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

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ABSTRACT

Gases evolve from nuclear waste melter feed during conversion to glass in response to heating. This paper is focused on oxygen mass balance based on the stoichiometry of feed melting reactions and evolved-gas analysis data. Whereas O_2-producing and -consuming batch-melting reactions are complete in the reacting and primary-foam layers of the cold cap, O_2 from redox reactions continues to evolve as long as melt temperature increases, and thus generates secondary foam. Also, we discuss the relationship between the oxygen mass balance and the temperature-dependent iron redox ratio and the O_2 partial pressure, as they evolve during the feed-to-glass conversion.

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 SO_2 and O_2.

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, Na_2O is supplied as soda, but can also be added in the form of soda ash [14] or sodium sulfate [15]; SiO_2 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 (Al_2O_3), nepheline ($NaAlSiO_4$), etc. [10,27,28]. In this study, we focus on the effect of the mineral source of Al_2O_3 on O_2 evolution that in turn influences the extent of foaming as the melter feed is converted to molten glass [10,27,28].

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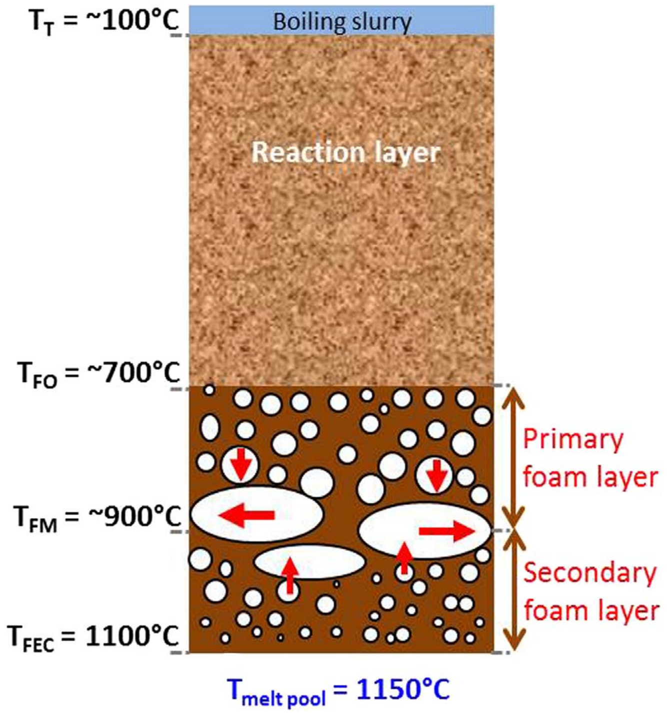

Fig. 1. Schematic of the cold cap (T_T is the cold cap top surface temperature, T_{FO} is the foam onset temperature, T_{FM} is the maximum foam temperature, and T_{FEC} is the effective foam collapse temperature).

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_2O_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_2O 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 into a continuous 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:

Table 1
Compositions of the glass and feed (to make 1 kg glass).

Glass composition	Mass %	Feed composition	Mass (g)
Al_2O_3	24.16	$Al(OH)_3$[(a)]	371.79
B_2O_3	19.12	H_3BO_3	341.59
Bi_2O_3	1.16	Bi_2O_3	11.67
CaO	5.74	CaO	10.87
Cr_2O_3	0.52	Cr_2O_3•$1.5H_2O$	6.20
F	0.67	NaF	15.00
Fe_2O_3	5.92	$Fe(OH)_3$	74.38
Li_2O	3.59	Li_2CO_3	89.22
Na_2O	9.64	NaOH	19.87
NiO	0.40	Na_2CO_3	106.57
P_2O_5	1.06	$NaNO_2$	3.48
PbO	0.41	$NaNO_3$	12.40
SiO_2	27.01	$Na_2C_2O_4$	1.26
SO_3	0.20	$Ni(OH)_2$	5.03
ZrO_2	0.40	PbO	4.17
		SiO_2	221.45
		Na_2SO_4	3.60
		$Zr(OH)_4$•xH_2O (x=0.654)	5.53
		$Fe(H_2PO_2)_3$	12.51
		$CaSiO_3$ (wollastonite)	97.07
Total	100.00	Total	1413.66

(a) For feeds containing boehmite and corundum, the equivalent masses are 285.94 g and 243.00 g, respectively [10].

$$NaNO_3 \rightarrow NaNO_2 + \tfrac{1}{2}O_2$$

$$NaNO_2 \rightarrow \tfrac{1}{2}Na_2O + NO + \tfrac{1}{4}O_2$$

$$Fe(H_2PO_2)_3 + 3O_2 \rightarrow \tfrac{1}{2}Fe_2O_3 + \tfrac{3}{2}P_2O_5 + 3H_2O$$

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_2O_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

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