Method to Reduce Molten Salt Penetration into Bulk Vitrification Refractory Materials - 8275

L.M. Bagaasen, P.R. Hrma, D-S Kim, M.J. Schweiger, J. Matyas, C.P. Rodriguez
Pacific Northwest National Laboratory
902 Battelle Boulevard, Richland WA 99352

K.S. Witwer
AMEC Nuclear Holdings Ltd., GeoMelt Division
1135 Jadwin Avenue, Richland, WA, 99352

ABSTRACT

Bulk vitrification (BV) is a process that heats a feed material consisting of glass-forming solids and dried low-activity waste (LAW) in a disposable refractory-lined metal box using electrical power supplied through carbon electrodes. The feed is heated to the point that the LAW decomposes and combines with the solids to generate a vitreous waste form. However, the castable refractory block (CRB) portion of the refractory lining has sufficient porosity to allow the low-viscosity molten ionic salt (MIS), which contains technetium (Tc) in a soluble form, to penetrate the CRB. This limits the effectiveness of the final waste form. This paper describes tests conducted to develop a method aimed at reducing the quantities of soluble Tc in the CRB.

Tests showed that MIS formed in significant quantities at temperatures above 300°C, remained stable until roughly 550°C where it began to thermally decompose, and was completely decomposed by 800°C. The estimated volume fraction of MIS in the feed was greater than 40%, and the CRB material contained 11 to 15% open porosity, a combination allowing a large quantity of MIS to migrate through the feed and penetrate the open porosity of the CRB. If the MIS is decomposed at temperatures below 300°C or can be contained in the feed until it fully decomposes by 800°C, MIS migration into the CRB can be avoided.

Laboratory and crucible-scale experiments showed that a variety of methods, individually or in combination, can decrease MIS penetration into the CRB. Modifying the CRB to block MIS penetration was not deemed practical as a method to prevent the large quantities of MIS penetration seen in the full-scale tests, but it may be useful to reduce the impacts of lower levels of MIS penetration. Modifying the BV feed materials to better contain the MIS proved to be more successful.

A series of qualitative and quantitative crucible tests were developed that allowed screening of feed modifications that might be used to reduce MIS penetration. These tests showed that increasing the specific surface area of the soil (used as the primary glass-forming solid in the baseline process) by grinding stopped MIS penetration nearly entirely for feeds that contained waste simulants with lower quantities of nitrate salts. Grinding soil significantly reduced MIS penetration in feeds with higher nitrate quantities, but it was necessary to add carbohydrates (sucrose or cellulose) to destroy a portion of the nitrate at low temperatures to reach the same low levels of MIS penetration seen for the lower nitrate feeds.

Developing feeds to reduce MIS penetration in full-scale BV applications resulted in two additional refinements. Soil-grinding to the necessary levels proved to be difficult and expensive, so the fine soil was replaced with readily available fine-grained glass-forming minerals. Cellulose was shown to have

less impact on dryer operation than sucrose and was chosen as the carbohydrate source to use in subsequent engineering- and full-scale tests.

INTRODUCTION

More than 200 million liters (53 million gallons) of highly radioactive and hazardous waste is stored at the U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State. DOE has committed to retrieving this waste and partitioning the less radioactive component, referred to as low-activity waste (LAW), from the highly radioactive constituents. The Waste Treatment and Immobilization Plant (WTP), currently under construction, is not designed with the capacity to treat the majority of the LAW within the timeframe agreed to between DOE, the Washington State Department of Ecology, and the U.S. Environmental Protection Agency. This agreement, called the Tri-Party Agreement, specifies that pretreatment and immobilization of all Hanford waste must be completed by the year 2028.

Several supplemental treatment technologies were evaluated by DOE's Office of River Protection (ORP) and its prime contractor at Hanford, CH2M Hill Hanford Group, Inc. AMEC's[1] bulk vitrification (BV) process, referred to as in-container vitrification (ICV)™,[2] was selected for further evaluation. This project is referred to as the Demonstration Bulk Vitrification System (DBVS). Thompson et al. [1] summarized the overall status, direction, and description of the DVBS program, and Witwer et al. [2] updated this summary in 2006 [2] and 2007 [3].

ICV™ PROCESS DESCRIPTION

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 of in an 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 baseline BV process includes a mixer/dryer to convert liquid waste into a dried, blended feed for vitrification. This is done by blending liquid LAW with glass-forming minerals (GFMs) and then drying the feed in a 10,000-liter vacuum dryer at temperatures ranging from 60 to 80°C. The mixture is brought to a suitable dryness, consistency, and particle size for transport to the BV container for subsequent melting at approximately 1250 to 1350°C by electrical resistance. Graphite flakes are added to the mix to form a conductive path for melt initiation. Electrical current is supplied by two graphite electrodes. The current design uses a "feed-while melt" process in which melting is initiated in a small quantity of staged batch, and additional batch is gradually loaded in increments until the container is filled with waste glass. A rigid castable refractory block (CRB) is used as the primary liner to protect the steel container from the glass melt. The CRB is made from Vibrocast 60PC,[3] a 60% alumina, mullite-based, low-cement castable designed to provide minimum porosity.

Extensive testing is done in parallel with the design of DBVS to find and fix any processing problems. Three different scales are used to test the system: laboratory (crucible) scale, engineering scale, and full scale. Laboratory-scale testing is done to develop glass formulations, test composition boundaries, and

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[1] AMEC is a leading provider of technical consultancy, engineering services and program and asset management to the nuclear industry.

[2] In-Container Vitrification™ is a registered trademark of AMEC Inc.

[3] E. J. Bartell Co., Spokane, Washington.

evaluate chemistry changes for limiting molten ionic salt (MIS)[4] formation and migration. Engineering-scale testing is used as a relatively low-cost screening method prior to full-scale testing.

Engineering-Scale Testing

Figure 1 is a photograph of the typical engineering-scale test equipment used at AMEC's test site. The engineering-scale tests used a container that is about $^1/_6$ linear scale relative to the full-scale container. Engineering-scale tests supply a variety of useful processing and waste-performance information. Three series of engineering-scale tests have been conducted: the 30-series qualitative tests, 31-series quantitative tests spiked with Re as a Tc surrogate, and the 32-series quantitative radioactive tests spiked with both Tc and Re.

Fig. 1. Engineering-scale test apparatus.

Full-Scale Testing

Figure 2 is a photograph of AMEC's testing area where full-scale tests are performed. The tests at this facility are simulant tests that can include low levels of heavy metals such as Cr and are known as the 38-series tests. This facility allows full-scale testing to identify and address problems in a controlled non-radioactive environment before the DBVS facility is built and operated on the Hanford Site. The current facility includes the prototypic 10,000-liter dryer/mixer, the ICV™ melter, and non-prototypic dry-waste transfer and off-gas treatment systems. Before 2007, the site did not have the 10,000-liter dryer, so waste feed was produced for tests by dry-blending waste-simulant chemicals with GFMs. Figure 3 shows a more detailed picture of the ICV™ assembly showing the graphite electrodes, feed chutes, and off-gas pipe.

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[4] Molten salt is salt is the low viscosity liquid that forms when the Hanford waste components initially melt.

Waste Simulants

The simulant used for glass-formulation development and testing to support the 2003 supplemental treatment selection process was a waste simulant known as the six-tank composite. After the selection process was completed, Hanford Tank 241-S-109 (S-109) was selected as the feed tank for DBVS operations, and testing was expanded to include glass compositions for simulants based on S-109 information. Table I shows that the main difference in the two simulants is that S-109 has higher nitrate and lower hydroxide and sulfate concentrations than the six-tank composite formulation. These differences are important with respect to MIS formation and transport.

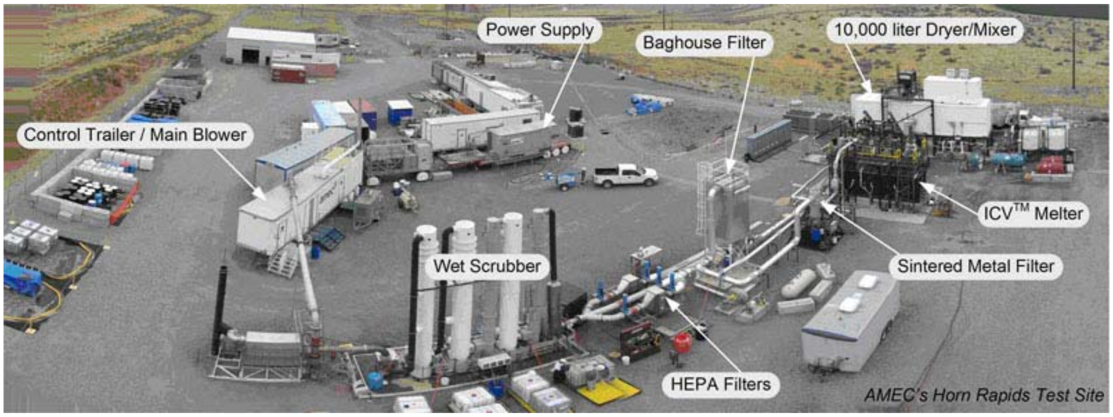

Fig. 2. AMEC's full-scale testing area.

Fig. 3. Full-scale ICV^{TM} test assembly at AMEC's site in Richland, WA.

Glass Formulations

A baseline glass-formulation and preliminary-waste envelope for the BV process was developed based on a constraint that required that the BV process use Hanford soil for glass-forming chemicals to the extent possible. Table II shows the final target glass compositions when the two waste simulants discussed in the preceding section were processed in full-scale (FS) tests, and Table III shows the recipe used to obtain these compositions.

Table I. Comparison of S-109 and Six-Tank Waste Simulants

	Moles/Mole of Na	
Species	S-109	Six-Tank Composite
Al	0.0088	0.0143
Ca	0.0002	0.0000
Cl	0.0014	0.0088
Cr	0.0028	0.0021
F	0.0011	0.0063
Fe	0.0009	0.0000
K	0.0008	0.0029
P	0.0109	0.0098
SO_3	0.0074	0.0180
NO_3	0.8241	0.5070
NO_2	0.0123	0.0848
CO_3	0.0338	0.0953
OH	0.0666	0.1479
Organic C	0.0050	0.0573

Table II. Target Compositions of Glasses Produced in FS-38B and FS-38C

Test	FS-38B	FS-38C
Waste Simulant	Six-Tank Composite	S-109
Component	Glass Composition (Mass Fraction Oxide/Halogen)	
Al_2O_3	0.0800	0.0800
B_2O_3	0.0500	0.0500
BaO	0.0005	0.0005
CaO	0.0288	0.0285
Cl	0.0018	0.0003
Cr_2O_3	0.0010	0.0013
F	0.0007	0.0001
Fe_2O_3	0.0400	0.0400
K_2O	0.0193	0.0186
MgO	0.0139	0.0137
MnO	0.0006	0.0006
Na_2O	0.2000	0.2000
P_2O_5	0.0054	0.0058
SiO_2	0.4730	0.4804
SO_3	0.0084	0.0035
SrO	0.0003	0.0002
TiO_2	0.0064	0.0064
ZrO_2	0.0700	0.0700
SUM	1.0000	1.0000

Table III. Feed Recipes for FS-38B and FS-38C Glasses

Test	FS-38B		FS-38C	
Materials	Mass, kg	Wt%	Mass, kg	Wt%
Six-tank composite simulant	19,331	36.1	-	-
S-109 simulant	-	-	21,252	38.1
HRTS soil	26,285	49.1	25,924	46.5
ZrO_2	3,080	5.8	-	-
$ZrSiO_4$	-	-	4,613	8.3
B_2O_3	2,200	4.1	2,200	3.9
SiO_2	2,374	4.4	1,426	2.6
$Al(OH)_3$	247	0.5	373	0.7
Total	53,516	100.0	55,787	100.0

EVOLUTION OF THE MOLTEN IONIC SALT CONCERN

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 be in a soluble form deposited in a vesicular glass layer located at the top of the BV melt and in the quartz sand previously used as insulation. Based on an initial risk assessment, the small amount of soluble Tc salt in the BV waste packages was projected to create a Tc concentration peak at early times in the groundwater extracted from a 100-meter down-gradient well [4]. 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 the deposition of soluble Tc salts. It was decided to use a CRB in place of a portion of the refractory sand layer and a bottom-up melting technique to reduce Tc deposition in the porous refractory sand and to eliminate the vesicular glass layer at the top of the melt.

Five Series 31 and two Series 32 quantitative engineering-scale tests were conducted in late 2004 and early 2005 to assess and reduce Tc migration. The CRB configuration for these tests is shown in Fig. 4 [5]. Table IV summarizes parameters for the seven tests. Tc and Re quantities in the CRB were estimated [6], and the levels of Re[5] and Tc in the CRB for each of the engineering-scale tests, normalized to the amount of material added to each test, are shown in Table V. The amount of leachable Re, excluding the results from Test 31D,[6] ranged from a high of 5.74 ± 0.44% to a low of 0.77 ± 0.06% with an average value of 2.11 ± 0.74%. These results were combined with the Tc results obtained from Tests ES-32A and -32B to determine a best estimate of 0.37 ± 0.12% for the amount of Tc that would be present as a soluble salt in the CRB [6]. This value is significantly lower than the earlier tests using a sand-only refractory and top-down melting technique, which indicated that 2 wt% of the Tc inventory was deposited in the sand insulation and vesicular glass layer after vitrification. Results from Tests ES-32A and -32B were also used to generate a Tc/Re mobility ratio of 0.17 to estimate CRB Tc levels from future tests that only contained Re. It is interesting to note that the only early ES test that used the S-109 simulant, ES-31B, showed the lowest level of Re in the CRB for this ES test configuration.

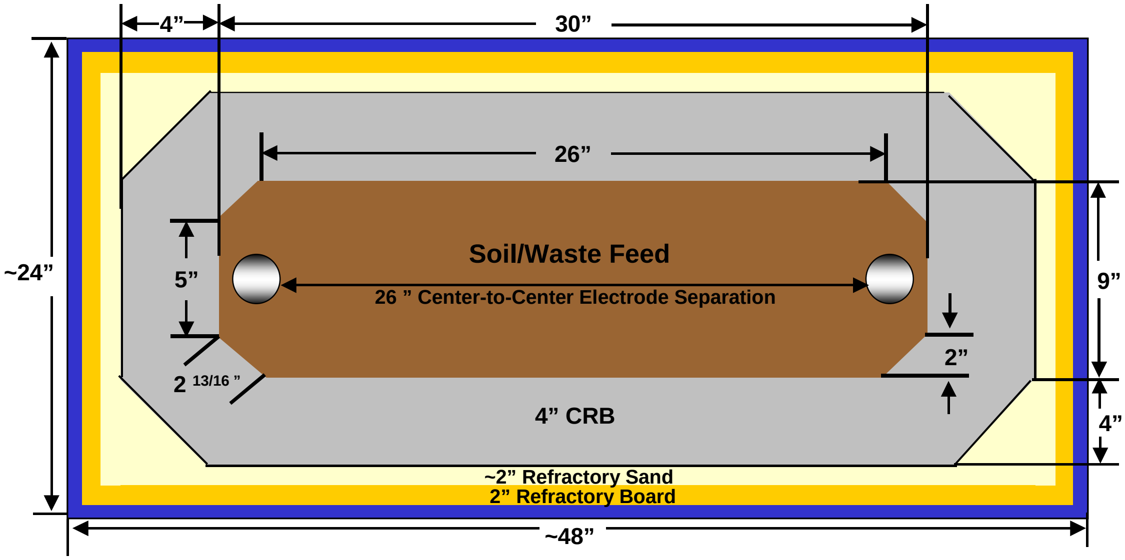

Fig. 4. Schematic plan view of the engineering-scale BV design.

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[5] Non-radioactive surrogate for Tc.

[6] 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. Quantitative engineering-scale tests.

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

Table V. Summary of engineering-scale soluble fraction test results.

Test ID	% Soluble Re in CRB[a]	% Soluble Tc in CRB[a]
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	5.74 ± 0.44	Not Spiked
ES-31D[b]	0.24 ± 0.03	Not Spiked
ES-31E	1.96 ± 0.16	Not Spiked
Average	2.11 ± 0.74	-
Best Estimate Using both Re and Tc Data		0.37 ± 0.12%

[a] All uncertainty values reported as ± 1 σ.
[b] ES-31D was not used in the calculation of the average.

Although ES testing showed that the soluble Tc fraction was significantly reduced by modifying the process, a small fraction of soluble Tc still remained in the CRB and was projected to result in a groundwater peak different than WTP glass. Also, the potential impacts of process scale on the quantity of soluble Tc that deposited in the CRB were not known. As a result, work was continued to both generate a better understanding of the mechanisms of deposition and to understand the scale-up impacts on Tc deposition in the CRB.

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 MIS 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. The testing program identified MIS migration as the predominant mechanism for movement of Tc into the CRB [7], and PNNL[7] had efforts underway to look at potential methods to further reduce the levels of MIS penetration.

Full-scale tests FS-38B and FS-38C were useful to help determine the scale-up impacts on Tc deposition in the CRB. Test FS-38B was performed in November 2005 and used the six-tank composite simulant (see Table I) with a Re spike to allow for a direct correlation to earlier engineering-scale tests. The test ran for 168 hours but was terminated with only $^{2}/_{3}$ of the planned simulant load added. Off-gas treatment system problems, aggravated by inclement weather and high condensate levels in the off-gas stream, forced early termination of the test. In addition, feed-delivery delays to the melt resulted in premature melt off of unprocessed feed on the melt surface, and the melt was covered by only a thin cold cap during much of the run. A consequence of this small cold cap was that Re retention in the melt was only 38% due to volatilization. However, analysis of the CRB found calculated Re levels of only 0.75 wt% and estimated Tc levels of only 0.13%.[8]

Full-scale test FS-38C was performed in May 2006. To better replicate the waste to be treated at the DBVS facility, S-109 simulant spiked with Re was used in FS-38C rather than the six-tank composite simulant. Based on earlier test results, Test 38C was operated with a significant feed pile above the molten glass to act as a cold cap and improve contaminant retention in the glass. All the planned feed material and clean cover-batch were melted, producing 44 metric tons of vitrified product.

The cold cap resulted in high single-pass Re and SO_3 retentions in glass of 70.9 wt% and 95 wt%, respectively but, combined with a shift to S-109 simulant, also significantly increased the quantity of MIS migration as can be seen in Fig. 5. This figure shows the FS-38C box after partial disassembly and the large quantity of clumped sand that was fused together from the penetration and subsequent thermal decomposition of large quantities of MIS. The FS-38C results led to an accelerated effort to devise methods to reduce MIS migration while allowing the continued use of cold caps in the BV process.

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[7] Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract number DE-AC05-76RL01830.

[8] Tests 38B did not feed radioactive Tc. Estimated Tc levels are based on Re analysis and calculations, adjusted for differences in Tc and Re behavior based on radioactive tests conducted with both Tc and Re.

Fig. 5. MIS penetration in 38C.
This view shows the outer wall of the CRB after the metal sides of the ICV™ box were removed, and the insulating sand was drained. Liquid MIS penetrated the CRB walls causing staining and clumping of the insulating sand.

PROGRESSION TO A MIS SOLUTION

An integrated process was used to generate a solution to the MIS migration problem. This process worked to minimize the impacts to the existing BV process design. The process started with a clear understanding of the problem, then looked at potential solutions to see what would be the most effective, and then conducted tests to determine the impacts to current equipment and designs. The final step was a set of scale-up tests that were used to show that the potential solution merited testing at full-scale. Highlights of each of the steps are discussed in the following sections.

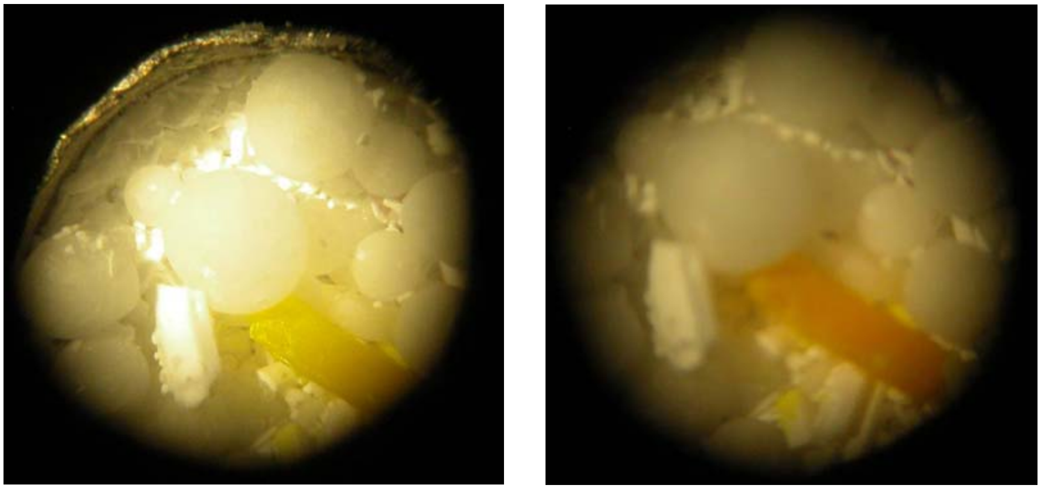
Developed a Conceptual MIS Migration Model

Previous work [7] described a conceptual model, supported by experimental evidence, that explained how a substantial portion of a well-dispersed and very-minute component (Tc) can segregate from a large volume of feed and migrate into a porous refractory wall that is contacted by that feed for a relatively short time at a relatively low temperature. The BV feed is a mixture of LAW and glass-forming solids. The LAW is a mixture of salts, predominantly nitrates. As the feed temperature increases, a single MIS phase that incorporates some B_2O_3 is formed from the LAW salts. The MIS wets the grains of feed solids, spreading over and bridging them, fills some of the space between the grains, and can freely migrate between the solid particles. The MIS begins to form at a temperature as low as 150°C, is fully developed by 450°C, and is nearly fully incorporated into a glass-forming phase by 800°C. The CRB contains fine open pores that adsorb the free MIS and are capable, provided that an ample supply of MIS is available, to transfer the MIS through the refractory wall and deposit it on its outer surface. The low viscosity of molten salts, which is close to that of water at ambient temperature, facilitates MIS penetration into the CRB. Because Tc is carried to the CRB by MIS, decreasing MIS migration into the CRB would proportionally decrease the concentration of the soluble Tc in the refractory lining.

Verified Model with Laboratory Evaluations and Full-Scale Tests

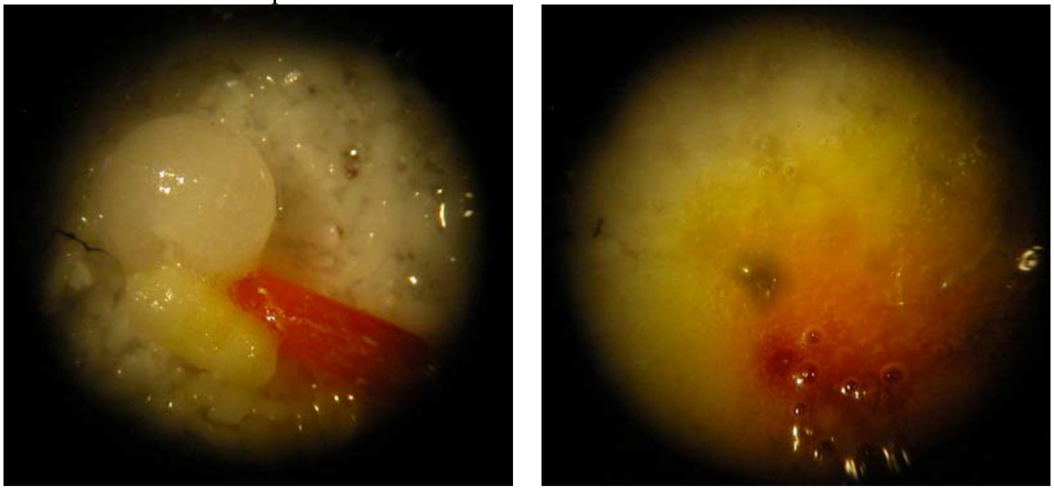
The progression of the formation and eventual thermal destruction of the molten salt was verified with hot-stage microscopy. The photos in Fig. 6 show the change of morphology of a dry-blended six-tank composite simulant with temperature. At 330°C, localized melting at the interface was apparent, but the MIS had not fully formed. At 450°C, the MIS had fully formed, and by 550°C, it was a clear liquid. The photo at 760°C shows the rapid thermal decomposition of $NaNO_3$.

There must be a sufficient volume of material to migrate and sufficient open porosity in the CRB material for the conceptual model for MIS migration to hold true. Calculations showed that the volume fraction of MIS in feed is large; for the six-tank LAW simulant, MIS makes 41.6 vol% of the condensed phase (excluding the void fraction) and can be as high as 46 vol% if all the B_2O_3 is dissolved in the MIS. This calculation demonstrates that there is enough volume of MIS to readily migrate to the CRB wall. Water absorption tests were combined with gas pycnometer tests to determine the total and open porosity in the CRB. Total porosity measurements were on the order of 22%, and the open (connected) porosity ranged from 11 to 15%, indicating that the there was sufficient open porosity for MIS penetration.



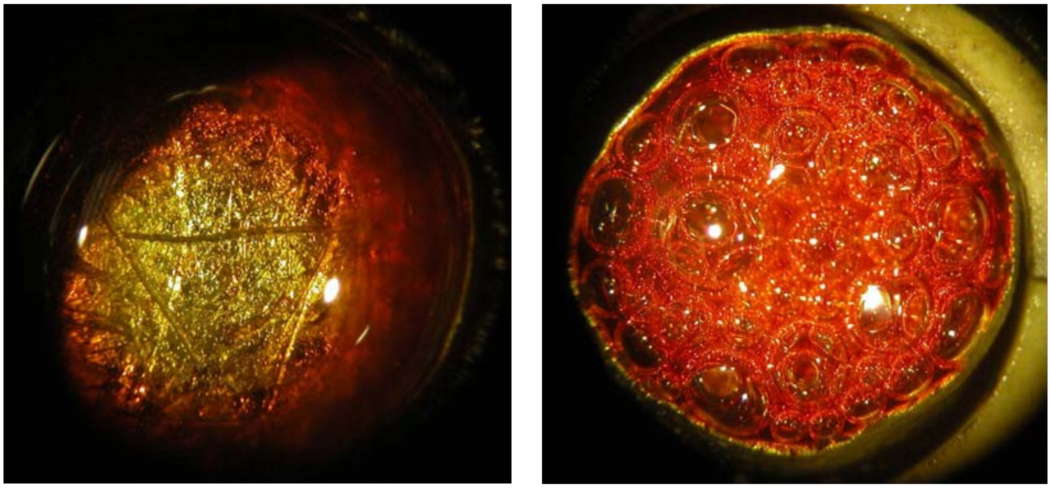
Room temperature

250°C



330°C

450°C



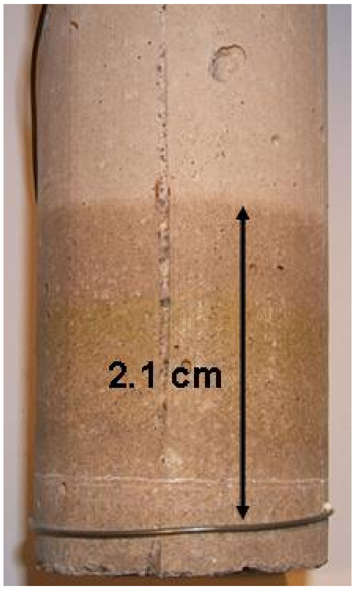
550°C

760°C

Fig. 6. Hot-stage microscopy images of dry LAW (six-tank composite) simulant.

Another portion of the model that had to be verified was the transport rates of the MIS through the CRB material. The FS-38C test results seemed to indicate that the MIS penetrated directly through the CRB, but several small cracks were present that could have played a role in transport of the MIS.

Experiments were conducted with a six-tank composite MIS simulant at 450°C to determine the penetration kinetics. Figure 7 shows that the capillary rise in the CRB material was more than 2 cm after only 3 hours, indicating that direct penetration of MIS into the refractory through capillary action was the predominant transport mechanism. Attempts to minimize CRB cracking would have little impact on MIS migration.



CRB sample in MIS at 450°C after 3 hours

Fig. 7. Capillary rise of MIS in the CRB material.

The results from the FS-38C test (see Fig. 5) in combination with laboratory tests showed that migration of MIS into the CRB was a major factor that would limit the effectiveness of the BV process if it were not addressed.

Developed Laboratory Tests to Measure MIS Migration

A key step in evaluating methods to reduce MIS migration and penetration was to develop a simple, low-cost, repeatable, quantitative test to measure the extent of MIS transport from feeds to the porous refractory. Early tests estimated MIS penetration depths on 2×2 cm rods of the CRB material that had been placed axially in Pt crucibles filled with feed and subjected to various heat treatments. Because of the non-uniformities in the CRB, these penetration depths were difficult to quantify. The process of tracking the Na penetration depths with scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) was expensive and time consuming.

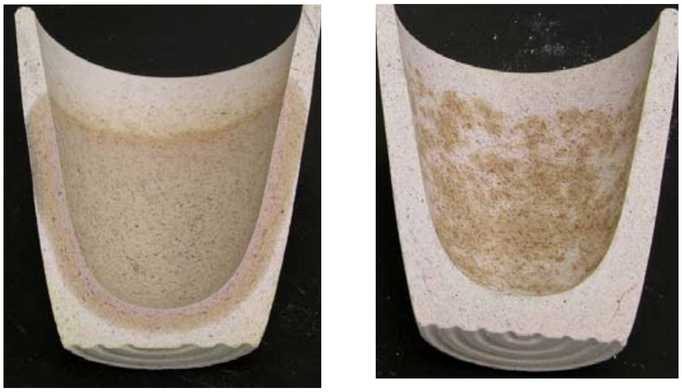
A successful MIS penetration measurement test involved heat treatment of feed in porous, commercial silica crucibles that were about 10 cm tall and 5 cm in diameter. The porous silica crucible walls are more uniform in composition, structure, and porosity than the CRB, and allowed easy detection of migrated MIS in sectioned samples. These simple tests were shown to be representative of the MIS migration data obtained with the more complicated CRB rod tests. The final procedure developed for these tests included the following steps:

1. The pre-weighed crucibles were filled with about 165 g of feed and re-weighed to determine the exact quantity of feed added.

2. The loaded crucible was heated at 5°C/min to 500°C and held for 30 min. This heat treatment was long enough to allow MIS to penetrate into the CRB but did not allow the feed to melt and adhere to the crucible walls.
3. After cooling, the feed was removed from the crucible, and the mass of the crucible (and any penetrated MIS) was measured. The mass of the feed was also measured to allow estimates of the extent of MIS reaction at 500°C. The mass difference in the crucible before and after heat treatment in contact with the feed gave an indication of the amount of MIS penetration except that the extent of decomposition of the MIS was unknown, and thus the fraction of the total MIS could not be obtained. This led to an additional heat-treatment step.
4. The empty crucible (with penetrated MIS) was heated at 5°C/min to 1000°C and held for 1 h. After cooling, the crucible was re-weighed and sectioned. This second heat treatment fully decomposed any penetrated MIS and brought the mass to a consistent basis for comparison. This allowed feeds that had additives that attempted to decompose the MIS at temperatures below 500°C to be compared to the performance of feeds where little or no decomposition occurred. This heat treatment also reacted the water-soluble MIS with the silica crucible and allowed for crucible sectioning and observation of the MIS penetration depths as shown in Fig. 8.
5. When comparing the result from different feeds, the final step was to correct the mass gained after heat treatment to 1000°C for the quantity of glass produced for different feeds. Making assumptions about the components that added to the quantity of MIS also allowed the 1000°C data to be expressed in terms of the fraction of total MIS penetrated.

Figure 9 shows why the 500°C temperature was chosen for the initial soak temperature and also supplies an example of the valuable insights that can be gained from a quantitative MIS penetration measurement method. Soak temperatures of 300, 400, and 500°C were investigated for feeds produced with the S-109 tank waste simulant that contained as-received and ground Hanford soil. The net mass gain after the subsequent heat treatment to 1000°C shows that little MIS penetration occurred at 300°C, but it increased with temperature at a decreasing rate. This mass gain correlates well with the MIS behavior seen in Fig. 6 where melting had just started at 330°C but was essentially complete at 450°C. The 400°C soak was necessary to melt the MIS-forming salts to allow penetration but most of the penetration was complete by 500°C, so higher temperatures were not necessary.

Figure 9 also demonstrates two other points that were important in generating a strategy to minimize MIS penetration levels. First, the penetration levels could be significantly reduced by increasing the specific surface area of the feed solids. The amount of penetrated MIS from feed with 2-min ground soil was about 73% less than the MIS penetration for feeds prepared with as-received soil at both 400°C and 500°C. The other point is that significant penetration did not occur at temperatures below 300°C, so decomposing the nitrate salts present in the wastes at temperatures below 300°C would be expected to reduce penetration.



Significant MIS penetration levels

MIS penetration reduced to low levels

Fig. 8. Example cross-sections of silica crucible results.

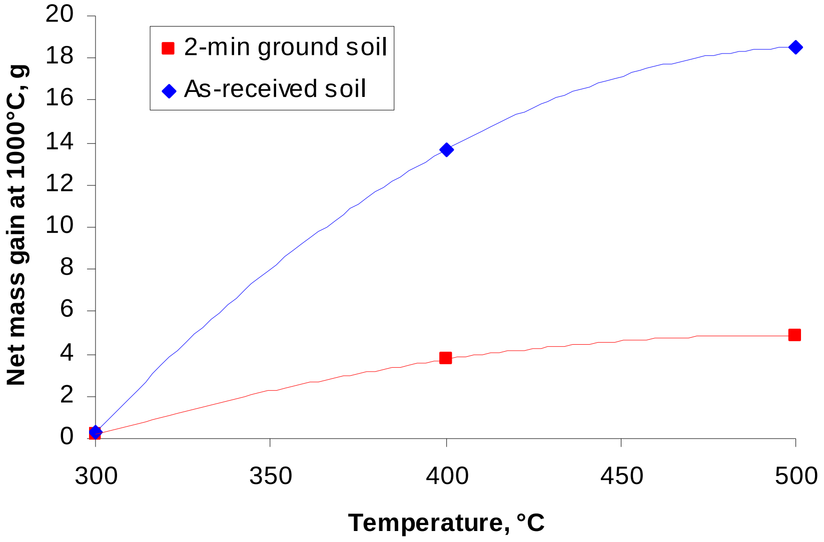


Fig. 9. Effect of temperature on MIS penetration to silica crucible from feed with S-109 simulant.

Identified Strategies to Reduce MIS Migration

Three main strategies to reduce the level of MIS migration into the CRB were explored. The first strategy involved surface treatments of the CRB that attempted to reduce the migration of the MIS. These treatments included surface glazes and tiles to block the MIS, sacrificial layers that would absorb the MIS and subsequently be dissolved in the glass, and carbon additions to the inner layer of the CRB to reduce the surface wetting. Some of the surface treatment strategies showed promise for reducing penetration when low levels of MIS were present but would not be effective for the high levels seen in the FS-38C test. After the FS-38C test demonstrated that MIS migration could be extensive at full scale, efforts were focused on the next two strategies.

The second strategy was to modify the feed to decrease the MIS mobility within the BV feed. Possible modifications included 1) increasing the specific surface area of solids and 2) adding organic carbon to the feed. Using solids with fine grains or grinding the existing solids (soil) reduces migration by bonding free MIS to solid grains by capillary forces. Adding organic carbon decreases the amount of

MIS in the feed by destroying its main components, nitrates and nitrites, at temperatures below 300°C (i.e., denitration). The laboratory silica crucible test discussed in the proceeding section was used to evaluate the effectiveness of various feed changes.

The third strategy was to limit the contact of the cold cap with the CRB while temperatures were in the range where MIS forms and migrates (300 to 700°C). This "controlled cold-cap" strategy represented a partial solution because the feed staged in the box before melt initiation would be in contact with the CRB as it was heated thorough the range where MIS forms. However, more than $^7/_8$ of the feed is added during the feed-while-melt process and could be added in a manner that minimized contact with the CRB. The impacts of this process change could only be effectively assessed using ES tests.

Demonstrated Feed-Modification Strategy at Laboratory Scale

The two aspects of the feed-modification strategy were investigated separately and in combination [8].

Effects of Particle Size

Initial tests showed that a few per cent of a high-surface-area additive (e.g., clay or diatomaceous earth) did not reduce MIS migration, and most of the solid fraction of the feed needed to have a higher surface area to be effective. To minimize impacts on the design, this higher surface area was initially obtained by grinding the Hanford soil used in the baseline process. Grinding was first performed in a laboratory-scale tungsten carbide mill in 20-g batches. As Fig. 10 shows, grinding the soil for 2 min decreased the sizes of nearly all particles. Increasing the grinding time to 5 min showed some further size reduction but also indicated that there was a practical limit to the particle-size reduction that could be obtained in the carbide mill.

Hanford soil samples were also sent to Praxair Specialty Ceramics (PSC), in Woodinville, WA, to develop a soil-grinding process that could be scaled up to produce the larger quantities of ground soil necessary for larger scale experiments. The specific surface areas of all the tested soils were measured with the Brunauer, Emmett, and Teller (BET) technique (a method for measuring surface areas). The as-received Hanford soil had a surface area of 5.74 m^2/g; 2-min grinding in a tungsten carbide mill increased it to 9.75 m^2/g and 5-min grinding to 10.78 m^2/g. The PSC methods included plate grinding and ball milling that produced a soil with a surface area of 8.00 m^2/g and a longer ball milling process that produced a surface area of 8.80 m^2/g.

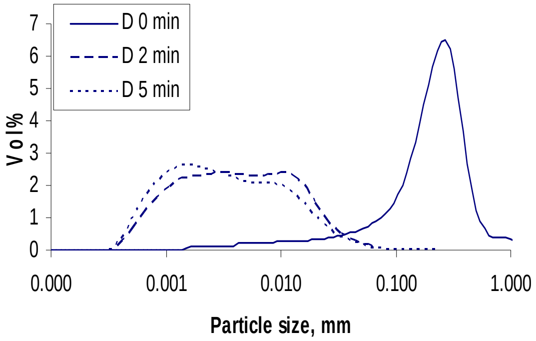


Fig. 10. Comparison of particle-size distribution of Hanford soil as received and ground for 2 and 5 min; samples were deagglomerated.

Initial tests conducted with the six-tank composite simulant indicated that grinding the soil to a surface area of 9.75 m^2/g would essentially stop MIS penetration (Fig. 11). However, tests with the S-109 simulant showed much higher penetration levels than the six-tank composite simulant. This is believed to be the result of a much higher NO_3 concentration in the S-109 waste. This simulant contains 0.82 moles of nitrate per mole of Na and has a higher nitrate concentration of more than 99% of all the projected feeds to the BV process [9]. This is thought to represent the worst case in terms of MIS penetration, and finding a solution for S-109 could potentially resolve this problem for all Hanford waste streams.

Figure 11 shows that the relationship between the soil surface area and the amount of MIS penetration for the S-109 simulant is linear and, in theory, a soil surface area of 12.76 would be high enough to prevent MIS migration in feeds with the S-109 simulant. However, in practice, PSC found it was difficult to develop a bench-scale process that could produce the particle size obtained in the laboratory mill without additional processing steps, including drying and prescreening. These additional steps would make processing the soil cost prohibitive. Therefore, alternate methods to obtain high-surface-area glass formers were investigated.

Standard GFMs were tested as a possible replacement for ground soil. The highest economically practical surface-area silica[9] was chosen for testing based on the soil experience that showed reduced MIS migration with higher surface areas. GFMs with the high-surface-area silica reduced MIS penetration levels by about 50%. Table VI shows the relative ratio of each of the GFMs used in testing. These ratios were chosen to simulate the oxide composition of the Hanford soil so that previous glass formulation data could be used. After testing, the surface area of each of the feed materials was measured, and the calculated mass of the weighted surface area for the GFM blend was only 4.16 m^2/g. This data point (see Fig. 11) does not fall on the line generated by the soil-grinding data, indicating that factors other than surface area play a role in MIS penetration. The greater effectiveness of the GFMs at lower surface areas was not studied further but is thought to be related to low-temperature reactions between the fine silica and sodium nitrates whereas the aluminosilicates in the soil are less reactive.

To summarize, a higher surface area of feed additives reduced MIS penetration, but grinding soil was not an economically practical way to control MIS migration in S-109 feeds. A GFM blend with a high-surface-area silica reduced MIS penetration in S-109 feeds by 50%. This was considered a practical limit achievable by particle-size reduction alone. This emphasized the necessity for a method to be used in conjunction with the finer GFMs for a complete solution to the MIS migration problem.

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[9] MIN-U-SIL 5 was used these tests. This material is a fine-ground silica (>97% less than 5 microns) produced by U.S. Silica Company, Berkeley Springs, WV.

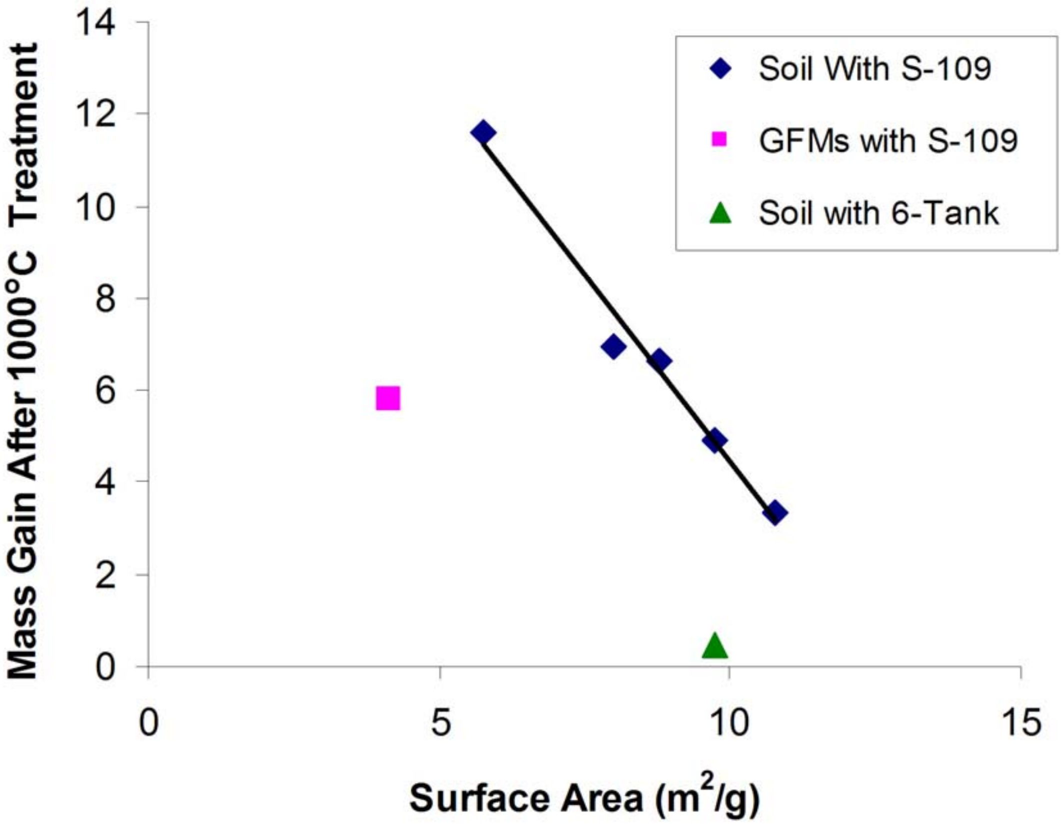


Fig. 11. Levels of MIS penetration as a function of surface area.

Table VI. Mass fractions and surface areas of GFMs used in testing.

Component	Oxide Composition	Mass Fraction	Surface Area by BET (m^2/g)	Mass Weighed Surface Area
MIN-U-SIL 5	SiO_2	0.519	5.15	2.67
Rutile	TiO_2	0.007	1.29	0.01
Zircon	$ZrSiO_4$	0.139	1.47	0.20
Olivine	$MgSiO_4$	0.034	3.87	0.13
Kyanite	Al_2SiO_5	0.180	2.26	0.41
Wollastonite	$CaSiO_3$	0.070	1.70	0.12
Hematite	Fe_2O_3	0.050	12.27	0.61
			Total	4.16

Effects of Carbohydrate Additions

Tests were conducted to determine the type and quantity of carbon source that would not prematurely react during vacuum drying of the BV feed, but would destroy the nitrates before they had a chance to migrate at temperatures ≥300°C. Denitration in the dryer is not desirable because the current system is not designed to handle the heat and NO_x generated. The carbon source also must not interfere with 1) drying operations, 2) transporting the dry feed from the dryer to the ICV™ box, and 3) melter operations. Efforts focused on two carbohydrate carbon sources that were known to be stable at dryer temperatures but reacted with MIS well below 300°C: water soluble sucrose and water in-soluble cellulose. Granular table sugar and alpha cellulose were chosen as the test materials. These materials react with the nitrate present according to the following exothermic reactions proposed by Smith et al. [10].

$$\text{Cellulose: } C_6H_{10}O_5 + 6\ NaNO_3 \rightarrow 3\ Na_2CO_3 + 3\ CO_2 + 5\ H_2O + 2\ N_2 + N_2O + O_2$$

$$\text{Sucrose: } C_{12}H_{22}O_{11} + 8\ NaNO_3 \rightarrow 4\ Na_2CO_3 + 4\ CO_2 + 11\ H_2O + 4\ N_2 + 4\ CO$$

The first screening tests determined the quantities necessary to reduce MIS penetration. Silica crucible tests described above were conducted using varying amounts of sucrose and cellulose. To compare the quantity added, the amounts are expressed in terms of a ratio in the moles of carbon added as carbohydrate to the moles of nitrogen present in the waste in the form of nitrates and nitrites. Figure 12 shows the effect of carbohydrate addition to an S-109 waste feed that contained as-received soil with a surface area of 5.74 m^2/g. Adding carbohydrates reduced the fraction of MIS penetrated with higher addition levels, resulting in reductions from nearly 0.5 to less than 0.05. The type of carbohydrate did not make a significant difference, and combinations of two different carbohydrates did not appear to be more effective than adding a single carbohydrate source. Although the higher levels were more effective in preventing MIS penetration, they also resulted in more rapid reactions and excessive foaming in the melt as can be seen in Fig. 13. The carbohydrate additions also showed less uniform effectiveness where penetration was eliminated in some areas but fully penetrated the crucible in other areas.

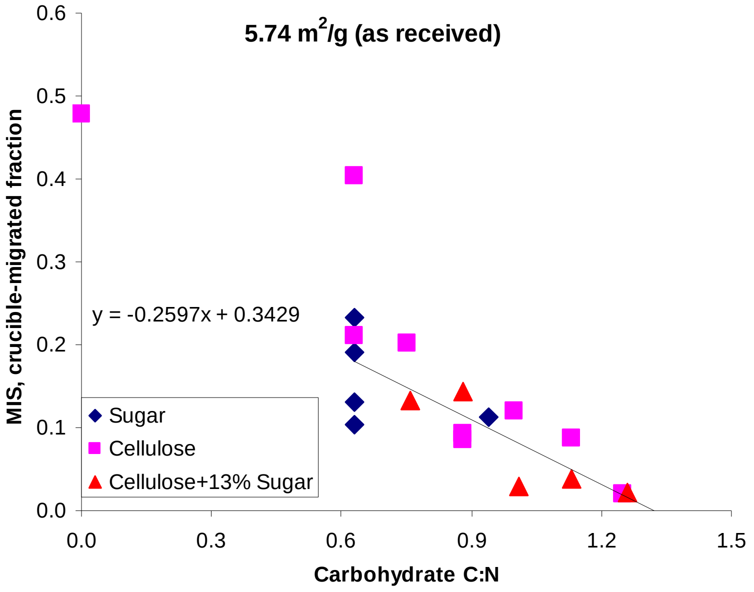
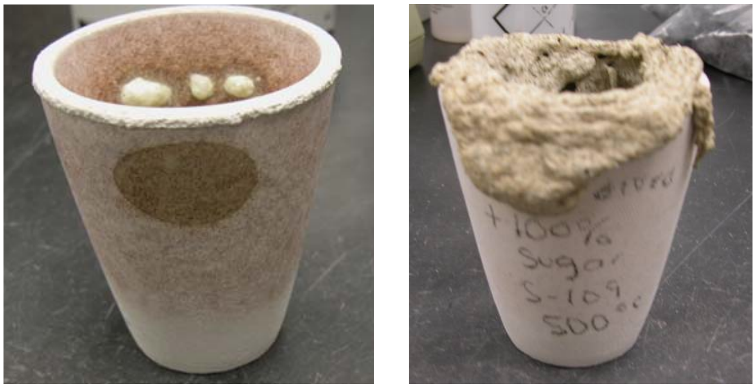


Fig. 12. Levels of MIS penetration as a function carbohydrate addition.



Non-uniform effectiveness of carbohydrate additions

Excessive foaming at high C:N ratios

Fig. 13. Potential concerns with carbohydrate additions.

Combined Effectiveness

Systematic tests were conducted with combinations of reduced feed particle sizes and carbohydrate additions. Figure 14 shows data generated with 2-min ground Hanford soil (9.75 m^2/g) and sucrose as well as confirmatory data obtained with GFMs and cellulose. C:N additions > 0.3 further reduced MIS migration; additions of about 0.7 C:N resulted in very low penetration levels. The data point for the ground soil/cellulose test and the GFM/cellulose test also showed that the combined effectiveness was similar to tests with sugar. This combination was felt to be effective at minimizing MIS migration and warranted equipment testing.

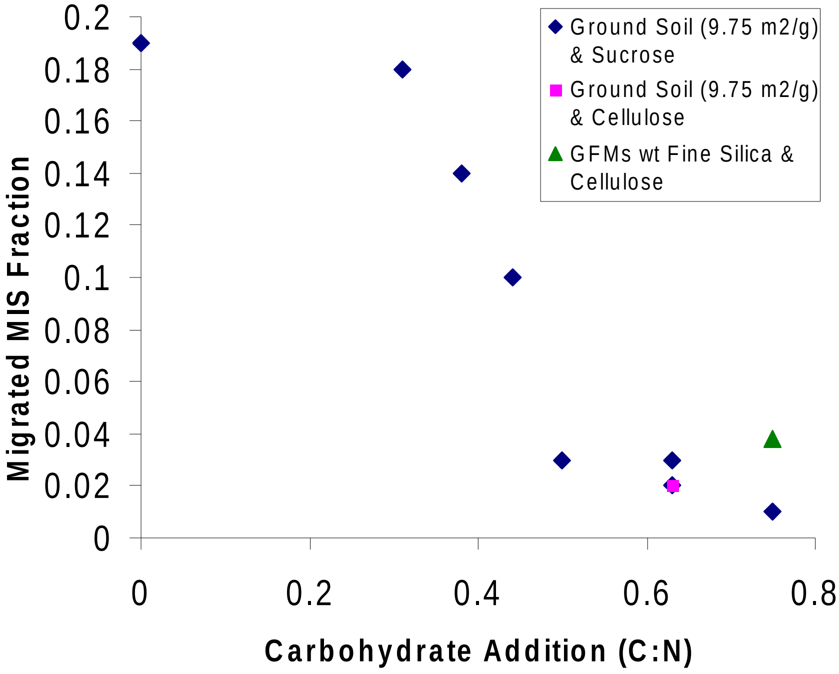


Fig. 14. Levels of MIS penetration as a function carbohydrate addition.

Bench-Scale Dryer Testing

As the feed changes necessary to reduce MIS migration became clearer, a series of tests was conducted to determine how these feed changes would impact dryer operations. These tests were conducted in the Littleford-Day 22-liter vacuum dryer system shown in Fig. 15. This bench-scale dryer is good for screening potential feed drying problems that might occur in the full-scale 10,000-liter dryer. The feeds were dried in the same manner as the full-scale system. Dry GFMs and carbohydrate material (sucrose or cellulose) were added to the dryer, and then the liquid waste simulant was slowly added while the dryer was put under vacuum (15 to 29 inches of Hg) and heated (60 to 80°C). The bed was maintained in a relatively dry condition (0.5 to 5 wt% moisture) until all the liquid simulant was added. Figure 16 shows the results of selected tests. The sucrose additions resulted in severe clumping of the feed. Dissolving the sucrose in the liquid simulant instead of adding it as a dry granular material also resulted in severe clumping. The cellulose material with Hanford soil, ground Hanford soil, or GMFs processed without problems and left low levels of residue in the dryer. These dryer tests indicated that cellulose was the only suitable carbohydrate and that ground Hanford soil and GFMs did not cause problems in the dryer operations.

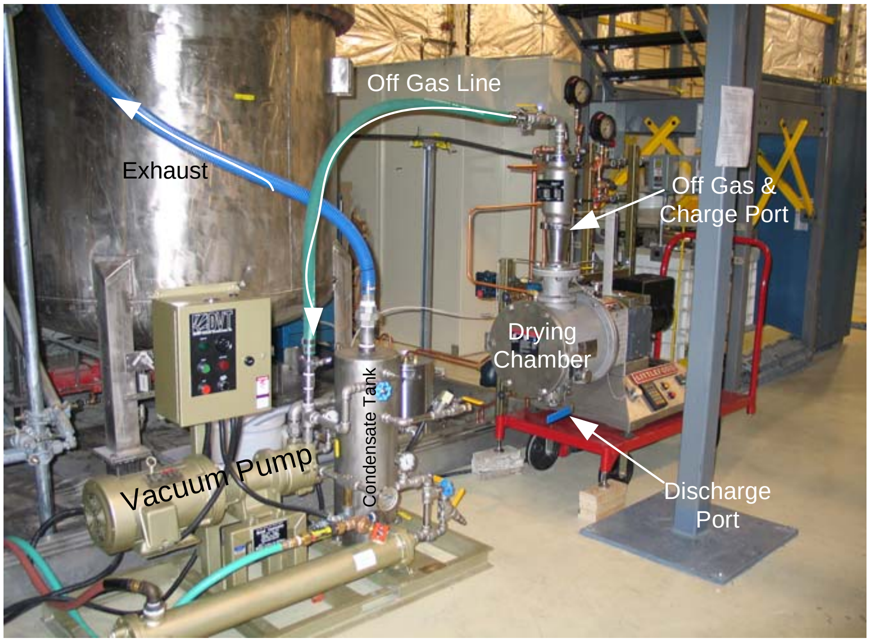


Fig. 15. 22-liter vacuum dryer system.

Feed clumping with Hanford soil and sucrose

Residue present after processing feed with Hanford soil and cellulose

Residue present after processing feed with GFMs and cellulose

Fig. 16. Compatibility of feeds with dryer operations.

Development of Meaningful Scale-Up Tests

As mentioned in the introduction, an earlier engineering-scale test was conducted with S-109 feed, but it showed no significant increase in MIS penetration levels. This indicated that the engineering-scale system configuration was not prototypic of the full-scale ICV™ with respect to MIS migration and penetration. New meaningful scale-up tests were needed to reduce the risk that the laboratory-generated MIS migration solutions would not be effective at full scale. Two tests were devised to accomplish this goal: the large CRB crucible test and an improved ES test. The first step in validating the usefulness of each of these tests was to make sure that the S-109 feed materials used in the FS-38C tests showed significant levels of MIS penetration.

Large CRB Crucible Tests

The large CRB crucible tests were designed to evaluate the rate of MIS migration into actual CRB material over time periods that were similar to those that might be expected in a full-scale operation. Large CRB crucibles were made from the same vibrocast material and manufactured by the same company[10] used for the ES and FS CRBs. The large crucibles held 7 to 9 kg of feed compared to 165 grams of feed use in the silica crucibles. Figure 17 shows the relative size of the silica and CRB crucibles. The heat-treatment steps for the large crucible were the same as the silica crucibles with the exception that the dwell time at 500°C was 20 hours instead of 30 minutes, and the dwell time at 1000°C was 2 hours instead of 1 hour.

Figure 17 also shows selected results from the large CRB tests and the corresponding results that were obtained in the silica crucibles for the same feeds. These results showed extensive MIS penetration for the baseline feed in both the large CRB crucible and silica crucible tests and similar reductions in MIS penetration when the GFM/cellulose formulation was used. These results indicated that the results obtained in the silica crucible tests were meaningful for CRB materials at a larger scale and could continue to be used to examine any future MIS migration questions.

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[10] E. J. Bartells Company, Spokane, WA.

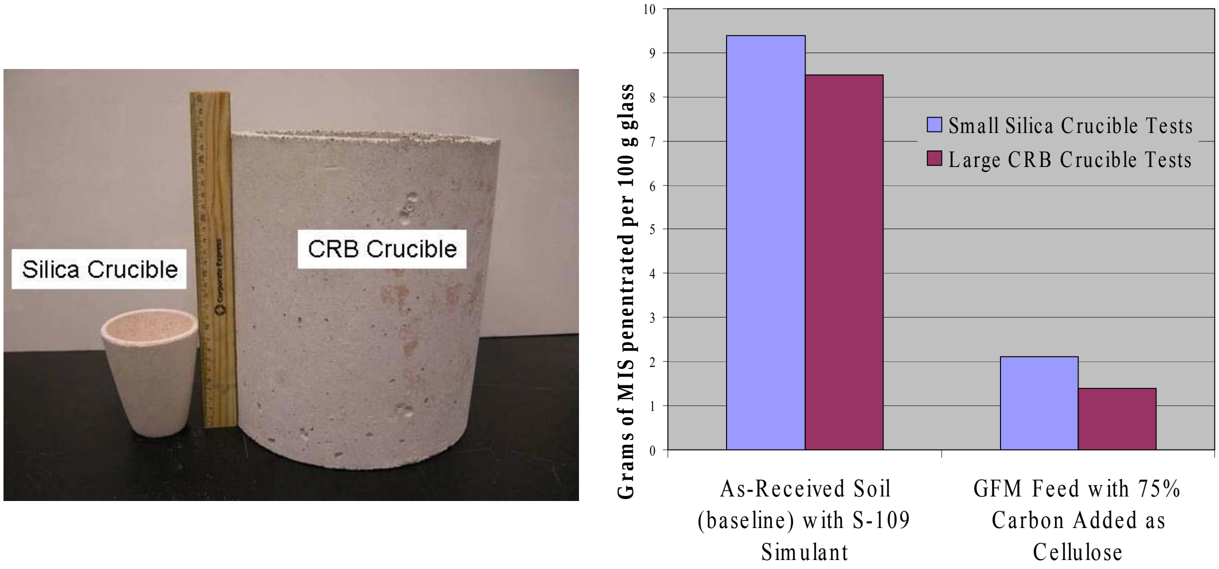

Fig. 17. Comparison of large CRB and silica crucible sizes and results.

Improved Engineering-Scale Tests

Evaluation of earlier ES tests indicated that the ES CRB design was too massive relative to the mass of feed processed when compared to the full-scale ICV™ system. The large CRB resulted in a large thermal mass that heated slowly and remained at low enough temperatures to inhibit MIS penetration. The early ES tests were also operated with minimal cold caps to prevent feed bridging and large bubble formation. The refractory design was updated with significant changes to more closely reflect the full-scale refractory design and increased the volume available for feed processing. A series of three interrelated tests were conducted to determine the path forward for additional FS testing [11].

Test ES-30J was the control test with the goal of repeating the MIS penetration seen in FS-38C with the improved ES test design. The same S-109 feed composition as that used with FS-38C was used with an aggressive feed schedule that would create a thick cold cap and have feed in contact with the CRB wall for long periods of time. Post-test ES-30J examination showed evidence of significant MIS penetration into the refractory lining. There were six locations of clumped sand that likely formed from MIS that penetrated through the CRB into the refractory silica sand lining. Figure 18 shows one of the clumped sand regions as viewed from above after removing the loose sand. The MIS penetration depth was determined with SEM-EDS analysis of the sodium levels in CRB cross sections. Sodium is the primary component in the MIS and is only present at low levels in the CRB, so analysis of sodium levels is a clear method to monitor MIS penetration depths. Figure 19 shows elevated sodium levels through the entire 80 mm CRB thickness, confirming MIS penetration to the outer surface of the CRB. The results of this test confirmed that the new engineering-scale ICV™ configuration was more representative of the full-scale ICV™ system than the earlier engineering-scale configuration used for test ES-31B.

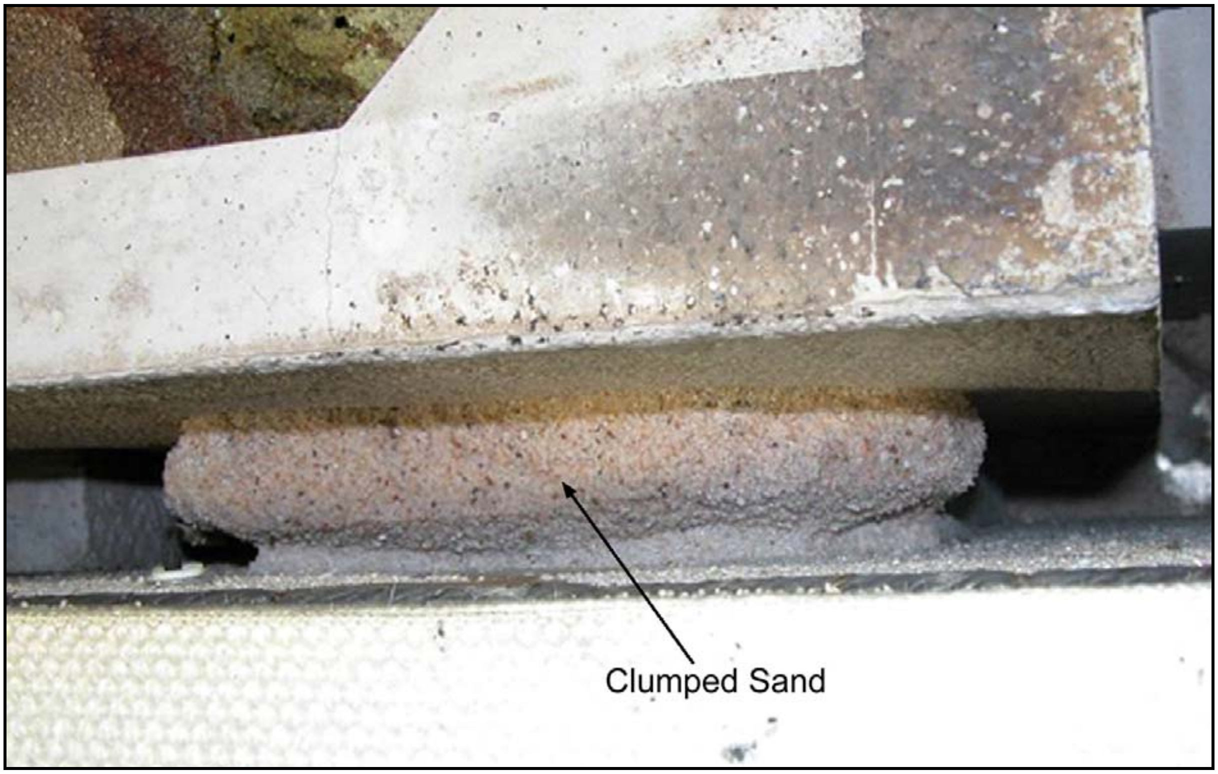

Fig. 18. Clumped sand outside of Test ES-30J CRB.

Test ES-30K used the same aggressive feed schedule as ES-30J with a reformulated feed that was composed of the S-109 simulant, GFMs with fine silica, and approximately 7.8-wt% cellulose (C:N ratio of 0.75). This test was used to determine the effects of the feed modifications alone. Initial post-test visual inspection revealed no MIS migration into the outer refractory sand layer. Subsequent SEM-EDS analyses of two CRB locations (Fig. 19) indicated much lower Na concentrations that penetrated to only 15 to 20 mm. These levels indicated that MIS penetration was 89 to 94% less than that seen in the ES-30J control test, and the modified formulation was very effective at reducing MIS penetration.

Test ES-31F used the GFM/cellulose feed composition used for ES-30K, but fed the ICV container using a schedule that produced a controlled cold-cap thickness. The feed rate was continually adjusted to produce a cold cap that was thick enough to reduce the melt surface temperatures for good contaminant retention, but did not allow unprocessed feed to build up against the CRB wall. Post-test visual examination of ES-31F indicated no MIS penetration through the refractory. Subsequent SEM-EDS analyses of two CRB locations (Fig. 19) indicated much lower Na concentrations that penetrated to only 5 to 18 mm. These levels indicated that MIS penetration was 93 to 98% less than that seen in the ES-30J control test. These results indicate that the controlled cold cap in combination with the modified feed formulation further reduced MIS penetration levels. Re levels in several CRB samples were measured to determine that the amount of Re present in the refractory was about 1.17% of total fed to the test. This Re level was similar to that obtained for earlier ES tests with the different CRB configuration.

The collective results from the three ES tests indicated that the modified GFM feed with cellulose (C:N ratio of 0.75) combined with a controlled cold cap was the best approach to test at full scale. Details of the FS-38D test are discussed in a related paper [12].

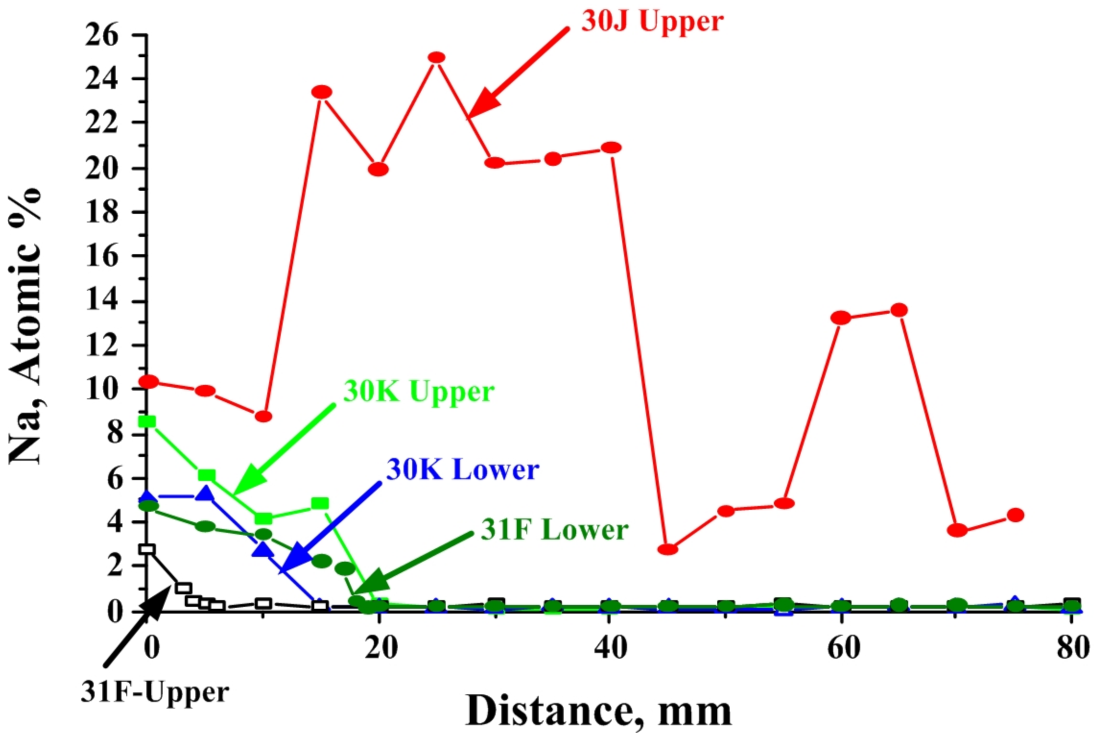

Fig. 19. SEM-EDS profile of Na concentration in ES-30J, ES-30K, and ES-31F CRB.

CONCLUSION

An integrated process was used to generate a solution to the MIS migration problem. This process accounted for the existing equipment and design of the BV process and worked to minimize the impacts.

The process started with developing a clear understanding of the problem and then looked at potential solutions based on that understanding. A key step in developing methods to reduce MIS migration was to develop the low-cost, quantitative silica crucible test to evaluate different methods. This test showed that increasing the specific surface area of the soil by grinding reduced MIS penetration. However, grinding enough soil to the required levels to prevent migration in S-109 feeds for FS operations was found to be impractical. GFMs with fine silica were shown to reduce MIS penetration of the high nitrate S-109 feeds by 50%. Adding sufficient quantities of carbohydrates (sucrose or cellulose) also reduced MIS, but levels necessary to significantly reduce MIS migration resulted in rapid reactions that caused feed foaming. Combining GFMs with fine silica with a lesser addition of sucrose or cellulose resulted in significant reductions of MIS migration. Bench-scale (22-liter) dryer tests indicated that sucrose would result in severe clumping; however, cellulose did not cause clumping and was a suitable carbohydrate.

Large CRB crucible tests and a series of three ES tests verified that a GFM feed with cellulose combined with a controlled cold-cap operating strategy was the best approach to move forward to full-scale testing.

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