U.S. DEPARTMENT OF **ENERGY**

Goethite Bench-Scale and Large-Scale Preparation Tests

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October 2011

Pacific Northwest
NATIONAL LABORATORY

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Summary

The Hanford Waste Treatment and Immobilization Plant (WTP) is the keystone for cleanup of high-level radioactive waste from our nation's nuclear defense program. The WTP will process high-level waste from the Hanford tanks and produce immobilized high-level waste glass for disposal at a national repository, low activity waste (LAW) glass, and liquid effluent from the vitrification off-gas scrubbers. The liquid effluent will be stabilized into a secondary waste form (e.g. grout-like material) and disposed on the Hanford site in the Integrated Disposal Facility (IDF) along with the low-activity waste glass. The major long-term environmental impact at Hanford results from technetium that volatilizes from the WTP melters and finally resides in the secondary waste.

Laboratory studies have indicated that pertechnetate ($^{99}TcO_4^-$) can be reduced and captured into a solid solution of α-FeOOH, goethite (Um 2010). Goethite is a stable mineral and can significantly retard the release of technetium to the environment from the IDF. The laboratory studies were conducted using reaction times of many days, which is typical of environmental subsurface reactions that were the genesis of this new process. This study was the first step in considering adaptation of the slow laboratory steps to a larger-scale and faster process that could be conducted either within the WTP or within the effluent treatment facility (ETF). Two levels of scale-up tests were conducted (25× and 400×). The largest scale-up produced slurries of Fe-rich precipitates that contained rhenium as a nonradioactive surrogate for ^{99}Tc. The slurries were used in melter tests at Vitreous State Laboratory (VSL) to determine whether captured rhenium was less volatile in the vitrification process than rhenium in an unmodified feed.

A critical step in the technetium immobilization process is to chemically reduce Tc(VII) in the pertechnetate (TcO_4^-) to Tc(IV) by reaction with the ferrous ion, Fe^{2+}—Fe^{2+} is oxidized to Fe^{3+}—in the presence of goethite seed particles. Rhenium does not mimic that process; it is not a strong enough reducing agent to duplicate the TcO_4^-/Fe^{2+} redox reactions. Laboratory tests conducted in parallel with these scaled tests identified modifications to the liquid chemistry necessary to reduce ReO_4^- and capture rhenium in the solids at levels similar to those achieved by Um (2010) for inclusion of Tc into goethite[1]. By implementing these changes, Re was incorporated into Fe-rich solids for testing at VSL. The changes also changed the phase of iron that was in the slurry product: rather than forming goethite (α-FeOOH), the process produced magnetite (Fe_3O_4)[1]. Magnetite was considered by Pacific Northwest National Laboratory (PNNL) and VSL to probably be a better product to improve Re retention in the melter because it decomposes at a higher temperature than goethite (1538°C vs. 136°C). The feasibility tests at VSL were conducted using Re-rich magnetite. The tests did not indicate an improved retention of Re in the glass during vitrification, but they did indicate an improved melting rate (+60%), which could have significant impact on HLW processing. It is still to be shown whether the Re is a solid solution in the magnetite as ^{99}Tc was determined to be in goethite.

Process modifications implemented during these scale-up tests to adapt to a plant process included:

- Purged reactor vessels and N_2-purged liquids were used to achieve anoxic conditions.

- Shorter reaction times—The reduction of ReO_4^- with Fe^{2+} and precipitation at elevated pH to form iron precipitates can be accomplished at room temperature in <1 h rather than over multiple days.

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[1] Unpublished data from laboratory studies conducted by Dr. Nikolla P. Qafoku to understand chemistry changes resulting from replacing $^{99}TcO_4^-$ with ReO_4^-.

- Higher concentrations of reagents can be used in the reactions—the lab-scale process batch mixed lower concentrations of reagents.

- Solids/liquids separation—the magnetite solids formed at the engineering scale filtered much better than typical WTP solids simulants. This enhances the possibility that the process could be incorporated into WTP and use the existing ultrafiltration (UF) capacity, which would be lower cost than a dedicated filtering system for the technetium removal process.

Acknowledgments

Acronyms and Abbreviations

APEL	Applied Process Engineering Laboratory
CUF	compact unit filter
DF	decontamination factor
DI	de-ionized
IDF	Integrated Disposal Facility
HLW	high-level waste
PEP	Pretreatment Engineering Platform
PNNL	Pacific Northwest National Laboratory
SBS	submerged bed scrubber
SS	stainless steel
TMP	transmembrane pressure
UDS	undissolved solids
UF	ultrafiltration
VSL	Vitreous State Laboratory
WTP	Hanford Waste Treatment and Immobilization Plant
XRD	x-ray diffraction

Contents

Figures

Tables

1.0   Introduction

The Hanford Waste Treatment and Immobilization Plant (WTP) is the keystone for cleanup of high-level radioactive waste from our nation's nuclear defense program. The WTP will process high-level waste from the Hanford tanks and produce immobilized high-level waste glass for disposal at a national repository, low-activity waste (LAW) glass, and liquid effluent from the vitrification off-gas scrubbers. The liquid effluent will be stabilized into a secondary waste form (e.g., some form of grout-like material) and disposed on the Hanford site in the Integrated Disposal Facility (IDF) along with the low-activity waste glass. The major long-term environmental impact at Hanford results from technetium that volatilizes from the WTP melters and finally resides in the secondary waste.

Laboratory studies using technetium (^{99}Tc) have indicated that technetium in the form of pertechnetate (TcO_4^-) can be reduced and captured into a solid solution of α-FeOOH, goethite (Um 2010). Geothite is a stable mineral and can significantly retard the release of technetium to the environment from the IDF. The goethite process could also be used to separate pertechnetate from the WTP effluent and direct the reduced technetium to the high-level waste melter where it could be incorporated into the HLW glass and sent to the national repository.

This study was the first step in considering adaptation of the laboratory process to a larger scale and one that could be conducted either within the WTP or within the effluent treatment facility (ETF). The initial scale-up of the lab-scale Tc stabilization process into a concept for a full-scale process that can be implemented for Hanford cleanup was executed in two steps. The first step was to conduct bench-scale testing using 12.5 liters of simulated submerged-bed scrubber effluent and then a 55-gallon scale test. The product from the larger-scale test was used in scaled melter tests to determine whether incorporating Tc into goethite has a measurable effect on the volatility of Tc in the HLW melter or whether the precipitated iron-rich solids have a negative impact on the resulting HLW glass. The scaled melter tests were conducted in a nonradioactive environment; therefore, a substitute for ^{99}Tc was needed for the test. Rhenium has been used extensively as a substitute for ^{99}Tc in vitrification studies; its atomic radius is similar to that of Tc, so it is expected to be incorporated similarly into the goethite solid structure and to be incorporated similarly into the vitrified product. The chemistry of rhenium is similar to that of technetium. It forms a similar oxidized species in the +7 oxidation state (TcO_4^- vs. ReO_4^-), and, when reduced, it forms a similar oxide in the +4 oxidation state (TcO_2 vs. ReO_2). Both oxides (IV) have reduced solubility and hence precipitate so they are not readily mobile in the environment.

Although Re is the element most similar to Tc, it is not a perfect substitute for Tc, and their behaviors are not identical; there are some differences that must be considered.

- First, the standard reduction potential of the ReO_4^- anion is significantly less than that of TcO_4^-: 0.51 V for ReO_4^- vs. 0.738 V for TcO_4^-. In the hypothesized reaction to form goethite, Fe^{+2} oxidizes to Fe^{+3} driven by the reduction of pertechnetate to form TcO_2. The difference between Re and Tc redox is illustrated in the redox equations below:

<u>Technetium</u>:

Oxidation:	$3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$	$\varepsilon^0 = -0.77$ V
Reduction:	$TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	$\varepsilon^0 = 0.738$ V
Net reaction:	$TcO_4^- + 3Fe^{2+} + 4H^+ \rightarrow TcO_2 + 3Fe^{3+} + 2H_2O$	$\varepsilon^0 = -0.032$ V

Rhenium:

Oxidation:	$3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$	$\varepsilon^0 = -0.77$ V
Reduction:	$ReO_4^- + 4H^+ + 3e^- \rightarrow ReO_2 + 2H_2O$	$\varepsilon^0 = 0.51$ V
Net reaction:	$ReO_4^- + 3Fe^{2+} + 4H^+ \rightarrow ReO_2 + 3Fe^{3+} + 2H_2O$	$\varepsilon^0 = -0.26$ V
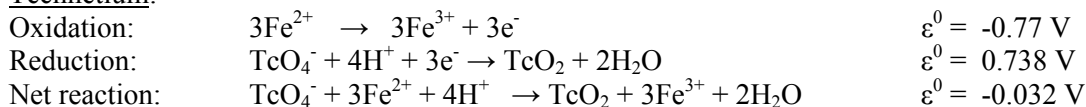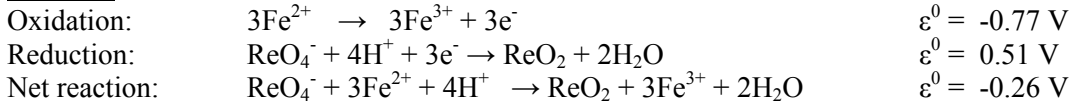
When applied to the reaction conditions established at the lab scale,[1] the redox potential for TcO_4^- leads to a predicted reduction of pertechnetate to TcO_2 of >99.9%, while the reduction of perrhenate to ReO_2 is <0.1%. (Note: The solution redox conditions do not account for heterogeneous reduction on the surface of goethite particles. Um (2010) showed that effective removal of Tc required the goethite particles.)

- Secondly, the solubility of the reduced rhenium oxide, ReO_2, is greater than that of the reduced technetium oxide, TcO_2, at the process pH (~12): 10^{-6} M for ReO_2 vs. 10^{-8} M for TcO_2. The ^{99}Tc stabilization process in goethite involves the oxidation of Fe^{2+} to Fe^{3+}, simultaneously reducing the pertechnetate to Tc(IV) and subsequently co-precipitating the Fe oxide and the Tc(IV)oxide.

Both of these differences between Re and Tc would lead to a lower expected capture efficiency for Re compared to Tc. Lab-scale tests were conducted separately to: 1) better understand how the fundamental differences between Re and Tc affect the process, and 2) verify experimental conditions so that sufficient Re could be incorporated into the solids for use in the melter test.

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[1] The lab-scale conditions established by Um (2010) were: 2.2×10^{-5} M TcO_4^-, 0.07 M Fe^{2+}, pH 2.

2.0 Background

The primary objective of the scaled tests was to adapt the lab-scale process appropriately to make it more suitable for incorporation into the WTP flow sheet and operation as a routine full-scale process. An additional objective was to produce a sufficient amount of goethite to determine whether the process could be used within WTP as a method to selectively remove ^{99}Tc from the secondary waste stream and incorporate the ^{99}Tc into the HLW glass for disposal in the national repository. Two scaled tests were conducted. The first test (bench scale) scaled the lab-scale process approximately 25× (12.5-L reaction vessel) and implemented changes to make the process more suitable for a routine full-scale process. The second test (engineering scale) scaled the process 400× (55-gal. drum) and produced enough solids for pilot-scale melter testing.

The scaled process tests were based upon the lab-scale process using ^{99}Tc (Um 2010). The steps of the lab-scale process are summarized in Table 2.1.

Table 2.1. Goethite Process Steps at Lab Scale

Step	Amount
1. Initial WTP submerged bed scrubber (SBS) simulant solution Add perrhenate	250 mL 2.2 E-5 M

2. Prepare separate seed slurry in DI water (goethite)
      Adjust pH of seed slurry to acid side using HNO_3
      Add $FeCl_2 \cdot 4H_2O$ to seed slurry
	2.75 g solids
	1.5−2.0
	3.48 g

3. Combine solutions and mix	1-2 days pH after mixing: 10.5
4. Prepare $Fe(NO_3)_3 \cdot 9H_2O$ solution	11.4 g in 100 mL
5. Prepare NaOH solution	2 M; 100 mL
6. Combine SBS-goethite slurry and 2-M NaOH	pH 13+
7. Add $Fe(NO_3)_3 \cdot 9H_2O$ solution	
8. Cook slurry	80°C for 7−10 days
9. Filter slurry and wash solids	

Adaptations to the lab-scale process that were incorporated into the scaled process were:

- Purged reaction vessels: Steps #1–4 were done in the lab in an oxygen-free hood using deaerated liquids. For the scaled tests, sealed and N_2-purged reaction vessels were used for reaction steps 1–4. DI water was purged with N_2 before solid reactants were added so that oxygen-free conditions could be maintained inside the vessel.

- Lower pH of Re-containing solution: The oxidation of Fe^{2+} solution (and concomitant reduction of ReO_4^-) are favored by lower pH. The off-gas scrubber effluents are expected to be alkaline. The initial lab-scale tests with TcO_4^- and scrubber effluent simulant ended up alkaline (pH 10.5) after mixing with the acidic (pH 1.5–2) slurry of Fe^{2+} and goethite seed. To enhance the reduction of ReO_4^-, this initial step was conducted at acid conditions.

- Shorter reaction time: The initial lab-scale tests allowed a reaction time of 1–2 days. Within WTP such long reaction times would be very difficult to accommodate. However, liquid redox reactions are generally fast, so such a long reaction time shouldn't be necessary. The scaled tests were conducted with shorter reaction times (i.e., 30 min–1 h).

- Solution concentrations: The bench-scale tests used more concentrated solutions for the initial Fe^{2+}, goethite seed and $Fe(NO_3)_3$ solutions. The same ratios of chemical reactants were used and the solutions were kept below solubility limits, but the amount of excess water was reduced from the system so more waste effluent could be processed in the available volume. This is a first step for conserving processing volume.

- Higher Re concentrations: Lab-scale tests using Re showed a significantly reduced capture efficiency of Re into the solids relative to the capture efficiency observed for Tc, but verified that some incorporation was achievable. To compensate for expected lower capture efficiency, a 90× higher concentration of Re (1×10^{-3} M) was used for both larger-scale tests.

- Filtering and washing solids: The lab-scale tests filtered the solids through a vacuum funnel to remove essentially all the free liquid and then washed the solids several times to remove soluble salts and any remaining soluble Tc. This facilitated analysis and made sure that the Tc analyzed in the solids was truly "immobile." It is preferred that in the full-scale system the goethite be maintained in slurry that can be transported with typical centrifugal pumps. The goethite process would most readily integrate into the WTP process at the ultrafiltration step. The dilute precipitated slurry would be combined with normal HLW sludge and ultrafiltration would be used to remove excess water and wash out soluble salts. The engineering-scale test filtered about 60 L of the goethite slurry using the compact unit filter (CUF) apparatus, which mimics the WTP ultrafilters. The remainder (150 L) of the engineering-scale test and the entire bench-scale test used a batch washing and settling process. After thorough mixing, the dilute slurry was allowed to settle, the supernatate was pumped out, clean water was added to dilute the dissolved material and then the settling, pump-out, and washing was repeated a number of times to achieve a reduction of soluble salts by at least a factor of 100 (e.g., decontamination factor [DF] > 100).

- Skip final conversion to goethite (α-FeOOH) on some product: the co-precipitation step doesn't form goethite directly, but rather ferrihydrite, $Fe(OH)_3$. The lab-scale tests converted the ferrihydrite to α-FeOOH by heating at 80°C for seven to ten days. Such long processing would be very difficult to accommodate within WTP, but it may not be necessary. The scaled tests produced two slurries for testing within the melter to determine whether the final solids need to be cooked or the uncooked form may behave the same in the melter.

3.0 Tests

3.1 Bench-Scale Test

The bench-scale test was executed in accordance with test instruction 57154-2.2.2-T4, *WP-2.2.2 Tc Removal using Goethite Precipitation Test Instruction: Goethite Bench-Scale Test w/Rhenium.* The steps of the process are summarized in Table 3.1.

Table 3.1. Process Steps for Bench-Scale Testing (25× lab scale) (To make up SBS and goethite seed slurry purge, use deaerated H_2O. Conduct steps 1−5 under N_2 blanket.)

Step	Amount

1. Initial SBS solution (deaerated)
    Adjust pH of SBS solution to acid side using HNO_3
    Add $NaReO_4$ to obtain a final simulant concentration of
	12.5 L
	1.5−2.0
	1×10^{-3} M

2. Prepare separate seed slurry in DI water [goethite] (deaerated)
    Adjust pH of seed slurry to acid side using HNO_3
    Add $FeCl_2 \cdot 4H_2O$ to seed slurry
    React
	135−140 g solids/L
	1.5−2.0
	174 g
	>1 h

3. Combine SBS solution and seed slurry and mix	30 min−1 h
4. Adjust pH (~400 g of 50% NaOH)	12−13
5. React	30 min−1 h
6. Prepare $Fe(NO_3)_3 \cdot 9H_2O$ solution	570 g in 4 L
7. Combine ferric nitrate solution and slurry and mix	
8. Maintain pH—may have to add NaOH	12−13
9. React	1 h

10. Settle and wash solids
    Settle slurry until solids interface appears stationary
    Pump out supernatant
    Add water until 4× volume, mix, settle, pump out supernatant
	Wash with 3× volume of water

11. Repeat washing, settling, supernate removal 4 more times (5 total)	5 total washes[a] (wash factor 1024×)
12. Mix settled slurry and separate into two fractions.	30 min−1 h
13. Cook one fraction of slurry[b]	80°C for 7 days

(a) If the washes do not settle add a small amount (e.g. ~ 0.1−1 g of a soluble calcium salt such as $CaCl_2$).
(b) One half of material will be converted to goethite [FeOOH] and the other maintained as ferrihydrite. VSL will determine whether there is any difference in melter test.

The apparatus used for the bench-scale test is shown in Figure 3.1.
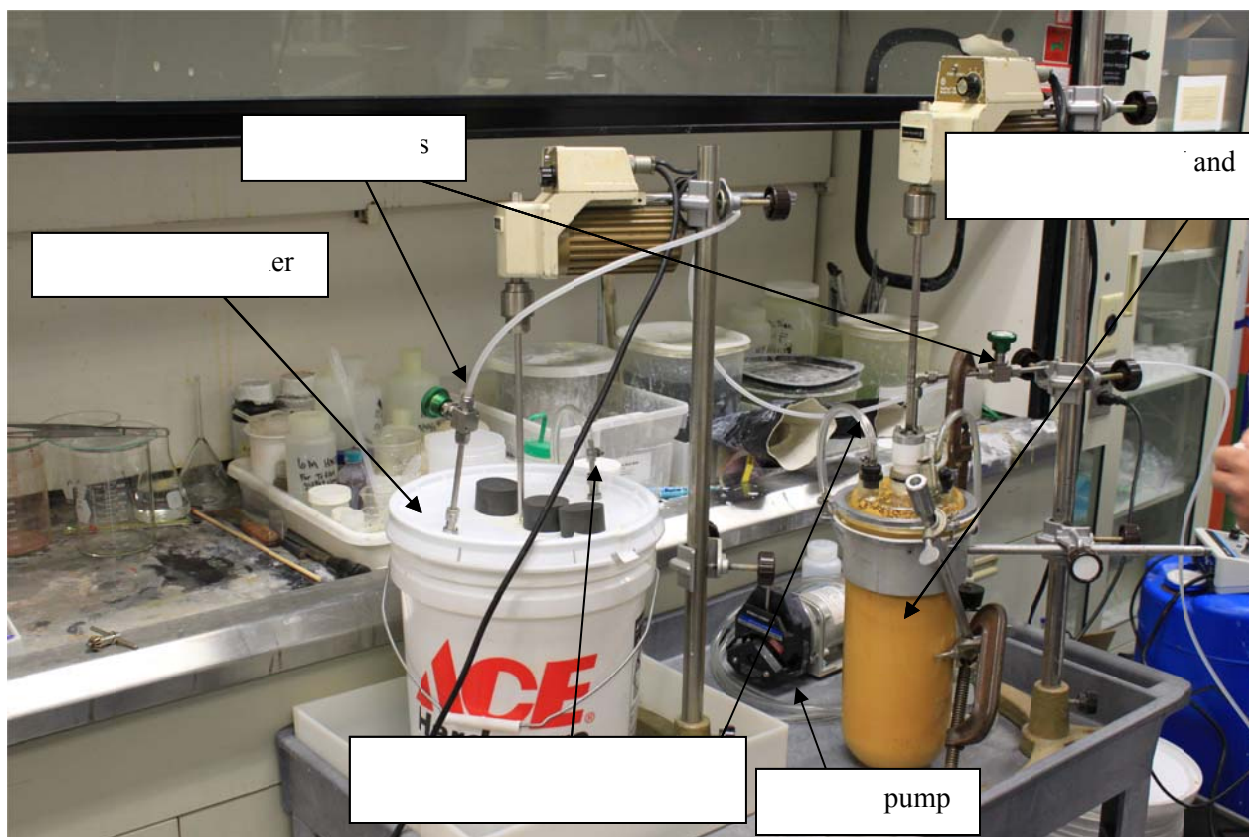
Figure 3.1. Bench-Scale Test Apparatus

Referring to Table 3.1 and Figure 3.1, the process steps were as described below.

Step 1) SBS Simulant. SBS simulant was made up using dry chemicals (including NaReO$_4$) and deionized water in the main reactor (5-gallon bucket). The pH was adjusted to 1.5−2 using HNO$_3$, and the solution was purged with N$_2$ overnight to remove dissolved oxygen from the solution.

Step 2) Goethite Seed with Fe^{2+}. Goethite-seed solids were combined with DI water and the resulting slurry was adjusted to pH 1.5−2 using HNO$_3$ in the pre-reactor. The slurry was purged with N$_2$ overnight to remove dissolved oxygen from the slurry. The prescribed amount (174 g) of solid Fe(Cl)$_2$•4H$_2$O was added through a port in the vessel lid while maintaining the N$_2$ purge. The slurry was then reacted for 2 h. Figure 3.1 shows the goethite slurry in the prereactor.

Step 3) Mixing and Reacting SBS Simulant and Fe^{2+}/Goethite. Using the transfer pump, the reacted goethite seed slurry was transferred into the main reactor, while maintaining deaerated conditions (N$_2$ purge). The slurry was mixed and reacted for 1.5 h. After the transfer, all the process steps were conducted in the main reactor; the prereactor (reaction flask) was not used again.

Steps 4−5) Precipitation of Fe^{2+}/Fe^{3+}. After the reaction time, the N$_2$ purge was stopped, the lid to the main reactor was removed and the pH was raised by adding 50% NaOH solution. Note: When the lid was removed, the technician recorded an odor similar to reduced sulfides coming from the solution. The solution was added slowly over ~20 min to prevent spattering from the mixing of concentrated caustic

solution into the acidic SBS-goethite slurry. As caustic was added, the color changed from orange to green at pH ~4. Further NaOH was added until the pH of the slurry was above 12. A total of 1058 g of solid NaOH was added (including initial NaOH added as 50% solution). The green color darkened as the pH was raised. (Photos were not taken at this time. Pictures of the material at the same process step were taken during the engineering-scale test and are shown in the next section.)

Steps 6−9) Armouring. After reacting for 20−30 min, 2257 mL of solution containing 570 g of $Fe(NO_3)_3 \cdot 9H_2O$ was added to the slurry. In high caustic, the Fe^{3+} precipitated as $Fe(OH)_3$, consuming OH^- and dropping the pH to 11.2. An additional 534 g of NaOH raised the pH back to 12. During this time the technician observed a smell of ammonia coming from the slurry. The additional $Fe(OH)_3$ precipitation was an "armouring:" adding a layer of iron-rich solids that didn't contain Re, intended to provide an additional barrier to protect the encapsulated Re. After reacting and mixing for an hour the "armoured" slurry was allowed to settle overnight.

Steps 10−11) Washing and Settling. After settling overnight a clear supernate (~55 vol%) sat on top of the settled solids (~45 vol%). The supernate was pumped out. The top of the settled solids appeared to be orange, similar to the original goethite (see Figure 3.2).

Figure 3.2. Initial Settled Solids after "Armouring"

Immediately below the orange film the bulk of the settled solids were still "pea soup" green. Whether the orange solids just settled more slowly and hence were the last to settle or the orange solids were green solids that reacted and became orange couldn't be determined. Deionized water was added to refill the

reactor; the reactor was mixed and then again settled. After four hours of settling, only 20% of the slurry formed clear supernate (Wash #1). It was determined that settling was going to be very time consuming, so the 20% supernate was removed and the remaining contents were transferred to a larger (10-gal) container and more water (~6 gal) added. After settling overnight the settled solids were about 20% of the volume and clear supernate 80% (Wash #2). The supernate was removed and deionized water added for another wash. Two more washes (#3 and #4) behaved the same as Wash #2. The fifth wash settled very poorly; after settling for 17+ h, a clear layer couldn't be distinguished. The settling was immediately accelerated by adding 200 g of granular $CaCl_2$ to liquid (it would form 0.01-M Ca when completely mixed) as a flocculent. After 5 h settling, the solids layer was somewhat smaller than had been obtained with any of the other settlings, indicating the settled solids slurry was denser than after earlier settling.

Table 3.2 summarizes the washing/settling.

Table 3.2. Bench-Scale Washing/Settling

Step	Settling Time (h)	Supernate (L)	Solids Slurry (L)
First settle	15	11.1	9.1
First wash	8	4.0	16.2
Second wash	16	32.4	9.1
Third wash	14	31.9	9.1
Fourth wash	15	30.4	8.4
Fifth wash	17 (before flocculant) 23 (after flocculant)	29.8	9.1
Wash factor $= \frac{9.1}{20.2} \times \frac{16.2}{41.5} \times \frac{9.1}{41.0} \times \frac{9.1}{38.8} \times \frac{8.4}{38.9} = \mathbf{.0020}$			DF = 500

Steps 12−13) Separation and Cooking. After the slurry solids were washed, approximately half the solids were separated and cooked in the oven at 80°C for seven days to convert the ferrihydroxide solids to goethite. Half the solids were retained "uncooked." Before "cooking," the slurry was brown; it noticeably changed to more orange by "cooking." Figure 3.3 shows the visual comparison.

Figure 3.3. Cooked Fe-Rich Solids (goethite) (left); Uncooked Fe-Rich Solids (right)

Solids from the cooked sample were analyzed by x-ray diffraction (XRD) and confirmed to be goethite (88%) with some remaining unconverted ferrihydroxide (9%). Analysis of the uncooked solids indicated that they were also mostly goethite (61%) with about 3× more ferrihydrite (25%) than the cooked sample.

Figure 3.4 shows example XRD spectra of the goethite-rich solids (top) and the "uncooked" solids (bottom).
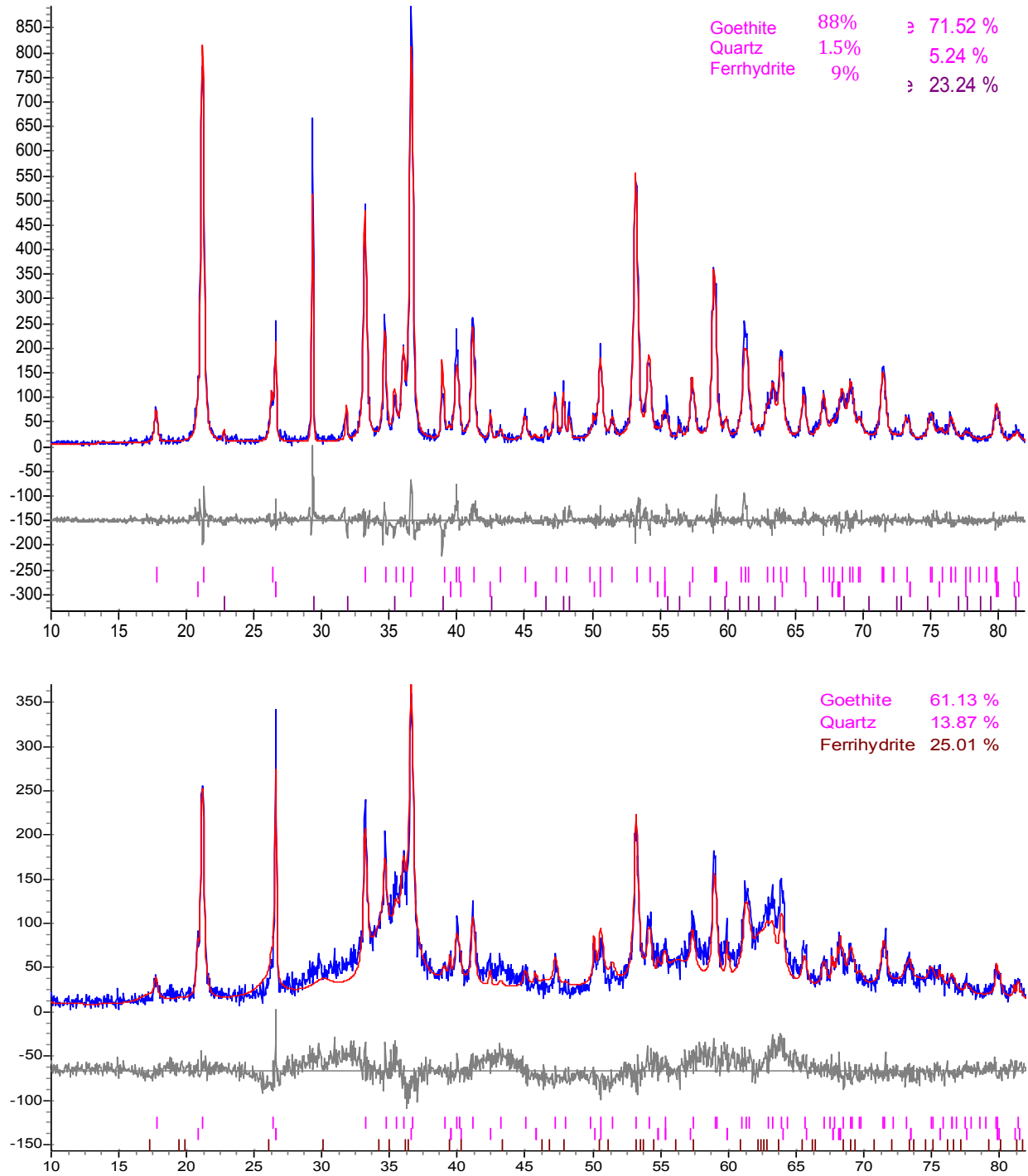
Figure 3.4. Example XRD Spectra: "Cooked" Product (top); "Uncooked" (bottom)

Overall, the process yielded 225 g of goethite solids as a 6.1 wt% slurry and 195 g of ferrihydroxide solids in 6.8 wt% slurry. The Re contents of the product solids were 12.7 µg/g and 12.9 µg/g for the uncooked and cooked products, respectively.

3.2 Engineering-Scale Test

The retention of Re in the goethite from the first scale-up was insufficient to support melter testing. Researchers at VSL indicated they would need at least 100 µg Re/g solids to quantify Re retention through melter testing. Additional modifications were made for the second scale-up to facilitate greater incorporation of Re into the solids.

Nitrate was eliminated from the solution. Nitrate is an oxidizer strong enough to oxidize reduced ReO_2 back to ReO_4^-. Rather than introduce ReO_4^- as a component in Hanford simulant, in which the largest component was $NaNO_3$, ReO_4^- was added directly as $NaReO_4$ in water.

Also, acidic conditions (pH 2) were created using HCl as the acid rather than HNO_3.

These changes were successful in lab-scale tests and proved successful at the engineering scale, too. The final product sent to VSL for melter testing included >2800 µg Re/g solids.

The bench-scale test was executed in accordance with test instruction 57154-2.2.2-T5, *WP-2.2.2 Tc Removal using Goethite Precipitation Test Instruction: Goethite Engineering-Scale Test w/Rhenium*. The steps of the process are summarized in Table 3.3.

Table 3.3. Process Steps for Engineering-Scale Test (400×)

Step	Amount
1. Prepare goethite seed	2.5 kg
Dissolve 13 kg of $Fe(NO_3)_3 \cdot 9H_2O$ into 150 L of H_2O	13 kg in 150 L H_2O
Add NaOH to raise pH to 11−12	~ 4 kg NaOH
Settle and wash solids to obtain a DF of ~100[a]	4 washes of 3× volume
Decant final supernatant, heat solids at 80°C overnight	
Deaerate slurry	
2. Initial Re solution in H_2O	110 L
Adjust pH of Re solution to acid side using HCl	1.5−2.0
Add $NaReO_4$ to obtain a 1×10^{-3} M Re concentration in final 150 L mixture	1.36×10^{-3} M in 110 L
De-aerate solution	
3. Prepare separate seed slurry in DI water [goethite] (deaerated)	2.5 kg solids in 40 L
Adjust pH of seed slurry to acid side using HCl	1.5−2.0
Add $FeCl_2 \cdot 4H_2O$ to seed slurry	4.5 kg
React (maintain anoxic)	>1 h
4. Combine Re solution and seed slurry and mix (maintain anoxic)	4−6 h
5. Adjust pH (~3 kg NaOH)	12−13
6. React (anoxic conditions no longer necessary)	30 min−1 h
7. Add solid $Fe(NO_3)_3 \cdot 9H_2O$ to slurry and mix	11.2 kg
8. Maintain pH—add NaOH (4.2 kg)	12−13
9. React	1 h
10. Separate ~15 gal for ultrafiltration and washing on CUF	
11. Settle and wash remaining solids	Wash with 2× volume of water.[a] Settle overnight.
Add flocculant	
Settle slurry until solids interface appears stationary	
Pump out supernatant	
Add water until 3× volume, mix, settle, pump out supernatant	
(a) DI water may be used if available. If DI water is limited, tap water may be used for the initial make-up and first two washes. DI water should be used for the last two washes.	

The second scale-up batch was prepared using drum reactors. Figure 3.5 shows the engineering-scale apparatus.
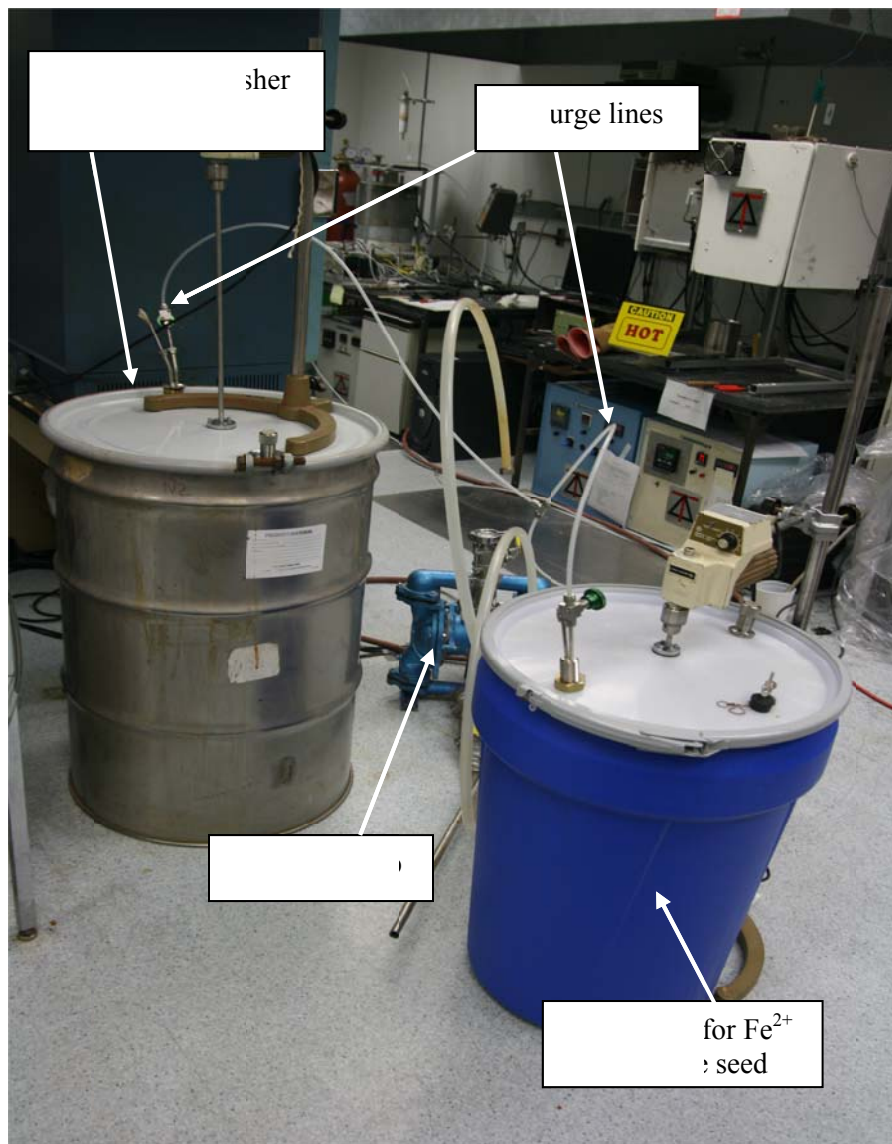
Figure 3.5. Engineering-Scale Apparatus

Referring to Table 3.3 and Figure 3.5, the process steps were similar to the bench-scale test, but had some differences as described below.

Step 1) Prepare Goethite Seed. The engineering-scale test required approximately 2.5 kg of initial goethite solids. The first steps of the engineering-scale process were to prepare sufficient goethite solids by precipitating ferrihydroxide solids by raising the pH of dissolved ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), washing and settling the solids, and cooking settled slurry to convert the ferrihydroxide solids to α-FeOOH (goethite). Seed preparation was essentially the same process as for Re (Tc) capture except without reaction with Fe^{2+}. VSL had requested that no Cl^- be added to the washes as a flocculant, as had

been done for the bench-scale test, because Cl⁻ in the goethite slurry would take the Cl⁻ content of the glass out of specification. For the goethite seed make-up, a polymer flocculent was initially used. Clarifloc® N-3300P was selected without testing because it was used at the Hanford K Basins to flocculate goethite particles and it was available onsite. Flocculent was made at 2.5 g Clarifloc solids to 500 g H_2O and 50 mL of solution added to ~200 L of slurry. The final Clarifloc addition rate was ~1¼ ppm. Flocculent was added for Washes #2 and #3. Wash #4 tried the settling without flocculant and it settled without difficulty. Wash #5, however, wouldn't settle. Figure 3.6 shows the washed slurry after settling overnight.

Figure 3.6. Goethite Seed Preparation, Wash #5

Five times the normal flocculant was added (6 ppm total) without success. Aluminum chloride was added under the hypothesis that it might be even more effective than $CaCl_2$, but it wasn't. The scaled testing was suspended for a day while flocculating tests were conducted using higher concentrations of Clarifloc and .01-M $CaCl_2$. Figure 3.7 shows the settled flocculation tests.
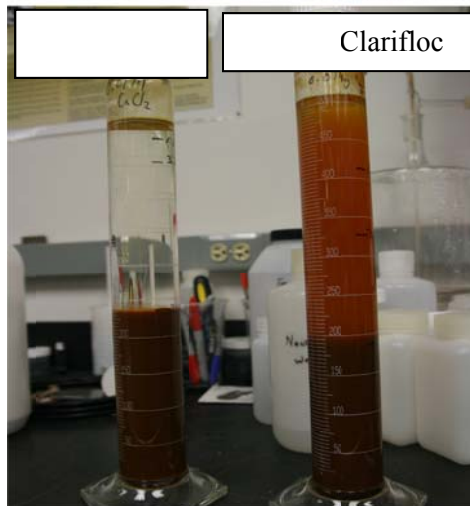
Figure 3.7. Goethite Seed Flocculation Tests

Clarifloc at 20 ppm settled faster and created denser-solids slurry, but the supernate remained cloudy. Supernate of $CaCl_2$ (.01 M) was clear. $CaCl_2$ was selected to complete washing, considering that the undesirable Cl^- would be washed out in the final product washing. Additional settling tests could be done before the final washing to identify a flocculent that didn't contain chloride. After settling, the supernate was removed and the solids slurry collected and cooked in the oven at 80°C for four days. XRD analysis indicated that the solids were entirely α-FeOOH (goethite). Figure 3.8 shows the prepared goethite seed solids.

Figure 3.8. Goethite Seed Solids for Engineering-Scale Test

Step 2) Re-solution. Rather than use SBS simulant as had been done in the bench-scale test, $NaReO_4$ was dissolved in 110 L deionized water in the main reactor and the pH adjusted to 2.0 with HCl. Consistent with the strategy to eliminate NO_3^- from the system, HCl was used rather than HNO_3. The solution was deaerated for three days until combined with the Fe^{2+} reacted goethite seed.

Step 3) Goethite Seed with Fe^{2+}. Goethite seed solids were combined with DI water to a total of 70 L and adjusted to pH 2.0 using HCl in the prereactor. The slurry was purged with N_2 for two days to remove dissolved oxygen from the slurry. After purging, the prescribed amount (4.5 kg) of solid $Fe(Cl)_2•4H_2O$ was added through a port in the vessel lid while maintaining the N_2 purge. The slurry was then reacted for 2½ h.

The ratio of Fe^{2+} to goethite seed solids was raised in this test to mimic the increase of Fe^{2+} concentration from .07 M to 0.1 M at the lab scale.

Step 4) Mixing and Reacting SBS Simulant and Fe^{2+}/Goethite. Using the transfer pump, the reacted goethite seed slurry was transferred into the main reactor, while maintaining deaerated conditions (N_2 purge). The slurry was mixed and reacted for 3.5−4 h. After the transfer, all the process steps were conducted in the main reactor (55-gal SS drum); the pre-reactor was not used again.

Step 5) Precipitation of Fe^{2+}/Fe^{3+}. After the reaction time, the N_2 purge was stopped, the lid to the main reactor removed, and the pH raised by adding solid NaOH. As caustic was added the color changed from orange (goethite) to green. The green color was thought to be $Fe(OH)_2$ ("green rust") (Um 2010), but no analyses were conducted to verify. Further NaOH was added until the pH of the slurry was above 12. A total of 2.5 kg of solid NaOH was added. The green color darkened as the pH was raised, becoming black when all the caustic was added (pH 13.3). See Figure 3.9 and Figure 3.10.

Figure 3.9. Initial NaOH Added (left); NaOH Mixed (right)

Figure 3.10. Precipitated Fe^{2+}/Fe^{3+} After All Caustic Added; pH = 13.3

The bench-scale test had formed the green color, which became darker as the pH increased, but never got as dark as in the engineering-scale test. This was the first indication that the solids formed in precipitation in the engineering-scale test were not identical to those in the bench-scale or lab-scale tests.

Steps 6−9) Armouring. The precipitated Fe^{2+}/Fe^{3+} reacted overnight, then 7.5 kg of solid $FeCl_3 \cdot 6H_2O$ was added directly to the slurry. The pH dropped from 13.3 to 12.1, but no additional NaOH was added.

After reacting and mixing for approximately 3 hours, a 20 L sample of the slurry was removed from the reactor (drum) and the remaining "armoured" slurry was allowed to settle over the weekend.

Steps 10−11) Washing and Settling. After settling, the clear supernate was pumped off and the slurry washed. Washing consisted of refilling the drum with H_2O, mixing, and resettling. The slurry was washed four times. Unlike in the bench-scale tests or the goethite seed preparation, flocculants were not needed. The washing steps are summarized in Table 3.4.

Table 3.4. Engineering-Scale Washing/Settling

Step	Settling Time (h)	Supernate (L)	Solids Slurry (L)
First settle	15	153.1	60.3
First wash	8	137.6	75.8
Second wash	16	137.6	75.8
Third wash	14	137.6	75.8
Fourth wash	15	155.6	54
Wash factor $= \frac{60.3}{213.4} \times \frac{75.8}{213.4} \times \frac{75.8}{213.4} \times \frac{75.8}{213.4} = .0126$			DF=79

Steps 12−13) Separation and Cooking. The settled slurry solids were combined with 5.5 L of concentrated washed slurry solids returned from the ultrafiltration/washing of the 20 L sample sent to the CUF (see Section 3.2.1). The combined washed slurry was split into two approximately equal fractions and one fraction was "cooked" in an oven at 80°C for nearly 4 days (89 h).

3.2.1   Final Product Analyses

Samples from both slurries ("cooked" and "uncooked") were analyzed by XRD. XRD indicated that 70% of the solids in both samples were magnetite (Fe_3O_4). A few attempts were made to convert the solids to goethite on lab-scale samples (longer heating, heating with mixing to promote oxidation, heating with NaOH) but they were not completely successful.

It was decided that the magnetite samples would be sent to VSL for melter testing. Between the two iron forms (goethite vs. magnetite), the magnetite would more likely improve incorporation of Re into the melt. Magnetite decomposes at 1538°C, while goethite dehydrates to an oxide at 136°C.

Analysis by inductively coupled plasma spectrometry of the digested solids for Re indicated that the modifications intended to improve Re retention were successful. The "cooked" and "uncooked" slurries contained 3044 µg Re/g solids and 2812 µg Re/g solids, respectively. Sixty-five percent (65%) of the initial Re in the solution was captured in the precipitated solids. Solids analysis of the "cooked" and "uncooked" products indicated the slurries were 11.84 wt% and 11.0 wt%, respectively.

3.2.2   Ultrafiltration/Washing of Precipitated Iron-Rich Slurry

The unwashed slurry solids from the engineering-scale test were initially dewatered to ~20 wt% solids and then washed with seven batches of 0.01 M NaOH simulating dewatering/washing as would be

done in the ultrafiltration system of WTP. The initial sample was measured to be 23 L and determined to be 3.9 wt% undissolved solids (UDS) using a Mettler moisture analyzer. During the initial dewatering step of the ultrafiltration, the permeate flux started at 0.5 gpm/ft^2 at a standard transmembrane pressure of 40 psid and decreased to 0.03 gpm/ft^2. At the end of dewatering, the solids content was measured to be 20.8 wt% UDS. The flux rates were significantly higher than UF flux rates for Hanford simulant slurries over comparable concentration ranges, which typically start at 0.04 gpm/ft^2 and decline to 0.01 gpm/ft^2. During seven batches of washing the slurry continued to filter significantly faster than typical Hanford simulant. Details of the UF performance are included in Appendix A.

3.3   Pilot-Scale Melter Testing of Fe-Rich Solids with Re

A series of melter tests were conducted at Vitreous State Laboratory (VSL) on a DuraMelter 10 small-scale ceramic continuous melter system using an AZ-101 HLW composition. The objective of the melter tests was to evaluate the effect of the iron and rhenium source on rhenium retention in the glass product. The tests employed melter feeds with four different iron and rhenium sources: the baseline iron hydroxide slurry without rhenium, the baseline iron hydroxide slurry with rhenium added as perrhenic acid, PNNL magnetite/goethite slurry with adsorbed rhenium, and PNNL heated magnetite/goethite slurry with adsorbed rhenium.

Measurements of glass production rates, melter operating conditions (temperatures, pressures, power, flows, etc.) were made throughout the tests. Qualitative observations of the cold cap and feed characteristics, such as pumpability and spreading across the melt surface, as well as ease of discharging glass were made throughout the tests. In addition, particulate loading and composition as well as acid gas concentrations were determined for the purpose of calculating a material mass balance around the melter during each test. Glass samples taken throughout the tests from the melt pool and the air-lift discharge were visually examined for secondary phases and analyzed for chemical composition. Particular emphasis was placed on rhenium distribution between the glass and the off-gas.

Notable observations made during the processing of the different feeds were as follows:

- Feed with goethite slurries as the iron source form a significantly more viscous melter feed. Dilution of the feed with additional water was required to produce a melter feed from the goethite slurries that could be processed. However, surprisingly little added water was required.

- Feed made with goethite slurries as the iron source processed about 60% faster than feed using iron hydroxide as an iron source when processed at a constant bubbling rate.

- The retention of rhenium in the glass product was essentially the same for feeds with iron hydroxide and perrhenic acid, heated goethite slurries with rhenium, and unheated goethite slurries with rhenium.

- The majority of the divalent iron present as magnetite in the goethite slurry was oxidized during the vitrification process.

- Solids carryover from the melter for feed with goethite slurries as the iron source was about half that measured for feed with iron hydroxide as the iron source.

Details of the melter testing are in the VSL report, VSL-11R2300-1, *Melter Testing for Technetium Removal Using Goethite Precipitation, 2011*. See Appendix B.

3.13

4.0 Conclusions

These tests indicate that primary unit operations of the technetium removal process using precipitation in Fe-rich solids can be adapted from labware, flasks, and shaker tables to plant processing equipment. The anoxic conditions necessary in the lab can be created using purged reaction vessels and deaerated liquids. The tolerable oxygen level in the anoxic conditions was not investigated in these initial tests, but these initial modifications were conducted in a straightforward manner without precision fits to the equipment. One can assume the oxygen levels were significantly reduced from normal air atmospheres, but were above zero; they would be easily achieved in a plant design without special seals or equipment.

Reaction times for the Fe^{2+}/goethite and the Fe^{3+} precipitation were conducted within 2 hours instead of over 1-2 days as had been done in the lab-scale baseline tests; they are suitable for plant processing.

During the preparation of goethite seed for the engineering-scale test, the final conversion of the precipitated Fe-rich solids to goethite was accomplished in 3½ days. This is too long for a plant process, and the need to convert to goethite is still not firmly established. This will have to be studied further.

Changes to the redox chemistry (elimination of nitrate and increased Fe^{2+}:goethite solids ratio) increased the retention of Re in the precipitated solids. There was also a noticeable change during the subsequent precipitation. The precipitated solids turned out to be magnetite (Fe_3O_4) rather than amorphous ferrihydrite solids that could readily be converted to goethite ($FeOOH$). The difference in oxidation of the iron in magnetite vs. goethite implies that the changes in redox chemistry also affected the crystal-growth solids formation of the precipitates. Further work must be done to determine the causes.

The formed magnetite solids settled better than the ferrihydrite precursors. The settling difference could be a result of several differences (e.g., particle size) that would need to be investigated further. The differences also led to a solids slurry that filtered better than the Fe-rich solids typically in Hanford simulant.

Rhenium captured in magnetite solids did not improve the retention of rhenium in vitrification. This would indicate that capturing technetium into magnetite (or goethite) would not improve its retention in the melter, which was one objective of this application for the technology. However, this work by itself does not disprove that possibility. Further understanding is needed of whether the Re incorporated fully into the solid matrix or might have simply co-precipitated before concluding that the Re-rich solids were completely comparable to the Tc/Fe solid solutions prepared in the initial lab tests. Further detailed characterization would need to be done before discounting the potential application.

An interesting positive result of the melter tests was that the melter feed rate improved about sixty percent when the iron was added as a precipitated magnetite/goethite vs. the baseline iron hydroxide as the iron source. The impact of a 60% increase in melter rate is potentially significant; melter rate is inherently a controlling factor in the overall processing of HLW through WTP. A full assessment is beyond the scope of this work, but potential impacts on the Hanford cleanup schedule are worthy of further consideration.

5.0   References

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Appendix A

Ultrafiltration of Engineering-Scale Fe-Rich Slurry

Appendix A

Ultrafiltration of Engineering-Scale Fe-Rich Slurry

Date:	**January 20, 2011**	Project No.:	**57154**
To:	**Gary Josephson**	Internal Distribution:	**Joseph Westsik**
From:	**Justin Billing**		
Subject:	**Goethite Ultrafiltration Tests**		

In November 2010, 23 L of caustic slurry containing goethite was received for ultrafiltration testing in the CUF filtration system. The stated objectives of the filtration tests were to concentrate the slurry from a nominal 1–2 wt% UDS to greater than 10 wt% UDS and to wash the concentrated solids to a decontamination factor of greater than 100 using 0.01 M NaOH. The results for this testing show that the caustic goethite slurry can be concentrated and washed at rates significantly exceeding filtration rates for comparable PEP simulant slurries.

Initial Dewatering

Before the slurry was added to the CUF slurry reservoir, a clean water flux test was performed with 0.01 M NaOH. The test lasted one hour and the flux remained stable at a typical level for this filter element of 2.36 gpm/ft^2 when adjusted from the tested transmembrane pressure (TMP) of 10 psid to the reference TMP of 40 psid. The received slurry was then added to the CUF slurry reservoir, mixed, and sampled (sample name ReGoet_IN). A brief preliminary filtration test was performed to determine the feasibility of dewatering over 20 L of slurry. The observed permeation rate was nearly 10× higher than typical waste simulant slurries (i.e. PEP simulant). Since the slurry could be readily dewatered in the CUF system, the system was back-pulsed once and the dewatering test began.

Over a duration of 1.73 hours, 19.936 kg of permeate (ρ = 1.03 g/mL) was dewatered into a clean, tared carboy container. The target operating conditions were:
- transmembrane pressure (TMP) = 40 psid
- axial velocity (AV)=15 ft/sec
- T_{slurry} = 25°C

The starting concentration was measured to be 3.88 wt% UDS using the Mettler moisture analyzer in lab 107 of the Applied Process Engineering Laboratory. The final concentration was measured to be 20.8 wt% UDS. The flux during dewatering started near 0.50 gpm/ft^2 and declined over the test to 0.03 gpm/ft^2. Flux during the dewatering of PEP simulant slurries over comparable concentration ranges typically starts at 0.04 gpm/ft^2 and declines to 0.01 gpm/ft^2. The flux of the goethite slurry was as much as 10× higher compared to PEP simulant slurry dewatering steps.

The permeate flow rate is converted to a filter flux by dividing it by the filter surface area. This flux is also corrected for minor variations in temperature and transmembrane pressure around

the target setpoints. The corrected permeate flux for the initial dewatering is given in Figure A.1. Actual process performance against the target operating conditions is shown in Figure A.2.
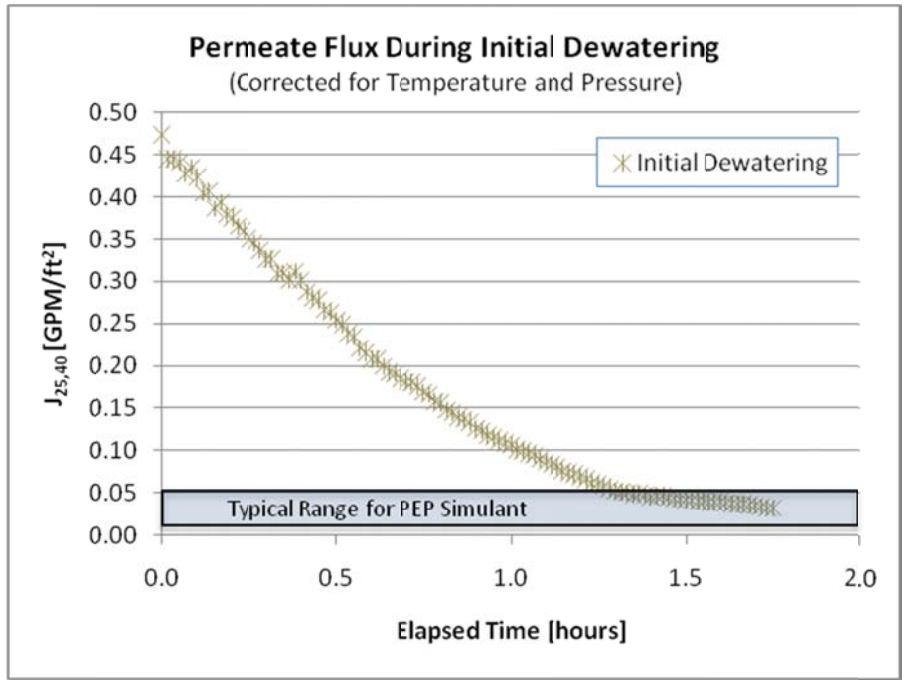
Figure A.1. Permeate Flux During the Initial Dewatering of the Caustic Goethite Slurry

The shaded box represents the typical range of permeate flux observed during dewatering of PEP simulant slurries.
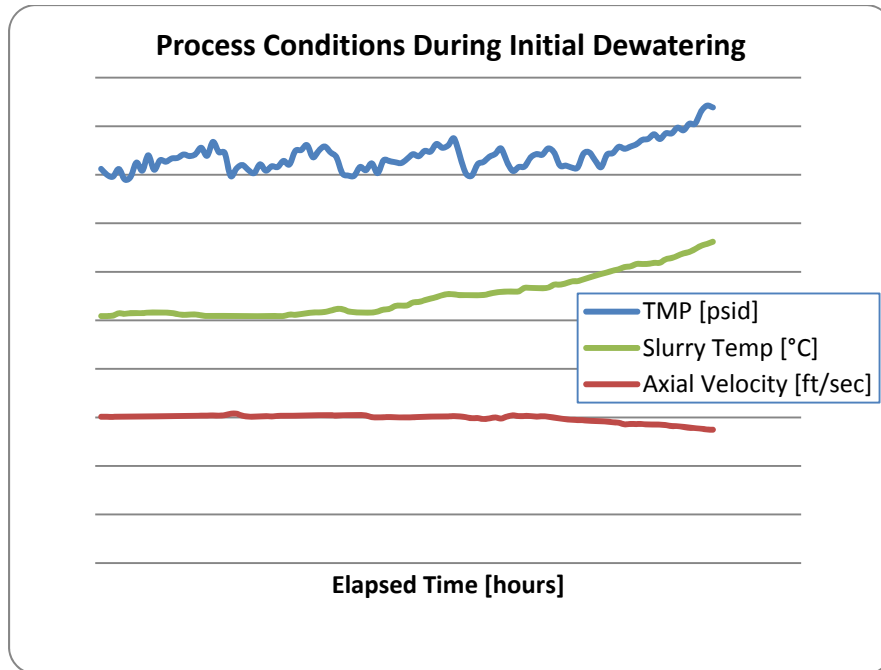
Figure A.2. Process Conditions During Initial Dewatering of Caustic Goethite Slurry

The Y axis is a dimensionless scale; the units for each of the three variables are given in the legend.

Multiplying the wt% UDS data for the initial slurry, ReGoet_IN, by the mass of slurry added (minus the sample mass), the mass of UDS in the CUF during dewatering was 0.953 kg. After dewatering 19.936 kg of permeate, the slurry mass was 4.629 kg. The predicted wt% UDS of the final sample would then be 20.6 wt% UDS by the following calculation. This agrees well with the measured value of 20.8 wt% UDS.

$$UDS_{Calc} = \frac{m_{UDS}}{m_{slurry}} = \frac{0.953kg}{4.629kg} = 20.6wt\%UDS$$

Slurry Washing

To wash the concentrated slurry with 0.01 M NaOH to a decontamination factor (DF) greater than 100, a series of equal-mass washes was planned. Since each equal-mass wash diluted the suspending phase by more than half (since the slurry was ~20 wt% UDS), the DF per wash was assumed to be two. To get a DF over 100, seven equal-mass washes were required ($2^7 = 128$). The DF on a volume basis will be higher because the volume of an equal mass of 0.01 M NaOH is greater than the volume of the denser, concentrated slurry. The washing approach was conservative to make sure the washing target was exceeded.

Each of the seven washes was dewatered at the same target operating conditions as the initial dewatering. The corrected permeate flux for each of the seven washes is shown in Figure A.3 and the operating conditions are shown in Figure A.4. As with initial dewatering, the flux during the washes was significantly higher than the flux observed for comparable PEP simulant slurries. To verify that the slurry had been successfully washed, permeate collected from Wash #7 was analyzed on the moisture analyzer and found to contain no measurable dissolved solids.

After dewatering Wash #7, the slurry was pumped from the reservoir. Due to the high UDS concentration, 0.01M NaOH was added as needed to rinse and flush the solids out of the system. The net mass of washed slurry recovered was within 0.16% of what was predicted by the run mass balance of material into and out of the system during processing.

The washed slurry was collected in a rinsed, labeled carboy and returned to Mike Schweiger.

Permeate Flux During Slurry Washing
(Corrected for Temperature and Pressure)

✳ Wash #1   ■ Wash #2   ▲ Wash #3   ✕ Wash #4   ✳ Wash #5   ● Wash #6   ✛ Wash #7

Typical Range for Concentrated, Washed PEP Simulant

$J_{25,40}$ [GPM/ft²]

Condensed Elapsed Time [hours]
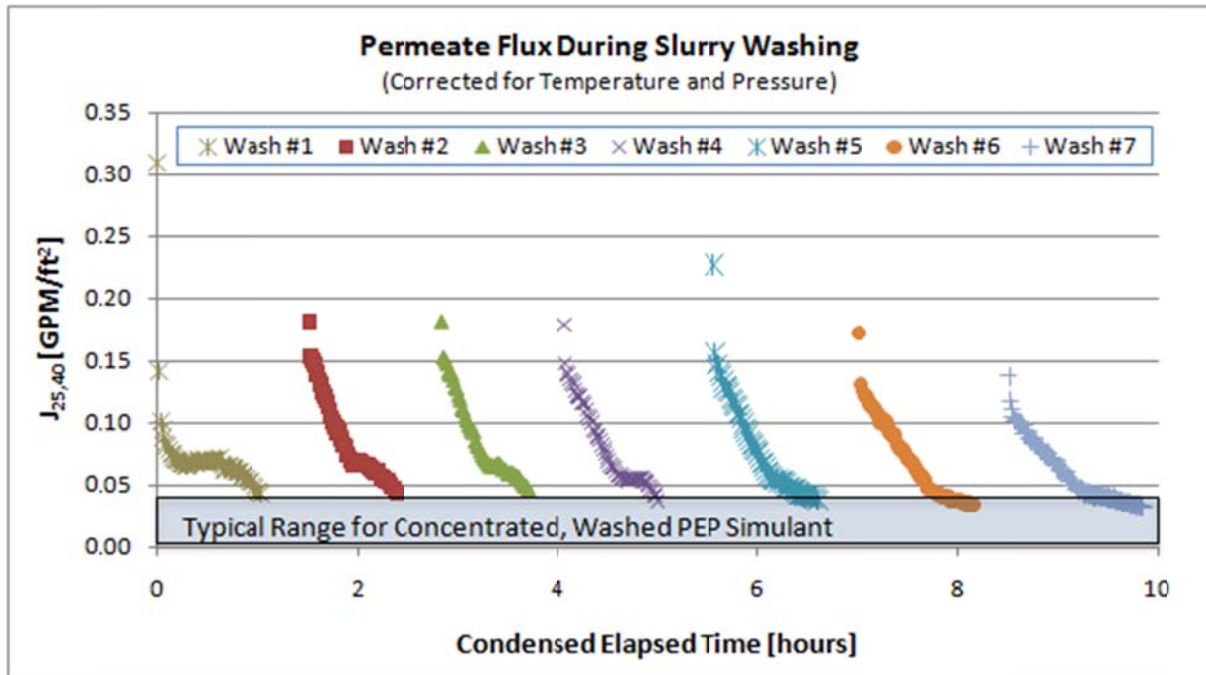
Figure A.3. Corrected Permeate Flux for Each of the Seven 0.01 M NaOH Washes

The shaded box represents the typical range of permeate flux observed during dewatering of comparable PEP simulant slurries. The time axis is condensed for the purpose of presentation; time periods of inactivity during washing have been omitted, including one overnight period, as washes were conducted on two consecutive days.
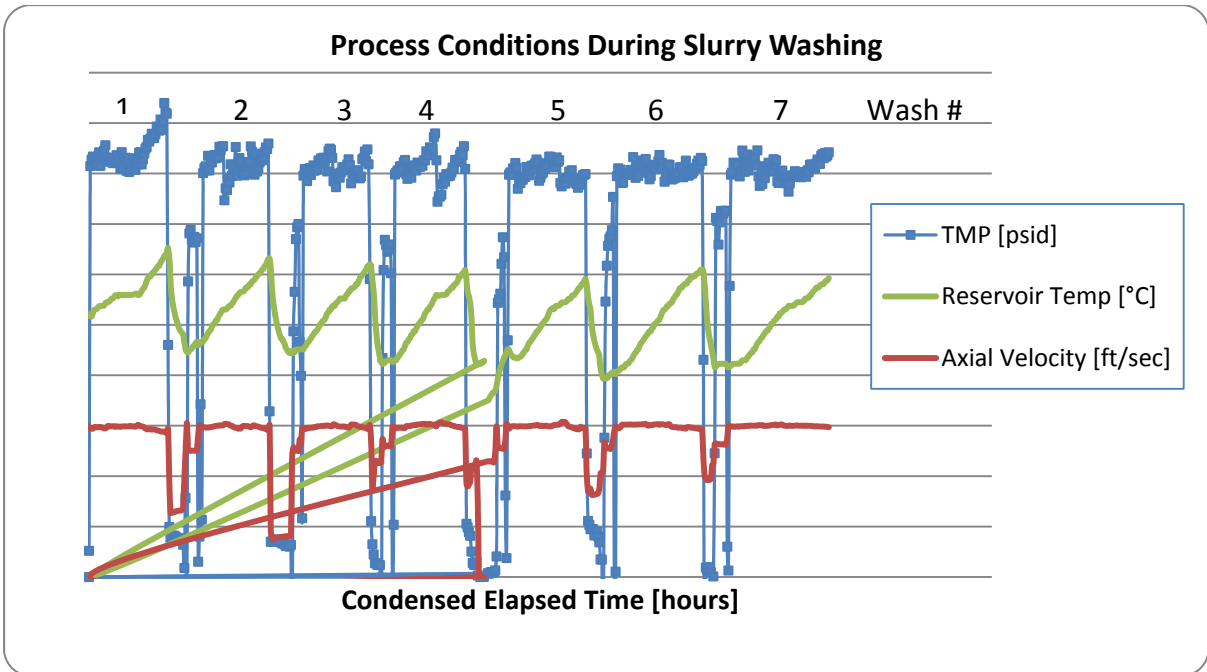
Figure A.4. Process Conditions During Dewatering Each of Seven Washes.

The Y axis is a dimensionless scale: the units for each of the three variables are given in the legend.

Processing notes

The initial dewatering and wash dewaterings produced concentrated slurry with challenging rheology and high yield strength. During processing, this change in rheological properties resulted in large (15 to 50 psid) axial pressure drops in the filter element as the dewatering neared completion. After a certain consistency was reached, the CUF heat-exchange system was not able to maintain slurry temperature and temperatures above 30°C were observed. Near the end of initial dewatering, it was also difficult to maintain the target axial velocity.

Appendix B

Melter Testing of Fe-Rich Solids from Technetium Removal Process

VSL-11R2300-1

Final Report

Melter Testing for Technetium Removal Using Goethite Precipitation

prepared by

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Washington River Protection *Solutions*, LLC
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August 15, 2011

Rev. 0, 9/22/11

Completeness of Testing:

This report describes the results of work and testing specified by WRPS. The work and any associated testing followed established quality assurance requirements. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Results required by the test program are reported. Also reported are any unusual or anomalous occurrences that are different from the starting hypotheses. The test results and this report have been reviewed and verified.

I. L. Pegg:_____   Date: ___9/22/11___
VSL Program Director/Principal Investigator

I. Joseph:_____   Date: ___9/22/11___
Energy*Solutions* Sub-Contract Manager

TABLE OF CONTENTS

List of Tables

4

List of Figures

List of Abbreviations

ASME	American Society of Mechanical Engineers
CUA	The Catholic University of America
DCP-AES	Direct Current Plasma Atomic Emission Spectroscopy
DM	DuraMelter
DOE	Department of Energy
DWPF-EA	Defense Waste Processing Facility-Environmental Assessment
EDS	Energy Dispersive X-ray Spectroscopy
HEPA	High-Efficiency Particulate Air Filter
HLW	High Level Waste
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
LAW	Low Activity Waste
M	Molarity
N	Normality
NIST	National Institute of Standards and Technology
NQA	Nuclear Quality Assurance
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QARD	Quality Assurance Requirements and Description
RPP	River Protection Project
RPP-WTP	River Protection Project-Waste Treatment Plant
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leaching Procedure
UTS	Universal Treatment Standards
VSL	Vitreous State Laboratory
WRPS	Washington River Protection *Solutions*, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

SECTION 1.0
INTRODUCTION

During vitrification of low activity waste (LAW) at the Hanford Tank Waste Treatment and Immobilization Plant (WTP), liquid effluents are produced in the primary off-gas treatment system that processes the exhaust gases from the LAW melters. That effluent stream, which contains captured hazardous and radioactive species from the melter exhaust, is then recycled and eventually becomes part of subsequent melter feed batches. Other constituents, such as sulfur and halides, are also recycled in this process and this can impact the LAW glass loadings that are achievable. Thus, breaking the melter recycle loop could have advantages with respect to reducing LAW glass volumes. However, this recycle stream cannot currently be diverted to liquid secondary waste treatment because of the levels of several constituents in the scrub solutions, particularly technetium. Researchers at Pacific Northwest National Laboratory (PNNL) have been investigating a process whereby the technetium could be precipitated from the off-gas recycle stream in the mineral goethite ((Tc, Fe)OOH). It could then be diverted to the high level waste (HLW) stream through the WTP pretreatment facility and the decontaminated liquid stream could be sent to secondary waste treatment. As part of the test program to develop the goethite precipitation process, it is necessary to assess the impacts of including this material in the HLW melter feed and the extent to which the captured technetium is volatilized during HLW vitrification. To support such testing, sufficiently large batches of material were prepared at PNNL using rhenium as a surrogate for technetium. These materials were shipped to the Vitreous State Laboratory (VSL) of the Catholic University of America (CUA) for testing on a DuraMelter 10 (DM10) small-scale joule-heated ceramic melter system. This report describes the testing that was performed with those materials.

1.1   Test Objectives

The principal objectives of the DM10 tests at the VSL were to demonstrate processing of a Hanford HLW waste stream combined with two different forms of iron-containing materials that were produced during the precipitation of rhenium from simulated LAW recycle streams. A simulant of an AZ-101 HLW composition based on an actual waste sample analysis, which was previously processed on a continuously fed melter, was selected for these tests. The goal of these tests was to compare Hanford HLW melter feed simulants, containing rhenium added directly or in various types of iron compounds, with respect to processing properties, rhenium retention, and off-gas compositions.

Specific objectives of these tests were to:

- Demonstrate on the DM10 melter acceptable processing (glass production rate, feed distribution across molten glass, glass redox, off-gas characteristics, melter feed mixing/pumping) of a Hanford HLW high-iron waste stream (AZ-101) with the iron

7

oxide source substituted with various forms of iron-containing materials produced at PNNL during rhenium precipitation.

- Determine rhenium retention in the DM10 glass product with three different iron sources and two different rhenium sources: (i) iron hydroxide with perrhenic acid (baseline); (ii) PNNL heated iron precipitate loaded with rhenium; and (iii) PNNL unheated iron precipitate loaded with rhenium.

- Determine rhenium emissions from the DM10 with the same three iron and rhenium sources.

- Characterize the chemical composition of each discharge glass with particular emphasis on rhenium and determine the iron oxidation state for glass from the end of each melter test for each feed composition.

- Sample and characterize discharge glass samples at the end of each test segment.

- Characterize the melter emissions (particulate, aerosol, and gaseous) to permit material mass balance across the melter for each iron and rhenium source, with particular emphasis on rhenium.

It should be noted that the testing involved complete replacement of the iron source in the melter feed by each of the rhenium-loaded goethite materials provided by PNNL. This approach was used in order to maximize any differences in rhenium retention and thereby optimize the sensitivity of the tests. However, if such a precipitation process were implemented, a more likely scenario in actual WTP operations would be that the goethite precipitate would form an additional iron stream to the melter feed, over and above that derived from the HLW solids.

1.2   Quality Assurance

Testing was performed according to the existing quality assurance program that is in place at VSL. That program is compliant with applicable criteria of 10 CFR 830.120; Office of Civilian Waste Management DOE/RW-0333P, Quality Assurance Requirements and Description (QARD) Revision 20; the American Society of Mechanical Engineers (ASME) NQA-1, 2004; and DOE Order 414.1 C, Quality Assurance. The requirements of DOE/RW-0333P were applicable to the following specific aspects of this work:

- Crucible melt preparation of HLW glasses
- Analysis of HLW crucible melt glasses

The program is supplemented by a Quality Assurance Project Plan for WRPS work [1] that is conducted at VSL. Test and procedure requirements by which the testing activities are planned and controlled are also defined in this plan. The program is supported by VSL standard operating procedures that were used for this work [2].

1.3   Melter System Description

Testing was conducted on one of the two DM10 melter systems installed at the VSL, shown in Figure 1.1. A schematic diagram of the DM10 system is shown in Figure 1.2 and the principal components of the system are described in the following sections.

1.3.1   Feed System

The feed container is mounted on a load cell for weight monitoring and is stirred continuously except for periodic, momentary interruptions during which the weight is recorded. The material in the feed container is constantly recirculated, which provides additional mixing. The recirculation loop extends to the top of the melter where feed is diverted from the recirculation loop into the melter through a Teflon-lined feed line and water-cooled feed tube. The feed rate is regulated by a peristaltic pump that is located in between the recirculation loop and the feed tube.

1.3.2   Melter System

A DuraMelter 10 (DM10) system was used for this work. The Monofrax K3 ceramic refractory-lined melter includes two MA 758 plate electrodes that are used for joule-heating of the glass pool and a bubbler for mixing the melt. The DM10 melter has a melt surface area of $0.02 \ m^2$ and glass inventory of about 8 kg. The glass product is removed from the melter by means of an air-lift discharge system.

1.3.3   Off-Gas System

For operational simplicity, the DM10 is equipped with a dry off-gas treatment system involving gas filtration operations only. Exhaust gases leave the melter plenum through a film cooler device that minimizes the formation of solid deposits. The film-cooler air has constant flow rate and its temperature is thermostatically controlled. Consequently, the exhaust gases passing through the transition line (between the melter and the first filtration device) can be sampled at constant temperature and air flow rate. The geometry of the transition line conforms to the requirements of the 40-CFR-60 air sampling techniques. Immediately downstream of the transition line are cyclonic filters followed by conventional pre-filters and HEPA filters. The temperature of the cyclonic filters is maintained above 150^oC while the HEPAs are held above 100^oC to prevent moisture condensation. The entire train of gas filtration operations is duplicated and each train is used alternately. An induced draft fan completes the system.

1.4   Experimental and Analytical Methods

The measurements and analyses that were performed in this work are detailed in controlled VSL technical procedures [2], which constitute part of the VSL QA program. This section provides a brief description of the equipment and experimental methods that were used.

1.4.1   Glass Preparation

Each crucible-melt glass was prepared from reagent grade or higher purity chemicals to produce a batch size of approximately 400 g. Crucible melts were prepared by melting the appropriate combination of well-mixed chemicals at 1150ºC for 120 minutes in a platinum or platinum-gold crucible. Mixing of the melt was accomplished mechanically with a platinum stirrer, beginning 15 minutes after the furnace temperature reached 1150ºC and continuing for the next 100 minutes. The molten glass was poured onto a graphite plate to cool, and the resulting glass was then distributed for analyses.

1.4.2   Compositional Analysis

Each glass sample was powdered and sieved to give -200 mesh material before analysis by X-ray fluorescence spectroscopy (XRF). An ARL 9400 wavelength dispersive XRF spectrometer running UniQuant™ was used for analysis. An additional analysis to quantify rhenium more precisely was also conducted using the XRF. This method involved analyzing a specific spectral line and the associated background for extended periods instead of using the UniQuant™ program. Boron and lithium were determined by total acid dissolution of ground glass samples in HF/HNO$_3$ and subjecting the resulting solutions to DCP-AES analysis.

1.4.3   Mössbauer Spectroscopy

Mössbauer spectroscopy is an analytical technique that utilizes the recoil-free emission and resonant absorption of gamma rays by nuclei bound in solids. The energies of the gamma ray emitter (source) and absorber (sample) have to be closely matched and, therefore, the number of elements that can be studied using this technique is limited. One of the elements that has been studied extensively using Mössbauer spectroscopy is iron. In this work, Mössbauer spectroscopy was used to measure the fraction of iron in the Fe^{2+} and Fe^{3+} states, which can be used as a measure of the redox state of the glass sample.

Mössbauer spectra were collected using an American Magnetic/Ranger Scientific MS-1200 system equipped with a ^{57}Co source in a rhodium matrix with glass powder as the sample. Both divalent and trivalent iron show doublet peaks in the Mössbauer spectra and the peak areas are proportional to the concentrations of the respective species in the glass. Even though the peaks overlap partially, software can be used to deconvolute the peaks and calculate the peak areas. The ratio of the areas of the Fe^{2+} and Fe^{3+} peaks is equal to the ratio of their

concentrations in the glass. The redox measurements are calibrated using a set of six standard glass samples ranging in Fe^{2+} to Fe_{total} values from 7 to 90%. The standards include a NIST traceable Obsidian Rock (SRM 278), five standard glasses analyzed by Corning, Inc. for their redox state, and the SRL-EA glass. The NIST Standard iron foil (SRM 1541) was used to calibrate the instrument and determine the zero velocity channels. Since Doppler shifts in energy are measured in Mössbauer spectroscopy, the velocity is a measure of the shift in energy; knowing the zero velocity channel therefore helps in identifying the Fe^{2+} and Fe^{3+} peaks.

1.4.4 Feed Rheology

A Haake rheometer (Model RS600) was used to measure the yield stress and the dependence of shear stress on shear rate of melter feeds. For measurement of shear stress vs. shear rate, the instrument employs a cylindrical rotor and a matching sample cup and is operated in controlled shear rate mode. The steady-state shear stress is determined for a range of shear rates from 0.1 s^{-1} to 1000 s^{-1}. The rheology data are analyzed for the onset of Taylor vortices and the affected data are so noted. Yield stress is determined using a vane rotor and matching sample cup. The measured torque versus time is monitored at a given shear rate and the maximum torque is used to calculate the yield stress. All measurements were made at $25^{o}C$; previous work [3], which examined a range of temperatures, showed a relatively weak effect of temperature.

1.4.5 Melter Exhaust Sampling and Analysis

The melter exhaust was sampled for metals/particles according to 40-CFR-60 Methods 3, 5, and 29 at steady-state operating conditions during each test segment. The concentrations of off-gas species that are present as particulates and gaseous species that are collected in impinger solutions were derived from laboratory data on solutions extracted from air samples (filters and various solutions) together with measurements of the volume of air sampled. Particulate collection required isokinetic sampling, which entails removing gas from the exhaust at the same velocity that the air is flowing in the duct (40-CFR-60, Methods 1-5). Typically, a sample size of 30 dscf was taken at a rate of between 0.5 and 0.75 dscfm. Total particulate loading was determined by combining gravimetric analysis of the standard particle filter and chemical analysis of probe rinse solutions. An additional impinger containing 2 N NaOH was added to the sampling train to ensure complete scrubbing of all acid gases. The collected materials were analyzed using direct current plasma atomic emission spectroscopy for the majority of the constituents and ion chromatography (IC) for anions.

SECTION 2.0
WASTE SIMULANT AND GLASS FORMULATIONS

2.1   HLW AZ-101 Waste Simulant

In a previous study, actual waste solids from tank AZ-101 were pretreated and analyzed at PNNL. The pretreatment started with washing of the solids (insoluble solids = 317.9 g) twice with 0.01 M NaOH solution (1000 g each), which was followed by caustic leaching with approximately 3 M NaOH at 85°C. After 8 hours of leaching, the slurry was then batch rinsed three times with 0.01 M NaOH (1200 g each). The resulting slurry, which had a solids content of 10.9 wt% with 130.2 g of total insoluble solids, was analyzed; the resulting chemical composition data are listed in Table 2.1. This composition [4] was the basis for the development of suitable glass composition for this waste for subsequent testing [5].

The AZ-101 simulant composition used for recent melter tests [6, 7] was also based on the actual waste analysis provided in Table 2.1. Uranium and most constituents at less than about half a weight percent oxide were omitted. Exceptions were chromium and sulfur, which were added to the waste simulant. Non-radioactive cesium was also added at the designated level of half a weight percent. The recipe for the resulting AZ-101 simulant is provided in Table 2.2. For the purpose of the present work, the concentrations of the volatile components (i.e., carbonate, nitrite, nitrate, and organic carbon) are assumed to be similar to those found for the AZ-102 HLW waste [8]. With the waste compositions defined, formulation of the HLW waste simulant proceeds in a straightforward fashion. In general, oxides and hydroxides are used as the starting materials, with slurry of iron (III) hydroxide (13% by weight) as the major constituent. Volatile inorganic components are added as the sodium salts, whereas organic carbon is added as oxalic acid.

2.2   Glass and Feed Formulation

Several glasses were developed and evaluated as candidates for the AZ-101 waste stream based on the actual waste sample analysis [5]. The glass deemed most suitable for the waste (HLW98-95) is compared to the nominal glass composition used for the previous [7] and current tests in Table 2.3. The additive type and oxide percentage, 68.25%, are the same in the two glasses. The small differences in the glass product composition are the result of removal of uranium and several constituents at low concentrations, the exclusion of cesium and technetium pretreatment products, and renormalization of the waste oxide composition. The only difference between the glass previously processed and the glass processed in the current tests is the exclusion of RuO_2 from the waste composition in the present tests. A summary of the properties of the HLW98-95 glass is provided in Table 2.4. The measured glass properties indicate that the glass meets all WTP processability, product quality, and contract requirements.

NOAH Technologies Corporation produced the waste simulant blended with glass forming additives under sub-contract to VSL according to the formulation provided in Table 2.5 for the tests with the nominal feed composition. NOAH was the supplier of simulant and feed samples used in previous testing for the WTP performed at VSL on the DM100 and DM1200 melter systems [8-19]. The waste simulant was received in 55-gallon drums and was thoroughly homogenized prior to use. The chemical additives that were used to produce the melter feeds were selected based on previous testing and the RPP-WTP Project baseline glass forming chemicals. Concentrated perrhenic acid was added to the baseline feed to achieve a rhenium concentration in the target glass of 0.05 wt% ReO_2 if all of it were to be retained in the glass product.

2.3   PNNL Iron-Rhenium Precipitate

Two samples of the iron-rhenium precipitate material prepared at PNNL were shipped to VSL for melter testing. These samples consisted of approximately 28 kg of "heated" material and 25 kg of "unheated" material. The heating process was intended to convert the precipitate to the goethite form. The results from analysis of the received material are provided in Table 2.6. Both materials are composed of about 89% water and 11% solids. The dried material was analyzed by x-ray fluorescence spectroscopy (XRF) and x-ray diffraction (XRD) to determine chemical composition and iron mineral type. As expected from the PNNL analysis and description, the material was mostly iron oxide (97.5%), with about half a weight percent rhenium oxide and about two percent contaminants in the form of aluminum, calcium, and chlorine. Additional analysis of the dried material involving microwave aided acid dissolution followed by direct current plasma – atomic emission spectroscopy (DCP-AES) solution analysis was also conducted at VSL. The results of this analysis are in good agreement with the XRF analysis with slightly higher aluminum contents and trace amounts of magnesium, sodium, and silicon. The results from direct XRF analysis of the dried solids for rhenium are about a third higher than the PNNL inductively coupled plasma (ICP) analysis. Given the low rhenium concentrations and the fact that the XRF calibration is designed primarily for a glass matrix, the ICP analysis was considered more accurate and was therefore used to calculate target rhenium concentrations for the feeds constituted with goethite slurries. The dominant mineral phases present in slurries estimated by PNNL (magnetite and goethite) were confirmed by XRD analysis at VSL. However, the iron hydroxide assumed to be present in the unheated slurry could not be confirmed by the XRD method; furthermore, any amorphous phases that may be present would not be detected.

The heated and un-heated materials received from PNNL were used to produce two separate melter feed batches. In each case, the thirteen percent $Fe(OH)_3$ slurry shown in Table 2.2 was replaced on a molar basis with each of the iron-rhenium slurries received from PNNL. The average solids content of eleven percent and the XRF measured iron content of 97.5 wt% iron oxide was used to calculate the amounts of slurry required for each of the feed batches. The small amounts of aluminum, calcium, and chlorine will result in a change of less than 0.1 wt% in the product glass. The concentrations of rhenium in the target glass were 0.043 and 0.042 wt% ReO_2 if all of it were to be retained in the glass product for the heated and unheated material,

respectively. Previous melter testing with rhenium at similar target concentrations has demonstrated that these concentrations are suitable for reliable measurements of rhenium concentrations in both the melter exhaust and product glass [20]. The iron oxide slurries were combined with the remaining constituents in the waste simulant, shown in Table 2.2 as well as glass forming additives shown in Table 2.5, and were thoroughly blended before transfer to the melter feed tank. At this juncture, the feed produced with goethite slurries were too viscous to be pumped into the feed tank, as shown in Figures 2.1 and 2.2. Water was added to each of the feeds until they were pumpable, resulting in an absolute increase in water content of about three percent.

2.4　Analysis of Feed Samples

2.4.1　General Properties

Feed samples from each unique feed composition were analyzed to confirm physical properties and chemical composition. Samples were taken at the end of the first four melter tests upon removal of remaining feed from the melter feed tank. Sample names, sampling dates, and measured properties are given in Table 2.7. Samples from similar iron sources have very similar measured pH, density, and glass conversion ratio. As expected, higher water contents and lower glass conversion ratios were measured for feeds formulated with the goethite slurries due to the required additions of water to the feeds using goethite slurries as the iron source. The measured glass conversion ratios were within ten percent of the target; however, the nominal feed was on average three percent above the target value and the feeds with the goethite slurries were on average six percent below the target value. For the purposes of calculating production rates from feed rates, the average measured glass conversion ratios of 0.36 and 0.33 were used for nominal feed and for the feeds from the goethite slurries, respectively.

2.4.2　Rheology

Samples of the melter feeds that were used for these tests were also subjected to rheological characterization. The results from rheological characterization of a variety of other melter feeds and waste simulants, as well as the effects of a range of test variables, are described in detail in a separate report [3]. Rheograms for the melter feeds, which show the feed viscosity versus shear rate, are presented in Figure 2.3; measured values for viscosity at selected shear rates and the yield stress are shown in Table 2.7. The measured range of feed viscosity and yield stress was relatively small compared to feed samples from previous tests, which included feeds that were deliberately adjusted to be more viscous or diluted with water to simulate lower waste solids content [16]. Yield stress values were higher for feeds with the goethite slurries (24-28 Pa vs. 17 Pa) than for the nominal feeds. Viscosity differences were smaller and only apparent at the lowest shear rates. Clearly, the yield stress and viscosity of the material prior to the addition of water to the feed (see Figures 2.1 and 2.2) were considerably higher than those of the feeds processed during the tests. Increases in feed viscosity have previously been observed in HLW melter feeds formulated with boehmite in place of $Al(OH)_3$ (yield stress of 159 Pa vs. 1 Pa) [21] in a similar fashion to the increases in viscosity for feeds in current tests formulated with goethite

in place of $Fe(OH)_3$. The goethite and iron hydroxide slurries showed similar pH values as did the boehmite and aluminum hydroxide slurries. Addition of about 2 wt% of water to the goethite slurry resulted in a slurry with viscosity and yield stress values similar to those of the iron hydroxide slurry. Additional work is needed to determine if the cause of the difference in slurry properties with goethite and boehmite is something unique to the chemical form or some other factor such as the particle size. It should be noted that the material referred to as "goethite" was actually about 60-65% magnetite with the remaining being goethite or goethite and iron hydroxide.

2.4.3   Chemical Composition

The chemical compositions of the feed samples were determined by first making a glass from the feed via crucible melt. The glass was subsequently crushed and analyzed directly by XRF. The boron and lithium concentrations were determined by DCP analysis of solutions generated by microwave aided acid dissolution. Data are compared to the target composition in Table 2.8. The results generally corroborate the consistency of the feed composition and show good agreement with the target composition for the major components. Of the oxides with a target concentration of one percent or greater, only the XRF values for iron oxide in the feed produced by NOAH and lithium oxide for feed formulated with goethite slurries had deviations of greater than 10% from target. No oxides with target concentrations of one percent or greater had deviations greater than fifteen percent from target. The absolute deviations for iron and lithium were less than 1.6 and 0.6 wt%, respectively. Rhenium was added to the NOAH feed in the form of perrhenic acid and therefore the surplus iron has no effect on the rhenium concentration. Boron and lithium concentrations measured by DCP were within nine and four percent of the target for feed produced from NOAH, respectively, and within three and fifteen percent of the target for feed constituted from goethite slurry, respectively, validating the use of the target values for normalizing the XRF data. Several oxides targeted at low concentrations in the glass including Ca, Cd, Cr, Mn, P, and S were observed in the feed at concentrations higher than the target, particularly in the feed obtained from NOAH. Similarly, potassium, magnesium, and titanium were measured at low concentrations in feed made by NOAH. The volatile trace element sulfur was measured at concentrations higher than target concentrations suggesting that sulfur is present as a contaminant in the glass forming additives or chemicals used to make the simulant. Given the low target concentrations, these surpluses are not expected to have any significant effect on glass properties or rhenium retention. Rhenium was also measured at low concentrations (0.004 wt%) in feed in which it was not intentionally included, consistent with the analysis of the glass product (see Section 4.1); therefore corrections were made to the measured rhenium concentration of glasses for determination of rhenium retention in the glass and total rhenium balance. In feed samples with rhenium added as perrhenic acid or originating with the goethite slurry, much of the rhenium is volatilized during crucible melting, as expected.

SECTION 3.0
MELTER OPERATIONS

Melter tests were conducted with HLW AZ-101 waste simulants containing various sources of iron and rhenium on the DM10 between 2/28/10 and 3/4/10. These tests produced over 100 kg of glass from almost 300 kg of feed. The tests, ranging from 10 to 24 hours in duration, were divided as follows:

- Pre-Test: Processed nominal AZ-101 feed ($Fe(OH)_3$ as iron source) with no added rhenium for 9 hours.

- Test 1: Processed nominal AZ-101 feed ($Fe(OH)_3$ as iron source) with no added rhenium for 24 hours to define rhenium background.

- Test 2: Processed nominal AZ-101 feed ($Fe(OH)_3$ as iron source) with rhenium added as perrhenic acid targeting 0.05 wt% ReO_2 in the glass product. Duration of 23.25 hours.

- Test 3: Processed AZ-101 feed with heated goethite obtained from PNNL as the iron source. Based on analysis of the material, the rhenium content was targeted at 0.043 wt% ReO_2 in the glass product. Duration was 19.5 hours, determined by the amount of heated goethite material received.

- Test 4: Processed AZ-101 feed with unheated goethite obtained from PNNL as the iron source. Based on analysis of the material, the rhenium content was targeted at 0.042 wt% ReO_2 in the glass product. Duration was 16.25 hours, determined by the amount of unheated goethite material received.

- Test 5: Processed nominal AZ-101 feed ($Fe(OH)_3$ as iron source) with rhenium added as perrhenic acid targeting 0.05 wt% ReO_2 in the glass product. Duration of 9.75 hours with bubbling increased to give maximum attainable product rate.

Attempts were made to replicate the melter configuration and operating conditions used for previous melter tests with HLW simulants [12-15, 21-24]. These conditions include a near complete cold cap, which is between 80-95% melt surface coverage for the DM10 since a 100% cold cap tends to lead to "bridging" in smaller melters. The bubbling rate was held constant at 1 lpm in all but the last test and the feed rate was adjusted to provide the desired complete cold cap (90-100% of melt surface covered with feed). In Test 5, the bubbling rate was adjusted to obtain the highest attainable production rate. Power was supplied to the electrodes to maintain a glass temperature of 1150°C throughout the tests. All tests targeted the same glass composition (HLW98-95 without U, minor constituents, and RuO_2) with the difference in feed composition being the iron and rhenium sources. This approach permitted the direct comparison of each iron source with respect to rhenium retention in the glass product at constant operating conditions. It also allowed the determination of ease of processing feed with the different sources of iron.

3.1   Melter Operations Data

Production rates, run conditions, and measured melter parameters for the five melter test segments are summarized in Table 3.1. Production rates, bubbling rates, glass temperatures, plenum temperatures, electrode power, and glass resistance are depicted over the course of the tests in Figures 3.1 – 3.4. The average production rates ranged between 850 and 1700 kg/m^2/day and increased with the use of the goethite slurry as an iron source and melt pool bubbling. At a constant bubbling rate of 1 lpm, glass production rates increased by 59% from an average of about 950 to 1500 kg/m^2/day with the use of the goethite slurry as an iron source. The significant increase in production rate was unexpected and potentially complicates comparisons of rhenium retention between the various feeds; Test 5 was therefore added to provide an additional basis for comparison. The increase in production rate occurred despite the goethite feed having a higher water content, which in previous melter tests has been demonstrated to decrease glass production rates [9, 13, 15, 21-23]. This increase is also about twice the increase observed in DM100 tests at constant bubbling while processing HLW feeds with Al(OH)$_3$ and boehmite (950 to 1200 kg/m^2/day). It is not clear whether the increase in the processing rate with goethite and boehmite as compared to the corresponding hydroxides is unique to the chemical form of the materials, or some other factor such as particle size. Additional work would be useful to investigate this point. As noted above, the material identified as "goethite" was actually about 60-65% magnetite with the remaining being goethite or goethite and iron hydroxide. In tests with high-Al glass formulations, feeds with aluminum oxide as the aluminum source showed the lowest processing rate, feeds with aluminum hydroxide showed higher rates, and feeds with boehmite showed the highest rates [21].

The increase in production rate with increase in melt pool bubbling rate in Test 5 was expected based on numerous melter tests documenting the effect of bubbling on processing rate [8-18, 22, 23]. The glass production rate in this test was closer to that observed in the tests with the goethite feeds, providing an additional basis for comparison.

Occasionally during the tests, dried feed bridged from the sides of the melter, thermowell, and electrodes, necessitating dislodging with a rod through the view port on top of the melter. Feed bridging is commonly observed in small melters and is not judged to be related to the feed formulations that were used in the melter tests; furthermore, this would not be expected to be an issue in larger melters where the walls are farther apart. Glass temperatures (2 and 4 inches from the melt pool floor) averaged within 8°C of the target glass temperatures throughout the tests. The glass temperature 4 inches from the melt floor varied more with the level of glass in the melter and changes in the cold cap than did the temperatures measured lower in the melt pool. The discharge temperature was maintained above 1000°C throughout the tests to prevent the freezing of glass in the chamber during discharge. Test average plenum temperature measurements were between 524 and 610°C in the thermowell and about 30 to 90°C cooler at the exposed thermocouple. This difference is opposite to that in most previous tests, indicating that the exposed thermocouple was partially shielded, or the thermowell was closer to a bubbling outlet. The gas temperature at the film cooler averaged between 266-292°C, as determined by the plenum temperature, the amount of added film cooler air, and the temperature of the added film cooler air. Power supplied to the melter increased from near 4 kW to almost 7 kW with

increasing feed rates. Glass pool resistance decreased by about 0.01 ohm when processing feed formulated with the goethite slurry. A vacuum of about 1 inch of water was maintained on the melter throughout the tests.

SECTION 4.0
GLASS PRODUCTS

Over one hundred kilograms of glass was produced in these tests. The glass was discharged from the melter periodically using an airlift system and collected in custom fabricated square carbon steel cans. The discharged product glass was sampled at the end of each test by removing sufficient glass from the top of the cans for total inorganic analysis. Product glass masses, discharge date, and measured rhenium content are given in Table 4.1. The glass pool samples were obtained by dipping a rod into the glass melt at the end of each test

4.1 Discharge Glasses

Discharge glass samples were crushed and analyzed directly by XRF. The target values for boron and lithium oxides, which are not determined by XRF, were used for normalizing the XRF data to 100 wt%. The XRF analyzed compositions of all discharged glass samples are provided in Table 4.2. The majority of the XRF analysis results compared very favorably to their corresponding target values and also corroborated much of the feed sample analyses (see Section 2.4.3). Of the oxides with a target concentration of one percent or greater, only the XRF values for aluminum, zinc, and zirconium oxides had deviations of greater than 10% from target in glass from Test 1, zinc from Test 2, and zirconium from Test 4. Deviations observed in glass from Test 1 occurred due to a lack of complete melter turnover during the test. Zinc and zirconium deviations in other tests were less than half an absolute weight percent and therefore are not expected to have any significant effect on glass properties. Minor constituent such as calcium, cadmium, chromium, manganese and phosphorous were over-represented in the glass product at about the same frequency and magnitude as in the feed samples (see Section 2.4.3). Potassium, magnesium, and titanium were measured at low concentrations in glasses, particularly in glass produced from feed made by NOAH. The volatile trace element sulfur was measured at concentrations higher than target concentrations while processing feed supplied from NOAH suggesting that sulfur is present as a contaminant in the glass forming additives or chemicals used to make the simulant.

The discharge glass compositions over the course of testing are illustrated in Figures 4.1-4.6. Most oxides approximate their respective target values and varied little during testing after three melt pool turnovers had been completed for each composition. At the beginning of testing, oxides of Na, Al, Fe, Zn, Zr, Cd, Cs, Ce and P increase in concentration at the expense of Si, Cr, B, and Li as the glass pool transitions to the target HLW AZ-101 composition. Many of the oxides such as those of silicon and sodium reach steady state concentrations during testing and vary little over the remainder of the tests. Examples of small differences between glass generated from feeds produced by VSL (Tests 3 and 4) and NOAH (Tests 1, 2, and 5) are higher concentrations of iron and cadmium while processing feed from NOAH and higher concentrations of cerium and cesium while processing feed made at VSL with goethite slurries.

Rhenium was measured at low concentrations (0.002 to 0.005 wt% ReO_2) prior to the intentional introduction in the feed due to trace level feed contamination or residual rhenium from previous melter tests. Upon addition to the feed in Test 2, the concentration in the glass increased to 0.014 wt% ReO_2 through the majority of Test 3 while processing the heated goethite slurry. The concentration of ReO_2 increases again to 0.017 wt% during Test 4 while processing feed with unheated goethite slurry and then again to 0.018 wt% during Test 5 while processing nominal feed containing rhenium added as perrhenic acid. As expected, rhenium concentrations were well below target concentrations as a result of volatilization from the cold cap and glass pool.

4.2   Glass Pool Samples

Glass pool dip samples were obtained at the end of each test to verify the composition of the glass pool, detect any secondary phases on the glass pool surface, and to determine the melt level to quantify the amount of glass in the melt pool. A list of all dip samples including sample names, sampling dates, measured rhenium content, measured iron oxidation state, glass pool depth, and secondary phase observations are given in Table 4.3. There was no visual evidence of secondary phases in any of the dip samples. The analysis of the glass pool samples corroborates the composition of the discharge glasses as shown in Table 4.4. The measured rhenium concentrations in the glass pool samples were the same as, or an absolute 0.001 wt% oxide higher than the discharge glass. No reduced iron was measured in glass from the end of tests processing nominal feed, as expected since all iron in that feed was trivalent. About two percent of the total iron in glass samples from the tests processing feed containing the goethite slurry was determined to be divalent. Approximately two thirds of the iron in the goethite slurry is in the form of magnetite (see Table 2.6), resulting in twenty two percent of the iron in the feed being divalent; therefore, twenty percent of the feed iron was oxidized during the vitrification process.

SECTION 5.0
MONITORED OFF-GAS EMISSIONS

The melter exhaust was sampled for metals/particles according to 40-CFR-60 Methods 3, 5, and 29 at steady-state operating conditions during each test segment. The concentrations of off-gas species that are present as particulates and gaseous species that are collected in impinger solutions were derived from laboratory data on solutions extracted from air samples (filters and various solutions) together with measurements of the volume of air sampled. Particulate collection required isokinetic sampling, which entails removing gas from the exhaust at the same velocity that the air is flowing in the duct (40-CFR-60, Methods 1-5). Typically, a sample size of 30 dscf was taken at a rate of between 0.5 and 0.75 dscfm. Total particulate loading was determined by combining gravimetric analysis of the standard particle filter and chemical analysis of probe rinse solutions. An additional impinger containing 2 N NaOH was added to the sampling train to ensure complete scrubbing of all acid gases. The collected materials were analyzed using DCP-AES for the majority of the constituents and ion chromatography (IC) for anions. Cesium was measured in solutions using atomic absorption. Melter emission fluxes are compared to feed fluxes in Tables 5.1 – 5.6. Notice the distinction that is made between constituents sampled as particles and as "gas". The "gaseous" constituents are operationally defined as those species that are scrubbed in the impinger solutions after the air stream has passed through a 0.3 µm heated filter. All thirteen samples are within the 90 – 110% limits for isokinetic sampling.

Particulate emissions from the melter constituted 0.43 to 0.75 percent of feed solids during tests with nominal feed and 0.19 to 0.35 of feed solids during tests with feed containing the goethite slurry. The level of carry-over for tests processing nominal feed is mostly within the range measured previously for iron rich, HLW simulants processed on the DM100 [10, 19] (0.57 - 1.47 percent) and on the DM10 [24] (0.39 - 1.29 percent). Conversely, overall solids carryover while processing feed constituted with the goethite slurry was below that measured in previous tests as well as the tests in this study with nominal feed. Much of the difference between nominal and feed with goethite slurry is attributable to iron carryover; 0.67 percent of iron is carried over in tests with the nominal feed as opposed to an average of only 0.05 percent in tests with the goethite slurry. The carryover of solids and most elements was highest during the test with elevated bubbling, as expected. The feed element emitted at the highest rate was clearly rhenium. Calculated sulfur carryover from the melter was also high; however, the measured values were affected by low target feed concentrations and probable low level sulfur contamination in the feeds, particularly the nominal feed (see Section 2.4.3). Other elements exhibiting volatile behavior include chromium, alkali metals, cadmium, and boron. It should be noted that while indicative, melter sampling results from the DM10 have the potential to be biased somewhat by frequent bridging of feed across the melt pool surface and the need to mechanically dislodge the deposits and therefore DM10 results should be verified in future testing on larger melters, as is typically done. Boron and sulfur were the only elements detected in the impinger solutions

collected downstream of the heated particle filter in the sampling train, which constitutes the "gas" fraction of the melter emissions.

SECTION 6.0
MASS BALANCE FOR RHENIUM IN GLASS AND EMISSIONS

The principal goal of this work was to determine a mass balance for rhenium while processing feed containing goethite slurries used to remove rhenium from solution for comparison with that for the baseline feed. During tests processing feeds with the different iron and rhenium sources, sufficient glass and melter exhaust samples were taken and analyzed to complete a rhenium mass balance for each feed and operating condition. A complete rhenium mass balance for the tests is given in Table 6.1. Two to three times more rhenium was detected in the melter exhaust as compared to the glass for each of the feed compositions and operating conditions tested. The total rhenium recoveries ranged from 79 to 132 percent depending on the method used for determining the amount of rhenium in the feed and for assessing the background amount of rhenium in the feed and melter system.

Total mass balance closure is not only dependent on the amounts measured in the glass product and melter exhaust but also the amount of rhenium in the feed and the amount of rhenium contamination in the melter system or in the feed streams. Initial rhenium mass balance calculations (see Table 3.1) were based on the PNNL analysis (see Table 2.6) in the tests with the goethite slurry and the background rhenium concentration measured in glass discharged from the DM10 while feeding the target glass composition with no added rhenium. Subsequent analysis of melter feed samples suggests that the rhenium observed in the glasses discharged during the initial test originated as contamination in the feed provided by NOAH used in Tests 1, 2, and 5 rather than as residual rhenium remaining in the melter. Also, VSL analysis of the goethite slurry indicated that the rhenium concentrations were 25 and 36 percent higher than indicated by the PNNL analysis. The effect of the assumptions used for the feed rhenium concentration and the background corrections are evaluated in Table 6.l. Also evaluated is the exclusion of an outlier rhenium emission result for Test 3. Three samples were taken showing rhenium emission rates as 7.73 mg/min, 7.00 mg/min, and 4.47 mg/min (see Table 5.3); average percent feed emitted was calculated with and without the low outlier. The total rhenium recoveries for samples using the PNNL analysis of the goethite slurries are all above 100%, and 119% or greater when omitting the low emission outlier from Test 3. Correcting the glass concentrations by subtracting the rhenium measured during Test 1 reduces the percentage retention in the glass by an absolute 6 to 8 percent. Exclusion of the low emission outlier from Test 3 results in an absolute increase in the amount of rhenium measured in the emissions and total recovery of 14 percent.

The effects of using either of the two feed sample analyses taken together with the calculated total recoveries suggest that the best approach for tests processing feed including the goethite slurries is the use of the VSL rhenium analysis without background correction of the discharged glass. The background correction should be applied to the tests with the NOAH feed since the feed samples indicate that the origin of the rhenium background appears to be trace level contamination of the NOAH feed.

Overall, the amount of rhenium retained in the glass for the tests varied within a relatively narrow range, indicating that the iron and rhenium sources do not have a large effect on rhenium retention in the glass product. Direct comparisons are complicated by the fact that the feeds made using goethite processed at a significantly higher rate than the baseline feed under the same conditions. Nevertheless, the rhenium retention values are generally bounded by those for the baseline feeds at (i) lower production rate and the same bubbling rate (Test 1) and (ii) approximately the same production rate but higher bubbling rate (Test 5). There appears to be no significant difference between the heated and unheated goethite slurries with respect to rhenium retention in the glass product.

SECTION 7.0
SUMMARY AND CONCLUSIONS

A series of melter tests were conducted on the DM10 using an AZ-101 HLW composition to evaluate the effect of the iron and rhenium source on rhenium retention in the glass product. The tests employed melter feeds with four different iron and rhenium sources: the baseline iron hydroxide slurry without rhenium, the baseline iron hydroxide slurry with rhenium added as perrhenic acid, PNNL magnetite/goethite slurry with adsorbed rhenium, and PNNL heated magnetite/goethite slurry with adsorbed rhenium. In four of the five tests, the bubbling rate was set at 1 lpm and the feed rate adjusted to provide the desired complete cold cap (90-100% of melt surface covered with feed) and target plenum temperature of $550 - 650^{o}C$ for each of the four feed types. One test using the baseline iron hydroxide slurry with rhenium added as perrhenic acid was conducted at a higher bubbling rate targeting the highest achievable production rate. Measurements of glass production rates, melter operating conditions (temperatures, pressures, power, flows, etc.) were made throughout the tests. Qualitative observations of the cold cap and feed characteristics such as pumpability and spreading across the melt surface as well as ease of discharging glass were made throughout the tests. In addition, particulate loading and composition as well as acid gas concentrations were determined for the purposes of calculating a material mass balance around the melter during each test. Glass samples taken throughout the tests from the melt pool and the air-lift discharge were visually examined for secondary phases and analyzed for chemical composition. Particular emphasis was placed on rhenium distribution between the glass and the off-gas.

The melter tests resulted in the production of over 100 kg of glass from feeds with iron hydroxide and goethite slurries. Notable observations made during the processing of the different feeds were as follows:

- Feed with goethite slurries as the iron source form a significantly more viscous melter feed. Dilution of the feed with additional water was required to produce a melter feed from the goethite slurries that can be processed. However, surprisingly little added water was required.

- Feed made with goethite slurries as the iron source processed about 60% faster than feed using iron hydroxide as an iron source when processed at a constant bubbling rate.

- The retention of rhenium in the glass product was essentially the same for feeds with iron hydroxide and perrhenic acid, heated goethite slurries with rhenium, and unheated goethite slurries with rhenium.

- The majority of the divalent iron present as magnetite in the goethite slurry was oxidized during the vitrification process.

- Solids carryover from the melter for feed with goethite slurries as the iron source was about half that measured for feed with iron hydroxide as the iron source.

SECTION 8.0
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Table 2.1. Analyzed Compositions of AZ-101 Envelope D Waste.

Analyte	AZ-101 Solid (µg/g dry solid)	Oxide[#]	Analyzed AZ-101 Solid (wt%)
Ag	902	Ag_2O	0.12%
Al	99873	Al_2O_3	23.71%
As	—	As_2O_3	—
B	91	B_2O_3	0.04%
Ba	1510	BaO	0.21%
Be	26	BeO	0.01%
Bi	150	Bi_2O_3	0.02%
Ca	7505	CaO	1.32%
Cd	14500	CdO	2.08%
Ce	5240	Ce_2O_3	0.77%
Cl	703	Cl	0.09%
Co	128	CoO	0.02%
Cr	2285	Cr_2O_3	0.42%
Cs	—	Cs_2O	—
Cu	584	CuO	0.09%
F	390	F	0.05%
Fe	202384	Fe_2O_3	36.35%
K	2000	K_2O	0.30%
La	5808	La_2O_3	0.86%
Li	115	Li_2O	0.03%
Mg	1540	MgO	0.32%
Mn	5364	MnO_2	1.07%
Mo	67	MoO_3	0.01%
Na	54545	Na_2O	9.24%
Nd	4290	Nd_2O_3	0.63%
Ni	9992	NiO	1.60%
P	4505	P_2O_5	1.30%
Pb	1728	PbO	0.23%
Pd	2300	PdO	0.33%
Rh	513	Rh_2O_3	0.08%
Ru	1600	Ru_2O_3	0.25%
SO_4	2410	SO_3	0.25%
Sb	—	Sb_2O_5	—
Se	—	SeO_2	—
Si	13055	SiO_2	3.51%
Sn	3600	SnO_2	0.37%
Sr	3412	SrO	0.51%
Te	—	TeO_2	—
Ti	178	TiO_2	0.04%
U	18500	UO_2	2.64%
Y	385	Y_2O_3	0.06%
Zn	278	ZnO	0.04%
Zr	65050	ZrO_2	11.05%
TOTAL	537186	TOTAL	100.0%

- Empty data field. [#] Oxide forms listed are those provided by the WTP Project

Table 2.2. Compositions of the AZ-101 Waste (Oxide Basis) and the HLW Waste Simulant to Produce 100 kg of Waste Oxides (21.5 wt% total solids).

AZ-101 HLW Waste Composition		AZ-101 HLW Waste Simulant	
Waste Oxide	Wt%	Starting Material	Target Weight (kg)[*]
Al_2O_3	24.62%	$Al(OH)_3$	37.995
CaO	1.40%	CaO	1.429
CdO	2.16%	CdO	2.184
Ce_2O_3	0.80%	CeO_2	0.847
Cr_2O_3	0.46%	Cr_2O_3	0.469
Cs_2O	0.50%	CsOH (50% solution)	1.064
Fe_2O_3	37.73%	$Fe(OH)_3$ (13% slurry)	372.255
La_2O_3	0.89%	La_2O_3	0.899
MnO	0.91%	MnO_2	1.127
Na_2O	10.60%	NaOH	10.402
Nd_2O_3	0.65%	Nd_2O_3	0.657
NiO	1.66%	$Ni(OH)_2$	2.135
P_2O_5	1.34%	$FePO_4 \cdot xH_2O$	3.560
SO_3	0.38%	Na_2SO_4	0.682
SiO_2	3.78%	SiO_2	3.808
SnO_2	0.66%	SnO_2	0.667
ZrO_2	11.46%	$Zr(OH)_4 \cdot xH_2O$	29.565
Carbonate	1.20[#]	Na_2CO_3	2.130
Nitrite	0.50[#]	$NaNO_2$	0.769
Nitrate	2.00[#]	$NaNO_3$	2.459
Organic Carbon	0.05[#]	$H_2C_2O_4 \cdot 2H_2O$	0.264
		Water	155.610
Oxide Total	100.00%	TOTAL	630.977

[*] Target weights adjusted for assay information of starting materials.
[#] Unit for volatile components is g/100 g of waste oxide.

Table 2.3. Composition of Nominal AZ-101 HLW Glass Formulation (wt%).

Oxide [#]	AZ-101 Waste			Glass Composition		
	Actual Blended Waste [4, 5]	Next Generation Melter Tests [7]	Goethite Melter Tests	Crucible Melt [5]	Next Generation Melter Tests [7]	Goethite Melter Tests
Ag_2O	0.12%	-	-	0.04%	-	-
Al_2O_3	23.06%	24.58%	24.62%	7.32%	7.80%	7.81%
B_2O_3	0.43%	-	-	10.64%	10.50%	10.50%
BaO	0.21%	-	-	0.07%	-	-
BeO	0.01%	-	-	0.00%	-	-
Bi_2O_3	0.02%	-	-	0.01%	-	-
CaO	1.34%	1.40%	1.40%	0.43%	0.44%	0.44%
CdO	2.02%	2.16%	2.16%	0.64%	0.69%	0.69%
Ce_2O_3	0.75%	0.80%	0.80%	0.24%	0.25%	0.25%
Cl	0.18%	-	-	0.06%	-	-
Cr_2O_3	0.45%	0.46%	0.46%	0.14%	0.15%	0.15%
Cs_2O	0.00%	0.50%	0.50%	0.00%	0.16%	0.16%
CuO	0.09%	-	-	0.03%	-	-
F	0.05%	-	-	0.02%	-	-
Fe_2O_3	35.31%	37.67%	37.73%	11.21%	11.96%	11.98%
K_2O	0.43%	-	-	0.14%	-	-
La_2O_3	0.83%	0.89%	0.89%	0.26%	0.28%	0.28%
Li_2O	0.03%	-	-	3.76%	3.75%	3.75%
MgO	0.31%	-	-	0.10%	-	-
MnO_2	1.04%	0.91%	0.91%	0.33%	0.29%	0.29%
MoO_3	0.01%	-	-	0.00%	-	-
Na_2O	10.80%	10.58%	10.60%	11.93%	11.86%	11.87%
Nd_2O_3	0.61%	0.65%	0.65%	0.19%	0.21%	0.21%
NiO	1.55%	1.66%	1.66%	0.49%	0.53%	0.53%
P_2O_5	1.26%	1.34%	1.34%	0.40%	0.43%	0.43%
PbO	0.23%	-	-	0.07%	-	-
PdO	0.32%	-	-	0.10%	-	-
Rh_2O_3	0.08%	-	-	0.02%	-	-
RuO_2	0.24%	0.15%	-	0.08%	0.05%	-
SO_3	0.37%	0.38%	0.38%	0.12%	0.12%	0.12%
SiO_2	3.80%	3.77%	3.78%	44.71%	44.70%	44.70%
SnO_2	-	0.66%	0.66%	-	0.21%	0.21%
SrO	0.49%	-	-	0.16%	-	-
TiO_2	0.04%	-	-	0.01%	-	-
UO_2	2.76%	-	-	0.88%	-	-
ZnO	0.04%	-	-	2.01%	2.00%	2.00%
ZrO_2	10.72%	11.44%	11.46%	3.40%	3.63%	3.64%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

- Empty data field. # Oxide forms listed are those employed by the WTP Project

Table 2.4. Summary of AZ-101 HLW Characterization Data for Crucible Glass.

Glass ID		HLW98-95
Oxides from AZ-101 Solids		30.69%
Oxides from Cs Pretreatment		0.81%
Oxides from Tc Pretreatment		0.25%
TOTAL Waste Loading		31.75%
Melt Temperature		1150 °C
Crucible Used		Pt/Au
Visual Observation of As-Melted Glass		Dark brown homogeneous translucent glass
SEM/EDS Observations after Heat Treatment at 950 °C for 70 hours (Premelt 1200 °C/1 hour)		Spinel crystals found concentrated at the bottom of the crucible. Rh and Ru incorporated into spinel crystals. 0.5 vol % of crystals
Meets Liquidus Temp. Requirement?		Yes
Viscosity (P) at	1000 °C	226
	1050 °C	144
	1100 °C	85.9
	1150 °C	54.1
	1200 °C	35.6
Conductivity (S/cm) at	1000 °C	0.203
	1050 °C	0.254
	1100 °C	0.308
	1150 °C	0.367
	1200 °C	0.428
7-Day PCT Normalized Concentration (g/l)	B	0.554 (DWPF-EA – 16.83)
	Li	0.585 (DWPF-EA – 9.51)
	Na	0.461 (DWPF-EA – 11.59)
	Si	0.317 (DWPF-EA – 3.53)
7-Day PCT Normalized Leach Rate (g/(m²-d))	B	0.0395 (DWPF-EA – 1.20)
	Li	0.0418 (DWPF-EA – 0.68)
	Na	0.0329 (DWPF-EA – 0.83)
	Si	0.0226 (DWPF-EA – 0.25)
pH after 7 days of PCT Leaching		10.34
TCLP Data and Associated UTS Limits (ppm)	Ag	<0.003 (UTS – 0.14)
	Ba	<0.4 (UTS – 21.00)
	Cd	0.10 (UTS – 0.11)
	Cr	0.01 (UTS – 0.60)
	Ni	0.07 (UTS – 11.00)
	Pb	<0.02 (UTS – 0.75)
Glass Transition Temperature (°C)		463
Density (g/ml)		2.713

Table 2.5. Compositions of the Nominal AZ-101 HLW Glass Formulation and the Glass Former Mix to Produce 100 g of AZ-101 HLW Glass.

Oxide [#]	AZ-101 Blended Waste (wt%)	Oxides from Glass Formers (as wt% in Glass)	Nomimal AZ-101 Glass Composition (wt%)	Glass Forming Additives	Typical Assay	Amount (g) to Produce 100 g of Glass
Al_2O_3	24.58%	-	7.81%	-	-	-
B_2O_3	-	10.50%	10.50%	$Na_2B_4O_7.10H_2O$	0.99	29.049
CaO	1.40%	-	0.44%	-	-	-
CdO	2.16%	-	0.69%	-	-	-
Ce_2O_3	0.80%	-	0.25%	-	-	-
Cr_2O_3	0.46%	-	0.15%	-	-	-
Cs_2O	0.50%	-	0.16%	-	-	-
Fe_2O_3	37.67%	-	11.98%	-	-	-
La_2O_3	0.89%	-	0.28%	-	-	-
Li_2O	-	3.75%	3.75%	Li_2CO_3	0.975	9.512
MnO_2	0.91%	-	0.29%	-	-	-
Na_2O	10.58%	8.50%	11.87%	Na_2CO_3	0.99	6.609
Nd_2O_3	0.65%	-	0.21%	-	-	-
NiO	1.66%	-	0.53%	-	-	-
P_2O_5	1.34%	-	0.43%	-	-	-
RuO_2	0.15%	-	0.05%	-	-	-
SO_3	0.38%	-	0.12%	-	-	-
SiO_2	3.77%	43.50%	44.70%	SiO_2	0.99	43.939
SnO_2	0.66%		0.21%			
ZnO	-	2.00%	2.00%	ZnO	0.99	2.020
ZrO_2	11.44%	-	3.64%	-	-	-
TOTAL	100.00%	68.25%	100.00%	-	TOTAL	91.130

[#] Oxide forms listed are those provided by the WTP Project
- Empty data field

Table 2.6. Characteristics of PNNL Iron-Rhenium Slurries for Melter Testing.

–			Heated Material	Unheated Material
Amount of slurry available for melter and small scale testing			28.0 kg	25.2 kg
PNNL	Measured solids content		13.0 wt%, 11.84 wt%	11.0 wt%
	Measured Density		1.09 g/ml	1.09 g/ml
	Measured Re content		3.044 mg/g	2.812 mg/g
	Approximate pH		8.5	8.5
	Estimated iron speciation		65-70% magnetite, 30-35% goethite	65-70% magnetite, 30-35% goethite and iron hydroxide
VSL	Measured solids content		10.83 wt%	11.14 wt%
	XRD measured mineral speciation*		59% magnetite, 41% goethite	66% magnetite, 34% goethite
	XRF Measured Composition[#]	Al_2O_3	0.83 wt%	0.84 wt%
		CaO	0.46 wt%	0.47 wt%
		Cl	0.26 wt%	0.22 wt%
		Cr_2O_3	0.03 wt%	0.03 wt%
		Fe_2O_3	97.5 wt%	97.6 wt%
		MnO	0.05 wt%	0.04 wt%
		ReO_2	0.46 wt%	0.45 wt%
	DCP Measured Composition[#]	Al_2O_3	0.95 wt%	0.95 wt%
		CaO	0.47 wt%	0.47 wt%
		Cl	NA	NA
		Cr_2O_3	0.03 wt%	0.03 wt%
		Fe_2O_3	97.4 wt%	97.5 wt%
		MnO	0.05 wt%	0.05 wt%
		ReO_2	0.45 wt%	0.50 wt%
		MgO	0.07 wt%	0.07 wt%
		Na_2O	0.41 wt%	0.35 wt%
		SiO_2	0.05 wt%	0.04 wt%

* Does not include amorphous iron phases; data obtained by Reitveld refinement of XRD patterns.
# Oxidation states not measured.
NA – Not Analyzed

Table 2.7. Characteristics of Melter Feed Samples from DM10 Goethite/Rhenium Tests.

Test	Iron Source	Date	Name	% Water	pH	Density (g/ml)	Glass Yield Measured (g/l)	Measured (kg/kg)	Target (kg/kg)	% Dev	Yield Stress (Pa)	Viscosity @1/s	@10/s	@100/s
1	Fe(OH)$_3$	3/1/2011	ENM-F-15A	57.88	11.32	1.37	492	0.359	0.350	2.69	17.6	67.3	12.54	1.77
2	Fe(OH)$_3$	3/2/2011	ENM-F-21A	58.15	11.20	1.36	491	0.361	0.350	3.14	17.1	68.7	15.23	2.16
3	Heated goethite	3/3/2011	ENM-F-36A	60.62	10.84	1.34	453	0.333	0.350	-4.80	24.3	82.6	13.96	1.72
4	Unheated goethite	3/4/2011	ENM-F-42A	61.42	10.90	1.32	430	0.325	0.350	-7.03	28.8	87.9	19.62	2.15

Table 2.8. XRF Analyzed Compositions for Vitrified Melter Feed Samples from DM10 Tests (wt%).

Test	1			2			3			4	
Sample	Target	ENM-F-15A	% Dev.	Target	ENM-F-21A	% Dev	Target	ENM-F-36A	% Dev	ENM-F-42A	% Dev
Al_2O_3	7.81	7.19	-7.87	7.81	7.15	-8.40	7.81	7.64	-2.13	7.08	-9.35
B_2O_3	10.50	9.68*	-7.80	10.49	9.58*	-8.71	10.49	10.66*	1.58	10.75*	2.44
CaO	0.44	1.38	NC	0.44	1.42	NC	0.44	0.55	NC	0.57	NC
CdO	0.69	0.92	NC	0.69	0.92	NC	0.69	0.63	NC	0.68	NC
Ce_2O_3	0.25	0.25	NC	0.25	0.26	NC	0.25	0.29	NC	0.30	NC
Cr_2O_3	0.15	0.25	NC	0.15	0.24	NC	0.15	0.18	NC	0.19	NC
Cs_2O	0.16	0.13	NC	0.16	0.12	NC	0.16	0.16	NC	0.19	NC
Fe_2O_3	11.98	13.45	12.26	11.97	13.57	13.33	11.97	11.74	-1.93	12.97	8.33
K_2O	§	0.54	NC	§	0.53	NC	§	<0.01	NC	<0.01	NC
La_2O_3	0.28	0.12	NC	0.28	0.13	NC	0.28	0.22	NC	0.22	NC
Li_2O	3.75	3.60*	-3.99	3.75	3.67*	-2.07	3.75	4.29*	14.46	4.21*	12.33
MgO	§	0.18	NC	0.00	0.17	NC	0.00	<0.01	NC	<0.01	NC
MnO	0.29	0.74	NC	0.29	0.81	NC	0.29	0.31	NC	0.32	NC
Na_2O	11.87	11.78	-0.79	11.86	11.80	-0.50	11.86	12.47	5.09	11.98	0.96
Nd_2O_3	0.21	0.22	NC	0.21	0.22	NC	0.21	0.18	NC	0.17	NC
NiO	0.53	0.61	NC	0.53	0.61	NC	0.53	0.54	NC	0.54	NC
P_2O_5	0.43	0.71	NC	0.43	0.73	NC	0.43	0.48	NC	0.45	NC
ReO_2	§	0.004	NC	0.05	0.032	NC	0.043	0.033	NC	0.035	NC
SiO_2	44.70	42.38	-5.18	44.67	42.04	-5.88	44.68	44.06	-1.38	43.53	-2.57
SnO_2	0.21	0.23	NC	0.21	0.22	NC	0.21	0.19	NC	0.21	NC
SO_3	0.12	0.27	NC	0.12	0.26	NC	0.12	0.09	NC	0.16	NC
TiO_2	§	0.04	NC	§	0.04	NC	§	<0.01	NC	<0.01	NC
ZnO	2.00	1.81	-9.29	2.00	1.86	-7.15	2.00	1.98	-1.10	2.05	2.77
ZrO_2	3.64	3.52	-3.39	3.64	3.61	-0.76	3.64	3.30	-9.34	3.38	-6.98
Sum	100.00	100.00	NC	100.00	100.00	NC	100.00	100.00	NC	100.00	NC

* DCP-AES analyzed results.

NC – Not calculated

Table 3.1. Summary of DM10 Melter Tests.

Test		1	2	3
	Feeding Interval	2/28/11 19:00 – 3/1/11 19:00	3/1/11 19:45 – 3/2/11 19:00	3/2/11 21:18 – 3/3/11 16:52
	Total	24 hr	23 hr 15 min	19 hr 34 min
	Interruptions	6 min	0 min	10 min
Feed	Origin	NOAH	NOAH + perrhenic acid	VSL+ heated goethite
	Glass Yield (kg/kg)	0.36	0.36	0.33
	Rhenium glass target	0	0.05	0.043
	Processed (kg)	62.57	47.80	81.715
	Processing rate (kg/hr)	2.61	2.06	4.15
Glass	Produced from feed (kg)	22.52	17.21	26.97
	Discharged (kg)	18.55	15.12	24.48
	Test Average Production Rate (kg/m^2/day)*	1073	846	1564
	Measured ReO$_2$ wt%	0.0035	0.014	0.015
	Background Corrected ReO$_2$ wt%	0.0035	0.0105	0.0115
	% Feed Rhenium	NA	21	27
Emissions	Average Rhenium Emission Rate (mg/min)	< 0.10	2.92	6.40
	% Feed Rhenium	NA	58	78
Total Rhenium Recovery (%)		NA	79	105
Test Average Glass Temperature (°C)	2" from floor	1150	1152	1152
	4" from floor	1143	1146	1142
Test Average Plenum Temperature (°C)	Thermowell	538	556	577
	Exposed	493	510	544
Test Average Melt Pool Bubbling (lpm)		1.0	1.0	1.0
Test Average Discharge Chamber Temperature (°C)		1031	1035	1040
Test Average Film Cooler Exhaust Outlet Temperature (°C)		266	270	288
Test Average Melter Pressure (inches water)		-0.90	-0.87	-0.86
Test Average Electrical Properties	Voltage (volts)	27.1	25.9	31.1
	Current (amps)	169	158	207
	Power (kW)	4.59	4.11	6.49
	Glass Pool Resistance (ohms)	0.161	0.164	0.151

* - Calculated from total feed processed

NA – Not Applicable

Table 3.1. Summary of DM10 Melter Tests (continued).

Test		4	5
	Feeding Interval	3/3/11 17:45 – 3/4/11 10:00	3/4/11 10:45 – 3/4/11 20:30
	Total	16 hr 15 min	9 hr 45 min
	Interruptions	0 min	0 min
Feed	Origin	VSL+ goethite	NOAH + perrhenic acid
	Glass Yield (kg/kg)	0.33	0.36
	Rhenium glass target	0.042	0.05
	Processed (kg)	63.915	40.46
	Processing rate (kg/hr)	3.93	4.20
Glass	Produced from feed (kg)	21.09	14.57
	Discharged (kg)	19.08	14.10
	Test Average Production Rate (kg/m^2/day)*	1483	1699
	Measured ReO$_2$ wt%	0.017	0.018
	Background Corrected ReO$_2$ wt%	0.0135	0.0145
	% Feed Rhenium	32	29
Emissions	Rhenium Emission Rate (mg/min)	7.12	7.66
	% Feed Rhenium	92	76
Total Rhenium Recovery (%)		124	105
Test Average Glass Temperature (°C)	2" from floor	1152	1152
	4" from floor	1144	1148
Test Average Plenum Temperature (°C)	Thermowell	610	524
	Exposed	524	479
Test Average Melt Pool Bubbling (lpm)		1.0	3.2
Test Average Discharge Chamber Temperature (°C)		1039	1035
Test Average Film Cooler Exhaust Outlet Temperature (°C)		292	282
Test Average Melter Pressure (inches water)		-0.92	-0.98
Test Average Electrical Properties	Voltage (volts)	31.3	30.0
	Current (amps)	215	186
	Power (kW)	6.80	5.65
	Glass Pool Resistance (ohms)	0.146	0.161

* - Calculated from total feed processed

Table 4.1. Listing of Glasses, Masses, Cumulative Masses, and Rhenium Concentrations from DM10 Tests.

Test	Iron/Rhenium Source	Date	Name	Mass (kg)	Cumulative Mass (kg)	ReO$_2$ (wt%)
Pre Test		2/28/11	DNM-G-147A	-	-	-
			DNM-G-147B	1.12	1.12	0.004
			DNM-G-149A	2.10	3.22	0.005
			DNM-G-149B	-	-	-
			DNM-G-151A	-	-	-
1	Baseline AZ-101 Feed, No Rhenium		DNM-G-151B	4.36	7.58	0.004
			DNM-G-151C	-	-	-
			DNM-G-151D	3.22	10.80	0.004
		3/01/11	ENM-G-9A	-	-	-
			ENM-G-9B	3.46	14.26	0.004
			ENM-G-9C	-	-	-
			ENM-G-9D	2.04	16.30	0.002
			ENM-G-10A	1.62	17.92	0.003
			ENM-G-10B	2.24	20.16	0.003
			ENM-G-10C	-	-	-
			ENM-G-13A	2.84	23.00	0.003
			ENM-G-13B	-	-	-
			ENM-G-13C	2.50	25.50	0.003
			ENM-G-13D	-	-	-
			ENM-G-13E	2.44	27.94	0.004
2	Baseline AZ-101 Feed, Perrhenic Acid	3/02/11	ENM-G-15A	1.88	29.82	0.007
			ENM-G-16A	2.00	31.82	0.010
			ENM-G-16B	1.82	33.64	0.014
			ENM-G-16C	2.10	35.74	0.013
			ENM-G-16D	1.86	37.60	0.013
			ENM-G-17A	1.82	39.42	0.014
			ENM-G-17B	1.66	41.08	0.014
			ENM-G-17C	1.98	43.06	0.014
3	Heated Goethite	3/03/11	ENM-G-21A	2.58	45.64	0.014
			ENM-G-26A	2.28	47.92	0.014
			ENM-G-26B	2.38	50.30	0.014
			ENM-G-29A	2.26	52.56	0.014
			ENM-G-29B	1.86	54.42	0.014
			ENM-G-29C	2.42	56.84	0.014
			ENM-G-29D	1.92	58.76	0.014
			ENM-G-29E	1.98	60.74	0.014
			ENM-G-31A	2.42	63.16	0.014
			ENM-G-31B	1.86	65.02	0.015
			ENM-G-36A	2.52	67.54	0.018
4	Unheated Goethite		ENM-G-36B	2.02	69.56	0.017
			ENM-G-37A	2.34	71.90	0.017
			ENM-G-37B	1.94	73.84	0.017

- Empty data field

Table 4.1. Listing of Glasses, Masses, Cumulative Masses, and Rhenium Concentrations from DM10 Tests (continued).

Test	Iron/Rhenium Source	Date	Name	Mass (kg)	Cumulative Mass (kg)	ReO$_2$ (wt%)
4	Unheated Goethite		ENM-G-37C	1.96	75.80	0.016
			ENM-G-41A	1.76	77.56	0.017
			ENM-G-41B	1.78	79.34	0.015
			ENM-G-41C	2.30	81.64	0.015
			ENM-G-41D	2.14	83.78	0.017
			ENM-G-42A	2.84	86.62	0.017
5	Baseline AZ-101 Feed, Perrhenic Acid	3/04/11	ENM-G-44A	2.74	89.36	0.017
			ENM-G-44B	2.02	91.38	0.019
			ENM-G-45A	2.08	93.46	0.018
			ENM-G-45B	1.92	95.38	0.019
			ENM-G-49A	1.98	97.36	0.018
			ENM-G-49B	1.92	99.28	0.017
			ENM-G-49C	1.44	100.72	0.018

Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%).

Test		PreTest		1							
Mass (kg)	Target	1.12	3.22	7.58	10.80	14.26	16.30	17.92	20.16	23.00	25.50
Sample		DNM-G-147B	DNM-G-149A	DNM-G-151B	DNM-G-151D	ENM-G-9B	ENM-G-9D	ENM-G-10A	ENM-G-10B	ENM-G-13A	ENM-G-13C
Al_2O_3	7.81	2.88	2.71	4.32	5.14	5.87	6.05	6.34	6.49	6.56	6.90
B_2O_3*	10.50	15.64**	14.67	13.19	12.45	11.88	11.63	11.46	11.26	11.08	10.95
CaO	0.44	0.84	0.84	1.07	1.13	1.26	1.26	1.30	1.30	1.36	1.36
CdO	0.69	0.16	0.15	0.51	0.59	0.73	0.56	0.70	0.72	0.80	0.79
Ce_2O_3	0.25	0.04	0.02	0.09	0.14	0.17	0.17	0.18	0.21	0.20	0.23
Cr_2O_3	0.15	0.43	0.43	0.40	0.35	0.32	0.29	0.28	0.28	0.28	0.26
Cs_2O	0.16	0.03	0.02	0.07	0.08	0.11	0.07	0.09	0.10	0.11	0.11
Fe_2O_3	11.98	3.53	2.90	7.23	8.62	10.65	10.49	11.21	11.49	12.07	12.19
K_2O	§	0.75	0.77	0.68	0.63	0.59	0.60	0.60	0.58	0.60	0.61
La_2O_3	0.28	0.02	0.01	0.06	0.08	0.10	0.11	0.10	0.11	0.12	0.12
Li_2O*	3.75	6.99**	6.38	5.45	4.98	4.62	4.46	4.35	4.23	4.11	4.03
MgO	§	0.28	0.30	0.25	0.25	0.18	0.20	0.22	0.23	0.24	0.20
MnO	0.29	0.16	0.12	0.42	0.52	0.66	0.65	0.70	0.71	0.75	0.75
Na_2O	11.87	5.38	5.01	7.19	8.36	9.06	9.59	9.34	10.23	10.07	10.57
Nd_2O_3	0.21	0.04	0.03	0.10	0.12	0.16	0.17	0.17	0.18	0.20	0.19
NiO	0.53	0.40	0.37	0.52	0.53	0.57	0.53	0.55	0.56	0.56	0.55
P_2O_5	0.43	0.17	0.15	0.36	0.46	0.58	0.59	0.61	0.62	0.63	0.64
ReO_2	§	0.004	0.005	0.004	0.004	0.004	0.002	0.003	0.003	0.003	0.003
SiO_2	44.70	59.87	62.89	54.22	51.34	47.46	48.01	46.81	45.54	44.78	44.15
SnO_2	0.21	0.04	0.04	0.12	0.15	0.17	0.14	0.18	0.17	0.20	0.19
SO_3	0.12	0.11	0.10	0.16	0.16	0.18	0.17	0.18	0.19	0.20	0.16
TiO_2	§	0.19	0.21	0.15	0.12	0.09	0.08	0.08	0.07	0.07	0.06
ZnO	2.00	0.89	0.83	1.26	1.35	1.57	1.48	1.57	1.60	1.70	1.68
ZrO_2	3.64	1.14	1.05	2.17	2.44	2.99	2.69	2.98	3.10	3.31	3.29
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the first discharged glass during Test 1.
§ - Not a target constituent
NC – Not calculated
** DCP-AES analyzed results.

Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%), (Continued).

Test	1			2							
Mass (kg)	Target	27.94		Target	29.82	31.82	33.64	35.74	37.60	39.42	41.08
Sample		ENM-G-13E	% Dev		ENM-G-15A	ENM-G-16A	ENM-G-16B	ENM-G-16C	ENM-G-16D	ENM-G-17A	ENM-G-17B
Al_2O_3	7.81	6.93	-11.30	7.81	6.95	6.96	6.97	7.12	7.21	7.10	7.26
B_2O_3*	10.50	10.85	3.35	10.49	10.79	10.73	10.69	10.66	10.63	10.61	10.59
CaO	0.44	1.36	NC	0.44	1.36	1.38	1.42	1.38	1.38	1.41	1.38
CdO	0.69	0.79	NC	0.69	0.86	0.81	0.83	0.76	0.83	0.85	0.78
Ce_2O_3	0.25	0.21	NC	0.25	0.23	0.24	0.24	0.24	0.23	0.24	0.24
Cr_2O_3	0.15	0.24	NC	0.15	0.24	0.24	0.24	0.23	0.21	0.21	0.21
Cs_2O	0.16	0.11	NC	0.16	0.11	0.10	0.11	0.09	0.11	0.11	0.09
Fe_2O_3	11.98	12.23	2.11	11.97	12.44	12.83	13.21	12.74	12.48	12.82	12.64
K_2O	§	0.56	NC	§	0.52	0.55	0.55	0.55	0.56	0.56	0.54
La_2O_3	0.28	0.12	NC	0.28	0.11	0.14	0.14	0.13	0.14	0.14	0.15
Li_2O*	3.75	3.97	5.91	3.75	3.93	3.90	3.87	3.85	3.83	3.82	3.81
MgO	§	0.19	NC	§	0.23	0.19	0.20	0.17	0.19	0.18	0.18
MnO	0.29	0.75	NC	0.29	0.77	0.80	0.83	0.81	0.79	0.82	0.80
Na_2O	11.87	11.06	-6.84	11.86	10.97	10.94	10.60	11.30	11.51	11.37	11.30
Nd_2O_3	0.21	0.20	NC	0.21	0.21	0.21	0.22	0.22	0.21	0.21	0.21
NiO	0.53	0.53	NC	0.53	0.55	0.57	0.57	0.55	0.53	0.53	0.53
P_2O_5	0.43	0.68	NC	0.43	0.69	0.69	0.70	0.70	0.70	0.71	0.73
ReO_2	§	0.004	NC	0.05	0.007	0.010	0.014	0.013	0.013	0.014	0.014
SiO_2	44.70	43.86	-1.87	44.67	43.57	43.09	42.85	43.07	43.01	42.66	43.15
SnO_2	0.21	0.19	NC	0.21	0.22	0.20	0.20	0.18	0.20	0.21	0.20
SO_3	0.12	0.16	NC	0.12	0.16	0.16	0.16	0.15	0.15	0.16	0.15
TiO_2	§	0.05	NC	§	0.05	0.05	0.05	0.05	0.05	0.05	0.05
ZnO	2.00	1.68	-15.89	2.00	1.68	1.75	1.82	1.73	1.69	1.73	1.69
ZrO_2	3.64	3.27	-10.03	3.64	3.36	3.45	3.51	3.30	3.34	3.47	3.32
Sum	100.00	100.00	NC	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the first discharged glass during Test 1.
§ - Not a target constituent
NC – Not calculated

**Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%),
(Continued).**

Test	2			3							
Mass (kg)	Target	43.06		Target	45.64	47.92	50.30	52.56	54.42	56.84	58.76
Sample		ENM-G-17C	% Dev.		ENM-G-21A	ENM-G-26A	ENM-G-26B	ENM-G-29A	ENM-G-29B	ENM-G-29C	ENM-G-29D
Al_2O_3	7.81	7.16	-8.33	7.81	7.39	7.31	7.43	7.52	7.54	7.71	7.78
B_2O_3*	10.49	10.57	0.74	10.49	10.55	10.54	10.53	10.52	10.52	10.51	10.51
CaO	0.44	1.39	NC	0.44	1.22	1.15	1.02	0.97	0.84	0.78	0.76
CdO	0.69	0.86	NC	0.69	0.79	0.83	0.80	0.71	0.69	0.65	0.67
Ce_2O_3	0.25	0.25	NC	0.25	0.24	0.27	0.27	0.25	0.27	0.28	0.27
Cr_2O_3	0.15	0.22	NC	0.15	0.21	0.22	0.22	0.20	0.21	0.20	0.20
Cs_2O	0.16	0.11	NC	0.16	0.12	0.13	0.16	0.14	0.15	0.15	0.16
Fe_2O_3	11.97	12.97	8.32	11.97	12.29	12.60	12.55	12.24	12.16	11.85	11.94
K_2O	§	0.55	NC	§	0.43	0.39	0.30	0.28	0.21	0.18	0.15
La_2O_3	0.28	0.14	NC	0.28	0.12	0.13	0.13	0.13	0.16	0.16	0.16
Li_2O*	3.75	3.80	1.31	3.75	3.79	3.78	3.77	3.77	3.76	3.76	3.76
MgO	§	0.14	NC	§	0.14	0.14	0.10	0.08	<0.01	0.06	<0.01
MnO	0.29	0.82	NC	0.29	0.71	0.69	0.60	0.55	0.50	0.45	0.43
Na_2O	11.86	11.11	-6.37	11.86	12.11	11.69	11.59	11.99	12.71	12.09	11.97
Nd_2O_3	0.21	0.22	NC	0.21	0.21	0.21	0.20	0.19	0.19	0.18	0.18
NiO	0.53	0.55	NC	0.53	0.48	0.56	0.55	0.50	0.55	0.52	0.53
P_2O_5	0.43	0.71	NC	0.43	0.68	0.64	0.61	0.57	0.54	0.54	0.52
ReO_2	0.05	0.014	NC	0.043	0.014	0.014	0.014	0.014	0.014	0.014	0.014
SiO_2	44.67	42.72	-4.37	44.68	43.11	43.09	43.45	43.81	43.46	44.54	44.47
SnO_2	0.21	0.21	NC	0.21	0.21	0.21	0.22	0.20	0.19	0.19	0.20
SO_3	0.12	0.16	NC	0.12	0.12	0.10	0.09	0.08	0.07	0.07	0.07
TiO_2	§	0.05	NC	§	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
ZnO	2.00	1.77	-11.38	2.00	1.71	1.81	1.87	1.88	1.91	1.85	1.90
ZrO_2	3.64	3.50	-3.72	3.64	3.30	3.46	3.52	3.38	3.36	3.25	3.34
Sum	100.00	100.00	NC	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the
first discharged glass during Test 1.
§ - Not a target constituent
NC – Not calculated

Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%), (Continued).

Test		3					4					
Mass (kg)	Target	60.74	63.16	65.02	67.54		Target	69.56	71.90	73.84	75.80	77.56	79.34
Sample		ENM-G-29E	ENM-G-31A	ENM-G-31B	ENM-G-36A	% Dev.		ENM-G-36B	ENM-G-37A	ENM-G-37B	ENM-G-37C	ENM-G-41A	ENM-G-41B
Al_2O_3	7.81	7.61	7.63	7.68	7.72	-1.06	7.81	7.67	7.67	7.69	7.47	7.46	7.48
B_2O_3*	10.49	10.51	10.50	10.50	10.50	0.06	10.49	10.50	10.50	10.50	10.50	10.50	10.50
CaO	0.44	0.73	0.70	0.65	0.65	NC	0.44	0.64	0.60	0.60	0.62	0.58	0.59
CdO	0.69	0.73	0.66	0.65	0.68	NC	0.69	0.68	0.60	0.60	0.66	0.61	0.66
Ce_2O_3	0.25	0.27	0.28	0.28	0.28	NC	0.25	0.30	0.27	0.28	0.28	0.28	0.27
Cr_2O_3	0.15	0.20	0.21	0.20	0.19	NC	0.15	0.20	0.19	0.19	0.20	0.19	0.19
Cs_2O	0.16	0.18	0.16	0.16	0.18	NC	0.16	0.17	0.15	0.15	0.18	0.17	0.18
Fe_2O_3	11.97	12.11	12.03	11.70	11.74	-1.96	11.97	12.03	11.69	12.05	12.33	12.14	12.15
K_2O	§	0.14	0.12	0.09	0.09	NC	§	0.08	0.07	0.07	0.05	0.06	0.05
La_2O_3	0.28	0.18	0.18	0.18	0.20	NC	0.28	0.20	0.20	0.20	0.21	0.20	0.20
Li_2O*	3.75	3.76	3.75	3.75	3.75	0.11	3.75	3.75	3.75	3.75	3.75	3.75	3.75
MgO	§	<0.01	<0.01	<0.01	<0.01	NC	§	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MnO	0.29	0.43	0.40	0.38	0.37	NC	0.29	0.36	0.34	0.34	0.34	0.33	0.33
Na_2O	11.86	12.26	12.63	13.16	13.00	9.59	11.86	12.68	13.46	12.29	12.31	12.97	12.81
Nd_2O_3	0.21	0.19	0.18	0.18	0.18	NC	0.21	0.17	0.17	0.17	0.18	0.18	0.18
NiO	0.53	0.55	0.55	0.52	0.53	NC	0.53	0.54	0.51	0.53	0.53	0.51	0.51
P_2O_5	0.43	0.51	0.51	0.49	0.48	NC	0.43	0.49	0.47	0.50	0.48	0.47	0.48
ReO_2	0.043	0.014	0.014	0.015	0.018	NC	0.042	0.017	0.017	0.017	0.016	0.017	0.015
SiO_2	44.68	43.93	43.85	43.99	43.89	-1.75	44.68	43.89	44.06	44.67	44.32	44.16	44.17
SnO_2	0.21	0.22	0.21	0.19	0.21	NC	0.21	0.21	0.18	0.18	0.21	0.19	0.20
SO_3	0.12	0.07	0.07	0.07	0.07	NC	0.12	0.07	0.07	0.06	0.07	0.07	0.06
TiO_2	§	<0.01	<0.01	<0.01	<0.01	NC	§	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ZnO	2.00	1.95	1.95	1.89	1.92	-3.79	2.00	1.96	1.87	1.93	1.95	1.94	1.93
ZrO_2	3.64	3.46	3.39	3.24	3.35	-8.04	3.64	3.40	3.15	3.22	3.34	3.22	3.28
Sum	100.00	100.00	100.00	100.00	100.00	NC	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the first discharged glass during Test 1.

§ - Not a target constituent

NC – Not calculated

Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%), (Continued).

Test		4					5				
Mass (kg)	Target	81.64	83.78	86.62		Target	89.36	91.38	93.46	95.38	97.36
Sample		ENM-G-41C	ENM-G-41D	ENM-G-42A	% Dev.		ENM-G-44A	ENM-G-44B	ENM-G-45A	ENM-G-45B	ENM-G-49A
Al_2O_3	7.81	7.41	7.42	7.37	-5.64	7.81	7.28	7.23	7.25	7.20	7.09
B_2O_3*	10.49	10.50	10.50	10.50	0.01	10.49	10.49	10.49	10.49	10.49	10.49
CaO	0.44	0.59	0.57	0.58	NC	0.44	0.65	0.82	0.89	0.98	1.09
CdO	0.69	0.65	0.64	0.58	NC	0.69	0.63	0.73	0.76	0.72	0.81
Ce_2O_3	0.25	0.28	0.29	0.30	NC	0.25	0.28	0.29	0.29	0.26	0.28
Cr_2O_3	0.15	0.19	0.18	0.19	NC	0.15	0.19	0.21	0.22	0.23	0.23
Cs_2O	0.16	0.18	0.18	0.15	NC	0.16	0.16	0.16	0.14	0.12	0.13
Fe_2O_3	11.97	12.33	12.06	12.53	4.62	11.97	12.52	12.99	13.07	12.82	13.31
K_2O	§	<0.01	<0.01	<0.01	NC	§	0.08	0.17	0.22	0.29	0.33
La_2O_3	0.28	0.20	0.20	0.22	NC	0.28	0.20	0.17	0.16	0.12	0.13
Li_2O*	3.75	3.75	3.75	3.75	0.02	3.75	3.75	3.75	3.75	3.75	3.75
MgO	§	<0.01	<0.01	<0.01	NC	§	<0.01	<0.01	0.07	0.09	0.13
MnO	0.29	0.33	0.32	0.33	NC	0.29	0.37	0.48	0.54	0.58	0.65
Na_2O	11.86	12.70	13.01	12.76	7.53	11.86	12.75	12.07	11.85	12.40	11.67
Nd_2O_3	0.21	0.17	0.18	0.18	NC	0.21	0.18	0.20	0.20	0.20	0.21
NiO	0.53	0.53	0.48	0.53	NC	0.53	0.53	0.56	0.57	0.55	0.57
P_2O_5	0.43	0.47	0.48	0.46	NC	0.43	0.49	0.53	0.56	0.59	0.61
ReO_2	0.042	0.015	0.017	0.017	NC	0.05	0.017	0.019	0.018	0.019	0.018
SiO_2	44.68	44.14	44.31	44.18	-1.10	44.67	43.83	43.27	43.06	42.95	42.52
SnO_2	0.21	0.20	0.20	0.18	NC	0.21	0.20	0.21	0.22	0.19	0.21
SO_3	0.12	0.07	0.06	0.07	NC	0.12	0.08	0.12	0.14	0.16	0.18
TiO_2	§	<0.01	<0.01	<0.01	NC	§	<0.01	<0.01	<0.01	<0.01	0.02
ZnO	2.00	1.96	1.90	1.97	-1.24	2.00	1.95	1.98	1.96	1.88	1.94
ZrO_2	3.64	3.32	3.25	3.17	-12.96	3.64	3.35	3.54	3.57	3.41	3.62
Sum	100.00	100.00	100.00	100.00	NC	100.00	100.00	100.00	100.00	100.00	100.00

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the first discharged glass during Test 1.
§ - Not a target constituent
NC – Not calculated.

Table 4.2. XRF Analyzed Compositions for Glass Discharged During DM10 Tests (wt%) (continued).

Test		5		
Mass (kg)	Target	99.28	100.72	
Sample		ENM-G-49B	ENM-G-49C	% Dev.
Al_2O_3	7.81	7.32	7.22	-7.45
B_2O_3*	10.49	10.49	10.49	0.00
CaO	0.44	1.06	1.14	NC
CdO	0.69	0.78	0.84	NC
Ce_2O_3	0.25	0.25	0.27	NC
Cr_2O_3	0.15	0.20	0.22	NC
Cs_2O	0.16	0.13	0.14	NC
Fe_2O_3	11.97	12.53	12.94	8.04
K_2O	§	0.34	0.38	NC
La_2O_3	0.28	0.13	0.12	NC
Li_2O*	3.75	3.75	3.75	0.00
MgO	§	0.09	0.15	NC
MnO	0.29	0.63	0.68	NC
Na_2O	11.86	11.93	11.85	-0.08
Nd_2O_3	0.21	0.20	0.21	NC
NiO	0.53	0.48	0.56	NC
P_2O_5	0.43	0.63	0.65	NC
ReO_2	0.05	0.017	0.018	NC
SiO_2	44.67	43.52	42.66	-4.50
SnO_2	0.21	0.20	0.22	NC
SO_3	0.12	0.16	0.18	NC
TiO_2	§	0.02	0.02	NC
ZnO	2.00	1.79	1.82	-8.77
ZrO_2	3.64	3.34	3.46	-4.98
Sum	100.00	100.00	100.00	NC

* Target values calculated based on simple well stirred tank model using the DCP-AES analyzed results for the first discharged glass during Test 1.
§ - Not a target constituent
NC – Not calculated

Table 4.3. List of Glass Pool Samples with Sampling Times, Measured Iron Oxidation State, Measured ReO$_2$ Concentrations and Observations of Secondary Phases.

Test	Date	Time	Sample I.D.	Fe^{2+}/ Fe$_{tot}$ (%)	ReO$_2$ (wt%)	Secondary Phases?	Depth of Glass Pool (inches)
Before 1	2/28/2011	9:05	DNM-D-147A	NA	0.003	No	8.00
End of 1	3/1/2011	19:35	ENM-D-15A	< 1.0	0.004	No	6.50
End of 2	3/2/2011	20:30	ENM-D-21A	< 1.0	0.014	No	6.75
End of 3	3/3/2011	17:20	ENM-D-36A	1.9	0.017	No	9.50
End of 4	3/4/2011	10:31	ENM-D-42A	2.3	0.018	No	8.00
End of 5	3/4/2011	21:00	ENM-D-49A	< 1.0	0.019	No	8.25

NA – Not analyzed

Table 4.4. Comparison of XRF Analyzed Compositions for Glass Pool and Discharge Glass Samples Taken from the End of DM10 Tests (wt%).

Test	1		2		3		4		5	
Type	Pool	Discharge	Pool	Discharge	Pool	Discharge	Pool	Discharge	Pool	Discharge
Name	ENM-D-15A	ENM-G-13E	ENM-D-21A	ENM-G-17C	ENM-D-36A	ENM-G-36A	ENM-D-42A	ENM-G-42A	ENM-G-49A	ENM-G-49C
Al_2O_3	6.89	6.93	7.05	7.16	7.73	7.72	7.32	7.37	7.09	7.22
B_2O_3*	10.85	10.85	10.57	10.57	10.50	10.50	10.50	10.50	10.49	10.49
CaO	1.37	1.36	1.43	1.39	0.67	0.65	0.57	0.58	1.09	1.14
CdO	0.83	0.79	0.85	0.86	0.69	0.68	0.62	0.58	0.81	0.84
Ce_2O_3	0.23	0.21	0.26	0.25	0.30	0.28	0.29	0.30	0.28	0.27
Cr_2O_3	0.25	0.24	0.23	0.22	0.21	0.19	0.20	0.19	0.23	0.22
Cs_2O	0.12	0.11	0.10	0.11	0.18	0.18	0.16	0.15	0.13	0.14
Fe_2O_3	12.80	12.23	13.49	12.97	12.02	11.74	12.72	12.53	13.31	12.94
K_2O	0.55	0.56	0.55	0.55	0.09	0.09	<0.01	<0.01	0.33	0.38
La_2O_3	0.12	0.12	0.14	0.14	0.18	0.20	0.22	0.22	0.13	0.12
Li_2O*	3.97	3.97	3.80	3.80	3.75	3.75	3.75	3.75	3.75	3.75
MgO	0.20	0.19	0.15	0.14	<0.01	<0.01	§	<0.01	0.13	0.15
MnO	0.78	0.75	0.85	0.82	0.38	0.37	0.33	0.33	0.65	0.68
Na_2O	10.82	11.06	10.85	11.11	12.17	13.00	12.26	12.76	11.67	11.85
Nd_2O_3	0.21	0.20	0.22	0.22	0.18	0.18	0.18	0.18	0.21	0.21
NiO	0.59	0.53	0.60	0.55	0.55	0.53	0.56	0.53	0.57	0.56
P_2O_5	0.67	0.68	0.71	0.71	0.51	0.48	0.47	0.46	0.61	0.65
ReO_2	0.004	0.004	0.014	0.014	0.017	0.018	0.018	0.017	0.019	0.018
SiO_2	43.17	43.86	42.34	42.72	44.17	43.89	44.15	44.18	42.52	42.66
SnO_2	0.21	0.19	0.20	0.21	0.21	0.21	0.19	0.18	0.21	0.22
SO_3	0.16	0.16	0.15	0.16	0.07	0.07	0.08	0.07	0.18	0.18
TiO_2	0.06	0.05	0.05	0.05	<0.01	<0.01	<0.01	<0.01	0.02	0.02
ZnO	1.76	1.68	1.83	1.77	1.98	1.92	2.03	1.97	1.94	1.82
ZrO_2	3.39	3.27	3.57	3.50	3.44	3.35	3.38	3.17	3.62	3.46
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

§ - Not a target constituent
* - Target values.

Table 5.1. Results from DM10 Test 1 Off-Gas Emission Samples.

		Feed[#] (mg/min)	3/1/11 11:52 – 12:52 5.46% Moisture, 101% Isokinetic		3/1/11 14:34 – 15:34 5.49% Moisture, 98.2% Isokinetic		3/1/11 16:39 – 17:39 6.15% Moisture, 99.7% Isokinetic	
			Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted
Particulate	Total[$]	18322	97.96	0.53	87.92	0.48	136.75	0.75
	Al	616	2.11	0.34	1.92	0.31	3.11	0.51
	B	486	6.04	1.24	5.60	1.15	8.36	1.72
	Ca	46.9	0.65	1.40	0.54	1.15	0.95	2.03
	Cd	92	1.53	1.66	1.60	1.73	2.35	2.55
	Cr	15.3	0.25	1.64	0.25	1.62	0.32	2.10
	Cs	22.5	< 0.10	< 0.44	< 0.10	< 0.44	0.17	0.74
	Fe	1248	7.15	0.57	6.77	0.54	10.70	0.86
	Li	260	1.15	0.44	1.14	0.44	1.62	0.63
	Mn	33.5	< 0.10	< 0.30	< 0.10	< 0.30	< 0.10	< 0.30
	Na	1312	8.89	0.68	8.46	0.64	12.67	0.97
	Nd	62.6	< 0.10	< 0.16	< 0.10	< 0.16	< 0.10	< 0.16
	Ni	62.1	0.32	0.52	0.25	0.41	0.44	0.71
	P	28.0	0.17	0.59	< 0.10	< 0.36	0.11	0.40
	Re	0	< 0.10	NC	< 0.10	NC	< 0.10	NC
	S*	7.2	1.93	27.0	1.76	24.6	2.67	37.3
	Sn	24.6	< 0.10	< 0.41	< 0.10	< 0.41	< 0.10	< 0.41
	Si	3114	13.14	0.42	11.34	0.36	18.90	0.61
	Zn	239	1.15	0.48	1.11	0.46	1.73	0.72
	Zr	402	0.88	0.22	0.70	0.18	1.28	0.32
Gas	B	486	2.21	0.46	2.20	0.45	2.61	0.54
	S	7.2	8.66	121	7.59	106	9.11	127

[$] - From gravimetric analysis of filters and particulate nitric acid rinses
[#] - Calculated from target composition and test average glass production rate
* - Calculated from analysis of filter particulate by water dissolution
NC – Not Calculated

Table 5.2. Results from DM10 Test 2 Off-Gas Emission Samples.

| | | Feed[#] (mg/min) | 3/2/11 11:11 – 12:11 4.56% Moisture, 101% Isokinetic | | 3/2/11 14:22 – 15:22 4.38% Moisture, 101% Isokinetic | | 3/2/11 16:10 – 17:10 4.50% Moisture, 98.2% Isokinetic | |
			Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted
Particulate	Total[$]	14369	91.48	0.64	62.18	0.43	108.03	0.75
	Al	485	2.10	0.43	1.30	0.27	2.52	0.52
	B	383	5.23	1.37	3.10	0.81	5.35	1.40
	Ca	36.9	0.57	1.54	0.32	0.86	0.69	1.88
	Cd	72.6	1.22	1.68	0.82	1.13	1.46	2.02
	Cr	12.1	0.14	1.20	0.12	1.01	0.16	1.30
	Cs	17.7	< 0.10	< 0.56	< 0.10	< 0.56	< 0.10	< 0.56
	Fe	984	7.17	0.73	4.23	0.43	8.47	0.86
	Li	205	1.01	0.49	0.62	0.30	1.20	0.58
	Mn	26.4	< 0.10	< 0.38	< 0.10	< 0.38	< 0.10	< 0.38
	Na	1034	8.28	0.80	5.37	0.52	9.40	0.91
	Nd	49.3	< 0.10	< 0.20	< 0.10	< 0.20	< 0.10	< 0.20
	Ni	48.9	0.32	0.66	0.19	0.39	0.38	0.77
	P	22.0	< 0.10	< 0.45	< 0.10	< 0.45	2.55	11.6
	Re	5.01	2.87	57.31	2.95	58.97	2.94	58.71
	S*	5.65	1.22	21.7	1.09	19.4	1.45	25.7
	Sn	19.4	< 0.10	< 0.51	< 0.10	< 0.51	< 0.10	< 0.51
	Si	2454	13.60	0.55	9.82	0.40	16.17	0.66
	Zn	189	1.20	0.63	0.65	0.34	1.38	0.73
	Zr	316	0.79	0.25	0.48	0.15	0.98	0.31
Gas	B	383	1.28	0.33	1.78	0.47	1.83	0.48
	S	5.65	4.24	75.1	5.08	90.0	6.64	118

[$] - From gravimetric analysis of filters and particulate nitric acid rinses
[#] - Calculated from target composition and test average glass production rate
* - Calculated from analysis of filter particulate by water dissolution

Table 5.3. Results from DM10 Test 3 Off-Gas Emission Samples.

| | | Feed[#] (mg/min) | 3/3/11 11:57 – 12:57 9.98% Moisture, 104% Isokinetic | | 3/3/11 14:33 – 15:33 9.34% Moisture, 102% Isokinetic | | 3/3/11 15:51 – 16:51 7.38% Moisture, 109% Isokinetic | |
			Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted
Particulate	Total[$]	27238	68.22	0.25	51.29	0.19	57.60	0.21
	Al	897	0.33	0.04	0.31	0.03	0.34	0.04
	B	707	3.08	0.44	1.62	0.23	1.35	0.19
	Ca	68.28	< 0.10	< 0.15	0.15	0.22	0.21	0.31
	Cd	134	2.35	1.75	1.60	1.19	0.95	0.71
	Cr	22.28	0.35	1.59	0.26	1.17	0.15	0.70
	Cs	32.77	0.28	0.85	0.39	1.19	< 0.10	< 0.31
	Fe	1819	0.54	0.03	0.36	0.02	0.30	0.02
	Li	378	0.97	0.26	0.64	0.17	0.32	0.08
	Mn	48.76	< 0.10	< 0.21	< 0.10	< 0.21	< 0.10	< 0.21
	Na	1912	9.15	0.48	6.52	0.34	4.60	0.24
	Nd	91.2	< 0.10	< 0.11	< 0.10	< 0.11	< 0.10	< 0.11
	Ni	90.4	< 0.10	< 0.11	< 0.10	< 0.11	< 0.10	< 0.11
	P	40.76	< 0.10	< 0.25	< 0.10	< 0.25	< 0.10	< 0.25
	Re	8.15	7.73	94.81	7.00	85.89	4.47	54.78
	S*	10.44	1.82	17.40	1.06	10.16	1.37	13.16
	Sn	35.91	< 0.10	< 0.28	< 0.10	< 0.28	< 0.10	< 0.28
	Si	4537	4.90	0.11	5.15	0.11	6.46	0.14
	Zn	349	0.15	0.04	0.12	0.03	0.12	0.04
	Zr	585	0.10	0.02	< 0.10	< 0.02	< 0.10	< 0.02
Gas	B	707	9.64	1.36	8.61	1.22	6.18	0.87
	S	10.44	6.56	62.8	6.80	65.2	5.04	48.3

[$] - From gravimetric analysis of filters and particulate nitric acid rinses
[#] - Calculated from target composition and test average glass production rate
* - Calculated from analysis of filter particulate by water dissolution

Table 5.4. Results from DM10 Test 4 Off-Gas Emission Samples.

| | | Feed[#] (mg/min) | 3/4/11 05:19 – 06:19 9.40% Moisture, 99.5% Isokinetic | | 3/4/11 06:37 – 07:37 9.54% Moisture, 98.6% Isokinetic | | 3/4/11 07:59 – 08:59 9.10% Moisture, 98.8% Isokinetic | |
			Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted
Particulate	Total[$]	25270	83.01	0.33	76.07	0.30	61.33	0.24
	Al	851	0.60	0.07	0.54	0.06	0.43	0.05
	B	671	4.88	0.73	4.28	0.64	2.60	0.39
	Ca	64.7	0.32	0.50	0.20	0.31	0.25	0.39
	Cd	127	2.61	2.05	2.25	1.77	1.59	1.25
	Cr	21.1	0.35	1.65	0.33	1.54	0.26	1.25
	Cs	31.1	0.33	1.07	0.36	1.16	0.29	0.94
	Fe	1724	1.53	0.09	1.39	0.08	0.93	0.05
	Li	359	1.16	0.32	1.09	0.30	0.79	0.22
	Mn	46.2	< 0.10	< 0.22	< 0.10	< 0.22	< 0.10	< 0.22
	Na	1813	11.34	0.63	10.24	0.56	7.78	0.43
	Nd	86.5	< 0.10	< 0.12	< 0.10	< 0.12	< 0.10	< 0.12
	Ni	85.7	< 0.10	< 0.12	< 0.10	< 0.12	< 0.10	< 0.12
	P	38.6	< 0.10	< 0.26	0.21	0.54	< 0.10	< 0.26
	Re	7.73	7.19	93.00	7.47	96.67	6.70	86.66
	S*	9.90	2.85	28.76	2.46	24.88	1.89	19.12
	Sn	34.1	< 0.10	< 0.29	< 0.10	< 0.29	< 0.10	< 0.29
	Si	4302	6.47	0.15	5.93	0.14	6.04	0.14
	Zn	331	0.33	0.10	0.29	0.09	0.18	0.05
	Zr	555	0.21	0.04	0.20	0.04	0.15	0.03
Gas	B	671	8.60	1.28	9.03	1.35	8.31	1.24
	S	9.90	3.22	32.5	5.23	52.9	3.23	32.6

[$] - From gravimetric analysis of filters and particulate nitric acid rinses
[#] - Calculated from target composition and test average glass production rate
* - Calculated from analysis of filter particulate by water dissolution

Table 5.5. Results from DM10 Test 5 Off-Gas Emission Samples.

| | | Feed# (mg/min) | 3/4/11 16:51 – 17:51 8.69% Moisture, 101% Isokinetic | |
			Output (mg/min)	% Emitted
Particulate	Total$	29295	206.55	0.71
	Al	974	4.48	0.46
	B	768	11.50	1.50
	Ca	74.2	1.18	1.59
	Cd	146	2.70	1.85
	Cr	24.2	0.55	2.26
	Cs	35.6	< 0.10	< 0.28
	Fe	1976	17.98	0.91
	Li	411	2.56	0.62
	Mn	53.0	< 0.10	< 0.19
	Na	2077	20.12	0.97
	Nd	99.0	< 0.10	< 0.10
	Ni	98.2	0.64	0.65
	P	44.3	0.25	0.57
	Re	10.1	7.66	76.16
	S*	11.3	4.01	35.4
	Sn	39.0	0.16	0.41
	Si	4928	22.81	0.46
	Zn	379	2.91	0.77
	Zr	635	1.44	0.23
Gas	B	768	3.60	0.47
	S	11.3	8.22	72.5

$ - From gravimetric analysis of filters and particulate nitric acid rinses
# - Calculated from target composition and test average glass production rate
* - Calculated from analysis of filter particulate by water dissolution

Table 5.6. Average Emissions Rates and Carryover for DM10 Tests.

		Test 1		Test 2		Test 3		Test 4		Test 5	
		Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted	Output (mg/min)	% Emitted
Particulate	Total$	107.54	0.59	87.23	0.61	59.04	0.22	73.47	0.29	206.55	0.71
	Al	2.38	0.39	1.97	0.41	0.33	0.04	0.52	0.06	4.48	0.46
	B	6.67	1.37	4.56	1.19	2.02	0.29	3.92	0.58	11.50	1.50
	Ca	0.71	1.53	0.53	1.43	0.18	0.26	0.26	0.40	1.18	1.59
	Cd	1.82	1.98	1.17	1.61	1.63	1.22	2.15	1.69	2.70	1.85
	Cr	0.27	1.78	0.14	1.17	0.26	1.15	0.31	1.48	0.55	2.26
	Cs	0.17	0.74	< 0.10	< 0.53	0.33	1.02	0.33	1.05	< 0.10	< 0.28
	Fe	8.21	0.66	6.62	0.67	0.40	0.02	1.28	0.07	17.98	0.91
	Li	1.31	0.50	0.94	0.46	0.64	0.17	1.01	0.28	2.56	0.62
	Mn	< 0.10	< 0.21	< 0.10	< 0.36	< 0.10	< 0.21	< 0.10	< 0.21	< 0.10	< 0.19
	Na	10.00	0.76	7.69	0.74	6.76	0.35	9.79	0.54	20.12	0.97
	Nd	< 0.10	< 0.11	< 0.10	< 0.19	< 0.10	< 0.11	< 0.10	< 0.11	< 0.10	< 0.10
	Ni	0.34	0.54	0.30	0.61	< 0.10	< 0.11	< 0.10	< 0.11	0.64	0.65
	P	0.14	0.50	2.55	11.58	< 0.10	< 0.25	0.21	0.54	0.25	0.57
	Re	< 0.10	NC	2.92	58.33	6.40	78.49	7.12	92.11	7.66	76.16
	S*	2.12	29.61	1.26	22.25	1.42	13.57	2.40	24.25	4.01	35.35
	Sn	< 0.10	< 0.29	< 0.10	< 0.49	< 0.10	< 0.29	< 0.10	< 0.28	0.16	0.41
	Si	14.46	0.46	13.20)	0.54	5.50	0.12	6.15	0.14	22.81	0.46
	Zn	1.33	0.56	1.08	0.57	0.13	0.04	0.27	0.08	2.91	0.77
	Zr	0.96	0.24	0.75	0.24	0.10	0.02	0.19	0.03	1.44	0.23
Gas	B	2.34	0.48	1.63	0.43	8.14	1.15	8.65	1.29	3.60	0.47
	S	8.45	118	5.32	94.2	6.13	58.8	3.89	39.3	8.22	72.5

$ - From gravimetric analysis of filters and particulate nitric acid rinses
* - Calculated from analysis of filter particulate by water dissolution

Table 6.1. Mass Distribution of Rhenium Based on Alternative Feed Analyses and Glass Background Corrections.

	Test	2	3	4	5
	Feed Origin	NOAH + Perrhenic Acid	VSL+ Heated Goethite Slurry	VSL+ Unheated Goethite Slurry	NOAH + Perrhenic Acid
Glass	Target ReO$_2$ wt% (Recipe amount – Tests 2 and 5, PNNL Feed Analysis – Tests 3 and 4)	0.05	0.043	0.042	0.05
	Target ReO$_2$ wt% (Recipe amount – Tests 2 and 5, VSL Feed Analysis – Tests 3 and 4)	0.05	0.05375	0.05712	0.05
	Measured ReO$_2$ wt%	0.014	0.015	0.017	0.018
	Background Corrected ReO$_2$ wt% (- 0.0035 wt% measured in Test 1)	0.0105	0.0115	0.0135	0.0145
Feed: Recipe amount - Tests 2 and 5, PNNL Feed Analysis – Tests 3 and 4 Glass: Background corrected	% Feed Rhenium in Glass	**21**	27	32	**29**
	% Feed Rhenium in Exhaust	**58**	78 (92)*	92	**76**
	% Total Rhenium Recovery	**79**	105 (119)	124	**105**
Feed: Recipe amount - Tests 2 and 5, PNNL Feed Analysis – Tests 3 and 4 Glass: No Background correction	% Feed Rhenium in Glass	NA	35	40	NA
	% Feed Rhenium in Exhaust	NA	78 (92)	92	NA
	% Total Rhenium Recovery	NA	113 (127)	132	NA
Feed: Recipe amount - Tests 2 and 5, VSL Feed Analysis – Tests 3 and 4 Glass: Background corrected	% Feed Rhenium in Glass	21	21	24	29
	% Feed Rhenium in Exhaust	58	62 (74)	68	76
	% Total Rhenium Recovery	79	84 (95)	91	105
Feed: Recipe amount - Tests 2 and 5, VSL Feed Analysis – Tests 3 and 4 Glass: No Background correction	% Feed Rhenium in Glass	NA	**28**	**30**	NA
	% Feed Rhenium in Exhaust	NA	62 **(74)**	**68**	NA
	% Total Rhenium Recovery	NA	90 **(102)**	**97**	NA

*- Values based on an average of two of the emission values without the low outlier are shown in parentheses.

NA – Not applicable.

Note: The recommended mass balance is shown by the bold entries shaded in blue.

Figure 1.1. DM10 melter and feed tank; off-gas system is in the background to the left.
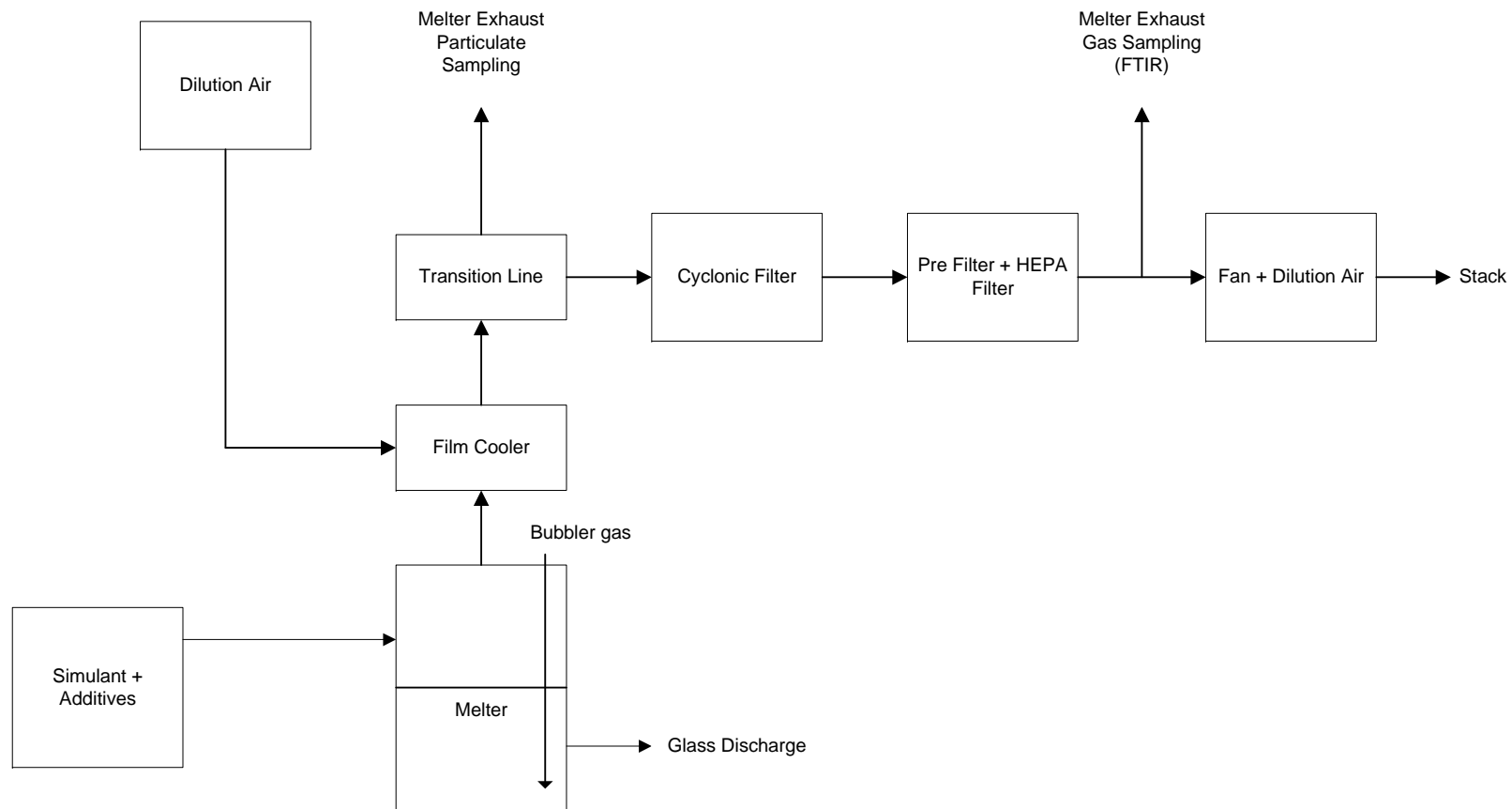
Figure 1.2. Schematic diagram of DM 10 vitrification system.

Figure 2.1. Feed composed of heated goethite slurry prior to mixing in additional water.

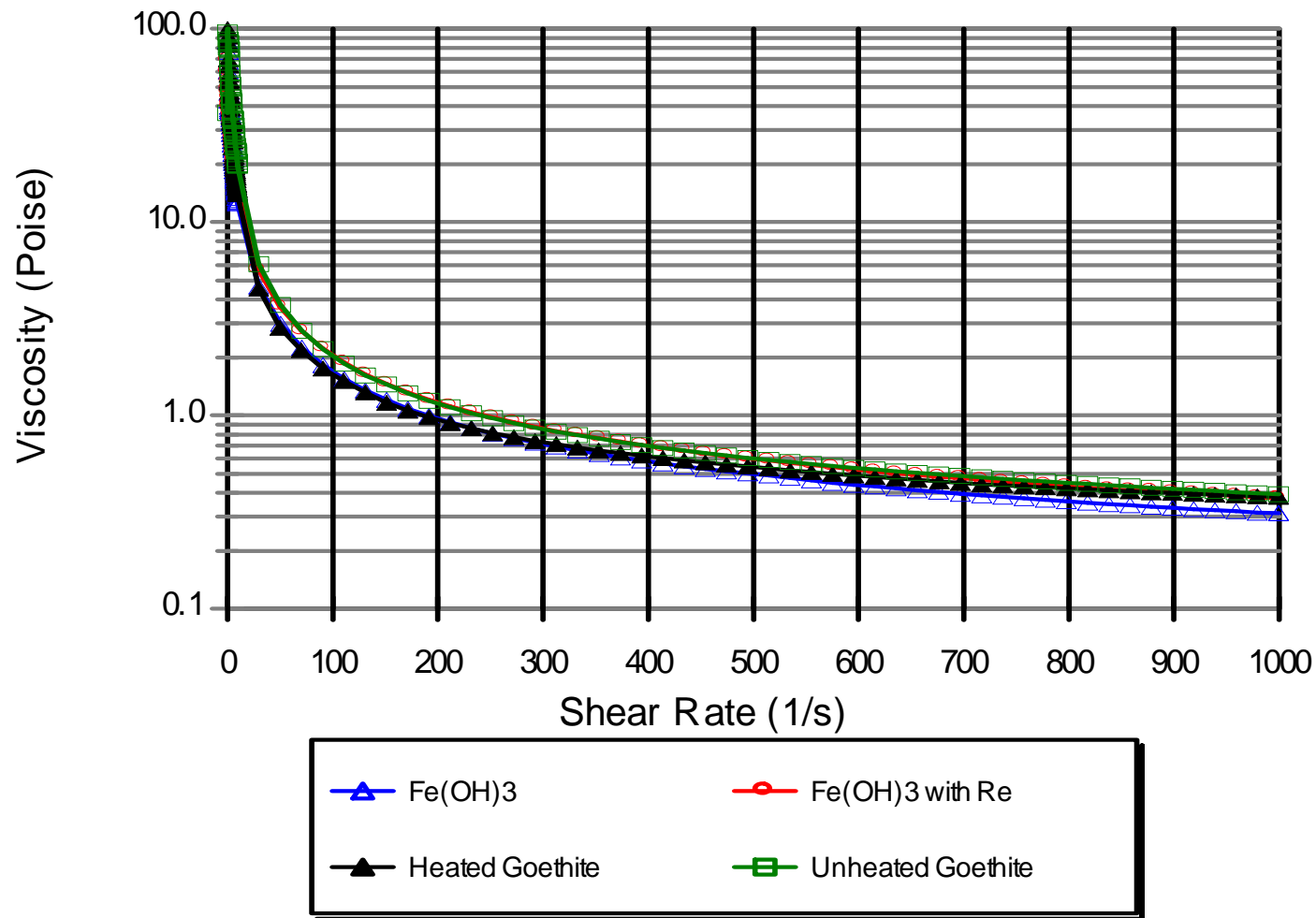**Figure 2.2. Feed composed of heated goethite slurry prior to mixing in additional water.**

Figure 2.3. Viscosity versus shear rate for each feed with each iron and rhenium source.
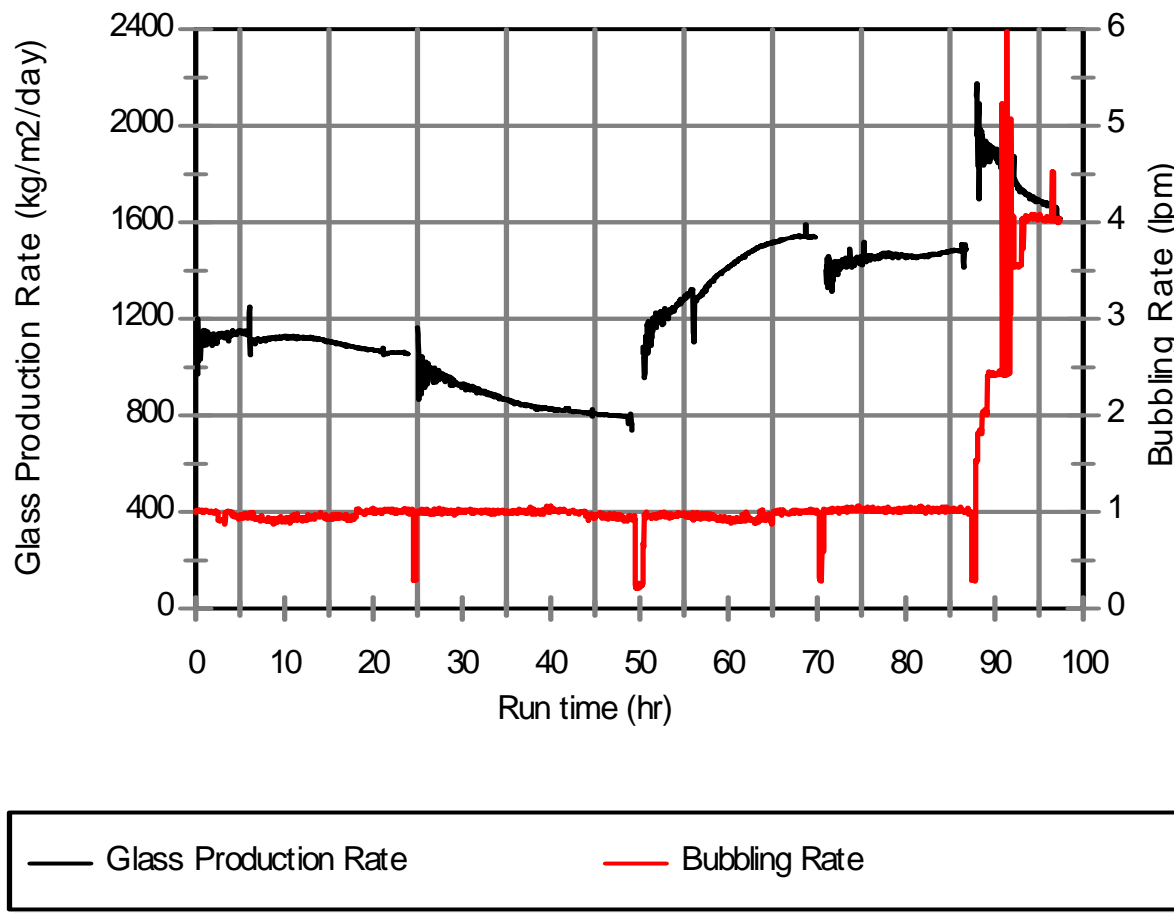
Figure 3.1. Glass production (cumulative) and bubbling rates for DM10 tests with goethite and rhenium.
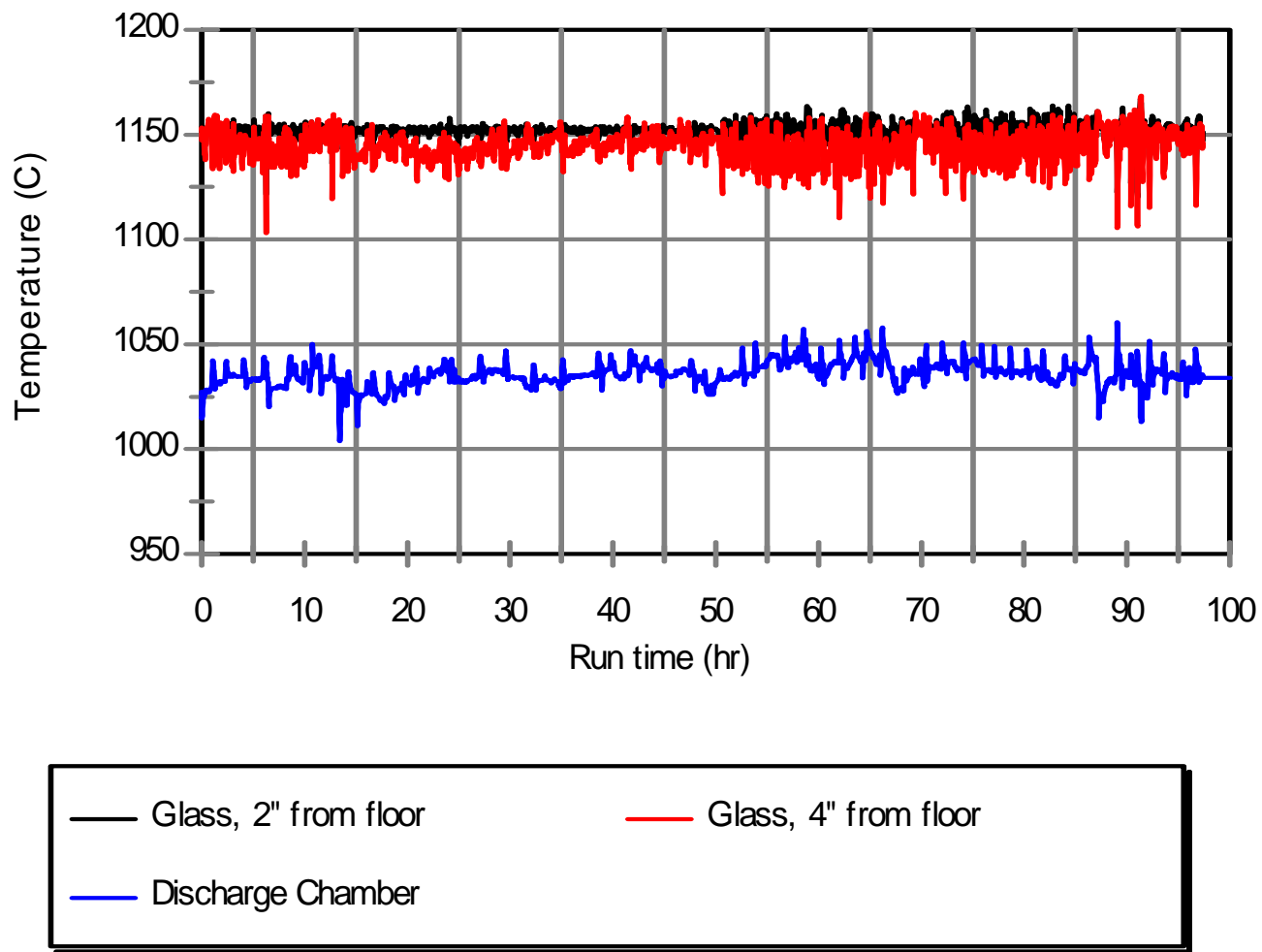
Figure 3.2. Glass temperatures for DM10 tests with goethite and rhenium.
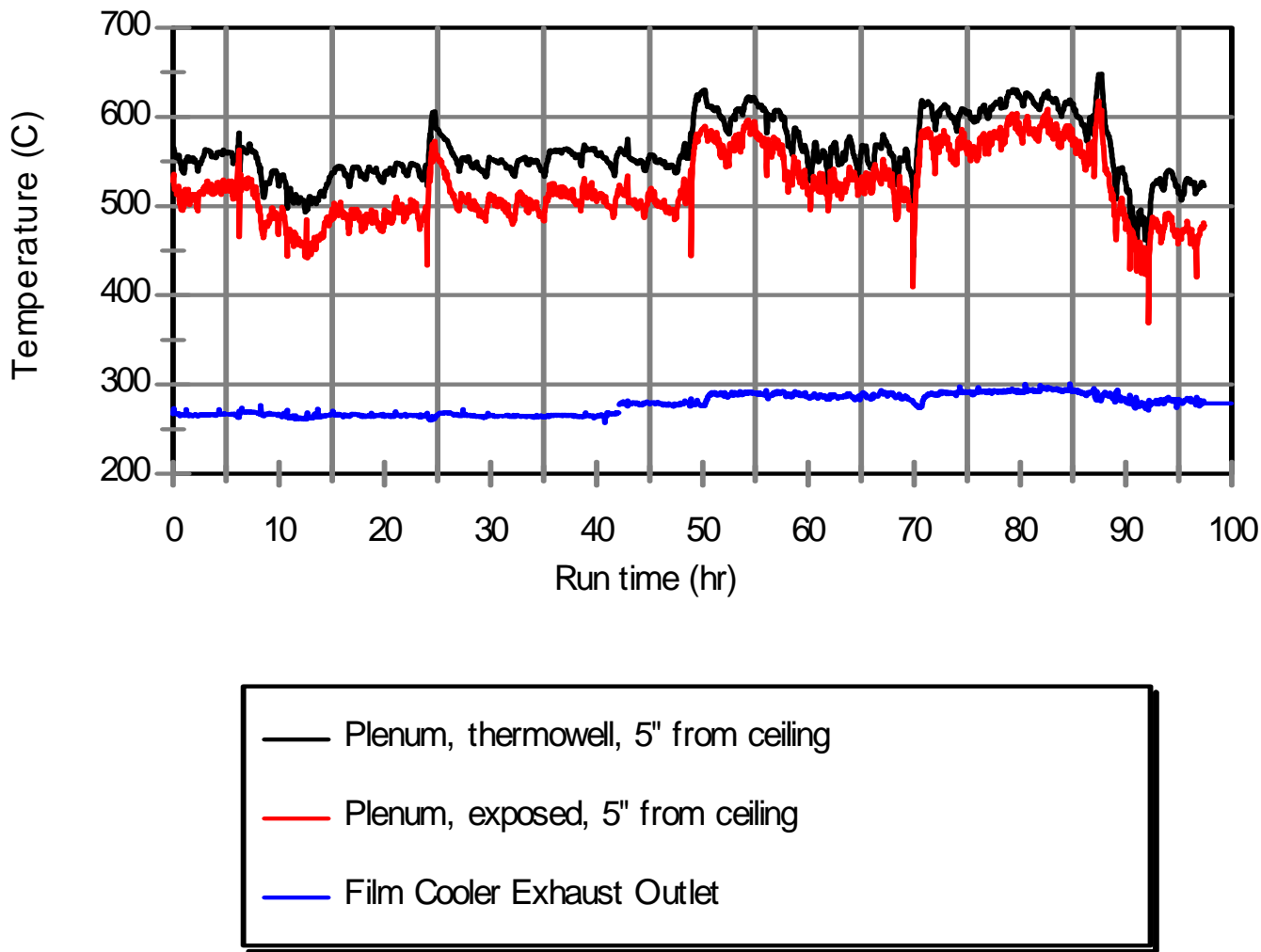
Figure 3.3. Plenum temperatures for DM10 tests with goethite and rhenium.
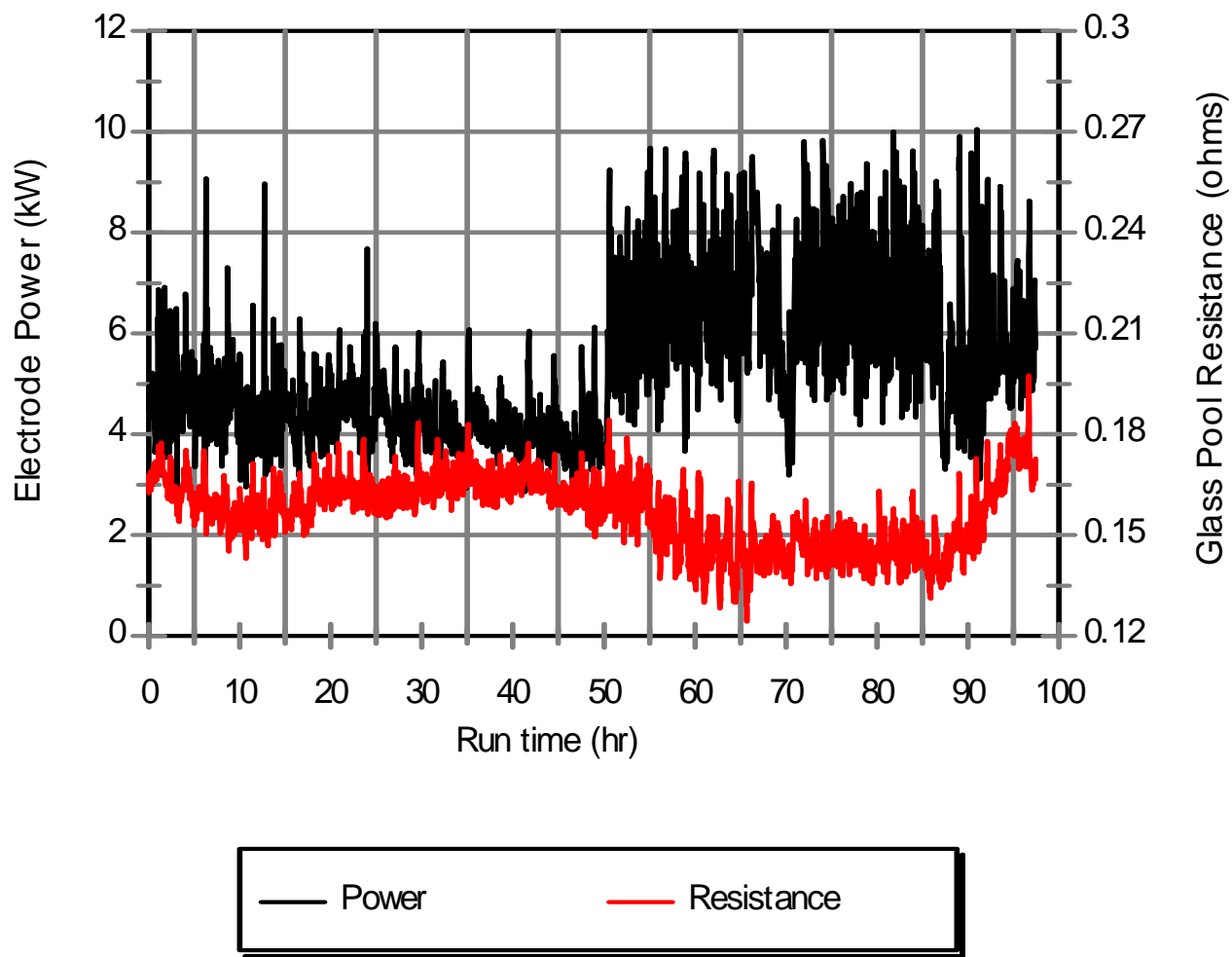
Figure 3.4. Electrode power and glass pool resistance for DM10 tests with goethite and rhenium.
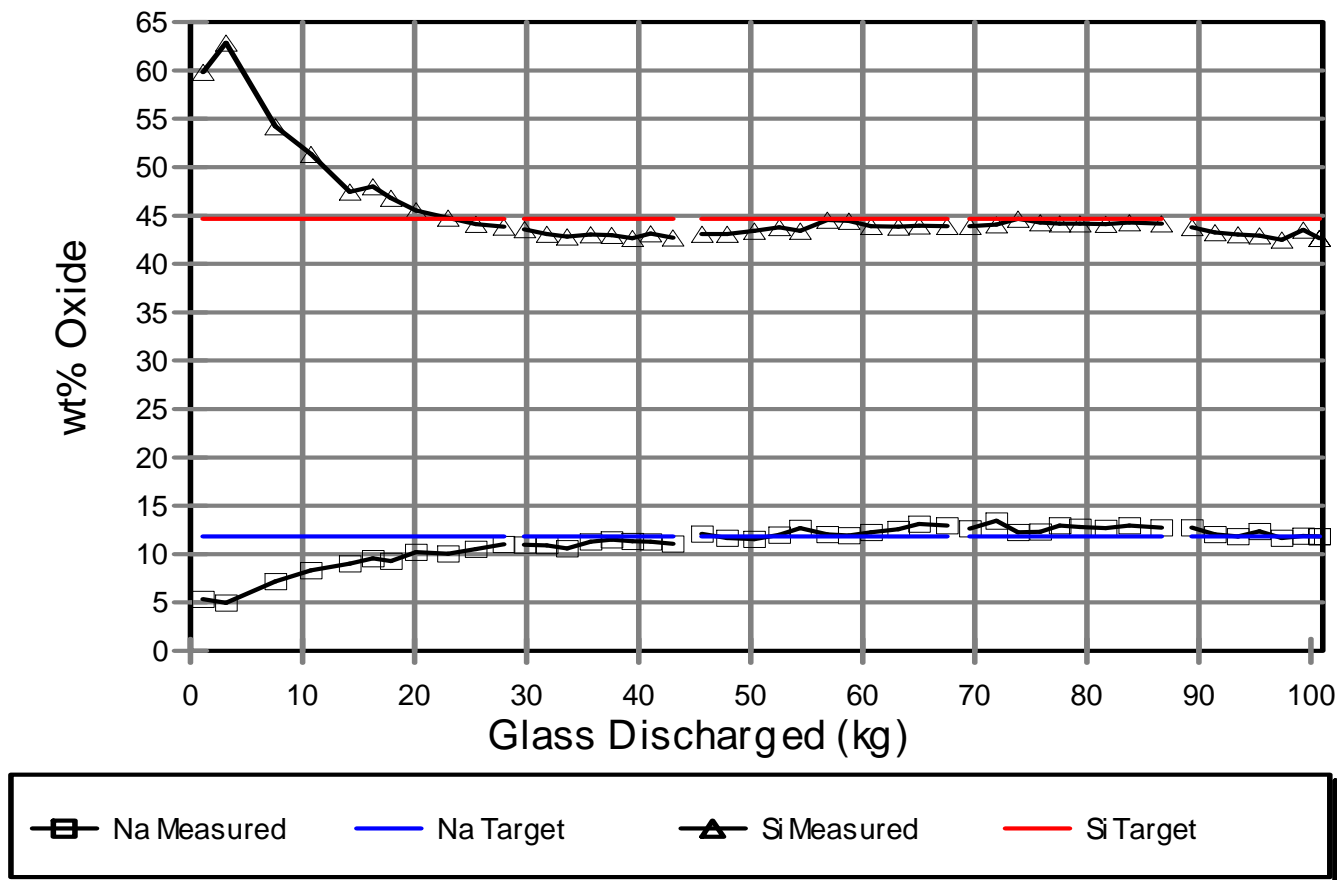
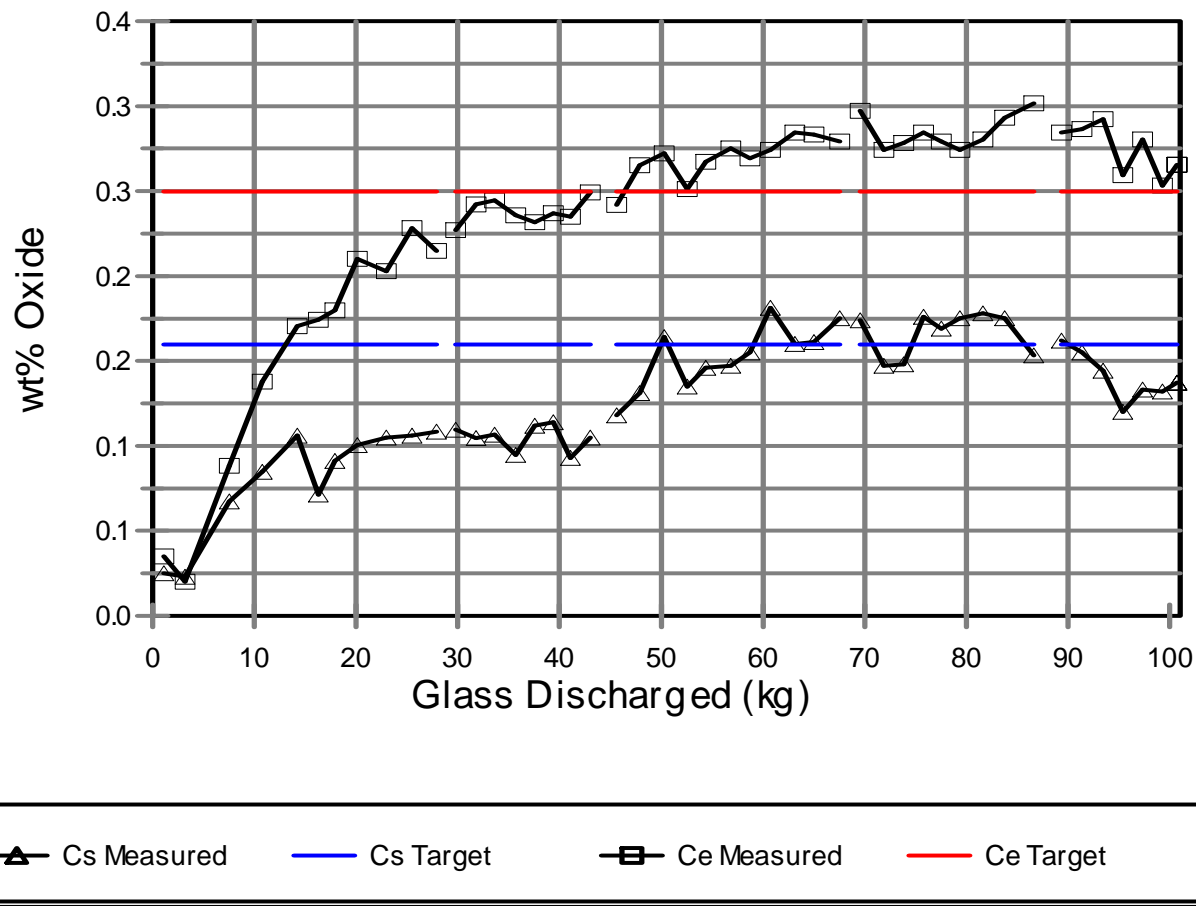**Figure 4.1. DM10 product and target glass soda and silica concentrations determined by XRF.**
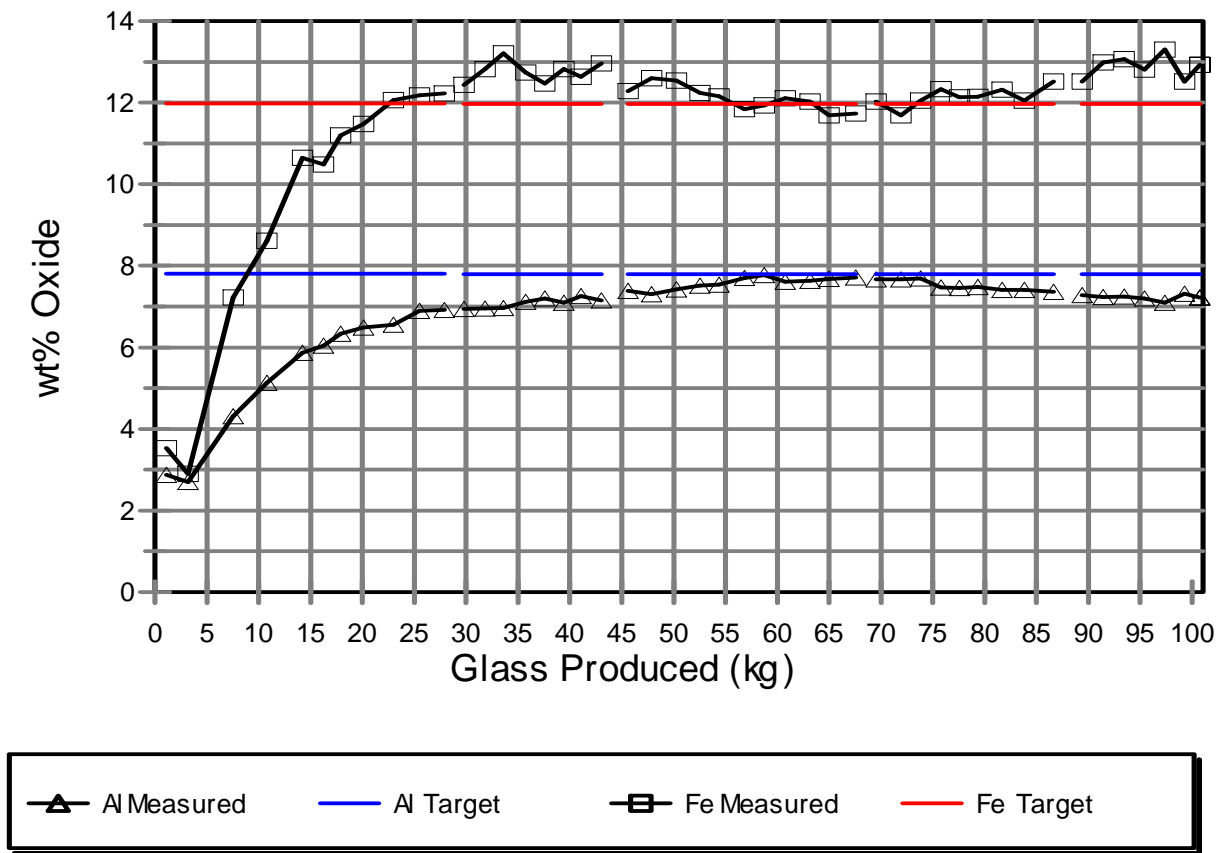
Figure 4.2. DM10 product and target glass aluminum and iron oxide concentrations determined by XRF.
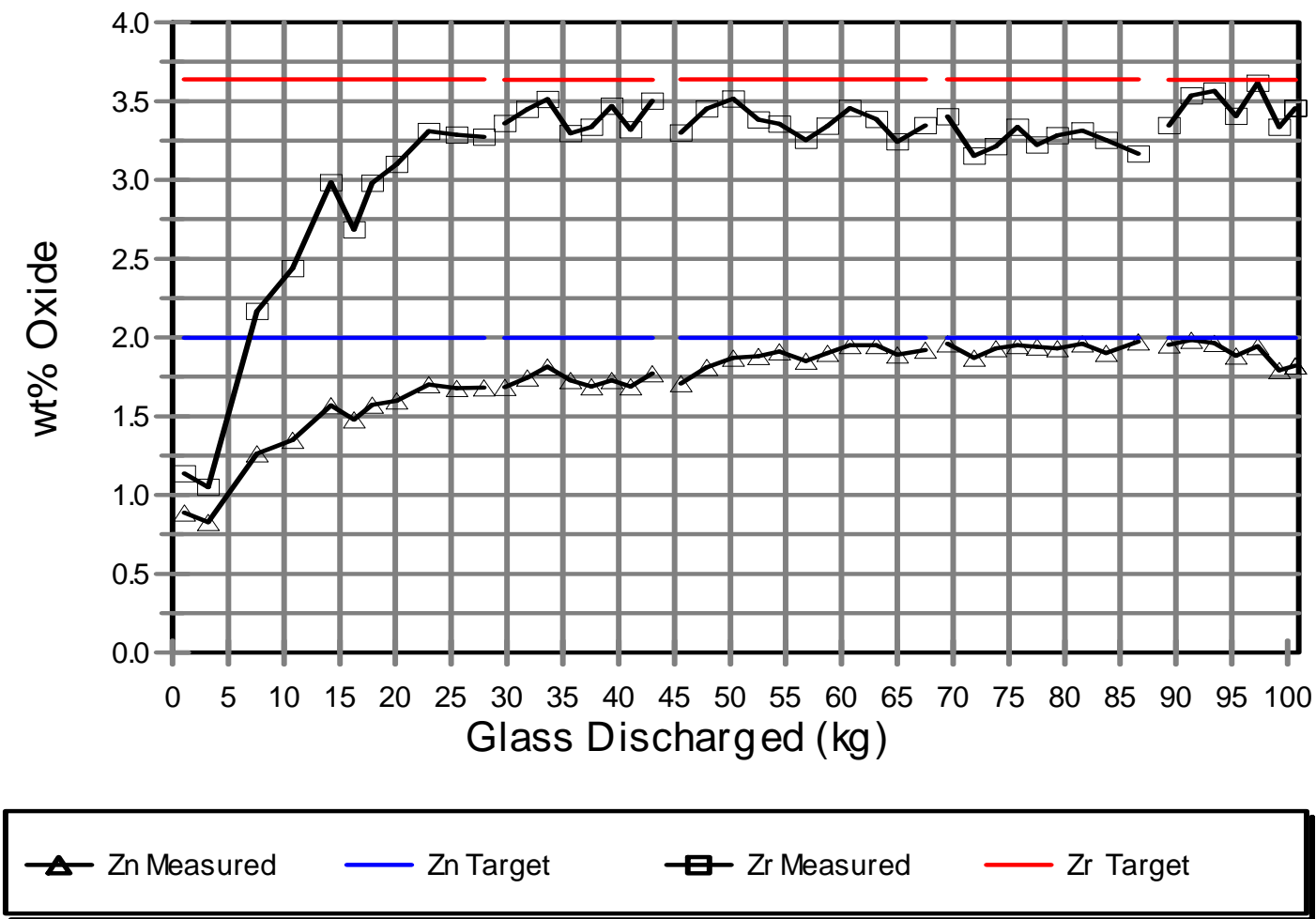
Figure 4.3. DM10 product and target glass zinc and zirconium oxide concentrations determined by XRF.
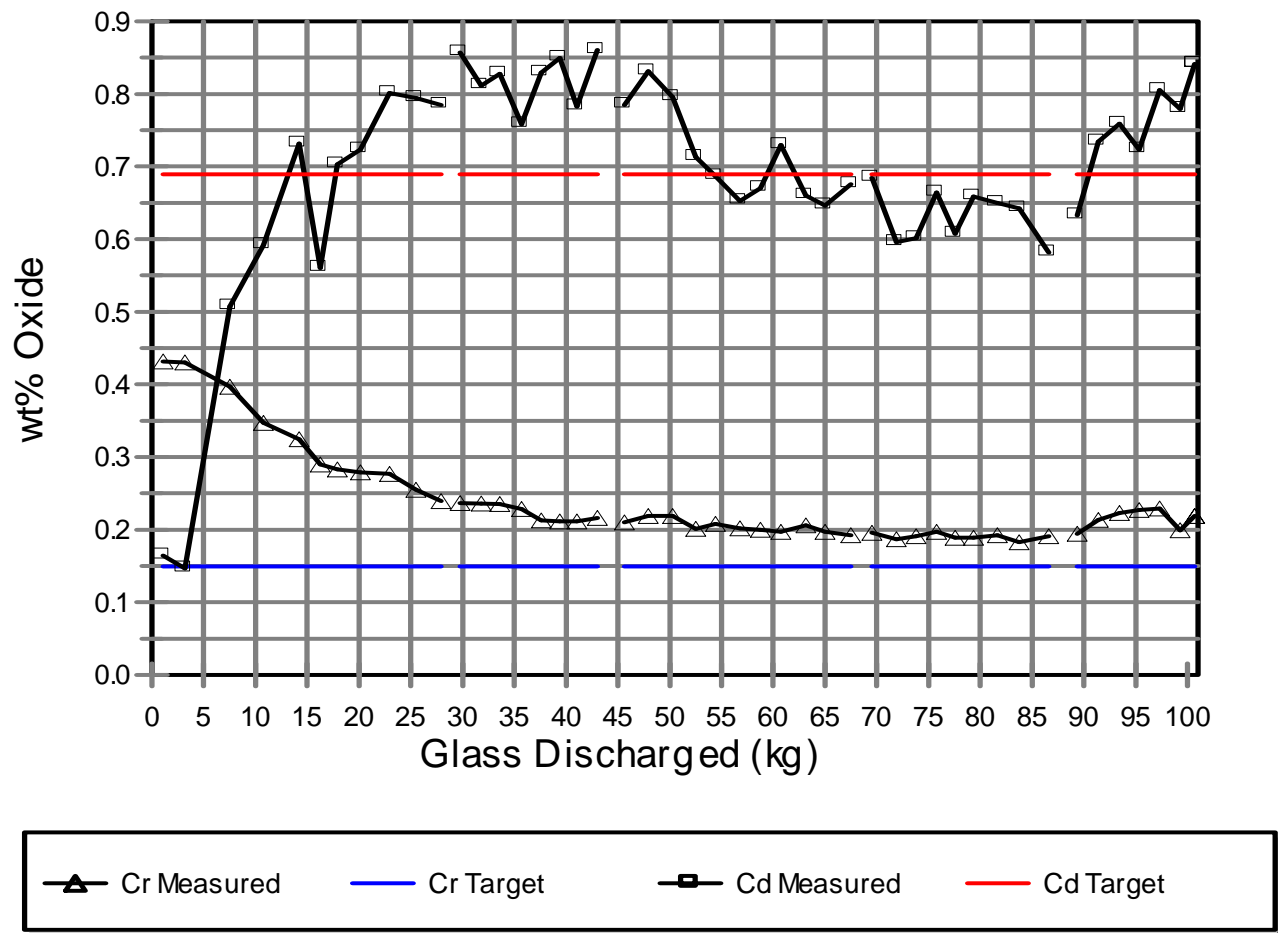
Figure 4.4. DM10 product and target glass chromium and cadmium oxide concentrations determined by XRF.

Figure 4.5. DM10 product and target glass cesium and cerium oxide concentrations determined by XRF.
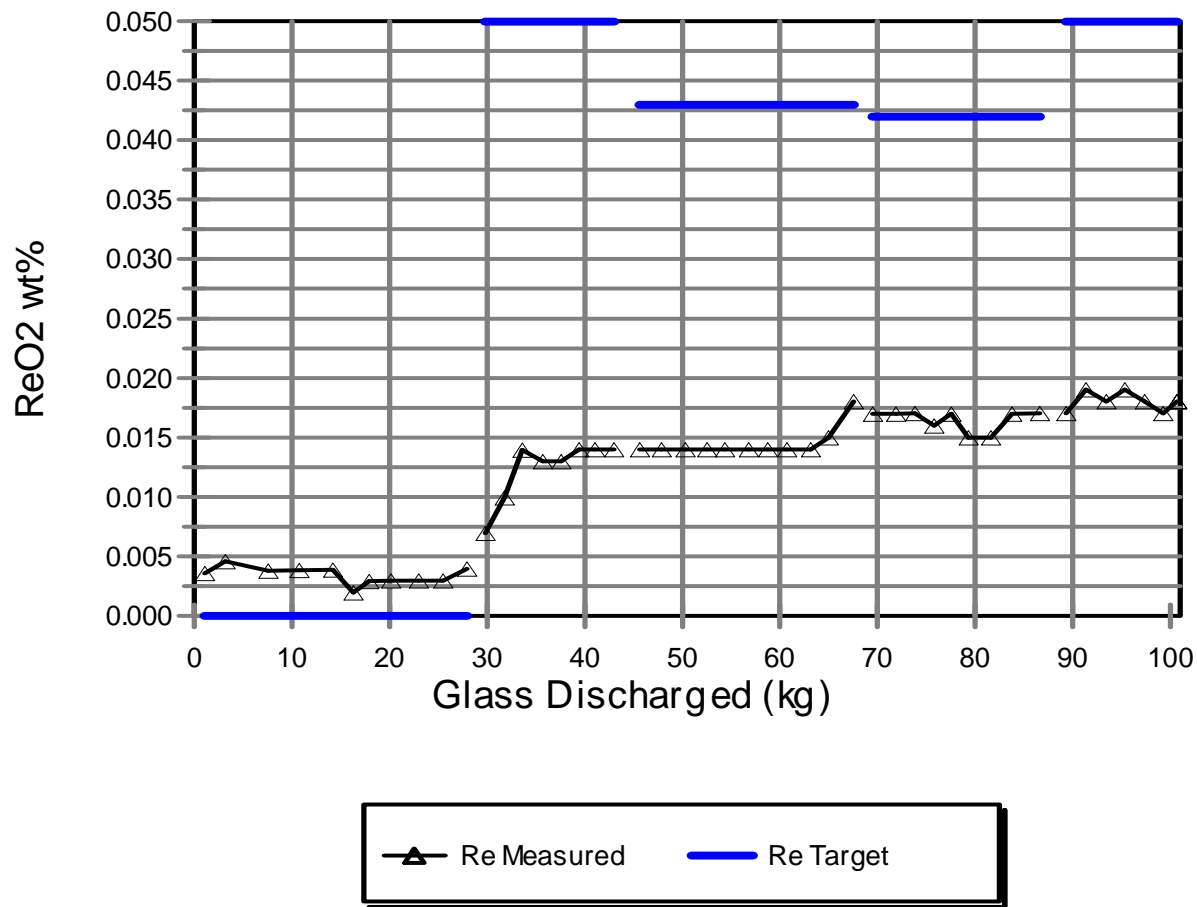
**Figure 4.6. DM10 product and target glass rhenium oxide concentrations determined by XRF.
Note: target values for Tests 3 and 4 are based on the PNNL analysis of the goethite slurries.**

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