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Technical Task Request HLW/DWPF/TTR-00-0016, Rev. 1:

Confirmation Run of the DWPF SME Cycle and Results of the Glass Analysis Using the Sludge-Only Flowsheet with Tank 40 Radioactive Sludge and Frit 200 in the Shielded Cells Facility (U)

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1.0 SUMMARY

Several basic data reports[1, 2, 3] have been issued concerning the recent demonstration of the Defense Waste Processing Facility (DWPF) Sludge Receipt and Adjustment Tank (SRAT) Cycle and Slurry Mix Evaporator (SME) Cycle conducted at the Savannah River Technology Center (SRTC) in support of Sludge Batch 2 (Macrobatch 3). This report describes in detail the SME cycle; glass fabrication, analysis, and acceptability; and the SME Redox Adjustment cycle.

For the SME cycle, water was added to the SRAT product* and then evaporated to simulate the addition and removal of decon water from the canister decontamination process. Frit 200 and dilute formic acid were then added to the SME vessel. Finally, the SME contents were concentrated to 45 wt% solids. During the SME cycle, no foaming was observed, and hydrogen gas generation was well below DWPF limits. It should be noted that SRTC followed DWPF's current antifoam addition strategy as recommended by Koopman[4] (addition of IIT747 antifoam prior to boiling, and every eight hours thereafter).

A small amount of SME product was then vitrified. The resulting glass was analyzed for chemical composition and evaluated using the Product Consistency Test (to measure the glass durability). Based on the chemical composition, the SME product was predicted to produce acceptable glass per the Product Composition Control System (PCCS)†. Also, as determined by the PCT, the glass was significantly more durable than the Environmental Assessment (EA) glass.

In the event that the redox of the SME would need to be adjusted, SRTC added concentrated formic acid to the remaining SME product to evaluate gas generation during the SME Redox Adjustment cycle. While there was some evidence of denitration and more carbon dioxide and hydrogen were produced than during the SME cycle (as expected), no foaming was observed, and hydrogen generation was still well below DWPF limits.

This demonstration was requested by the DWPF through a Technical Task Request (HLW/DWPF/TTR-00-0016, Rev. 1)[5].

2.0 INTRODUCTION

The DWPF is currently processing and immobilizing radioactive sludge slurry into a durable borosilicate glass. After successfully processing Sludge Batch 1B (Macrobatch 2) for approximately 3 years, the DWPF was in need of a new batch of radioactive sludge slurry to continue canistered waste form production. The next batch of radioactive sludge slurry to be processed by the DWPF is called Sludge Batch 2 (Macrobatch 3). Sludge Batch 2 is a mixture of the sludge slurry that was transferred from Tank 8 and the sludge slurry that already existed in Tank 40. Tank 40 is one of the two tanks (the other feed tank is Tank 51) that directly feeds the DWPF.

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* The SRAT product produced in the Shielded Cells is described in Reference 11, "Confirmation Run of the DWPF SRAT Cycle Using the Sludge-Only Flowsheet with Tank 40 Radioactive Sludge and Frit 200 in the Shielded Cells Facility (U)."

† The glass was not acceptable for chromium (see Reference 27). However, the chromium is attributed to contamination from the steel grinder used to prepare the glass for analysis.

Prior to processing a new sludge batch in DWPF, SRTC-Immobilization Technology Section (ITS) must analyze and confirm that each sludge batch produces an acceptable glass[6]. Part of this effort is to perform a glass variability study using nonradioactive simulants and frit (glass forming chemicals) to verify the applicability of the composition/PCT correlation[7]. Another portion of this sludge qualification effort is to perform process testing using nonradioactive sludge slurry simulants prior to processing the actual radioactive material in the Shielded Cells[4]. Finally, an actual sample of the radioactive material is processed in the Shielded Cells and glass is produced to demonstrate the acceptability of the sludge batch[8,9,10].

To perform the Shielded Cells demonstration, twelve dip samples (220 mL/each dip sample) were obtained from Tank 40, prior to sludge washing, and sent to the SRTC Shielded Cells Facility. The samples were combined and an initial composition of the radioactive sludge slurry was obtained. Since the sludge was unwashed and sodium concentration of the sludge slurry did not meet the DWPF acceptance criteria, a demonstration of the Tank Farm's Extended Sludge Processing (ESP) was performed by the Waste Processing Technology Section (WPTS). The sludge slurry was washed to a target endpoint of 0.55M Na (± 0.05M Na) in the supernate to meet the acceptance criteria of the DWPF. Upon receipt of the washed sludge slurry from WPTS, a demonstration of the DWPF "Sludge-Only" flowsheet was performed using approximately one liter of sludge slurry. The DWPF "Sludge-Only" flowsheet calls for processing radioactive sludge slurry using nitric acid, concentrated formic acid, and Frit 200 through the Chemical Processing Cell (CPC) of DWPF.

Information concerning processing, offgas data, and analyses of the final washed sludge slurry composition and final SRAT product can be found in a previous report[11]. Information concerning the SME cycle, vitrification, non-radioactive chemical analyses of the SME product, Product Consistency Test results, and SME Redox Adjustment Cycle are presented in this report. Radionuclide analyses of the SME product will be reported in a later report.

3.0 DESCRIPTION OF THE SYSTEM AND CALCULATIONS USED TO PERFORM THE SME CYCLE AND GLASS FABRICATION

The sections below provide a description of the system used in the Shielded Cells to perform the Tank 40 demonstration and the data used to calculate the amounts of glass frit needed to complete the SME cycle.

3.1 Experimental Equipment Description

The SRAT/SME vessel used in this confirmation run is a glass cylinder approximately 13 inches in height and 6 inches in diameter. The SRAT/SME vessel has a capacity of approximately 2 liters, and the top of the SRAT/SME vessel has a series of ports and openings. These ports and openings are for the installation of equipment (i.e. pH probe, thermocouple, agitator, etc.) and process lines (acid addition, air purge, etc.). The condenser, mercury/condensate trap, and cold trap connected to the SRAT/SME vessel are also made out of glass.

To supply heat to the SRAT/SME vessel, a heating mantle is used. Also, a laboratory chiller unit is used to supply the chilled water for the condenser. Figure 1 is a picture taken in the Mockup Cells of the system prior to installation in the Shielded Cells.
Figure 2 is a picture of the top portion of the vessel showing the ports/openings for the SRAT/SME vessel.

Figure 1 - Picture of the SRAT/SME Vessel in the Mockup Cells of the Shielded Cells Facility

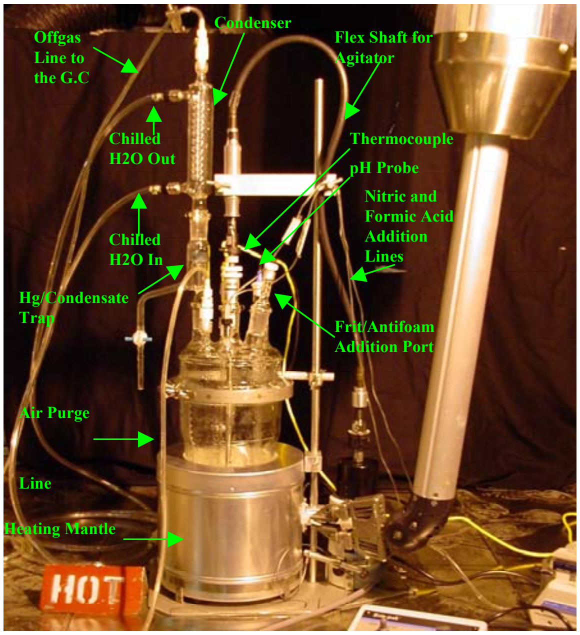
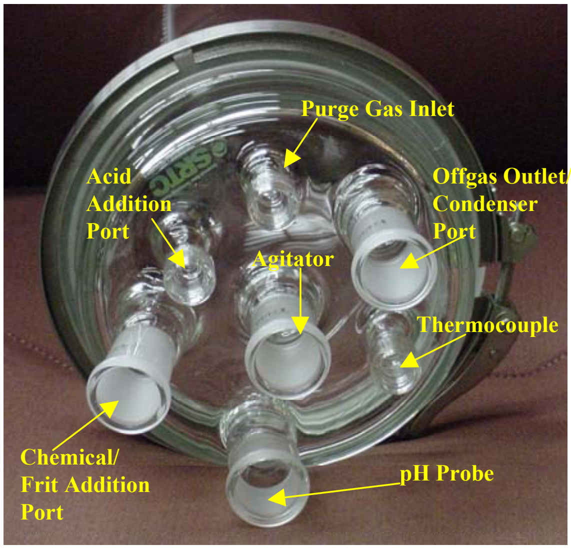


Figure 2 - Picture of the Top View of the Connections/Ports for the SRAT/SME Vessel Prior to Entry into the Shielded Cells



The SRAT/SME is purged using air with 0.5% (nominal) helium. By measuring the helium in the vessel purge, gas generation rates can be calculated. The purge gas composition is measured using a Varian CP-2002 Micro-GC gas chromatograph (GC). Column A contains a Molsieve 5A column with argon carrier gas. It separates helium, hydrogen, oxygen, and nitrogen. Column B contains a PoraPlot Q column with nitrogen carrier gas. It separates carbon dioxide and nitrous oxide. The GC is located in a radiohood behind the Shielded Cells.

A CM FURNACES Model 1708 BL bottom loading box furnace was used to vitrify the SME product. The furnace was equipped with a programmable controller that enabled the control of furnace heatup.

3.2 Calculations for the Blending of the Frit 200 and SRAT Product Compositions

To determine the amount of Frit 200 to be added to the SRAT product for the SME cycle, SRTC provided Waste Disposition (WD) Engineering with the SRAT product volume and composition[12]. WD Engineering used this information to complete the blending calculations. The results of the calculations were documented in a memo and transmitted to SRTC prior to the start of the SME cycle[13]. Table 1 presents the SRTC SRAT product composition[11], the Frit 200 composition (from WD Engineering), and resulting calculated blend composition for the SRTC SME cycle.

Table 1 - Information Used to Complete the Blending Calculations for the SRTC SME Cycle

	SRTC SRAT Product	**Frit 200**	**Calculated SRAT Product/ Frit 200 Blend**
Wt% Total Solids	20.2	45.0	51.00
Calcined Wt% Solids	15.7	45.0	46.70
Specific Gravity	1.15	1.30	1.463
Elements	**Ave. Elemental Wt. % (dried slurry basis)**	**Ave. Elemental Wt. % (vitrified basis)**	**Elemental Wt. % (vitrified basis)**
Al	5.56	0.36	2.262
B	0.03	3.59	2.554
Ca	2.19	0.18	0.915
Cr	0.15	--	0.054
Cu	0.04	--	0.015
Fe	22.3	0.04	8.076
K	0.04	0.12	0.097
Li	0.07	2.23	1.605
Mg	1.77	1.17	1.465
Mn	2.97	--	1.072
Na	7.88	8.07	8.567
Ni	1.13	--	0.408
Si	0.99	32.32	23.282
Ti	0.02	0.03	0.029
U	6.85	--	2.472
Zr	0.02	--	0.006
Volume Weight	722 mL N/A	N/A 329.76 g	N/A

4.0 DESCRIPTION OF THE SME CYCLE, GLASS FABRICATION, GLASS ANALYSIS, AND SME REDOX ADJUSTMENT CYCLE

4.1 SME Cycle

Initiation – Heating and Agitation
Initiation of the SME cycle began at 0715 on 17 October 2001 when the agitator to the SME vessel was turned on. Heatup of the vessel began at 0730 when power was supplied to the heating mantle.

Antifoam was added at 0835 when the vessel temperature reached 50°C. Additional antifoam was added every eight hours thereafter.

Decon Water Addition and Removal
At 1044, with the SME contents boiling, water was added to the vessel to simulate the addition of water from the decontamination of five canisters. Water addition took approximately 50 minutes. This water was then boiled off over the next nineteen hours.

Frit/Formic Acid Addition
On 18 October 2001 at 0720, the first of two frit additions began. First, dry frit was poured into the vessel. Second, dilute formic acid was pumped into the vessel. Third, the vessel contents were boiled to reduce the volume to its original level. Beginning at 1430, the second frit/formic acid addition/concentration was begun.

Final Concentration
Upon reaching approximately 45 weight percent total solids, during the SME cycle, the condensate collection rate decreased from approximately 0.24 mL/min to approximately 0.12 mL/min. The heat to the vessel was increased, but the condensate rate remained unchanged. This indicated that the target weight percent total solids of 51% was not achievable due to the inability to transfer more heat to the vessel. At 2300 on 18 October 2001, with WD Engineering concurrence, the SME cycle was concluded when heat to the vessel was turned off.

Antifoam Additions
The antifoam strategy (as recommended by Koopman[4]) of adding 100 ppm of IIT747 antifoam before boiling and refreshing with additions of 100 ppm antifoam every eight hours thereafter was followed. It should be noted that for the Shielded Cells SME cycle the first antifoam addition occurred when the vessel temperature reached 50°C rather than just before boiling. No unscheduled antifoam additions were required during the SME cycle.

Following the SME cycle, the SME product was sampled for weight percent total solids and density measurements. A sample was also removed for vitrification (see following section). The remaining SME product was left in the vessel for the SME Redox Cycle (see Section 4.4). Table 2 lists some of the key processing parameters during the SME Cycle. Appendix B shows the calculations used for the SME cycle.

Table 2 - Processing Parameters During the SRTC SME Cycle

Parameter	Value	Comment
Purge Rate	20.5 cc/min	SRTC purge is 1/3 of DWPF scale for better gas measurement sensitivity.
SRTC SME Volume	722 mL	For comparison purposes, it is assumed that the DWPF SME volume is 6,000 gal.
Decon Water Volume and Addition Rate	602 mL at 12 mL/min	This corresponds to the decon water for 5 canisters. (1,000 gal/can, SME volume of 6,000 gal).
Frit Addition	329.76 g	Calculated by WD Engineering.
Dilute Formic Acid Added	335.3 g at 1.5 wt%	Rather than mixing frit and formic acid as DWPF, SRTC added the frit and acid separately in two equal batches (frit, acid, then frit, acid).
IIT747 Antifoam Added	1.66 mL of a 5 wt% solution per addition	This amount of antifoam solution is intended to give an antifoam concentration in the vessel of 100 ppm.

Note that the values above are those actually used during the SME cycle. They may be slightly different than the calculated values given in Appendices A and B.

4.2 Glass Preparation

The glass was prepared remotely by drying and melting the SME product slurry in a 100-mL platinum crucible in a programmable electric furnace in Cell 1 of the Shielded Cells. The crucible was partially filled with 102.5 grams of the SME product slurry (45.3 wt. % solids). The crucible was placed in a drying oven in Cell 1 at 40°C, heated to 106°C, and held for 6.5 hours to dry. After drying, a thin layer of white material was noted on the surface. This material was probably dried salts that were soluble in the slurry. The crucible containing the SME product was then set in a kyanite catch crucible and placed into the furnace. The furnace was programmed to ramp up to 1150°C in four hours. When the furnace reached 1150°C, the temperature was maintained for 4 hours. The heating steps (drying, ramped heating, and high-temperature hold) are to ensure dryness, decomposition of the nitrates and any residual nitrites, and to provide the opportunity to produce a homogeneous melt. The crucible was then removed from the furnace at temperature. The glass was quenched by setting the crucible in a shallow pan of water (i.e., water only had contact with the outside of the crucible) and then allowed to cool to ambient temperature in the cell. The cooled glass was then removed from the crucible and stored in a labeled jar.

4.3 Glass Analysis and Evaluation

The measured elemental composition of the glass was obtained by dissolving samples of the ground glass and analyzing the resulting solutions using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES). Dissolution of the glass samples was performed remotely in the Shielded Cells of SRTC. A portion of the glass sample was dissolved in quadruplicate by two separate dissolution methods, mixed acid dissolution and sodium peroxide fusion, according to approved procedures[9]. The acid dissolution method uses boric acid to complex the fluorine used to help dissolve the glass. Thus, the boron content of the glass cannot be obtained by this method. The sodium peroxide fusion uses sodium peroxide to convert the glass to hydroxide salts that are then dissolved in acid. Thus, the sodium content of the glass cannot be obtained by this method. All fusions were performed in zirconium crucibles; thus, the zirconium content of the glass could not be obtained by this method. The silicon in the glass is best determined by the peroxide fusion method because of incomplete dissolutions by the mixed acids. Calcium, copper, and iron are present as impurities in the zirconium crucibles, so these elements were determined by the mixed acid dissolution. Uranium was determined by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). This technique is not applied to the solutions from the peroxide fusion method because the high concentration of the sodium affects the performance of the instrument. Thus uranium was determined by analyzing solutions from the mixed acid dissolution.

The samples for the dissolutions were obtained from the glass that was ground in a stainless steel grinder and then sieved for the PCT (see below). The glass used for dissolutions passed through a 200-mesh (<74 µm) sieve. Since the glass was ground in a stainless steel grinder, some stainless steel contamination was present in the glass samples used for dissolutions[‡]. The additional iron from the steel does not significantly affect the final glass composition or property predictions because of the large amount of iron already in the glass. However, the chrome addition from the stainless steel, albeit small in an absolute sense, can affect the Cr concentration in the final glass. A standard glass with a composition similar to the DWPF glass, Analytical Reference Glass-1 (ARG-1)[14], was also dissolved and analyzed concurrently with the Tank 40/Frit 200 glass. Results for oxides present in amounts greater than one weight percent were within five percent of the published values. This indicates that the dissolutions were complete and the analytical procedures were performed correctly.

A qualitative measure of glass composition and an assessment of homogeneity with respect to crystallization were obtained by examining a glass sample using a Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Spectroscopy (EDS).

In addition to composition, the glass quality was evaluated using the Product Consistency Test (PCT) Part A[15]. The PCT, a crushed glass leach test using ASTM Type I water, was performed in quadruplicate in Cell 14 on crushed, ground samples of the glass. The test, which was performed at 90°C for seven days, included the Environmental Assessment (EA)[16] glass, appropriate blanks, and standard ARM-1 glass.

The concentrations of several elements and radionuclides in the leachate were measured using ICP-ES, Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS), and radioactive counting techniques. The concentrations were used along with the measured chemical composition of the glass to calculate the average normalized releases in terms of grams of glass dissolved per liter of leachate based on specific elements and radionuclides in the glass.

4.4 SME Redox Adjustment Cycle

Initiation – Heating and Agitation
The SME Redox Adjustment Cycle began on 12 December 2001 at 0717 when the vessel agitator and heater were turned on. Upon reaching 50°C in the vessel (0817), a 100 ppm addition of IIT747 antifoam was made.

Formic Acid Addition

[‡] With the concurrence of WD Engineering (personal communication between S. L. Marra (SRTC) and J. E. Occhipinti (WDE)), a stainless steel grinder was used with the knowledge that grinding of the glass could impart stainless contamination to the ground glass. This was done because it relieved scheduling problems in the SRTC shielded cells.

Formic acid addition began at 1008, and was completed at 1155. The vessel temperature remained approximately 91°C during the addition. Due to the uncertainty of foam potential from the acid additon, an antifoam addition was made at 1215. It should be noted that no foaming was observed.

Reflux

At 1450, boiling was observed, and the vessel was allowed to reflux (i.e., no condensate was removed during boiling). At 1850, the process was stopped by turning off the heater and agitator, and discontinuing offgas sampling. Table 3 lists some of the key processing parameters. Appendix C shows the calculations used for the SME Redox Adjustment cycle.

Table 3 - Processing Parameters During the SME Redox Adjustment Cycle

Parameter	Value	Comment
Purge Rate	14.5 cc/min	SRTC purge is 1/3 of DWPF scale for better gas measurement sensitivity.
SME Product Wt% Total Solids	45.3	DWPF targets between 45 and 51 wt% total solids for SME product.
SRTC Final SME Product Volume	540 mL	For comparison purposes, it is assumed that the DWPF final SME product volume is 6,000 gal.
Formic Acid Added	25.2 mL of 90 wt% (22.8 M)	This corresponds to 280 gal of formic acid added to 6000 gal of SME Product in the DWPF
Reflux Time	4 hours	DWPF does not reflux the SME after a formic acid addition. SRTC refluxed the vessel several hours to measure worst case hydrogen generation.
IIT747 Antifoam Added	1.24 mL of a 5 wt% solution per addition	This amount of antifoam solution is intended to give an antifoam concentration in the vessel of 100 ppm.

Note that the values above are those actually used during the SME redox adjustment cycle. They may be slightly different than the calculated values given in Appendix A and C.

5.0 RESULTS AND DISCUSSION OF THE SME CYCLE, GLASS ANALYSIS AND EVALUATION, AND SME REDOX ADJUSTMENT CYCLE

5.1 Weight Percent Solids, Weight Percent Calcined Solids, and Density Measurements for the Tank 40 SME Product

Quadruplicate measurements of the total weight percent solids for the sludge slurry were completed remotely in the SRTC Shielded Cells. Mixed portions of a sample of SME product were pipetted into four labeled, pre-weighed PMP® beakers. After the addition of the mixed SME product, the PMP® beakers were weighed and placed into a drying oven at 115°C overnight. The samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. To check the accuracy and precision of the method, three samples of a 15 wt. % NaCl standard solution were also weighed and dried (in labeled PMP® beakers) along with the SME product samples. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard[29]. The averages, standard deviations (Std. Dev.), and the percent relative standard deviations

(% RSD) of the calculated results of the weight percent solids for the SME product are presented in Table 4.

To determine the weight percent dissolved solids, a mixed sample of the SME product was filtered through a Nalgene® filter resulting in a clear supernate. The clear supernate was then mixed and four samples were pipetted into four labeled, pre-weighed PMP® beakers. The same procedure was followed for the SME supernate samples as for the SME product samples (see above paragraph). The averages, standard deviations (Std. Dev.), and the percent relative standard deviations (% RSD) of the calculated results of the weight percent dissolved solids for the supernate are presented in Table 4.

Duplicate measurements of the calcined solids were completed in the Shielded Cells Facility for the SME product. Mixed portions of a sample of SME product were pipetted into two pre-weighed alumina crucibles. The crucibles were weighed and then dried overnight at 115°C in a drying oven. By removing excess water from the samples, the risk of splattering material from the crucibles when heated to the calcine temperature is minimized. The samples were removed from the drying oven and allowed to cool for ~5 minutes before they were weighed. The samples were then placed into a muffle furnace and heated to 1000°C. The samples were held at 1000°C for ~ 2 hours. The muffle furnace was turned off and the samples were allowed to cool inside of the muffle furnace. The samples were then removed from the muffle furnace, weighed, and the calcined solids were calculated. The averages, standard deviations (Std. Dev.), and the percent relative standard deviations (% RSD) of the calculated results of the calcine solids for the sludge slurry are presented in Table 4.

Density measurements of the SME product were completed remotely in the Shielded Cells Facility by using heat sealed pipette tips. The pipette tips are first sealed and then calibrated with water to obtain the volume. Four density measurements were completed for the SME product. The sealed pipette tip was first weighed and then a mixed sample of SME product was pipetted into the sealed pipette tip. The sealed pipette tip containing the SME product sample was weighed and a density calculated. The results of the density measurements, along with the standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD), are presented in Table 4.

The supernate obtained for the weight percent dissolved solids measurement was also used to complete the SME product supernate density measurements. The same density procedure (see above paragraph) was followed to obtain the results for the SME supernate. The results of the density for the SME supernate sample with the standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) are presented in Table 4.

Weight percent insoluble solids, weight percent soluble solids, and the vitrification factor are presented in Table 4. These values are calculated using the weight percent total solids, dissolved solids, and calcined solids results described above. The calculations are shown in Appendix D.

Table 4 - Weight Percent Solids, Weight Percent Calcined Solids, Density Measurements, and Vitrification Factor for the Tank 40 SME Product

	Average	Std. Dev.	% RSD
Weight Percent Total Solids [a, b] **(g total dried solids/100 g SME product)**	45.3 wt%	0.52	1.1
Weight Percent Dissolved Solids [a, c] **(g dissolved solids/100 g SME product supernate)**	7.64 wt%	0.062	0.81
Weight Percent Calcined Solids [c, d] **(g calcined solids/100 g SME product)**	41.6 wt%	1.1	2.6
Density of the SME Product [e]	1.36 g/mL	0.035	2.6
Density of the SME Product Supernate [b]	1.04 g/mL	0.0024	0.23
Weight Percent Insoluble Solids (g insoluble solids/100 g SME product)	40.8 wt%	0.57	1.4
Weight Percent Soluble Solids (g soluble solids/100 g SME product)	4.5 wt%	0.77	17
Vitrification Factor (g glass/mL SME product)	0.566	0.021	3.7

[a] The samples for weight percent solids measurements were dried overnight in a drying oven at 115°C.
[b] Average of three results.
[c] Average of two results.
[d] Samples were calcined at 1000°C.
[e] Average of four results.

5.2 SME Cycle Gas Production

The SME vessel was purged using air with 0.5% (nominal) helium. The helium was used as a tracer to calculate flow out of the vessel and gas generation rates. The composition of the gas produced during the SME cycle was measured using a GC located in a hood outside of the SRTC Shielded Cells. The GC was capable of measuring helium, hydrogen, oxygen, nitrogen, carbon dioxide, and nitrous oxide. It should be noted that many of the oxides of nitrogen were likely produced in the SME cycle, but the GC was only capable of measuring nitrous oxide.

Figure 3 shows the hydrogen (H_2), carbon dioxide (CO_2), and nitrous oxide (N_2O) concentrations during the SME cycle. Table 5 lists the maximum concentrations and generation rates, on a DWPF basis, of H_2, CO_2, and N_2O (see Appendix A for details of conversion from SRTC to DWPF basis).

Figure 3 - SRTC Scale Hydrogen, Carbon Dioxide, and Nitrous Oxide Concentrations and pH in the Offgas During the SME Cycle

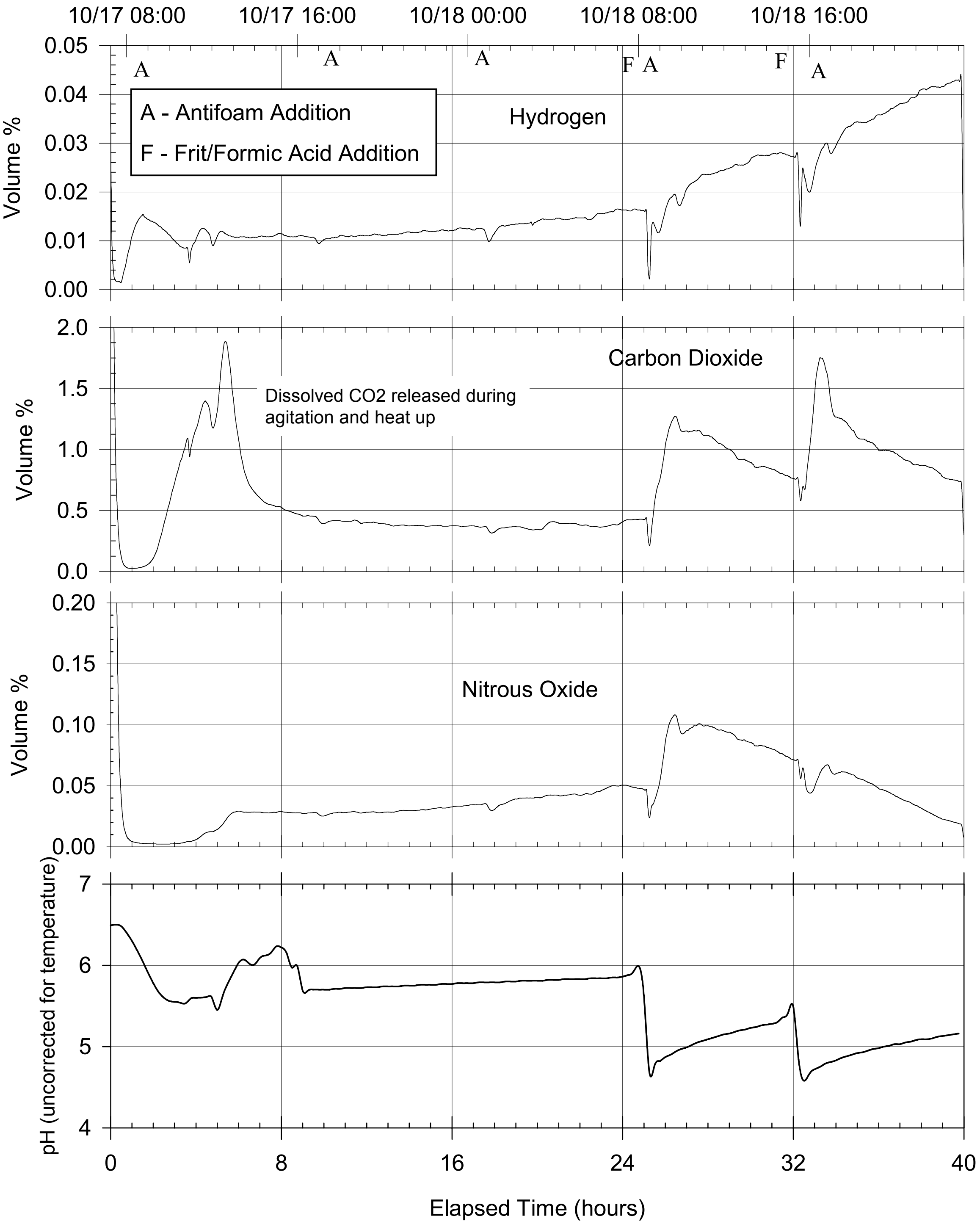


Table 5 - Maximum Hydrogen, Carbon Dioxide, and Nitrous Oxide Generation During the SME Cycle

	SRTC Scale Maximum Gas Concentration (Vol. %)	DWPF Scale Maximum Gas Concentration † (Vol. %)	DWPF Scale Maximum Generation Rate † (lb/hr)
Hydrogen	4.3E-02	1.5E-02	3.0E-03
Carbon Dioxide	1.9E00	6.7E-01	3.0E00
Nitrous Oxide	1.1E-01	3.9E-02	1.7E-01

† Appendix A provides the inputs and assumptions used for calculating gas generation during the SME cycle.

As can be seen from Figure 3, H_2, CO_2, and N_2O were produced following the frit/formic acid additions. The H_2 and CO_2 were likely the result of catalytic decomposition of formic acid, and the N_2O may be evidence of reaction between nitric and formic acids (see the discussion of the SME Redox Adjustment Cycle, Section 5.6, for a more detailed discussion of the chemistry).

5.3 Chemical Composition of Vitrified SME Product

Table 6 shows the elemental weight percents of the major components in the glass made from the SME product. Table 7 presents the same data, with the elements converted to their oxide forms. Table 7 also shows the calculated composition of the glass based on the blend (see Section 3.2). Except for Cr_2O_3, CuO, K_2O, NiO, TiO_2, and ZrO_2, the measured values agree well with the calculated. As mentioned earlier, the glass was ground for analysis in a stainless steel grinder. This could account for the higher than predicted chromium and nickel values. Copper contamination could have resulted from the brass sieve used to sieve the glass for dissolution. Potassium, titanium, and zirconium are minor constituents in the glass, and the difference between predicted and analyzed result could be analytical error.

Table 6 - Required Elements (excluding oxygen) for Checking the SME Acceptability for the Tank 40 /Frit 200 SRTC Vitrified SME Product

Element	Weight Percent [*, a]	Element	Weight Percent [*, a]
Al	2.26E00 (± 7.3E-02, 3.2E00)	Mg	1.50E00 (± 5.7E-02, 3.8E00)
B [c]	2.55E00 (± 3.9E-02, 1.5E00)	Mn	1.07E00 (± 3.6E-02, 3.4E00)
Ca [c]	9.27E-01 (± 4.6E-02, 5.0E00)	Na [c]	8.83E00 (± 4.4E-02, 4.9E-01)
Cr [b]	2.26E-01 (± 1.6E-02, 7.2E00)	Ni [b]	4.74E-01 (± 1.3E-02, 2.7E00)
Cu [c]	7.14E-02 (± 1.2E-03, 1.7E00)	P	2.46E-01 (± 1.5E-02, 5.9E00)
Fe [b, c]	8.26E00 (± 1.6E-01, 2.0E00)	Si [c]	2.48E01 (± 3.5E-01, 1.4E00)
K [d]	1.36E-01 (± 6.8E-04, 5.0E-01)	Ti	4.87E-02 (± 2.3E-03, 4.8E00)
Li	1.63E00 (± 2.7E-02, 1.6E00)	U [c, e]	2.53E00 (± 5.7E-02, 2.3E00)
		Zr [c]	9.45 E-02 (± 2.7E-03, 2.9E00)

[*] The SME product was vitrified at 1150°C. The resulting glass was dissolved. The results are presented as elemental weight percent in the glass.

[a] Results are determined by Inductively Coupled Plasma-Emission Spectroscopy unless otherwise indicated and are the average of eight sample results of dissolved glass. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

[b] Slightly contaminated with Cr, Ni, and Fe from the stainless steel Tekmar grinder used to grind the glass. Calculated values for Cr, Ni, and Fe for the blend of Tank 40 and Frit 200 were 0.054 wt. %, 0.408 wt. %, and 8.08 wt% respectively[13].

[c] Average of four results.

[d] Results determined by Atomic Adsorption method.

[e] Results determined by Inductively Coupled Plasma-Mass Spectroscopy method.

Table 7 - Average Measured and Calculated Composition (Major Oxide Wt%) of the Vitrified SME Product

Oxide	Measured Composition (wt%)	Calculated Composition [b] (wt%)
Al_2O_3	4.27E+00	4.27E+00
B_2O_3	8.21E+00	8.22E+00
CaO	1.30E+00	1.28E+00
Cr_2O_3	3.30E-01	7.89E-02
CuO	8.94E-02	1.88E-02
Fe_2O_3	1.18E+01	1.16E+01
K_2O	1.64E-01	1.17E-01
Li_2O	3.51E+00	3.45E+00
MgO	2.49E+00	2.43E+00
MnO	1.38E+00	1.38E+00
Na_2O	1.19E+01	1.16E+01
NiO	6.03E-01	5.19E-01
SiO_2	5.31E+01	4.98E+01
TiO_2	8.12E-02	4.84E-02
UO2	2.87E+00	2.80E+00
ZrO_2	1.28E-01	8.10E-03
Total	1.02E+02	9.76E+01

5.4 Product Consistency Test (PCT)

The PCT is a standard ASTM leach test[15]. The test is a crushed glass leach test using ASTM Type I water. It was performed in Cell 14 on quadruplicate samples of crushed, ground Tank 40/Frit 200 glass following the ASTM-1285-97 procedure. The test, which was performed at 90°C for seven days, included the appropriate blanks and standards (Approved Reference Material-1 (ARM-1) glass) and a multi element analytical standard. The results for the ARM-1 standard glass and the blanks indicated that the test was acceptable. The Tank 40/Frit 320 glass was included in this PCT and the results for the standards and blanks are given in Appendix B of the Tank 40/Frit 320 Report[17]. The Environmental Assessment (EA) glass was included in the PCT test in order to compare its durability with that of the Tank 40/Frit 200 glass.

The concentrations of several elements and radionuclides in the leachates were measured using Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES), Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS), and radioactive counting techniques. The PCT procedure requires the measurement of Na, Li, and B, because these are the major elements in the glass that are the best indicators of the durability of the glass. We measured the concentrations of radionuclides detected in the leachates to determine if any had normalized releases larger than those for Na, B, or Li. The measured concentrations of the radionuclides were used along with their measured concentrations in the glass to calculate the average normalized releases in terms of grams of glass dissolved per liter of leachate based on a specific element or radionuclide in the glass. The normalized releases were calculated using the following equation.

$$NR_i = \frac{C_i}{F_i \cdot 10}$$

where NR_i = the normalized release based on element i
C_i = the concentration (ppm) of i in the leachate
F_i = the weight percent of i in the glass.

Results are presented for boron, sodium, lithium, and silicon in Table 8 as the average of the normalized releases. Values for the pH of the leachates are also presented. Values predicted using the PCT/chemical composition correlations from THERMO[18] are also presented. The average measured values for the EA glass are also presented along with published values[16]. Silicon is not required by the WAPS[19] but is provided because it is a major component of the glass. The leachate pH was measured as part of the PCT protocol and provides a secondary indication of glass durability. Typically, the higher the leachate pH, the lower the durability.

Table 8 - Normalized PCT Results for Major Nonradioactive Element in Tank 40 Frit 200 Glass and for the Environmental Assessment Glass

Element	Measured [a] (g Glass/L)	Predicted [b] (g/L)	Measured /Predicted	Measured EA [a] (g/L)	Published EA [c] (g/L)
B	0.887±0.011 (1.1)	0.64	1.4	18.6±0.5(2.5)	16.7
Na	0.809±0.009 (1.2)	0.64	1.3	14.0±0.3(2.2)	13.3
Li	0.867±0.008 (1.1)	0.68	1.3	9.96±0.19(1.9)	9.57
Si	0.504±0.004 (0.80)	N/A	N/A	4.3±0.1(2.1)	3.9
pH	9.9	N/A	N/A	11.6	11.9

[a] Based on quadruplicate samples of the Tank 40/Frit 200 and EA glass. For each glass, the standard deviation of the mean is given as the uncertainty along with the percent relative standard deviation (in parenthesis) based on the leachate analyses only.
[b] Predicted by Reference 27.
[c] Published results for EA glass are taken from Reference 16.

The normalized elemental release ranges reported in Table 8 indicate that the Tank 40/Frit 200 glass met the PCT acceptance criterion as defined in the WAPS[19] . This criterion states that the durability of the glass produced must be at least two standard deviations lower than the EA glass[16] in a PCT test. The fact that the Tank 40/Frit 200 glass is more durable than the EA glass is also indicated by the lower final pH value for the leachates of the Tank 40/Frit 200 glass. For some reason the measured releases for boron, lithium, and sodium were all slightly higher than the the published values for the EA glass even though the ARM glass releases were acceptable (see Reference 18). The agreement between the measured and predicted normalized releases in Table 8 for the Tank 40 Frit 200 glass is similar to that observed for the Frit 320 glass[18].

Table 9 presents the normalized releases calculated for several radionuclides in the Tank 40/Frit 200 glass. Results for B, Na, Li, and Si are repeated in Table 9 for ease in comparing their results with those for the radionuclides. Weight percents of the elements in the glass along with their concentrations in the leachates are presented to illustrate the large range in these measured values (24.8 to 8.9E-05 wt% and 125 to 4.8E-05 ppm, respectively).

Table 9 - Normalized PCT Results for Major Nonradioactive Elements and Several Radionuclides in Tank 40 Frit 200 Glass [a]

Element	Wt. % In Glass	Leachate Concentration (ppm)	Normalized Release (Grams Glass/L)
B	2.55	22.6	0.89(1.2%)
Na	8.83	71.4	0.81(1.1%)
Li	1.63	14.1	0.87(0.9%)
Si	24.8	125.	0.50(0.80%)
Sr-90	1.1E-03	8.5E-05 [b]	0.0077(9.6%)
Tc-99	2.3E-04	2.1E-03 [c]	0.91(2.2%)
Cs-137	8.9E-05	1.45E-04 [d]	0.16(5.1%)
Th-232	6.5E-03	4.0E-03 [c]	0.061(12%)
Np-237	4.6E-04	1.1E-04 [c]	0.024(58%)
U-238	2.53	3.73 [c]	0.15(8.7%)
U-235	9.7E-03	1.6E-02 [c]	0.16(4.8%)
Pu-239	3.4E-03	1.4E-03 [c]	0.041(5.4%)
Pu-240	3.2E-04	1.3E-03 [c]	0.041(8.7%)
Am-241	2.7E-04	4.8E-05 [d]	0.018(6.0%)

[a] Based on quadruplicate samples of the Tank 40/Frit 200. For the normalized releases, the standard deviation of the mean based only on the leachate analyses is given in parenthesis.
[b] Measured by beta counting after special separation.
[c] Measured by ICP-MS
[d] Measured by gamma counting.

Note that the only radionuclide that has a normalized release similar to B, Na, or Li is Tc-99. This has been observed in another PCT test with a DWPF type glass[20] and a leach test using a small monolith of a DWPF type glass doped with Tc-99[21].

Normalized releases for U and Cs-137 are nominally 5-6X lower than those for B, Na, or Li, while the other radionuclides have even lower releases. It should be noted that in this PCT test, the vessels were not rinsed with acid after the test to strip those radionuclides that may have sorbed on the walls of the vessel. Thus normalized releases for some of the radionuclides that have low solubilities could be higher than what is reported in Table 9. Such radionuclides are Sr-90 and Pu. From the data in Table 9, the normalized release for Sr-90 is ~100X lower than those for B, Na, or Li, while that for Pu is ~20X lower. In a PCT at SRS[22] with two different radioactive glasses where the vessels were acid stripped, the normalized releases for Sr-90 were 25 to 250X lower than those for B, Na, or Li. For Pu, the releases were 4 to 10X lower. Results for Cs-137 were 4-5X lower than those for B, Na, or

Li, in agreement with the results calculated from Table 9. Thus it appears that sorption on the vessel walls can be a factor but not large enough to make the measured releases for these elements to be as large as those for B, Na, or Li. Sorption on the walls has been shown not to occur with Tc-99[21]. Thus its release given in Table 9 is the total release for Tc-99. Based on the data in Table 9 and the results published in Reference 22, it can be said that of all the radionuclides measured, only Tc-99 has a release rate similar to B, Na, or Li, the elements that are to be measured in the PCT.

5.5 Examination of the Tank 40/Frit 200 Glass by Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Spectroscopy (EDS) were used to examine the vitrified SME product. One sample of approximately 0.015 grams of vitrified SME product was prepared for analysis. The sample was from glass that had been ground, washed, and sieved for the PCT. A typical micrograph for the sample is shown in Figure 4. EDS analysis of the sample showed that the main glass components were Si and Fe (see Figure 5). The arrow in Figure 4 indicates a particle whose image is shown in Figure 6 at a larger magnification.

Figure 4 - SEM Micrographs of the Vitrified SME Product Sample at 50x

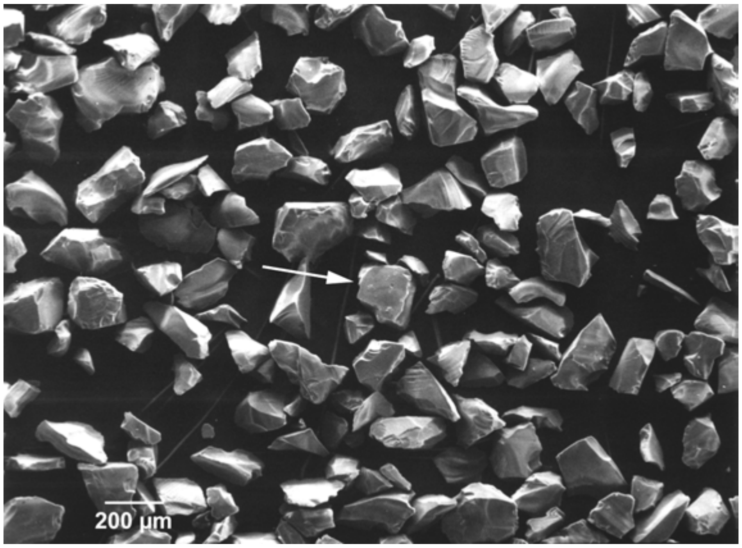
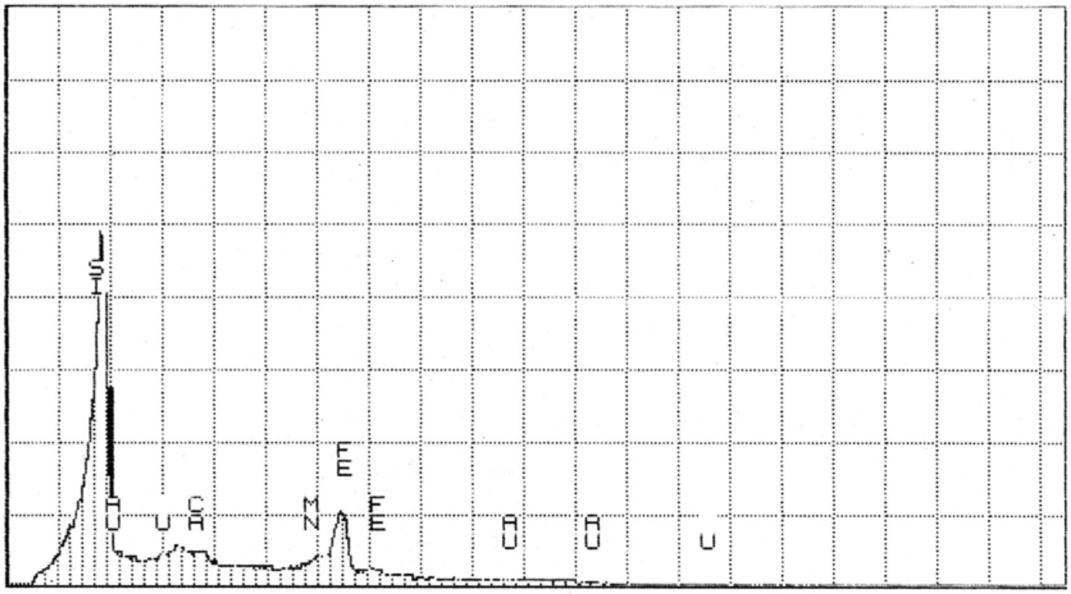


Figure 5 - EDS Spectrum of Vitrified SME Product †

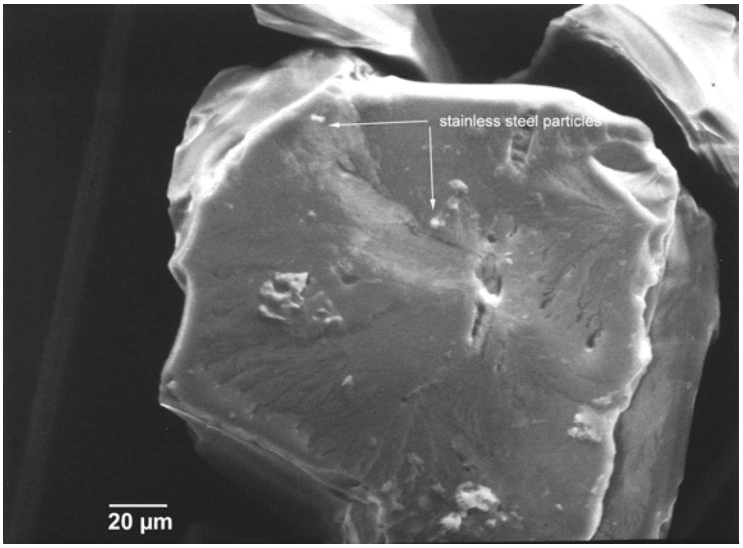


† The Au in the spectra is due to the Au alloy used to coat the samples for analysis.

Figure 6 is a more magnified view of the particle indicated by the arrow in Figure 4. This micrograph shows smaller particles adhering to the surface. The majority of these smaller particles are glass and are not stainless steel; however, two of the particles (indicated by the arrows in Figure 6) are stainless steel. Apparently, as evidenced by the measured and calculated compositions in Table 7, this slight stainless steel contamination was sufficient to increase the Cr above that predicted by PCCS from the composition of the blend.

No crystals were detected in any of the particles examined by SEM.

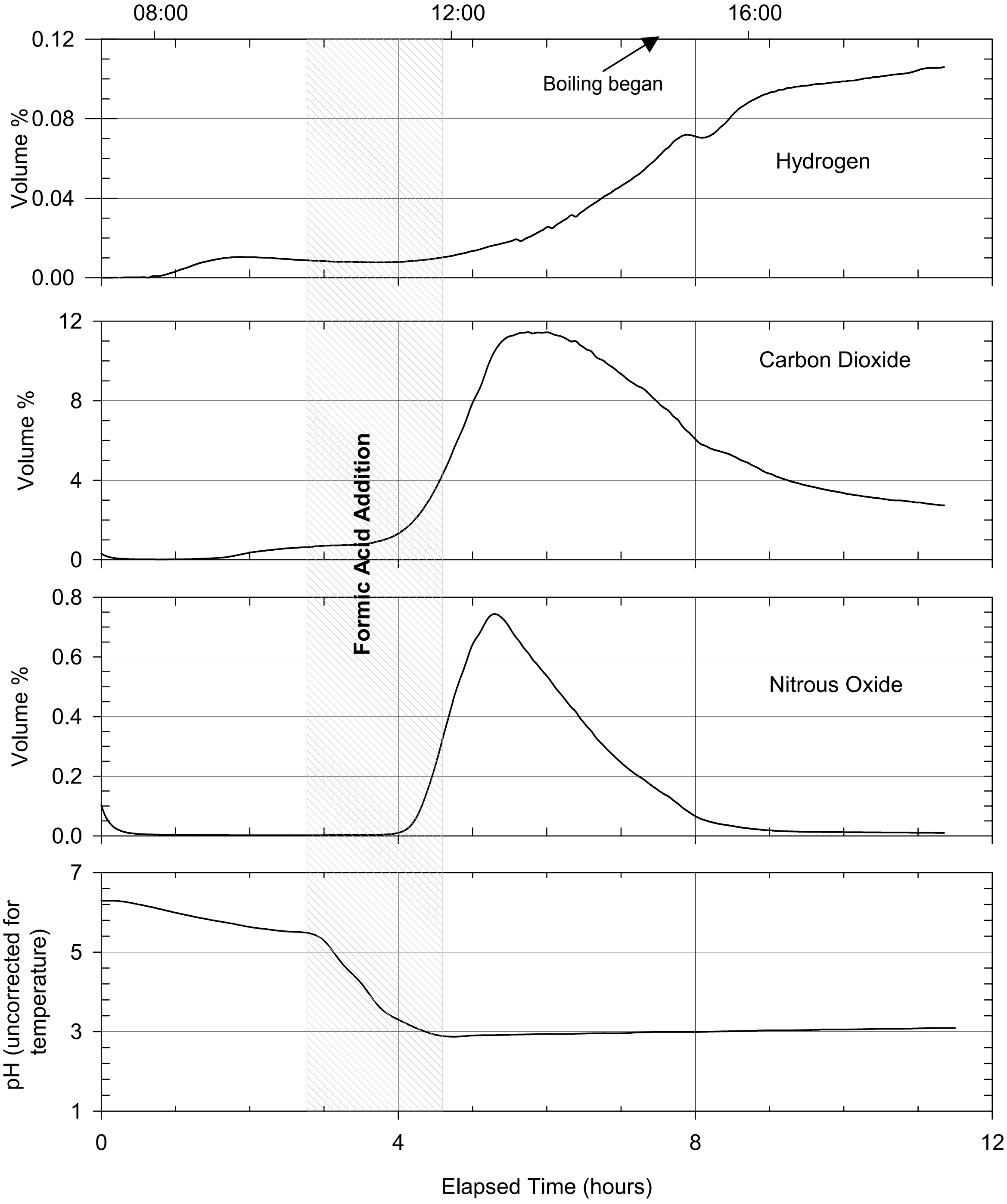
Figure 6 - SEM Micrograph of the Representative Particle Identified in Figure 4 at 500x



5.6 SME Redox Adjustment Cycle

SRTC scale gas concentration and pH during the SME Redox Adjustment Cycle are presented graphically in Figure 7.

Figure 7 - SRTC Scale Hydrogen, Carbon Dioxide, and Nitrous Oxide Concentrations and pH During the SME Redox Adjustment Cycle



As can be seen from Figure 7, as formic acid was added to the vessel, carbon dioxide and nitrous oxide evolved, and pH decreased. Hydrogen generation increased after the formic acid addition was complete and as the vessel temperature was increased from ~90°C to boiling. Maximum gas concentrations and generation rates are presented in Table 10. A description of calculations is given in Appendix A.

Table 10 - Maximum Observed Gas Concentrations and Generation Rates During the SRTC SME Redox Cycle

Gas	SRTC Scale Maximum Gas Concentration (Volume %)	DWPF Scale Maximum Gas Concentration (Volume %)	DWPF Scale Maximum Gas Generation Rate (lb/hr)
Hydrogen	0.11	0.036	0.0071
Carbon Dioxide	11.4	3.7	20.6
Nitrous Oxide	0.74	0.24	1.3

The primary reaction for hydrogen generation is:

$$\mathrm{HCOOH} \xrightarrow{\text{catalyst}} \mathrm{H_2} + \mathrm{CO_2}$$

This reaction is highly dependent on nitrite content (hydrogen evolves after nitrite is destroyed), the vessel temperature, and the amount of excess formic acid[23]. Since most of the nitrite in the SME product was destroyed in the SRAT cycle, the nitrite content did not delay the production of hydrogen. This is confirmed by the fact that hydrogen concentration was rising as nitrous oxide concentration was rising, as seen in Figure 7. During the SRAT cycle, the hydrogen concentration did not increase until after the nitrous oxide concentration peaked.

The factors contributing to hydrogen generation during the redox cycle were vessel temperature and the amount of formic acid added to the vessel. The hydrogen concentration remained fairly constant until completion of the formic acid addition, and then increased as the vessel was heated to boiling.

The large amounts of carbon dioxide and nitrous oxide are likely the result of a denitration reaction (a reaction between nitric acid and formic acid). As pH drops to 3 with a formic acid concentration greater than nitric acid concentration, the following reaction can occur[24]:

$$\mathrm{2HNO_3} + \mathrm{4HCOOH} \rightarrow \mathrm{N_2O} + \mathrm{4CO_2} + \mathrm{5H_2O}$$

It is believed this reaction was slowing before the end of the reflux period. Nitrous oxide concentration was approaching zero, and pH was beginning to increase.

6.0 ACCEPTABILITY OF THE GLASS USING PRODUCT COMPOSITION CONTROL SYSTEM (PCCS)

WD Engineering evaluated the acceptability of the Tank 40/Frit 200 glass based on two compositions. One was the glass composition calculated from the SME blend and the other was the measured composition of the final glass.

The acceptability of the glass from the SME blend was documented by WD Engineering[13]. The SME blending calculations determined the amount of Frit 200 to be added to the Macrobatch 3 SRAT Product. The SME blend, based on a calculated composition of the glass, met all the PCCS constraints (including that for Cr) except the homogeneity constraint. However, the calculated composition for the glass contained a concentration of aluminum oxide greater than 4 wt%. This aluminum oxide concentration was sufficient to reduce the application of the homogeneity constraint from the MAR to the PAR[25,26].

WD Engineering also performed a SME acceptability calculation based on the measured composition of vitrified SME product[27]. All constraints were met with the exception of the chromium constraint. As was noted in Section 5.5, there was chromium contamination from the grinder used to prepare the glass for PCT . This contamination was detected in the SEM analysis. In the SME blending calculations[12] the predicted composition of the glass did meet the Cr constraint.

7.0 QUALITY ASSURANCE

The following certified NIST traceable standard gases (from Air Liquide) were used to calibrate the GC for the SME and Redox Adjustment cycles:

	He	H_2	O_2	N_2O	CO_2	N_2
CalGas 1	0.80	1.00	12.00	15.00	25.00	Balance
CalGas 2	0.20	0.10	20.00	0.10	1.00	Balance

Each calibration gas was sampled until a steady reading on the GC was obtained to establish a calibration curve for each species immediately before each cycle.

All samples generated in the Shielded Cells for this task were tracked per L1 2.21 Procedure, "Radioactive Sample Receiving, Labeling and Tracking". All sludge dissolution samples were submitted with standards to check that dissolutions were complete and the analytical procedures were performed correctly[8,9].

Data are recorded in notebooks WSRC-NB-2000-00166[28], WSRC-NB-2001-00162[29], and WSRC-NB-2001-00163[30].

8.0 CONCLUSIONS

Based on the data presented in this report, the following conclusions can be drawn from the Tank40/Frit 200 SME cycle, vitrification, and formic acid addition cycle in the SRTC Shielded Cells:

- The maximum hydrogen generation rate during the SME cycle (0.0030 lb/hr on a DWPF basis) was well below the DWPF hydrogen design basis rate of 0.223 lb/hr.
- For the major elements, the measured composition of the glass was very close to the composition calculated by WD Engineering. The calculated composition of the glass from SME blending calculations met all the PCCS constraints, except homogeneity at the MAR. The measured composition failed the Cr constraint because of Cr contamination from the stainless steel grinder.

- The glass produced from this demonstration met the durability acceptance criterion as defined in WAPS[19]. The releases of B, Na, and Li in the PCT were all significantly less than their respective releases from the EA glass.
- In the PCT, the only radionuclide that had a normalized release equal to that for B, Li, or Na was Tc-99. All other radionuclides detected in the leachates (Sr-90, Cs-137, Th-232, Np-237, U, Pu, and Am-241) had lower normalized releases.
- The glass contained no crystals as determined by SEM examination; however, SEM is a surface analysis technique. (The glass was too radioactive for analysis by X-ray diffraction which is a bulk analysis technique.)
- The maximum hydrogen generation rate during the Redox Adjustment cycle (0.0071 lb/hr on a DWPF basis) was well below the DWPF hydrogen design basis rate of 0.223 lb/hr.
- During the Redox Adjustment cycle, there was evidence of denitration after the formic acid addition.

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APPENDIX A – INPUTS AND ASSUMPTIONS USED FOR CONVERTING FROM SRTC TO DWPF SCALE

Table A-1. SRTC and DWPF Sludge Volumes and Purge Rates Used for SME Cycle and Redox Adjustment Cycle

	SME Cycle SRTC Basis	SME Cycle DWPF Basis	Redox Cycle SRTC Basis	Redox Cycle DWPF Basis
Sludge Volume	0.722 L	22710 L (6000 gal)	0.540 L	22710 L (6000 gal)
Purge Rate (F_{in})	20.5 sccm	1.869×10^6 sccm (66 scfm)	14.5 sccm	1.869×10^6 sccm (66 scfm)

Note that the purge rates above are those actually observed during the SME cycle and SME redox adjustment cycle. They are slightly different than the purge rates given in Appendix B (19.8 sccm for the SME cycle) and Appendix C (14.8 sccm for the redox adjustment cycle).

Definition of Standard Conditions:

Temperature = 21.1°C or 70°F (This is the temperature used by SRS flow calibration personnel)

Pressure=1 atm

Assumption: The gasses produced behave as ideal gasses, i.e. volume %=mole %, and 1 mole = 2.41×10^4 cc (calculated using ideal gas law PV=nRT, with P = 1 atm and T = 21.1°C)

Conversion of the SRTC Volume % to DWPF Volume %

To convert from SRTC to DWPF scale volume %, one must adjust for differences in sludge volumes and purge rates.

$$vol\,\%\,DWPF = vol\%\,SRTC \cdot \frac{DWPF\ Sludge\,Volume}{SRTC\ Sludge\,Volume} \cdot \frac{SRTC\ Purge\ Rate}{DWPF\ Purge\ Rate} \tag{A-1}$$

For the SME Cycle:

$$\frac{22710\,\text{L DWPF Sludge}}{0.722\,\text{L SRTC Sludge}} \cdot \frac{20.5\,\text{sccm SRTC purge}}{1.869 \times 10^6\ \text{sccm DWPF purge}} = 0.345\frac{\text{vol\% DWPF}}{\text{vol\% SRTC}}$$

For the Redox Adjustment Cycle:

$$\frac{22710\,\text{L DWPF Sludge}}{0.540\,\text{L SRTC Sludge}} \cdot \frac{14.5\,\text{sccm SRTC purge}}{1.869 \times 10^6\ \text{sccm DWPF purge}} = 0.326\frac{\text{vol\% DWPF}}{\text{vol\% SRTC}}$$

Calculation of Gas Generation Rate

The DWPF scale gas generation rate is calculated by

1. Calculating the flow out of the SRTC vessel
2. Calculating the gas generation rate in the SRTC vessel by multiplying the measured volume % by the flow rate out of the vessel
3. Converting the SRTC generation rate from cc/min to lb/hour

4. Scaling the SRTC rate to DWPF basis

1. The flow rate out of the vessel is calculated by a helium balance.

$$F_{out} = F_{in} \cdot \frac{c_{He}}{x_{He}} \quad \text{(A-2)}$$

   where c_{He} is the volume % helium in the purge gas, and *Fin* is flow into vessel (purge rate) and x_{He} is the measured volume % helium.

2. The SRTC gas generation rate is then:

$$SRTC\ Gas\ gen\ rate = \frac{x_i}{100} \cdot F_{out} \quad \text{(A-3)}$$

   where x_i is the measured vol % of gas *i*.

3. The SRTC gas generation rate (SGGR) is then converted from cc/min to lb/hr:

$$\text{SGGR cc/min} \cdot \frac{\text{mol}}{\text{2.41E4 cc}} \cdot \frac{M_i\ \text{g}}{\text{mol}} \cdot \frac{1\ \text{lb}}{454\ \text{g}} \cdot \frac{60\ \text{min}}{1\ \text{hour}} \quad \text{(A-4)}$$

   where M_i is the molecular weight of gas *i*.

4. To scale the gas generation rate from SRTC to DWPF, the ratio of sludge volumes is used:

$$Gen\ Rate\ Scale\ Factor = \frac{DWPF\ Sludge\ Volume}{SRTC\ Sludge\ Volume} \quad \text{(A-5)}$$

Combining the above:

$$DWPF\ Gas\ Gen\ Rate = F_{in} \cdot \frac{x_i}{100} \cdot \frac{c_{He}}{x_{He}} \cdot \frac{\text{mol}}{\text{2.41E4 cc}} \cdot \frac{M_i\ \text{g}}{\text{mol}} \cdot \frac{1\ \text{lb}}{454\ \text{g}} \cdot \frac{60\ \text{min}}{1\ \text{hour}} \cdot \frac{DWPF\ Sludge\ Vol}{SRTC\ Sludge\ Vol} \quad \text{(A-6)}$$

In the SME cycle, little gas was generated as evidenced by a variation of +/-10% on the output helium concentration. Therefore, it was assumed that flow into the vessel was equal to flow out of the vessel, and c_{He} was equal to x_{He}. Substituting known values, and combining terms, Equation A-7 becomes:

$$SME\ Cycle\ DWPF\ Gas\ Gen\ Rate = x_i \cdot M_i \cdot 3.54 \times 10^{-2} \quad \text{(A-7a)}$$

For the SME Redox Cycle, c_{He} is equal to 0.48%, as measured by the GC[*]. Inputting known values and combining terms, Equation A-7 reduces to:

$$SME\ Redox\ Cycle\ DWPF\ Gas\ Gen\ Rate = x_i \cdot \frac{M_i}{x_{He}} \cdot 1.605 \times 10^{-2} \quad \text{(A-7b)}$$

---

[*] The purge gas contains 0.46% helium. However, after purging the vessel, the GC recorded 0.48% helium. This difference is within the expected accuracy of the GC calibration, and the as measured value is used for calculations.

Table A-2. SME Cycle Maximum Gas Concentrations and Generation Rates

	H_2	CO_2	N_2O
Molecular Weight (M_i)	2.0	44.0	44.0
SRTC Scale Maximum Vol. % (x_i)	0.043	1.9	0.111
DWPF Scale Maximum Vol. % (Eq. A-1)	0.015	0.67	0.039
DWPF Scale Generation Rate (lb/hr) (Eq. A-7a)	0.0030	3.0	0.17

Table A-3. SME Redox Adjustment Cycle Maximum Gas Concentrations and Generation Rates

	H_2	CO_2	N_2O
Molecular Weight (M_i)	2.0	44.0	44.0
He Vol. % at Maximum Gas Concentrations (x_{He})	0.48	0.39	0.43
SRTC Scale Maximum Vol. % (x_i)	0.11	11.4	0.74
DWPF Scale Maximum Vol. % (Eq. A-1)	0.036	3.7	0.24
SRTC Scale Vol% at Max Gas Generation Rate	0.11	11.4	0.73
He Vol% at Max Gas Generation Rate	0.48	0.39	0.41
DWPF Scale Generation Rate (lb/hr) (Eq. A-7b)	0.0071	20.6	1.3

APPENDIX B – CALCULATIONS FOR THE SME CYCLE

Scaling Factor for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of SRAT Product for the Shielded Cells:	0.72	Liters
Volume of SRAT Product for the DWPF:	6000	Gallons
or Volume of SRAT Product for the DWPF:	22710	Liters

$$\text{Ratio=}\quad \frac{\text{Volume of SRAT Product for the Shielded Cells}}{\text{Volume of SRAT Productt for the DWPF}}$$

$$\text{Ratio=}\quad \frac{0.722\ \text{Liters}}{22710\ \text{Liters}}$$

Ratio= 3.18E-05

Flow Rates for Decon Water and Dilute Formic Acid/Water Additions During the SME Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of SRAT Product for the Shielded Cells:	0.722	Liters
Volume of SRAT Product for the DWPF:	6000	Gallons
or Volume of SRAT Product for the DWPF:	22710	Liters
DWPF Flow Rate:	100	Gallons/min
or DWPF Flow Rate:	378.5	Liters/min

$$\text{Ratio=}\quad \frac{\text{(Volume of SRAT Product for the Shielded Cells)*(DWPF Flow Rate)}}{\text{Volume of SRAT Product for the DWPF}}$$

$$\text{Ratio=}\quad \frac{0.722\ \text{Liters*}\quad 378.5\ \text{Liters/min}}{22710\ \text{Liters}}$$

Shielded Cells Flow Rate = 0.0120 Liters/min
or
Shielded Cells Flow Rate= 12.0 mL/min

Decon Water Calculations for the Shiedled Cells SME Cycle

Decon Water Calculations for the Shielded Cells SME Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of SRAT Product for the Shielded Cells:	0.722	Liters
Volume of SRAT Product for the DWPF:	6000.00	Gallons
or Volume of SRAT Product for the DWPF:	22,710.00	Liters
Volume of Decon Water used in DWPF (= 1 Can):	1,000.00	Gallons
Volume of Decon Water used in DWPF (= 1 Can):	3785	Liters

$$\text{Ratio=}\quad \frac{\text{Volume of the SRAT Product for the Shielded Cells*Volume of Decon Water used in DWPF}}{\text{Volume of the SRAT Product for the DWPF}}$$

$$\text{Ratio=}\quad \frac{0.72\ \text{Liters *}\quad 3785\quad \text{Liters}}{22710.00\ \text{Liters}}$$

Decon Water Addition for Shielded Cells per Canister= 0.120 Liters
or
Decon Water Addition for Shielded Cells per Canister= 120.40 mL
5 Canisters per SME Cycle= 602.00 mL

Antifoam Additions for Shielded Cells

	Amount	Units
Volume of SRAT Product for the Shielded Cells:	0.722	Liters
Density of Sludge:	1.15	g/mL
Concentration of Antifoam :	100	ppm
Weight percent solution wanted:	5	wt.%
Approximate Density of Antifoam Solution:	1	g/mL

To make 50 mLs of 5 wt.% antifoam solution, you will need to add the following:

Antifoam Required:	5	g
Water Required:	95	g
Total Solution wt:	100	g
Check of calculations:	(5/100)*100	
Wt. % of Antifoam:	5	wt.%

Calculation for Amount of Antifoam to be Added During SRAT and SME Cycles

$$\text{Grams of antifoam=}\quad \frac{\text{(Volume of Sludge)*(Density of Sludge)*(Weight of Antifoam)*(1000mL/L)}}{1000000\ \text{g Slurry}}$$

Grams of antifoam= 0.08303 g

$$\text{mL of Antifoam Solution to Add=}\quad \frac{\text{(Grams of Antifoam Required)}}{\text{(Made up Solution)*(Density of Solution)}}$$

mL of Antifoam Solution to Add= 1.66 mL

Formic and Frit Slurry Calculation for the Shielded Cells SME Cycle
Amount of dry frit calculated by WD-E 329.76 g

To make a 50 wt.% solution:
Amounts Needed:

Frit & Water	659.52 g	= 329.76g/0.5
Dry frit	329.76 g	= 329.76
Water	329.76 g	= 659.52-329.76

Formic Acid (1.5 Wt. %) Required for 50 wt.% Solution:
Amounts needed:

Using 100 wt.% formic acid:	4.95 g	= 329.76*0.015
Using 90 wt.% formic acid:	5.50 g	= 4.95/0.90

Amounts Required for Shielded Cells Preparation:

Dry Frit 200 Required:	329.76 g
Amount of Water Required:	329.76 g
Amount of Formic Required:	5.50 g

Add amount of formic to the amount of water required.

Divide the frit amount by 2. Place in separate poly bottles.

Purge Rate for the SME Cycle

Assumptions for Scaling Factor:

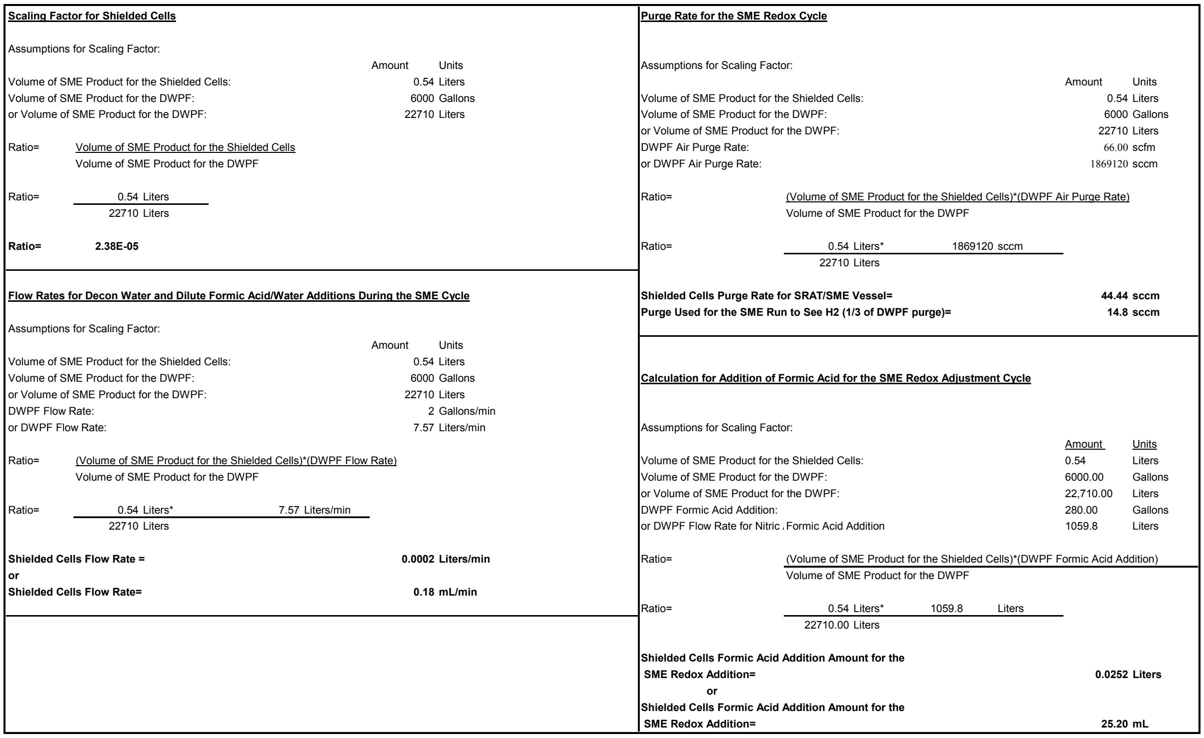
	Amount	Units
Volume of SRAT Product for the Shielded Cells:	0.722	Liters
Volume of SRAT Product for the DWPF:	6000	Gallons
or Volume of SRAT Product for the DWPF:	22710	Liters
DWPF Air Purge Rate:	66.00	scfm
or DWPF Air Purge Rate:	1869120	sccm

$$\text{Ratio=}\quad \frac{\text{(Volume of SRAT Product for the Shielded Cells)*(DWPF Air Purge Rate)}}{\text{Volume of SRAT Product for the DWPF}}$$

$$\text{Ratio=}\quad \frac{0.722\ \text{Liters*}\quad 1869120\ \text{sccm}}{22710\ \text{Liters}}$$

Shielded Cells Purge Rate for SRAT/SME Vessel= 59.42 sccm
Purge Used for the SME Run to See H2 (1/3 of DWPF purge)= 19.8 sccm

APPENDIX C – CALCULATIONS FOR THE SME REDOX CYCLE



Scaling Factor for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of SME Product for the Shielded Cells:	0.54	Liters
Volume of SME Product for the DWPF:	6000	Gallons
or Volume of SME Product for the DWPF:	22710	Liters

Ratio= Volume of SME Product for the Shielded Cells / Volume of SME Product for the DWPF

Ratio= 0.54 Liters / 22710 Liters

Ratio= 2.38E-05

Flow Rates for Decon Water and Dilute Formic Acid/Water Additions During the SME Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of SME Product for the Shielded Cells:	0.54	Liters
Volume of SME Product for the DWPF:	6000	Gallons
or Volume of SME Product for the DWPF:	22710	Liters
DWPF Flow Rate:	2	Gallons/min
or DWPF Flow Rate:	7.57	Liters/min

Ratio= (Volume of SME Product for the Shielded Cells)*(DWPF Flow Rate) / Volume of SME Product for the DWPF

Ratio= 0.54 Liters* 7.57 Liters/min / 22710 Liters

Shielded Cells Flow Rate = 0.0002 Liters/min
or
Shielded Cells Flow Rate= 0.18 mL/min

Purge Rate for the SME Redox Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of SME Product for the Shielded Cells:	0.54	Liters
Volume of SME Product for the DWPF:	6000	Gallons
or Volume of SME Product for the DWPF:	22710	Liters
DWPF Air Purge Rate:	66.00	scfm
or DWPF Air Purge Rate:	1869120	sccm

Ratio= (Volume of SME Product for the Shielded Cells)*(DWPF Air Purge Rate) / Volume of SME Product for the DWPF

Ratio= 0.54 Liters* 1869120 sccm / 22710 Liters

Shielded Cells Purge Rate for SRAT/SME Vessel= 44.44 sccm
Purge Used for the SME Run to See H2 (1/3 of DWPF purge)= 14.8 sccm

Calculation for Addition of Formic Acid for the SME Redox Adjustment Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of SME Product for the Shielded Cells:	0.54	Liters
Volume of SME Product for the DWPF:	6000.00	Gallons
or Volume of SME Product for the DWPF:	22,710.00	Liters
DWPF Formic Acid Addition:	280.00	Gallons
or DWPF Flow Rate for Nitric . Formic Acid Addition	1059.8	Liters

Ratio= (Volume of SME Product for the Shielded Cells)*(DWPF Formic Acid Addition) / Volume of SME Product for the DWPF

Ratio= 0.54 Liters* 1059.8 Liters / 22710.00 Liters

Shielded Cells Formic Acid Addition Amount for the SME Redox Addition= 0.0252 Liters
or
Shielded Cells Formic Acid Addition Amount for the SME Redox Addition= 25.20 mL

APPENDIX D – CALCULATION OF THE WEIGHT PERCENT SOLUBLE AND INSOLUBLE SOLIDS AND VITRIFICATION FACTOR

The soluble and insoluble weight percent solids can be calculated by using the following equations[†] once the weight percent total solids and dissolved solids have been obtained.

$$W_{is} = \frac{(W_{ts} - W_{ds})}{(1 - W_{ds})} \qquad \text{Eq. 1}$$

$$W_{ss} = W_{ts} - W_{is} \qquad \text{Eq. 2}$$

where W_{ds} is the weight fraction of dissolved solids (weight of dissolved solids/weight of supernate)
W_{ts} is the weight fraction of total solids (weight of total solids/weight of sludge slurry)
W_{is} is the weight fraction of insoluble solids (weight of insoluble solids/weight of sludge slurry)
W_{ss} is the weight fraction of soluble solids (weight dissolved solids/weight of sludge slurry)

Converting the weight percent total and dissolved solids from Table 4 into weight fractions and inserting into Equations 1 and 2 yields:

$$W_{is} = \frac{(0.453 - 0.0764)}{(1 - 0.0764)} = 0.408$$

$$W_{ss} = 0.453 - 0.408 = 0.045$$

Multiplying the above results by 100 to convert to percent yields:

40.8 wt% insoluble solids
4.5 wt% soluble solids.

The vitrification factor is defined as the grams of glass per mL of SME product. For this calculation, the weight percent calcined solids was used. A sample of SME product was calcined at 1000°C. The resulting "calcine" was black and shiny, resembling glass. Therefore, the vitrification factor is calculated as follows:

wt% calcined solids/100 x density of SME product, or

$$\frac{41.6\text{ g calcined solids}}{100\text{ g SME product}} \cdot \frac{1.36\text{ g SME product}}{\text{mL SME product}} = 0.566\text{ g glass/mL SME product}$$

[†] M.S. Hay and N.E. Bibler, "Characterization and Decant of the Tank 42 Sludge Sample ESP-200 (U)", WSRC-RP-98-00406, Rev. 0, June 12, 1998.