Numerical simulation of bubble growth in foam glass containing polyvalent ions

A. Steiner, J. van der Schaaf and R.G.C. Beerkens Eindhoven University of Technology, Glass Technology Group, P.O. Box 513, 5600MB Eindhoven, The Netherlands

Abstract

The conversion of fly ashes from municipal solid waste (MSW) incinerators into foam glass is a promising way for their detoxification and reuse as an added value product. The foaming properties of glass melts strongly depend on the glass properties such as viscosity, surface tension, composition and oxidation state and also on the interaction of the glass with the used foaming agent (carbon). In this paper, a physical - chemical model is presented, which can be used to calculate how foam glass compositions need to be adjusted to comply with foam glass specifications. The model involves simultaneous mass and momentum transfer between an expanding bubble and a finite volume of gas releasing glass around the bubble. The model also includes the effect of polyvalent ions on the gas forming reactions at the glass-bubble interface. Regarding the concentrations of the polyvalent ions, it appears that during foaming the oxidized form of the polyvalent ion, i.e. the chemically dissolved oxygen, is responsible for the oxygen transport through the glass. It is also shown, that the influence of the moving boundary on the diffusion characteristics and thus on the bubble growth is very important. The model is a good tool to predict and control the foamability of glass melts.

Introduction

Fly ashes from municipal solid waste (MSW) incinerators contain considerable amounts of environmentally harmful components [1]. Their leaching characteristics make it critical to store them on landfills without any prior treatment [2]. The detoxification and reuse of these fly ashes by a thermal process is a proven and successful method, however most of the time, this results in another waste stream [3]. Alternatively foam glass, a promising added value product, can be made from these silicate waste streams. The final foam glass product contains small homogeneously distributed closed gas bubbles, and is used as construction material for heat and sound insulation.

A silicate glass powder, mixed with a foaming agent, will start foaming during heating above the softening point. At temperatures lower than the actual foaming temperatures, the glass particles sinter together, which results in small closed bubbles, in which the foaming agent is enclosed (1- $7 \cdot 10^8$ bubbles/cm³ [4]). When the temperature is further increased, the foaming agent starts either decomposing into at least one gaseous component (oxidized foaming agent, e.g. CaCO₃) or reacting with the oxygen in the glass (reducing foaming agent e.g. carbon). Here carbon is used as foaming agent. It will react with the physically and chemically dissolved oxygen available at the glass - bubble interface. The chemically dissolved oxygen in form of e.g. ferric iron can be reduced at the interface into ferrous iron and oxygen. The gas forming reactions of the carbon plus the oxygen from the glass, produce CO and CO₂. This increases the pressure in the bubble, which is the driving force for the bubble growth. At a certain pressure and viscosity the glass relaxes and the bubble will grow. The diffusion process of chemically and physically dissolved oxygen from the glass towards the bubble is therefore the rate determining step for bubble growth. In addition to the viscosity, the bubble growth or foaming behavior also depends on the glass properties such as surface tension, composition, and oxidation state, and on process parameters such as heating rate, powder particle size, and residence



Figure 1: Schematic representation of foam model



Figure 2: Bubble growth caused by either physically dissolved O_2 or Fe^{3+} diffusion at 900° C. A difference of a factor $\approx 10^5$ is observed. R=radius, $R_0=radius$ at t=0

time. The bubble size and the foam height of the final product have an important influence on the insulation characteristics of the foam glass.

The use of waste glasses as raw materials for foam glass production requires compositional corrections. In order to optimize the foaming process and the use of waste glasses, a physical chemical model was developed to predict the bubble growth and foam height in foam glass as a function of the glass properties, the redox state of the glass and the process parameters. A physical description of the problem involves simultaneous mass and momentum transfer between an expanding bubble and a finite volume of glass around the bubble. For simplicity, coalescence of bubbles and hydrodynamic interaction between the bubble and highly viscous glass is neglected. The problem then reduces to the solving of diffusion equations for the mass transport in the glass with a moving boundary and a source term describing chemical equilibrium reactions of multiple polyvalent ions in the glass.

Model Theory

The dissolution or growth of an isolated spherical gas bubble surrounded by a fluid has been subject to extended research [5–8]. Most bubble dissolution and growth models were used in describing the elimination of gas bubbles in glass melts. The results are based on approximate and numerical solutions, incorporating one or more diffusing gases [9–12]. The effect of redox reactions on diffusion profiles and on bubble growth was first presented by Beerkens et al. [13, 14]. In these papers an effective diffusion coefficient is derived, based on thermodynamic equilibrium of polyvalent ions at all positions in a molten glass melt. Based on this approach, Yoshikawa et al. [15, 16] developed a model for transient bubble growth in glass melts. They also give an approximation for the moving bubble boundary. Both authors only consider an infinite glass melt volume and one sort of polyvalent species in the glass melt. Regarding the cellular structure of foam glass, as schematically shown in figure 1, only a limited amount of glass is available for one bubble. This requires a model which includes the influence of the surrounding bubbles. Following the approach of Arefmanesh and Advani [17], one bubble with an initial radius surrounded by a finite volume of glass around the bubble is considered for the modelling.

The thermodynamic equilibrium state of polyvalent ions in the glass is important for the foaming behavior, because it determines the concentrations of physically and chemically dissolved oxygen. Waste glasses often contain considerable amounts of multiple polyvalent species e.g. iron and sulfate. Glasses melted from municipal solid waste incinerator fly ashes can contain up to 3 wt.% Fe₂O₃ and 0.5 wt.\% SO_3 . Polyvalent ions in glass melts show mutual interaction, which influences the individual concentrations of the oxidized and reduced forms [18]. If the velocity of chemical relaxation (e.g. 1s at 550°C for an iron doped soda lime silicate glass [19]) is faster than diffusion or the diffusion



Figure 3: Influence of the bubble growth on the molar oxygen flux at the glass - bubble interface f(x) = 0



Figure 4: Bubble growth between 600 and 900° C as a function of the Fe^{3+} concentration in the glass (left) and heating rate (right), R=radius, R_0 =radius at t=0

coefficients of the different species respectively, it is obvious that the thermodynamic equilibrium between the different polyvalent ions in the glass influences the concentrations of physically and chemically dissolved oxygen in the glass and thus the bubble growth.

The mathematical formulation of the model consists of one partial differential equation for each diffusing species with appropriate initial and boundary conditions plus three ordinary differential equations, one equation for the molar flux at the glass bubble interface, one to describe the heating rate and one for the bubble growth. It should be mentioned, that the problem is non-isothermal and that all material properties, e.g. viscosity, surface tension, and diffusion coefficient are temperature dependent.

Results and Discussion

The following results are calculated for a soda lime silicate glass with only iron as polyvalent ion. The initial radius for all calculations was 32μ m with a shell thickness of 4/3 of the initial radius, based on closed packing of the cells. The reaction considered at the glass bubble interface is the reduction of ferric iron to the ferrous state producing oxygen according to:

$$\mathrm{Fe}^{3+} \leftrightarrows \mathrm{Fe}^{2+} + \frac{1}{4} \mathrm{pO}_2 \tag{1}$$

In a first attempt, the influence on bubble growth of the diffusion of physically dissolved oxygen on the one hand, and Fe₂O₃ on the other hand was evaluated, according to the approach of Beerkens et al. [13]. The result is shown in figure 2. The influence of the diffusion of physically dissolved oxygen on the bubble growth negligibly small. The influence of Fe³⁺ is a factor $\approx 10^5$ larger. In the latter case the bubble does not grow anymore after 50 seconds, because all chemically dissolved oxygen is converted. This is explained by the difference in initial equilibrium concentration of the physically dissolved oxygen $(10^{-8} \text{ mol/m}^3)$ and the Fe₂O₃ (400 mol/m³). Any distortion of the oxygen - polyvalent ion equilibrium by diffusion is always compensated by the thermodynamic equilibrium but only up to equilibrium concentration, which is very low for oxygen. In case of Fe³⁺ diffusion, the influence of the physically dissolved oxygen on the Fe³⁺ concentration profile is negligible.

Figure 3 shows that the influence of bubble growth on the molar oxygen flux at the glass bubble interface is very high. Without bubble growth only 6.6% of the available chemically dissolved oxygen was converted, whereas with bubble growth a conversion of 100% was obtained. One effect of bubble growth is the increasing surface available for mass transport, but another large effect is the compression of the concentration profiles due to the expanding bubble and the thinning of the glass melt shell. This shortens the diffusing distances, increases the slope of the concentration profiles at the interface and thus increases the molar oxygen flux into the bubble.

Figure 4 shows the bubble growth as a function Fe^{3+} concentration and heating rate. It can be seen that the Fe^{3+} content in the glass determines the maximum foam height, whereas the heating rate determines the time at which the desired foam height is reached. The results are similar to literature data [4,20], and will be validated experimentally.

Conclusion and outlook

The model presented in this paper shows that, for foam glass production, diffusion of the chemically dissolved oxygen in form of polyvalent ions is responsible for the oxygen transport through the glass. When multiple species of polyvalent ions are present in the glass, the physically dissolved oxygen concentration needs to be modelled, because it links the different thermodynamic redox reaction equilibria. It is also demonstrated, that the moving boundary has an important effect on the bubble growth and cannot be neglected.

With the developed model, the foaming process (temperature, glass composition, heating rate, viscosity etc.) of waste glasses can be designed, optimized and controlled. The latter is especially important, because of the strongly altering waste glass compositions. The model is going to be extended to incorporate multiple polyvalent ions.

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