Transport of Technetium and Rhenium into Refractory Materials during Bulk Vitrification

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ABSTRACT

Bulk vitrification (BV) was selected as a potential supplemental waste treatment process to support the commitment for cleanup of low-activity waste (LAW) stored in large waste storage tanks at the U.S. Department of Energy's Hanford Site. In the BV process, LAW, soil, and glass-forming chemicals are mixed, dried, and placed within a castable refractory block (CRB) and sand, all within a metal box. Electric current, supplied through two graphite electrodes in the box, melts the waste feed and produces a durable glass waste form. During engineering-scale tests of BV, a small fraction of radioactive technetium-99 (Tc) and rhenium (Re) (a nonradioactive surrogate) were transferred out of the LAW glass feed and molten LAW glass and deposited on the surface and within the pores of the CRB. Tc is a primary risk driver for long-term performance of immobilized LAW; therefore, even small fractions of Tc present in a readily leachable form rather than immobilized in a glass matrix can impact long-term performance of the immobilized waste.

Laboratory and engineering-scale studies were undertaken to reduce or eliminate the readily leachable Tc in the CRB. These studies focused on 1) understanding the mechanisms of the transport of Tc/Re into the CRB during vitrification, and 2) evaluating various means of protecting the CRB against the deposition of leachable Tc/Re. The tests used either Re as a chemical surrogate for Tc, or Re and Tc together.

A conceptual Tc/Re transport model was developed based on observed laboratory experiments to attempt to explain the transport behavior seen in engineering-scale tests. At temperatures below 650°C, molten ionic salt (MIS) containing Tc and Re penetrates by capillarity from the feed into the CRB open porosity. At approximately 650 to 750°C, the MIS decomposes through the loss of NO_X, leaving mainly sulfate and chloride salts. The Na_2O formed during decomposition of the nitrates reacts with insoluble grains in the feed and the aluminosilicates in the CRB to form more viscous liquids that reduce further liquid penetration into the CRB. At 750 to 950°C, a continuous glass phase traps the remains of the MIS in the form of inclusions in the bulk glass melt. At 950 to 1200°C, the salt inclusions in the glass slowly dissolve but also rise to the surface. The Tc/Re salts also evaporate from the free surface of the glass melt that is rapidly renewed by convective currents. The vapors condense on cooler surfaces in the upper portion of the CRB, the box lid, and the off-gas system.

Results of the engineering-scale tests helped to validate the conceptual transport model of Tc/Re deposition and improved the understanding of likely mechanisms of deposition in the CRB. As a result, there is increased potential that Tc deposition can be controlled and reduced to ensure that the BV waste form will provide acceptable performance.

INTRODUCTION

Radioactive tank waste at the Hanford Site in Richland, Washington, has been generated by more than 40 years of nuclear materials production operations. Baseline plans for disposing of these wastes include the separation of low-activity and high-level fractions of the waste, followed by vitrification of both fractions to produce immobilized high-level waste and low-activity waste (LAW) forms. The immobilized high-level waste will be disposed in a deep geologic repository, while the immobilized LAW will be disposed in a shallow burial facility at Hanford. Separation and vitrification operations will be performed in the Waste Treatment Plant (WTP) that is currently under construction at the Hanford Site. However, the capacity of the WTP is insufficient to process all of the tank waste and support the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) milestone to complete tank waste treatment by 2028.[1] Therefore, the U.S. Department of Energy's Office of River Protection, Washington State Department of Ecology, and U.S. Environmental Protection Agency agreed to cooperatively develop approaches to supplement tank waste treatment by providing additional LAW treatment capacity, supplemental to the WTP [1].

After assessing dozens of technologies for supplemental treatment, and then testing and evaluating three preferred LAW immobilization approaches in 2002 and 2003, bulk vitrification (BV) was selected for a pilot supplement treatment test and demonstration facility [2]. The goal is to further evaluate BV through simulant and real waste testing to support a Tri-Party Agreement milestone (M-62-11) associated with a final decision on treatment of the balance of tank waste that is beyond the capacity of the WTP.

BV combines LAW and glass-forming chemicals within a large disposal container and melts the contents using electrical resistance heating. It employs a disposable melter where the waste form and melter (i.e., steel container) are disposed in a LAW burial ground after the vitrified waste form has cooled. Because the BV melter is used only once, some of the processing constraints of the baseline joule-heated, continually fed ceramic melters can be avoided. The BV In-Container Vitrification[TM][2] process studied here mixes and dries LAW, soil, and glass forming chemicals, and then melts the mixture at approximately 1250 to 1500°C by electrical resistance [3,4]. Graphite flakes are added to the mix to form a conductive path for melt initiation. Electrical current is supplied by two graphite electrodes imbedded in the batch. The design concept used in early testing employed top-down melting of a large, single batch of waste and soil, which was surrounded by an insulating primary liner of quartz sand to protect the steel container from the glass melt. The current design uses bottom-up melting, in which, after melt initiation of a batch, an additional batch is gradually loaded in increments until the container is filled with waste glass. A rigid castable refractory block (CRB), rather than quartz sand, is used as the primary liner to protect the steel container from the glass melt.

Engineering- and full-scale tests of bottom-up melting were conducted as part of the development and qualification of the BV process. The current full-scale BV design uses steel containers that are 2.3 m (tall) × 2.3 m (wide) × 7.32 m (long) (7.5 ft × 7.5 ft × 24 ft). The engineering-scale tests used a container that is about 1/6th linear scale relative to the full-scale container. The engineering-scale tests were conducted to gather information on a variety of process variables that cannot be obtained with crucible-scale tests. Both engineering-scale and full-scale steel containers employed refractory materials to insulate the container walls from the high-temperature glass melt. The glass melt was in direct contact with a CRB, which was surrounded by quartz sand.

Results of the early engineering-scale and full-scale tests of top-down melting suggested that a small portion of the waste stream technetium-99 (Tc) would end up in a soluble form deposited in a vesicular

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[1] The current Tri-Party Agreement requirement is for vitrification of all tank wastes
[2] In-Container Vitrification[TM] is a registered trademark of AMEC Inc.

glass layer located at the top of the BV melt and in the quartz sand used as an insulator. Based on an initial risk assessment, the small amount of soluble Tc salt in the BV waste packages is projected to create a Tc concentration peak at early times in the groundwater extracted from a 100-meter down-gradient well [5]. This peak differed from predicted baseline WTP glass performance, which showed an asymptotic rise to a constant release rate. Because of the desire by regulatory agencies to achieve essentially equivalent performance to WTP glass with supplemental treatment technologies, the BV process was modified in an attempt to minimize deposition of soluble Tc salts. The use of a CRB, in place of a portion of the refractory sand layer, and a bottom-up melting technique were chosen to reduce Tc deposition in the porous refractory sand and to eliminate the vesicular glass layer at the top of the melt.

Several bottom-up melting engineering-scale tests were conducted to evaluate the modified BV process and quantify the deposition of soluble Tc or rhenium (Re), the nonradioactive surrogate of Tc. Results showed that the bottom-up melting process eliminated the vesicular glass layer on the melt surface, and the CRB significantly reduced Tc deposition in the refractory liner. Although significant reduction in the soluble Tc fraction was achieved through process modification, a small fraction of soluble Tc still remained in the CRB and was projected to result in a groundwater peak different than WTP glass. To ensure that the amount of Tc deposition can be minimized and controlled to achieve consistently acceptable levels, an understanding of the mechanisms of deposition was desired. Two likely mechanisms of Tc transport from the LAW glass feed and molten LAW glass and deposition to the external and internal surfaces of the CRB were hypothesized: 1) low-temperature molten salt penetration, and 2) high-temperature Tc evaporation-condensation. A testing program was developed and implemented to evaluate the capability of these two mechanisms to transport Tc and Re into the CRB during vitrification.

EXPERIMENTAL APPROACH AND METHODS

Most of this experimental work used a representative Hanford tank waste simulant referred to as the "six tank composite" and a baseline glass composition that has been shown to have acceptable durability at Na_2O waste loadings of 20 wt%[3] [3,6]. Table I shows that Hanford tank waste and representative simulants consist primarily of sodium nitrate/nitrite and sodium hydroxide with lesser amounts of sodium sulfate, phosphate, carbonate, chloride, and fluoride. The waste also includes some aluminum cations and small quantities of organic sodium (Na) salts. Table II shows the oxide/halogen composition of the baseline glass and the contributions from the waste simulant and the Hanford soil that is the main glass-forming ingredient in the baseline glass formulation. The B_2O_3 and ZrO_2 that are part of the final glass composition are added as separate glass additives.

The experimental approach involved several sets of tests that focused on different aspects of Tc/Re penetration into the CRB. One set of laboratory tests focused on the reactions that occurred as the BV feed was converted from a mixture of salts and oxide materials into a glass. These tests included thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of the simulated LAW and glass feed material, and "cold finger" tests (CFT) designed to look at melt progress and the composition of evolved species as a function of temperature. A second set of tests looked at CRB/melt interface interactions through laboratory immersion tests that assessed the penetration of molten ionic salt (MIS) alone and when combined with glass formers as a function of temperature. The third set of tests involved examinations of the CRB materials used during engineering-scale testing and included methods to

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[3] A few experiments were conducted with another waste simulant for Hanford Tank S-109 dissolved saltcake, as waste from that tank is expected to be used in large-scale radioactive BV tests. The S-109 simulant has the same main components as the six-tank composite, but has a nitrate level that is about 60% higher and a sulfate concentration that is about 60% lower.

Table I. Composition of "Six Tank Composite" Simulant [6]

Reagent	Mass (g)	Mole/L	Dry Wt%
H_2O	860		
$Na_2C_2O_4$	1.58	0.0118	0.416
CH_3COONa	10.79	0.132	2.84
$NaNO_3$	196.11	2.308	51.63
KNO_3	1.25	0.0124	0.329
$NaOH$	29.58	0.740	7.79
$Al(NO_3)_3 \cdot 9H_2O$	23.90	0.0637	6.292
Na_2CO_3	50.35	0.475	13.25
Na_2SO_4	12.78	0.0900	3.364
Na_2CrO_4	1.68	0.0104	0.442
$Na_3PO_4 \cdot 12H_2O$	18.70	0.0492	4.923
$NaCl$	2.56	0.0438	0.674
NaF	1.33	0.0316	0.350
$NaNO_2$	29.26	0.424	7.702
$CsNO_3$	1.0E-05	5.1E-08	2.63E-6

Table II. Compositions of Simulant, Hanford Soil, and Resulting Glass in Mass Fraction of Oxides and Halogens

Component	Simulant	Soil[a]	Glass
Al_2O_3	0.0188	0.1294	0.0915
B_2O_3	0.0000	0.0000	0.0500
BaO	0.0000	0.0007	0.0005
CaO	0.0000	0.0404	0.0274
Cl	0.0090	0.0000	0.0018
Cr_2O_3	0.0046	0.0001	0.0010
Cs_2O	4.19E-8	0.0000	8.47E-9
F	0.0035	0.0000	0.0007
Fe_2O_3	0.0000	0.0627	0.0425
K_2O	0.0034	0.0217	0.0154
MgO	0.0000	0.0197	0.0134
MnO	0.0000	0.0010	0.0007
Na_2O	0.8987	0.0272	0.2000
P_2O_5	0.0203	0.0021	0.0055
SiO_2	0.0000	0.6830	0.4631
SO_3	0.0418	0.0000	0.0084
SrO	0.0000	0.0004	0.0003
TiO_2	0.0000	0.0116	0.0079
ZrO_2	0.0000	0.0000	0.0700
SUM	1.0000	1.0000	1.0000

[a]Soil was taken from a location adjacent to the Hanford Site.

estimate the total mass of Tc/Re present in the CRB and measurements to determine the level of Re/Tc penetration into the refractory material. The following subsections describe each set of tests.

Thermal Gravimetric Analysis and Differential Thermal Analysis

TGA and DTA were used to study the nitrate/nitrite decomposition behavior of 1) simulated LAW alone [7] and 2) glass feed material that included both simulated LAW and glass-forming materials (Hanford soil, B_2O_3 and ZrO_2)[8]. A TGA/DTA instrument was used that simultaneously measures mass changes (TGA) and relative, to an inert material, temperature changes (DTA) as the sample temperature was increased at a known and controlled heating rate. A heating rate of 1°C/min was used for the LAW simulant, while 4°C/min was used for the glass batch.

Cold Finger Tests

The CFT were designed to look at melt progress and the composition of evolved species as a function of temperature for different feed variations. These tests were conducted with both Tc and Re to determine if there was a significant difference between the behavior of Tc and the proposed Re surrogate.

Three of the six feed variation cases in the original study [7] are discussed in the following:

Case 1 - Baseline: A baseline feed with a final glass composition shown in Table II and target concentrations of 4.3 mg/kg Tc and 8.1 mg/kg Re in glass. This Tc concentration is the approximate average level expected in Hanford tank waste, and the higher Re mass concentration yields a molar concentration equal to the Tc level. This feed establishes a baseline performance for the cold finger and allows for direct comparison with engineering-scale test (ES-32A and -32B) results for Tc.

Case 2 - No sulfate: A feed of the same makeup as the baseline, but without sulfate in the feed. The Na_2SO_4 in the simulant was replaced by the same moles of Na_2CO_3 to keep the Na concentration in the feed the same as that in the baseline feed. This case determines if the behavior of Tc is influenced by sulfur (S) in the feed.

Case 3 - Pre-melted glass: A pre-melted glass with Tc and Re spiked to compensate for the expected loss during melting. This case determines the extent to which volatility from the glass contributes to the Tc/Re deposition as opposed to deposition from the reacting feed.

For Cases 1 and 2, Tc/Re-spiked simulant (baseline or sulfate removed) was mixed with additives and soil in the proportion necessary to produce 200 g of glass. Case 3 used 200 g of crushed, pre-melted glass that had been prepared by melting the baseline feed spiked with Tc and Re.

The dried feeds (or pre-melted glass in Case 3) were tested by heating in a 4–in.-diameter platinum-20% rhodium crucible with a water-cooled cold finger, as shown in Fig. 1. The Inconel cold finger tubing was placed in the head space of the crucible through a loose-fitting crucible lid. The temperature of cooling water was kept below 90ºC. The crucible and cold finger assembly were placed in a box furnace and ramp heated in air at 5°C/min, starting from 80°C and air quenched at one of the following final temperatures: 600°C—nitrate beginning to thermally decompose; 800°C—nitrate all reacted; 1000°C—glass melt forming; or 1200°C—glass melt fully formed.

The pre-melted glass in Case 3 was ramp heated at 5°C/min from 500°C to 1200°C and held at 1200°C for 1 and 5 h before air quenching.
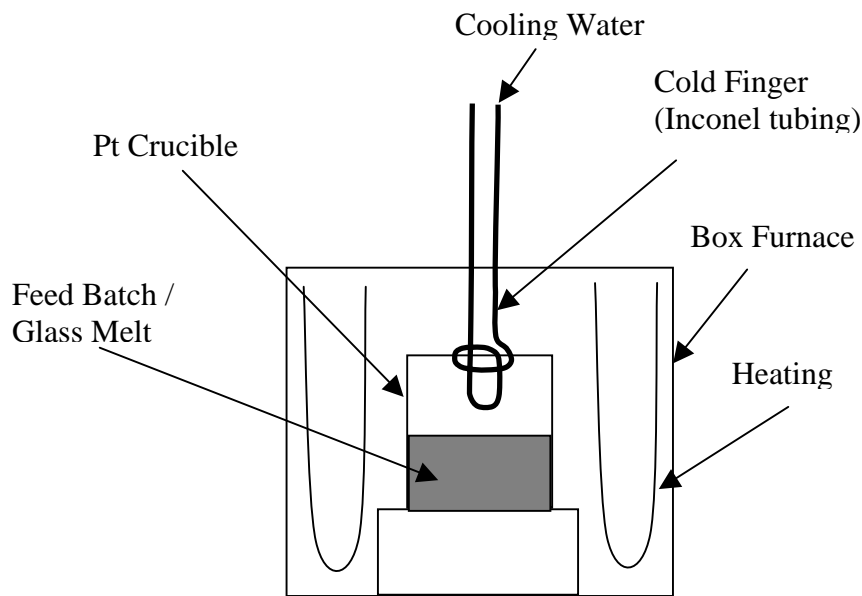
Fig. 1. Schematic of experimental setup for "cold finger" crucible feed melting tests

The following analyses were conducted for each set of tests:

- Feed wash samples: Approximately 20 g of samples were taken from the dried feed materials before conducting feed melting tests. As-dried feeds were washed with ~20-mL deionized water, the wash was then filtered thorough a 0.45-μm filter and analyzed for Tc and Re via inductively-coupled plasma-mass spectrometry and for anions via ion chromatography.

- Crucible rinse samples: All partly reacted feed and glass materials remaining in the platinum crucible were washed using ~200-mL deionized water. The wash solutions from all tests were filtered through a 0.45-μm filter and analyzed for Tc and Re via inductively-coupled plasma-mass spectrometry and for anions via ion chromatography.

- Condensate samples: The condensate materials attached to the cold finger were collected by first scraping the deposits with a razor blade and then rinsing the cold finger with deionized water. Both the soluble and insoluble materials were mixed into 15- to 50-mL solution, depending on the amount of condensate materials collected. Condensate samples from all tests were analyzed for Tc and Re via inductively-coupled plasma-mass spectrometry; for major glass components via inductively coupled plasma-atomic emission spectroscopy; and for anions, including halogens, via ion chromatography. Selected condensate samples from tests performed at 1000 and 1200°C were analyzed by X-ray diffraction.

- Glass samples: Representative glass samples from tests performed at 1200°C were analyzed for Tc and Re via inductively-coupled plasma-mass spectrometry and for major glass components via inductively coupled plasma-atomic emission spectroscopy after glass digestion or total fusion.

- Crucible contents: For Case 1, X-ray diffraction was used to identify the main crystal phases present in the baseline feed at temperatures ranging from 200 to 1200°C.

Immersion Tests

Two types of refractory immersion tests were conducted: an MIS test and a melter feed immersion test [8]. In the MIS immersion test, an MIS was prepared by pre-melting the salts shown in Table I at a temperature of 400°C before quenching. Coupons (2-cm cubes) of the refractory material were

suspended by platinum wire in a tall platinum crucible with large particles of the quenched MIS. The crucibles were heated in a box furnace to temperatures ranging from 400 to 700°C for 6 to 24 h. Cross sections of the coupons were examined in the scanning electron microscope using energy dispersive spectroscopy dot map techniques to determine the level of penetration.

In the melter feed immersion tests, a refractory rod (12- to 20-mm cross section and 10- to 12-cm length) was inserted into a platinum crucible and held in position by a platinum lid with a central opening (see Fig. 2). Melter feed enriched in sodium sulfate and Re_2O_7 was added to the crucible so that ~25 mm of the lower end of the rod would be immersed in molten glass. The assembly was heated gradually (5°C/min) to the set temperature. The rod was removed from the melt at the end of the heat treatment. Both the exposed surface and a fracture surface perpendicular to the exposed surface were examined optically and by scanning electron microscopy-energy dispersive spectroscopy.
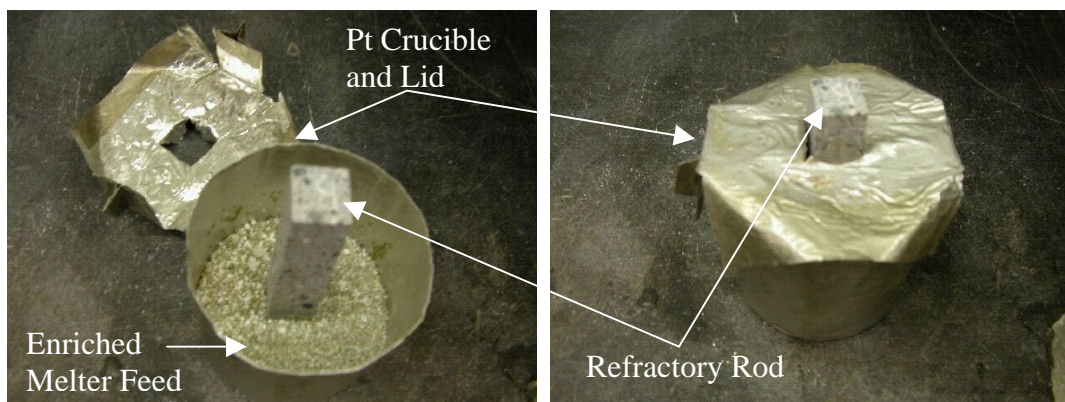

Fig. 2. Partially immersed refractory rod setup

Engineering-Scale CRB Tests

A schematic plan view of the engineering-scale BV waste package configuration is shown in Fig. 3. The engineering-scale tests used a container that is about 1/6th linear scale relative to the full-scale container. The engineering-scale metal test containers were lined with a 5.1 cm (2 in.) layer of duraboard insulation, a 5.1-cm (2-in.) layer of quartz sand, and a 10.2-cm (4-in.) CRB wall. Engineering-scale tests supply a variety of useful processing and waste performance information; however, this paper focuses on measurements of the quantities of soluble Tc and Re that are deposited in the CRB.

Seven quantitative engineering-scale tests were conducted in late 2004 and early 2005. Five of these tests involved waste simulant spiked with Re (31 series), while two of the tests involved waste simulant containing both Re and Tc (32 series). The objective of three of the tests, ES-31A, -31B, and -32A, was to determine whether modifications to the earlier BV process design reduced the leachable fraction of Re/Tc contained in the BV waste package compared to 2003 test results. These first three tests used a sprayed-on, non-fired calcium-fluoride glaze material (RX-14) in an attempt to minimize Re and/or Tc penetration into the CRB. Although these tests illustrated a reduction in the soluble fraction of Re/Tc compared to results from 2003, it was clear that further improvements were possible. Therefore, three additional tests; ES-31C, -31D, and -31E, were conducted to evaluate alternative approaches to minimizing the amount of soluble Re in the BV waste package. These alternative approaches included the use of pre-fired refractory glazes (Ferro-Frit 3225 and sodium silicate), a simulated denitrated feed that contained reduced Re [e.g., Re(IV) instead of Re(VII) oxidation state], and refractory tiles. One additional engineering-scale test, ES-32B, was conducted to evaluate the performance of the BV process using actual Hanford tank waste. Table III summarizes parameters for the seven tests.
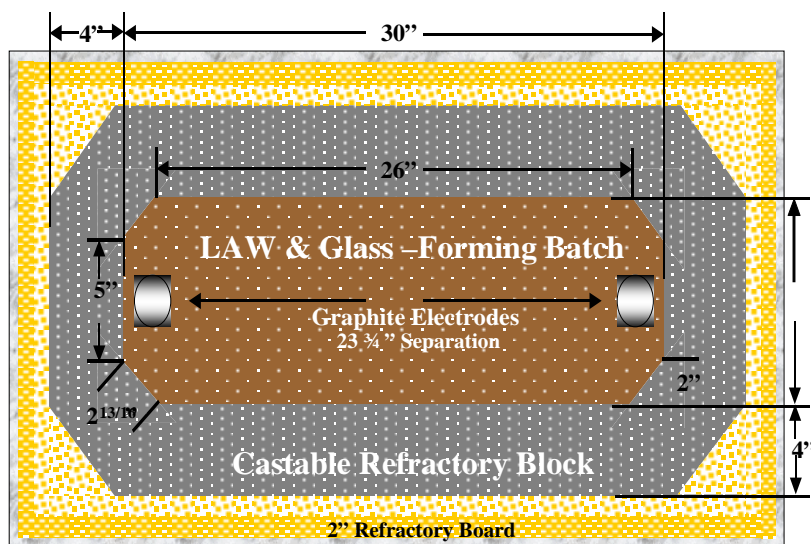
Fig. 3. Schematic plan view of the engineering-scale BV design

Table III. Quantitative Engineering-Scale Tests

Test ID	Waste Simulant	Tc/Re Spike Materials	Total Energy (Kwh)	Modifications
ES-31A	6-Tank Composite	Re	488	CRB coated with sprayed-on RX-14 glaze material
ES-31B	S-109	Re	570	CRB coated with sprayed-on RX-14 glaze material
ES-32A	6-Tank Composite	Tc, Re	639	CRB coated with sprayed-on RX-14 glaze material
ES-31C	6-Tank Composite	Re	921	Ferro-Frit 3225 and sodium silicate pre-fired glazes applied to CRB
ES-31D	6-Tank Composite	Re	738	Denitrated feed, reduced Re (Re IV)
ES-32B	6-Tank Composite	Tc, Re	645	5% tank waste added to simulant
ES-31E	6-Tank Composite	Re	664	Greystone tiles added to ¾ of box

Tc and Re levels in the CRB were estimated using grab sampling, centrifuge sample extraction, and inductively-coupled plasma-mass spectrometry analysis approaches described elsewhere [9]. Grab samples from the CRB wall were taken at multiple vertical depths and at the CRB base. An estimate of the total fraction of Re and/or Tc that may dissolve and leach as a soluble salt from the CRB was estimated by 1) determining the concentration of each contaminant in each grab sample, 2) finding the average concentration of samples taken at the same vertical depth, 3) multiplying the average concentration by the mass of CRB at each depth, 4) summing the total mass of contaminant in the four wall sections and the base, and 5) dividing by the mass of contaminant added to the test. The calculation yields the fraction of inventory in the CRB available for leaching.

Additional tests were conducted to determine the depth of Re penetration into the CRB. Segments of the CRB grab samples taken from Tests ES-31A and ES-31B were analyzed individually. The extraction process was used for segments broken or cut into samples with a thickness as small as 18 mm, but smaller samples did not produce adequate extract after centrifuge operations. A second sample of the ES-31B CRB was used to determine the concentration distribution of Re in the refractory wall as a function of depth from the interface with the molten glass. Material was removed from the CRB sample by grinding off ~1-mm layers of CRB material starting from the molten glass interface. The powder removed during each dry grinding operation was collected in a plastic bag, with a total of 10 samples obtained. The ground samples were leached in water (added at 2.5 mL per gram of refractory powder) in a teflon container at 90°C for 24 h. The leachate was filtered and sampled for analysis by inductively-coupled plasma-mass spectrometry.

RESULTS AND MECHANISM FOR Tc/Re TRANSPORT

The potential levels of Tc deposition into refractory materials during the BV process is shown by the results of Re- and Tc-spiked engineering-scale tests.[4] These tests showed that the concentrations of Re and Tc varied greatly in different areas of the CRB. Generally, the base of the CRB showed low levels of Re and Tc, while the walls of the CRB showed two different patterns. In some cases, the wall contained higher concentrations in the upper portions, while other tests showed a more level concentration as a function of wall height. In tests where both Re and Tc were spiked, the amount of Re in the CRB was higher than that seen for Tc, but the ratio of Re to Tc was relatively constant, indicating that Re is a good conservative transport surrogate for Tc. Table IV shows the estimated levels of Re and Tc in the CRB for each of the engineering-scale tests normalized to the amount of material added to each test. Although individual CRB samples showed a wide range of Re and Tc concentrations, the total calculated amount of Re and Tc in the CRB was relatively consistent considering the variation in process parameters for each test. The amount of leachable Re, excluding the results from Test 31D[5], ranged from a high of 4.82 ±0.44% to a low of 0.77 ±0.06%, with an average value of 1.96 ±0.09%. These results were combined with the Tc results obtained from Tests ES-32A and -32B to determine a best estimate of 0.34 ±0.02% for the amount of Tc that would be present as a soluble salt in the CRB [10]. This value is significantly lower than the earlier tests using a sand-only refractory and top-down melting technique, which indicated 2wt% of the Tc inventory deposited in the sand insulation and vesicular glass layer after vitrification.

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[4] Engineering-scale test results are considered preliminary. Full-scale test results will provide more accurate data. Full-scale Re surrogate results will be available in 2006, and full-scale Tc results will be available from large-scale radioactive tests.

[5] Test ES-31D evaluated the impacts of a denitrated feed on the BV process. Results were useful to help understand potential transport mechanisms, but are not thought to represent feeds that will be processed by BV.

Table IV. Summary of Engineering-Scale Soluble Fraction Test Results

Test ID	% Soluble Re in CRB	% Soluble Tc in CRB
ES-31A	1.51 ±0.15%	Not Spiked
ES-31B	0.77 ±0.06%	Not Spiked
ES-32A	1.55 ±0.12%	0.37 ±0.03%
ES-32B	1.13 ±0.11%	0.17 ±0.02%
ES-31C	4.82 ±0.44%	Not Spiked
ES-31D	0.22 ±0.03%	Not Spiked
ES-31E	1.96 ±0.16%	Not Spiked

At first glance, it is difficult to understand how a portion of a well-dispersed but very minute component (4.3 mg/kg of Tc in the final glass) can segregate from a large volume of feed (typically 130 kg for an engineering-scale test) and end up in a soluble form in the CRB. Based on results of experiments described earlier, a conceptual model for the mechanism of Tc/Re segregation from melter feed into the CRB has been proposed [8,16]. The conceptual model shows that, when considering some intricacies of the conversion process from melter feed to molten glass, a plausible mechanism governing this segregation can be constructed. The conceptual model consists of five steps that are discussed below with supporting experimental results. The first two steps are associated with the initial stage of feed melting, while Steps 3 through 5 are associated with the glass-forming stage.

Conceptual Model: Initial Feed Melting – Steps 1 and 2

BV melter feed is a mixture of Hanford aluminosilicate soil, ZrO_2, B_2O_3, and LAW, which is a mixture of salts (see Table I) that melts and forms a single MIS phase incorporating some or all B_2O_3. In Step 1, the MIS forms, starting at temperatures as low as 200°C, and wets and bridges the grains of the higher melting soil minerals and ZrO_2 components of the feed, filling some of the space between the grains. The MIS contains the Tc and Re. Some of the MIS near the CRB wall is drawn into the pores between the refractory grains of the CRB by capillary forces. The MIS penetration is a complex process affected by temperature gradients in the feed and CRB, pore sizes, and decomposition rates of MIS components. This step is portrayed schematically in Fig. 4.

As the temperature increases from 650 to 750°C, the nitrate and nitrite salts (~66 mass% of LAW simulant) are decomposed [7,11-16] in Step 2, leaving behind less reactive salts such as sulfate, chloride, borate, and chromate, and highly reactive Na_2O. Tc and Re are probably present in this phase as pertechnetate and perrhenate. The further fate of Tc/Re depends on whether the feed is far from or close to the interface with the CRB. Grains of soil and zirconia react with the Na_2O generated from the decomposed nitrates and other salts, creating intermediate crystalline phases and the initial glass-forming melt. This stage is schematically portrayed in Fig. 5.

Tables V and VI describe the key elements/assumptions in Steps 1 and 2 of the conceptual model and list test results that supply supporting evidence. The tests in these and subsequent tables are referred to as the test type (e.g., TGA/DTA, CFT) or the specific engineering-scale test that was conducted (e.g., ES-31B, ES-32A). The following are supporting results for each set of experiments and supplies examples of the data collected. Complete experimental results are reported elsewhere [7,8,16]. TGA curves of both the LAW simulant alone and the glass feed (e.g., simulant, soil, glass-forming additives) show similar behavior. Little mass loss occurs before 550°C. The mass loss rate increases and peaks at 650°C, while the mass loss levels out after 800°C. DTA curves for both simulant and feed show an endothermic peak that begins at 200°C and continues to 600°C. These curves are consistent with endothermic MIS melting

Bulk Feed/Melt   Interface Between Feed/Melt and CRB
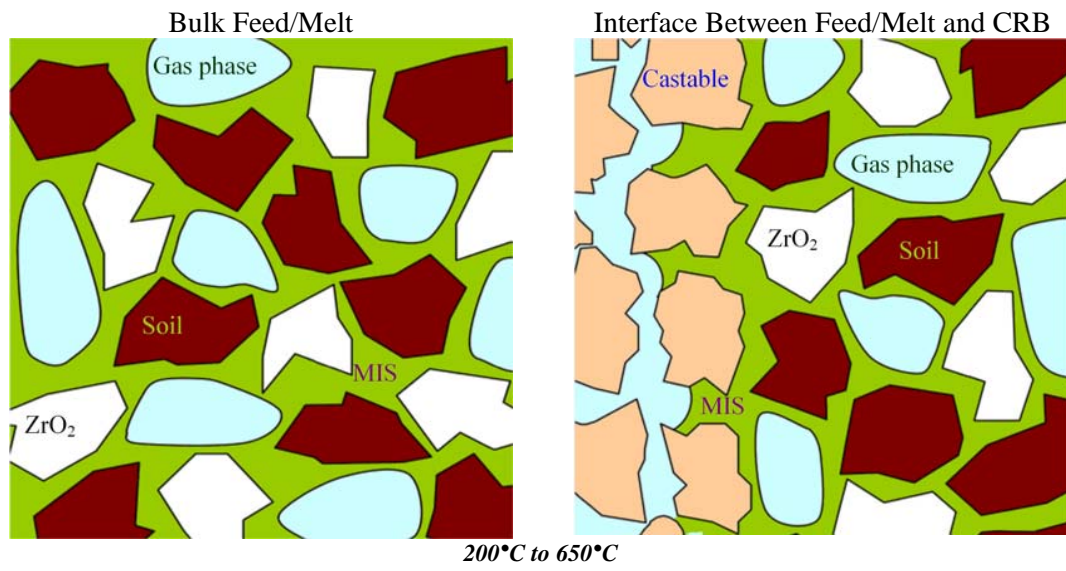
200°C to 650°C
Grains of soil (brown) and zirconia (white) become coated and bridged by MIS and borates (green). Gas bubbles (light blue) fill the remaining space. The MIS is drawn into the pores between the refractory grains (salmon) of the CRB by capillary forces. The pores in the CRB are partially filled with fine-grained material (not shown in the pictures).

Fig. 4. Step 1 - MIS melts and penetrates the CRB

Bulk Feed/Melt   Interface Between Feed/Melt and CRB
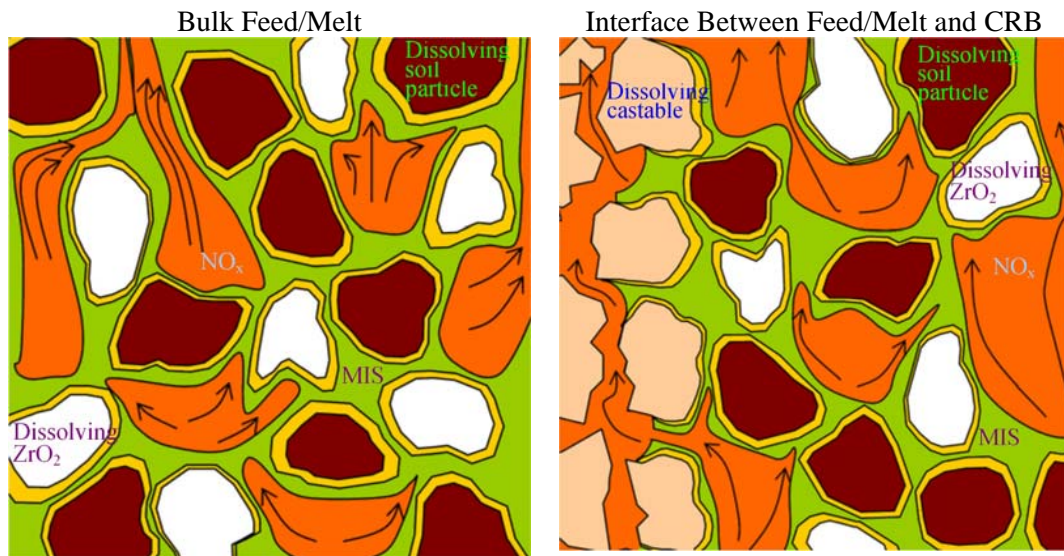
650°C to 750°C
Most of the molten salts decompose, releasing NO_x (bright orange) and other gases. NO_x gas rises toward the surface in large bubbles and through open channels. Grains of soil (brown) and zirconia (white) react with Na_2O from nitrates and other salts, creating intermediate crystalline phases and the initial glass-forming melt (mustard). Molten salt that has penetrated the CRB also decomposes, releasing NO_x and creating an intergranular glass phase.

Fig. 5. Step 2 - MIS decomposes and reacts with refractory components

starting at 200°C with little decomposition (e.g., weight loss) occurring until 550°C. Total mass loss for MIS at 750°C is greater than 50%.

Fig. 6 shows the crystal phases, identified through X-ray diffraction, present in a crucible melt after heating and quenching at temperatures from 200 to 1200°C. Nitrate is present at temperatures as high as 600°C but absent in samples heated to 800°C. The relatively constant amount of soil crystal phases (e.g., quartz, ZrO_2) at temperatures of 600°C and below, and the decrease in these phases with an increase in sodium aluminosilicates (e.g., nosean and nepheline) and sodium zirconia silicate, also support the theory that the soil particles and ZrO_2 do not react with the MIS until the nitrates decompose to release Na_2O.

Fig. 7 shows the crucible rinse and cold finger condensate concentrations of Tc/Re in the CFT for the baseline feed. The condensate results show that the Tc/Re do not volatilize from the melt until temperatures are higher than 800°C, while the rinse results indicate that much of the Tc/Re remains in a readily soluble form (i.e., associate with the nitrate MIS) until 600°C. The 800°C condensate data show that the Tc/Re is not volatilizing to a significant extent but is partially present in a soluble form that indicates that part of the Tc/Re is associated with the sulfate/chloride MIS present after nitrate decomposition. This assumption is further supported by Fig. 8 that shows the crucible rinse and condensate Tc/Re concentrations for the no-sulfate feed. When sulfate is not present, no Tc/Re shows up in the 800°C crucible rinse after the nitrate decomposes.

Preparation of the MIS for the immersion tests showed that LAW simulant feed components will form an MIS by heating for a few minutes at 400°C. Energy dispersive spectroscopy dot maps of Na showed that the molten salt fully penetrated the 2-cm CRB coupons in as little as 6 h at temperatures as low as 400°C. Although penetrated with MIS, the structural integrity of the CRB coupons was good for 6-h exposures to 700°C. The coupons severely degraded when held at 800°C for 24 h, indicating that the CRB will react with Na_2O formed when the nitrates decompose. The melter feed immersion tests showed that the presence of soil and glass formers reduced the depth of MIS penetration into the CRB coupon to less than 1 cm, but MIS penetration still occurred.

The engineering-scale test results also support the initial feed melting conceptual model. Fig. 9 shows the extent of penetration of Na, S, and Cl into an ES-31B refractory sample taken from the lower third of the CRB wall. The figure also shows the Re distribution in a refractory sample taken from the upper third of the ES-31B CRB wall. Although these were taken from different positions, Fig. 9 shows that Na penetrated to 12 mm and is present at higher concentrations than S and Cl, indicating that Na penetrated mainly as $NaNO_3$ or NaOH. The Re profile indicates that it is mainly present in the first 18 mm and falls off rapidly at greater depths into the refractory wall. The Na, S, and Cl profiles along with the Re profile support the theory that Re is carried into the CRB with the $NaNO_3$/NaOH phase but penetrates to a lesser degree after the MIS decomposes. The ES-31D test that used a waste feed with NaOH in place of $NaNO_3$ and $NaNO_2$ to simulate a denitrated feed also indicates that the mobility of the MIS may play a role in transporting Tc/Re. An MIS based mostly on NaOH would be expected to be much more viscous and transport less Re/Tc than the nitrate MIS, and this test showed the lowest CRB levels. The presence of Na, S, and Re behind low permeable tiles placed in the CRB for ES-31E also supports the theory of nitrate MIS penetration that carries Tc/Re.

Table V. Supporting Experimental Results for Step 1 - MIS Melts and Penetrates the CRB

Description	Key Elements/ Assumptions	Evidence/Basis	
		Test	Result
The first step in the melting process is the formation of MIS in the feed that includes all Tc/Re within the porosity of the soil and other insoluble grains. The MIS penetrates the CRB open porosity as the interface temperature increases from approximately 200 to 650°C along with its highly concentrated Tc/Re. *Grains of soil and zirconia become coated and bridged by MIS and borates. Gas bubbles fill the remaining space. The MIS is drawn into the pores between the refractory grains by capillary forces.*	All Tc/Re is contained within the MIS.	MIS Immersion[a]	Oxy-ionic salts are mutually soluble ($KTcO_4$ melts at 532°C, $NaTcO_4$ at 378°C). MIS preparation for immersion tests show that eutectic MIS forms at 400°C.
		CFT[b]	CFT show large quantity of soluble Tc remaining at 600°C.
	Tc is not yet volatilizing from the melt.	CFT[b]	Tc was non-detectable below 600°C and in very small amounts at 800°C in condensate materials.
	MIS forms and penetrates the CRB open porosity.	MIS and Glass Feed Immersion[a]	MIS and glass feed immersion show MIS penetration into CRB coupons.
		ES-31B Refractory Analysis[c]	Engineering-scale refractory analysis shows Na penetration to 12 mm and is present at higher concentrations than S and Cl, indicating that Na penetrated mainly as $NaNO_3$ or NaOH.
		TGA/DTA[d]	Nitrate begins melting as low as 200°C and is not fully decomposed until >650°C. Adequate temperature range for MIS formation and penetration.
		ES-31D[c]	This test with NaOH rather than nitrate/nitrite resulted in significantly lower Re deposition—possibly the result of less penetration of a highly viscous NaOH MIS.
		ES-31E[c]	CRB samples from behind tiles show Na, S, and Re deposition.

[a] See [8] for MIS and glass feed immersion test results.
[b] See [7] for CFT results.
[c] See [10] for engineering-scale test results.
[d] See [7] and [8] for TGA/DTA results.

Table VI. Supporting Experimental Results for Step 2 - MIS Decomposes and Reacts with Refractory Components

Description	Key Elements/ Assumptions	Evidence/Basis	
		Test	Result
As the temperature rises from 650 to 750°C, the MIS loses most of the NO_x, leaving mainly sulfate and chloride salts. The Na_2O from nitrates reacts with refractory grains in the feed (soil, ZrO_2) and to some extent the aluminosilicates in the CRB, forming viscous glass-forming liquid.

Most (80 to 90%) of MIS decomposes, releasing NO_x; NO_x gas rises toward the surface in large bubbles and open channels. Grains of soil, zirconia, and CRB react with Na_2O from MIS, creating intermediate crystalline phases and the initial glass-forming melt. | Nitrate decomposition is nearly complete at 750°C. | CFT[a] | Nitrate decomposition is first observed at 600°C and is complete by 800°C. |
		TGA/DTA[b]	Mass loss from waste begins at >550°C and ends by 800°C.
	Na_2O from MIS starts to react with soil, ZrO_2, and CRB.	CFT[a]	Formation of Na aluminosilicate and Na zirconia silicate minerals at 800°C indicates Na_2O reaction with soil and ZrO_2.
		MIS Immersion Tests[c]	CRB coupons severely degraded only after 800°C exposures, indicating that the CRB is stable in contact with MIS but reacts with Na_2O formed when the nitrates decompose.
		Feed Immersion Tests[c]	Penetration of CRB is 6 to 10 mm. CRB swells at >1100°C, indicating MIS reaction with CRB.
	MIS shrinks as nitrates decompose, leaving chloride and sulfate salts.	TGA[b]	TGA of MIS alone shows 50% mass loss.
		CFT[a]	Crucible washes at 800°C show <5% of the batched NO_3 but 20 to 30% of the batched Cl and S.
	Tc/Re stays in MIS as MIS begins reaction with CRB.	Engineering-Scale Tests[d]	Nosean and nepheline form in engineering-scale CRB tests. These tests generally showed lower Re concentrations in the CRB base, possibly resulting from higher base temperatures and more Tc/Re incorporation in a glassy phase.
		CFT[a]	Tc volatility in CFT is low at <800°C. Tc/Re to S/Cl ratio in condensate increases at >800°C.

[a] See [7] for CFT results.
[b] See [7] and [8] for TGA/DTA results.
[c] See [8] for MIS and glass feed immersion test results.
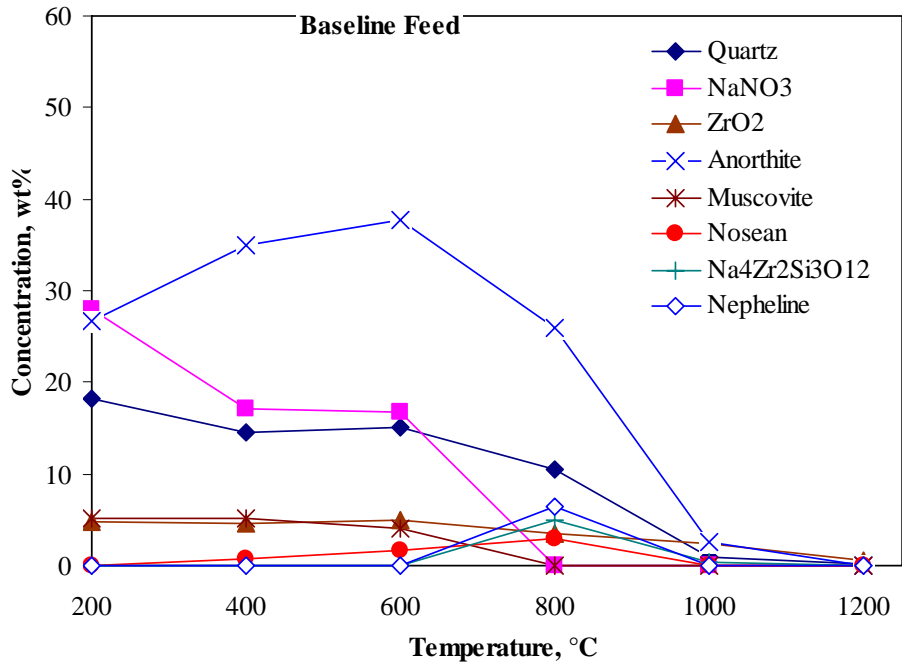[d] See [10] for engineering-scale test results.

Fig. 6. X-ray diffraction phase identification on baseline feeds quenched at the specified temperature
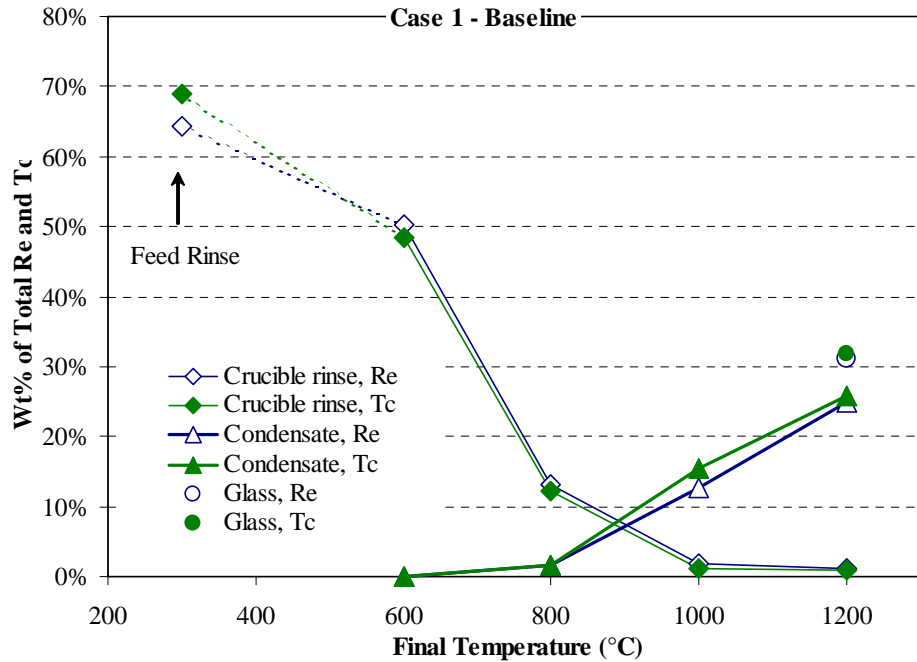

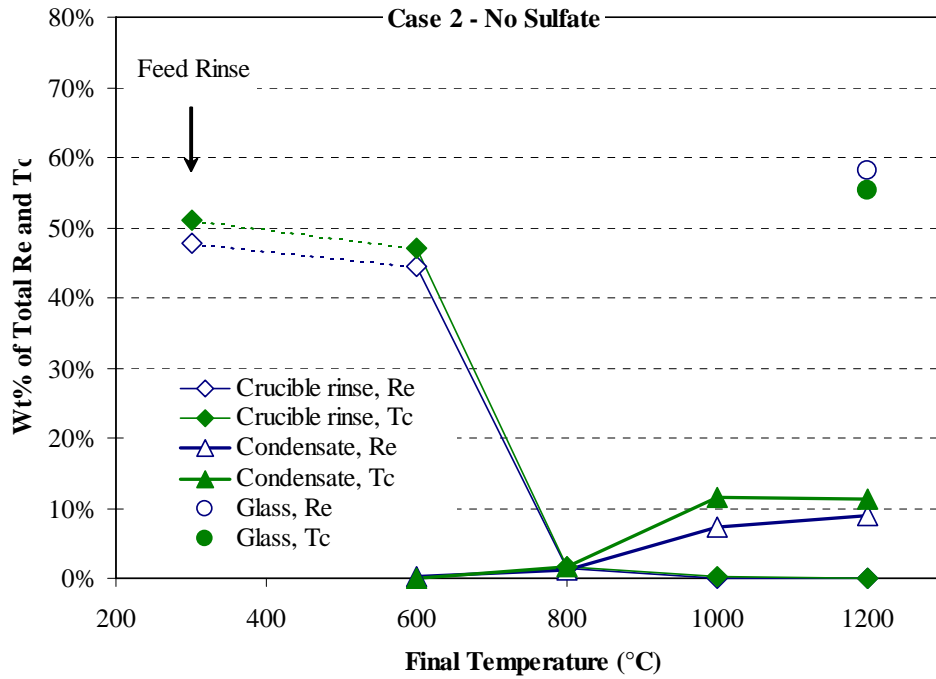Fig. 7. Wt% of total Re and Tc versus final temperature for Case 1— Baseline Feed

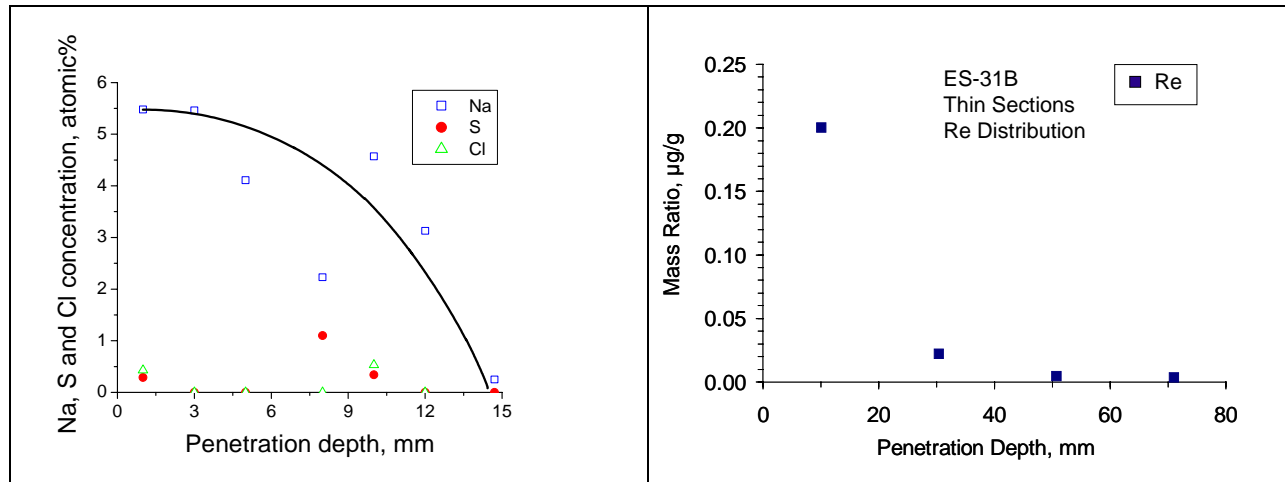Fig. 8. Wt% of total Re and Tc versus final temperature for Case 2—No-Sulfate Feed

Fig. 9. Atomic fractions of Na, S, and Cl and Re concentrations in ES-31B CRB as functions of distance from the interface with molten glass

Conceptual Model: Glass Formation – Steps 3, 4, and 5

As the waste feed conversion process transitions into the glass formation phase, alkali oxides formed from the decomposition of nitrites, nitrates, carbonates, and hydroxides react with silicate and aluminosilicate components of the soil grains, creating a glass-forming melt. As the melt fuses in Step 3, the open space between solid grains shrinks into closed pores that become bubbles (Fig. 10). In Step 4, the residual salt phase (sulfates and chlorides) is trapped into spherical inclusions that may or may not contain gas (Fig. 11). Because the density of inclusions is lower than the density of molten glass, the inclusions tend to ascend to the top surface of the melt. Some inclusions can stay in the melt for a long time due to their small size and entrainment in melter circulation currents. Sulfate and chloride salts containing chromates, perrhenates, and pertechnetates are also left behind in the CRB pores. Whereas sulfate and chlorate inclusions rise to the surface in molten glass, they stay in the CRB and may evaporate and condense at colder portions of the porous CRB, distributing Tc and Re to greater depths into the CRB wall.

In Step 5, sulfate- and chloride-rich inclusions reach the glass melt surface, where they gradually evaporate (Fig. 12). Remaining sulfate melt forms patches of salt at the glass surface. The chloride-rich inclusion may convert to gas while still in the glass-forming melt (NaCl boils at 1465°C). The sulfate melt keeps dissolving in molten glass as long as the glass melt remains below SO_3 saturation levels. However, the SO_3 solubility limit in the glass sharply decreases as the temperature approaches 1400°C. Some glass components, such as alkali borates, also readily volatilize.

The vapors of the sulfate and chloride MIS precipitate on colder surfaces such as the box lid or the upper portions of the CRB wall. Vapor condensation may occur on a hot refractory surface if the condensate reacts with the CRB components. Once on the CRB in a sufficient quantity, this MIS can also penetrate into the pores of the CRB by capillary forces.

Iron oxides in the soil may be reduced to iron metal along with Tc/Re oxides through a reaction with remaining graphite flake (starter path) and on the surface of graphite electrodes (Fig. 12 and Eq. 1 and 2):

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2 \qquad \text{(Eq. 1)}$$

$$2Tc_2O_7 + 7C \rightarrow 4Tc + 7CO_2 \qquad \text{(Eq. 2)}$$

Carbon dioxide escapes to the melt surface in the form of bubbles. Metallic iron makes droplets that form alloys with Tc/Re and other easily reduced metal like phosphorus and sink to the bottom of the melt when they reach a sufficient size to overcome convective currents in the glass melt. Droplets that reach the bottom can fuse and create an ingot.

Bulk Feed/Melt   Interface Between Feed/Melt and CRB


~750°C to 950°C
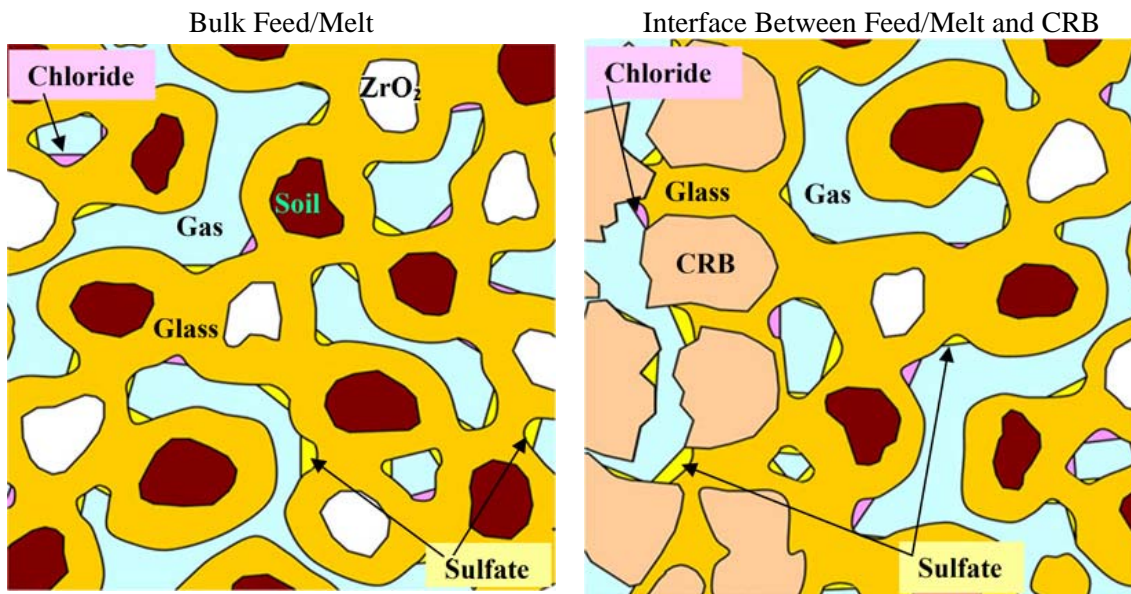
Grains of soil and zirconia (brown and white) continue to dissolve in the glass-forming melt (mustard) that becomes connected. The gas phase is partly connected and partly confined in bubbles. Extremely fluid sulfate (yellow) and chloride (pink) salts, the remains of the MIS, are trapped in gas bubbles and channels (light blue). Chromates, perrhenates, pertechnetates, and other thermally stable MIS are components of the sulfate and chloride phases. Sulfate and chloride salts, containing chromates, perrhenates, and pertechnetates, are also left behind in the CRB pores.

Fig. 10. Step 3 - Glass melt becomes continuous

Bulk Feed/Melt   Interface Between Feed/Melt and CRB

950°C to 1200°C
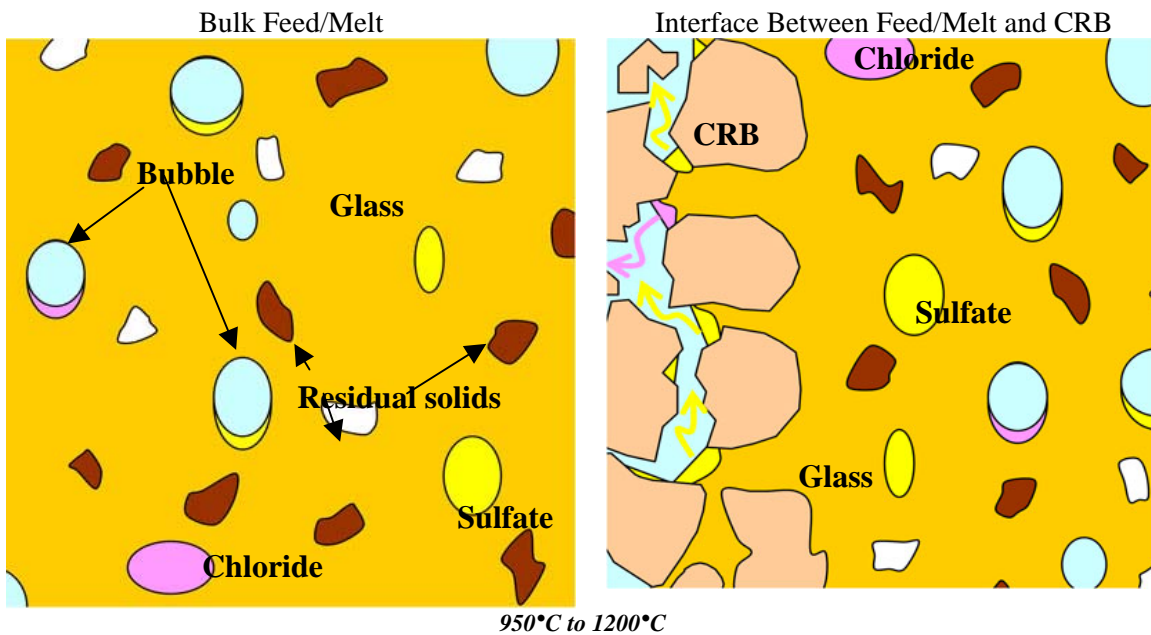
Solid grains are nearly entirely dissolved. Sulfate and chlorate salts form inclusions in the glass phase and are also present in bubbles. Whereas sulfate and chlorate inclusions rise to the surface in molten glass, they stay in the CRB; they may evaporate only to condense at colder portions of the porous CRB, distributing Tc and Re to greater depths into the CRB wall (as indicated by yellow and pink areas).

Fig. 11. Step 4 - Remaining solids dissolve and remaining MIS segregates
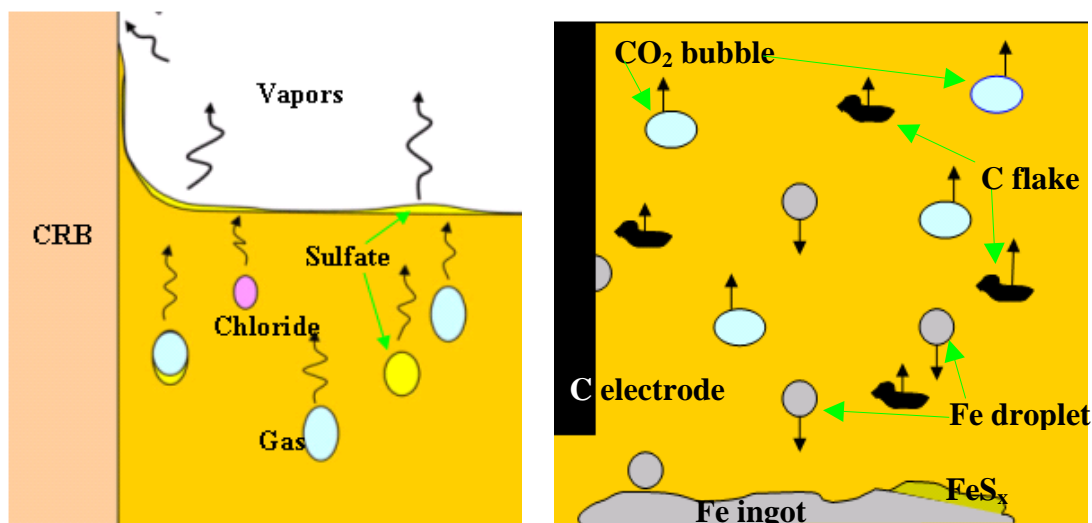
1200° to 1400°C

A fraction of sulfate and chloride phases with Tc/Re salts reach the top surface of the molten glass, where they are deposited as a thin layer and evaporate. Salt vapors and volatile components from glass (such as sodium borate) condense on the upper portions of the CRB, on the box lid, and in the off-gas system. Iron oxides in the soil are reduced to iron metal along with Tc/Re oxides through reaction with the remaining graphite flake (starter path) and on the graphite electrodes surface. Metallic iron makes droplets that form alloys with Tc/Re and other easily reduced metal like phosphorus and sink to the bottom of the melt when they reach a sufficient size to overcome convective currents in the glass melt. Iron sulfide may form at the iron-glass interface.

Fig. 12. Step 5 - MIS reaches melt surface and vapors transport to exposed CRB

Tables VII through IX describe the key elements/assumptions in each step of the glass-formation phase of the conceptual model and list test results that supply evidence that the conceptual model is valid. The tests in these and subsequent tables are referred to as the test type (e.g., TGA/DTA, CFT) or the specific engineering-scale test that was conducted (e.g., ES-31B, ES-32A). The following are supporting results for each set of experiments and supply examples of the data collected. Complete experimental results are reported elsewhere [7,8,10,16].

TGA curves of both the LAW simulant alone and the glass feed (e.g., simulant, soil, and glass-forming additives) show that a small amount of weight loss occurs between 750 and 800°C. The TGA of the glass feed shows that the weight loss is very small from 800 to 1100°C, but that additional weight loss occurs at temperatures higher than 1100°C. This is consistent with the assumption that the MIS decomposition reactions are essentially complete by 800°C, but that additional volatilization will occur at higher temperatures.

Fig. 6 showed that the crystal phases present in a crucible melt after heating and quenching at 800°C are essentially gone at 1000°C, indicating that a glassy melt has formed at this point in the melting process.

Table VII. Supporting Experimental Results for Step 3 - Glass Melt Becomes Continuous

Description	Key Elements/ Assumptions	Evidence/Basis	
		Test	Result
At 750 to 950°C, a continuous glass phase starts to form and traps the remains of the MIS in dispersed inclusions. *Grains of soil and zirconia continue to dissolve in the glass-forming melt that becomes connected. Extremely fluid sulfate and chloride salts, the remains of the MIS, are trapped in gas bubbles or separate phases in the bulk melt and also left behind in the CRB pores. Chromates, perrhenates, pertechnetates, and other thermally stable salts are components of the sulfate and chloride phases.*	Gas bubbles continue to evolve as a glassy melt forms.[a]	CFT[b]	The quantity of Cl in the cold finger condensate is very low at 800°C but increases significantly at 1000°C. Crystalline phases present at 800°C are essentially gone at 1000°C, indicating that a glassy phase has formed.
		TGA/DTA[c]	TGA shows some continued mass loss to 800°C.
	Potassium and Na perrhenates and pertechnetates concentrate in the MIS phases, rather than dissolving in the glass melt.	CFT[b]	Sulfate significantly influences Tc/Re volatilization. No-sulfur test indicates significant increase in glass retention (30 to 40%) and decrease in condensate concentrations (15 to 25%).

[a] Gases contain CO_2 from carbonates and remnants of NO_x at 750 to 800°C; CO_2 also evolve from carbon-iron reaction; NaCl evaporates at 800 to 1000°C.
[b] See [7] for CFT results.
[c] See [7] and [8] for TGA/DTA results.

Table VIII. Supporting Experimental Results for Step 4 - Remaining Solids Dissolve and Remaining MIS Segregates

Description	Key Elements/ Assumptions	Evidence/Basis	
		Test	Result
At 950 to 1200°C, the salt inclusions in the glass slowly dissolve but also rise to the surface, where they volatilize and condense on cooler surfaces. The salt inclusions in the CRB continue to react and form a glassy phase that incorporates some of the Tc/Re but also evaporates and condenses in colder portions of the CRB, distributing Tc/Re as they condense.	Tc/Re within chloride and sulfate MIS rise to surface, volatilize, and condense on cooler surfaces.	CFT[a]	Tc, Re, and Cl quantities in the cold finger condensate increase significantly in the baseline feed test at 1000 and 1200°C. S also is present in the condensate for the 1200°C baseline feed test. At least 10 to 20 wt% of the batched sulfate is present in a soluble form (e.g., an MIS salt) at 1000 and 1200°C.
		TGA/DTA[b]	TGA of glass feed shows additional weight loss that starts at 1100°C.
Solid grains are nearly entirely dissolved. Sulfate and chloride salts form inclusions in the glass phase and are also present in bubbles. While sulfate and chloride inclusions rise to the surface in molten glass, they stay in the CRB where they may evaporate only to condense in colder portions of the porous CRB, distributing Tc and Re at greater depths into the block.	Sulfates and chlorides remain in CRB pores. Re and Tc penetrate to greater depths.	ES-31B Refractory Analysis[c]	S and Cl are present in the CRB pores after completion of the engineering-scale test. Distribution of Re in the CRB wall indicates that Re concentration drops off significantly with depth but penetrates further than the MIS constituents.
		Feed Immersion Tests[d]	Feed immersion tests also showed S and Cl in the CRB after heating to 1200°C
[a] See [7] for CFT results [b] See [7] and [8] for TGA/DTA results. [c] See [10] for engineering-scale test results. [d] See [8] for feed immersion test results.			

Table IX. Supporting Experimental Results for Step 5 - MIS Reaches Melt Surface and Vapors Transport to Exposed CRB

Description	Key Elements/ Assumptions	Evidence/Basis	
		Test	Result
At 1200° to 1400°C, the sulfate and chloride MIS reaches the glass melt surface and volatilizes. Tc/Re also volatilize directly from molten glass. The vapors penetrate CRB pores and condense on cooler surfaces of the CRB, hood, and off-gas system. Without the Na$_2$O from the nitrate and the higher temperatures seen in the lower CRB region, in the upper region Tc/Re are not incorporated in the glass phase and remain in a leachable form. *A large fraction of sulfate and chloride MIS reach the top surface of the molten glass, where they deposit as a thin layer and evaporate. Their vapors and volatile components from glass (such as sodium borate) condense on upper portions of the CRB, the hood, and the off-gas system. Iron oxides in the soil are reduced to iron metal through reaction with remaining starter path graphite and on the graphite electrode surfaces. Metallic iron makes droplets that form alloys with Tc/Re and other easily reduced elements, such as phosphorus, and sink to the bottom of the melt when they reach a sufficient size to overcome convective currents in the glass melt.*	Tc/Re within the melt also volatilize directly and condense on cooler surfaces.	CFT[a]	Pre-melted glass lost ~30% of Tc and Re in 5 h at 1200°C.
	Sulfate/ chloride MIS reaches the surface of the glass melt and volatilizes and condenses.	CFT[a]	1 wt% of the batched sulfate and 7 wt% of the batched Cl was collected in the cold finger condensate at 1200°C for the baseline feed. 7 wt% of the batched sulfate and 18 wt% of the batched Cl was collected in the cold finger for the pre-melted glass held at 1200°C for 5 h.
		ES-31B[b]	Re deposition was lower in ES-31B than in other engineering-scale tests with nitrate feed. The distribution of Re in the CRB was also relatively level from top to bottom (upper CRB portions were not elevated). Tank S-109 feed for ES-31B had a lower S/Na ratio (0.0074 vs. 0.018) than tests with the six-tank composite feed. Lower sulfate levels may reduce overall deposition in the CRB, particularly in the upper portions.
	Iron and Tc/Re within the melt are reduced by carbon. Iron inclusions form and scavenge additional iron and Tc/Re from the melt.	ES-32B[b]	Formation occurred of small dispersed iron metal inclusions and several large inclusions with high concentrations of Tc/Re compared to the bulk glass.

[a] See [7] for CFT results.
[b] See [10] for engineering-scale test results.

Fig. 13 shows the crucible rinse and cold finger condensate quantities of Cl, SO_4, and NO_3 in the CFT for the baseline feed. Fig. 14 shows the crucible rinse and cold finger condensate quantities of Cl and SO_4 in the CFT for the pre-melted feed. Fig. 15 shows the Tc/Re quantities in the glass and cold finger condensate for pre-melted glass held at 1200°C for 1 and 5 h. Collectively, these figures support the assumptions that the Tc/Re is associated with the sulfate/chloride MIS that does not completely incorporate in the glass and that these MIS phases volatilize and in turn promote the volatilization of Tc/Re. For example, Fig. 13 shows that, for the baseline feed, the quantity of Cl in the cold finger condensate is very low at 800°C but increases significantly at 1000°C and that 1 wt% of the batched sulfate and 7 wt% of the batched Cl was collected at 1200°C. Fig. 15 shows that 7 wt% of the batched sulfate and 18 wt% of the batched Cl was collected in the cold finger from the pre-melted glass held at 1200°C for 5 h. Figs. 7 and 15 show that the Tc/Re quantities collected on the cold finger are also significantly higher at 1000 and 1200°C for both the baseline feed and the pre-melted glass.

Fig. 13 also shows that at least 10 to 20 wt% of the batched sulfate is present in a soluble form at 1000 and 1200°C.
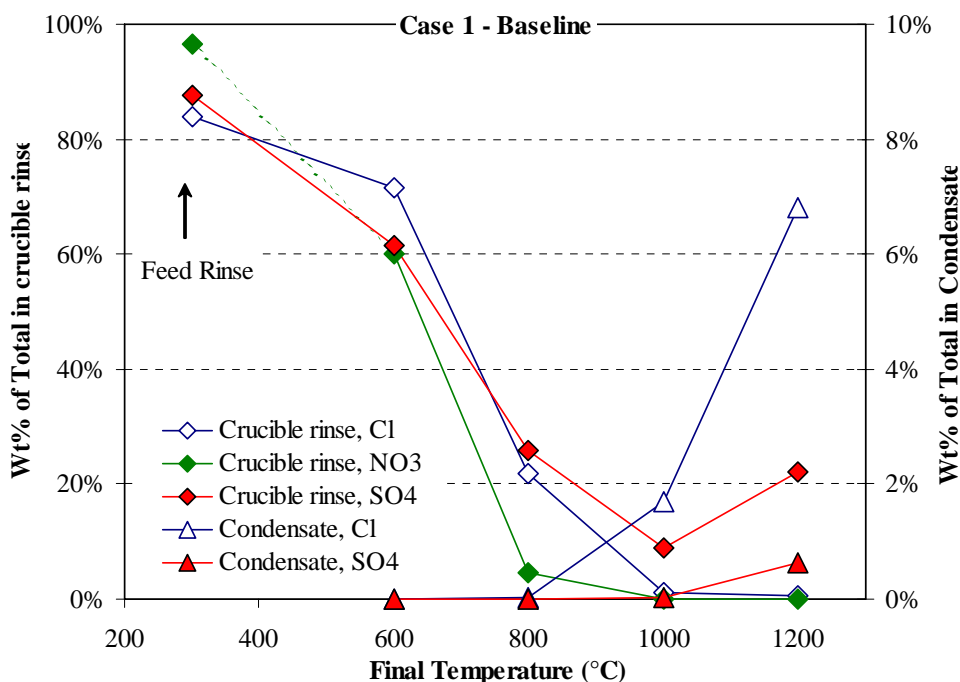

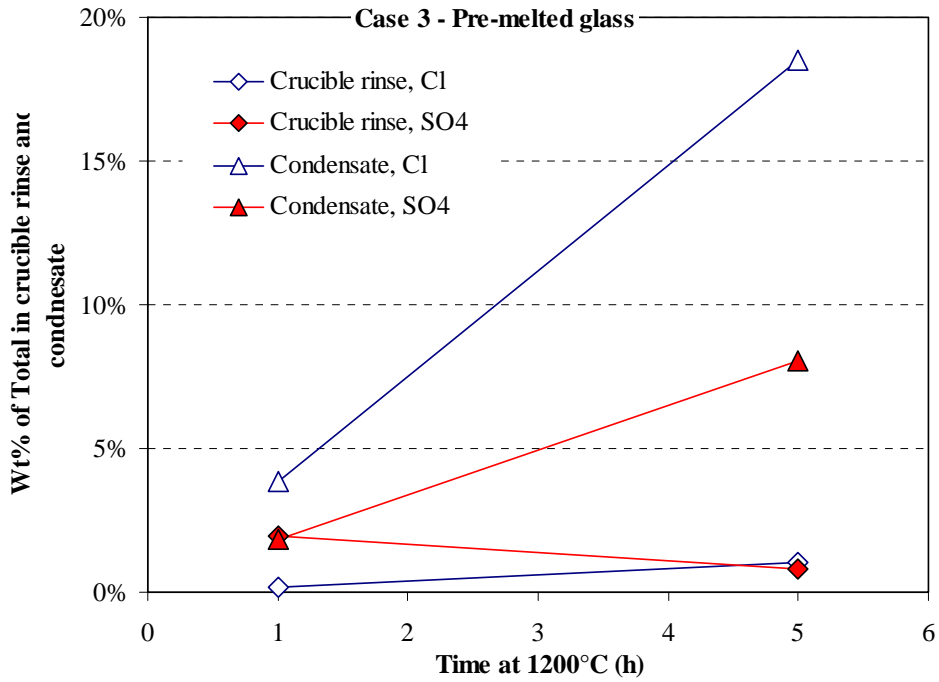Fig. 13. Wt% of total anions versus final temperature for Case 1—Baseline Feed

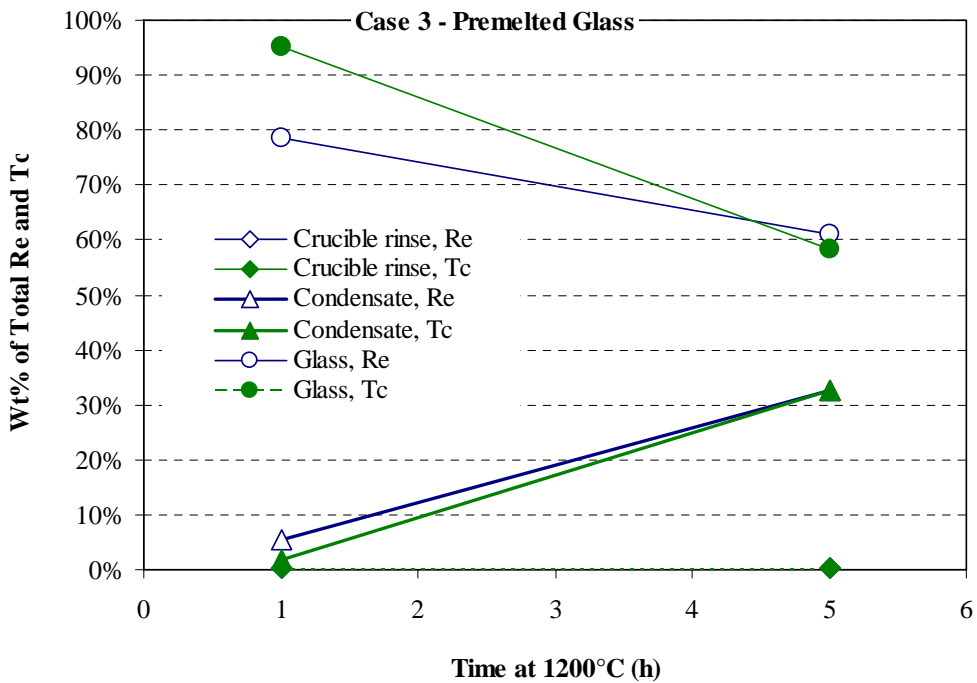Fig. 14. Wt% of total anions versus time at 1200°c for Case 3—Pre-Melted Glass

Fig. 15. Wt% of total Re and Tc versus final temperature for Case 3—Pre-Melted Glass

The no-sulfate feed test results (see Fig. 8) indicate a significant increase in Tc/Re glass retention of 30 to 40% and a decrease in condensate quantities by 15 to 25% when compared to the baseline feed. This result also supports the assumption that sulfate MIS impacts Tc/Re retention. Fig. 15 also supports the assumption that fully melted glass continues to volatilize Tc/Re since pre-melted glass shows cold finger quantities of ~30% of Tc and Re after heating for 5 h at 1200°C.

The melter feed immersion tests showed that S and Cl were present in the CRB after heating to 1200°C. Fig. 9 also shows that S and Cl are present in the ES-31B refractory sample after test completion and that small quantities of Re penetrate to depths greater than the MIS constituents. These results support the assumption that the sulfate/chloride MIS remains in the CRB and that Tc/Re penetrates, at lower concentration, deeper into the refractory wall.

The lower total quantity of Re in the ES-31B CRB (Table IV) is also consistent with the assumption that sulfate plays an important role in the ability of glass to retain Re. This test used Tank S-109 feed, which had a 60% lower S/Na ratio (0.0074 vs. 0.018) than tests with the six-tank composite feed. Lower sulfate levels may reduce overall deposition in the CRB, particularly in the upper portions.

Fig. 16 shows metal inclusions taken from the glass and an ingot taken from the base of the ES-32B glass melt. The ingot was composed of approximately 93 wt% iron, 6 wt% P, 0.35 wt% S, and 0.01wt% Tc and Re. These results support the assumption that iron oxides in the soil can be reduced to iron metal, which forms alloys with Tc/Re and other easily reduced elements (e.g., phosphorus and S). The inclusion and ingot show that the metal can either stay suspended in the glass or sink to the bottom of the melt when it reaches a sufficient size to overcome convective currents in the glass melt.
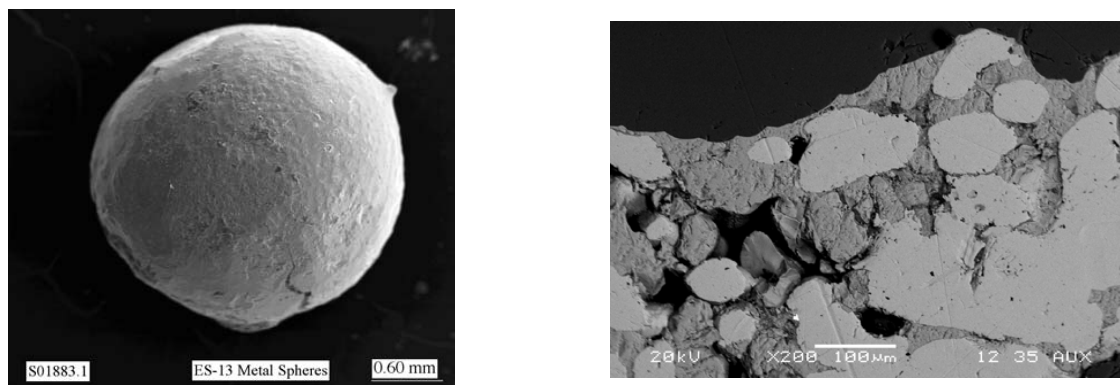

Fig. 16. Iron inclusion in a BV glass (left) and ingot of iron accumulated at the BV melt bottom (right) from ES-32B. The ingot is composed of approximately 93 wt% iron, 6 wt% P, 0.35 wt% S and 0.01 wt% Tc

SUMMARY AND CONCLUSIONS

Based on engineering-scale BV test results, a small fraction of Tc and Re deposits on the surface and within the pores of the CRB during vitrification. Tc is a primary risk driver for long-term performance of immobilized LAW; therefore, controlling and minimizing the amount of Tc deposition is desired to ensure consistently acceptable levels. A testing program was developed and implemented to evaluate likely mechanisms of Tc transport and deposition, with the goal of developing an understanding of the mechanism to guide the BV process design, testing, and operations.

Based on observed laboratory and engineering-scale test results, a plausible conceptual model has been developed for Tc/Re transport into the CRB during the BV process. In the process, especially during startup, the feed/glass refractory interface is exposed to a moving temperature gradient that starts at ambient temperature and proceeds to 1200°C or greater. Considering the evolution of the temperature field within the CRB, the Tc/Re transport scenario can be outlined as proceeding in the following stages/steps:

Initial Feed Melting

1. The first step in the melting process is the formation of an MIS in the feed that includes all the Tc/Re within the porosity of the soil and other insoluble grains. By capillarity, this MIS penetrates the CRB open porosity as the interface temperature increases from 200 to 650°C.

2. At approximately 650 to 750°C, the MIS decomposes through the loss of NO_x, leaving mainly sulfate and chloride salts. The Na_2O formed in the decomposition of the nitrates also starts to react with insoluble grains in the feed (soil and ZrO_2), and to some extent the aluminosilicates in the CRB, to form more viscous liquids that reduce further liquid penetration into the CRB.

Glass Formation

3. At 750 to 950°C, a continuous glass phase starts to form that traps the remains of the MIS in the form of inclusions in the bulk glass melt.

4. At 950 to 1200°C, the salt inclusions in the glass slowly dissolve but also rise to the surface. The salt inclusions in the CRB continue to react and form glassy phases that may incorporate some of the Tc/Re but also evaporate and condense in colder portions of the porous CRB, distributing Tc/Re as they condense. The Tc/Re salts also evaporate from the free surface of the glass melt that is rapidly renewed by convective currents.

5. Available data support the conclusion that a substantial fraction of Tc/Re deposits is incorporated into a durable glass phase as the maximum temperatures are reached in the lower CRB regions.

    - At 1200 to 1400°C, the low-density inclusions of sulfate/chloride MIS continue to reach the surface of the glass melt, where they volatilize and condense on cooler surfaces in the upper portion of the CRB, the box lid, and the off-gas system. The condensate from the sulfate/chloride MIS penetrates the CRB and deposits Tc/Re in the upper portions. Without the Na_2O from the nitrate decomposition and the higher temperatures seen in the lower sections of the box, the Tc/Re deposits in the upper region of the CRB are not incorporated in a refractory glass phase and remain in a leachable form.

    - An additional mechanism of Tc removal from molten glass is the partitioning of metallic Tc into droplets of metallic iron. Metallic iron can be reduced from Fe_2O_3 (4 to 8 mass%

of Hanford soil), mainly by the unoxidized residue of carbon used as the starter path for electric melting. A fraction of the iron droplets may coalesce and sink to the melt bottom and form Tc-containing ingots.

The conceptual model concludes that both low-temperature molten salt penetration and high-temperature evaporation and condensation mechanisms play significant roles in the transport of Tc/Re. Therefore, methods to control and minimize the amount of Tc deposition must focus on parameters affecting both liquid and vapor-phase transport. For example, molten salt penetration of the CRB should be significantly affected by molten salt contact time with the CRB, and CRB permeability and wetability. Process and feed conditions that encourage adsorption and rapid decomposition of the MIS and MIS decomposition products may limit Tc/Re transport. Vapor-phase transport should be significantly affected by temperature and time; therefore, long melt times at high temperatures should be avoided. The conceptual model of the mechanism of Tc/Re transport and deposition during the BV process is based on direct and indirect evidence from experimental studies. Additional testing, especially at larger scale, will provide data needed to fill gaps in the model, decrease data uncertainty, assess the impact of scale on Tc/Re transport behavior, and evaluate design and operational regimes to control and reduce Tc/Re deposition.

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REFERENCES

1. U.S. Department of Energy (DOE). 2002. *Performance Management Plan for the Accelerated Cleanup of the Hanford Site*. DOE/RL-2002-47, Rev. D, U.S. Department of Energy, Richland, Washington.

2. R.E. Raymond, R.W. Powell, D.W. Hamilton, W.A. Kitchen, B.M. Mauss, and T.M. Brouns. 2004. *Initial Selection of Supplemental Treatment Technologies for Hanford's Low-Activity Tank Waste*. In Proceedings of WM'04 Symposia. WM-4524/RPP-19763-FP, CH2M HILL Hanford Group, Inc. Richland, Washington.

3. D.S. Kim, J.D. Vienna, P.R. Hrma, M.J. Schweiger, J. Matyáš, J.V. Crum, D.E. Smith, G.J. Sevigny, W.C. Buchmiller, J.S. Tixier, J.D. Yeager, and K.B. Belew. 2003. *Development and Testing of ICV Glasses for Hanford LAW*. PNNL-14351, Pacific Northwest National Laboratory, Richland, WA.

4. L. Thompson, L. McClure, and D. Hamilton. 2005. *Status and Direction of the Bulk Vitrification Program for the Supplemental Treatment of Low Activity Tank Waste at Hanford*. In Proceedings of WM'05 Symposia. WM-5138, AMEC Earth and Environmental, Inc., Richland, WA.

5. F.M. Mann, B.P. McGrail, D.H. Bacon, R.J. Serne, K.M. Krupka, R.J. Puigh, R. Khaleel, and S. Finfrock. 2003. *Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies*. RPP-17675, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

6. S.D. Rassat, L.A. Mahoney, R.L. Russell, S.A. Bryan, and R.L. Sell. 2003. *Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis*. PNNL-14194 Rev.1, Pacific Northwest National Laboratory, Richland, WA.

7. D.S. Kim, C.Z. Soderquist, J.P. Icenhower, B.P. McGrail, R.D. Scheele, B.K. McNamara, L.M. Bagaasen, M.J. Schweiger, J.V. Crum, J.D. Yeager, J. Matyáš, L.P. Darnell, H.T. Schaef, A.T. Owen, A.E. Kozelisky, L.A. Snow, and M.J. Steele. 2005. *Tc Reductant Chemistry and Crucible Melting*

Studies with Simulated Hanford Low-Activity Waste. PNNL-15131, Pacific Northwest National Laboratory, Richland, WA.

8. P.R. Hrma, L.M. Bagaasen, A.E. Beck, T.M. Brouns, D.D. Caldwell, M.L. Elliott, J. Matyáš, K.B.C. Minister, M.J. Schweiger, D.M. Strachan, B.P. Tinsley, and G.W. Hollenberg. 2005. *Bulk Vitrification Castable Refractory Block Protection Study*. PNNL-15193, Pacific Northwest National Laboratory, Richland, Washington

9. E.M. Pierce, B.P. McGrail, L.M. Bagaasen, D.W. Wellman, J.V. Crum, K.N. Geiszler, and S.R. Baum. 2004. *Progress Report on the Laboratory Testing of Bulk Vitrification Cast Refractory*. PNNL-14935, Pacific Northwest National Laboratory, Richland, WA.

10. E.M. Pierce, B.P. McGrail, L.M. Bagaasen, E.A. Rodriguez, D.M. Wellman, K.N. Geiszler, S.R. Baum, L.R. Reed, J.V. Crum, and H.T. Schaef. 2005. *Laboratory Testing of Bulk Vitrified Low-Activity Waste Forms to Support the 2005 Integrated Disposal Facility Performance Assessment.* PNNL-15126, Rev. 1., Pacific Northwest National Laboratory, Richland, Washington.

11. C.V. Thomason and F.W. Wilburn. 1960. The Application of Differential Thermal Analysis and Thermogravimetric Analysis to the Study of Reactions between Glass Materials: Part 2. Sodium Carbonate System with Minor Batch Additions. *Physics and Chemistry of Glasses* 1:52-69.

12. O. Abe, T. Utsunomiya, and Y. Hoshino. 1983. The Reaction of Sodium Nitrate with Silica. *Bulletin of the Chemical Society of Japan* 56: 249-433.

13. P.A. Smith, J.D. Vienna, and P. Hrma. 1995. The Effect of Melting Reactions on Laboratory-Scale Waste Vitrification. *Journal of Materials Research* 10: 2137-2149.

14. P. Hrma, J. Matyáš, and D.S. Kim. 2002, The Chemistry and Physics of Melter Cold Cap. *9th Biennial International Conference on Nuclear and Hazardous Waste Management, Spectrum '02*, American Nuclear Society.

15. J. Matyáš, P. Hrma, and D.S. Kim. 2004. Analysis of Feed Melting Processes. *Ceramic Transactions* 155: 69-78.

16. P. Hrma, J. Matyáš, A.E. Beck, M.J. Schweiger, D.D. Caldwell, B.P. Tinsley, D.M. Strachan, M.L. Elliott, L.M. Bagaasen, T.M. Brouns, and G.W. Hollenberg. 2005. Bulk Vitrification Castable Refractory Block protection Against Molten Ionic Salt Penetration. *Proceedings of International Symposium on Radiation Safety Management*, Daejeon, S. Korea, 233-250.