

## ORIGINAL ARTICLE

# Real-time monitoring of crystal accumulation in the high-level waste glass melter using an electrical conductivity method

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**Abstract**

During the vitrification of high-level radioactive waste (HLW) in HLW melter in the Waste Treatment and Immobilization Plant located in Washington State, spinel crystals  $[\text{Fe}, \text{Ni}, \text{Mn}, \text{Zn}]^{2+}[\text{Fe}, \text{Cr}]_2^{3+}\text{O}_4$  may precipitate from glass and accumulate in the melter riser, preventing the discharge of molten glass into canisters. Therefore, an effort is being made to develop an electrical conductivity method to monitor crystal buildup in the melter riser. A vertically configured electrical conductivity (EC) probe with an alumina shaft and Pt-10%Rh-electrodes was designed and tested in standard conductivity solutions and glass melts both with and without spinel crystals. The EC probe measured conductivity in conductivity solutions within 10% of their certified values and showed a linear relationship with increased spinel layer thicknesses. Testing in silicate glass containing spinel crystals allowed for the determination of spinel conductivity as a function of temperature. The conductivities of spinel crystals of 20–24 S/m at 800°C were in excellent agreement with the conductivity of trevorite ( $\text{NiFe}_2\text{O}_4$ ) crystals at 800°C reported in the literature. The conductivities of spinel crystals and measured changes in the conductivity across the accumulated layer allowed for a successful measurement of spinel crystal accumulation in simulated HLW glass.

**KEYWORDS**

electrical conductivity, high-level waste glass, spinel crystals

## 1 | INTRODUCTION

During production of defense weapons from the 1940s through the 1980s, millions of gallons of radioactive waste were generated and subsequently stored in underground tanks at the Hanford Site in Washington State. This waste will be removed from the underground storage tanks, separated into a low-activity waste and high-level waste and vitrified at the Hanford Tank Waste Treatment and Immobilization Plant as part of a U.S. Department of Energy agreement with the U.S. Environmental Protection Agency and the state of Washington.

Joule-heated ceramic melter will be used to convert radioactive waste into stable borosilicate glass for long-

term storage and disposal. The projected operation of these melter is limited by spinel crystals, which are the primary solid phase predicted to precipitate from high-level waste (HLW) glasses at Hanford.<sup>1</sup> The spinel crystals can grow larger than 200  $\mu\text{m}$  during melter idling when the temperature in the riser of the melter is expected to drop as low as 850°C.<sup>2,3</sup> Limited mixing and low temperatures can lead to excessive crystal accumulation in the riser, and could potentially block the discharge of the molten glass into canisters.<sup>2-4</sup> To resolve this issue, various options are being explored, including the development of crystal-tolerant glasses<sup>1</sup> and methods to monitor spinel crystal accumulation. One method under consideration is an electrical conductivity method which is based on the assumption that the

spinel crystals have conductivities different from those of the glass, and therefore, their gradual accumulation can be assessed through the changes in measured conductivities during melter operation.

Because of the need to advance theoretical ideas on the formation of the structure of glass from melts and increased interest in the electric melting of glass, Okhotin et al.<sup>5</sup> developed an automatic measuring circuit and a cell suitable for laboratory and production measurements of conductivity. A short time later, Baucke and Frank<sup>6</sup> introduced the absolute resistivity measurement of glass melts, which consisted of two parallel electrodes immersed in a melt with resistivity determined according to the Equation 1:

$$\rho = \frac{RA}{L} \quad (1)$$

where  $\rho$  is electrical resistivity ( $\Omega\cdot\text{m}$ ),  $A$  is the surface area of the electrodes ( $\text{m}^2$ ),  $L$  is the distance between the electrodes (m), and  $R$  is the resistance ( $\Omega$ ). The principle was expanded by applying a cell constant ( $K$ ,  $\text{m}^{-1}$ ) to the measurement of the resistivity of glass melts.<sup>7,8</sup> This geometric factor is defined as,

$$K = \frac{L}{A} \quad (2)$$

and is determined from conductivity measurements of standard solutions at room temperature, with the assumption that the obtained  $K$  does not change with temperature. Because conductivity ( $\sigma$ ,  $\Omega^{-1}\cdot\text{m}^{-1}$ ) is the reciprocal of the resistivity, Equation 1 becomes,

$$\sigma = \frac{1}{\rho} = \frac{K}{R} \quad (3)$$

Utilizing vertically arranged parallel electrodes with a laboratory-determined geometric factor ( $K$ ) will allow for the detection of conductivity of the glass melt during melter operations. Borosilicate glass and spinel crystals have different mechanisms which allow charge to pass through each. These mechanistic differences will produce a measurable change in conductivity as spinel accumulates between the Electrical Conductivity (EC) probe leads.

The electrical conductivity of silicate glasses results from the migration of charge through monovalent cations in the silicate network such that,

$$\sigma = n_e e \mu \quad (4)$$

where  $n_e$  is the effective charge carrier concentration,  $e$  is the charge for the single charge species, and  $\mu$  is its electrical mobility.<sup>9</sup> At temperatures below the glass transition

temperature ( $T_g$ ), these glasses follow a temperature-activated mechanism represented by the Arrhenius law and a free-volume mechanism described by Cohen and Turnbull<sup>10</sup> that assumes random density fluctuations create “free” volume allowing for molecular transport.<sup>11</sup> Electrical conduction in silicate glasses is further dependent on the concentration of cations and their bond strength to the network where  $\text{Na}^+\text{-BO}_4^-$  bonds with bridging oxygen transform into  $\text{Na}^+\text{-BO}_2\text{O}^-$  bonds with nonbridging oxygen. At temperatures above  $T_g$  there is a sharp increase in conductivity as cation transport increases due to the breaking of the glassy network.<sup>12</sup> This rapid conductivity increase above  $T_g$  tends more towards a Vogel-Fulcher-Tammann (VFT) behavior rather than the Arrhenius law.<sup>13</sup>

Spinel crystals are composed of a closely packed oxygen lattice with cations in tetrahedral and octahedral positions. The electrical conductivity of these crystals at elevated temperatures is due to the electron transfer between different valence cations (e.g.,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}$ ) at the octahedral sites.<sup>14</sup> In addition, the electrical transport properties of spinel crystal increases with density, largely due to atomic mass and cell volume.<sup>15</sup> Spinel crystals in HLW melters have been found with densities of  $\sim 5.3 \text{ g/cm}^3$ <sup>1</sup>—on the high end of typical spinel densities that range from 4.4 to 5.4  $\text{g/cm}^3$ ,<sup>15</sup> therefore, spinel crystals in HLW melters would have comparatively high electronic transport properties. Trevorite is the principal spinel expected in the HLW melters and has been found to have a conductivity near 20 S/m.<sup>14,16</sup>

Based on mechanism changes that occur due to increasing or decreasing the glass/spinel fraction within the borosilicate glass melt, a method for determining spinel accumulation could be developed using vertically arranged parallel electrodes located at the bottom of the riser of the joule-heated ceramic melter. The development of such a method would facilitate the processing of high level waste-loaded crystal-tolerant borosilicate glasses while decreasing the cost and risk of HLW vitrification.<sup>17</sup> This paper describes the investigation of the feasibility of this method for the monitoring of crystal accumulation using standard conductivity solutions, spinel crystals, and laboratory glass melts.

## 2 | MATERIALS AND METHODS

Certified NaCl standard solutions with conductivities of 1-20 S/m were purchased from Ricca Chemical (Arlington, TX) and used for probe calibrations. Sodium silicate glass was used to determine the conductivities of spinel crystals as a function of temperature and to observe changes in conductivity with different thicknesses of accumulated layers. This glass was produced by drying

sodium silicate solution at 90°C overnight, grinding dry cake in a tungsten mill for 2 minutes, heating the powder from room temperature to 550°C at 5°C/min, and grinding melted/sintered product in a tungsten mill for 2 minutes. This synthesis approach allowed production of a sodium silicate powder with a minimal tendency for foaming during melting. High-Ni-Fe glass (Ni1.5/Fe17.5)<sup>18</sup> was used as a simulant of HLW glass for laboratory testing of the probe function. A simulated HLW glass, high-Ni-Fe glass, was produced from Hanford waste tank 241-AZ-101 simulant described by Hrma et al.<sup>19</sup> where additional Ni and Fe were added as oxides (Fe<sub>2</sub>O<sub>3</sub>, NiO). The precursors were homogenized in an agate mill for 5 minutes, melted in a Pt/10%Rh crucible in air at 1200°C for 1 hour, air-quenched, and ground in a tungsten carbide mill for 2 minutes. The glass powder was then remelted under the same conditions, air-quenched, and ground before using it for the test. Table 1 shows the composition of the High-Ni-Fe glass in mass fraction of oxides. The spinel crystals for all testing were produced from the High-Ni-Fe glass by heat-treatment in a double crucible<sup>20</sup> for 7 days at 850°C. The crystals were recovered from the layer accumulated at the bottom of the crucible through overnight treatment with heated (60°C) 20% HNO<sub>3</sub> to dissolve the glass, and then treated with 5% HF to dissolve the residual silica gel. The morphology of crystals is shown in the Figure 1. X-ray diffraction of the spinel crystals confirmed that the primary crystalline phase was trevorite (NiFe<sub>2</sub>O<sub>4</sub>).

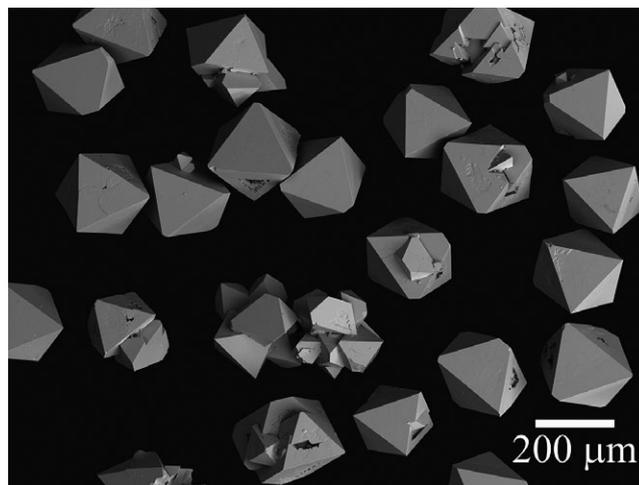
All standard and silica laboratory conductivity measurements were done using a Solartron 1470E impedance analyzer coupled with a Solartron 1400 frequency analyzer (Leicester, UK). A small-amplitude alternating-current

(AC) signal was supplied to the probe leads over a range of frequencies while providing impedance phase and magnitude to establish resistive, capacitive, and inductive behavior. The analysis sequence included a 100 seconds open circuit followed by an impedance sweep of a constant potential with 0 V of applied potential and 10 mV of AC amplitude. The frequency sweep was done on a log scale from 10<sup>-1</sup> to 10<sup>6</sup> Hz. The parameters for testing were developed to find the optimum electrical signal for a variable test matrix. A sinusoidal potential excitation was analyzed as a sum of sinusoidal functions or a Fourier series. The impedance was evaluated with Nyquist<sup>21</sup> and Bode<sup>22</sup> plots. A Nyquist plot is a polar plot of the frequency response function of a linear system and represents the actual impedance of the probe (real component) and the inductive and capacitive character of the probe (imaginary component). A Bode plot shows the gain and phase response of a given system for different frequencies and represents the impedance magnitude (real or imaginary components of the impedance) and phase angle as a function of frequency.

The probes were designed and constructed similar to Figure 2 (i.e., a 42 cm tall, 4 mm diameter alumina sheath housing two Pt/10%Rh wires). A hole was drilled 1 cm from the bottom of the sheath to allow one wire to be bent and protruded from the sheath (the bare wire was used in place of the plate to limit crystal settling on the upper electrode). This created a ~1 cm vertical path length between the top wire and the 16 mm<sup>2</sup> paddle that was welded to the bottom wire. A change in conductivity will occur and can be quantified as spinel crystals accumulate between the two leads. The probes were calibrated with standard NaCl solutions at room temperature using Equation 3 to calculate an average *K* value for each probe.

**TABLE 1** Composition of High-Ni-Fe (Ni1.5/Fe17.5) glass in mass fraction of oxides and halogens

Component	Ni1.5/Fe17.5	Component	Ni1.5/Fe17.5
Al <sub>2</sub> O <sub>3</sub>	0.0784	NiO	0.0150
B <sub>2</sub> O <sub>3</sub>	0.0763	P <sub>2</sub> O <sub>5</sub>	0.0031
BaO	0.0009	SiO <sub>2</sub>	0.3848
CaO	0.0054	SO <sub>3</sub>	0.0008
CdO	0.0062	TiO <sub>2</sub>	0.0003
Cr <sub>2</sub> O <sub>3</sub>	0.0016	ZnO	0.0002
F	0.0001	ZrO <sub>2</sub>	0.0397
Fe <sub>2</sub> O <sub>3</sub>	0.1750	Cl	0.0002
K <sub>2</sub> O	0.0032	Ce <sub>2</sub> O <sub>3</sub>	0.0019
Li <sub>2</sub> O	0.0190	CoO	0.0001
MgO	0.0012	CuO	0.0004
MnO	0.0033	La <sub>2</sub> O <sub>3</sub>	0.0021
Na <sub>2</sub> O	0.1781		



**FIGURE 1** Scanning electron microscope image of spinel crystals

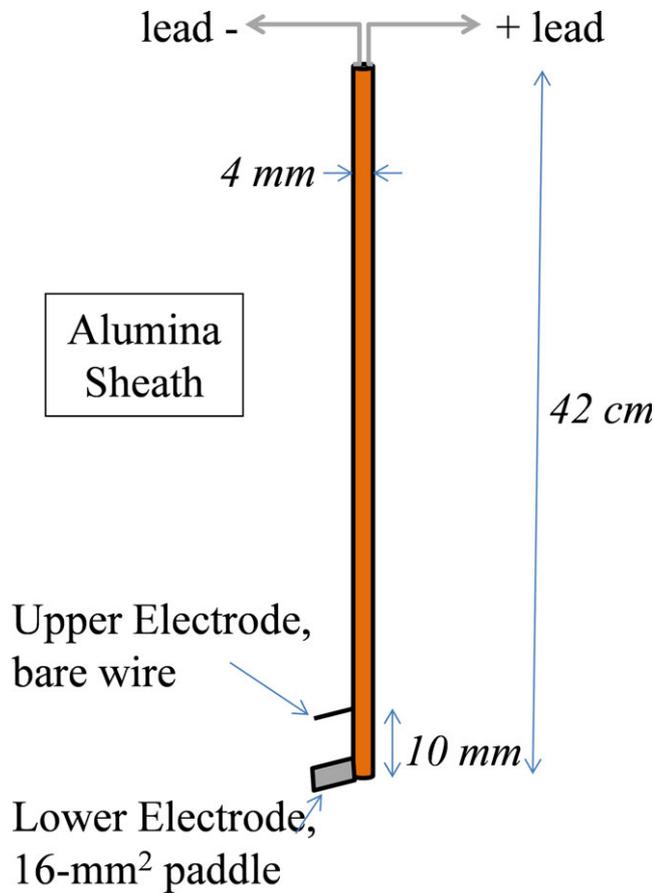


FIGURE 2 Probe design

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Probe calibration

The  $K$  values for prepared probes were used to calculate conductivities of solutions from measured resistances. Figure 3 compares the calculated conductivities with standard (certified) conductivities of standard solutions. Each probe had slightly different geometrical properties, which were captured in their  $K$  values and resulted in minor differences in probe slopes. The small differences in  $K$  values ( $292\text{--}315\text{ m}^{-1}$ ) and the  $\pm 10\%$  agreement with certified conductivities of standard solutions provided confidence in the accuracy of the probes.

#### 3.2 | Standard conductivity solutions with spinel crystals

Two standard solutions with conductivities of 10 and 20 S/m were used to evaluate the impact of an accumulated layer of crystals on the resulting glass/crystal matrix conductivity. These conductivities were selected based on conductivity measurements of glass melts reported by

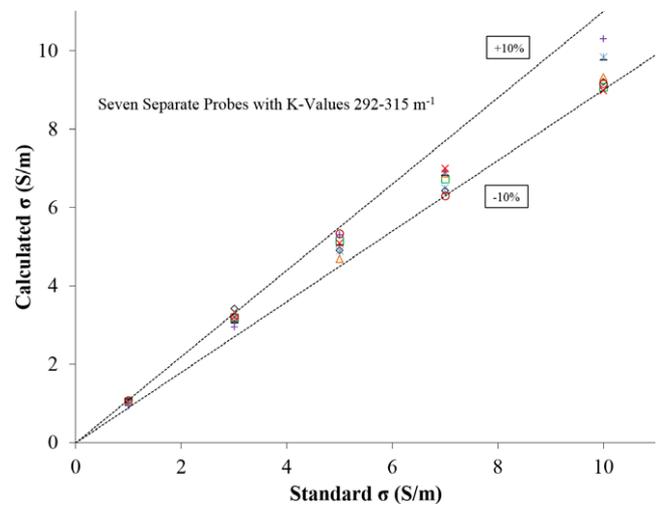
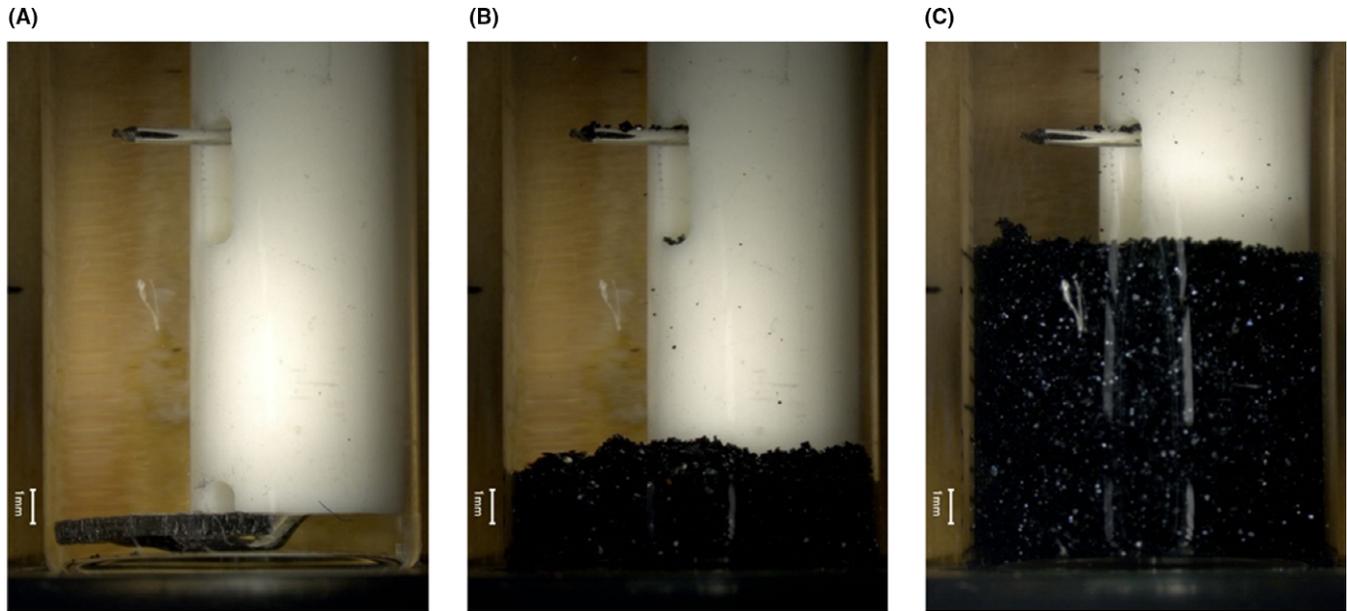


FIGURE 3 Calculated vs theoretical conductivities and cell constants ( $K$ ) obtained for calibrated probes

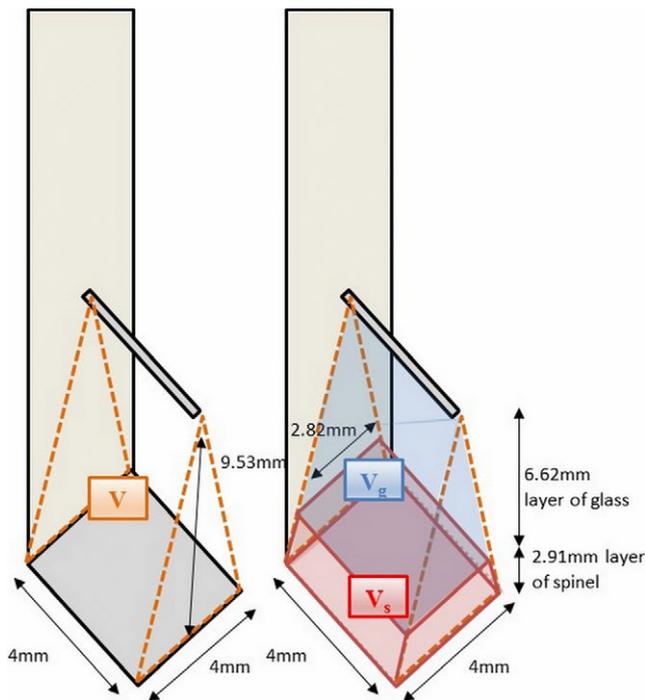
Crum et al.<sup>23</sup> The conductivity was measured for various thicknesses of spinel accumulations. At the same time, photomicrographs of the accumulated spinel layer between the upper and lower leads of the probe were collected with a VHX-2000 Digital Microscope (Keyence, Itasca, IL). The microscope was equipped with a  $5\times\text{--}5000\times$  magnification high resolution zoom lens and utilized high dynamic range 16-bit resolution through RGB data from 54 million pixels to produce images which were analyzed with image analysis to determine the spinel layer thickness. Figure 4 shows an example of crystals accumulated to different thicknesses. Because the probe consists of a flat plate on the lower electrode and a bare wire on the upper electrode, it was theorized that electrical current would pass through the solution/spinel layer in a three-dimensional triangular path. Therefore, the change in conductivity due to spinel would be related to the volume that the spinel occupied within that electrical path. This relationship can be addressed using the following formula:

$$\sigma_s \left( \frac{V_s}{V} \right) + \sigma_g \left( \frac{V_g}{V} \right) = \sigma_m \left( \frac{V}{V} \right) \quad (5)$$

where  $V$  is the total volume between the probe leads,  $\sigma_s$  is the conductivity of the spinel crystal,  $V_s$  is the volume occupied by spinel crystal between the probe leads,  $\sigma_g$  is the conductivity of the standard solution (or glass melt),  $V_g$  is the volume occupied by the standard solution (or glass melt) between the probe leads, and  $\sigma_m$  is the measured conductivity of the standard solution (or glass melt)/crystal environment. Figure 5 depicts the method of determining the volume terms as an example for probe 2-9.



**FIGURE 4** Accumulated layers of spinel crystals in 10 S/m standard conductivity solution. Layer thicknesses: (A) 0 mm; (B) 1.9 mm; (C) 7.2 mm



**FIGURE 5** Volume determination method (example: Probe 2-9)

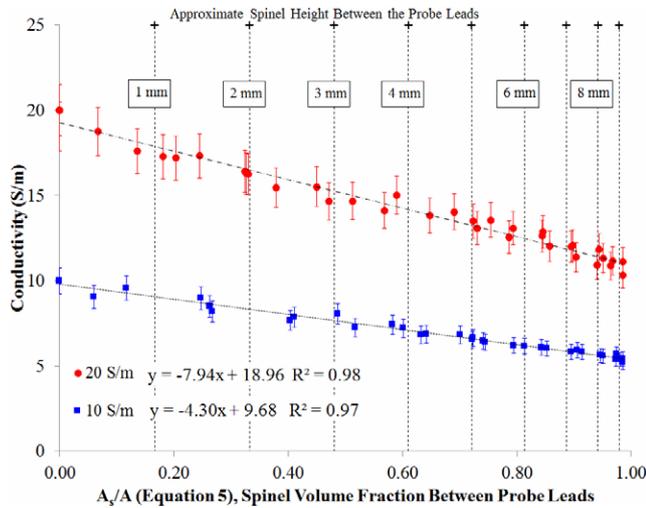
Applying Equation 5 and assuming that the conductivity of the glass ( $\sigma_g$ ) and the conductivity of the spinel ( $\sigma_s$ ) are constant, and that the volume fraction of glass ( $V_g/V$ ) occupies the remainder of A such that  $1 - V_g/V = V_s/V$ , the measured conductivity ( $\sigma_m$ ) can be expressed as a function of spinel volume fraction ( $V_s/V$ ):

$$\sigma_m = \left( \frac{V_s}{V} \right) * (\sigma_s - \sigma_g) + \sigma_g \quad (6)$$

Experimental data in Figure 6 show a linear decrease in conductivity with increased thickness of accumulated spinel layer. Calculating the conductivity of the spinel ( $\sigma_s$ ) at room temperature for both 10 and 20 S/m solution tests gives values of 5 and 10 S/m, respectively. This indicates that the spinel volume fraction ( $V_s/V$ ) consists of both spinel crystal and conductivity solution. The conductivities of the solutions that did not contain any crystals were within 5% of the certified values, verifying the probes' functionality. Figure 6 also contains estimations of spinel height ( $\pm 5\%$ ) between the probe leads. This number was generated using the known measurements of the probe (i.e., bottom electrode area and distance between electrodes) and the experimentally generated spinel volume fraction ( $V_s/V$ ).

### 3.3 | Conductivity as a Function of Temperature and Spinel Thickness in Silica Glass

To evaluate conductivity as a function of temperature and spinel layer thickness it was necessary to conduct experiments with a glass that would not produce spinel crystal. This was accomplished using sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) powder. Riser temperatures in HLW melters at the Hanford Waste Treatment and Immobilization Plant (WTP) can drop to 850°C. Therefore, laboratory testing included temperatures spanning a range from 675 to 875°C. Conductivity of molten glass below  $T_g$  (in the case of this glass, 490°C)



**FIGURE 6** Change of conductivity with increased thickness (volume occupied) of accumulated layer in standard solutions having conductivities 10 and 20 S/m

**TABLE 2** Molten glass testing parameters

Test	Parameters
1	Sodium silicate powder only
2	Sodium silicate powder+1.16 mm layer ( $V_s/V=0.21$ ) of spinel crystals
3	Sodium silicate powder+1.89 mm layer ( $V_s/V=0.32$ ) of spinel crystals
4	Sodium silicate powder+2.91 mm layer ( $V_s/V=0.52$ ) of spinel crystals

From Equation 5 where  $V_s/V$  is the fraction of the total electrical path length volume occupied by spinel crystal between probe leads.

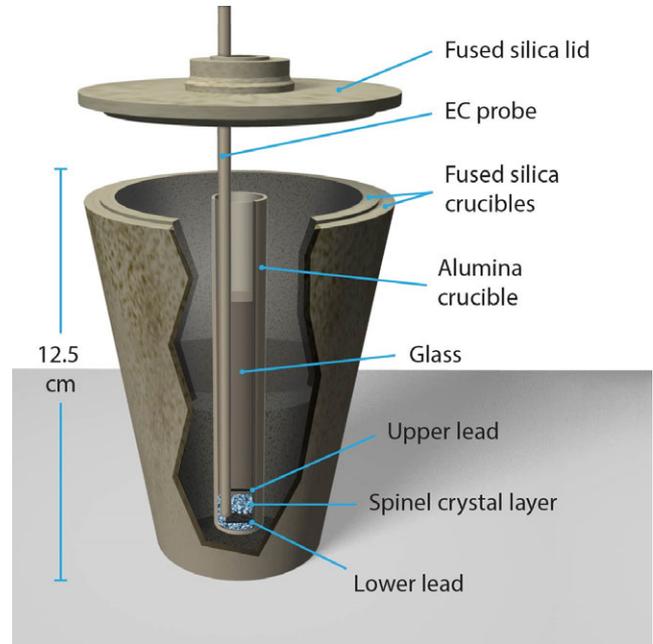
has been found to be an exponential function with temperature<sup>24,25</sup> such that:

$$\sigma = \sigma_0 \exp\left(\frac{-E_\sigma}{k_B T}\right) \quad (7)$$

where  $\sigma$  is the measured conductivity,  $\sigma_0$  is a preexponential factor,  $E_\sigma$  is activation energy,  $k_B$  is the Boltzmann's constant, and  $T$  is temperature in K. Above  $T_g$ , VFT behavior has been observed:

$$\sigma = \sigma_0 \exp\left(\frac{-E_\sigma}{k_B(T - T_{0\sigma})}\right) \quad (8)$$

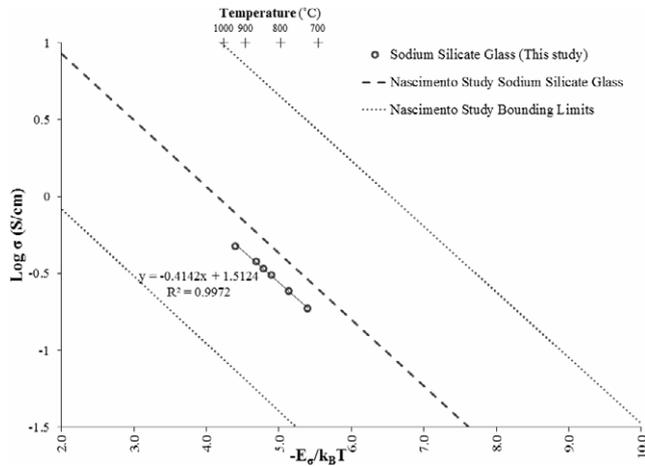
where  $T_{0\sigma}$  is the ideal glass transition temperature. Using this information, four separate tests were performed with different quantities of sodium silicate and spinel crystals (Table 2).



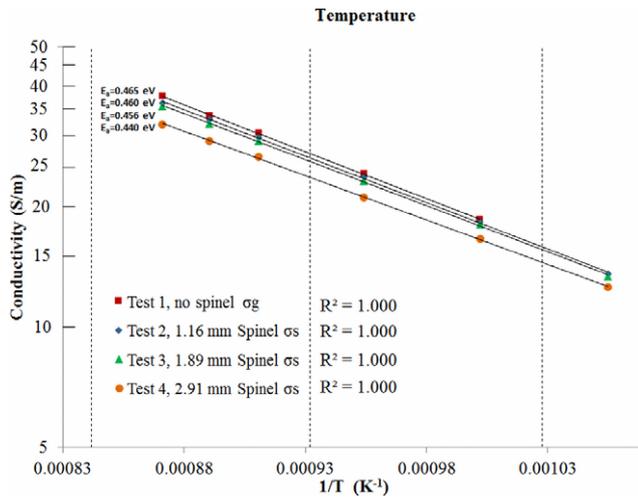
**FIGURE 7** Assembly to monitor crystal accumulation in the glass melt including a detail of electrical conductivity probe

Figure 7 depicts the assembly in which molten glass measurements were performed. The probe was positioned vertically at the bottom of the alumina crucible and, if the test included spinel, the crystals were placed in the crucible followed by sodium silicate powder which filled the crucible to approximately 3/4 of the whole volume. A lid with a hole was placed on the crucible and the entire assembly was transferred into a Deltech furnace with the end leads from the probe attached to the Solartron analyzer cables for conductivity measurements. The furnace was heated at 5°C/min from room temperature to 1200°C with a 60 minutes hold at this temperature. The glass was then cooled stepwise at 5°C/min and held for 3 hours at the following temperatures: 875, 850, 825, 775, 725, and 675°C. Conductivity measurements were taken midway through the hold at each temperature.

The first test (Test 1) measured the electrical conductivity of sodium silicate (spinel-free glass) at elevated temperatures. Nascimento<sup>26</sup> compiled and reported 205 binary sodium silicate glasses as a plot of the log of the conductivity ( $\sigma$ , as S/cm) vs the Arrhenius exponential function ( $-E_\sigma/k_B T$ ). The results of Test 1 are presented in Figure 8 in the same graphical manner with the bounding limits established by Nascimento. Using a best fit linear line and comparing with the Nascimento study, Test 1 showed that sodium silicate measured with the EC probe was nearly identical to the literature study (i.e., both have a y-intercept near 1.5 and a slope near -0.42) and provided further confidence in the probe performance.



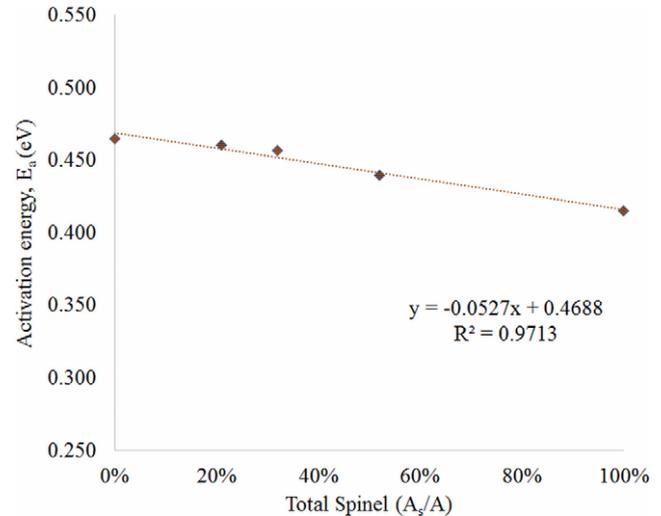
**FIGURE 8** Arrhenius plot of conductivity measured in sodium silicate glass at high temperature



**FIGURE 9** Conductivity vs  $1/\text{temperature}$  (in  $\text{K}^{-1}$ ) with differing layers of spinel

The spinel crystals used to conduct Tests 2-4 were extracted from High-Ni-Fe glass<sup>20</sup> as described in Section 2 (Figure 1 and Table 1). The distance between probe electrodes as well as the depth of the spinel crystal layer were determined after the crucible had cooled and could be cross sectioned and measured. Assuming the Arrhenius relationship described in Equation 7 and plotting each of the tests outlined in Table 2 as conductivity vs  $1/T$  results in Figure 9.

This plot shows that an exponential relationship does exist between conductivity and temperature in glass melts and further indicates that spinel crystals and the thickness of the crystal layer has an effect on the conductivity behavior of the glass/crystal environment. The conductivity curves for the four tests converge at a temperature between 430 and 440°C. This is the temperature range at which the



**FIGURE 10** Activation energies of glass/spinel matrices

conductivity of the spinel crystal and glass are the same. Using Equation 7 to calculate activation energies for each glass/spinel system shows that a linear relationship exists between the activation energy and the degree of spinel impedance in the electrical pathway (Figure 10).

Further, using the additive property (Equation 4) of conductivity with area terms established for each probe (based on post testing cross section measurements, Table 3) along with the relationship of conductivity with temperature (Equation 5), the conductivity of spinel crystal at various temperatures ( $\sigma_s$ ) can be determined (Table 4).

The conductivity for trevorite ( $\text{NiFe}_2\text{O}_4$ ) crystal at 800°C is reported in the literature<sup>14,16</sup> as 20 S/m. The values obtained in this study at 800°C were in excellent agreement at 20-24 S/m. Figure 11 shows the calculated spinel conductivities as a function of temperature

It is important to note that conductivity measurements taken at room temperature decreased with increased spinel volume fraction between electrodes (Figure 6) as did the measurements taken at elevated temperatures in sodium silicate glass. Results in Table 4 show that sodium silicate glass at 850°C has a conductivity of 33.7 S/m whereas the spinel conductivity at the same temperature is ~29 S/m. Spinel buildup would thus induce a decrease in overall conductivity. Typical High-Ni-Fe glass that will be used in the melters, however, has a spinel free conductivity of ~20 S/m at 850°C, which would be much lower than that of the spinel crystal at the same temperature. Therefore, during the planned melter operation, an increase in spinel buildup would induce an increase in overall conductivity—the opposite reaction than either the measurement of spinel in conductivity solution at room temperature or the measurement of spinel in sodium silicate glass at 850°C.

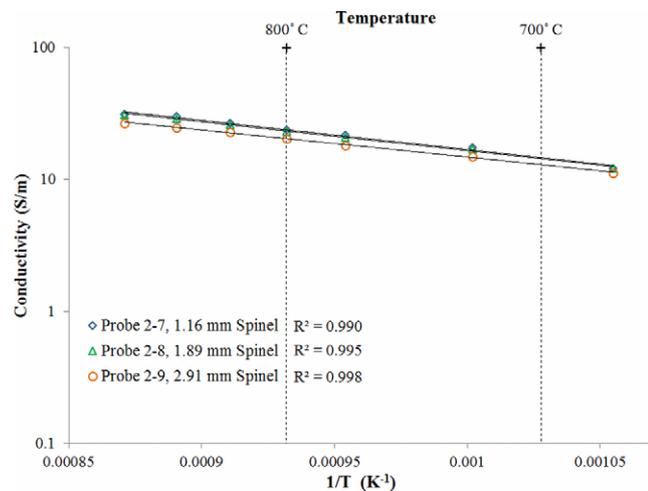
**TABLE 3** Area values used in spinel conductivity calculations

Test	Spinel depth, mm	Distance between probe leads, mm	Total volume, $V$ ( $\text{mm}^3$ )	Volume occupied by spinel, $V_s$ ( $\text{mm}^3$ )	Volume occupied by glass, $V_g$ ( $\text{mm}^3$ )
Test 2	1.16	9.53	152.5	32.2	120.3
Test 3	1.89	10.47	167.5	52.9	114.6
Test 4	2.91	9.28	148.5	76.8	71.6

**TABLE 4** Sodium silicate glass ( $\sigma_g$ ) and calculated spinel ( $\sigma_s$ ) conductivity at various temperatures

Temperature ( $^{\circ}\text{C}$ )	Test 1, conductivity of sodium silicate glass, $\sigma_g$ (S/m)	Test 2, 1.16 mm spinel, $\sigma_s$ (S/m)	Test 3, 1.89 mm spinel, $\sigma_s$ (S/m)	Test 4, 2.91 mm spinel, $\sigma_s$ (S/m)
875	37.65	31.13	31.08	26.93
850	33.71	29.93	28.82	24.89
825	30.41	26.81	26.17	23.05
<b>800</b>	27.08	<b>23.83</b>	<b>23.36</b>	<b>20.44</b>
775	24.14	21.89	21.00	18.10
725	18.51	17.34	16.99	14.86
675	13.96	12.19	12.13	11.28

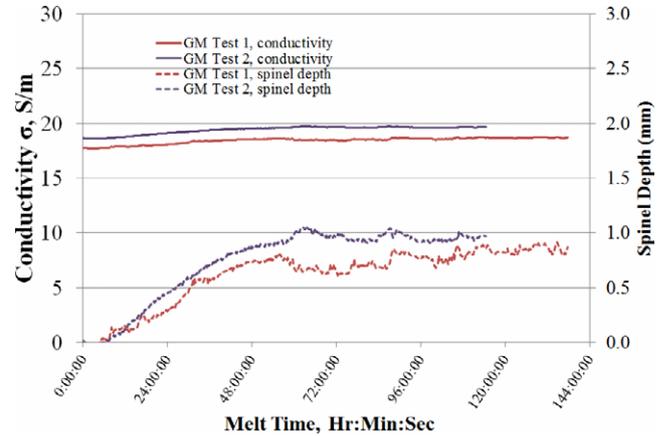
The bold values are indicative of a constant temperature (800C) that conductivities were compared across.



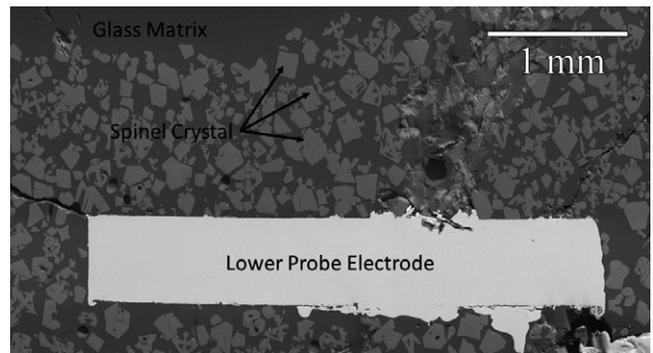
**FIGURE 11** Spinel conductivity as a function of  $1/\text{temperature}$  ( $\text{K}^{-1}$ )

### 3.4 | Laboratory glass melt testing

Two laboratory tests with a high-Ni-Fe glass and conductivity probes were completed at the temperature (850°C) expected in the riser during idling of HLW melter and



**FIGURE 12** Laboratory glass melt (GM) results



**FIGURE 13** Cross section of GM Test 2

were conducted using the same assembly as described in the silicate glass test (see Figure 7). Both conductivity probes were the same in design to those previously described (see Figure 2) and were calibrated with standard conductivity solutions to determine individual geometric factors ( $K, \text{m}^{-1}$ ; Equation 2). One test was idled for 5 days and the other for 6 days, with conductivity measurements taken every 12 minutes. The results are shown in Figure 12; estimated spinel depth was calculated using Equation 5.

At the beginning of testing the glass (presumably spinel-free after heating to 1200°C and holding at this temperature for 1 hour) had a conductivity of  $\sim 17.5\text{--}18.5$  S/m at 850°C. Since the conductivity of spinel at 850°C is higher (29 S/m) than the glass at the same temperature, the gradual buildup of spinel crystal results in an overall increase of measured conductivities. Assuming the spinel occupation of the entire area between electrodes produces a conductivity of 29 S/m at 850°C, and using Equation 5 with the known distance between the probe electrodes, a thickness of spinel layer can be determined. A cross section from glass melt (GM) Test 2 (Figure 13) show a 1.1 mm thick layer which verified the 1.0 mm thick layer as measured

with the conductivity probe (see Figure 12). The experimental accumulation rate for the testing was determined to be 0.02 mm spinel/h. This represents the first data generated that addresses spinel accumulation in HLW glass and can provide a basis for accumulation rates inside the melter.

## 4 | CONCLUSIONS

An electrical conductivity method to monitor crystal accumulation in the riser of a Joule-heated ceramic melter is currently being developed. Results in standard conductivity solutions were within 10% of certified values and provided confidence in the integrity and accuracy of the probe. Testing of the EC probe in standard conductivity solutions with varying thicknesses of accumulated layers of spinel showed a linear decrease in conductivity with increased layer thickness. Testing in sodium silicate glass with well-defined thicknesses of spinel layers enabled determination of the effect of temperature on the conductivity of glass and spinel crystals and the effect of crystal accumulation on glass conductivity. These tests showed the Arrhenius behavior of glass melts with respect to temperature and allowed for the determination of conductivity of spinel crystals at various temperatures. The conductivity of spinel crystals at 800°C, 20-24 S/m, was in good agreement with data from literature. Testing of the EC probe in simulated HLW glass provided a platform to assess crystal accumulation under HLW melter conditions. The changes in the conductivity suggested accumulation of crystals to a layer 1.0 mm thick. This value agreed well with 1.1 mm thick layer as determined from a cross section of the glass melt and probe after testing was completed.

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