melting and fining, if the number of glass defects could be reduced and the overall quality could be improved. Simulation techniques also could be effective for this purpose. Therefore, the following recommendations are proposed to reduce the energy consumption and CO_2 emission.

1) Optimization of the present melting and fining processes using numerical simulation implementing principles of melting and fining together with outcome from laboratory experiments;
2) Application of uniformly-mixed fine batch;
3) Application of helium gas to improve glass quality or to reduce temperature and time required for fining.

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VÝZVA KE ZLEPŠENÍ PROCESŮ TAVENÍ SKLA A ČEŘENÍ

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Procesy tavení skla spotřebovávají velké množství topných olejů a topných plynů, což má za následek emise spalin, které globálně přispívají ke skleníkovému efektu. Proto je žádoucí navrhnout ekologicky neškodnou technologii tavení skla. Jako realistický přístup zvolila firma NEG zkoumání faktorů důležitých pro výkon technologie tavení skla. V této zprávě jsou řešeny a budou diskutovány dva základní faktory, tedy příprava rovnoměrně rozmíchaného čeřeného kmene a urychlení čeření. Sklářskou pec lze považovat za reaktor, kde probíhá fyzikální a chemické míchání za zvýšené teploty,

obvykle vyšší než 1 500 °C. Aby mohl proces výroby skla probíhat za nižších teplot, je zapotřebí lepší příprava sklářského kmene poblíž fyzikálně rovnoměrných podmínek. Z tohoto důvodu bylo zkoumáno, zda lze chování taveniny zlepšit mletím kmene v kulovém mlýně. Analýza plynů uvolňovaných při reakcích kmene a vyhodnocení zbytkového oxidu křemičitého analýzou XRD prokázaly, že mletí urychluje reakce mezi složkami kmene. Tyto výsledky naznačují, že mletí kmene by mohlo zlepšit chování při tavení a čeření a snížit teplotu tavení. Použití plynného helia může urychlit proces čeření při tavení skla. Byl zkoumán efekt čeření difuzí helia povrchem skloviny aplikací heliové atmosféry, a to v laboratorních podmínkách a při poloprovozní zkoušce. Tyto výsledky naznačily, že rozpouštění helia ve sklovině je velmi účinné při eliminaci bublinek. Tato difuzní metoda, kdy helium proniká povrchem tavené skloviny z heliové atmosféry, je však považována za vhodnou jen pro výrobu v malém měřítku, kde může být sklovina v přímém kontaktu s heliovou atmosférou po dlouhou dobu. Probublávání helia sklovinou je považováno za účinné jako předběžné kondicionování, zvláště u vanových pecí s velkou výrobní kapacitou. Laboratorní pokus s bubláním helia taveninou ukázal výhody i nevýhody. Předností je to, že lze takto v tavenině rozpustit velké množství helia, což vede ke zvětšení bublinek. Nevýhodou je, že by se tak do taveniny mohlo dostat velké množství nových bublin a mohlo by dojít ke ztrátě určitého množství čeřicího plynu ze skloviny. Proto by bylo třeba vyvinout optimální návrh procesu.