Balance of oxygen throughout the conversion of a high-level waste melter feed to glass


1. Introduction

Vitrification is an established method to immobilize nuclear waste. The waste is mixed with glass-forming and -modifying additives and charged into a melter. In a joule-heated melter into which the feed is charged as slurry, melter feed forms the cold cap that floats on molten glass [1-2]. The cold cap consists of two layers (Fig. 1): the reaction layer, from which gases are freely escaping through open pores [3-7], and the foam layer, in which gases are trapped. Pokorny et al. [8] and Chun et al. [9] analyzed the kinetics of gas-evolving feed reactions and Rodriguez et al. [5] identified the gases using evolved-gas analysis (EGA).

Residual gases are trapped in bubbles when the glass-forming melt becomes connected. As bubbles grow, the bubbly melt turns to primary foam that eventually collapses [1,10]. Unless foaming is extremely vigorous, primary foam bubbles descend with melt and merge into cavities that escape sideways. Bubbles also ascend from the glass melt to form secondary foam (Fig. 1). Secondary bubbles originate from multivalent oxides that release oxygen in response to increasing temperature and from sulfate that releases SO2 and O2.

Foam tends to insulate the reaction layer from heat incoming from molten glass below. Foam can be destabilized by promoting forced convection in the melt (usually by bubbling gas [11]) or decreasing melt viscosity via glass composition or higher temperature [12]. Since the sources of gas are raw materials, modifying the feed makeup is another efficient way of affecting foaming.

In commercial glass batches, the raw materials are selected according to the cost, ease of melting, and efficient removal of bubbles [13]. For example, Na2O is supplied as soda, but can also be added in the form of soda ash [14] or sodium sulfate [15]; SiO2 is commonly introduced as silica sand or crushed quartz of a controlled grains-size [16-19]. Special additives are used for enhancing bubble removal, such as sulfate in combination with carbon or fining agents that change the redox state on heating (e.g., combination of sodium nitrate and antimony) [20].

Typically, about half of the waste glass mass originates from the waste. The rest are glass forming and modifying additives the mineral form of which can be chosen to maximize the rate of melting via their effect on the extent and the mode of foaming. Quartz (silica) grain size can vary between 1 µm and 1 mm [12,21]. Alkali and alkaline earth oxides can be introduced as nitrates or carbonates [22]. Feeds could contain reducing agents (e.g., sucrose [23] or oxalic acid [24]). Feed components can be calcined or pre-vitrified to frit [25,26]. Alumina can be added as boehmite [AlO(OH)], gibbsite [Al(OH)3], corundum (Al2O3), nepheline (NaAlSiO4), etc. [10,27,28]. In this study, we focus on the effect of the mineral source of Al2O3 on O2 evolution that in turn influences the extent of foaming as the melter feed is converted to molten glass [10,27,28].
In the melter feed, oxidizing components, such as nitrates and nitrites, coexist with reducing components, such as organics. Therefore, O$_2$ is both produced and consumed throughout the feed-to-glass conversion process. Compositions of the melter feeds are given in Section 2. In Sections 3 and 4, we estimate amounts of O$_2$ evolved, consumed, and released from melter feeds with different Al$_2$O$_3$ sources. Section 5 presents approximation functions that relate O$_2$ release rate to temperature and time. Then, in Section 6, we use oxygen mass balance to estimate the equilibrium iron redox ratio. Finally, in Section 7, we use the oxygen analyzer data to describe the approach of O$_2$ partial pressure to equilibrium with the atmosphere.

2. Melter feeds for high-alumina high-level waste (HLW) glass

Table 1 shows the composition of a high-alumina HLW glass and of the associated melter feed containing gibbsite as the alumina source. Feeds with boehmite and corundum mineral sources of alumina were also prepared. These three feeds are simplified versions of melter feeds designed and tested at the Vitreous State Laboratory [23,24]. Feed chemicals were mixed with deionized water to make slurry that was then dried and milled to powder (see [12,29] for details). The chemicals marked red in Table 1 evolve O$_2$ and the one marked blue consumes it.

### 3. Reactions involving O$_2$ at $T < 650$ °C

Before the glass-forming melt becomes connected, massive amounts of H$_2$O and CO$_2$ gases are generated from feed reactions together with small amounts of CO, NO, and NO$_2$ gases [5,10,28]. As glass-forming melt begins gradually to connect, the viscous phase (above approximately 650 °C, Section 4), residual gases are trapped in closed pores [12,29,30]. As pores expand, the melt turns into foam. When foam starts collapsing, the trapped gases are released while O$_2$ continues to evolve.

The following O$_2$-evolving and O$_2$-consuming reactions are irreversible and complete before glass-forming melt becomes connected:

- NaNO$_3$ → NaNO$_2$ + ½ O$_2$
- NaNO$_2$ → ½Na$_2$O + NO + ¼O$_2$
- Fe(H$_2$PO$_2$)$_3$ + 3 O$_2$ → ½Fe$_2$O$_3$ + 3P$_2$O$_5$ + 3H$_2$O

These reactions are schematic; in reality, oxyionic salts react with other feed components producing sodium borates, silicates, aluminates, etc. [31]. In the feed of composition listed in Table 1, NaNO$_3$ and NaNO$_2$ would produce 2.334 and 1.571 g O$_2$ per kg glass, respectively. EGA also detected the formation of small amounts of NO$_2$ at 380–560 °C. These amounts were equivalent, in g O$_2$ per kg glass, to 0.028 from the feed with gibbsite, 0.030 from the feed with boehmite, and 0.032 from the feed with corundum. Hence, the actual O$_2$ release from NaNO$_3$ in the feed with gibbsite, per kg glass, was 2.306 g.

The O$_2$-consuming chemicals in the feed (Table 1) are oxalate and hypophosphate. The oxalate could either react with nitrate or decompose, producing CO. The latter reaction would produce 0.268 g CO per kg glass. EGA data showed that 0.246 g CO per kg glass was released at 550 °C. The hypophosphate consumed 4.792 g O$_2$ per kg glass, which exceeds the O$_2$ from oxyionic salts. This explains why no O$_2$ was detected at temperatures below 650 °C from feeds containing boehmite and corundum. The small amount of O$_2$ liberated from the feed with gibbsite below 750 °C could possibly originate from Fe$_2$O$_3$ (neglecting the minute amount of O$_2$ from another multivalent oxide, CrO$_3$), see Section 6. As shown in Section 4, most of the O$_2$ was released into the atmosphere at temperatures above 850 °C.

### 4. Reactions involving O$_2$ at $T > 650$ °C

The release rate of gases from the feeds was measured using the EGA, a gas chromatograph with mass spectrometric detector (Agilent 6890N/5973N) connected to a silica glass tube in the furnace. Feed samples of ~1 g were heated to 1150 °C at 10 K min$^{-1}$ under He flowing at 50 ml min$^{-1}$. The temperature was then held constant at 1150 °C for about 13 min.

Note that an EGA sample represents a tiny amount of melter feed as it moves through the cold cap (Fig. 1) from top to bottom. The heating...
in the melt pool below. As the glass composition (Table 1) indicates, most of the O₂ is produced by the reversible reaction [34–37]

\[
\text{Fe}_2\text{O}_3 \leftrightarrow 2\text{FeO} + \frac{1}{2}\text{O}_2
\]

Local equilibria of multivalent components, such as Fe, S, or Cr, are functions of local composition and temperature and all depend on the local value of the partial pressure of O₂ [38–40], which, therefore, determines their mutual interaction [36,41]. As the melt becomes uniform with respect to composition and temperature (when residual solids dissolve and diffusion with convection eliminate concentration gradients), the partial pressure of O₂ continues to equilibrate with the atmosphere (Section 7) by a slow process of O₂ diffusion [42].

Although the 0.2 mass% SO₃ in glass (Table 1) is below the solubility limit [43,44], a small fraction of sulfate decomposed by the reaction [37,45,46]

\[
\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2
\]

By EGA of the feed with gibbsite, SO₂ began to evolve at 1100 °C and reached 6.7% of total present in the feed during 13 min at 1150 °C (releases during the constant-temperature interval are not shown in Fig. 2). The corresponding amounts of O₂ released from SO₂ were, in g per kg glass, 0.027 from the feed with gibbsite, 0.028 from the feed with boehmite, and 0.001 from the feed with corundum. Oxygen evolution from Fe₂O₃ is examined in Sections 5 and 6.

5. Approximation functions

Apart from the minute release from sulfate, gaseous O₂ was supplied by Fe₂O₃ dissolved in molten glass. The Fe redox ratio, Fe(II)/Fe(III), increased as long as the temperature increased, and approached equilibrium with the atmosphere when the temperature was held constant at 1150 °C. Fig. 3 displays O₂ release rate data measured with EGA during both increasing temperature (solid data points) and constant temperature (open data points). The lines represent two approximation functions fitted to data. For the increasing-temperature segment,

\[
\xi_i = \xi_0 \left[ 1 + \tanh \left( \frac{T - T_i}{T_R} \right) \right]
\]

(1)

where \(\xi\) is the gas evolution rate, \(T\) is the temperature, and \(\xi_0\), \(T_0\), and \(T_R\) are temperature-independent coefficients; subscript \(U\) stands for the increasing-temperature segment. For the constant-temperature segment (the decay curve, which is controlled by O₂ diffusion),

\[
\xi_D = \xi_0 \exp \left( \frac{T - \Delta T}{T_R} \right)
\]

(2)

where \(t\) is the time, \(\Delta T\) is defined by the intercept between the approximation functions defined by Eqs. (1) and (2), and \(\xi_0\) and \(T_R\) are temperature-independent coefficients; subscript \(D\) stands for the constant-temperature segment. Table 2 lists coefficient values of both functions for all three feeds. Coefficients of Eq. (1), except \(\xi_0\), depend on the alumina source. Coefficients of Eq. (2) do not depend on the alumina source, indicating that the melt was homogeneous and compositionally uniform at 1150 °C.

Integrating the right hand side of Eq. (1) yields the total release of O₂ from Fe₂O₃, \(\Xi_U\), during the increasing-temperature segment:

\[
\Xi_U = \xi_0 \sum_{i} \Delta T_i \left[ T_i - T_1 + T_1 \ln \left( \frac{T_2 - T_0}{T_1} \right) \frac{\cosh \left( \frac{T - T_0}{T_R} \right)}{\cosh \left( \frac{T_1 - T_0}{T_R} \right)} \right]
\]

(3)

where \(T_1 = 875 °C\) and \(T_2 = 1150 °C\) are the integration limits. Alternatively, based on measured data, we have \(\Xi_U = \sum_{i=1}^{n} \xi_i \Delta T_i\), where \(\xi_i\) is the \(i\)th measured value, \(\Delta T_i\) is the temperature interval between consecutive data points, and \(n\) is the number of data points (the data are displayed in Figs. 3 and 4). The results listed in Table 2 show that

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Fig. 2. Gas evolution rates from feeds with (a) gibbsite, (b) boehmite, and (c) corundum.
both methods yielded nearly identical values.

Integrating the right hand side of Eq. (2) from \( t = 0 \) to \( \infty \), we obtain for the \( O_2 \) release, \( \Xi_D \), as Fe redox approaches equilibrium at constant temperature, the formula

\[
\Xi_D = \frac{\xi(\Delta t)}{t_R}
\]  

(4)

Table 2 lists the resulting values. Because \( \Delta t < < t_R \), the \( \Xi_D \) value is virtually same for all three feeds.

Strictly speaking, the numerical coefficients of approximation functions proposed above depend on the glass composition and the heating rate. The glass-forming melt composition changes as the residual solids continue dissolving within the foam layer and even in the melt below the cold cap [47] and, as mentioned in Section 4, the heating rate varies during the passage of melter feed through the cold cap. These are secondary effects that are beyond the scope of this work, but can be taken into account in mathematical models [48].

The effect of alumina source on the \( O_2 \) release rate function, \( \xi(\xiT) \), is attributable mainly to the effect of the reaction path that the original mineral (gibbsite, boehmite, or corundum) turns into alumina embedded into glass structure [10,27] on foam stability. After gibbsite and boehmite lose the chemically bonded water, they become partly amorphous gels and partly transient aluminoborate minerals [2], whereas corundum persists up to a high temperature (800 °C, [27]).

The main foam stability determining factor in molten glass is the viscosity [49,50]. As is well known, water affects melt viscosity [51]. Gibbsite and boehmite release water at temperatures below 500 °C [5]. This water escapes before it can affect melt viscosity, especially in the EGA test, where the sample is small and the He atmosphere is dry. It is also unlikely that water from feed hydroxides would influence foam stability under the cold cap. Over the decades of viscosity testing of waste glasses, no effect of starting chemicals on melt viscosity was detected.

6. Fe redox

If \( Fe_2O_3 \) were fully reduced to \( FeO \), the amount of \( O_2 \) produced would be 5.931 g kg\(^{-1}\) glass. The actual amount of \( O_2 \) produced from \( Fe_2O_3 \) is 5.931z g kg\(^{-1}\), where \( z = Fe(II)/Fe(total) \) is the fraction reduced, the value of which can be obtained from the oxygen balance:

\[
O_2 \text{ evolved} = O_2 \text{ consumed} + O_2 \text{ released}
\]

As shown in Sections 2 and 3, \( O_2 \) was evolved from nitrates, nitrites, sulfate, and \( Fe_2O_3 \), and simultaneously consumed by iron hypophosphate. As shown in Section 5, the amount of \( O_2 \) released was \( \Xi = \Xi_U + \Xi_D \). Table 3 summarizes the numerical values of \( O_2 \) evolved, consumed, and released for feeds with gibbsite, boehmite, and corundum. The \( O_2 \) released from \( Fe_2O_3 \) was computed using the \( O_2 \) balance shown above. Based on this value, the fraction reduced, \( z \), and the redox ratio, \( \Gamma = Fe(II)/Fe(III) \), were then determined.

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**Table 2**

Coefficient values of functions for evolved \( O_2 \) gas for the feeds with different alumina sources.

<table>
<thead>
<tr>
<th>Source</th>
<th>Gibbsite</th>
<th>Boehmite</th>
<th>Corundum</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi_0 )</td>
<td>1.28 mg kg(^{-1}) K(^{-1})</td>
<td>1.28</td>
<td>1.28</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>989 °C</td>
<td>1027</td>
<td>952</td>
</tr>
<tr>
<td>( T_R )</td>
<td>69.9 K</td>
<td>83.1</td>
<td>78.3</td>
</tr>
<tr>
<td>( \Xi_U )</td>
<td>0.413 g kg(^{-1})</td>
<td>0.336</td>
<td>0.493</td>
</tr>
<tr>
<td>( \Xi_D )</td>
<td>0.415 g kg(^{-1})</td>
<td>0.344</td>
<td>0.499</td>
</tr>
</tbody>
</table>

\( ^{a} \) integration based on approximation function, Eq. (3).

\( ^{b} \) integration based on data.
7. Oxygen partial pressure

Oxygen partial pressure, $p_{O_2}$, determines the redox state of all multivalent species in molten glass [38–40]. The $\Gamma$ values listed in Table 3 (29% for the feed with gibbsite) are higher than the 2–4% reported for melts equilibrated in air at 1150 °C [52]. The difference is caused by the lower $p_{O_2}$ present in He used as a carrier gas in the EGA equipment ($p_{O_2} = 1.40$ Pa).

The equilibrium constant, $K$, of the reaction $4Fe^{3+} + O_2 \rightarrow 2Fe^{2+}$ is $K = \Gamma^4 p_{O_2}$. Where the activity of $O_2$ is included in $K$. Thus, dropping, for simplicity, the subscript $O_2$ and using subscripts $A$ and $F$ for air and the He gas used in the EGA equipment, we can write $K_A$ = $p_A(p_A/p_0)^{4/3}$. For the feed with gibbsite (Table 3), $K_A$ = 0.290. The $p_{O_2}$ in the He gas was $p_{O_2} = 1.40$ Pa. Since $p_A = 2.1 \times 10^{18}$ Pa, we obtain $K_A$ = 0.026. This value lies between 2% and 4% as expected.

The Fe redox equilibrium is also affected by formation of spinel, typically a solid solution of magnetite ($Fe_3O_4$), trevorite ($NiFe_2O_4$), and nichromite ($NiCr_2O_4$) [53]. For magnetite, $\Gamma = 0.5$ and $z = 0.533$. These values are higher than $\Gamma$ and $z$ values of glass at equilibrium with He atmosphere at 1150 °C (Table 3). Considering the small content of spinel in glass at 1150 °C (~1%) [48] and the small difference of Fe(II)/Fe(total) in spinel and in the melt [53], we can conclude that spinel formation has a negligible effect on the $O_2$ balance.

The $p_{O_2}$ in the glass melt was measured with an oxygen analyzer (GS Rapidox II). About 400 g powder feed containing gibbsite was heated at 10 K min$^{-1}$ to 1150 °C at which the temperature was held constant for 90 min. Fig. 4 displays $p_{O_2}$ versus time elapsed since 1150 °C was reached. After the initial rapid change, the $p_{O_2}(t)$ function was exponential:

$$p = p_\infty - (p_0 - p_\infty) \exp\left(-\frac{t}{t_k}\right)$$

(5)

where $p$ is the oxygen partial pressure (dropping the subscript $O_2$) and $p_0$, $p_\infty$, and $t_k$ are constant coefficients. Fitting Eq. (5) to data at $t > 40$ min, while imposing $p_\infty = 0.21$ bar, yielded $p_0 = 0.18$ bar and $t_k = 70.8$ min ($R^2 = 0.995$), indicating that equilibrium with air would be attained at ~5 h.

The chemical analysis of bubbles in quenched samples detected 97.4% $O_2$ at 1050 °C and 83.6% $O_2$ at 1150 °C, along with some $CO_2$ and $N_2$ and trace amounts of $SO_2$. The pressure in bubbles in molten glass is ~1 bar considering that hydrostatic pressure and capillary pressure are negligible. With the $p_{O_2}$ values in the melt as high as those shown in Fig. 4, it is not surprising that the oxygen content in bubbles was high.

8. Conclusions

Batch melting reactions that occur in the reaction layer and the primary foam layer of the cold cap, including those producing and consuming $O_2$, are generally irreversible. Multivalent oxides, such as $FeO_3$, undergo reversible reactions in molten glass producing $O_2$, the cumulative amount of which increases as temperature increases. Consequently, the redox reactions play a major role in the formation of secondary foam. The approximation functions defined by Eqs. (1) and (2) represent $O_2$ evolution from $FeO_3$ during both the non-isothermal and isothermal EGA. The EGA in conjunction with stoichiometric calculations allows estimation of both actual and equilibrium redox ratio of the dominant redox constituent ($FeO_3$) and the associated $O_2$ partial pressure as functions of temperature.

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References
