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Predictive modeling of crystal accumulation in high-level waste glass melters processing radioactive waste

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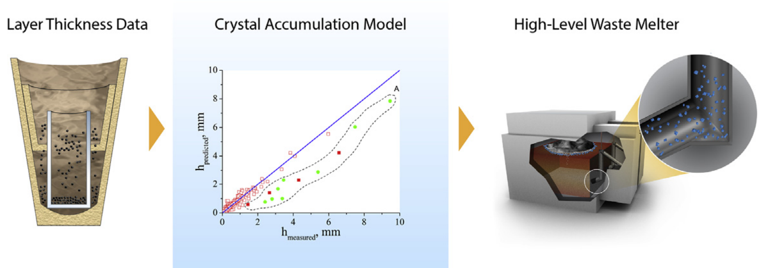
HIGHLIGHTS

- Spinel formers can encourage high agglomeration of crystals, producing thick layers.
- Liquidus temperature constraint cannot prevent crystal accumulation.
- Model developed predicts well the accumulation of single crystals and small agglomerates.
- Noble metals optimization of concentration can eliminate crystal accumulation.

GRAPHICAL ABSTRACT



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ABSTRACT

The effectiveness of high-level waste vitrification at Hanford's Waste Treatment and Immobilization Plant may be limited by precipitation/accumulation of spinel crystals [(Fe, Ni, Mn, Zn)(Fe, Cr)$_2$O$_4$] in the glass discharge riser of Joule-heated ceramic melters during idling. These crystals do not affect glass durability; however, if accumulated in thick layers, they can clog the melter and prevent discharge of molten glass into canisters. To address this problem, an empirical model was developed that can predict thicknesses of accumulated layers as a function of glass composition. This model predicts well the accumulation of single crystals and/or small-scale agglomerates, but excessive agglomeration observed in high-Ni-Fe glass resulted in an underprediction of accumulated layers, which gradually worsened over time as an increased number of agglomerates formed. The accumulation rate of ~53.8 ± 3.7 μm/h determined for this glass will result in a ~26 mm-thick layer after 20 days of melter idling.

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1. Introduction

The U.S. Department of Energy is building a Tank Waste Treatment and Immobilization Plant at the Hanford Site in eastern Washington to remediate a large inventory of high-level waste (HLW) that is being temporarily stored in underground tanks. This chemically complex waste will be vitrified into a durable borosilicate glass in Joule-heated ceramic melters (Fig. 1). An effort is being made to fully utilize this technology and increase the loading of Hanford tank wastes in glass while meeting glass property and composition constraints, and melter lifetime expectancies. . An evaluation of these constraints showed that one of the major factors that limit the waste loading for many HLW compositions at Hanford, high Fe_2O_3 wastes with and without Cr_2O_3, MnO, and NiO, is the precipitation and settling of spinel crystals $[Fe, Ni, Mn, Zn]^{2+}[Fe, Cr]_2^{3+}O_4$ in the melter [1]. These crystals do

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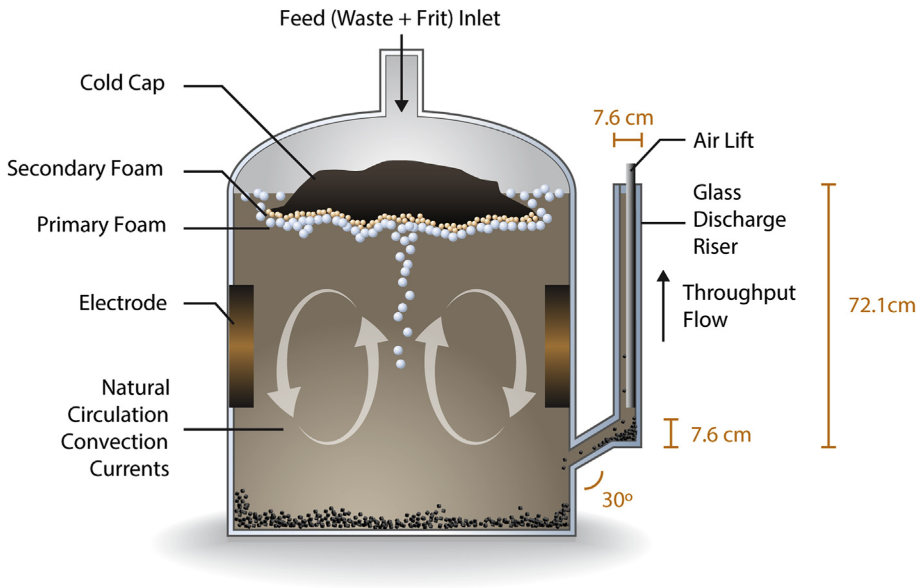

Fig. 1. Schematic cross section of a Joule-heated ceramic melter with dimensions of the glass discharge riser.

not affect glass durability [2]; however, they can accumulate in a layer thick enough to clog the melter and prevent discharge of molten glass into canisters [3]. Currently, to avoid the risk of crystal accumulation, glass formulations are constrained by the liquidus temperature (T_L) of glass (1050 °C) [4] or the temperature $T_{0.01}$ at which the equilibrium fraction of spinel crystals in the melt is 1 vol % (nominally below 950 °C) [5]. These constraints were enforced to ensure that crystals would not exist in molten glass or would be present in concentrations low enough to prevent any significant settling during the melter lifetime. However, they limit the waste loading too far below of what would be theoretically possible [5,6]. For example, without T_L constraint, the waste-glass volume could decrease by 12–16% [5].

Matyáš et al. [7] showed through mathematical simulation that T_L has little effect on the rate of crystals settling and, in contrast, the crystal size is the main rate-limiting factor. In addition, the current T_L constraint cannot prevent the precipitation of spinel crystals in the cooler regions (~850 °C) of the glass discharge riser during numerous and extended melter idling periods ranging from 20 to 100 days [8,9]. At this temperature, octahedral spinel crystals (Fig. 2) bigger than 200 μm can precipitate from the glass [10]. These crystals rapidly settle, forming thick sludge layers at rates up to 0.6 mm/d [11]. This would result in a ~10 mm-thick layer after 17 d of melter idling. Considering multiple idling periods and the fact that the spinel sludge cannot be easily dissolved or redistributed [12,13], a thick layer can form, which can clog the riser, and prevent pouring of molten glass during normal operation.

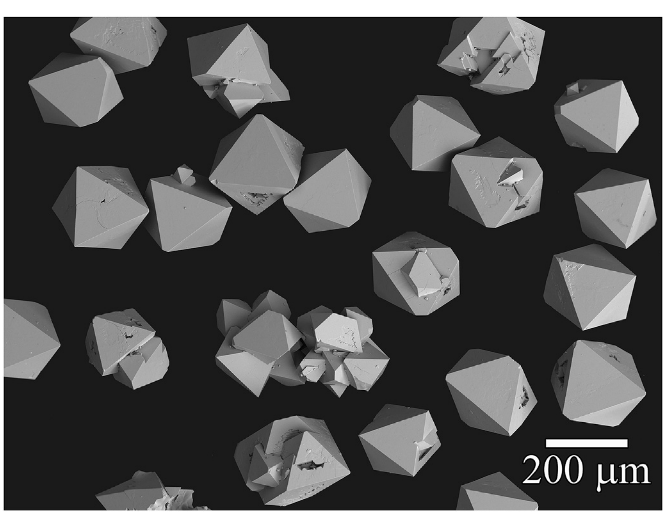

Fig. 2. Backscattered electron SEM image of spinel crystals. Crystals were extracted from Ni1.5/Fe17.5 glass heat treated at 850 °C for 4 days.

In the past, only a few studies were published on settling of spinel crystals in molten glasses [11,14–16] and transparent liquids [17,18]. More attention was focused on finding a glass composition for a given waste composition that would meet T_L and $T_{0.01}$ constraints while maximizing the waste loading. This was accomplished by combining the mathematically formulated relationships between glass properties and glass composition with experimental data from studies investigating the equilibrium fraction of spinel [19–21] and spinel crystallization kinetics [10,22,23] in HLW borosilicate glasses. While these studies provided useful insights on the crystal fraction and size, they did not assess the rate of settling/accumulation of crystals in the melter.

Our long-term objective is to replace the T_L and $T_{0.01}$ constraints with an empirical model that can relate the crystal accumulation in the riser to glass composition [11]. When coupled with glass property models [24], this model would allow formulation of crystal-tolerant glasses with high waste loading. Our preliminary empirical model showed good agreement between model-estimated and observed thicknesses of accumulated layers [17]. However, this model was only a linear function of the mass fractions of seven major components and covered limited compositional space. To make the model more robust, the effect of other components (present in the waste and additives) on crystal accumulation needs to be assessed, including the effect of crystal agglomeration.

In the study reported here, a matrix of 43 glasses was formulated, varying the concentration of 23 components. Labab-scale crucible tests were used to investigate the effect of individual components on the accumulation rate of spinel crystals in the glass discharge riser. Data collected on thicknesses of accumulated layers versus time were used to determine component coefficients for an