IMPACT OF PARTICLE AGGLOMERATION ON ACCUMULATION RATES IN THE GLASS DISCHARGE RISER OF HLW MELTER

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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The logo for the Office of River Protection features the text "Office of River Protection" in a bold, sans-serif font. The text is white and is set against a dark, wavy background that resembles a river or a stylized wave.

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IMPACT OF PARTICLE AGGLOMERATION ON ACCUMULATION RATES IN THE GLASS DISCHARGE RISER OF HLW MELTER

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ABSTRACT

The major factor limiting waste loading in continuous high-level radioactive waste (HLW) melters is an accumulation of particles in the glass discharge riser during a frequent and periodic idling of more than 20 days. An excessive accumulation can produce robust layers a few centimeters thick, which may clog the riser, preventing molten glass from being poured into canisters. Since the accumulation rate is driven by the size of particles we investigated with X-ray microtomography, scanning electron microscopy, and image analysis the impact of spinel forming components, noble metals, and alumina on the size, concentration, and spatial distribution of particles, and on the accumulation rate. Increased concentrations of Fe and Ni in the baseline glass resulted in the formation of large agglomerates that grew over the time to an average size of $\sim 185 \pm 155 \mu\text{m}$, and produced $>3 \text{ mm}$ thick layer after 120 h at 850°C . The noble metals decreased the particle size, and therefore significantly slowed down the accumulation rate. Addition of alumina resulted in the formation of a network of spinel dendrites which prevented accumulation of particles into compact layers.

INTRODUCTION

The most common and potentially problematic solids that can form and accumulate in joule heated melters vitrifying high-level radioactive waste (HLW) are spinel crystals $[(\text{Fe}, \text{Ni}, \text{Mn}, \text{Zn})(\text{Fe}, \text{Cr})_2\text{O}_4]$, RuO_2 , and their combination. There is a worry that these solids can growth into large particles or form large agglomerates in the glass discharge riser of the melter during a frequent and periodic idling from 20 to 100 days^{1,2} when the temperature of the molten glass can drop in some areas to as low as 850°C . This, together with the stagnant melts and small inner diameter of the riser ($\sim 76 \text{ mm}$), provide ideal conditions for accumulation of particles/agglomerates into a few centimeters thick robust layer³, which may clog the riser and thereby prevent molten glass from being poured into canisters.

A question arises whether it would be possible to control the accumulation rate of spinel crystals through optimization of noble metals concentration in radioactive wastes. A small concentration of noble metals may be sufficient to nucleate enough spinel crystals to limit their growth to a size of $10 \mu\text{m}$ or less. However, high concentrations of noble metals are not favorable because of their tendency to form large agglomerates⁴. These rapidly settling agglomerates can also form due to interactions of spinel crystals with noble metal particles.⁵ Another factor that can greatly affect the accumulation of spinel crystals in glasses containing high concentrations of spinel forming components is an addition of Al_2O_3 or Li_2O . These components tend to promote the formation of a network of large spinel dendrites which prevents building the dense settled layers.⁵

This laboratory study investigated particle agglomeration (size, concentration of agglomerates and their spatial distribution) and accumulation rates in three HLW glass

compositions with X-ray microtomography (XMT), scanning electron microscopy (SEM), and image analysis. Also, an attempt was made to measure an average composition of spinel crystals from elemental dot maps that were produced with an energy dispersive spectroscopy (EDS).

EXPERIMENTAL

HLW Glass Compositions

Table I shows compositions for three glasses (Ni1.5/Al10, Ni1.5/Fe17.5, and Ni1.5/Fe17.5/Ru0.015) used in the particle agglomeration study. The varied components were Al₂O₃, Fe₂O₃, NiO, and RuO₂/Rh₂O₃. The remaining components were kept in the same proportions as in the baseline glass.³ Glass batches were prepared from AZ-101 simulant and additives (H₃BO₃, Li₂CO₃, Na₂CO₃, and SiO₂). Additional Al, Fe, Ni, and Rh were added as Al₂O₃, Fe₂O₃, NiO, and Rh₂O₃. Ruthenium was added in the form of ruthenium nitrosyl nitrate solution drop by drop to SiO₂ that was dispersed on a Petri dish. The SiO₂ cake was dried in oven at 105 °C for 1 hour, quenched, and hand-mixed in the plastic bag with the rest of the glass batch. Then, the glass batch was milled in an agate mill for 5 min to ensure homogeneity. Glasses were produced in Pt-10%Rh crucibles following a two-step melting process: melting of homogenized glass batches at 1200 °C for 1 h and remelting of produced glasses at the same temperature and time after quenching and grinding.

Table I. Composition of glasses in mass fraction of oxides and halogens.

Component	BL	Ni1.5/Al10	Ni1.5/Fe17.5	Ni1.5/Fe17.5/Ru0.015 ^(a)
Al ₂ O ₃	0.0821	0.1000	0.0784	0.0783
B ₂ O ₃	0.0799	0.0776	0.0763	0.0762
BaO	0.0009	0.0009	0.0009	0.0009
CaO	0.0057	0.0055	0.0054	0.0054
CdO	0.0065	0.0063	0.0062	0.0062
Cr ₂ O ₃	0.0017	0.0017	0.0016	0.0016
F	0.0001	0.0001	0.0001	0.0001
Fe ₂ O ₃	0.1451	0.1409	0.1750	0.1750
K ₂ O	0.0034	0.0033	0.0032	0.0032
Li ₂ O	0.0199	0.0193	0.0190	0.0190
MgO	0.0013	0.0013	0.0012	0.0012
MnO	0.0035	0.0034	0.0033	0.0033
Na ₂ O	0.1866	0.1812	0.1781	0.1780
NiO	0.0064	0.0150	0.0150	0.0150
P ₂ O ₅	0.0032	0.0031	0.0031	0.0031
SiO ₂	0.4031	0.3913	0.3848	0.3846
SO ₃	0.0008	0.0008	0.0008	0.0008
TiO ₂	0.0003	0.0003	0.0003	0.0003
ZnO	0.0002	0.0002	0.0002	0.0002
ZrO ₂	0.0416	0.0404	0.0397	0.0397
Cl	0.0002	0.0002	0.0002	0.0002
Ce ₂ O ₃	0.0020	0.0019	0.0019	0.0019
CoO	0.0001	0.0001	0.0001	0.0001
CuO	0.0004	0.0004	0.0004	0.0004
La ₂ O ₃	0.0022	0.0021	0.0021	0.0021
Nd ₂ O ₃	0.0018	0.0017	0.0017	0.0017
SnO ₂	0.0010	0.0010	0.0010	0.0010
Total	1.0000	1.0000	1.0000	1.0000

^a Added 0.0003 Rh₂O₃ and 1.5E-4 RuO₂

Particle Agglomeration

Figure 1 shows the testing assembly for the lab-scale study of the particle agglomeration. The assembly consisted of an alumina crucible with an outer and inner diameter of 18 and 15 mm, respectively, and height 80 mm that was positioned on the alumina plate inside a Pt-crucible with an inner diameter of 30 mm and height 100 mm. The fabricated glasses were first melted in Pt/10%Rh crucibles at 1200 °C for an hour, and then the crucibles were removed one by one from the melting furnace, and molten glass poured into each of four assemblies that were rested on the 508-mm-diameter platform inside the big Deltech furnace at 850 °C. These assemblies were covered with a lid and removed (air-quenched) at different times up to 5 days. The alumina crucibles were core-drilled from assemblies and were investigated with XMT for the size and distribution of agglomerates. Then, the thin sections were prepared from middle of the crucible for optical microscopy and SEM-EDS observations, and an image analysis.

Figure 1. Cross-section of testing assembly.

X-ray Microtomography

XMT analysis was conducted using an NSI X-View Digital X-ray Imaging and Microfocus Computed Tomography (XMCT) system (North Star Imaging Inc., Rogers, Minnesota). X-rays were generated by a microfocus X-ray source (Comet Feinfocus model 160.48 160 kV) and collected by a PaxScan® 2520V flat panel digital X-ray detector with an active imaging area of 203 × 254 mm. This system is capable of spatial resolution of 6 μm in the focal plane for an object ~6 mm in diameter. Data acquisition and image reconstruction were conducted with X-View IW and efX-ct software's (North Star Imaging Inc., Rogers, Minnesota), respectively.

The X-ray tube voltage and current were adjusted to 110 kV and 340 μA, respectively, to produce an optimal luminosity contrast with values between 3500 and 6500. An X-ray detector response was optimized with dark and light field calibrations (gain or wedge), which were performed with the crucible removed from the field of view to create a uniform background response. The core-drilled alumina crucibles were put in the middle of the rotating stage that was positioned 89.8 mm from the center axis of rotation and X-ray tube, which resulted in a resolution of 18.7 μm (the smallest particle that can be detected). Each crucible was imaged in three separate sections (bottom, middle, and top) at 1 frame per second, with two images collected per 0.25° of rotation over 360°. Subsequently, the off-set calibration of stage with a

medium sized NSI calibration tool was performed on each section to correct stage movement errors, and images were reconstructed with efX-ct software.

Two-dimensional (XY) slice reconstructions of the bottom, middle, and top sections of the crucible were segmented with AVIZO Fire 7.0[®] image processing software (Visualization Science Group, Burlington, MA) to capture location and shape of particles. The size and count of particles was quantified with a three-dimensional volume quantification algorithm. The data were exported into Matlab, where each crucible volume was sectioned into 32x 2.5-mm tall cylinders to obtain size, count, and volume fraction of particles as a function of distance from the bottom of the crucible.

Scanning Electron Microscopy and Image Analysis

The YZ thin-sections of entire crucibles were polished, carbon coated and analyzed with JEOL JSM-5900 SEM (SEMTECH Solutions Inc., North Billerica, Massachusetts). The operating conditions were 15 kV acceleration voltage and working distance 34 mm. SEM images of rectangle areas (4×3 mm for Ni_{1.5}Fe_{17.5} and Ni_{1.5}/Al 10 glasses, and 1.3×1 mm for Ni_{1.5}Fe_{17.5}/Ru_{0.015} glass) were centered along z-axis and were taken every 5 mm starting from the bottom and moving up to the top of the crucible. Clemex Vision PE 6.0 image analysis software (Clemex Technologies Inc., Québec, Canada) was used to analyze the images for the size and surface area fraction of particles.

Energy-Dispersive X-ray Spectroscopy for Composition Analysis

Elemental dot maps were collected with a SEM JEOL 7001F/TTLS (JEOL Ltd., Tokyo, Japan) equipped with an Energy-Dispersive X-ray Spectroscopy (EDS) silicon drift detector (SDD, 30mm active area). The microscope was setup at working distance of 10 mm at an accelerating voltage of 15kV and probe current of 2-10 μ A. The SDD peaking time was between 0.8 - 3.2 μ s to maintain a count rate of 150 – 200 keps and a dead time of 30 - 50%. Maps were collected in a drift corrected mode with a resolution of 1024×800 pixels, 200 μ s/pixel, and copulation of 256 frames.

RESULTS AND DISCUSSION

Figure 1 shows the spatial distribution of spinel crystals, air voids, and cracks in the two-dimensional XMT cross-sections for Ni_{1.5}/Fe_{17.5} glass heat-treated at 850 °C for 96 h. These cross-sections are for the box with dimensions of $30 \times 7 \times 7$ mm which was extracted from the center of the bottom section of the crucible. The y-z plane visualizes projection of all crystals onto one plane. The high concentration of nickel and iron in the glass resulted in the formation of large spinel crystals/agglomerates with an average size $> 100 \mu$ m. These sparsely-distributed particles rapidly settled and accumulated in > 3 mm thick layer.

Figure 2A and B show the size and volume distribution of particles for the entire crucible in the Ni_{1.5}/Fe_{17.5} glass heat-treated at 850 °C for 24 and 96 h. The low grey-level contrast of XMT in the layer (96 h) resulted in an overestimation of the particle size ($> 450 \mu$ m) and occupied volume (> 86 %). The image analysis was not able to correctly resolve the individual particles but clumped them together into big clusters. The size of particles and their volume distribution was quite uniform after 24 h up to 10 mm below the glass level, and ranged from 100 to 130 μ m and 1-2 vol %, respectively. In contrast, particles of an average size $\sim 185 \pm 155 \mu$ m were identified in the 30-mm region above the bottom after an additional 72 h of settling. This indicates that the particles grew as they settled with a rate $\sim 1.1 \mu$ m/h.

Figure 1. X-ray microtomography cross-sections for Ni_{1.5}/Fe_{17.5} glass (850 °C - 96 h); glass is blue and gray, spinel crystals are yellow, cracks and air voids are white. All the crystals are projected onto y-z plane.

Figure 2. Size (A) and volume distribution (B) of particles vs. distance from the bottom of the crucible (0 mm – bottom, 80 mm – top) for Ni_{1.5}/Fe_{17.5} glass (850 °C for 24 and 96 h).

Table II shows the distribution of particle sizes as determined with image analysis from SEM images for Ni_{1.5}/Fe_{17.5}, Ni_{1.5}/Fe_{17.5}/Ru_{0.015}, and Ni_{1.5}/Al₁₀ glasses. Figure 3 shows the surface area occupied by the particles as a function of distance from the bottom of the crucible for the same glasses. Addition of Ni and Fe to baseline glass resulted in the formation of large particles that grew over the time, e.g., 90 % of all particles were smaller than 85 ± 56 and 126 ± 111 μm after 24 and 96 h, respectively. These large particles were initially uniformly distributed throughout the sample but got concentrated in ~ 25 -mm region at the bottom after 49 and 96 h. The settling of particles within this region produced compact 0.5- and 3-mm-thick layers with particles covering ~ 34 % of area, respectively. Figure 4 visualizes the layers accumulated in Ni_{1.5}/Fe_{17.5} glass after 49 and 96 h at 850 °C. In contrast, addition of noble metals to high-Ni-Fe glass resulted in the uniform distribution of particles with a size below 30 μm (D₉₀) even after 120 h at 850 °C. Because of the smaller particles the accumulated layers were only 79 and 168 μm thick after 72 and 120 h, respectively. Figure 5 shows the layers accumulated in Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass after 72 and 120 h at 850 °C. Addition of Al to

high-Ni glass produced a network of spinel dendrites with “arms” as long as 1 mm. These dendrite locked structure prevented accumulation of particles into thick layer. The dendrites slowly grew (see Table II) and dendritic network got more compacted over the time (~1 % after 24 h vs. ~3 % after 72 h). Figure 6 shows an example of the 3D network of spinel dendrites that formed in high-Ni-Al glass after 72 h at 850 °C. Figure 7 shows thin sections of dendrites for the same glass heat-treated at 850 °C for 24 and 72 h.

Table II. Distribution of particle sizes for Ni1.5/Fe17.5, Ni1.5/Fe17.5/Ru0.015, and Ni1.5/Al10 glasses heat-treated at 850 °C for different times; D10, D50, and D90 – 10, 50, 90% of crystals are smaller than these values, respectively.

Glass	Time, h	D10, μm	D50, μm	D90, μm
Ni1.5/Fe17.5	24	27 $\pm$ 22	51 $\pm$ 36	85 $\pm$ 56
	96	41 $\pm$ 48	74 $\pm$ 64	126 $\pm$ 111
Ni1.5/Fe17.5/Ru0.015	72	9 $\pm$ 6	21 $\pm$ 9	28 $\pm$ 10
	96	12 $\pm$ 6	20 $\pm$ 9	27 $\pm$ 10
	120	12 $\pm$ 8	21 $\pm$ 8	29 $\pm$ 13
Ni1.5/Al10	24	21 $\pm$ 14	36 $\pm$ 16	55 $\pm$ 24
	48	16 $\pm$ 9	41 $\pm$ 17	63 $\pm$ 27
	72	20 $\pm$ 14	47 $\pm$ 28	71 $\pm$ 38

Figure 3. Surface area fraction in % occupied by the particles for Ni1.5/Fe17.5 (A), Ni1.5/Fe17.5/Ru0.015 (B), and Ni1.5/Al10 (C) glasses heat-treated at 850 °C for different times.

A

B

Figure 4. SEM images of accumulated layers for Ni_{1.5}/Fe_{17.5} glass heat-treated at 850 °C for 49 h (A, 469 μm) and 96 h (B, 3111 μm).

A

B

Figure 5. SEM images of accumulated layers for Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass heat-treated at 850 °C for 72 h (A, 79 μm) and 120 h (C, 168 μm).

Figure 6. Optical image of spinel dendrite network at the bottom of crucible for Ni_{1.5}/Al₁₀ glass heat-treated at 850 °C for 72 h.

Figure 7. SEM images of dendrites in a 2D plane for Ni_{1.5}/Al₁₀ glass heat-treated at 850 °C for 24 h (A) and 72 h (B). The surface area fraction of dendrites increased with time.

Figure 8 shows an elemental dot map for Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass heat-treated at 850 °C for 96 h. Glasses containing high concentration of Ni and Fe, and some noble metals precipitated spinel crystals with a layer enriched with Cr and Na. Chromium is partitioned in the glass as Cr³⁺ and Cr⁶⁺ in an approximately 50:50 ratio.⁶ Since some Cr³⁺ is used for spinel crystals there is an extra Cr⁶⁺ that can wet the crystals and form NaCrO₄ layer. To test this hypothesis, a several higher magnification line scans were made to determine the changes in composition across the crystals. Figure 9 shows a location of line scan through a selected crystal containing a RhO₂ particle. Figures 10A and B visualize changes in the concentration of Na, Cr, Rh, Fe, Ni, and Mn along this line scan. The line scans revealed that higher concentration of Na in the skin of crystals is an artifact from charging but Cr enrichment in ~2.5-µm layer was real. This was confirmed by higher average concentration of Cr in the crystals that formed/grew in Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass. Table III shows an elemental composition of spinel crystals in the Ni_{1.5}/Fe_{17.5}, Ni_{1.5}/Fe_{17.5}/Ru_{0.015}, and Ni_{1.5}/Al₁₀ glasses heat-treated at 850 °C at different times.

Figure 8. Elemental dot map for Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass heat-treated at 850 °C for 96 h.

Figure 9. Location of line scan through a spinel crystal that formed in the Ni_{1.5}/Fe_{17.5}/Ru_{0.015} glass after 72 h at 850 °C.

Figure 10. Concentration profiles of Na, Cr, and Rh (A), and Fe, Ni, Cr, and Mn (B) along the line scan in Figure 9.

Table III. Composition of spinel crystals in atomic % for Ni_{1.5}/Fe_{17.5}, Ni_{1.5}/Fe_{17.5}/Ru_{0.015}, and Ni_{1.5}/Al₁₀ glasses heat-treated at 850 °C at different times.

Glass	O	Cr	Mn	Fe	Ni
Ni _{1.5} /Fe _{17.5} -850°C-49h	81.37	0.17	0.11	11.32	7.02
Ni _{1.5} /Fe _{17.5} /Ru _{0.015} -850°C-96 h	81.22	0.42	0.15	11.45	6.75
Ni _{1.5} /Al ₁₀ -850°C-48 h	82.26	0.35	0.11	10.79	6.49

CONCLUSION

The experimental study of spinel accumulation indicated that high concentrations of spinel-forming constituents in the glass can produce settling layers of a few mm thick in a few days. Adding ~ 0.9 wt% of NiO and ~ 3.4 wt% of Fe₂O₃ to baseline glass resulted in the formation of large particles/agglomerates that got bigger over the time to an average size of ~185±155 µm, and produced >3 mm thick layer after 120 h at 850 °C. The accumulation of these layers can be significantly suppressed by noble metals (RuO₂, RhO₂). These components slowed down or stopped the spinel accumulation because of their effect on decreasing the average crystal size. Adding ~ 0.015 wt% of RuO₂ to high-Ni-Fe glass decreased the crystal size and prevented agglomeration of particles. This resulted in the layer less than 0.2 mm thick after 120 h at 850 °C. Adding of ~ 1.8 wt% Al₂O₃ to high-Ni glass resulted in the formation of a network of spinel dendrites that prevented accumulation of particles into a compact spinel layer. There is a reasonable chance that the spinel crystals locked in this non-compacted layer can be removed with glass during the pouring into canisters. X-ray tomography proved to be a useful non-destructive technique to evaluate an agglomeration of large particles and to provide a spatial distribution of particles in the relatively large glass volumes.

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