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Pacific Northwest
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Tc Reductant Chemistry and Crucible Melting Studies with Simulated Hanford Low-Activity Waste

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Richland, WA 99352

Summary

The FY 2003 risk assessment (RA) (Mann et al. 2003) of bulk vitrification (BV) waste packages used 0.3 wt% of the technetium (Tc) inventory as a leachable salt and found it sufficient to create a significant peak in the groundwater concentration in a 100-meter down-gradient well. Although this peak met regulatory limits, considering uncertainty in the actual Tc salt fraction, peak concentrations could exceed the maximum concentration limit (MCL) under some scenarios so reducing the leachable salt inventory is desirable.

The main objective of this study was to reduce the mobile Tc species available within a BV disposal package by reducing the oxidation state of the Tc in the waste feed and/or during melting because Tc in its reduced form of Tc(IV) has a much lower volatility than Tc(VII). Reduced Tc volatility has a secondary benefit of increasing the Tc retention in glass. This study consisted of four main test activities:

1. Reduction of Tc(IV) in tank waste simulant: Determine the feasibility of controlling the volatility of technetium during BV process by reducing it from the relatively volatile Tc(VII) to the less volatile Tc(IV) in a tank waste simulant.
2. Reduction of Re(VII) in simplified simulant: Investigate Re(VII) reduction in a simplified simulant spiked with orders of magnitude more Re than that expected for Tc in tank waste to quickly screen reducing agents that might effectively reduce Re(VII) and keep it in a reduced state for an extended time.
3. Thermal denitration of sucrose/simulant mixtures: Investigate sucrose denitration as a pretreatment of alkaline Hanford low-activity waste (LAW) using thermoanalytical methods and determine the effects of temperature and sucrose concentration on the denitration of a simulated Hanford LAW.
4. Crucible feed melting tests: Investigate the behavior of Tc volatilization from feeds with reduction treatments, feed with no sulfate, and pre-melted glass using crucible-scale melting tests with a cold finger condenser.

Several potential methods of reducing the Tc(VII) contained in a tank waste simulant and keeping it in a less volatile, reduced state were proposed and tested including: finely divided metallic iron, dithionite, and borohydride. None of the initially proposed reductants were successful. Finely divided iron (25-nm particles) did not reduce pertechnetate in a tank waste simulant. Neither dithionite nor borohydride reduced pertechnetate under basic conditions of the tank waste simulant. Furthermore, when $TcO_2{\cdot}nH_2O$ (the reduced form of technetium) was added to tank waste simulant, it was quickly oxidized back to TcO_4^- by the waste simulant even when air was excluded.

A broader set of screening experiments were conducted to determine the feasibility of reducing technetium in caustic waste streams considered for bulk vitrification (BV). A long list of potential reducing agents was tested using a simplified simulant spiked with orders of magnitude more Re than that expected for Tc in tank waste. The high Re concentrations allowed quick Raman screening analyses to be conducted to determine the reductant's ability to effectively reduce Re(VII) and keep it in a reduced state for an extended time. $SnCl_2$ was found to be an effective, although temporary reducing agent for Re in simulated LAW feeds. Stable reduction was demonstrated by removing water with addition of anhydrite ($CaSO_4$). Results with other binders, including bentonite clay and poly acrylic acid were inconclusive. Several additional water binders and reductants remain to be investigated.

Thermal sucrose denitration of a simulated Hanford LAW was investigated as a pretreatment step to reduce the thermal oxidizing potential of Hanford wastes during vitrification using thermogravimetric analysis (TGA), differential thermal analysis (DTA), and nitrate/nitrite analysis of residual solids. The results of these thermal sucrose denitration studies indicate that Hanford LAW can be effectively denitrated at 400°C. It was shown that this process is an effective approach for removing nitrate and nitrite from Hanford LAW.

A feed melting reduction study found that adding sucrose at a carbon to nitrogen ratio (C/N) of 1 and carbocite at a C/N of 0.5 provided reducing conditions sufficient to keep the melt at a relatively reduced state up to high temperatures. These additions were selected for use in the crucible feed melting tests for Tc volatilization under reducing glass melt conditions. However, crucible scale tests showed that keeping the melt in a reduced state did not reduce Tc/Re volatilization. This was true even when feed without nitrates and spiked with reduced Tc and Re were used. Crucible scale tests showed that feed with no sulfate had noticeably reduced Tc/Re volatilization compared to the baseline feed. Although removal of sulfate is not directly applicable for process enhancement, the information gained from these tests is valuable for understanding Tc volatilization and may point to other possible process enhancements such as controlling the BV operational parameters to minimize the sulfate layer formation. It was also found that significant volatilization of Tc and Re occurs from a pre-melted glass sample, although the volatilization rate from glass is much lower than the rate from melting glass feed materials.

The added understanding of Tc volatilization and related mechanisms obtained from the crucible melt studies includes:

- Re and Tc behave similarly and both readily volatilize from both glass and melting feed.
- Tc/Re volatilization from melting feed is higher than pre-melted glass and is likely a result of the low viscosity of the initial glass-forming melt, enhanced mixing by reaction gases generated during melting, and the higher surface area of the foamy/bubbly melt that exist at temperatures below ~1000°C.
- The sulfate in the feed promotes volatilization through formation of a salt layer concentrated with Re and Tc. Volatilization of Re and Tc is much higher from the salt layer than from the glass. Enhanced sulfate bubble transport at high temperatures may also play a role at higher temperatures.

Reference

Mann FM, BP McGrail, DH Bacon, RJ Serne, KM Krupka, RJ Puigh, R Khaleel, and S Finfock. 2003. *Risk Assessment Supporting the Decision on the Initial Selection of Supplemental ILAW Technologies.* RPP-17675 Rev 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

Abbreviations and Acronyms

AES	atomic emission spectroscopy
AICHE	American Institute of Chemical Engineers
AMEC	AMEC Earth and Environmental, Inc.
ARC	accelerating rate calorimetry
ASR	Analytical service request
BRL	Below reporting limit
BV	bulk vitrification
CS	case stone
CRB	castable refractory block
DIW	deionized water
DOE	U.S. Department of Energy
DTA	differential thermal analysis
DTG	differential thermal gravimetric analysis
EDTA	ethylene diamine tetraacetate
EPR	electron paramagnetic resonance
ES	engineering-scale
HRTS	Horn Rapids Test Site
IC	ion chromatography
ICP	inductively coupled plasma
ILAW	immobilized low-activity waste
IR	infra red
LAW	low-activity waste
LRB	laboratory record book
MCL	maximum concentration limit
MDL	method detection limit
MS	mass spectrometry
MS	matrix spike (only in Appendix B)
NMR	nuclear magnetic resonance
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium-Uranium Extraction
QA	quality assurance
RA	risk assessment
SBMS	Standards Based Management System
SR	steam reformation

SwRI	Southwest Research Institute
T	temperature
TG	thermal gravimetric
TIC	total inorganic carbon
TOC	total organic carbon
TGA	thermal gravimetric analysis
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

Unit Abbreviations

°C	degrees Centigrade
Ci	curie
cpm	counts per minute
g	gram
h	hour
K	Kelvin
L	liter
µg	microgram
µm	micrometer
M	molarity / mole
mCi	millicurie
min	minute
mg	milligram
mL	milliliter
nm	nanometer
wt%	weight percent

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1.0 Introduction

The Hanford Site has the largest volume of high-level radioactive tank waste in the United States stored in 177 underground tanks containing 53 million gallons of waste and 200 million Curies of radioactivity. The life-cycle cost for cleanup has been estimated at nearly $50 billion over 50 years. The Waste Treatment and Immobilization Plant (WTP) is under construction and will immobilize both high-level waste for disposal at a national repository and low activity waste (LAW) for on-site disposal at Hanford. However, vitrification of the high volume of LAW is the rate-limiting step in the WTP and results in the 50-year project duration. The DOE accelerated cleanup mission for the Hanford Site is a strategic initiative to accelerate tank waste treatment by increasing the capacity of the WTP and using supplemental technologies for waste treatment and immobilization for as much as 70% of the LAW. Three supplemental treatment technology options (bulk vitrification [BV], steam reformation [SR], and cementation or cast stone [CS]) were evaluated in 2003 for immobilizing LAW. Detailed discussions of the preliminary FY 2003 risk assessment (RA) results are included in Mann et al. 2003. These results helped support the decision to proceed with a pilot-scale test and demonstration facility to further evaluate BV as a potential supplemental treatment technology for treating LAW at Hanford (Raymond et al. 2004). The use of this supplemental waste form would help DOE meet the long-term groundwater protection criteria for disposing of waste in a shallow land burial facility.

The FY 2003 risk assessment (Mann et al. 2003) of BV waste packages used 0.3 wt% of the technetium (Tc)[a] inventory as a leachable salt and found it sufficient to create a significant peak in the groundwater concentration in a 100-meter down-gradient well (see Figure 1.1)[b]. Although this peak met regulatory limits, considering uncertainty in the actual Tc salt fraction, peak concentrations could exceed the maximum concentration limit (MCL) under some scenarios so reducing the leachable salt inventory is desirable. The current immobilized low-activity waste (ILAW) by the WTP does not show this peak. CH2M Hill Hanford Group, Inc. (CH2M Hill) has requested that the soluble fraction of Tc in the BV box be significantly reduced; the ideal goal (not a requirement) is to reduce the amount of soluble salt in the BV waste package to the point that peak concentrations in the 100-meter down-gradient well do not exceed the highest levels seen for WTP glass. Early attempts to include a castable refractory block (CRB) in place of the refractory sand layer and using a bottoms-up melting technique have eliminated the two main areas where soluble Tc was depositing in the previous process design. However, the refractory block is still quite porous, and early analyses have shown that larger than desired quantities of Re (a chemical surrogate for Tc) are depositing in the pores of the CRB. Based on these early results, a BV performance enhancement task team was organized to explore possible ways to reduce the amount of soluble Tc in the BV waste package. This team developed three main approaches to reduce the problem: (1) modifying the chemistry of the Tc in the BV feed to reduce volatilization, (2) improving the refractory materials to reduce the places for soluble material to collect, and (3) changing the BV operating parameters to better control Tc volatilization. This report summarizes the results from the initial laboratory and crucible scale work for the Tc chemistry modification approach.

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[a] Technetium used in this study was all ^{99}Tc. The symbol "Tc" is used for "^{99}Tc" throughout this report.

[b] The Tc concentrations from BV, WTP, and Steam Reformer are considered comparable because they are several orders of magnitude less than the permitted level.

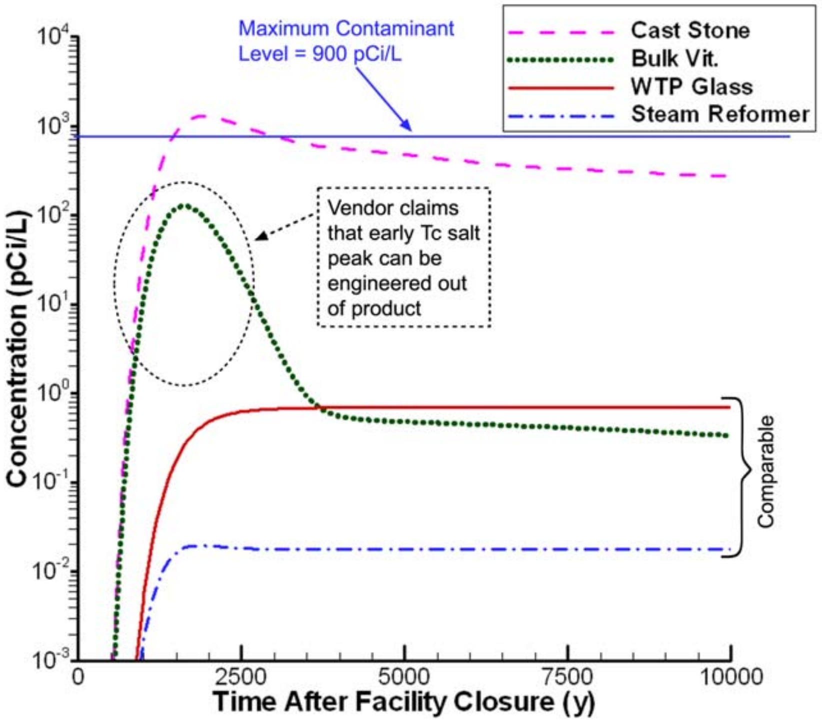

Figure 1.1. Tc Concentration in 100-m Downgradient Well (from Mann et al. 2003)

As stated above, the main objective of this study was to reduce the mobile Tc species available within a BV disposal package by reducing the oxidation state of the Tc in the waste feed and/or during melting because Tc in its reduced form of Tc(IV) has a much lower volatility than Tc(VII). Reduced Tc volatility has a secondary benefit of increasing the Tc retention in glass. The specific objectives of the Tc chemistry modification study were to:

1. Study the effect of feed variation on Tc volatilization behavior at crucible scale
    a. Determine if finely divided iron-particle additives or other selected reductant/treatment will significantly reduce Tc migration during a simulated BV process with nitrate salts present.
    b. Determine if the reduction of nitrates by reductant addition to the feed is sufficient to significantly reduce Tc migration during a simulated BV process.
    c. Determine if the reduction of Tc combined with the removal of nitrate is sufficient to significantly reduce Tc migration during a simulated BV process. If this were successful, a pretreatment process such as high temperature drying would have to be developed to remove nitrate from the feed before melting.
    d. Measure how much Tc removal occurs from a pre-melted glass at crucible scale (to help determine the relative importance of volatility from glass vs. transport from reacting feed).
    e. Measure the impact of sulfate on Tc volatilization at crucible scale.
2. Help to determine the dominant mechanisms for Tc migration in the BV process.

This study consisted of four main test activities:

1) Reduction of Tc(IV) in tank waste simulant: Determine the feasibility of controlling the volatility of technetium during BV process by reducing it from the relatively volatile Tc(VII) to the less volatile Tc(IV) in the tank waste simulant.
2) Reduction of Re(VII) in simplified simulant: Investigate Re(VII) reduction in a simplified simulant spiked with orders of magnitude more Re than that expected for Tc in tank waste to quickly screen reducing agents that might effectively reduce Re(VII) and keep it in a reduced state for an extended time.(a)
3) Thermal denitration of sucrose/simulant mixtures: Investigate sucrose denitration as a pretreatment of alkaline Hanford low activity waste (LAW) using thermoanalytical methods and determine the effects of temperature and sucrose concentration on the denitration of a simulated Hanford LAW.
4) Crucible feed melting tests: Investigate the behavior of Tc volatilization from feeds with reduction treatments, feed with no sulfate, and pre-melted glass using crucible-scale melting tests with a cold finger condenser.

The results of these four test activities are summarized in four main sections of this report, Sections 5.0 through 8.0. Each section contains its test approaches, results and discussion, and summary and/or conclusions. Overall conclusions are included in a separate Section 9.0.

(a) This activity was added when the first activity did not identify an effective reducing agent.

2.0 Quality Assurance

All the tests in this report were proof-of-principle(a) in nature and performed under the Pacific Northwest National Laboratory's (PNNL's) Standards Based Management System (SBMS) and the Supplemental Technologies Support Program's Tank Waste Support Quality Assurance Plan, Rev. 6. The SBMS Quality Assurance Program meets DOE Order 414.1A and 10CFR 830, Subpart A. Staff Training is documented and Test Plans, Procedures, and Instructions are approved and in project records.

(a) Proof-of-principle testing indicates that the tests performed in this study provide qualitative information necessary to understand Tc migration mechanisms during the BV process but are not intended to supply quantitative data for major project decisions without further verification.

3.0 Records

Records for this report are the data sheets from the test instructions, applicable procedures, and any laboratory record book (LRB) pages used to record data and test information. These include instrument calibrations, test set up and standards, data logging, hand calculations, and review comments and signatures. Copies of all test records are provided to the project records custodian for storage in accordance with the quality assurance (QA) plan.

4.0 Simulant Description

The simulant used in this study was the 5 M sodium "6 tank composite" simulated Hanford LAW (also called FY 2003 simulant) developed by Rassat et al. (2003), which has been used in most of the recent BV engineering-scale tests. Table 4.1 shows the reagent masses used to prepare 1 L of simulant (a six-tank composite saltcake solution). The simulant was spiked with 0.0090 g/L Re_2O_7 to provide a target concentration of 8.1 ppm Re (metal basis) in glass, which is the molar equivalent to 4.3 ppm Tc in glass, based on the baseline glass formulation (Kim et al. 2003) at 20 wt% Na_2O with 12 wt% total additive and using Horn Rapids Test Site (HRTS) soil. The 4.3 ppm Tc is the same as used in recent radioactive engineering-scale tests ES-32A (or ES-12) and ES-32B (or ES-13). A total of 25 L of Re-spiked simulant was prepared and distributed for various tests described in the following sections. The Tc was spiked on an as needed basis at 0.00367 g/L of Tc metal (added as 0.00671 g/L NH_4TcO_4 or 0.062 mCi/L), which will provide 4.3 ppm Tc in glass.

The measured density of the simulant was 1.23 g/cm^3, which is very close to the calculated value of 1.24 g/cm^3 (Rassat et al. 2003). The composition of simulant in terms of oxides and halogens that will remain in glass is given in Table 4.2. The compositions of HRTS soil and the resulting glass from the baseline formation are also in Table 4.2.

Table 4.1. Composition of 5 M Sodium "6 Tank Composite" Simulant (Rassat et al. 2003)

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

Table 4.2. Compositions of Simulant, HRTS Soil, and Resulting Glass in Mass Fraction of Oxides and Halogens

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

5.0 Reduction of TcO_4^- in Tank Waste Simulant

In this phase of the work, experiments were conducted to determine the feasibility of controlling the volatility of technetium during BV process by reducing it from the relatively volatile Tc(VII) to the less volatile Tc(IV) (Darab and Smith 1996) directly in the BV feed.

During BV melting tests made with tank waste simulant spiked with pertechnetate, the technetium evaporated out of the melt and collected on the hood and other cooler surfaces, and part also absorbed into the CRB containing the melt. The mechanism that transports the pertechnetate out of the melt at temperature is not known, but it appeared that the technetium was being moved to the surface of the melt where part could evaporate, and part could absorb into the CRB. One mechanism proposed is that fused sulfate and chlorate salts float to the surface of the glass and scavenge pertechnetate along the way, carrying it to the surface. (Certain salts such as sodium sulfate and chlorate are known to accumulate on the surface of the melt.) It was postulated that if the technetium mobility were reduced during the initial stages of melting, then the technetium would have a greater tendency to remain in the BV melt which tends to have highly reducing conditions due to excess carbon.

Several potential methods were considered to immobilize the technetium during the initial stages of melting. Darab et al.(a) reported that pertechnetate could be reduced by metallic iron on a zirconia substrate in the presence of tank waste simulant. Iron does not normally react with strong base (NaOH can be fused in iron crucibles), but iron is more reactive when finely divided (at a small enough particle size it becomes pyrophoric, for example) and we regarded it worth testing. Considered as possibilities for testing were reduction of the pertechnetate by finely divided iron and reduction by some other reagent such as dithionite, tin(II), and borohydride. Adsorption onto an anion exchanger was briefly considered, but then abandoned, because organic anion exchangers would decompose to volatile organics during vitrification. Reduction by metallic aluminum and metallic zinc were considered, but then abandoned, because both metals will readily dissolve in strong base and will reduce nitrate and nitrite to compounds such as NH_3 and NH_2OH, adding unwanted volatile components to the waste stream.

The reducing agents that were ultimately tested included finely divided metallic iron, dithionite, and borohydride. Reduction of perrhenate in tank waste simulant by Sn(II) was tested in another phase of this project and is reported in Section 6.0 of this report.

5.1 Reduction of Pertechnetate by Finely Divided Metallic Iron

The first test of reduction of pertechnetate used finely divided metallic iron as the reducing agent. A sample of iron on ZrO_2 (the same material previously reported to reduce pertechnetate in tank waste simulant) was obtained for testing and a supply of 25-nm iron particles and 1- to 6-μm iron particles were purchased.

(a) JG Darab et al. 1999. *Removal of pertechnetate anions from simulated aqueous radioactive tank waste using supported zero-valent iron*. Abstracts of Papers of the American Chemical Society 218: U1060-U1060 111-NUCL Part 1 (meeting abstract).

The 25-nm iron was chosen for testing because that was the smallest size that can be handled in air without a pyrophoricity hazard. The 1- to 6-µm iron was chosen because it was the next largest size available on short notice. The 1- to 6-µm size was not tested because reduction by iron was abandoned after the first test; using 25-nm-size iron failed to reduce pertechnetate in waste simulant.

The tank waste simulant used in this work (Table 4.1) included the oxidizing agents nitrate, nitrite, and chromate. Nitrate and nitrite are present in high enough concentration to potentially overwhelm any added reducing agent. However, at room temperature and under basic conditions, neither is a strong oxidizing agent.

5.1.1 Experimental Method for Reduction by Finely Divided Metallic Iron

A series of eight tank waste simulant samples were spiked with TcO_4^- and ReO_4^- and reacted with metallic iron to measure the extent of reduction of TcO_4^- and ReO_4^- under varying conditions. Each sample consisted of 50 mL of tank waste simulant in a 50-mL septum-sealed polyethylene Erlenmeyer flask with a magnetic stir bar, metallic iron, and TcO_4^- and ReO_4^- spike. The test matrix is summarized in Table 5.1.

Table 5.1. Test Matrix for Reduction by Finely Divided Metallic Iron

Test	Spike	Reductant	Quantity of Reductant
#1	NH_4TcO_4	25 nm iron	0.5× stoichiometric
#2	NH_4TcO_4	25 nm iron	1.0× stoichiometric
#3	NH_4TcO_4	25 nm iron	5.0× stoichiometric
#4	NH_4TcO_4	Iron on ZrO_2	1.0× stoichiometric
#5	NH_4TcO_4	Iron on ZrO_2	1.0× stoichiometric
#6	NH_4TcO_4	None	
#7	NH_4TcO_4	None	
#8	$TcO_2 + ReO_2$	None	

The stoichiometric amount of iron was calculated using the assumption that the reduction would proceed by these reactions:

$$2MO_4^-{}_{(aq)} + 3Fe + 4H_2O \rightarrow 2MO_{2(s)} + 3Fe(OH)_2 + 2OH^- \text{ (M = Tc or Re)} \quad (5.1)$$

$$2CrO_4^{-2}{}_{(aq)} + 3Fe + 4H_2O \rightarrow 2CrO_2^-{}_{(aq)} + 3Fe(OH)_2 + 2OH^- \quad (5.2)$$

$$O_2 + 2Fe \rightarrow 2FeO \quad (5.3)$$

Using those stoichiometries, the quantities of reductant were calculated and summarized in Table 5.2.

One spike solution was prepared for Tests #1 - #7. The NH_4TcO_4 spike concentration was 0.671 mg/mL (0.00623 mCi/mL) and 1.00 mL was used in each test.

A second set of spike solutions were prepared for test #8. The TcO_2 spike was made by dissolving solid $(NH_4)_2TcCl_6$ in 0.5 M HCl to make a final concentration of 1.29 mg/mL (6.23 µCi/mL). The ReO_2 spike was made by dissolving solid $(NH_4)_2ReCl_6$ in 0.5 M HCl to make a final concentration of 1.61 mg/mL. Both solutions were bright yellow when they were first prepared, but turned dark brown within an hour as the $TcCl_6^{2-}$ and $ReCl_6^{2-}$ partially hydrolyzed. No precipitate formed in either spike solution. When this solution is made basic, hydrous TcO_2 and hydrous ReO_2 precipitate immediately. Since the waste simulant is basic, the spike turns to TcO_2 and ReO_2 on contact with the sample. This way, the spikes are not air sensitive until the moment they are added to the sample. One-half mL of each spike solution was used in Test #8.

Table 5.2. Calculated Quantities of Reductant

Compound	grams/50 mL	Moles	Electrons per mole	equiv
NH_4TcO_4	3.36E-4	1.85E-6	3	5.56E-6
NH_4ReO_4	4.98E-4	1.86E-6	3	5.57E-6
Na_2CrO_4	8.40E-2	5.19E-4	3	1.56E-3
O_2 (5 mL air)	7.50E-4	4.69E-5	4	1.87E-4
			Sum =	1.75E-3
	0.5 X stoichiometric			
	Mole of Fe required =	4.39E-4		
	grams of Fe required =	2.45E-2		
	1.0 X stoichiometric			
	Mole of Fe required =	8.77E-4		
	grams of Fe required =	4.90E-2		
	5.0 X stoichiometric			
	Mole of Fe required =	4.39E-3		
	grams of Fe required =	2.45E-1		

The flasks, filled with 50 mL of liquid, had an average headspace of about 3 mL. The stir bar was added first, then the simulant, then the TcO_4^- spike, then the TcO_2+ReO_2 spike (in Test #8), and finally the iron. After the iron was added, the flasks were capped immediately to exclude air.

The temperature at the beginning of the test was 23ºC. At the end of the first day, the temperature was 24.5ºC.

The TcO_2 + ReO_2 control sample did not turn dark when the spike was added. A readily visible amount of black TcO_2 and black ReO_2 was expected to instantly form when the acidic spike was added to the basic tank waste simulant, but there was no discernable color change.

The samples were stirred with magnetic stir bars throughout the test. Samples of slightly over 1 mL each were withdrawn from the flasks at regular intervals with a syringe through the septa. After withdrawing each sample, air sucked back into the flask, slightly increasing the headspace.

To measure the pertechnetate in the samples, the samples were centrifuged to remove iron and other solids and then 0.5 mL of each centrifuged sample was mixed with 4.5 mL of water in a liquid scintillation vial. A total of 1.00 mL of this solution was passed through a column with 1.0 mL of EiChrom TEVA resin. The TcO_4^- loads onto the resin, but the waste simulant salts and lower oxidation states of technetium pass through. Each column was washed with 10 mL of deionized water, and then the TEVA resin was withdrawn from the column and placed in a glass liquid scintillation vial. A total of 15 mL of liquid scintillation cocktail was added to each vial, and then the vials were counted for Tc beta. This method was intended to avoid measuring precipitated TcO_2 and any other non-pertechnetate species in the sample.

5.1.2 Results of Reduction by Finely Divided Metallic Iron

No reduction of pertechnetate was observed when simulant spiked with pertechnetate was reacted with iron. All the technetium in the samples was found in solution. It would not centrifuge out and therefore did not precipitate as TcO_2 or stick to the iron. Also, all the technetium in the sample loaded onto the TEVA resin, implying that it was in the chemical form TcO_4^-. Furthermore, the simulant appeared to very quickly oxidize the TcO_2 to TcO_4^-. No black TcO_2 formed when the $(NH_4)_2TcCl_6$ spike solution was added to the simulant, and all of the $(NH_4)_2TcCl_6$ added originally was found as TcO_4^- in the subsequent measurements.

The iron did not appear to react with the chromate, either. If the CrO_4^{2-} had been reduced by iron, then the color should have changed as the yellow CrO_4^{2-} was consumed, and green Cr(III) was formed. No such color change occurred; even after several days, the samples with iron looked exactly the same color as the blank with no iron. The iron itself remained magnetic throughout the test and collected readily on the magnetic stir bar when the stirring motor was turned off.

Table 5.3 shows the fraction of total technetium found as pertechnetate. The expected analytical uncertainty (the sum of random and systematic) in the pertechnetate measurement is approximately 3% at 1 standard deviation for the sum of random and systematic errors.

Table 5.3. Fraction of Total Technetium Found as Pertechnetate

Sample	0.5 hour	1 hour	4 hours	7 hours	24 hours	48 hours
25 nm Fe, 0.5× stoic	0.983	0.976	0.967	0.968	0.966	0.958
25 nm Fe, 1.0× stoic	0.950	0.960	0.948	0.957	0.972	0.955
25 nm Fe, 5.0× stoic	0.963	0.971	0.943	0.958	0.974	0.961
Fe on ZrO_2 #1, 1× stoic	0.910	0.912	0.899	0.890	0.912	0.911
Fe on ZrO_2 #2, 1× stoic	0.941	0.969	0.946	0.953	0.951	0.967
TcO_4^- control #1	0.972	0.972	0.957	0.961	0.970	0.964
TcO_4^- control #2	0.967	0.964	0.953	0.963	0.971	(a)
TcO_2 control	0.959	0.949	0.938	0.942	0.977	0.481

(a) Sample not measured.

These data show that there was no reduction by 25-nm iron and little or no reduction by Fe on ZrO_2. The 25-nm iron particles caused no measurable reduction even after 4 days. Only the Fe on ZrO_2 samples show any indication of reduction of pertechnetate, but just barely outside expected analytical uncertainty (about 3 standard deviations). The TcO_2 control was apparently oxidized completely to TcO_4^- at the beginning of the test. (The 48-h TcO_2 control result of 0.481 is probably an analytical error considering that no reducing agent was present.) The results do not change with time. The results for the 25-nm iron are not statistically different from the two pertechnetate controls.

5.2 Reduction of Pertechnetate in Tank Waste Simulant by Dithionite and Borohydride

5.2.1 Test of Borohydride

Several milligrams of NH_4TcO_4 (in water) was added to a 25-fold molar excess of $NaBH_4$ in NaOH solutions of varying concentration in a capped 15-mL centrifuge tube, protected from air. The total volume in each test was 15 mL. The tests were done at room temperature. Table 5.4 summarizes the conditions and results of the borohydride tests.

Table 5.4. Conditions and Results of the Borohydride Tests

Test	NaOH molarity	mg NH_4TcO_4	mg $NaBH_4$	Result
#1	0.00	7.98	41.7	Reduced to TcO_2 on contact
#2	0.10	7.98	41.7	No reaction
#3	0.50	7.98	41.7	No reaction
#4	1.00	7.98	41.7	No reaction
#5	5.00	7.98	41.7	No reaction
#6	10.00	7.98	41.7	No reaction

Test # 1 (water with no NaOH) reacted on contact to give a dark brown precipitate of TcO_2. The solution bubbled H_2 gas and overflowed the centrifuge tube. The solution turned pale lavender, which faded after several hours to a clear solution with a dark precipitate.

Tests #2 through #6 (which all had NaOH added) gave no visible reaction, even after 7 weeks of standing at room temperature.

These tests had enough TcO_4^- to give an obvious color change if even a small fraction of the TcO_4^- were reduced, yet Tests #2 through #6 remained completely colorless.

5.2.2 Test of Dithionite

NH_4TcO_4 was mixed with a fivefold molar excess of $Na_2S_2O_4$ in water and in 0.1 M NaOH. The test volume was 15 mL. The tests were done in capped 15-mL centrifuge tubes, protected from air, at room temperature. Table 5.5 summarizes the conditions and results of the dithionite tests.

Table 5.5. Conditions and Results the Dithionite Tests

Test	NaOH molarity	mg NH_4TcO_4	mg $Na_2S_2O_4$	Result
#1	0.00	7.98	38.5	No reaction at first; TcO_2 precipitated after several weeks.
#2	0.10	7.98	38.5	No reaction.

This test shows that dithionite does not reduce TcO_4^- in 0.1 M hydroxide and requires days or weeks to reduce TcO_4^- in water.

If a reducing agent is unable to reduce TcO_4^- under basic conditions in the absence of oxidizing agents such as air, nitrate, nitrite, and chromate, then it is unlikely to reduce TcO_4^- in actual waste with all those oxidizing agents present. Neither borohydride nor dithionite were investigated any further.

5.3 Measurement of the Rate of Oxidation of TcO_2 by Tank Waste Simulant

5.3.1 Experimental Method

Atmospheric oxygen is known to readily oxidize TcO_2 to TcO_4^- under basic conditions. The rate that tank waste simulant oxidizes TcO_2 to TcO_4^- was measured directly by spiking simulant with TcO_2 and then measuring the TcO_4^- that formed. To distinguish between oxidation of TcO_2 by air and oxidation by tank waste simulant, duplicate tests were run with one exposed to air and the other protected from air. Tests were also run with Na_2CO_3 + NaOH solution, the same pH as the simulant but without any oxidizing agents.

A total of five tests were run, including a blank. The test conditions are summarized in Table 5.6. For each test, 50 mL of simulant (or Na_2CO_3 + NaOH solution) was measured into a flask with a stir bar, and then a solution of $(NH_4)_2TcCl_6$ was added. The $(NH_4)_2TcCl_6$ solution immediately hydrolyzed to $TcO_2 \cdot nH_2O$ on contact with the basic solution. Each test used about 4.2 mg of TcO_2, enough to make a bulky dark brown precipitate. Two of the tests were immediately capped with septum-sealed caps to protect the solution from air. The other three tests were done in air. All the tests were run at room temperature. Samples were periodically withdrawn and analyzed for TcO_4^-.

Table 5.6. Test Conditions for Oxidation Rate of TcO_2

Test	Solution	TcO_2 spike	Exposed to air?	Flask
#1	Simulant	1 mL	Yes	125-mL Erlenmeyer
#2	Simulant	1 mL	No	50-mL septum-sealed
#3	NaOH + Na_2CO_3	1 mL	Yes	125-mL Erlenmeyer
#4	NaOH + Na_2CO_3	1 mL	No	50-mL septum-sealed
Blank	Simulant	[none]	Yes	125-mL Erlenmeyer

The simulant was the same material left over from the iron reduction tests (see Table 4.1). The NaOH + Na_2CO_3 solutions used the same amounts that went into the simulant so that the pH was about the same, but oxidizing agents were absent (0.74 M NaOH + 0.475M Na_2CO_3).

5.3.2 Pertechnetate Measurement

The pertechnetate was separated and measured independently of the TcO_2 by a solvent extraction that took the TcO_4^- into the organic phase and left TcO_2 behind in the aqueous phase. To measure the TcO_4^-, a 0.1-mL sample of the test solution was pipetted into a vial with 5 mL of 0.1 M HNO_3 and 0.05 mL of 0.1 M Ph_4AsCl solution in water. A total of 5 mL of methyl isobutyl ketone was added, and the mixture was shaken and then centrifuged to separate the phases. The TcO_4^- extracts into the methyl isobutyl ketone as Ph_4AsTcO_4. An aliquot of the organic phase (0.05 mL) was measured into 15 mL of Packard brand Ultima Gold liquid scintillation cocktail and counted for Tc.

The pertechnetate measurement is prone to high bias from air oxidation of TcO_2. The pertechnetate measurement was originally attempted with dilute NaOH, not 0.1 M HNO_3. However, in dilute NaOH, the TcO_2 oxidized so fast that it was impossible to complete the analysis fast enough to avoid an unacceptably high bias. A test of the extraction using 0.1 M NaOH, 10 M NaOH, 0.1 M HCl, water, and 0.1 M HNO_3 showed that 0.1 M HNO_3 had the least trouble with air oxidation of TcO_2 during the TcO_4^- analysis. This pertechnetate analysis recovers the pertechnetate well with only minor interference from TcO_2. A test of this method gave the results summarized in Table 5.7 for analysis of four TcO_4^- solutions and four TcO_2 suspensions.

Table 5.7. Recovery of TcO_4^- and TcO_2

TcO_2 spike concentration:	2.44E+7	dpm/mL	
TcO_4^- spike concentration:	3.29E+7	dpm/mL	
Vol used for each spike:	0.0497	mL	± 0.2%
Total vol:	5.033	mL	± 0.1%
Vol counted:	0.0497	mL	± 0.2%

Instrument bkg =	32.00	cpm
Instrument count length =	5.00	min
Counting efficiency =	0.97	counts/decay

Sample	gross cpm	count length	dpm ± 1s		Fraction Recovered
TcO_4^- spike 1	15113	2.65	15548	± 0.5%	0.964
TcO_4^- spike 2	15510	2.58	15957	± 0.5%	0.989
TcO_4^- spike 3	15728	2.55	16182	± 0.5%	1.003
TcO_4^- spike 4	15149	2.65	15585	± 0.5%	0.966
TcO_2 spike 1	1496	5.00	1509	± 1.2%	0.126
TcO_2 spike 2	1483	5.00	1496	± 1.2%	0.125
TcO_2 spike 3	1449	5.00	1460	± 1.2%	0.122
TcO_2 spike 4	1413	5.00	1424	± 1.2%	0.119
Blank 1	34	5.00	2	± 181.7%	
Blank 2	38	5.00	6	± 64.4%	

The average recovery of the TcO_4^- spikes was 0.98 ± 0.02, which is quantitative recovery. However, the average recovery of the TcO_2 spikes was only 0.12 ± 0.003.

5.3.3 Results of the TcO_2 Oxidation Test by Tank Waste Simulant

The tank waste simulant oxidizes TcO_2 quickly, with or without air. TcO_2 oxidizes in Na_2CO_3 + NaOH solution, but not as fast.

All four tests spiked with TcO_2 were dark brown with suspended TcO_2 at first. Judging from the dark color of the TcO_2, the simulant sample exposed to air oxidized its TcO_2 the fastest—it appeared to take about 5 h to completely eliminate the dark color. Three hours into the test, the simulant sample exposed to air had turned much lighter, but the simulant protected from air was still dark. Both Na_2CO_3 + NaOH samples were still dark. Five hours into the test, the simulant sample exposed to air looked nearly as light as the blank, but the other samples still had dark TcO_2. Over the next few days, the TcO_2 in all the samples faded completely.

However, according to the TcO_4^- analysis, both simulant samples oxidized their TcO_2 immediately. All of the technetium appeared as TcO_4^- at the first sampling, even though the samples still had a dark precipitate. Either the dark precipitate in the two simulant samples was something other than TcO_2, or the TcO_2 in these samples was oxidizing very fast during the pertechnetate analysis, ruining the pertechnetate data. (The simulant has nitrite and chromate, which could possibly oxidize TcO_2 on contact under the acidic conditions of the TcO_4^- analysis, and skew the TcO_4^- data.)

The fraction of TcO_2 oxidized, according to the TcO_4^- analysis, is given in Table 5.8 and plotted in Figure 5.1.

Table 5.8. Fraction of TcO_2 Oxidized with Elapsed Time

Elapsed time, h:min	simulant in air		simulant, no air		NaOH + Na_2CO_3 in air		NaOH + Na_2CO_3, no air	
0:00								
0:06	0.942	± 0.054	0.933	± 0.054	0.520	± 0.048	0.610	± 0.049
0:27	0.914	± 0.053	1.007	± 0.055	0.642	± 0.049	0.647	± 0.049
0:52	0.993	± 0.055	1.012	± 0.055	0.707	± 0.050	0.740	± 0.051
1:12	0.921	± 0.053	0.926	± 0.053	0.762	± 0.051	0.721	± 0.050
3:22	0.910	± 0.053	0.991	± 0.055	0.846	± 0.052	0.805	± 0.052
5:22	0.936	± 0.054	0.974	± 0.054	0.855	± 0.052	0.840	± 0.052
24:15	0.930	± 0.054	0.929	± 0.054	1.062	± 0.056	0.911	± 0.053
48:12	0.994	± 0.055	0.865	± 0.052	1.017	± 0.055	0.897	± 0.053

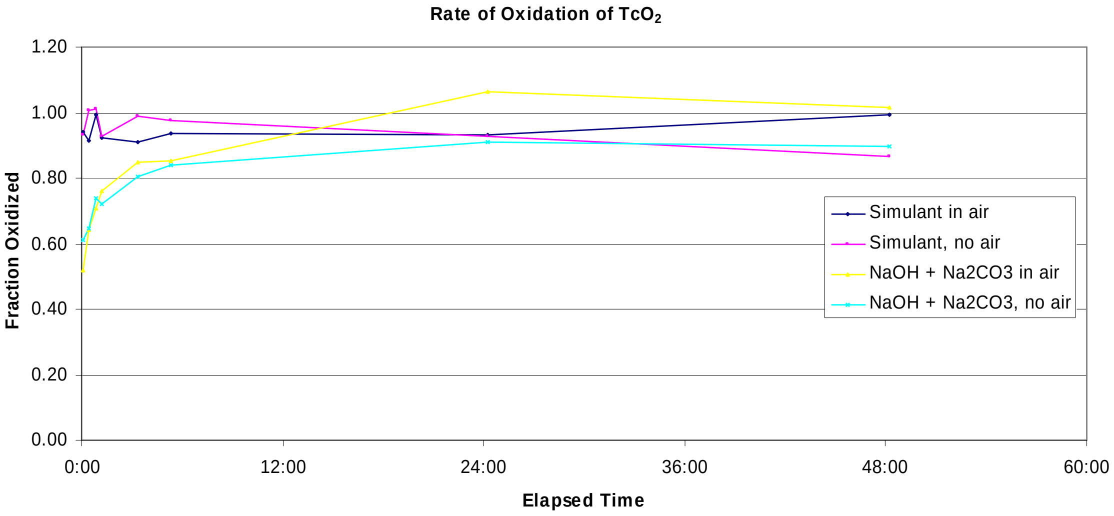

Figure 5.1. Plot of Fraction of TcO_2 Oxidized as a Function of Elapsed Time

According to the pertechnetate analysis data, the simulant, whether exposed to air or not, oxidized the TcO_2 on contact. The Na_2CO_3 + NaOH solution took several hours to completely oxidize the TcO_2.

5.4 Summary of Results

None of the reductants tested could reduce pertechnetate directly in tank waste simulant and keep it in a lower oxidation state. Finely divided iron (25-nm particles) did not reduce pertechnetate in simulant. Neither dithionite nor borohydride reduced pertechnetate under basic conditions. Furthermore, when $TcO_2 \cdot nH_2O$ (the reduced form of technetium) was added to tank waste simulant, it was quickly oxidized back to TcO_4^- by the waste simulant, even when air was excluded.

It appears that TcO_4^- is difficult to reduce directly in tank waste, and as discussed in Section 5.3, is reoxidized back to TcO_4^- within hours by the tank waste at room temperature. Stabilization of the reduced technetium was not considered in this work. The reduced technetium could, for example, potentially be stabilized against re-oxidation by complexing it with organic such as ethylene diamine, but any organic complexant used to stabilize the reduced technetium would have downstream processing consequences that would need to be evaluated.

The tank waste simulant was spiked with NH_4ReO_4 when it was prepared. If the technetium reduction tests had been successful, then the rhenium would have been measured concurrently with technetium (by inductively coupled plasma-mass spectrometry [ICP-MS]) to test whether perrhenate is a suitable substitute for pertechnetate. The technetium reduction tests were not successful, and no rhenium measurements were made.

6.0 Reduction of Re(VII) in Simplified LAW Simulant

Reduction of an aqueous species can be accomplished by several methods but addition of a reducing agent in which electrons are transferred from the reductant to the target element is the most straightforward approach. Hence, this work focused on evaluating reducing agents. It is also possible to drive a redox reaction by applying an external electrical potential on the system, i.e. electrolysis. The substance that is reduced gains electrons and "plates out" (or precipitates) at the cathode. However, no electrolysis experiments were attempted in this study.

As mentioned in Section 5.0, the reduced form of technetium, Tc(IV), is known (Darab and Smith 1996) to be less volatile during heating and fusion. None of the potential reducing agents tested in Section 5.0 with the Tc-spiked tank waste simulant could directly reduce Tc(VII) and keep it in a lower oxidation state. This section summarizes investigations performed on a simplified simulated waste that contains the main components of the anticipated tank waste, including high concentrations of nitrate (NO_3^-), sodium (Na^+) and hydroxide (OH^-), to evaluate reduction of technetium in the LAW stream prior to fusion in the bulk vitrification process. Because of the large number of experiments that were carried out, rhenium was used as a surrogate for technetium. Rhenium (Re) like Tc is a class VIIB element in the Periodic Table, and its aqueous complexation, volatility, oxidation state and reduction-oxidation (redox) potentials are similar (Cotton and Wilkinson 1996, Brookins 1986).

6.1 Experimental Approach

6.1.1 Materials Preparation

Heptavalent rhenium was used in the form of perrhenate (ReO_4^-) as a proxy for the pertechnetate (TcO_4^-) ion in the LAW simulant. The concentration of Re (in the form of potassium or sodium perrhenate) in the mixture was 10 g/L; this concentration greatly exceeds the concentration of Tc in actual LAW feeds by three to four orders of magnitude. The high concentrations of Re were required because of the relatively low sensitivity of the laser Raman system available for analysis of the Re oxidation state in solution. It was also desired to generate sufficient precipitated Re in the simulant so that solid phase characterization could be performed by powder x-ray diffraction. Most experiments were performed with a simplified LAW feed consisting of 5 M $NaNO_3$ solution pH adjusted to a value near 13 using ~0.2 M NaOH. The simplified feed was used to eliminate interferences in the Re-O Raman bands that were observed in Re-free LAW feed simulant (Rassat et al. 2003). However, when successful reduction was observed in the simplified feed, confirmation experiments were performed with the full LAW feed simulant. All fluid and sample preparation was performed in an anaerobic glove box. In some mixtures, hexavalent chrome Cr(VI) was used as a colorimetric indicator of the relative redox state of the simulant. Ostensibly, reduction of Cr is indicated when the aqueous solution turns to green from yellow. If Cr is reduced, it was expected that Re may also be reduced as sufficient reductant was added to ensure complete reduction of both Cr and Re.

6.1.2 Analytical Devices and Techniques

The valence state of Re in solution was checked by Raman spectroscopy, in which the 974 cm^{-1} stretch was assigned to dissolved ReO_4^- (969 cm^{-1} in the solid) and the 2331 cm^{-1} stretch characteristic of solid

ReO_2. Because ReO_2 is exceedingly insoluble, detectable Raman bands for dissolved Re(IV) were not expected nor were they found. Raman spectroscopy was selected as the principle analytical method because it is rapid (each analysis requires less than a minute), non-destructive/non-invasive to the sample, and inexpensive. Sample unknowns were analyzed and compared with scattering peaks of well-characterized standard materials. X-ray diffraction (XRD) techniques were also used, in this case to determine the presence and specific crystalline form of Re-bearing solid compounds, such as $NaReO_4$, Re_2O_3, Re_2O_5, and ReO_2. As discussed below, the ability to identify Re-bearing solids was crucial to confirming or questioning the interpretation of the Raman spectroscopic data.

6.1.3 Reducing Agents

Prospective reducing agents were added to the LAW feed simulants in an anaerobic chamber. The reducing agents included colloidal Fe^0, $SnCl_2$, $PdCl_2$, $MnCl_2$, $FeCl_2$, Na-EDTA, Na-thiosulfate ($Na_2S_2O_3$), Na-dithionite ($Na_2S_2O_4$), and Mg- and Mn-sulfate (SO_4^{2-}). In select experiments solid TiO_2, Ti_2O_3, Al- and Pd-metal as well as apatite [$Ca_5(PO_4)_3{\cdot}(OH, F)$] were added as possible catalytic substrates. In a final experiment, H_2 gas was bubbled across the surface of a solid platinum strip, which typically would exert a strongly reducing environment. Solutions were subjected to Raman analysis before and after the reducing agents were added. In many of the experiments, a white or black solid precipitated after mixing the synthetic waste stream with a reductant. Solid precipitates, where present, were analyzed and identified using XRD techniques.

Because of the large amount of Re added to the feed simulants, an equal amount (on a mol equivalent basis) of reductant was required to be added to ensure that Re(VII) could be completely reduced. These additions typically greatly exceeded the solubility of oxyhydroxide compounds, such as SnO, $Fe(OH)_2$, etc. The net result was acidification of the starting solutions through reactions such as:

$$SnCl_2 + H_2O \rightarrow SnO + 2Cl^- + 2H^+ \qquad (6.1)$$

Because this occurs as an artifact of the large Re and subsequent reductant additions, the solutions were titrated back to approximately pH 12 by addition of NaOH.

6.2 Results and Discussion

6.2.1 Experiments with Reducing Agents

Raman analyses of the starting reagents yielded the required baseline from which peak assignments on the unknown samples could be assigned. Figure 6.1 displays results of Raman spectroscopy on the solid $NaReO_4$ standard. The diagram shows a prominent peak at ~959 cm^{-1} that is assigned to a Re(VII)**—**O stretching vibration (Mattigod et al. 2005). Further results of spectroscopic analyses on a dilute ReO_4^- solution showed that there is a peak shift between Re(VII) in solution compared to that of the solid. In solution, the ReO_4^- Raman peak appears at ~974 cm^{-1}, whereas in the solid, the peak is located at 969 cm^{-1} (Figure 6.1).

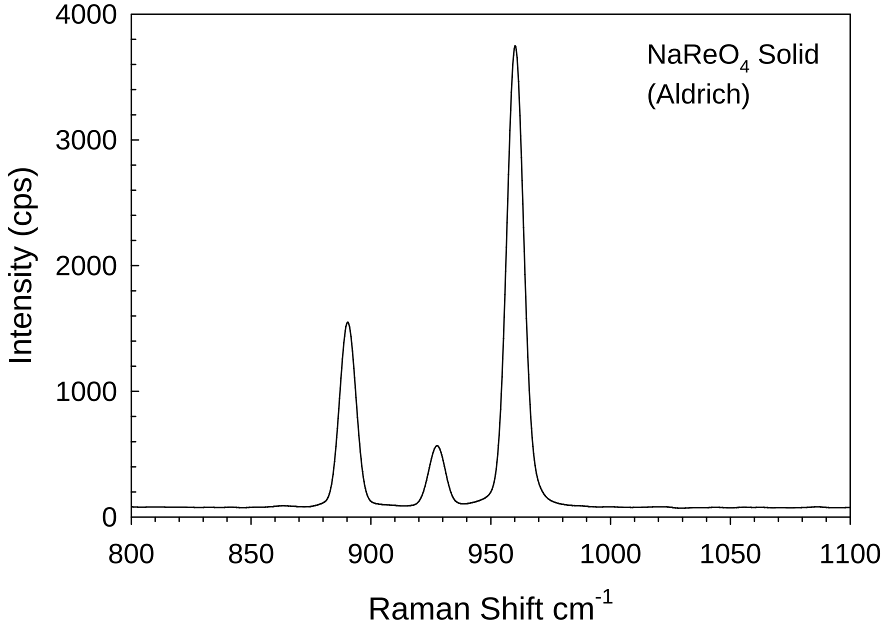

Figure 6.1. Raman Spectrum of $NaReO_4$(s) Standard

The location of the main Raman peak for solid ReO_2 is at 2331 cm^{-1} (Figure 6.2). No detectable Raman bands were evident for dissolved Re(IV) because of the low solubility of the parent oxide. Next, a synthetic waste stream solution was examined using Raman analyses to assure that interferences or peak overlaps with the Re peak would not occur. A representative Raman spectrograph of the results is exhibited in Figure 6.3. Results for a 5 M $NaNO_3$ aqueous solution mixed with $NaReO_4$ (in the absence of a reductant) are shown. The bottom trace is the spectrograph taken immediately after mixing while the top trace corresponds to an analysis taken 24 hours after mixing. In both traces the prominent peak at ~1060 cm^{-1} corresponds to the N–O stretch of the nitrate (NO_3^-). The ReO_4^- peak is clearly visible at the lower wave number of ~974 cm^{-1}. Note that the scale between the two traces is different, such that the ReO_4^- peak and the broad features at ~1350 and 1700 cm^{-1} are exaggerated in the 24-hour experiment. At present, we have not made peak assignments for these features. The results indicate that Re at the concentrations added (10 g/L) is sufficiently high to be detected in solution. Fortunately, the very large band associated with NO_3^- is sufficiently far away from the stretch for ReO_4^- that it does not interfere with the measurement.

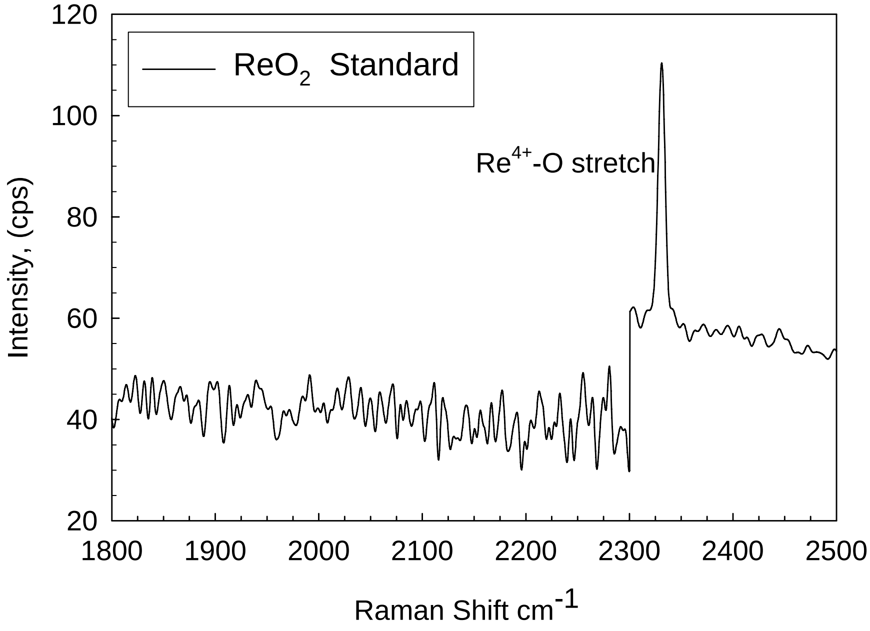

Figure 6.2. Raman Spectrum of ReO$_2$(s) Standard

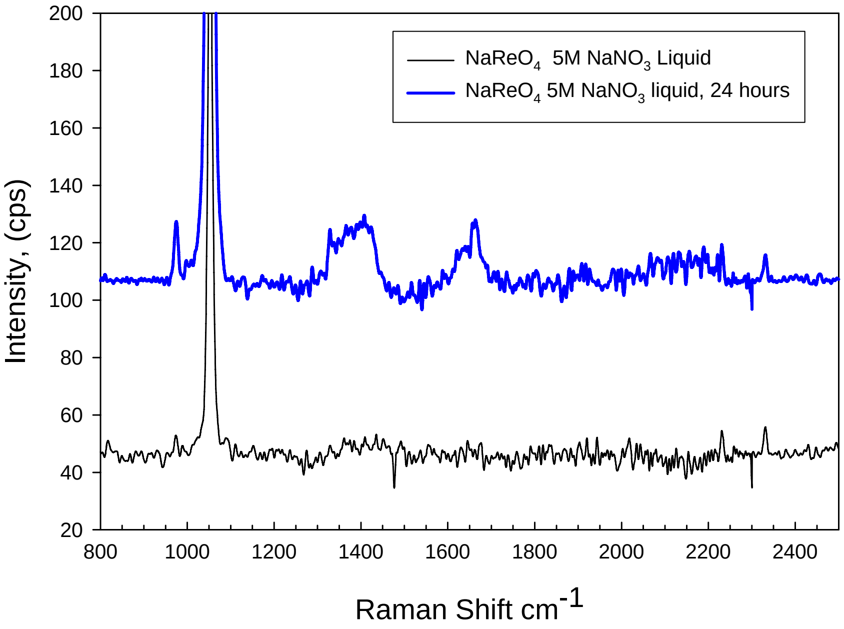

Figure 6.3. Raman Spectrum of Dissolved NaReO$_4$ in 5 M NaNO$_3$ Solution

The first reductant material used was zero valent iron. Because of the large number of papers in the literature on the use of Fe^0 for subsurface contaminant remediation, including Tc, there was an initial expectation that Fe^0 would be an effective reducing agent for the LAW feed. In fact, no change in the 974 cm^{-1} Raman peak for perrhenate was observed in any of our tests using Fe^0. Numerous combinations of zero valent iron with the catalytic substrates mentioned previously were also tried. None of the combinations were found to have any effect. Out of the list of reducing agents and substrates tested in this study, only $SnCl_2$ was found to actually reduce the Re(VII) in the LAW feed. As shown in Figure 6.4, Raman analyses taken immediately after mixing the feed simulant with $SnCl_2$ show the disappearance of the 974 cm^{-1} Raman band for perrhenate. Unfortunately, subsequent analyses taken at later times show the reappearance of the 974 cm^{-1} peak in less than 24 hr at room temperature.

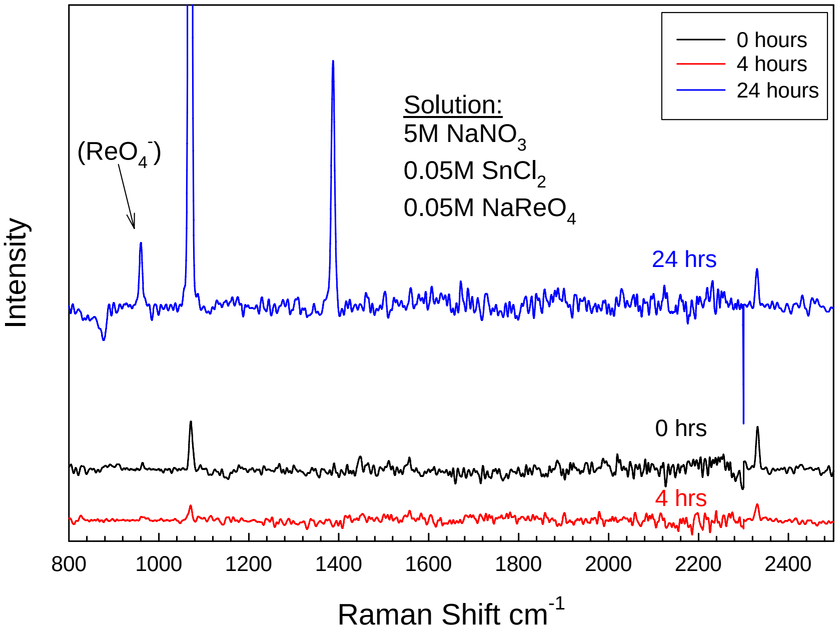

Figure 6.4. Raman Spectrum of $NaReO_4$(s) Standard

The second sequence of experiments involved drying the solutions containing reduced Re in an attempt to stop the reoxidation process. The solutions were dried and the resulting precipitates were characterized by XRD. Figure 6.5 shows the XRD tracings of a ReO_2 solid in 5M $NaNO_3$ along with two 5M $NaNO_3$ solutions containing $NaReO_4$ and $SnCl_2$. The high temperature pattern corresponds to a sample that was heated until the solid turned white. The other two solutions were heated to dryness and then cooled. The major reflection for $NaNO_3$ (29.377 °2θ) has been truncated to allow for more detail in the tracings. Examination of the ReO_2 tracing shows a slight oxidation of Re to $NaReO_4$ after 24 hours. Rhenium in the reduced form (ReO_2) is still present, which is evident by the weak broad reflection at 2.417 Å (37.175 °2θ). Solutions starting out with $NaReO_4$, and subsequently reduced by $SnCl_2$, then dried, contained no detectable ReO_2 phase. Rhenium in solution reoxidized and precipitated as $NaReO_4$ (Figure 6.5). Different combinations of drying temperatures on the bench top and anaerobic chamber were tried and no differences were noted. Rhenium is spontaneously reoxidized in the LAW feed, most probably by nitrate reduction. The need to dry the feed at elevated temperature for blending with glass forming additives would significantly speed up the reoxidation reaction making it untenable for use in the BV process flow sheet. Numerous combinations of $SnCl_2$ with added solid substrates were tried but no extension in the duration of the Re reduction was observed.

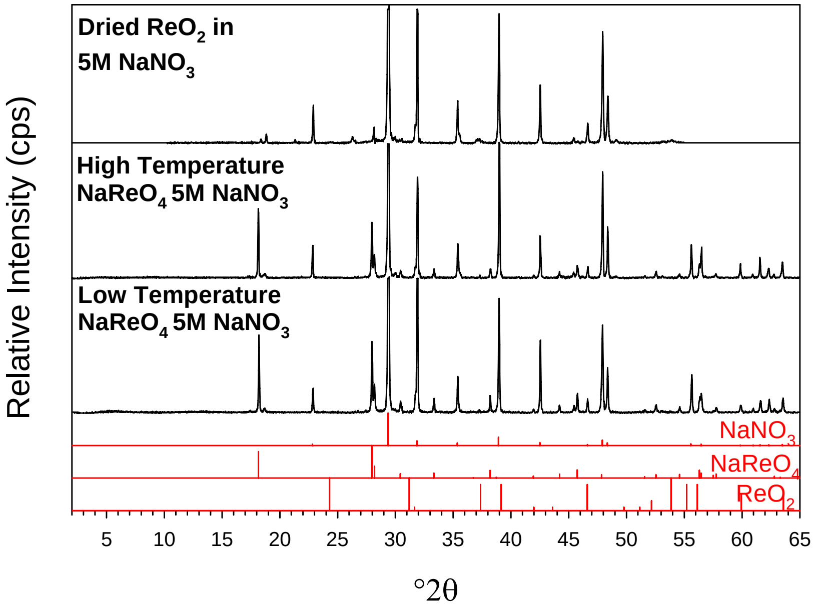

Figure 6.5. XRD Tracing of Dried 5M $NaNO_3$ Solutions Containing Either ReO_2 or 0.05M $NaReO_4$ and $SnCl_2$

6.2.2 Experiments with Water Binders

The oxidation-reduction reactions with Re in the LAW feed are mediated by water. Hence, if water could be removed or its activity lowered sufficiently without heating (evaporation) before Re reoxidized, it was hypothesized that reoxidation reactions might be halted. To test this hypothesis, a series of experiments was performed where excess (or free) water was "removed" by adding water-binding materials to the feed simulant. The materials investigated included drierite ($CaSO_4$), bentonite (a mixture of clay minerals, mainly smectite and illite), and poly (acrylic acid) or ($[-CH_2CH(CO_2H)-]_n$).

A 5M $NaNO_3$ solution was prepared containing 0.05M $NaReO_4$ and the reducing agent, $SnCl_2$. Reduction of the ReO_4 was confirmed by Raman spectroscopy in the liquid sample where the characteristic ReO_4^- stretch was absent. "Excess" or free water was removed by adding drierite ($CaSO_4$; also known as the mineral anhydrite). The mixture was gently dried on a hot plate before being placed inside an atmospherically controlled XRD holder. The solid was examined by XRD within a few hours. Dominating the XRD pattern (Figure 6.6) is drierite ($CaSO_4$) and $NaNO_3$. The primary reflection for a reduced form of Re (ReO_2) was detected at 3.659Å (24.305 °2θ). Raman analysis taken of the same dried solid did not show the characteristic Re(IV)-O band (974cm^{-1}). Subsequent experiments in which the solids were dried for various lengths of time and a variety of temperatures, either inside or outside the anaerobic chamber, indicated that the drierite kept Re in the reduced state on the scale of several days. Therefore, the results of these experiments confirmed our hypothesis and suggest the possibility of maintaining the lower oxidation state of Re by removing free water. However, $CaSO_4$ would not be a water absorber of choice because the addition of large amounts of sulfate into the waste feed is expected to cause numerous problems in the BV process.

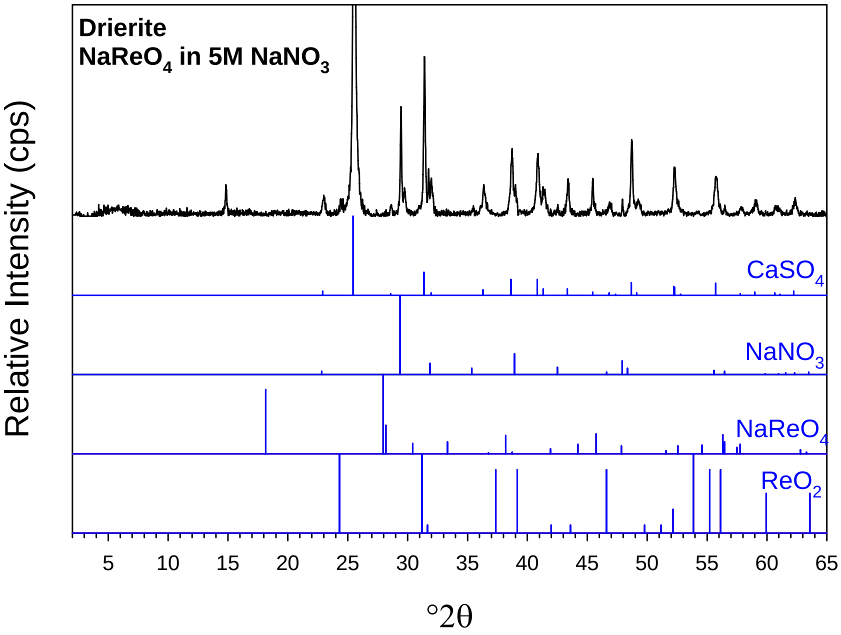

Figure 6.6. XRD Graph of Drierite Added to a 5M $NaNO_3$ Solution Containing 0.05M $NaReO_4$ and $SnCl_2$

Results with the other binders were less conclusive. Experiments with bentonite and poly acrylic acid were conducted in the same manner as described above. Similar to the Raman data collected from the drierite experiments, the characteristic ReO_4^- peak was generally absent for bentonite and poly acrylic acid solids. However XRD results of the bentonite sample were inconsistent; no known Re-bearing crystalline phase was detected. Due to the elastic nature of the poly acrylic acid, this material was not examined by XRD. The results from the experiments with bentonite and poly acrylic acid were not definitive. Rhenium may have been fully or partially reduced. Additional experiments and use of alternative analytical methods, such as nuclear magnetic resonance (NMR) or electron paramagnetic resonance (EPR) may be required to conclusively determine the Re oxidation state in these binders.

6.3 Summary

Experiments were conducted to determine the feasibility of reducing heptavalent (7^+) to tetravalent (4^+) technetium in caustic waste streams considered for BV. Volatilization of Tc(VII) is greater than that of Tc(IV) at the high temperatures used in vitrification processes. A method to reduce technetium in the low-activity waste stream may lower overall Tc volatilization and condensation on refractory and other surfaces in the BV container and so reduce peak release rates to groundwater. Simple analogs of the LAW waste feed were made up using a 5M $NaNO_3$ plus sufficient NaOH to raise the pH to 13. In place of Tc, Re was used, which behaves chemically much in the same manner as Tc. Simulated feed compositions were mixed in an anaerobic chamber using de-aerated water. The perrhenate ion, ReO_4^-, was added to the mixture as either $NaReO_4$ or $KReO_4$. A long list of potential reducing agents, with or without solid substrates, was then added to the waste stimulant to determine the most efficacious candidate and to test the longevity of the reduced state. The presence or absence of oxidized and reduced Re was determined by Raman spectroscopy where changes in the stretching mode vibration Re–O were indicative of the oxidation state of Re. Peak assignments were made in comparison to $NaReO_4$ and ReO_2 peaks in water or as a solid. In summary, $SnCl_2$ appears to be the only candidate that effectively reduces Re(VII), but the length of time in this state is only ~24 hours, regardless of whether the specimen was made up inside or outside the anaerobic chamber. An additional set of experiments was performed to test a hypothesis that binding up excess water could halt the reoxidation of Re. Drierite (anhydrous $CaSO_4$), bentonite clay, and poly acrylic acid were added as potential water binders. Both Raman and XRD analyses confirmed that Re was maintained in a reduced state with the drierite binder. However, neither the Raman nor XRD results were conclusive regarding the Re oxidation state in the bentonite or poly acrylic acid binders. Additional experiments and use of alternative analytical methods, such as NMR or EPR may be required to conclusively determine the Re oxidation state in these binders.

6.4 Additional Options

If it is determined that a reduced Tc could significantly improve the retention within the glass melt, there are additional research options that can be explored. One possible avenue of research that has not yet been performed is to affect reduction of Re(VII) by electrolysis methods. By supplying a potential to the waste stream via an appropriate cathode (with an appropriate anode either in the waste stream or in a half-cell connected to the waste stream via a salt bridge), reduction of Re could be accomplished. The ideal scenario would be that ReO_2 would precipitate or “plate out” on the cathode. The electrode potential for the Tc(VII)—Tc(IV) couple is well known (and is similar to that of the Re analogs) and many investigators believe that the most consistent value is 0.746 V (Rard et al 1999). However, because other dissolved metals will be present in the waste stream (Fe, Cr, Al, etc.), precipitation of oxides and oxy-hydroxides of other elements would likely occur as well. Under these conditions, the cathode might become coated with precipitates and need frequent cleaning to remain effective.

A variety of other methods aimed at Tc immobilization have been advanced in the literature. For example, investigators have proposed using sorbents to collect Tc; activated carbon (Gu et al. 1996), custom “extraction disks” (Fiskum et al. 2000), and synthetic resins (Liang et al. 1996) have all been championed. Other investigators have suggested using natural minerals, especially magnetite (Cui and Erikson 1996, Farrell et al. 1999), as a source of electrons for Tc reduction. Other investigators have advanced “green rust” as a sorbent (Pepper et al. 2003). The proposed use of “green rust” (actually a layered hydrous oxide of Fe^{2+} and Fe^{3+} with interlayer sulfate or carbonate complexes) is interesting, because the high selectivity for Tc (>99.8%) from the waste stream, even in the presence of high concentrations of $NaNO_3$. The data indicate that Tc(VII) is reduced to Tc(IV) and remains in this lower oxidation state despite exposure to air. Interestingly, the “green rust” converts to a goethite-like phase upon oxidation, yet Tc(IV) remained reduced. Another promising technology has demonstrated that extraction of pertechnetate from synthetic waste streams possessing high salinity is possible through use of an organometallic molecule with the name [cyclopentadienyliron(II)arene]cyclotriguiasylene. The organometallic complex is highly selective with respect to pertechnetate (>95%) into nitromethane, despite the presence of competing anions. Additional experiments would be needed to determine if any of these compounds are effective Re/Tc reductants in LAW feed. Of course, achieving stable Re/Tc reduction in the feed is only the first step. Maintenance of the reduced state during the vitrification process at higher temperatures would also require investigation.

6.5 Conclusions and Recommendations

Based on the findings reported above, $SnCl_2$ was found to be an effective, although temporary reducing agent for Re/Tc in simulated LAW feeds. A hypothesis regarding the effectiveness of using water absorbers to prevent Re reoxidation was conclusively confirmed with $CaSO_4$ at room temperature. Initial tests were unable to determine the exact oxidation state or chemical form of Re when using bentonite or poly acrylic acid water binders. Although a large number of experiments were performed in this study in an attempt to achieve Re reduction in LAW feeds, several additional approaches remain to be investigated. Hence, if it is found that a reduced Tc could improve the retention within the glass melt, it is recommended to continue a modest research program to examine these additional approaches and determine if a viable method of Re/Tc reduction in LAW feeds can be identified.

7.0 Thermal Denitration of LAW Simulant by Sucrose

The objective of studying thermal denitration of LAW simulant by sucrose was to assess the potential for denitrating the Hanford LAW stream to potentially help to ensure that reduced Tc remain reduced during the LAW feed melting step within BV. Sucrose denitration was a method that may be compatible with a BV flowsheet (with limited modification) and was chosen to evaluate experimentally.

Thermochemical denitration using carbonaceous materials offered promise based on Smith's studies (Smith et al. 1999), which found that simulated radioactive wastes could be successfully denitrated between 250° and 400°C, producing a significant fraction of the off-gases as N_2 and CO_2. High-temperature calcinations of this type of waste rely on thermal decomposition and produce only the toxic and corrosive oxides of nitrogen as off-gases.

To investigate sucrose denitration as a pretreatment of alkaline Hanford LAW, we used the thermo-analytical methods of thermogravimetric (TG) and differential thermal analysis (DTA), to determine the effects of temperature and sucrose concentration on the denitration of a simulated Hanford LAW based on a recipe given in Table 4.1. To confirm the denitration efficiency, we also analyzed the residual nitrate and nitrite concentration from selected tests.

This section provides a description of the equipment and the results of our studies.

7.1 Experimental

To investigate sucrose denitration of Hanford LAW, we used TG and DTA to study the thermal behavior of a simulated LAW with sucrose added at 1) a stoichiometric amount, 2) a 10% stoichiometric excess, and 3) a 20% stoichiometric excess; we assumed that the reaction proceeds via the formation of N_2 and CO_2.

In this section, we describe the equipment used, the composition of the waste, and the preparation of the sucrose-containing simulated LAW.

7.1.1 Description of Test Equipment and Experimental Approaches

For these studies, we used a Seiko (Model 320) TG and DTA instrument that simultaneously measures mass changes (TG) and relative, to an inert material, temperature changes (DTA) as the sample temperature is increased at a known and controlled heating ramp (1°C/min) in flowing nitrogen (150 mL/min). Initial plans were to heat at 5°C/min; however, when testing at 5°C/min, several samples underwent very rapid reactions, ejecting sample material from the sample pan.

Samples were run for the most part in an inert purge to simulate the anaerobic conditions that should exist in the waste as it is molten and being vitrified. Two TG experiments were run to assess the impact of oxygen on the weight loss of the sucrose/simulant mixtures.

This report presents the results of the TG analyses as both the mass change and the mass change rate (differential thermal gravimetric analysis [DTG]). If a mass change occurs simultaneously with a reaction that produces or requires heat, the DTG provides a directly comparable presentation to that of the DTA, thus allowing an easier correlation between types of reactions. The DTA provides information on whether the reaction is heat-producing (exothermic) or requires heat (endothermic). The DTA can also be used for quantifying the heat required for an endothermic reaction or the exothermic heat produced. The latter is complicated for gas-producing reactions because the portion of the reaction heat contained within the gaseous products is swept away by the flowing gas and not seen by the instrument.

To produce enough reacted sample for residual nitrate and nitrite analyses, we heated 0.1 g of the test samples to 400°C in sealed stainless steel or titanium containers that had been purged with nitrogen. These samples were leached using several treatments of deionized water (DIW) and analyzed using ion chromatography (IC) to measure residual anions. The residual gases in the sealed containers were identified by infrared (IR) spectroscopy on a Nicolet 750 infrared spectrophotometer using a gas cell fitted with NaCl windows. Some of the residual solids were examined by X-ray diffraction on a Scintag (PAD III) X-ray diffractometer (XRD).

7.1.2 Preparation of Test Samples

Sucrose was added to the supplied simulated waste described in Section 4.0 (Table 4.1) at a schedule providing a 2% stoichiometric excess, an 11.6% stoichiometric excess, and a 21.7% stoichiometric excess to convert the nitrate and nitrite to gases. Based on the work of Smith et al. (1999), the stoichiometry of the reaction used to prepare the sucrose/simulant mixtures was assumed to produce N_2, CO_2, and CO gas as the only gaseous products per the reactions:

$$C_{12}H_{22}O_{11} + 8NaNO_3 + 2NaOH = 4N_{2(g)} + 6CO_{2(g)} + 4CO_{(g)} + 12H_2O_{(g)} + 2Na_2CO_3 + 3Na_2O \quad (7.1)$$

$$C_{12}H_{22}O_{11} + 14NaNO_2 + 2NaOH = 7N_{2(g)} + 9CO_{2\,(g)} + 3CO_{\,(g)} + 12H_2O_{(g)} + 8Na_2O \quad (7.2)$$

Table 7.1 lists the amount of sucrose added to each of four 25-mL stock simulant solutions. Freeze drying was used to remove the water to provide uniformity in the stock sucrose-simulant samples and to ensure that no or minimal denitration occurred as water was removed.

Table 7.1. Recipe for Preparation of Sucrose-Doped Simulated Hanford LAW

Test Material	Volume (mL)	Sucrose (grams)	Freeze Dried Mass, (grams)	Initial Color	Final Color
Simulant	25.00	0	9.4968	yellow	yellow
2% Stoichiometric Excess	25.00	2.78	12.2722	yellow	green
11.6% Stoichiometric Excess	25.00	3.04	12.5408	yellow	green
21.7% Stoichiometric Excess	25.00	3.32	12.8199	yellow	green

Upon completion of two 24-h freeze-dry cycles, the solid solutions were bright yellow in color. Over a 3-day period, the sucrose-doped solids discolored and finally turned dark green as shown in Figure 7.1. A potential explanation for this is the reduction of chromate to chromium oxide, and the reaction may have been photochemically initiated. The pure simulant remained bright yellow for several months. The dried solid solutions were stored in a desiccator, under a dynamic vacuum, over the course of their use.

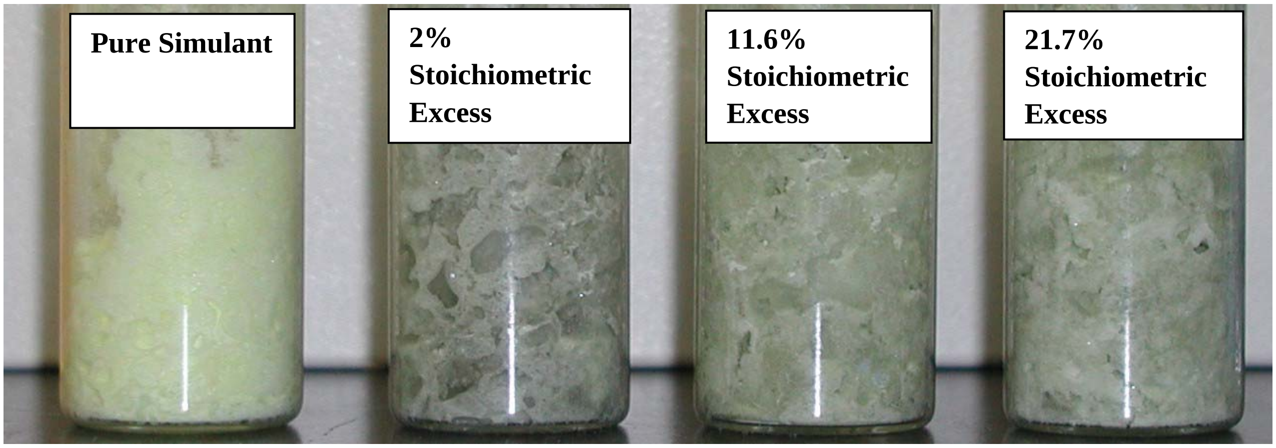

Figure 7.1. Freeze-Dried Simulant After Three Days

To ensure that we had sufficient mass to determine the residual nitrate and nitrite, residual samples were prepared by heating in a sealed system using stainless steel containers purged with nitrogen gas. Mass loss in these preparations was measured and, to gain some insight into the reaction pathway, residual gases were analyzed by infrared spectrometry after collecting the gas sample. The vessels were weighed again after release of the off-gases. Additional four sealed containers were charged with an approximately 0.1 to 0.5-g sample and were heated to 400°C in an oven at 40°C/min. Three of these experiments were repeated at 1°C/min. Several IR spectra of the off-gases from the eleven (total) sealed container experiments were obtained. These helped to qualitatively identify the product distribution at 400°C. The powder residues from the bomb experiments were rerun in triplicate by TG in air to observe any residual heat release.

The residual nitrate and nitrite concentrations were determined using IC after leaching the cooled powdered residue several times with deionized water. The residues did not dissolve completely. The X-ray diffraction analysis of the dried, leached residues provided no useful information concerning their identity; presumably, the powders were amorphous.

7.2 Results and Discussion

This section presents and discusses previous studies that investigated denitration of wastes and reaction of organics with nitrates and nitrites and provides the results of our studies on the sucrose-denitration of simulated Hanford LAW.

7.2.1 Historical Studies of Sucrose Denitration and Organic-Nitrate/Nitrite Reactions

Sucrose denitration of radioactive wastes has been considered for denitrating tank wastes in the DOE complex. Hanford's Plutonium-Uranium Extraction (PUREX) plant used sugar denitration of its acidic high level wastes based on Bray's (1963) study, which found that the reaction between sucrose and nitrate/nitrite was controllable and effective. Later Eaton's (1995) and Smith's (Smith et al. 1999) studies indicate that sucrose offers promise as a thermal denitrating agent for high-pH salt wastes.

Other related studies, such as those of Beitel (1976a; 1976b; 1976c; 1977), Turner and Miron (1994), and Scheele et al. (1995), investigated the thermal reactivity and sensitivity of reactions between nitrate and nitrite with carbon and various organic complexant salts. These studies were performed to support thermal hazard evaluations of mixed organic and nitrate/nitrite wastes.

7.2.1.1 Stoichiometry and Product Distribution of Sucrose/Alkaline Simulant Mixtures

The reaction between nitrate and nitrite with sucrose is complex and can follow a number of different pathways. An optimum sucrose reduction of nitrate in caustic waste can be written as:

$$5C_{12}H_{22}O_{11} + 48NaNO_3 + 72NaOH \rightarrow 60Na_2CO_{3(s)} + 24N_{2(g)} + 91H_2O_{(g)} \qquad (7.3)$$

Smith et al. (1999) found that this product distribution usually did not occur because NO_x, CO, CO_2, and small amounts of hydrogen gas are released from the reacting melt, indicating incomplete reduction of the nitrate/nitrite nitrogen and incomplete oxidation of the sucrose carbon. Factors causing sucrose reactions with nitrate to have product distributions that are incongruous with Equation (7.3) include the physical nature of the sample or operational parameters. One can write chemical equations that provide insight to this complex behavior by increasing the nitrate concentration relative to the amount of sucrose. Typical product distributions with increasing nitrate and are shown in Equations (7.4a-c) (Smith et al. 1999). A comparison of product distributions measured by Smith to those described by Equations (7.4a-c) supports incomplete oxidation of sucrose and reduction of nitrate/nitrite. In practice, hot spots occur in the sample, which could result in direct thermal decomposition of nitrate (Smith et al. 1999) into NO_x and Na_2O or in inefficient conversion of nitrate to nitrogen gas. Equation (7.4a) more closely represents the observed product distribution than that shown in Equation (7.3). This stoichiometry was chosen as representative to prepare the sucrose/simulant mixtures.

$$C_{12}H_{22}O_{11} + 8NaNO_3 + 2NaOH \rightarrow 4N_{2g} + 6CO_{2g} + 4CO_g + 12H_2O_g + 2Na_2CO_3 + 3Na_2O \qquad (7.4a)$$

$$C_{12}H_{22}O_{11} + 10NaNO_3 + 2NaOH \rightarrow 4N_{2g} + 9CO_{2g} + 12H_2O_g + N_2O_g + 3Na_2CO_3 + 3Na_2O \qquad (7.4b)$$

$$C_{12}H_{22}O_{11} + 12NaNO_3 + 2NaOH \rightarrow 5/2N_{2g} + 9CO_{2g} + 12H_2O_g + N_2O_g + 5NO_g + 3Na_2CO_3 + 4Na_2O \qquad (7.4c)$$

7.2.1.2 Reactivity of Organic/Waste Mixtures

When considering any process that involves the exothermic reaction of a strong oxidant such as nitrate or nitrite with an organic reductant, such as denitration with sucrose, the process designer must consider the thermal reactivity hazards of the process. Factors to be considered are energy density (J/g), the reaction rates and mechanisms, the amount of gas produced, the thermal conductivity of the system, the heat absorption capacity of the mixture constituents, and other interdependent chemical and physical parameters.

The American Institute of Chemical Engineers (AICHE) provides both general guidance and detailed strategies for assessing processes or chemical mixtures for potential chemical reactivity hazards (Heemskerk et al. 1995). AICHE's general guidelines provide an approach to assess thermal hazards principally based on energy density. These guidelines are as follows:

1. A chemical system has the potential to be a thermal reactivity hazard if the experimental enthalpy of decomposition is -200 to -300 J/g (-50 to -70 cal/g); the risk is dependent on operational parameters such as heating rate.
2. A substance is capable of deflagration if its exothermic enthalpy of decomposition is greater (exothermic sense) than -1000 J/g (-250 cal/g).
3. A substance is capable of detonation if its exothermic enthalpy of decomposition is greater (exothermic sense) than -3000 J/g (-700 cal/g).

If the hazard screen identifies a potential hazard, AIChE suggests approaches including using thermoanalytical methods such as DTA, DSC, TG, and accelerating rate calorimetry (ARC) to identify reaction onset temperatures, enthalpies, and other factors that control the reactivity. For additional discussion, see Scheele et. al. (1995).

Because the amount of energy generated per gram of sucrose is similar to that from elemental carbon, Beitel, in his studies investigating the thermal reactivity of mixtures of organics and $NaNO_3$ and $NaNO_2$ (Beitel 1976a; 1976b; 1976c; 1977) often used charcoal as a surrogate for the organics of interest. In these studies, he found that mixtures of nitrate and charcoal produce enough energy for self-sustaining reactions near 550°C.

$$5C + 4NaNO_3 \rightarrow 2Na_2CO_{3s} + 2N_{2g} + 3CO_{2g} - 1572\ \text{kJ} \tag{7.5}$$

Beitel (1976a; 1976b; 1976c; 1977) investigated the reactivity of nitrate hydrocarbon fuel mixtures (including sugar) that ranged from fuel rich to fuel poor. Key findings from these were as follows:

1. Below 380°C, combustion did not occur with varying sucrose-to-nitrate ratio.
2. For mixtures containing 20% moisture or greater, combustion did not occur.
3. For nitrate/fuel mixtures with greater than 95% or less than 35% nitrate, combustion did not occur.
4. For nitrate/fuel mixtures between 60 and 85% nitrate, rapid burning was observed.
5. 95% nitrate/fuel mixtures reacted explosively above 400°C if the organic was liquid or volatile.

Several of his observations are relevant to denitration of the Rassat-recipe simulant. His first observation indicates that for the sucrose/nitrate mixture to combust, the mixture must be above 380°C under his test conditions. With respect to his second observation, our freeze-dried Rassat simulant contained only waters of hydration, and thus a water content well below the 20% moisture criteria was required to prevent combustion. The simulant with its 70 wt% nitrate content and its >35% and <95% nitrate/fuel content after adding sucrose could combust based on his second and third findings. Although not presented yet, we observed a caramel-like liquid after heating sucrose and sucrose/LAW mixtures above 200°C in nitrogen, and so based on his fifth finding, our sucrose/LAW mixtures could be susceptible to rapid reactions.

Our earlier studies (Scheele et al. 1996) using DSC, TG, and ARC to investigate the reactivity of 2, 6, and 10 wt% total organic carbon (TOC) mixtures of Hanford complexants such as acetate, citrate, and EDTA and nitrate and/or nitrite, found that:

- onset temperature for self-sustaining reactions began as low as 175°C

- onset temperature was dependent on TOC content
- reactivity was dependent on the nature of the organic with simpler molecules being more thermally sensitive
- endothermic reactions such as melting of sodium nitrate will stop or slow reactions
- reactions are complex.

With respect to sucrose denitration of Hanford LAW, our earlier investigations suggest that the sucrose-containing LAW should support self-sustaining reactions under adiabatic conditions. The complexity of the sucrose should mitigate a reactivity hazard.

7.2.2 Thermal Behavior/Reactivity of Sucrose and Simulated Waste

To understand and distinguish thermally induced reactions between sucrose and simulated waste, we used TG and DTA to investigate the thermal behavior of 1) sucrose, 2) the Rassat-simulated waste, and 3) three sucrose-doped simulated LAW mixtures.

7.2.2.1 Thermal Behavior of Sucrose

As sucrose is heated in nitrogen, the only thermally induced reactions should be melting and thermal decomposition, both endothermic reactions. Figure 7.2 shows a TG curve for the decomposition of pure sucrose under a nitrogen flow. The solid melts at 186°C and nearly simultaneously decomposes. The endothermic melting and decomposition reactions are indicated by the downward signature in the DTA curve. The greatest weight loss occurred near 200°C and continued to about 500°C. Within this temperature range, a dark brown caramel formed in significant yield. This liquid is stable under a nitrogen purge and tends to creep along surfaces at temperatures lower than 300°C and evaporates to approximately 75 wt% loss at 730°C. Complete mass loss of all sucrose degradation products was observed only for temperatures exceeding 900°C. As expected for combustion of an organic, burning the liquid caramel decomposition product in air was exothermic; the TG instrument thermocouples recorded combustion temperatures exceeding 1000°C when burned in air.

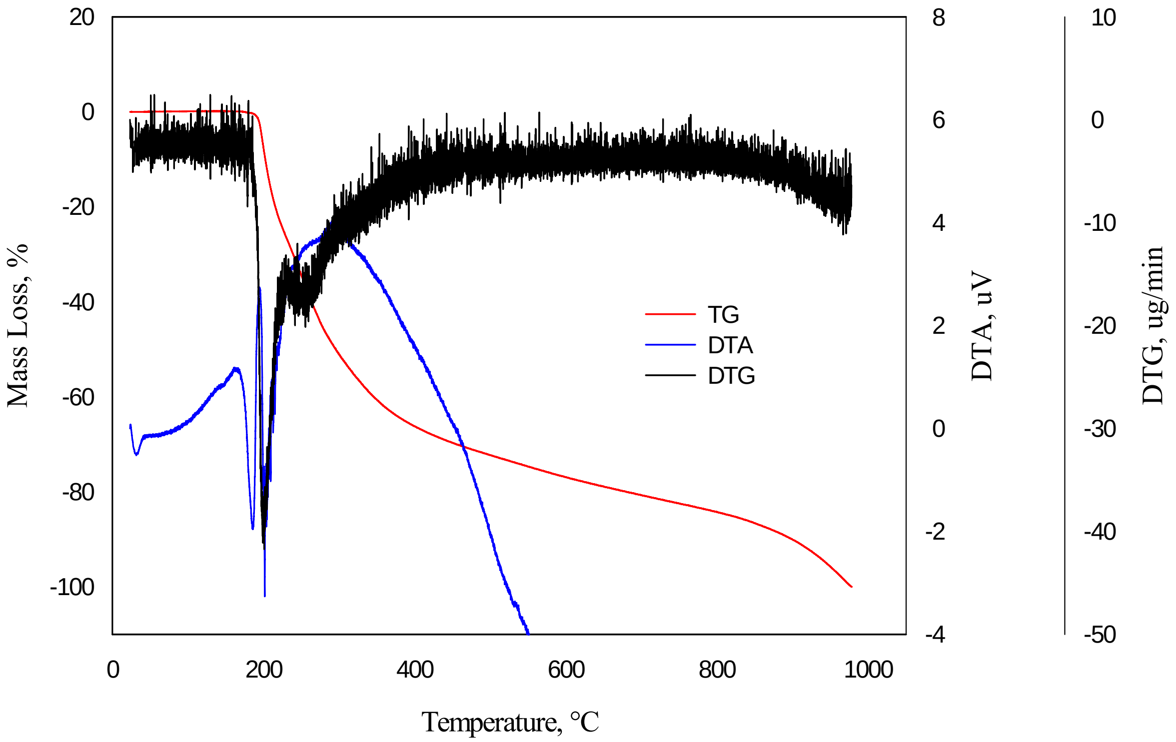

Figure 7.2. Thermal Decomposition of Sucrose as Measured by TG and DTA

7.2.2.2 Thermal Behavior of Pure Simulant

In the six-tank composite simulant given in Table 4.1, we expect endothermic melting reactions, endothermic thermal decompositions such as the dehydration of hydrates, and endothermic thermal decompositions such as decomposition of sodium carbonate, and exothermic reactions between the organic salts sodium oxalate and acetate and the nitrate and nitrite, as we saw in earlier work (Scheele et al. 1995; Wahl et al. 1996). The thermal behavior will thus be a complex combination of endothermic thermal decompositions and thermally induced exothermic reactions.

The conditions and results from four TG analyses of the simulant are reported in Table 7.2. Figure 7.3 shows a representative TG curve for the combination of decompositions and thermochemical reactions between organics and nitrate/nitrite The weight loss between 25°C and 50°C is postulated to be mostly loss of physisorbed water (see Appendix A). Potential decompositions include those of $Al(NO_3)_3.9H_2O$, which could occur between 74 and 150°C, and $Na_3PO_4.12H_2O$ (100°C); this combined 3.5 wt% loss was not observed; the absence of these losses may be explained by the formation of aluminum hydroxide or the efficiency of our freeze-drying. Thermal loss of waters of hydration in the reacting metal salt mixture or decomposition of hydrous oxides (NaOH) typically requires temperatures exceeding 100°C for the hydrates and 400°C for hydroxides.

Table 7.2. Thermogravimetric Testing Parameters for Rassat Simulated Hanford LAW

Sucrose/Simulant Composition	Atmosphere @150 mL/min	Ramp Rate, °C/min	% Wt loss from 50 to 500°C
Simulant	N_2	1	4.080
Simulant	N_2	1	3.757
Simulant	N_2	1	5.792
Avg			4.43
StdDev			1.18

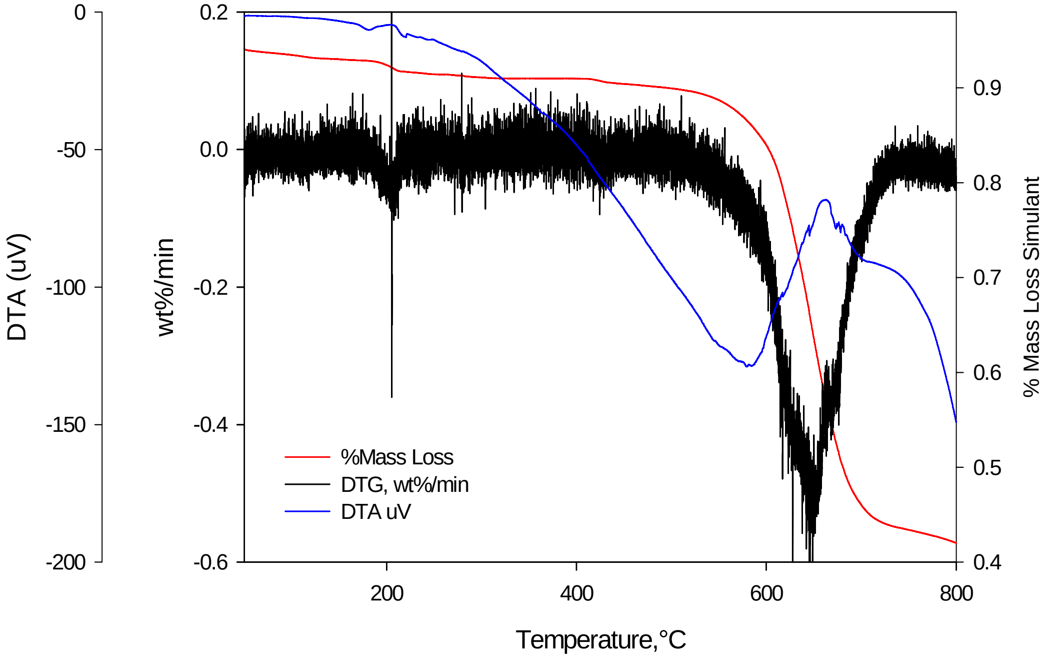

Figure 7.3. Thermal Behavior of Rassat Simulated Hanford LAW as Measured by TG and DTA

The slight mass losses between 50 and 500°C are likely partially due to gradual release of the water. Further, the lack of a distinct (peak) endothermic DTA signal for this water loss is consistent with evaporative loss from the heated mix rather than discrete loss events, as occurs for pure compounds and hydrates.

Other expected low-temperature reactions below 500°C include the reaction of sodium acetate and sodium oxalate with sodium nitrite and nitrate (Scheele et al. 1995; Wahl et al. 1996). The DTA measured a small exotherm, and the TG observed a mass loss near 200°C, which is consistent with nitrate or nitrite reaction with organics such as these. The expected mass loss from the pure simulant due to acetate and oxalate reaction with nitrate and/or nitrite is about 2.5%. The measured mass loss for three trials for this event was 3.1±0.6%.

Consistent with the behavior of sodium nitrate reported by Scheele et al. (1995), the TG and DTG curves indicate onset of the nitrate loss near 500°C, and this continued to about 730°C. The total mass loss from 50 to 730°C averaged as 52.4±1.7 wt%.

7.2.2.3 Sucrose Thermal Denitration of Simulated Hanford LAW

To test sucrose as a denitrating agent for Hanford LAW, we tested a variety of sucrose/simulant mixtures having 2%, 10%, and 20% excesses of sucrose. We assumed the reaction stoichiometries provided in Equations (7.1) and (7.2), which were based on Smith's (Smith et al. 1999) reported stoichiometry adjusted for the presence of sodium hydroxide. We used TG, DTA, and a sealed-container approach to determine the thermal behavior of these mixtures.

Thermogravimetric Testing Results. The conditions and results from TG studies of the sucrose-doped simulants are reported in Table 7.3. Assuming the stoichiometries of Equations (7.1) and (7.2), the predicted mass losses for the tested near-stoichiometric, 10% excess, and 20% excess mixtures are 38.5, 37.6, and 36.8%, respectively. In comparison, we measured between 100 and 400°C an average 32 ±8 wt% loss for the near-stoichiometric mix (2% excess), 42±4 wt% loss for the 12% excess mix, and 42±5 wt% loss for the 22% excess mix; the variability is at the 95% confidence level. Aiding in identifying the 100 to 400°C reaction range as the temperature range for sucrose denitration was based on the corresponding exothermic reaction observed by the DTA.

Although the predicted losses lie within the 95% confidence intervals of the measured losses, there is not absolute coincidence. This is not surprising given the number of potential reaction pathways with the potential formation of sodium carbonate or loss of CO_2 and the volatilization of the sucrose itself. For example, the 12 and 22% excess sucrose mixtures lost more than predicted, which could suggest that rather than reacting to form Na_2CO_3, some CO_2 left the mixture.

The TG results indicate that complete denitration can be achieved with excess sucrose. The results for the 2-wt% excess mixture indicate that complete denitration is nearly achieved, assuming the reaction path is via Equations (7.1) and (7.2). Most of the experiments with 2 wt% excess indicate very nearly complete denitration.

Figure 7.4 shows representative TG curves for the thermal behavior of the three sucrose/simulant mixtures. As can be seen by comparing Figure 7.4 with Figure 7.3, denitration begins at 180°C with sucrose present, compared to 500°C for the pure simulant; the exception being that some denitration occurs as a result of the acetate and oxalate in the simulant itself. These results indicate that sucrose effectively reduces the thermal denitration onset. It is valuable to note that the reduction reaction begins shortly after sucrose melts and begins to decompose; see Figure 7.2.

Figure 7.4 shows that qualitatively, the 2%, 11.6%, and 21.7% stoichiometric excess sucrose mixtures exhibit the same reaction profile, indicating that sucrose concentration does not affect the reaction mechanism with the denitration reaction complete by 400°C when the mixture is heated at 1°C/min. In addition, Figure 7.4 shows that the reaction between sucrose and the nitrate and nitrite in the LAW proceeds via a complex reaction mechanism as well illustrated by the DTG curve (the DTG curve has been smoothed for purposes of clarity).

Table 7.3. Results of TG Testing of Sucrose/Simulated Hanford LAW

Sucrose/Simulant Composition	Atmosphere (150 mL/min)	Heat Rate (°C/min)	Mass loss from 100 to 400°C (wt%)	Mass loss from 100 to 500°C (wt%)	Mass loss from 100 to 600°C (wt%)	Mass loss from 100 to 730°C (wt%)
2% Stoichiometric Excess	N_2	1	36.59	38.9	40.3	48.4
2% Stoichiometric Excess	N_2	1	34.68	35.14	35.47	35.75
2% Stoichiometric Excess	N_2	1	25.62	26.12	27.31	NA
2% Stoichiometric Excess	N_2	1	32.32	33.18	33.59	33.81
Avg			32.3	33.3	34.17	38.07
StdDev			4.78	5.37	5.37	5.77
11.6% Stoichiometric Excess	N_2	1	44.27	45.34	45.61	45.74
11.6% Stoichiometric Excess	N_2	1	42.95	43.93	44.15	44.33
11.6% Stoichiometric Excess	N_2	1	43.39	45.73	NA	NA
11.6% Stoichiometric Excess	N_2	1	39.00	40.38	41.76	NA
11.6% stoichiometric excess	N_2	1	36.24	37.50	39.052	39.24
Avg			41.17	42.58	44.88	45.03
StdDev			3.41	3.53	2.87	3.41
21.7% Stoichiometric Excess	N_2	1	43.92	45.02	45.32	45.53
21.7% Stoichiometric Excess	N_2	1	47.35	48.53	48.745	48.97
21.7% Stoichiometric Excess	N_2	1	44.562	47.087	NA	NA
21.7% Stoichiometric Excess	N_2	1	37.87	39.50	41.54	43.2056
21.7% Stoichiometric Excess	N_2	1	37.52	39.11	40.95	41.46
Avg			42.24	43.85	44.14	44.79
StdDev			4.35	4.30	3.62	3.24
21.7% Stoichiometric Excess	Air	1	34.85	35.16	37.65	46.50

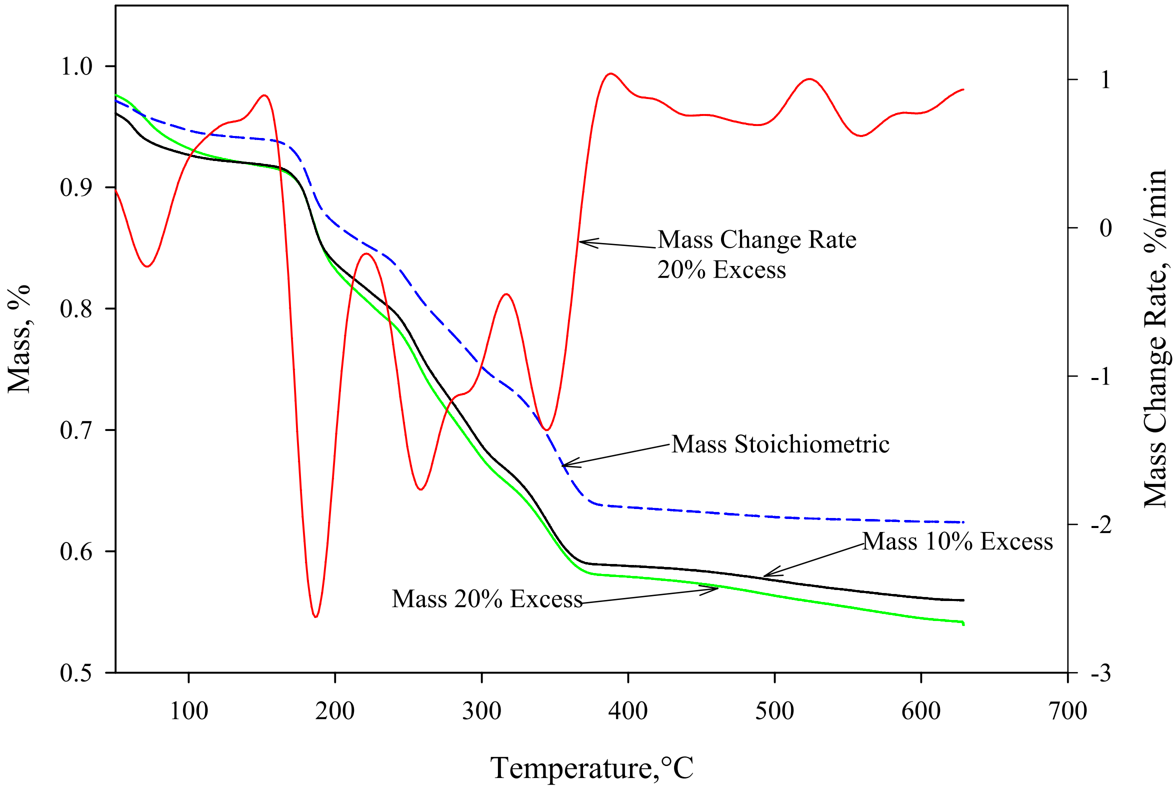

Figure 7.4. Thermal behavior of 2%, 11.6%, and 21.7% Sucrose Stoichiometric Excess Additions to Simulated Hanford LAW as Measured by TG

While resolving the denitration reaction(s) into their reaction pathways is beyond the scope of this work, we can speculate on the nature of each of the discrete steps observed for the sucrose LAW mixtures. The initial mass loss up to 100°C is caused by the evaporation of free water or waters of hydration in a salt such as $Al(NO_3)_3$. The second mass loss beginning at 180°C is near the melting point of sucrose and is likely is the first step of the reaction of sucrose or the acetate or oxalate with nitrate or nitrite; our past work (Scheele et al. 1995) with organic complexant and nitrate or nitrite reactions suggest that nitrite will react first. Options to gain more knowledge about the chemical mechanism would be to analyze the off-gases using IR or mass spectroscopy.

Although not important to our studies to determine the effectiveness of the sucrose denitration process, the chemical mechanism could affect the volatility of Tc. It is possible that if the denitration reaction produces oxides of nitrogen, they still contain enough oxidizing power to oxidize the Tc to volatile forms. By developing a process that produces N_2 rather than NO_x, one could prevent the formation of NO_x to the benefit of the goal to control Tc volatility.

The final experiment of the 21.7% excess sucrose mixture used an air purge with the expectation that the sucrose-nitrate reaction may be inhibited or the efficiency reduced by air oxidation of sucrose. The weight loss result for the single run was only slightly lower than the average of five TG trials of the

21.7% sucrose-doped simulant run under a nitrogen purge. A similar result was observed by Smith (Smith et al. 1999). This suggests that the efficiency of the sucrose denitration is not significantly impacted by the presence of air.

Several events occurred during our TG experiments that indicate the reaction(s) between sucrose and nitrate/nitrite can be very rapid and gassy. Thermal ejection of sample mass was observed near 180°C for >15-mg samples of the sucrose/simulant mixtures heated at >5°C/min. Additionally, upon quenching the reaction between 250 and 350°C, a brown viscous liquid formed. This liquid spattered with heat and tended to migrate out of the TG sample pan. Complete removal of the caramelized sucrose required heating the pure sucrose sample under oxygen. The reaction with oxygen was exothermic and resulted in rapid self-heating of the sample to temperatures exceeding 1000°C. The caramelized material was removed completely when reacted with nitrate in the sucrose/simulant mixtures.

In summary, our TG tests indicate that sucrose effectively denitrates the Rassat-recipe LAW. The results also indicate that excess sucrose greater than a 2% stoichiometric excess relative to Equations (7.1) and (7.2) are needed to completely denitrate the LAW in an open system. We also saw that performing sucrose denitration is not inhibited or prevented by doing the process in air, at least with a 20% sucrose excess.

Sealed Container Testing of Sucrose-Doped Simulated LAW. We discovered during the TG testing that in some samples the sucrose caramelized and coated the sample pan and its holder preventing removal of the sample pan without dissolving the caramel in water or burning the carbon in air. This prevented us from quantitatively recovering the residual material from the TG testing for nitrate and nitrite analysis for all samples.

To provide samples for residual nitrate and nitrite analysis, we heated 0.1 to 0.5 g samples of the three sucrose/simulant mixtures in a sealed container to 400°C based on TG results indicating completion of the sucrose denitration by 400°C. The residual samples were leached and analyzed using IC.

We also measured mass losses and analyzed the residual gases. The residual gases from the sealed container reactions were also identified by IR spectrometry.

Weight Loss and Residual Gas Composition. The weight-loss data and the identities of the residual off-gases as recorded from the four experiments are reported in Table 7.4. The mass losses for the reactions using 2%% stoichiometric and 11.6 stoichiometric excess sucrose were considerably lower than those measured in the TG experiment and the 38 wt% expected based on predicted reaction stoichiometry [see Equations (7.1) and (7.2)]. These results are not consistent with the residual nitrate and nitrite results that showed complete denitration for these samples. The mass-loss data from the sealed container testing, using 21.7% stoichiometric excess sucrose, were more similar to the TG results at 400°C.

The residual gases observed after this static closed test are affected by two processes and possibly a third. The first, of course, is the reaction mechanism, and the second is the reaction of the product gases with the product solids, which can include sucrose, sucrose fragments from incomplete reaction, or sucrose thermal decomposition products. For example, produced NO_2 or NO can react with residual excess sucrose, and they will disappear from the residual gases. A third possible mechanism exists where "hot spots" and poor mass transport within the static samples and poor mass transport produce areas that have low local sucrose concentration and cause the nitrate/nitrite to decompose to form volatile NO_x before additional sucrose is encountered to complete the reduction. Table 7.4 shows that the residual gas composition was markedly different at sucrose concentrations below the 21.7% stoichiometric excess sucrose mixture.

Table 7.4. Mass Change and Off-Gases from Sealed Container Testing

Sucrose/Simulant Composition	Initial/Final Sample Mass (grams)	Ramp, °C/min	Mass Loss, %	Residual-gases
2% Stoichiometric Excess	0.550/0.4356[a]	40	20.8	Large N_2O, NO_2, small CO_2, very little H_2O,CO, NO
11.6% Stoichiometric Excess	0.1501/0.1189	40	20.8	Large N_2O, NO_2, small CO_2. Very little H_2O,CO, NO
21.6% Stoichiometric Excess	0.1092//0.0693	40	36.5	Large CO_2, small N_2O very little CO, NO was absent
21.6% Stoichiometric Excess	0.0926/0.0579	40	37.5	Large CO_2, smaller N_2O, CO and NO were absent[a]

(a) The residual gases were expanded into the IR cell at 360°C

Figure 7.5 shows the IR spectra of the residual gases in progression from the stoichiometric to the excess sucrose mixtures. To better qualitatively address the CO_2 to N_2O ratio from the off-gas spectra, the regions that NO, NO_2, and water vapor appear are not shown; N_2 gas, the optimal product of the sucrose denitration reaction(s), is not observable by IR.

NO and NO_2 were clearly present in some samples as itemized in Table 7.4. The IR spectra of the off-gases indicate that the reaction by the 2% stoichiometric and 11.6% stoichiometric excess sucrose results predominantly in formation of N_2O, NO_2, and smaller amounts of NO and CO. The presence of these oxidizing gases in the residual gases indicates that the reaction does not proceed totally by the most desirable reaction, producing only N_2.

The reaction by the 21.7% stoichiometric sucrose resulted in the formation of predominantly CO_2 and smaller amounts of N_2O, which indicates that this excess sucrose concentration was a sufficient quantity to consume the NO and NO_2 formed in the initial stages of the reaction or that the NO and NO_2 reacted with the excess sucrose remaining after the denitration reaction.

The lack of water vapor in the residual-gas spectra in general might be caused by condensation of water vapor back onto the activated solids on cooling of the sample. In one experiment, the gases from the 21.7% stoichiometric excess sucrose reaction were expanded into the IR cell at 360°C. The presence of NO, NO_2, and water were still difficult to detect in the IR spectrum.

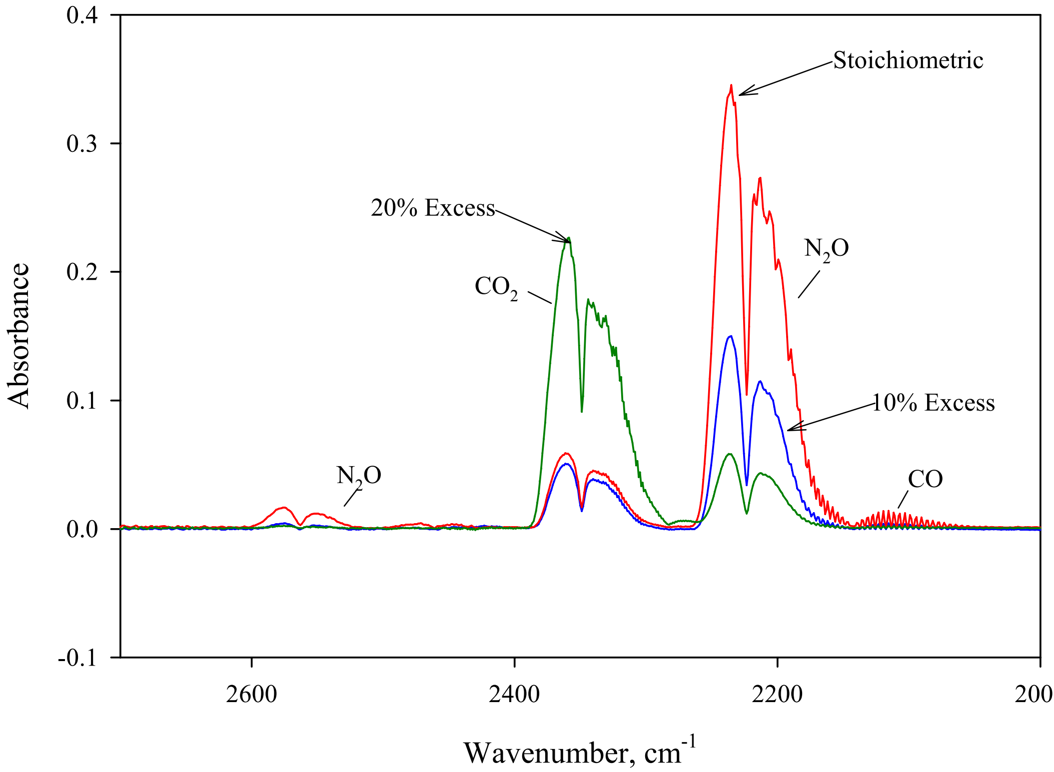

Figure 7.5. IR Spectra of Residual Gases from Sealed Container Tests for Stoichiometric, 10%, and 20% Stoichiometric Excess Sucrose and LAW Mixtures

The closed sealed container experimental mass loss data at high ramp rate and the IR data indicate that nitrate loss proceeds with evolution of NO_x and CO, even at fairly high ratios of sucrose to simulant. While nitric oxide and nitrogen dioxide are nonflammable gases, they will accelerate the burning of combustible materials. Potentially of greater importance is the potential for these strongly oxidizing gases to oxidize technetium to a more volatile species.

Residual Nitrate and Nitrite in LAW after Sucrose Treatment. To recover the residual nitrate and nitrite, the solid residues from each sealed container experiment were each leached three times in small volumes of deionized water. The combined leaches for each experiment were analyzed for anions by IC.

As shown in Table 7.5, sucrose effectively denitrated the simulated LAW. The sucrose denitration efficiencies ranged from 99.5 to 99.9% for nitrate and 92 to 100% for nitrite; the latter assumes that nitrite is not a product of the sucrose nitrate reaction. Table 7.5 also provides the chloride behavior, which, because of its not being affected by the thermal and chemical processes, provides a good reference behavior. When none of the analyte was observed, we assumed none present. Appendix B provides an analogous comparison for SO_4^{2-}, PO_4^{3-}, and $C_2O_4^{2-}$.

The oxalate data provided in Appendix B is interesting because it appears that high concentrations of sucrose suppressed the reaction of the simulant oxalate concentration to some extent. Alternatively, oxalate might be a product of the sucrose reaction with nitrate/nitrite.

Because chloride is stable in the caustic melt and not volatile near 400°C, its concentration was not altered in the sealed-container experiments, and it provides an indicator of treatment and leaching efficiency. The percent difference provides an indication of the scatter in the overall data set. This includes uncertainty in the known starting simulant composition. The assumption that the samples were initially prepared as homogeneous samples by the freeze-drying technique may not be completely valid as some of the final anions data returned with a concentration slightly higher than the initial value. The analytical data is for the most part consistent with some loss of product or speciation to insoluble or low solubility residual solid products.

Table 7.5. Effects of 400°C Thermal Treatment on Chloride, Nitrate, and Nitrite Content

Sucrose/Simulant Composition	**Cl^- Change, %**	**NO_3^- Change, %**	**NO_2^- Change, %**
2% Stoichiometric Excess	-6.33	-99.5	-98.6
2% Stoichiometric Excess	-1.21	-99.9	-100
2% Stoichiometric Excess	-2.25	-99.9	-95.5
11.6% Stoichiometric Excess	0.0	-99.9	-100
11.6% Stoichiometric Excess	-17.4	-99.8	-100
11.6% Stoichiometric Excess	-2.9	-99.8	-92.1
21.7% Stoichiometric Excess	-6.2	-99.9	-100
21.7% Stoichiometric Excess	-9.9	-99.8	-100

These experiments show that sucrose effectively denitrates a simulated Hanford LAW. Thus, this process offers promise denitrating Hanford LAWs.

Oven Testing of the Sucrose/Simulant Mixtures: The Effect of Heating Rate. The mass-loss data shown in Table 7.5 for the sealed-container experiments does not compare well with the TG mass-loss data shown in Table 7.3. This would suggest rather poor denitration in the sealed containers. However, the residual nitrate/nitrite analyses indicate complete or nearly complete denitration in these experiments. The outstanding experimental variable used for the first set of oven runs was the high ramp rate of the oven, and it is likely that the ramp rate was responsible for poor mass-transport properties in the samples. Indeed, as shown in Table 7.6 when the sucrose/simulant mixtures were rerun at both 40 and 1°C/min, the weight-loss performance improved to match the TG result, and the major observable off-gases by IR for the 21.7% mixture were again CO_2 and N_2O.

Based on Smith et al. (1999), who associated inefficient denitration with direct thermal decomposition of the nitrate by local hot spots in the sample, we suspect these results implicate fast ramp rates with inefficient reaction between sucrose and the simulant. The data in Table 7.5 and Table 7.6 are consistent with increasing conversion of all nitrate and nitrite to higher nitrogen gas yield by the use of low ramp rates and excess sucrose concentrations.

Table 7.6. Mass Change and Measured Off-Gases from Oven Testing

Sucrose/Simulant Composition	Initial/Final Sample Mass (grams)	Ramp, °C/min	% Weight Loss	Off-Gases by IR
2% Stoichiometric Excess	0.1065/0.0155	40	14.6	NM
2% Stoichiometric Excess	0.1792/0.0257	40	14.3	NM
11.6% Stoichiometric Excess	0.1110/0.0304	40	27.4	NM
11.6% Stoichiometric Excess	0.1150/0.0198	40	17.2	NM
2% Stoichiometric Excess	0.1132/0.0365	1	32.2	CO_2, N_2O, NO_2, CO
11.6% Stoichiometric Excess	0.1534/0.0775	1	49.5	CO_2, N_2O, CO
21.7% Stoichiometric Excess	0.0798/0.0384	1	48.1	CO_2, N_2O

We recovered 77.5 mg of powdered residues from the reaction of the 11.6% stoichiometric excess sealed container test for TG/DTA. These had previously been run at a ramp of 1°C/min to 400°C in a sealed container to determine if any exothermic reactions could be induced because of the excess sucrose . These residues were dark brown, soft powders. The XRD powder patterns of the residues were nearly featureless, implying the presence of fairly amorphous reaction products.

We analyzed the powders in triplicate on the TGA/DTA to 1000°C. The results are presented in Table 7.7. The heat release from the three samples was similar to that described for Exotherm I near 180°C for the 11.6% sucrose/simulant mixture. Because the mass and heat loss were the same for different mass samples, the data are most consistent with the presence of unreacted or partially decomposed sucrose reaction products near 400°C. These data are also consistent with the decomposition curve for pure sucrose. From Figure 7.2, about 30 wt% residual mass remained on thermal decomposition of the pure sucrose at 400°C.

The enthalpy of the residual sucrose/waste reaction product on the powder was an average endothermic 532 J/g or 0.13 kcal/g of sucrose/simulant mixture (see Table 7.7). The reaction was endothermic, which indicates that subsequent to the denitration reaction, there should be little possibility of heat release from residual organic compounds (from excess sucrose).

Table 7.7. Mass Loss and Enthalpy from Residues from 11.7% Excess Sucrose Sealed Container Tests

Sucrose/Simulant Composition	Initial Sample Mass, mg	Ramp, °C/min	% Weight Loss	Energy J/g	Average (StdDev) J/g
11.7% Stoichiometric Excess	5.562	1	27.2	519	532 (11)
11.7% Stoichiometric Excess	9.237	1	27.3	535	
11.7% Stoichiometric Excess	8.747	1	27.3	541	

DTA Results. As mentioned earlier, the DTA assisted in identifying the sucrose reaction onset through its observation of exothermicity. The DTA also can be used with proper calibration to measure energetics or reaction heats. Because it is an open system where the product gases are swept away with their latent heat from an exothermic reaction, DTA will under-measure exothermic reaction heats for gas-producing reactions (Scheele et al. 1995; Wahl et al. 1996).

Recognizing the limitations of this calorimetric method for the exothermic gas-producing sucrose denitration of LAW, we analyzed the obtained data resulting from our simultaneous TG/DTA experiments to obtain an order of magnitude estimate of the reaction heat (ΔH). In this testing, the measured reaction heats were nevertheless reproducible.

The heats released during several thermochemical denitration reactions run at a temperature ramp rate of 1°C/min are listed in Table 7.8 for the three ratios of sucrose/simulant mixtures used. As shown in Figure 7.6, four exothermic reactions occur between 125 and 400°C with each exotherm corresponding to a significant mass loss as evidenced by the DTG. In contrast, Smith et al. (1999) observed only two exotherms producing about 1 kJ/g of 80% sodium nitrate-containing simulated waste. We have no explanation for the difference in observed reaction steps other than our test material has much more nitrite.

Inspection of Figure 7.6 finds no obvious endotherms as would be expected for the decomposition of sucrose (~200°C) or the melting of sodium nitrate (308°C) or the melt of the mixed sodium nitrate/nitrite (200 to 308°C, depending on the nitrate/nitrite ratio). A possible explanation for the absence of observed endothermic behavior may be that because the reaction between the oxidant and the fuel occurs simultaneously with melting; we have observed this behavior in past studies. Alternatively, the compound itself no longer exists by the time the pure compound melts. If endothermic events occur simultaneously with exothermic events, the endothermic or exothermic event can be masked. In any event, the measured enthalpy will be lower than actual.

Table 7.8. Heat Release for Sucrose/Simulant Reactions as Measured by DTA at 1°C/min

Sucrose/Simulant Composition	Exotherm I Peak Temp, C	Enthalpy J/g_{sample}	Mean (StdDev) J/g_{sample}	Exotherm II Peak Temp, C	Enthalpy J/g_{sample}	Mean (StdDev) J/g_{sample}	Exotherm III Peak Temp, C	Enthalpy J/g_{sample}	Mean (StdDev) J/g_{sample}
2% Stoichiometric Excess	179	-530	-560 (30)	250	-1200	-860 (300)	365	-730	-1100 (410)
2% Stoichiometric Excess	173	-590		241	-730		340	1400	
2% Stoichiometric Excess	179	-560		252	-640		345	1050	
11.6% Stoichiometric Excess	181	-600	-580 (25)	253	-500	-550 (50)	350	520	-970 (400)
11.6% Stoichiometric Excess	170	-550		251	-510		350	1300	
11.6% Stoichiometric Excess	178	-580		252	-590		358	1100	
21.68% Stoichiometric Excess	179	-880	-770 (120)	253	-360	-450 (80)	362	720	-880 (200)
21.68% Stoichiometric Excess	181	-650		253	-500		360	810	
21.68% Stoichiometric Excess	179	-780		251	-480		362	1100	

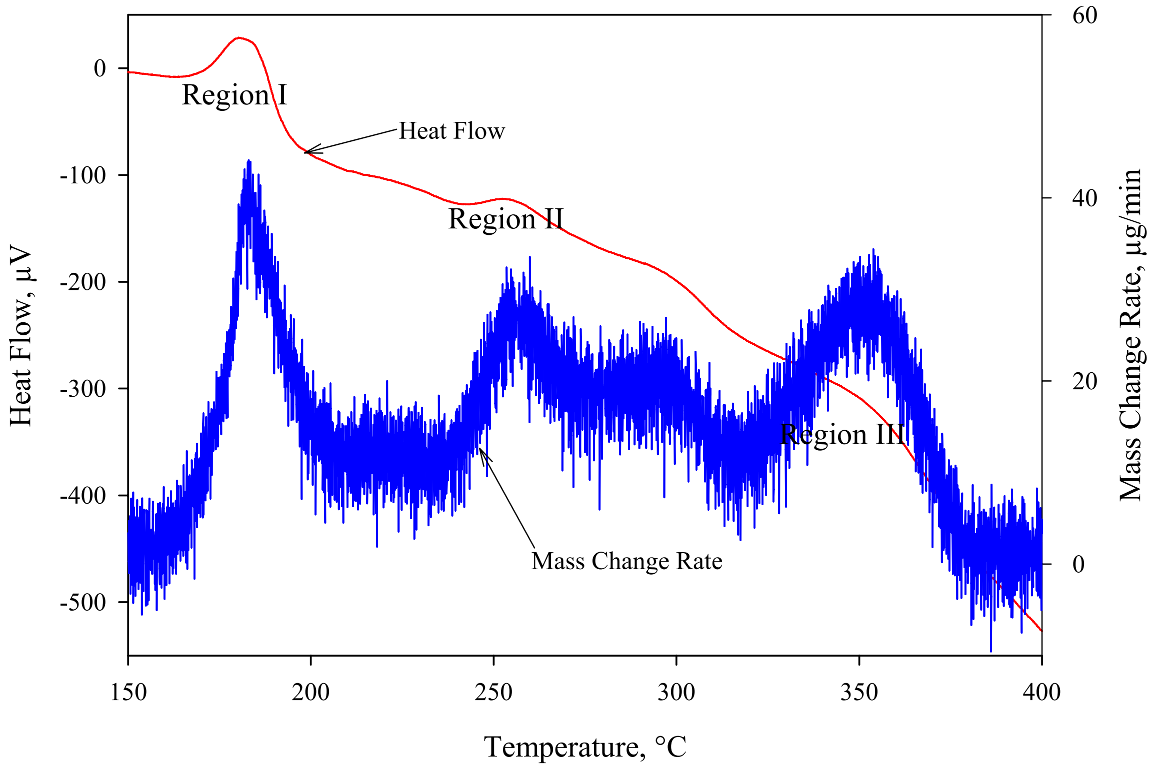

Figure 7.6. DTA (enthalpy) and DTG (weight loss) of a 21.7% Sucrose/Simulant Mixture

The peak positions of the exotherms reported in Table 7.8 were measured by taking the derivative of the DTA curve and selecting the zero crossing position. The magnitude and the often large uncertainty of the measured heat data are similar to Smith's (Smith et al. 1999) thermochemical denitration heats determined by calorimetric methods.

As shown in Figure 7.6, the first event (Region I) between 160 and 190°C released between -500 to -900 J/g sample. The measured heat release was somewhat reproducible and appeared to increase slightly with the amount of sucrose added. This indicates that the reaction between sucrose and nitrate and/or nitrite begins at 160°C. The apparent influence of sucrose concentration on the reaction enthalpy suggests that at the lower concentrations, there is insufficient sucrose for the first stage of the reaction to complete; given the tentative nature of DTA measurement of exothermic reactions, this is very speculative conjecture.

The second region (Region II) displayed two exotherms between 200 and 250°C that were difficult to resolve from sample to sample. The measured heat-release data were quite variable and showed no correlation to the amount of sucrose added. Using Smith's observation of only two exotherms in his sucrose denitration studies with his low nitrite (10^{-4} M) simulant with one corresponding to our designated Region I and Region III, we speculate that the nitrite reaction with sucrose may occur in Region II.

The third exotherm between 275 and 350°C was the largest, releasing between -500 and -1100 J/g of sample. The weight loss associated with this Region III exotherm was consistent with the denitration reaction. The liquid caramel product that formed by sucrose decomposition near 230°C was absent at 400°C.

For reference purposes, heats that range from -1000 to -1500 J/g may imply a low to medium potential for exothermic deflagration (Heemskeerk et al. 1995).

In summary, the DTA showed that the four distinct steps in the sucrose denitration of simulated Hanford LAW are exothermic with a total reaction enthalpy release exceeding -2 kJ/g sample. The nature of the reactions, whether nitrate or nitrite or whether succeeding steps are dependent on earlier steps, is unknown and would require additional investigations to identify the gases and/or solid products.

7.3 Summary

In support of PNNL efforts to develop an effective approach to reduce technetium volatilization during BV process of Hanford's LAW, we investigated thermal sucrose denitration of a simulated Hanford LAW as a pretreatment step to reduce the thermal oxidizing potential of Hanford wastes during vitrification. To investigate thermal sucrose denitration, we used the thermoanalytical methods TG, DTA, and nitrate/nitrite analysis of residual solids to determine the effects of temperature and sucrose concentration on the efficiency of thermal sucrose denitration of a simulated Hanford LAW. It is hoped that removing the highly oxidizing nitrate and nitrite from the waste will prevent or significantly reduce technetium volatilization during vitrification.

In these studies, we investigated sucrose contents at near-stoichiometric, at a 10% stoichiometric excess, and a 20% stoichiometric excess, assuming stoichiometries (Smith et al. 1999) for nitrate and nitrite as given by Equations (7.1) and (7.2).

Our TG/DTA studies using a flowing nitrogen atmosphere show that sucrose denitration is a complex set of reactions requiring at least four exothermic reaction steps to achieve complete denitration by 400°C. The denitration produces multiple nitrogen products including N_2O, NO, NO_2, and we suspect N_2 and carbon products of CO, CO_2, and we also suspect Na_2CO_3. Some of the testing suggests that the sucrose treatment level affects the nitrogen product distribution with lower nitrogen oxidation states resulting at higher sucrose treatments. Higher nitrogen oxidation states may maintain the technetium in a more volatile oxidation state; this may make the denitration pathway important.

Table 7.9 shows that denitration is effective when compared to the expected mass losses of 38.5, 37.6, and 36.8 wt% for the 2, 12, and 22 wt% excess sucrose. These results indicate that a 12% excess is required to achieve complete denitration; this assumes the stoichiometries presented in Equations (7.1) and (7.2), which are but two of a multitude of possible reaction paths. In contrast, the nitrate and nitrite analyses of the residual solids arising from closed container testing found nearly complete denitration with >99.5% destruction for all tested sucrose treatment levels.

Table 7.9. % Mass Loss on Thermal Reaction of Sucrose/Simulant Mixtures

Composition, % Stoichiometric Excess	Average mass loss from 100 to 400°C, wt%	Average mass loss from 100 to 500°C, wt%	Average loss from 100 to 600°C, wt%	Average loss from 100 to 730°C, wt%
2%	32.3 (4.78)[(a)]	33.3 (5.37)	34.17 (5.37)	38.07 (5.77)
11.6%	41.17 (3.41)	42.58 (3.53)	44.88 (2.87)	45.03 (3.41)
21.7%	42.24 (4.35)	43.85 (4.30)	44.14 (3.62)	44.79 (3.24)

(a) Standard deviation of trials.

From an operational standpoint, we found that lower heating rates (1°C/min vs 5°C/min) were needed to prevent rapid gas releases that carried molten material from the experimental container. In some experiments, the sucrose formed a caramel-like material that crept out of its container. This organic was easily oxidized in air at elevated temperature.

Our measurement of order-of-magnitude reaction enthalpies for the different sucrose treatment levels using the DTA found average total reaction enthalpies ranging from 2.0 kJ/g to 2.5 kJ/g with the 10 and 20% stoichiometric excesses having the lower measured reaction enthalpy. It should be mentioned that the DTA typically under-measures exothermic reaction enthalpies because gases produced carry away reaction heat. The measurement of reaction enthalpies for these denitration reactions is complicated by the likely hidden occurrence of endothermic reactions such as melting.

The DTA-measured order-of-magnitude reaction heats are presented in Table 7.10. Both the magnitude and the uncertainty of the measured heat data are in accord with recent thermochemical denitration data reported by Smith et al. (1999). It should be noted that Heemskeerk et al. (1995) consider heats that range from -1000 to -1500 J/g a low to medium potential for exothermic deflagration.

Table 7.10. Heats of Release Related to Thermochemical Denitration of Sucrose/Simulant Mixtures

Sucrose/Simulant Composition Stoichiometric Excess	Exotherm I Mean Peak Temp, °C	Average Energy J/g_{sample}	Exotherm II Mean Peak Temp, °C	Average Energy J/g_{sample}	Exotherm III Mean Peak Temp, °C	Average Enthalpy J/g_{sample}
2%	179	-560 (30)	249	-860 (300)	350	-1100 (410)
11.6%	178	-580 (25)	252	-550 (50)	355	-970 (400)
21.68%	180	-770 (120)	253	-450 (80)	361	-880 (200)

7.4 Conclusions

Our studies investigating the thermal sucrose denitration of simulated Hanford LAW using TG/DTA and residual nitrate and nitrite analyses of 400°C closed system thermal tests indicate that Hanford LAW can be effectively denitrated at 400°C; TG/DTA typically provides onsets higher than are needed for isothermal success.

Other conclusions can also be drawn from our studies:

- The residual nitrate and nitrite analyses of the residual solids produced in a closed container show that sucrose very effectively denitrates simulated LAW (>99.5% destruction), converting the nitrate and nitrite to gaseous products.
- The TG analyses indicate that the effectiveness of sucrose improves with increasing sucrose content with a 10% excess needed to ensure complete denitration, assuming the reference reaction mechanism.
- The sucrose denitration reaction is complex, proceeding to completion via at least four steps.
- Our closed-container preparations suggest that sucrose concentration affects the denitration pathway with less NO_x observed with increasing sucrose; this conclusion is complicated by the potential back reaction of NO_x with residual sucrose or any remaining organic reaction products.
- The nitrogen in the waste is not necessarily converted to N_2; rather, N_2O, NO, and/or NO_2 can also be produced. The actual fate of the nitrate and nitrite nitrogen could affect the volatility of technetium with the oxidizing NO_x having a potential to maintain the Tc in its more volatile oxidation state.
- An organic caramel-like substance forms in the absence of oxygen; this substance is easily oxidized by air.
- Our closed container testing coupled with the TG testing suggests that the nature of the product nitrogen gases depends on gas sweep rate, thermal ramp rate, and possibly sample homogeneity.
- The heating rate affects the reaction rate with lower heating rates (1 vs 5°C/min) required to prevent splattering of LAW.

Our sucrose denitration studies showed that this process is an effective approach for removing nitrate and nitrite from Hanford wastes. Albeit the reaction mechanism itself is complex, requiring at least four steps to achieve complete denitration with production of N_2, N_2O, NO, and NO_2, we are supposing that N_2 forms because we did not analyze for it.

7.5 Recommendations

Although sucrose thermal denitration appears attractive, the reaction pathway, reaction energetics, the reaction rate, and selected operational parameters could be important operationally and with respect to achieving the ultimate goal of preventing/controlling technetium volatility. Controlling the reaction path to produce nitrogen products that are non-oxidizing or have low oxidizing potential could maintain technetium in a less-volatile oxidation state. Knowing the reaction energetics and kinetics would provide important information to design the process and equipment to accommodate heat produced, to prevent rapid thermal reactions, and to control the rate of off-gassing.

If denitration is chosen for further evaluation, the following suggested experiments should be pursued:

- Perform accelerating rate calorimetric (ARC) experiments to measure accurate heats of reaction over several compositional profiles, including nitrate/nitrite, light organic content, and ammonia,.
- Perform studies using TG/DTA and ARC that will determine reaction kinetics and verify that uncontrolled exothermic reactions will not occur. Include the effects of glass forming diluents that are part of the feed material that is added to the BV process.
- Characterize reaction off-gases from TG/DTA experiments to determine the effects of operational parameters, such as heating rate and sucrose concentration, on the nitrogen products. Studies could also investigate technetium volatility. Methods could include in-line IR, mass spectroscopy (MS), and gas chromatography.
- Characterize residual solids using such methods as x-ray diffraction spectrometry, IC to determine anions, and total organic carbon/total inorganic carbon (TOC/TIC) to identify solid products and for mass balance. XRD could identify and quantify mineral forms that may trap significant nitrate, such as cancrinite.
- Use a slower heating rate or isothermal TG/DTA tests to obtain a more accurate (lower) actual onset temperature for complete denitration.

8.0 Crucible Feed Melting Tests to Measure Glass Reduction and Tc Volatilization

This section describes the experimental methods and test results from feed melting reduction tests using sucrose and carbon. This section also describes the experimental methods and results from cold finger crucible melting tests conducted to investigate the behavior of Tc volatilization from the baseline feed and the feeds with reduction treatments, feed with no sulfate, and pre-melted glass.

8.1 Crucible Feed Melting Tests for Reduction of Nitrates by Sucrose and Carbon

The preliminary feed melting tests for glass reduction was performed to determine the concentration of reductants (sucrose and carbon) required to significantly reduce the oxidation potential of nitrates during melting and to understand the role of reductant on the feed/glass redox and phase evolution of nitrates and melting reaction products as a function of temperature during initial feed melting.

8.1.1 Experimental

The effect of reductant concentration on the reduction of nitrates and on the redox state of glass (or partially melted feed) during heating of dried feed was initially evaluated by crucible feed melting and iron redox measurements. The feed makeup to make 200 g glass shown in Table 8.1 was used in each test.

Table 8.1. Baseline Feed Makeup to Produce 200 g Glass

Simulant	234.35	mL	(Table 4.1)
HRTS soil (dried)	135.59	g	(Table 4.2)
ZrO_2	14.00	g	
B_2O_3	10.00	g	

The slurry feeds with varying addition of sucrose and carbon were dried according to the following procedure before testing in the crucible:

- Initially, the wet feed was dried by stirring the feed contained in a 4-L stainless steel beaker placed on a hot plate while Ar gas was introduced into the beaker close to the feed surface. This process continued until the feed became thick and dry enough to prevent segregation of salt phases during further drying
- The partially dried feed in the stainless steel beaker was transferred to the oven and kept at 85°C for 16 h (typically overnight) with Ar flowing.

Each dried feed was heated at 5°C/min, starting from 80°C to 800°C, and then air-quenched. The redox of iron was measured as an indication of the redox state of the partially melted feed. The result of this set of reduction tests was used for the Case 3 cold finger crucible feed melting test described in Sections 8.2.1.

Wet colorimetry was used to measure the ratio of Fe(II) to Fe(total). Glass samples were ground in a tungsten carbide mill for 2 min and fine glass powder samples were dissolved using a mixture of sulfuric and hydrofluoric acid. Buffer solution containing 25ml of 4% Boric acid solution, 7 ml of saturated potassium hydrogen phthalate solution, and 2ml of concentrated ammonium hydroxide was added to prevent air oxidization of Fe(II) in the solution and to complex the excess fluoride ion. The ferrous ion in the solution was chelated by three molecules of phenanthroline forming an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 2.9 to 9. Ammonium hydroxide was added to adjust pH between 2.9 to 3.5 ensuring the rapid color development in the presence of an excess of phenanthroline. The absorption of light by orange-red complex was measured using an ultra-violet visible near infrared (UV-VIS-NIR) spectrophotometer (Cary 500 Scan, Varian) with Cary WinUV software at 510nm. Spectrophotometer was calibrated with a certified iron solution at seven different calibration points. The total iron in the sample was determined by reducing the ferric ion to a ferrous ion with hydroquinone at room temperature and quantified spectrophotometrically at a wavelength of 510 nm.

The nitrates reduction study included non-radioactive crucible testing and analyses of partially reacted feeds to understand the role of reductant on the feed/glass redox and phase evolution of nitrates and melting reaction products as a function of temperature during initial feed melting. The feeds without and with a fixed addition of sucrose (as determined from the initial reduction tests described above in this Section) were heated at 5 °C/min starting from 80°C to 200, 400, 600, 800, 1000 and 1200°C and air-quenched. All samples were analyzed for crystalline phases and iron redox.

The amount of crystalline phases in partially reacted feed or glass was determined by the semiquantitative XRD. The internal standard for quantitative XRD was 5 wt% CaF_2. The sample mass of 1 to 2 g (±0.0001 g) was milled for 2 min in the tungsten-carbide milling chamber. The powder was mounted in an XRD sample holder. Scanning proceeded with 0.04° 2-θ step size, 6-s dwell time, and from 5 to 70° 2-θ scan range.

8.1.2 Results from Feed Melting Redox Study with Varying Reductant Addition at a Fixed Final Temperature

Table 8.2 summarizes the results of feed melting and redox measurements after heat treating the feeds at 5°C/min from 80 to 800°C. The stoichiometry of sucrose and carbon for the tests described in this section was defined as the carbon to nitrogen (from nitrates and nitrite) molar ratio, C/N = 1, for convenience, which is different from that used in Section 7.0 [see Equations (7.1) and (7.2) for comparison]. Figure 8.1 shows the iron redox data as a function of total C/N ratio in various feeds.

The results given in Table 8.2 and Figure 8.1are summarized as below:

- Drying the feed under Ar or air atmosphere did not make any difference in the redox results. Air drying was used in later tests.
- The feed height (H) to feed width (W) ratio resulted in a large redox difference in the glass product. The H/W ratio was ~0.5 or less for the Pt crucible compared to ~1 for the alumina crucible, where W is the width of crucible at the feed surface. The larger H/W ratio (or lower surface area to volume ratio) in the alumina crucible is likely to be more efficient in reducing the feed.

Table 8.2. Results of Feed Melting Redox Tests after Heating at 5°C/min from 80 to 800°C

Sample ID	Total C/N	Sucrose C/N	Carbon C/N	Crucible	Drying Atmos.	Fe^{2+}/ Fe(total)	NOTES
RSS-0	0	0	NA	Pt	air	0.025	Baseline
RSS-1	1	1	NA	Pt	air	0.031	
RSS-1 Ar	1	1	NA	Pt	Ar	0.066	
RSS-1 Ar-b	1	1	NA	Pt	Ar	0.034	Rerun of RSS-1 Ar
RSS-1.5Ar-p	1.5	1.5	NA	Pt	Ar	0.207	
RSS-2Ar	2	2	NA	Pt	Ar	0.107	
RSS-2p	2	2	NA	Pt	air	0.099	
RSS-1.5Ar-a	1.5	1.5	NA	alumina	Ar	0.715	
RSS-2	2	2	NA	alumina	air	0.655	
RSS-2-b	2	2	NA	alumina	air	0.237	Rerun of RSS-2, ignited during drying
RSS-2-c	2	2	NA	alumina	air	0.040	Rerun of RSS-2, violently reacted and overflowed during melting
RSS-1.25-CC	1.25	0.75	0.5	Pt	air	0.402	Carbocite used as carbon source
RSS-1.5-CC	1.5	1	0.5	Pt	air	0.539	Carbocite used as carbon source
RSS-1.25-CL	1.25	0.75	0.5	Pt	air	0.176	Lampblack used as carbon source
RSS-1.5-CL	1.5	1	0.5	Pt	air	0.289	Lampblack used as carbon source

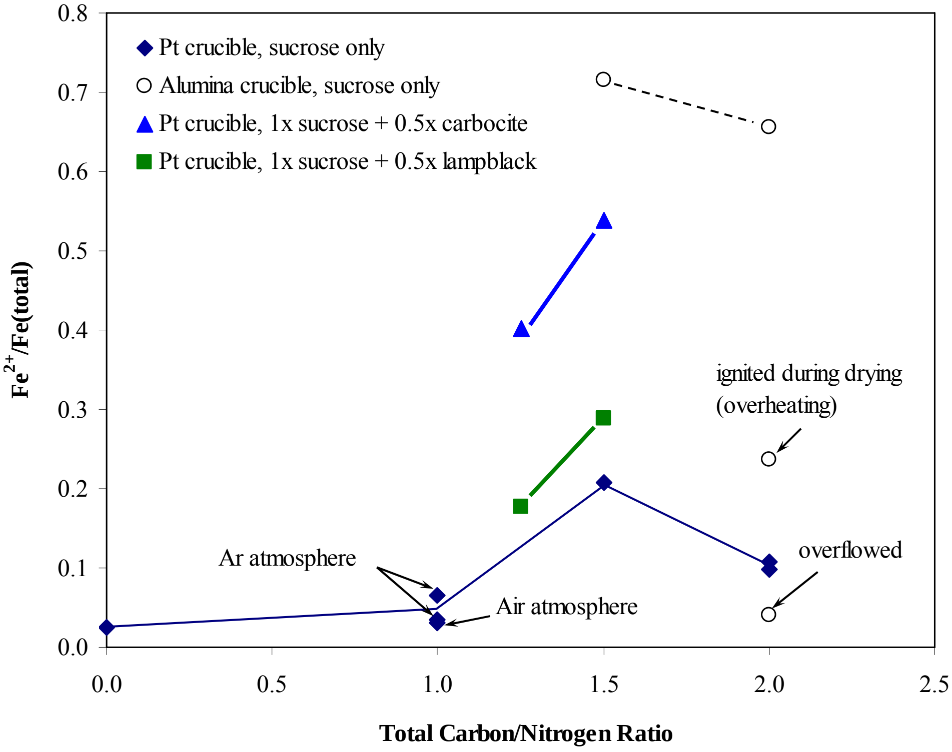

Figure 8.1. Iron Redox as a Function of Reductant Addition

- The feed with C/N = 2 tested in the alumina crucible did not produce reproducible results because of ignition during drying when the feed was overheated by error or because of violent reaction during melting. There was no violent reaction when the Pt crucible was used.
- Using sucrose at a C/N ratio of 1 makes little difference in redox compared to the baseline feed without reductant. The redox increases as the C/N increases from 1 to 1.5 but decreases when the C/N increases further to 2.
- The redox increased when the carbocite or lampblack was used to partly replace the sucrose at C/N = 1.5. Carbocite appeared to be a better reductant than lampblack.

Based on these results, a reductant consisting of sucrose at C/N =1 and carbocite at C/N = 0.5 was used for the Case 3 reduced nitrates feed for the cold finger test described in Section 8.2.1. There was no ignition or violent reaction with sucrose at C/N = 1 during crucible melting tests with the cold finger.

8.1.3 Results from Redox and Melting Reaction Progress Study as a Function of Final Temperature

These experiments were performed in two sets, several months apart. The initial set of experiments (June to July 2004) were performed for 600, 800, and 1200°C final temperatures for both baseline and reduced feeds. The second set of experiments (Nov. to Dec. 2004) were performed for 200, 400, and 1000°C. Figure 8.2 shows the results of redox measurements as a function of final temperature for the baseline and feed with reduced nitrate. Each set of test results is shown by separate symbols. Evaluation of the data shown in Figure 8.2 clearly indicates that there is a bias or mismatch between these two sets of data. The possibility of analytical bias of the redox measurement was ruled out because two separate measurements on the same samples showed almost identical results (note that 800°C results have two data points for both baseline and reduced feeds). Careful comparison of test conditions used in each set of experiments revealed that all the partially-reacted feed or glass from the first set of experiments were ground for better homogeneity before taking samples for redox and XRD measurements whereas a small sample was taken from the second set of experiments without grinding all the partially-reacted feed or glass. This difference in sampling method is believed to be the reason for apparent mismatch between these two sets of data. To check the effect of sampling method, two samples from the second set of tests were re-measured after grinding all the materials. Figure 8.2 shows that the sampling method had a significant effect although it did not seem to explain all the bias.

It can be seen from Figure 8.2 that the redox increases in the reductant feed but decreases in the baseline feed with increasing temperature starting from approximately 600°C. The fraction of Fe^{2+} in the baseline feed becomes oxidized by air during heating whereas the reduced feed maintains its reducing condition up to 1200°C. The redox ratio of 0.66 in the reduced feed heated to 1200°C is comparable to those observed in the glasses from large-scale (LS) tests (Hrma et al. 2005), which ranged from 0.38 to 0.80 for LS-2 and from 0.41 to 0.52 for LS-3.

Figure 8.3 and Figure 8.4 show the XRD results on the semi-quantitative concentrations as a function of final temperature for baseline and reduced nitrate feeds, respectively. Figure 8.3 and Figure 8.4 clearly show through the disappearance of $NaNO_3$ that the feeds with reductants become denitrated before 400°C whereas the baseline feed becomes denitrated between 600 and 800°C. The nosean, Na4Zr2Si3O12, and nepheline phases formed as intermediate reaction products during feed melting between 600 and 800°C

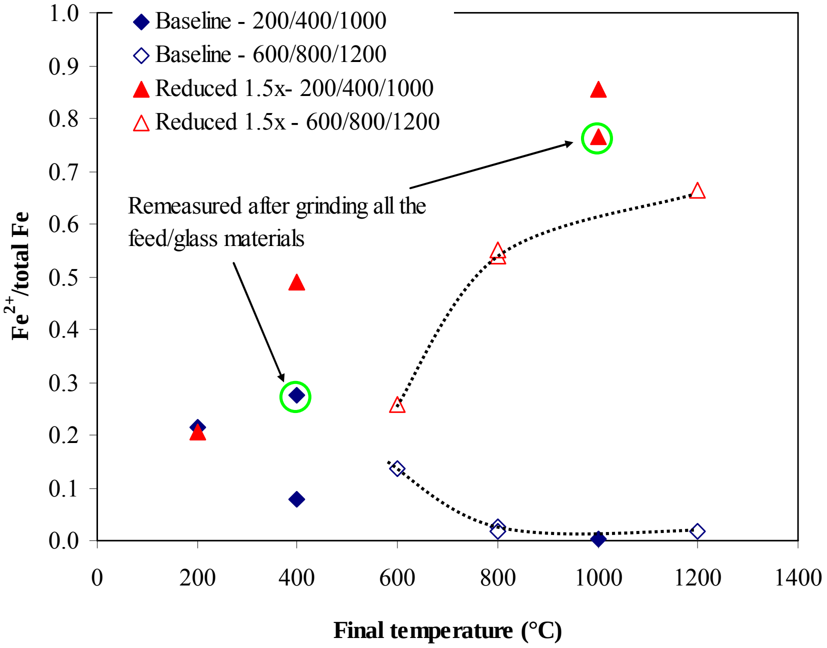

Figure 8.2. Fe Redox as a Function of Final Temperature for the Baseline Feed and Feed with Sucrose and Carbocite Reductants

and then disappeared before 1200°C was reached. There was no noticeable difference between two feeds in terms of melting reactions other than nitrate difference, indicating that the addition of reductant did not have significant effect on the feed reaction path.

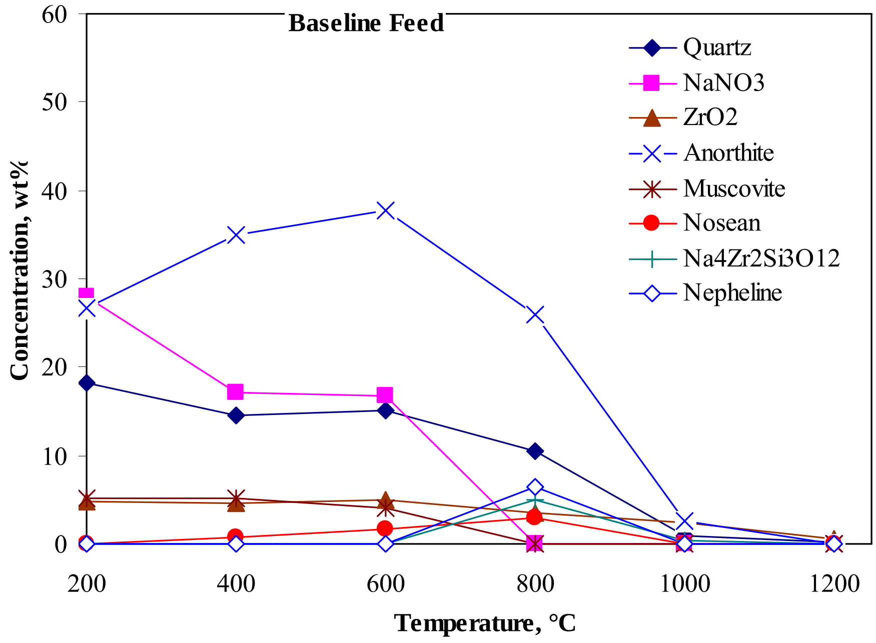

Figure 8.3. XRD Phase Identification on Baseline Feeds Quenched at the Specified Temperature

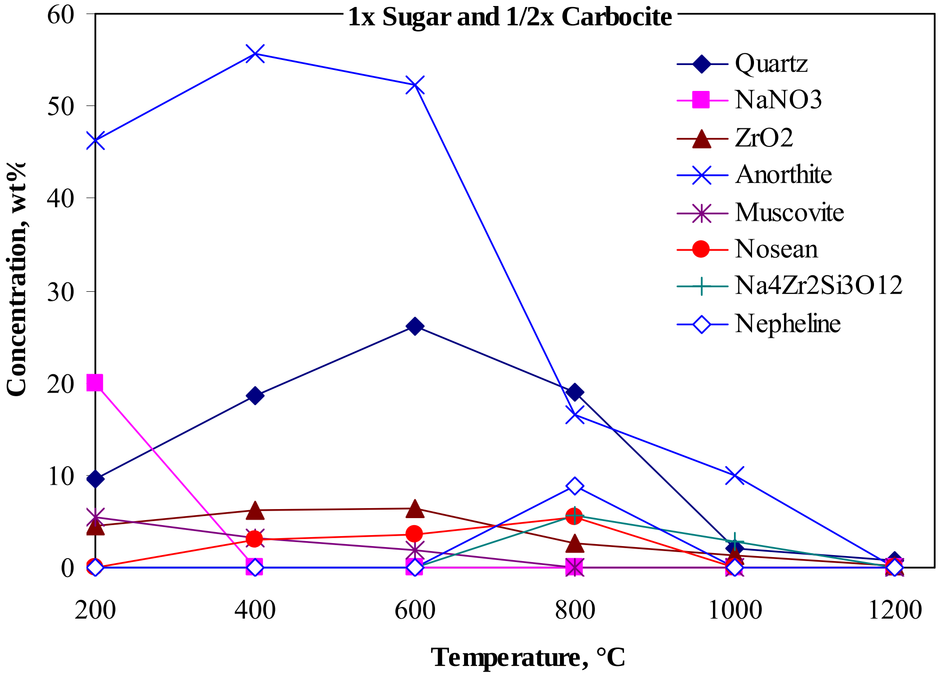

Figure 8.4. XRD Phase Identification on Reduced Nitrates Feeds Quenched at the Specified Temperature

8.2 Crucible Feed Melting Tests with Cold Finger

The crucible feed melting tests with cold finger was performed to study the effect of feed variation on Tc and Re volatilization behavior at crucible scale and to help to determine the dominant mechanisms for Tc migration in the BV process. Because all the tests in this study were performed to provide proof-of-principle information only, systematic evaluation of the reproducibility of the test results based on multiple test runs and multiple sample measurements were not performed.

8.2.1 Experimental

The feed variations or glass tested in each test case included the following:

Case 1 - Baseline: A baseline feed with target concentrations of 4.3 ppm Tc and 8.1 ppm Re in glass. This baseline feed allows for direct comparison with engineering-scale (ES) 32A and 32B test results for Tc and gives a result for the "do nothing case" at crucible scale.

Case 2 - Reduced Tc: This case was not tested. The plan was to use a feed of the same make up as baseline with the Tc treated by selected reduction treatment developed from the Tc reduction study in Section 5.0. However, none of the reductants tested could reduce pertechnetate in the waste simulant and keep it in a reduced state, as described in Section 5.0.

Case 3 - Reduced nitrates: A feed of the same make up as baseline with sucrose and carbon added to the feed: 19.61 g sucrose and 4.13 g carbocite[(a)] in addition to those given in Table 8.1. This level of sucrose and carbon roughly corresponds to one stoichimetric addition of sucrose based on the assumption for reaction stoichiometry used in Section 7.1.2. This case determines the effectiveness of nitrate reduction during melting by adding sucrose and carbon at crucible scale.

Case 4 - No sulfate: A feed of the same make up as baseline, without any sulfate in the feed. The 12.78 g of Na_2SO_4 in the simulant (see Table 4.1) was replaced by the same moles of Na_2CO_3 (9.54 g to make a total of 59.89 g Na_2CO_3 in addition to existing 50.35 g) to keep the Na concentration in the feed the same as in the baseline feed. The resulting feed recipe uses 234.05 mL simulant instead of 234.35 mL given in Table 8.1 for a baseline feed. This case determines if the volatility of Tc is strongly influenced by S in the feed.

Case 5 - No nitrates and reduced Tc/Re: A feed made up to have the same ultimate glass composition with the Tc in the reduced form and no nitrates present. This feed was spiked with reduced Tc and Re added as TcO_2 and ReO_2 in $SnCl_2$ solution, which, as discussed in Section 6.0, was determined to be a partially effective reducing agent. Nitrates and nitrites were replaced by hydroxides and carbonates to make the glass composition the same as the baseline glass. (See below for details of the Case 5 feed makeup.) This case determines the impact of reduced Tc in the feed without nitrates on the Tc volatilization. This feed makeup was the same as used in ES-31D.

Case 6 - Pre-melted glass: A pre-melted glass from a separate crucible melting with Tc spiked to compensate for the expected loss during melting. This case determines the extent to which volatility from the glass contributes to the Tc migration as opposed to migration from the reacting feed. This test was conducted only at the final temperature of 1200°C.

For test cases 1-5, Tc-spiked simulant (baseline) or Tc-spiked and modified (reduction treatments or sulfate removal) simulant as summarized above was mixed with additive and soil in the proportion to produce the baseline glass composition given in Table 4.2. The feed necessary to produce 1000 g glass was prepared, and the amount to make 200 g glass was used for each test. The slurry feeds were dried following the procedure described in Section 8.1.1. Case 6 used a pre-melted glass and started with 200 grams of crushed glass.

Table 8.3 shows the composition of the no nitrate simulant used for the preparation of Case 5 feed. The feed make up for Case 5 to produce 200 g glass is given in Table 8.4. The carbocite was added to help keep the Re and Tc in a reduced state during melting. The Tc was added as an $(NH_4)_2TcCl_6$ solution and Re was added as ReO_2. Because of concerns that the Re and Tc may oxidize if they are added to the aqueous simulant, a solution containing ReO_2, $(NH_4)_2TcCl_6$, and $SnCl_2$ was mixed with a small amount of soil, carbocite, and other simulant chemicals (CH_3COONa, $Na_2C_2O_4$, $Na_2B_4O_7$, $Na_2CrO_4.4H_2O$) and dried separately before it was mixed with the dried main feed. The dried main feed that was prepared following the same procedure described in Section 8.1.1.

[(a)] Carbocite is a carbon material typically used in commercial glass plants to control the redox state of glass. Produced by Shamokin Graphite, Shamokin, PA 17872, USA. Carbocite contains approximately 75 to 77 wt% C with 17 to 19 wt% ash, 6 to 7 wt% volatiles, 0.5 to 0.6 wt% sulfur, and 1.5 to 2.5 wt% moisture.

Table 8.3. Composition of No-Nitrate Simulant Used in Case 5 Feed

Reagent (used in baseline)	Baseline, Mass (g)	Reagent (replaced for Case 5)	Case 5, Mass (g)	Dry Wt%
$Na_2C_2O_4$	1.58		1.58	0.64
CH_3COONa	10.79		10.79	4.40
$NaNO_3$	196.11	NaOH	92.29	37.64
KNO_3	1.25	K_2CO_3	0.85	0.35
NaOH	29.58		29.58	12.07
$Al(NO_3)_3{\cdot}9H_2O$	23.9	Al(OH)3	4.97	2.03
Na_2CO_3	50.35		50.35	20.54
Na_2SO_4	12.78		12.78	5.21
Na_2CrO_4	1.68	$Na_2CrO_4.4H_2O$	2.43	0.99
$Na_3PO_4{\cdot}12H_2O$	18.7		18.70	7.63
NaCl	2.56		2.56	1.04
NaF	1.33		1.33	0.54
$NaNO_2$	29.26	NaOH	16.96	6.92
$CsNO_3$	1.00E-05	Cs_2CO_3	8.36E-06	3.41E-08

Table 8.4. Case 5 (No Nitrates and Reduced Re and Tc) Feed Makeup to Produce 200 g Glass

Materials	Mass (g)	Note
Simulant (dry)	57.46	(Table 8.3)
HRTS soil (dried)	135.59	(Table 4.2)
ZrO_2	14	
B_2O_3	10	
ReO_2	1.90E-03	
TcO_2	1.14E-03	
Carbocite	1.65	

The pre-melted glass for Case 6 was prepared by melting the baseline feed spiked with Tc to make 400 g glass using the following procedure:

- Heat at 750ºC for 30 min to drive the nitrates off.
- Melt at 1200ºC for 1 h. Melt by placing the feed contained in a Pt crucible into a furnace maintained at a specified temperature. This step did not form a reasonably homogeneous glassy phase.
- Melt at 1350ºC for 1 h, poured into a steel plate, and crushed. Separated salt phase was observed.
- Re-melt crushed glass (including the salt) at 1350ºC for 1 h. A typical homogeneous glass material was obtained, but the separated salt phase was still present.
- Use 200 g glass for each run, which was the same target mass of glass as used in the other tests with simulant + soil + additive feeds.
- Make pre-melted glass with Tc and Re spiked to add 30% more than the baseline target described in Section 4.0 to compensate for the expected loss during melting. The analyzed Re and Tc was used as a basis for “fraction of total Re/Tc” calculation.

The dried feeds (or pre-melted glass in Case 6) were tested by heating in a Pt-20%Rh crucible with a water-cooled cold finger, as shown in Figure 8.5. The temperature of cooling water was kept below 90ºC though the surface temperature of the cold finger was not monitored or estimated. Figure 8.6 shows the approximate dimensions of the Pt crucible and cold finger.

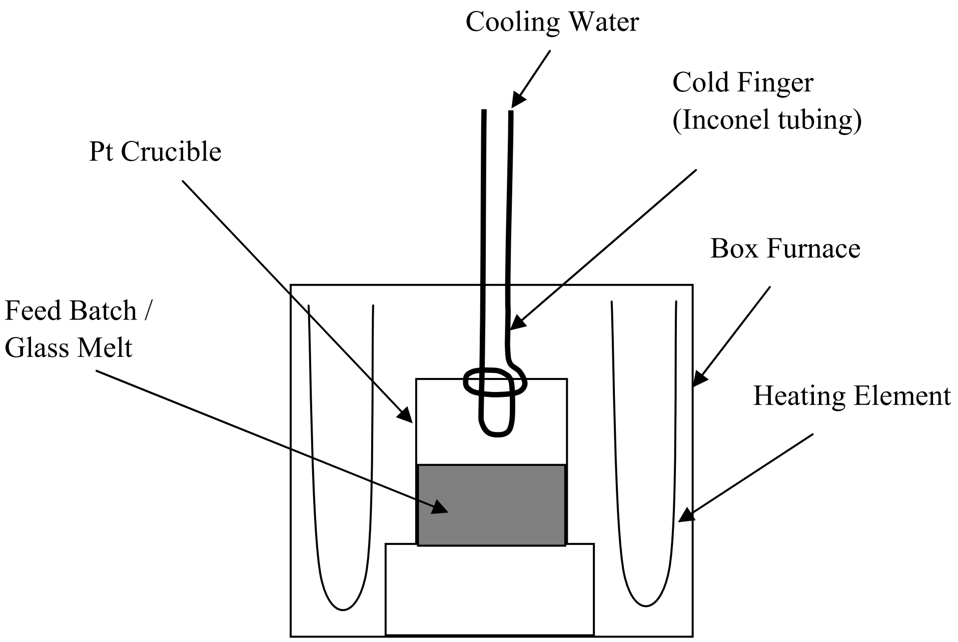

Figure 8.5. Schematic of Experimental Setup for Crucible Feed Melting Tests

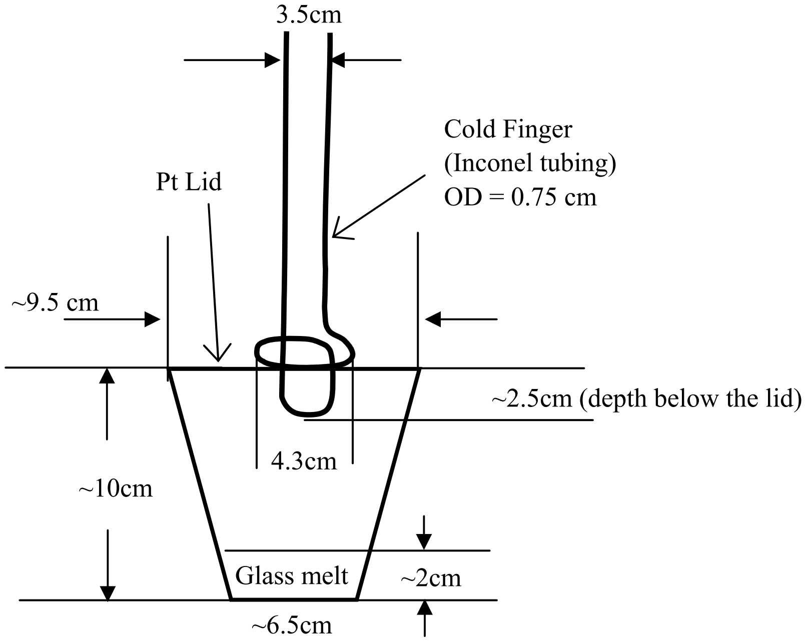

Figure 8.6. Approximate Dimensions of Crucible and Cold Finger

The dried feeds in all cases except for Case 6 were ramp heated at 5°C/min, starting from 80°C and terminated at one of the following final temperatures before air quenching:

- 600°C—nitrate beginning to thermally decompose
- 800°C—nitrate all reacted

- 1000°C—glass melt forming
- 1200°C—glass melt fully formed.

The pr-emelted glass in Case 6 was ramp heated at 5°C/min from 500°C to 1200°C and held at 1200°C for 1 and 5 h. The 5 h was the maximum time the current cooling system could be used before starting to overheat.

The heat-treated samples were quenched after reaching the preset final temperature or after preset time at 1200°C in Case 6. The following samples were analyzed:

- Feed wash samples: Approximate 20 g of samples were taken from the dried feed materials before conducting feed melting tests. As-dried feeds were washed with ~20 mL DIW, the wash was then filtered thorough a 0.45-µm filter, and analyzed for Tc and Re via ICP-MS and for anions via IC.
- Crucible rinse samples: All the partly reacted feed and glass materials remaining in the Pt crucible were washed by ~200 mL DIW. The wash solutions from all tests were filtered thorough a 0.45-µm filter and analyzed for Tc and Re via ICP-MS and for anions via IC.
- Condensate samples: The condensate materials attached to the cold finger were collected by first scrapping the deposits with razor blade and then rinsing the cold finger with DI water. Both the soluble and insoluble materials were mixed into 15- to 50-mL solution, depending on the amount of condensate materials collected. Condensate samples from all tests were analyzed for Tc and Re via ICP-MS, for major glass components via ICP-AES, and for anions, including halogens via IC. Selected condensate samples from 1000 and 1200°C tests were analyzed by XRD before submitting for chemical analysis to determine the crystalline form of deposit materials. The condensate samples to be analyzed by XRD were split in approximately half for chemical analyses and XRD. The chemical analyses samples were sent immediately after each test to obtain preliminary results that were used to support planning efforts for engineering scale tests.
- Glass samples: The representative glass samples from 1200°C tests in all cases were analyzed for Tc and Re via ICP-MS and for major glass components via ICP-AES. Grinding all the glass into fine powder to homogenize the glass sample was not performed because of constraints of handling the radioactive samples.

All the chemical analyses were performed at Southwest Research Institute (SwRI).(a)

The current test methods to determine the volatilization behavior of Tc and Re using cold finger setup involves many factors that can increase the variability of data generated. The main sources of variability are:

- Efficiency of cold finger condensation depending on the test configuration control, such as depth of cold finger into the crucible and the position of the lower part of the cold finger within the opening of the lid. The estimated relative difference in condensation efficiency caused by the difference in test configuration is not expected to be higher than 10%.
- Sample loss during handling of condensate samples. A small fraction (typically less than 5%) of sample loss was experienced but was not considered in evaluation of Re and Tc results from condensate samples except for the Case 1, 1200°C and Case 4, 1200°C samples. It was estimated that roughly 10% more material (compared to other tests) was lost during handling of these two condensate samples and the total Re and Tc data were adjusted to compensate for these losses.

(a) Department of Analytical and Environmental Chemistry, 6220 Culebra Rd., San Antonio, Texas, 78238 USA.

- Inhomogeneity of glass samples. A small sample was taken from the resulting glass pieces instead of grinding all the resulting glass materials that .
- Efficiency of feed rinse (based on small sample) and crucible rinse (depends on pore structure that may not be reproducible).
- Analytical uncertainty.

Among these factors, the analytical uncertainty was within ±10%, based on all the duplicate analysis results of Re and Tc on selected samples (duplicate analyses were performed on at least one sample in each set of samples that consisted of typically 2 to 10 samples).

8.2.2 Results from Crucible Feed Melting Tests with Cold Finger

This section describes the results of the cold finger crucible tests. Results include the analyses of Re and Tc by ICP-MS on crucible rinse, condensate, and glass samples, anions by IC on crucible rinse and condensate samples, glass component by ICP-AES on glass and condensate samples, and identification of crystalline phases by XRD on condensate samples.

8.2.2.1 Re and Tc Results by ICP-MS

Although systematic studies were not performed to check the reproducibility of the current crucible melting tests with cold finger, there are two sets of data that can provide an indication of the uncertainty resulting from the analyses of glass samples as shown in Table 8.5. The relative difference in Table 8.5 includes both sample variation (indication of inhomogeneity) and analytical uncertainty.

Table 8.5. Re and Tc analyses Result for Replicate Samples

Sample	Re (mg/Kg)	Tc (mg/Kg)
TcCruc-C5-1200-Glass	2.19	1.898
TcCruc-C5-1200-Glass (repeat)	2.3	1.678
Relative Percent Difference	5.0%	-11.6%
TcCruc-C6-1200-1 h-Glass	1.61	0.907
TcCruc-C6-1200-1 h-Glass (repeat)	1.955	0.964
Relative Percent Difference	21.4%	6.3%

The feed preparation for Case 5 was different from other feeds in that caking was encountered during drying of the main feed. Due to suspected problems with the Case 5 feed, a second Case 5 feed was prepared and tested. However, preparation of the second Case 5 feed indicated that the caking was not associated with a specific preparation problem but was the nature of the denitrated feed. Therefore, it was determined that both Case 5 feeds were good for testing. All the data on Case 5 in this report are from the second Case 5 feed. The first Case 5 feed was run at 1200°C only and was used to help estimate the test-to-test variability in the data as summarized in Table 8.6.

Table 8.6. Re and Tc Analyses for Test Samples Resulting from Two Separate Feed Preparations

	Case 5-1 (First Case 5)		Case 5-2 (Second Case 5)		Relative Percent Difference	
Sample	Re (mg/Kg)	Tc (mg/Kg)	Re (mg/Kg)	Tc (mg/Kg)	Re	Tc
TcCruc-C5-1200-Condensate	19	7.304	22	8.472	15.8%	16.0%
TcCruc-C5-1200-Crucible Rinse	0.192	0.041	0.339	0.043	76.6%	5.1%
TcCruc-C5-1200-Glass	2.19	1.898	2.52	2.165	15.1%	14.1%

Based on limited data presented in Table 8.5 and Table 8.6 the reproducibility for condensate and glass samples seems to be good considering all the factors that can increase the variability discussed in Section 8.2.1. However, as indicated in Table 8.6, results from crucible rinse samples may involve higher variability than condensate or glass samples.

Table 8.7 summarizes the results of Re and Tc analyses by ICP-MS on all feed rinse, crucible rinse, condensate, and glass samples collected from all the tests performed in this study. The “amount in sample” is the mass of Re and Tc analyzed in each sample, and the “wt% of total target” is the fraction of total added to the feed (Cases 1, 3, 4, and 5) or analyzed in pre-melted glass (Case 6). Analysis of dried feed was not performed and assumed that all the Re and Tc added was retained in the feed. The total target amount of Re and Tc added to the feed to produce 200 g glass was 1.62 mg for Re and 0.86 mg for Tc.

Table 8.7. Summary of ICP-MS Results for Re and Tc for All Samples

	Amount in Sample		Wt% of Total Target	
	Re (mg)	Tc (mg)	Re (wt%)	Tc (wt%)
Case 1—Baseline				
Feed Rinse	1.04	0.593	64.22	69.00
Crucible Rinse, 600°C	0.814	0.416	50.25	48.39
Crucible Rinse, 800°C	0.214	0.106	13.21	12.29
Crucible Rinse, 1000°C	0.0314	0.0100	1.94	1.16
Crucible Rinse, 1200°C	0.0173	0.00781	1.07	0.91
Condensate, 600°C	0.00089	0.000018	0.05	0.00
Condensate, 800°C	0.0255	0.0132	1.57	1.54
Condensate, 1000°C	0.204	0.133	12.57	15.44
Condensate, 1200°C	0.404	0.222	24.93	25.86
Glass, 1200°C	0.506	0.273	31.23	31.73
Case 3—Reduced nitrates by sugar and carbon				
Feed Rinse	1.23	0.687	76.13	79.87
Crucible Rinse, 600°C	0.129	0.0605	7.96	7.04
Crucible Rinse, 800°C	0.0306	0.00880	1.89	1.02
Crucible Rinse, 1000°C	0.0120	0.00407	0.74	0.47
Crucible Rinse, 1200°C	0.0173	0.00658	1.07	0.76
Condensate, 600°C	0.00100	0.000971	0.06	0.11
Condensate, 800°C	0.00770	0.00611	0.48	0.71
Condensate, 1000°C	0.508	0.217	31.35	25.23
Condensate, 1200°C	0.475	0.222	29.31	25.87
Glass, 1200°C	0.280	0.189	17.28	21.98
Case 4—No sulfate				
Feed Rinse	0.774	0.439	47.75	51.02

Table 8.7. Summary of ICP-MS Results for Re and Tc for All Samples

	Amount in Sample		Wt% of Total Target	
	Re (mg)	**Tc (mg)**	**Re (wt%)**	**Tc (wt%)**
Crucible Rinse, 600°C	0.722	0.404	44.57	46.99
Crucible Rinse, 800°C	0.0236	0.0136	1.46	1.59
Crucible Rinse, 1000°C	0.00162	0.00111	0.10	0.13
Crucible Rinse, 1200°C	BRL	0.000171	BRL	0.02
Condensate, 600°C	0.00308	0.000105	0.19	0.01
Condensate, 800°C	0.0172	0.0135	1.06	1.57
Condensate, 1000°C	0.120	0.100	7.41	11.58
Condensate, 1200°C	0.145	0.0979	8.93	11.39
Glass, 1200°C	0.940	0.475	58.02	55.27
Case 5—No nitrate, reduced Tc/Re				
Feed Rinse	0.0502	0.228	3.10	26.47
Crucible Rinse, 600°C	0.312	0.122	19.26	14.14
Crucible Rinse, 800°C	0.0324	0.00398	2.00	0.46
Crucible Rinse, 1000°C	0.0764	0.0298	4.72	3.46
Crucible Rinse, 1200°C	0.0509	0.00641	3.14	0.75
Condensate, 600°C	0.000600	0.000655	0.04	0.08
Condensate, 800°C	0.0122	0.00490	0.75	0.57
Condensate, 1000°C	0.345	0.231	21.30	26.87
Condensate, 1200°C	0.595	0.227	36.70	26.36
Glass, 1200°C	0.504	0.433	31.11	50.35
Case 6—Pre-melted glass				
Glass, 0 h	0.410(a)	0.191(a)	19.47(b)	17.05(b)
Crucible Rinse, 1200°C 1 h	0.00121	0.000654	0.30	0.34
Crucible Rinse, 1200°C 5 h	0.00176	0.000723	0.43	0.38
Condensate, 1200°C 1 h	0.0222	0.00327	5.41	1.71
Condensate, 1200°C 5 h	0.133	0.0620	32.51	32.53
Glass, 1200°C 1 h	0.322	0.181	78.54	95.18
Glass, 1200°C 5 h	0.250	0.111	60.98	58.27

BRL: below reporting limit

(a) Amount analyzed in pre-melted glass, which was used as the total basis for all other Case 6 results

(b) Calculated using the actual amount of Re and Tc (30% more than normal feed to compensate the estimated loss) added in the feed used to prepare pre-melted glass as a total basis.

For Case 6, the pre-melted glass was prepared with 30% more Re and Tc spike than the other feeds. The analyses of this pre-melted glass showed that only 19.5% and 17.1% of the Re and Tc added to the feed were retained in glass. The low retention may be attributed to the high temperature of 1350°C used for glass preparation as described in Section 8.2.1. The observed segregated salt phase might have also contributed to the Re and Tc loss. The amount of Re and Tc in the pre-melted glass determined by chemical analysis was used as the basis to calculate the wt% of total target for Case 6 samples.

Figure 8.7 through Figure 8.11 show the wt% of total Re and Tc added to the feed analyzed in the feed rinse, crucible rinse, condensate, and glass samples as a function of final temperature for five feeds tested in this study. Figure 8.12 shows the same plots for all the crucible rinse samples and Figure 8.13 for all the condensate samples. Figure 8.14 and Figure 8.15 show the Re and Tc plots for condensate samples separately. Figure 8.16 compares the wt% of total Re and Tc retained in the 1200°C glass samples for

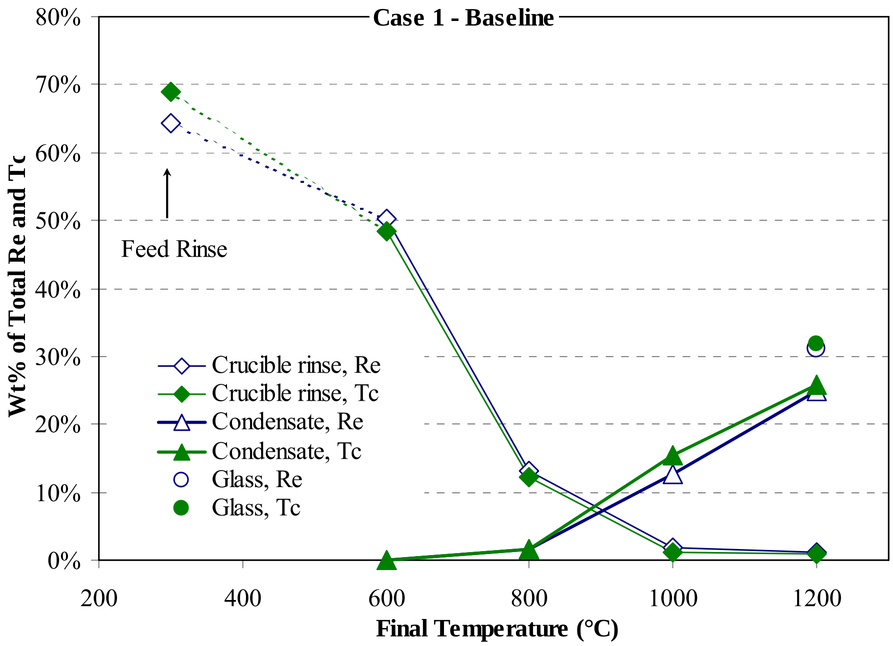

Figure 8.7. Wt% of Total Re and Tc Versus Final Temperature for Case 1—Baseline Feed

four of the test cases that started with feed material. Figure 8.17 and Figure 8.18 compare the wt% of total Re and Tc in glass and condensate samples, representing total recovery of Re and Tc from the present experimental setup.

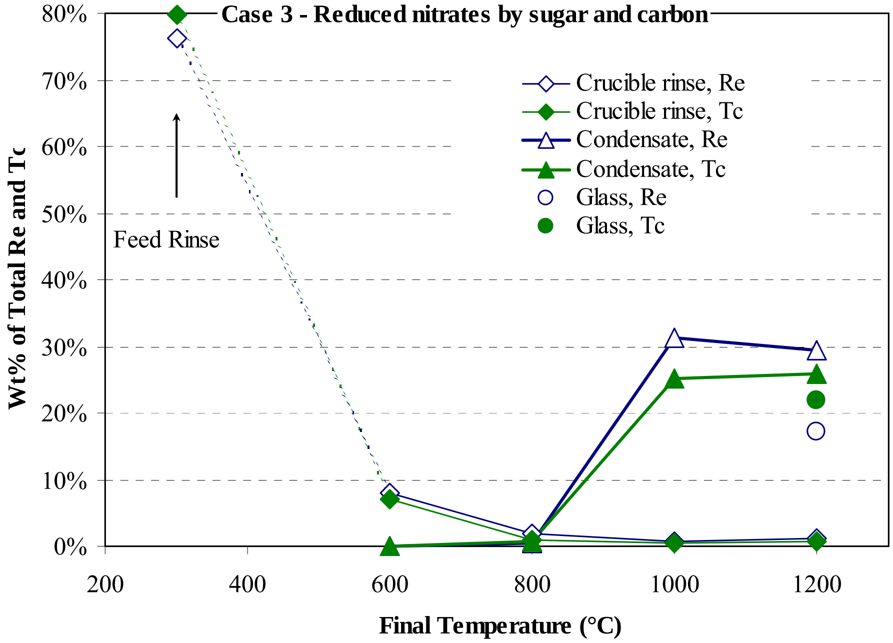

Figure 8.8. Wt% of Total Re and Tc Versus Final Temperature for Case 3—Reduced Nitrates Feed

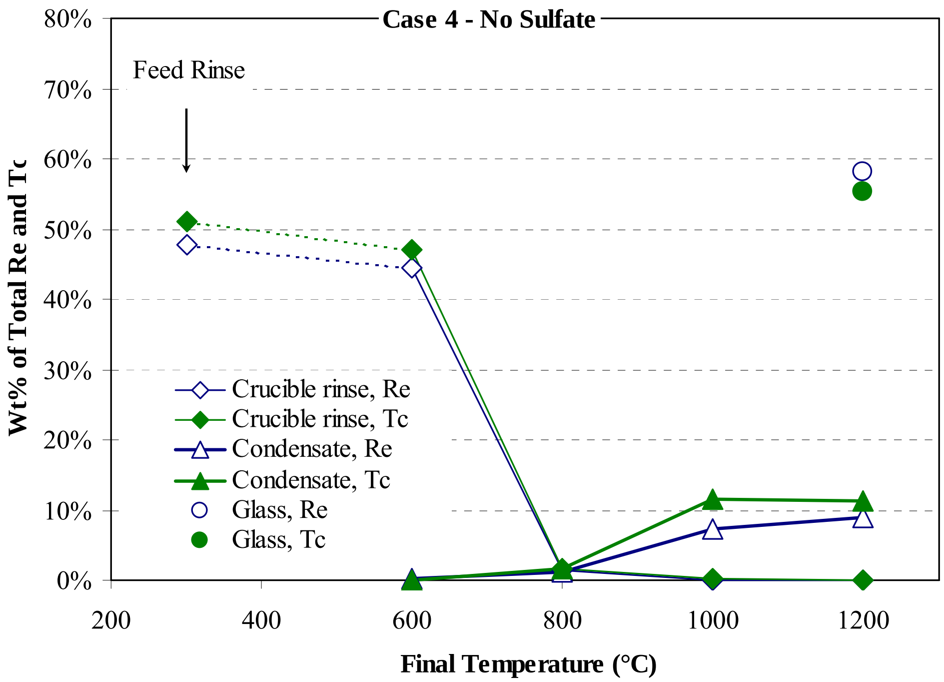

Figure 8.9. Wt% of Total Re and Tc Versus Final Temperature for Case 4—No Sulfate Feed

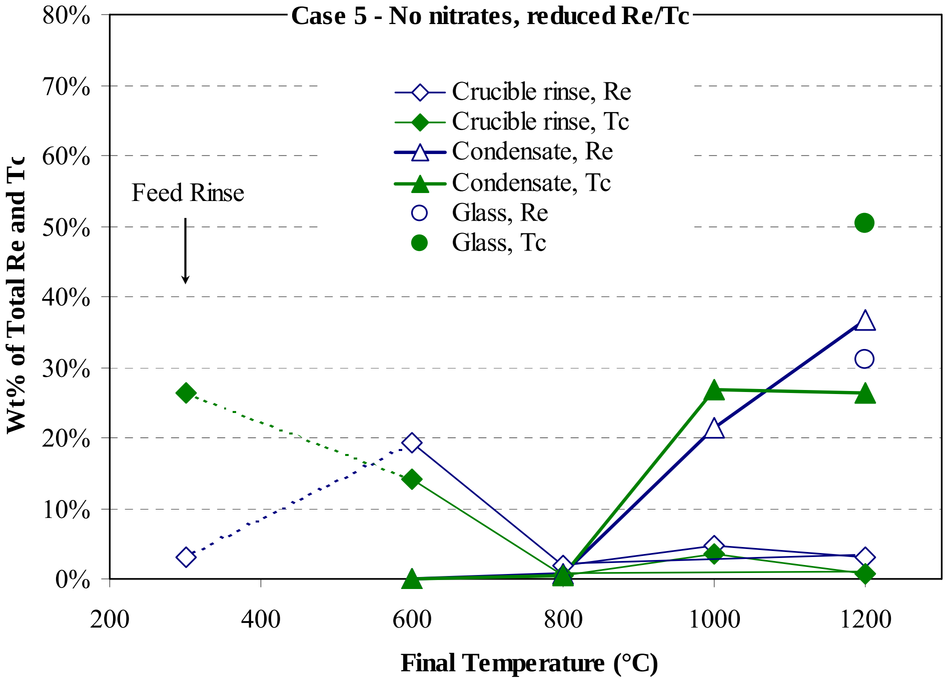

Figure 8.10. Wt% of Total Re and Tc Versus Final Temperature for Case 5—No Nitrates Feed

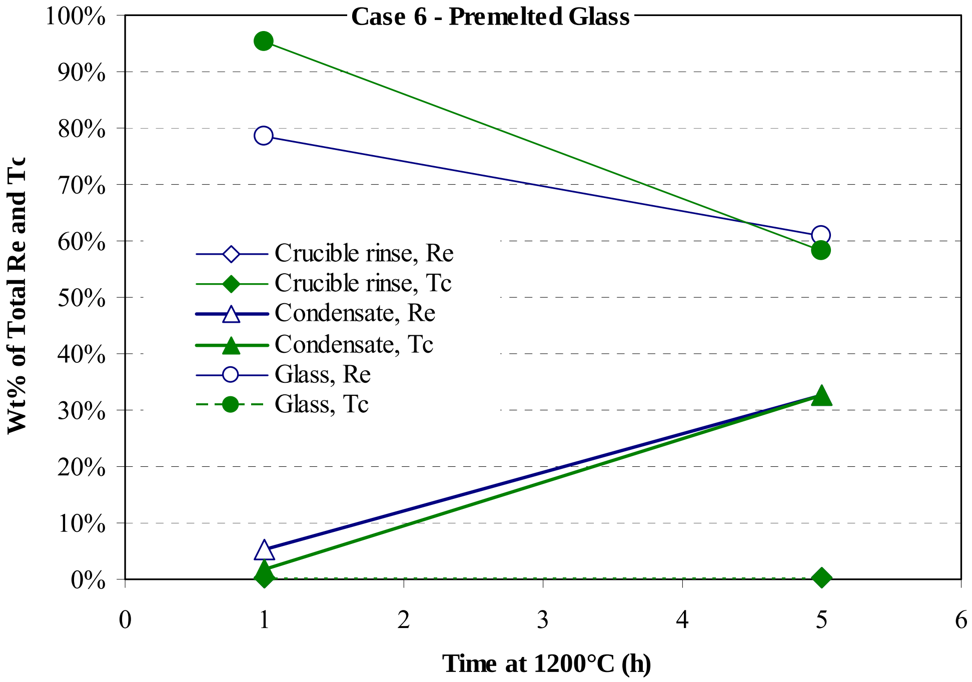

Figure 8.11. Wt% of Total Re and Tc Versus Final Temperature for Case 6—Pre-Melted Glass

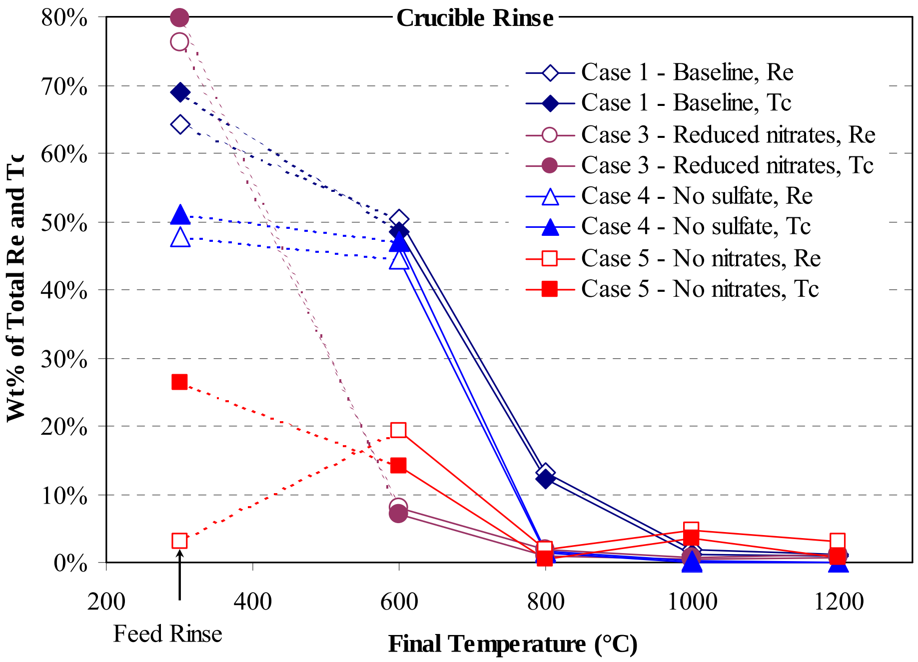

Figure 8.12. Wt% of Total Re and Tc Versus Final Temperature in Feed and Crucible Rinse Samples

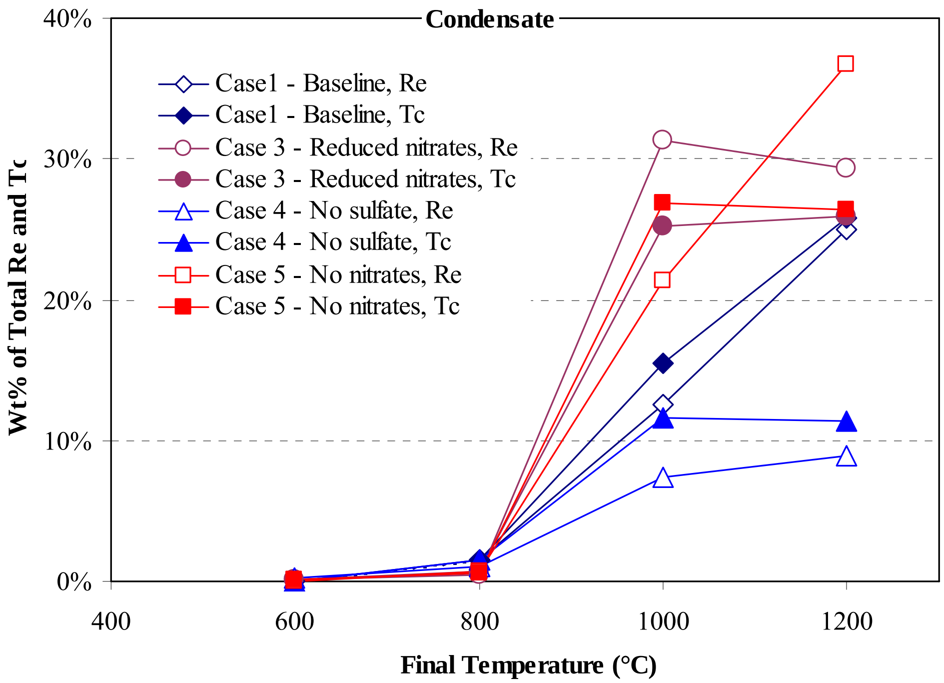

Figure 8.13. Wt% of Total Re and Tc Versus Final Temperature in Condensate Samples

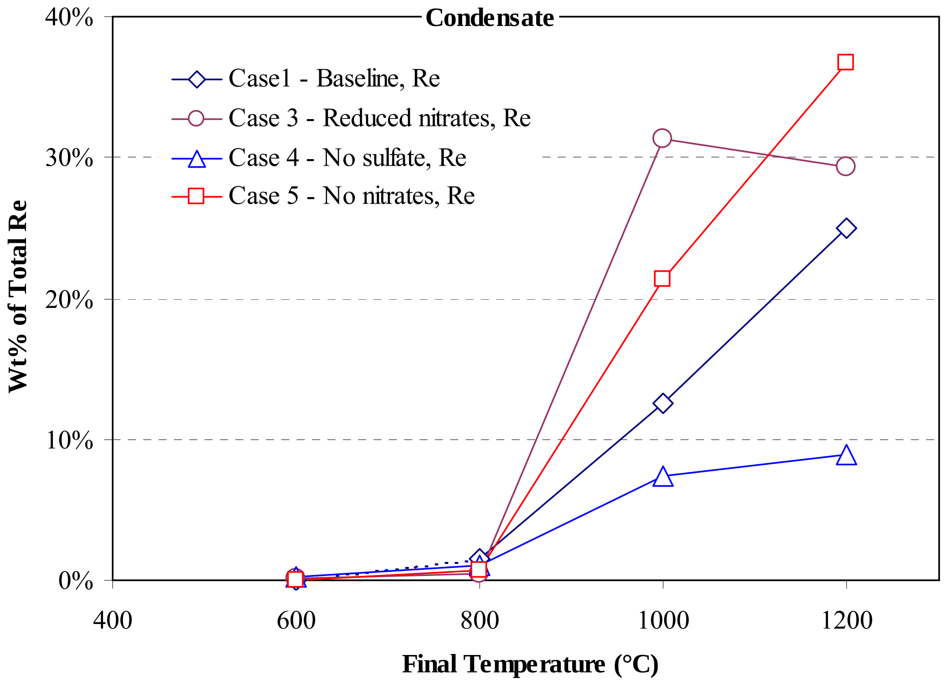

Figure 8.14. Wt% of Total Re Versus Final Temperature in Condensate Samples

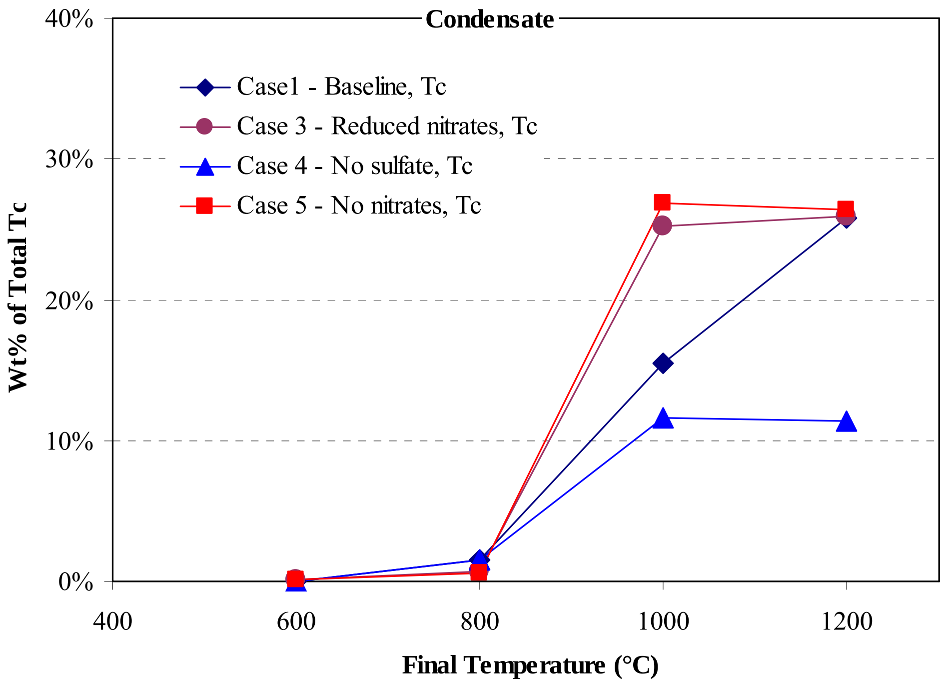

Figure 8.15. Wt% of Total Tc Versus Final Temperature in Condensate Samples

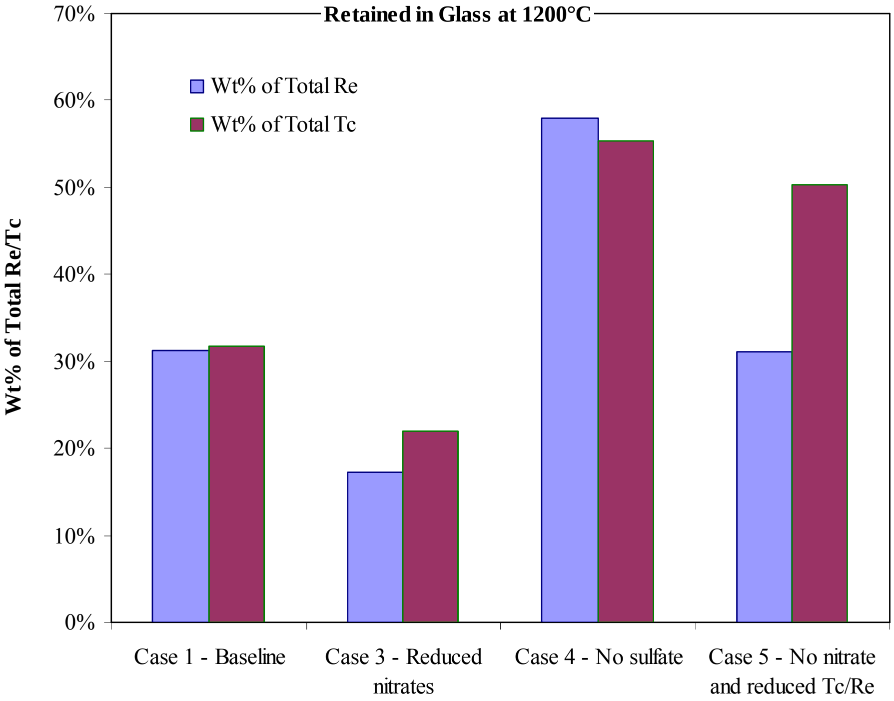

Figure 8.16. Comparison of Wt% of Total Re and Tc Retained in Glass after 1200°C Test

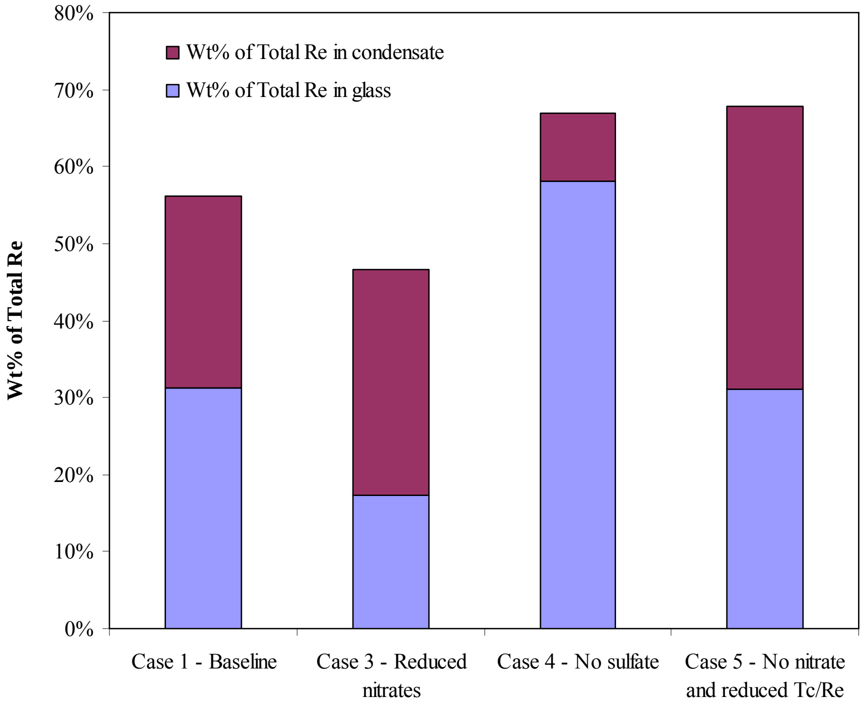

Figure 8.17. Wt% of Total Re in Condensate and Glass Samples after 1200°C Tests

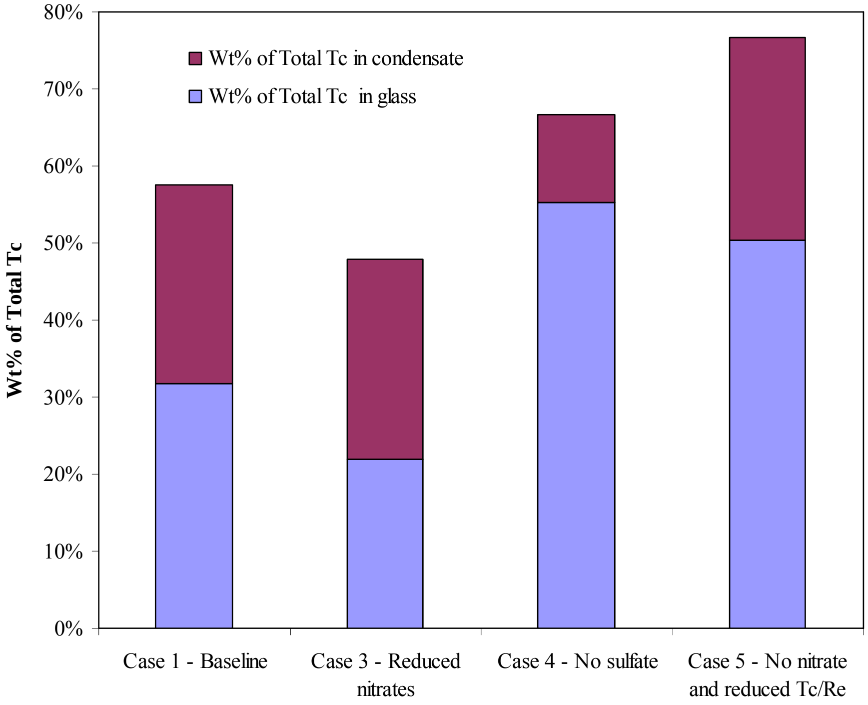

Figure 8.18. Wt% of Total Tc in Condensate and Glass Samples after 1200°C Tests

The data in Table 8.7 and Figure 8.7 through Figure 8.18 are summarized below:

- In all but a few isolated cases, the Re and Tc behaved in a similar manner indicating that Re is a good volatilization surrogate for Tc.
- Based on the condensate sample results, measurable volatilization of Re and Tc starts to occur only above 800°C (Figure 8.7 through Figure 8.10).
- Based on the crucible rinse sample results, most Re and Tc in the feed becomes insoluble (incorporate into glass forming melt) below 1000°C for the baseline feed and below 800°C for three other feeds. Pre-melted glass shows no Re and Tc in the crucible rinse samples as expected (Figure 8.7 through Figure 8.11).
- The no-sulfate (Case 4) feed had the lowest volatilization of Re and Tc as indicated by the amount measured in the condensate and the highest retention in the glass (Figure 8.17 and Figure 8.18).
- Feeds with reduced nitrates, either by reductants added to the slurry feed (Case 3) or using reduced Re/Tc with no nitrates (Case 5), increased the Re/Tc volatilization or had no effect within experimental uncertainty (Figure 8.14 and Figure 8.15).
- Significant volatilization occurs from the pre-melted glass sample, although the volatilization rate is much slower than the rate observed in the melting feed: the volatilization rate of Tc was ~16 wt%/h for the baseline feed between 1000 and 1200°C tests (10.4 wt% during 40 min) compared to ~8 wt%/h for pre-melted glass at 1200°C between 1- and 5-h tests (Figure 8.11) (30.8 wt% during 4 h).
- The cold finger setup efficiency for capturing volatile Re and Tc seems to be relatively high. The sum of wt% of total in condensate and retained in glass ranged from 47 to 68% for Re and 48 to 77% for Tc from 1200°C tests of Cases 1 to 5 (see Figure 8.17 and Figure 8.18). For Case 6, as shown in Figure 8.11, the amount of Re and Tc deposited in condensate is roughly comparable to the amount lost from the glass sample (36.9 wt% was lost while 30.8 wt% was condensed for Tc and 17.6 wt% was lost while 27.1 wt% was condensed for Re). Noting that the condensation efficiency cannot be greater than 100%, it is likely that the rate of Tc and Re volatilization from pre-melted glass obtained from one set of tests in this study could have been an overestimation.

These results are discussed in connection with the anions and glass component analytical results in the following sections.

8.2.2.2 Anion Results by IC

Table 8.8 summarizes the calculated masses of anions in the baseline feed to produce 200 g glass for comparison with the analyzed results from condensate and crucible rinse samples. Table 8.9 summarizes the results of anion analyses by IC on feed rinse, crucible rinse, and condensate samples collected from all tests performed in this study. The data values for crucible rinse and condensate samples given in Table 8.9 are the masses of each anion analyzed in total crucible rinse, and condensate samples obtained by multiplying the analyzed concentration by the amount of water used in collecting the samples. For

Table 8.8. Calculated Total Mass of Anions in the Baseline Feed to Produce 200 g Glass

Anion	Cl^-	F^-	NO_3^-	NO_2^-	PO_4^{2-}	SO_4^{2-}
Mass in the feed to produce 200 g glass (g)	0.364	0.141	36.485	4.572	1.095	2.026

Table 8.9. Summary of IC Results on Feed Rinse, Crucible Rinse, and Condensate Samples

Sample	Cl^- (mg)	F^- (mg)	NO_3^- (mg)	NO_2^- (mg)	PO_4^{3-} (mg)	SO_4^{2-} (mg)
Case 1—Baseline						
Feed Rinse	305.83	36.04	35175.43	3964.17	109.50	1777.62
Crucible Rinse, 600°C	260.00	80.00	21868.36	1504.31	127.80	1248.00
Crucible Rinse, 800°C	79.60	24.80	1717.60	235.83	98.60	524.00
Crucible Rinse, 1000°C	4.18	BRL	BRL	BRL	6.75	182.00
Crucible Rinse, 1200°C	2.61	0.65	BRL	BRL	9.06	447.00
Condensate, 600°C	0.02	0.02	0.71	0.01	BRL	0.01
Condensate, 800°C	0.07	0.22	25.01	BRL	BRL	0.05
Condensate, 1000°C	6.12	0.59	10.15	BRL	BRL	0.51
Condensate, 1200°C	24.83	5.58	7.86	BRL	BRL	12.62
Case 3—Reduced nitrates by sugar and carbon						
Feed Rinse	273.17	41.11	26533.87	3101.17	90.70	1567.44
Crucible Rinse, 600°C	34.60	17.42	BRL	BRL	172.20	1418.00
Crucible Rinse, 800°C	1.04	0.24	0.54	BRL	3.82	17.78
Crucible Rinse, 1000°C	1.55	BRL	BRL	BRL	0.85	87.20
Crucible Rinse, 1200°C	4.24	0.46	BRL	BRL	2.02	350.00
Condensate, 600°C	0.18	0.08	0.05	BRL	BRL	0.02
Condensate, 800°C	0.76	0.25	0.03	BRL	BRL	0.11
Condensate, 1000°C	9.01	1.45	BRL	BRL	BRL	9.65
Condensate, 1200°C	14.52	2.16	0.21	BRL	BRL	14.05
Case 4—No sulfate						
Feed Rinse	293.16	33.39	29439.72	3200.71	88.76	9.09
Crucible Rinse, 600°C	280.00	82.20	19743.50	1366.36	127.20	25.60
Crucible Rinse, 800°C	9.52	2.66	131.92	10.05	19.06	1.59
Crucible Rinse, 1000°C	0.89	BRL	BRL	0.29	0.34	2.06
Crucible Rinse, 1200°C	0.07	BRL	BRL	BRL	0.04	0.15
Condensate, 600°C	0.05	0.06	5.99	0.01	0.00	0.03
Condensate, 800°C	0.25	0.10	16.49	0.02	BRL	0.06
Condensate, 1000°C	12.11	0.92	14.43	BRL	BRL	0.16
Condensate, 1200°C	11.97	3.66	11.91	BRL	0.02	0.35
Case 5—No nitrate, reduced Tc and Re						
Feed Rinse	115.03	61.44	BRL	BRL	161.22	831.89
Crucible Rinse, 600°C	10.50	21.80	BRL	BRL	152.80	798.00
Crucible Rinse, 800°C	1.60	0.57	BRL	BRL	7.72	50.60
Crucible Rinse, 1000°C	19.54	1.08	BRL	BRL	1.53	828.00
Crucible Rinse, 1200°C	13.80	BRL	BRL	BRL	13.37	349.50
Condensate, 600°C	0.04	0.05	0.02	0.01	BRL	0.17
Condensate, 800°C	1.05	0.36	0.02	BRL	BRL	0.29
Condensate, 1000°C	11.36	0.96	BRL	BRL	BRL	5.13
Condensate, 1200°C	25.22	3.15	BRL	BRL	BRL	53.78
Case 6—Pre-melted glass						
Crucible Rinse, 1200°C 1 h	0.64	BRL	BRL	BRL	0.18	39.00
Crucible Rinse, 1200°C 5 h	3.72	0.06	BRL	BRL	0.11	16.54
Condensate, 1200°C 1 h	13.92	2.22	BRL	BRL	BRL	37.80
Condensate, 1200°C 5 h	67.35	6.36	BRL	BRL	0.10	163.47
BRL: below reporting limit						

feed rinse samples, about 20 g of feed sample was washed, and the result was used to calculate the amount of anions in the feed used to produce 200 g glass. Table 8.10 summarizes the wt% of total anions in the feed rinse, crucible rinse, and condensate samples, calculated by dividing the mass of each anion given in Table 8.9 with the mass of each anion added in the feed given in Table 8.8. Among these anions (Cl, F, NO_3, NO_2, PO_4, and SO_4) the discussion in this section will focus on NO_3, SO_4, and Cl. The reasons for focusing only on these 3 anions are as follows: SO_4 had significant effect on Re and Tc volatilization as discussed in Section 8.2.2.1: NO_3 behaved similarly to NO_2 but was present at a higher concentration than NO_2; Cl behaved similarly to F but was present at a higher concentration than F and NaCl was identified as the primary phase in condensate samples by XRD (see Section 8.2.2.4); and PO_4 does not form a separate salt phase unlike SO_4 and was not found in any of the condensate samples.

Figure 8.19 through Figure 8.23 show the change of the wt% of total anions in crucible rinse (starting from feed rinse) and condensate rinse as a function of the final temperature or time at 1200°C. The significant findings from these results are:

- Nitrates in the crucible rinse sample of the baseline (Case 1) and no sulfate (Case 4) feeds disappear before 800°C. Nitrates were not found in crucible rinse samples of the reduced nitrates (Case 3) and no nitrates (Case 5) as expected. For Case 3, this indicates that denitration was completed before 600°C.
- Sulfate in the crucible rinse of Case 1, Case 3, and Case 5 feeds decreases to a very low level or zero between the 800 and 1000°C range, but reappears and tends to increase as the final temperature increases. It is believed that the sulfate in the crucible rinse samples decreases and becomes almost zero when the glass-forming melt forms and traps all the gas bubbles that contain the sulfate layer (Hrma et al. 2003 and 2004) preventing the penetration of water (the present method of collecting a crucible rinse sample does not break the glass or partially reacted feed calcine into smaller pieces or powder). However, as the temperature increases, bubbles rise to the melt surface and form a separated salt layer that can be easily dissolved by a crucible rinse as in the 1000 and 1200°C crucible rinse samples.
- Cl starts to volatilize above 800°C while sulfate starts above 800 or 1000°C. The volatilization of Cl is significantly faster than sulfate. However, unlike sulfate, the Cl in crucible rinse samples disappears before 800 or 1000°C without reappearing, except for Case 5 feed that showed a slight increase of Cl at 1000 and 1200°C. The reason for this reappearing of Cl in Case 5 feed is not understood.
- In Case 6, all NO_3 and NO_2 and part of the Cl, F, PO_4, and SO_4 would have been lost during preparation of the pre-melted glass. A small fraction of Cl and sulfate is present in crucible rinse samples. As in the feed melting cases, the volatilization from glass is faster for Cl than for sulfate.

Comparison of above results on sulfate with the results on Re and Tc in crucible rinse samples from 1000 and 1200°C tests (Figure 8.7 through Figure 8.10) suggest that the sulfate salt phase in these 1000 and 1200°C crucible rinse samples did not have a high concentration of soluble Re and Tc in any cases. In baseline Case 1, for example, 9 to 22 wt% of total SO_4 was analyzed in the crucible rinse samples from 1000 and 1200°C tests whereas only 1 to 2 wt% of total Re or Tc was detected. In contrast, the crucible rinse sample from 800°C test had 26 wt% of total SO_4 and 13 wt% of total Re and 12 wt% of total Tc, indicating the sulfate in the 800°C crucible rinse sample had a high concentration of soluble Re and Tc. The decrease of Re and Tc in the crucible rinse samples as temperature increases from 800°C to 1200°C

Table 8.10. Wt% of Total Anions in Feed Rinse, Crucible Rinse, and Condensate Samples

Sample	Cl^- (wt%)	F^- (wt%)	NO_3^- (wt%)	NO_2^- (wt%)	PO_4^{3-} (wt%)	SO_4^{2-} (wt%)
Case 1 – Baseline						
Feed Rinse	84.03	25.56	96.41	86.70	10.00	87.76
Crucible Rinse, 600°C	71.44	56.73	59.94	32.90	11.67	61.61
Crucible Rinse, 800°C	21.87	17.58	4.71	5.16	9.01	25.87
Crucible Rinse, 1000°C	1.15	BRL	BRL	BRL	0.62	8.99
Crucible Rinse, 1200°C	0.72	0.46	BRL	BRL	0.83	22.07
Condensate, 600°C	0.01	0.01	0.00	0.00	BRL	0.00
Condensate, 800°C	0.02	0.16	0.07	BRL	BRL	0.00
Condensate, 1000°C	1.68	0.42	0.03	BRL	BRL	0.03
Condensate, 1200°C	6.82	3.95	0.02	BRL	BRL	0.62
Case 3 - Reduced nitrates by sugar and carbon						
Feed Rinse	75.06	29.15	72.73	67.83	8.28	77.38
Crucible Rinse, 600°C	9.51	12.35	BRL	BRL	15.73	70.01
Crucible Rinse, 800°C	0.29	0.17	0.00	BRL	0.35	0.88
Crucible Rinse, 1000°C	0.43	BRL	BRL	BRL	0.08	4.31
Crucible Rinse, 1200°C	1.17	0.33	BRL	BRL	0.18	17.28
Condensate, 600°C	0.05	0.06	0.00	BRL	BRL	0.00
Condensate, 800°C	0.21	0.17	0.00	BRL	BRL	0.01
Condensate, 1000°C	2.48	1.03	BRL	BRL	BRL	0.48
Condensate, 1200°C	3.99	1.53	0.00	BRL	BRL	0.69
Case 4 - No sulfate						
Feed Rinse	80.55	23.67	80.69	70.00	8.11	NA
Crucible Rinse, 600°C	76.94	58.29	54.11	29.88	11.62	NA
Crucible Rinse, 800°C	2.62	1.89	0.36	0.22	1.74	NA
Crucible Rinse, 1000°C	0.24	BRL	BRL	0.01	0.03	NA
Crucible Rinse, 1200°C	0.02	BRL	BRL	BRL	0.00	NA
Condensate, 600°C	0.01	0.05	0.02	0.00	0.00	NA
Condensate, 800°C	0.07	0.07	0.05	0.00	BRL	NA
Condensate, 1000°C	3.33	0.65	0.04	BRL	BRL	NA
Condensate, 1200°C	3.29	2.59	0.03	BRL	0.00	NA
Case 5 - No nitrate, reduced Tc and Re						
Feed Rinse	31.61	43.56	BRL	BRL	14.72	41.07
Crucible Rinse, 600°C	2.89	15.46	BRL	BRL	13.96	39.40
Crucible Rinse, 800°C	0.44	0.41	BRL	BRL	0.71	2.50
Crucible Rinse, 1000°C	5.37	0.76	BRL	BRL	0.14	40.88
Crucible Rinse, 1200°C	3.79	BRL	BRL	BRL	1.22	17.25
Condensate, 600°C	0.01	0.03	0.00	0.00	BRL	0.01
Condensate, 800°C	0.29	0.25	0.00	BRL	BRL	0.01
Condensate, 1000°C	3.12	0.68	BRL	BRL	BRL	0.25
Condensate, 1200°C	6.93	2.23	BRL	BRL	BRL	2.66
Case 6 – Pre-melted glass						
Crucible Rinse, 1200°C 1 h	0.18	BRL	BRL	BRL	0.02	1.93
Crucible Rinse, 1200°C 5 h	1.02	0.04	BRL	BRL	0.01	0.82
Condensate, 1200°C 1 h	3.82	1.57	BRL	BRL	BRL	1.87
Condensate, 1200°C 5 h	18.51	4.51	BRL	BRL	0.01	8.07
BRL: below reporting limit NA: Not applicable						

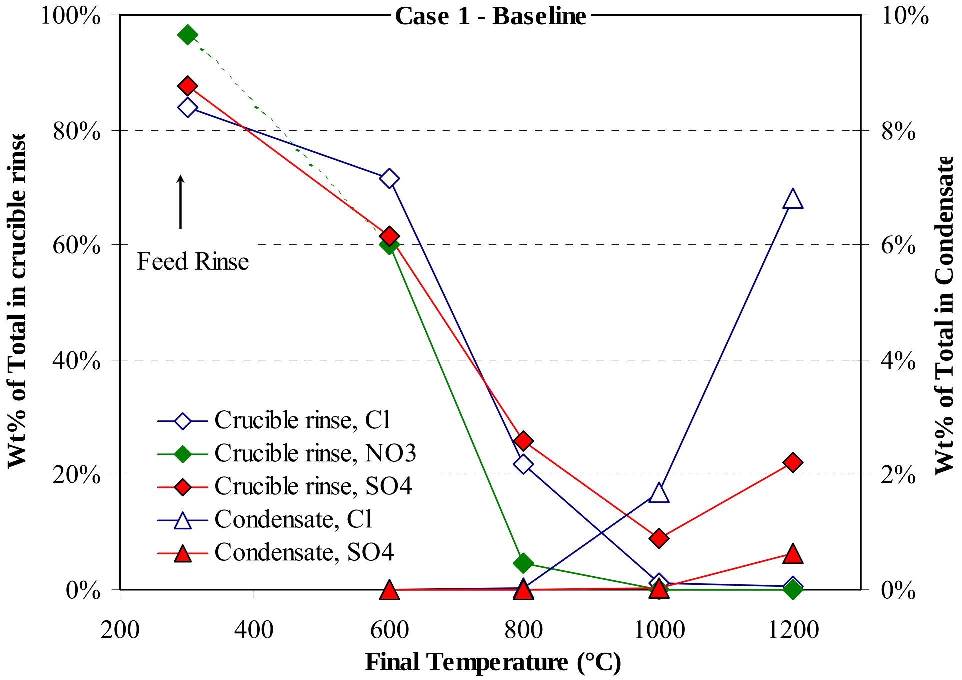

Figure 8.19. Wt of Total Anions Versus Final Temperature for Case 1—Baseline Feed

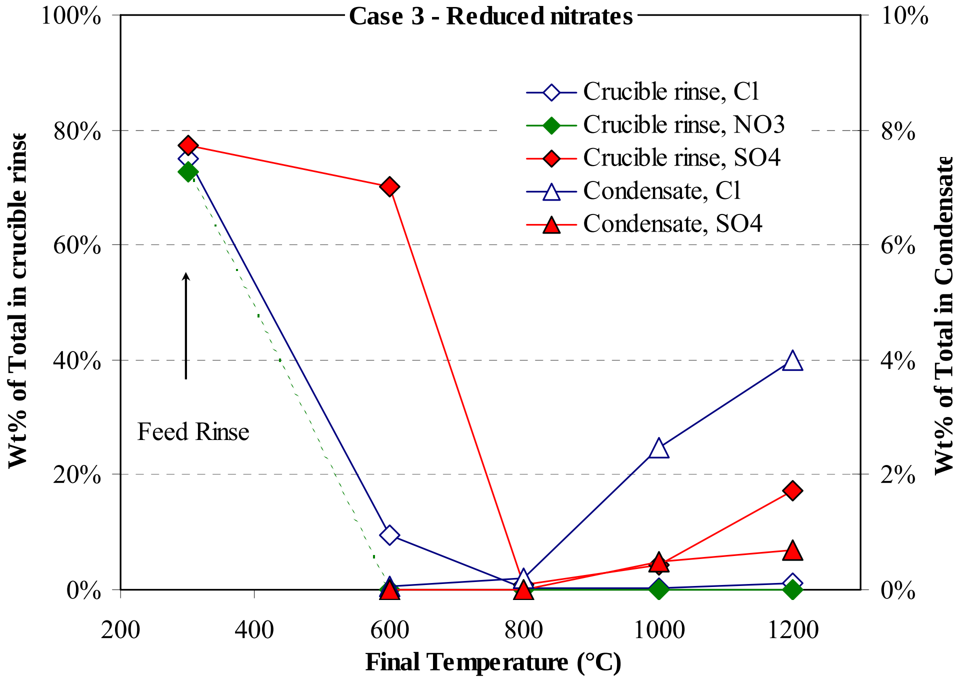

Figure 8.20. Wt of Total Anions Versus Final Temperature for Case 3—Reduced Nitrates Feed

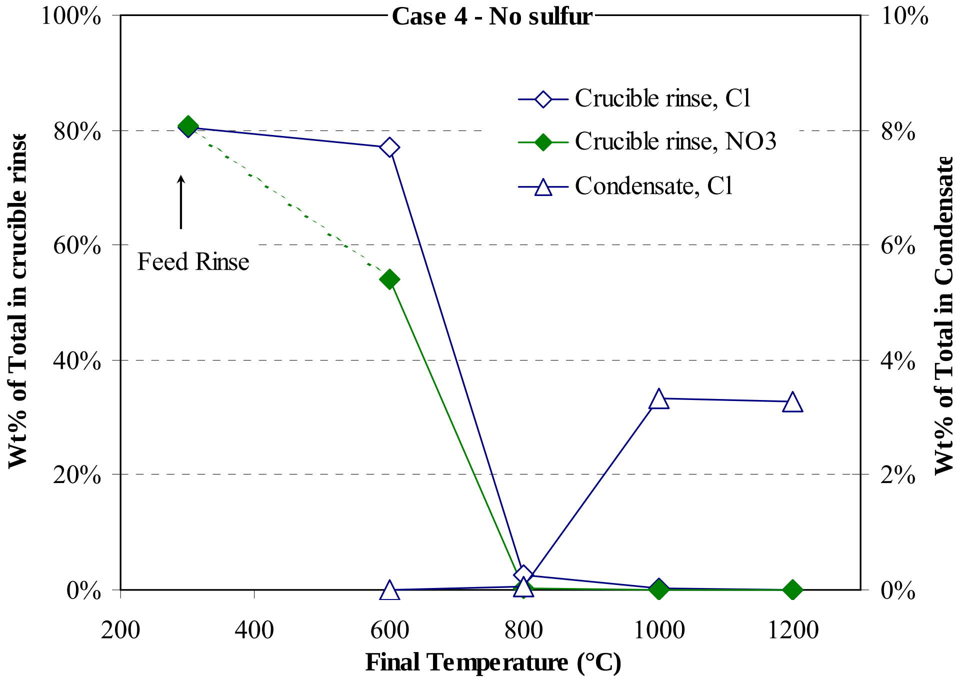

Figure 8.21. Wt of Total Anions Versus Final Temperature for Case 4—No Sulfate Feed

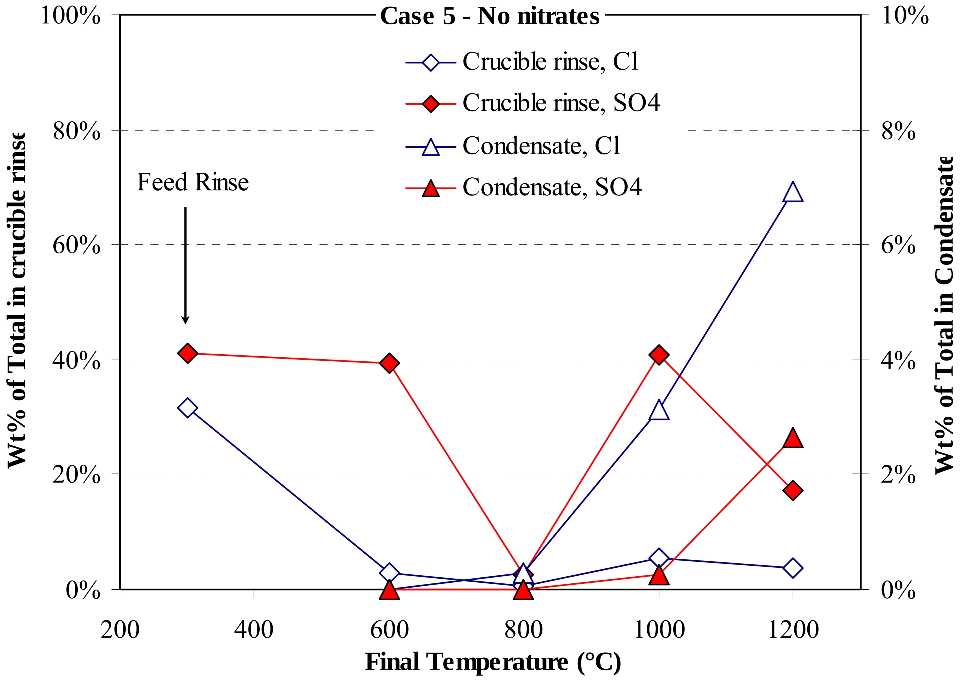

Figure 8.22. Wt of Total Anions Versus Final Temperature for Case 5—No Nitrates Feed

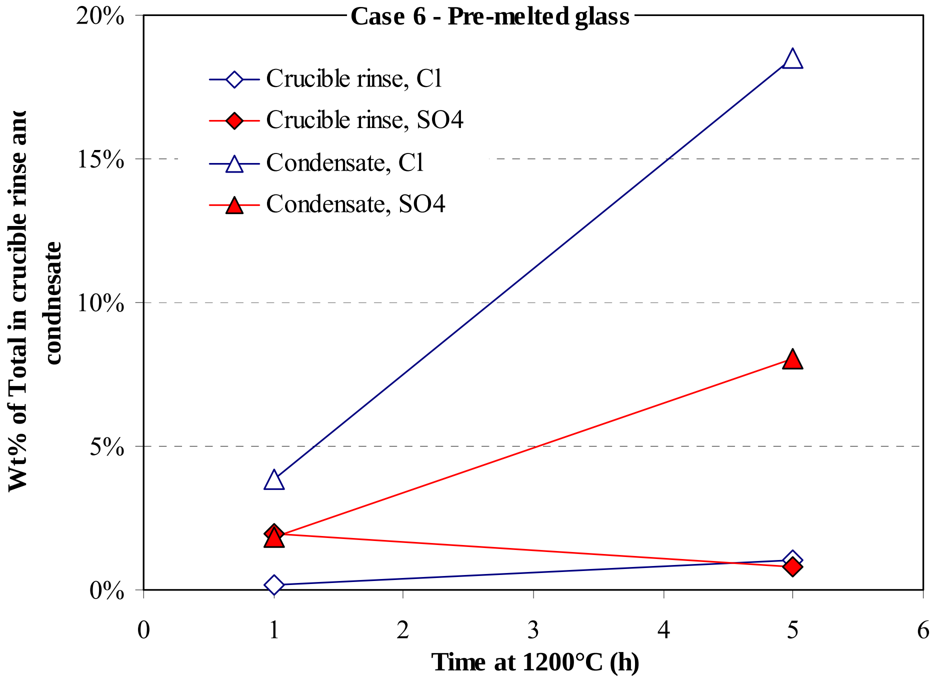

Figure 8.23. Wt of Total Anions Versus Time at 1200°C for Case 6—Pre-melted Glass

suggests that the Re and Tc contained in the separated salt layer volatilizes very fast leaving the separated sulfate layer without Re and Tc. This fast volatilization of Re and Tc from salt layer seems to partly explain the higher volatilization of Re and Tc in the baseline feed compared to the no-sulfate feed.

- Based on these results, it is likely that Re and Tc volatilize much faster than any other volatile species in the feed assuming that the condensation efficiency of the cold finger capturing the volatile species is the same for all volatile species, i.e. the cold finger condenses the similar fraction of the volatilized mass for each species.
- Comparison of volatilization from pre-melted glass in Figure 8.11 and Figure 8.23 indicates that Re and Tc volatilize faster than Cl or any other volatile species in the glass.

8.2.2.3 Glass Components Results by ICP-AES

Table 8.11 summarizes the results of glass components analyses by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on the glass samples collected from 1200°C tests of Cases 1, 3, 4, and 5, pre-melted glass used for Case 6 tests (designated as Case 6 0 h), and Case 6 1200°C 1- and 5-h tests. Table 8.11 also compares the analytical results with the target glass composition for those components reported after excluding Cl, F, and SrO that cannot be analyzed by ICP-AES or were present below reporting limit from Table 4.2. One of the purposes of the ICP-AES analyses on glass samples was to check if there was any error in feed preparation, which also involves the composition of simulant.

Table 8.11 shows that the analyzed compositions agree with the target reasonably well except that SO_3 is lower than target levels, which is as expected due to its high volatility. There was no indication that any feed preparation errors occurred.

Table 8.11. Summary of ICP-AES Results on Glass Samples (composition in wt)

Oxide	Case 1 1200°C	Case 3 1200°C	Case 4 1200°C	Case 5 1200°C	Case 6 0 h(a)	Case 6 1 h	Case 6 5 h	Target(b)
Al_2O_3	9.54	9.40	8.99	9.17	9.38	9.17	9.39	9.15
B_2O_3	4.78	4.94	4.41	4.16	4.98	4.34	4.88	5.00
BaO	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05
CaO	2.95	3.27	2.84	3.11	3.18	3.07	3.19	2.74
Cr_2O_3	0.08	0.10	0.09	0.09	0.09	0.08	0.09	0.10
Fe_2O_3	5.05	5.24	4.55	4.98	5.03	4.79	5.05	4.25
K_2O	1.56	1.73	1.59	1.73	1.79	1.72	1.71	1.54
MgO	1.46	1.52	1.63	1.50	1.50	1.48	1.52	1.34
MnO	0.08	0.08	0.07	0.08	0.08	0.08	0.08	0.07
Na_2O	20.40	20.08	19.96	19.82	19.66	19.71	19.88	20.00
P_2O_5	0.52	0.61	0.58	0.57	0.58	0.57	0.54	0.55
SiO_2	44.99	44.76	43.95	44.60	44.71	44.74	43.92	46.31
SO_3	0.54	0.19	0.000	0.322	0.30	0.58	0.26	0.84
TiO_2	0.85	0.90	0.78	0.87	0.85	0.83	0.85	0.79
ZrO_2	6.47	6.58	6.23	6.43	5.93	5.92	5.96	7.00
LOI @ 1000°C	2.34	1.21	2.56	2.09	2.25	1.39	2.28	-
SUM	101.66	100.65	98.29	99.57	100.35	98.53	99.65	99.73

(a) Represent pre-melted glass used for Case 6 tests.

(b) Excluding the components that cannot be analyzed by ICP-AES (Cl and F) or were present below the reporting limit (SrO) from Table 4.2.

Table 8.12 summarizes the results of glass components analyses by ICP-AES on the condensate samples collected from all tests performed in this study. The data values given in the table are the masses of each element analyzed in total condensate samples obtained by multiplying the analyzed concentration by the amount of water used in collecting condensate samples. Table 8.12 shows only the elements that were present at more than 10 mg/kg in at least one sample. Even among these elements, the concentrations of the non-volatile components, Al, Ca, Cr, Fe, Mo, and Si, do not show any systematic change with feed variations or with temperature, indicating that they are present in condensate samples as impurities in cold finger materials or contamination by feed materials because of dusting during the initial melting stage of the dried feed. The data evaluation is conducted only on the volatile components, B, K, Na, and S.

Table 8.13 summarizes the wt% of total target mass of element in the 200 g glass analyzed in condensate samples for B, K, Na, and S, which were obtained by dividing the mass of element in condensate samples given in Table 8.12 with the calculated target mass of element given in Table 8.14. The data in Table 8.13 are plotted in Figure 8.24. General trends in the ICP-AES results in Table 8.13 and Figure 8.24 are:

- When sulfate was present in the feed, it showed the highest volatilization rate among four volatile components. This was also true for the glass sample (Case 6).
- Potassium shows the next highest volatilization, and B and Na had similar volatilization rates for both feed and pre-melted glass samples.
- The highest volatilization of sulfate was observed in Case 5 (no nitrate) feed. The trend of increasing volatilization with temperature resembled the baseline feed but proceeded at a rate approximately four times higher than the baseline.
- Glass itself shows significant volatilization with a much higher rate for sulfate than any other components analyzed by ICP-AES.

Table 8.12. Summary of ICP-AES Results on Condensate Samples

Element	Case 1 600°C (mg)	Case 1 800°C (mg)	Case 1 1000°C (mg)	Case 1 1200°C (mg)	Case 3 600°C (mg)	Case 3 800°C (mg)	Case 3 1000°C (mg)	Case 3 1200°C (mg)	Case 4 600°C (mg)
Al	0.068	0.204	0.19	0.075	0.021	0.039	0.561	0.355	0.048
B	0.023	0.083	0.264	3.76	0.022	0.031	0.664	1.715	0.049
Ca	0.168	0.273	0.073	0.123	0.033	0.08	0.103	BRL	0.185
Cr	0.003	0.014	0.057	0.585	BRL	0.014	0.326	0.358	0.004
Fe	BRL	0.053	0.098	0.324	BRL	0.063	1.122	0.971	BRL
Mo	BRL	0.04	0.018	0.914	BRL	BRL	0.076	0.833	0.005
K	BRL	2.25	2.362	7.303	BRL	0.085	2.003	4.101	0.087
Si	0.22	0.42	BRL	0.035	BRL	BRL	BRL	BRL	0.047
Na	0.056	6.47	5.306	18.916	0.056	0.338	7.278	30.466	0.614
S	BRL	0.015	0.133	3.632	BRL	BRL	2.901	2.202	BRL

Element	Case 4 800°C (mg)	Case 4 1000°C (mg)	Case 4 1200°C (mg)	Case 5 600°C (mg)	Case 5 800°C (mg)	Case 5 1000°C (mg)	Case 5 1200°C (mg)	Case 6 1 h (mg)	Case 6 5 h (mg)
Al	0.085	0.114	0.108	0.113	0.123	0.279	0.149	0.149	0.158
B	0.057	0.411	1.714	BRL	BRL	0.441	2.42	4.369	32.659
Ca	0.191	BRL	0.132	0.06	0.096	0.056	0.062	0.048	BRL
Cr	0.004	0.055	0.11	BRL	0.095	0.167	0.482	0.559	2.085
Fe	BRL	0.122	0.127	0.023	0.368	0.442	0.775	0.288	0.148
Mo	0.01	0.019	0.407	0.006	0.011	0.044	0.144	0.156	0.599
K	1.491	4.492	3.913	BRL	0.093	2.257	8.517	7.638	49.75
Si	0.205	0.116	0.087	0.046	0.082	0.091	BRL	BRL	BRL
Na	3.945	10.271	8.6	0.336	0.576	6.036	30.464	19.975	124.207
S	0.022	BRL	0.042	0.031	0.056	1.383	14.686	10.356	53.135

BRL: Below reporting limit

Table 8.13. Wt% of Target Element in 200 g Glass in Condensate Samples

Element	Case 1 600°C (wt)	Case 1 800°C (wt)	Case 1 1000°C (wt)	Case 1 1200°C (wt)	Case 3 600°C (wt)	Case 3 800°C (wt)	Case 3 1000°C (wt)	Case 3 1200°C (wt)	Case 4 600°C (wt)
B	0.0008	0.0027	0.0085	0.1211	0.0007	0.0010	0.0214	0.0552	0.0016
K	0.0000	0.0880	0.0924	0.2856	0.0000	0.0033	0.0783	0.1604	0.0034
Na	0.0002	0.0218	0.0179	0.0637	0.0002	0.0011	0.0245	0.1027	0.0021
S	0.0000	0.0023	0.0198	0.5398	0.0000	0.0000	0.4312	0.3272	0.0000

Element	Case 4 800°C (wt)	Case 4 1000°C (wt)	Case 4 1200°C (wt)	Case 5 600°C (wt)	Case 5 800°C (wt)	Case 5 1000°C (wt)	Case 5 1200°C (wt)	Case 6 1 h (wt)	Case 6 5 h (wt)
B	0.0018	0.0132	0.0552	0.0000	0.0000	0.0142	0.0779	0.1407	1.0516
K	0.0583	0.1757	0.1530	0.0000	0.0036	0.0883	0.3331	0.2987	1.9458
Na	0.0133	0.0346	0.0290	0.0011	0.0019	0.0203	0.1027	0.0673	0.4186
S	0.0033	0.0000	0.0062	0.0046	0.0083	0.2056	2.1827	1.5391	7.8970

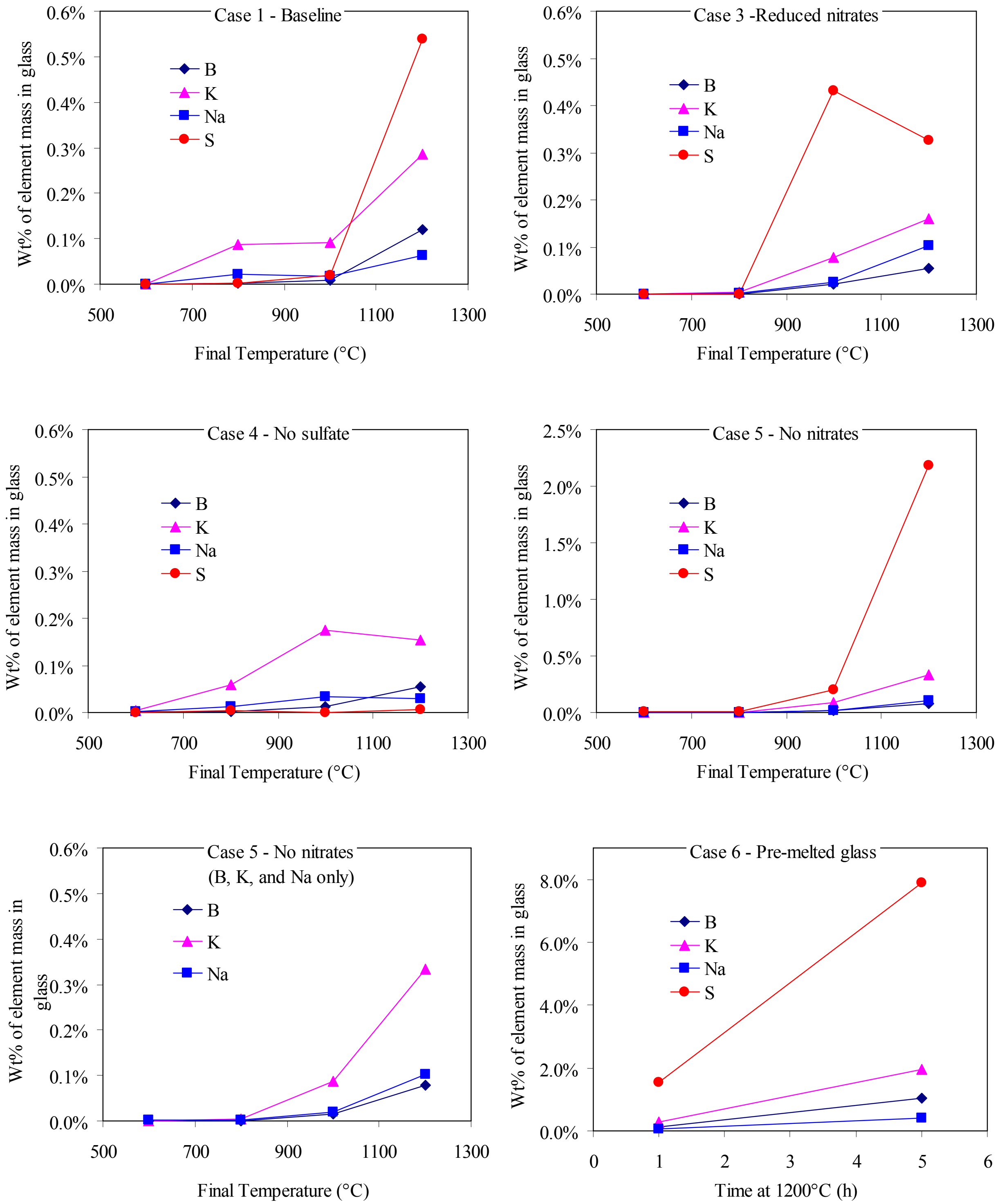

Figure 8.24. Wt% of Target Element in 200 g Glass Analyzed in Condensate by ICP-AES

Table 8.14. Calculated Target Mass of Elements in 200 g Glass

Element	B	K	Na	S
Mass in 200 g glass (g)	3.106	2.557	29.674	0.673

8.2.2.4 XRD of Condensate Samples

Table 8.15 summarizes the XRD analysis results on selected condensate samples. The XRD scan patterns are included in Appendix C. XRD samples were collected for all 1000°C and 1200°C tests except the Case 5 1000°C and Case 6 1200°C 1-h samples because the amount of condensate materials was too small to reserve samples for XRD. Some condensate materials, especially Case 5 samples, were also very difficult to handle because they were very light and tended to dust away. The semi-quantitative analyses using an internal standard material were not performed because of small sample size.

The main finding of the XRD results is the positive identification of the $K(Re,Tc)O_4$ phase (denotes a solid solution of $KReO_4$ and $KTcO_4$ phases that have almost identical XRD peak patterns) in most of the condensate samples. The $K(Re,Tc)O_4$ phase was not identified in Case 4 1000°C and 1200°C samples and the Case 6 1200°C 5-h sample. However, the lack of $K(Re,Tc)O_4$ peaks in these samples could be because the amount of condensate sample was too small or the concentration of Re and Tc was too low.

NaCl was the primary phase in all condensate samples (after considering the relative intensity ratio [RIR] of the phases identified), which agrees with the high volatilization rate of Cl as discussed in subsection 8.2.2.2. Nitrates were observed only in 1000°C condensate samples of Case 1 and Case 4 feeds, indicating that the nitrates in feeds without reductants will partially volatilize and condense as the feed was heated through lower temperatures. At higher temperatures, the condensate sample is dominated by other phases so the nitrates do not show up. The results from the Case 6 1200°C 5h test suggests that NaCl and alkali sulfates are the main volatile components from glass, which agree with the IC results shown in Figure 8.23.

Table 8.15. Summary of Qualitative XRD Results on Cold Finger Condensate Samples

Test Case	Condition	Positive or highly probable matches[(a)]
Case 1—Baseline	1000°C	$NaCl > NaNO_3 > KNO_3 \sim K(Re,Tc)O_4$
	1200°C	$NaCl >> Na_2SO_4 \sim NaK_3(SO_4)_2 > K(Re,Tc)O_4$
Case 3—Reduced nitrates by sugar and carbon	1000°C	$NaCl >> K(Re,Tc)O_4$
	1200°C	$NaCl >> K(Re,Tc)O_4$
Case 4 - No sulfate	1000°C	$NaCl > NaNO_3 > Fe_2PO_5$
	1200°C	$NaCl >> KCl$
Case 5—No nitrate, reduced Tc/Re	1200°C	$NaCl >> CaS > Na_2SO_4 \sim NaK_3(SO_4)_2 \sim NaClO_4 \geq K(Re,Tc)O_4$
Case 6—Pre-melted glass	1200°C 5 h	$NaCl > NaKSO_4$
(a) >>, >, and ~ symbols are to show the order of relative XRD peak intensities as a rough indication of dominat phases, not quantitative phase fraction.		

8.3 Summary

From the feed melting reduction study, adding sucrose at C/N =1 and carbocite at C/N = 0.5 resulted in the iron redox of 54%, which was the best attainable within the limited conditions tested with the Pt crucible configuration, and was selected as the condition for use in the crucible feed melting tests for Tc volatilization. It was found that the redox is very sensitive to the drying condition and melting test configuration, and that it is difficult to obtain a highly reduced state using sucrose only (mainly because the reaction involving sucrose completes at a lower temperature as found in Section 7.0). The combination of sucrose and carbon appeared to be effective in maintaining a reduced melt up to a high temperature range through removing nitrates by sucrose at lower temperatures and maintaining the reduced state with carbon from carbocite at higher temperatures. It should be noted that the proper amount of sucrose and carbon necessary to keep the feed/melt reduced will be different for different crucible geomtries and also for ES or full-scale processing.

General findings from the crucible feed melting studies with cold finger are as follows:

- Significant volatilization of Re and Tc begins only above 800°C.
- Re and Tc behave very similarly with only a few exceptions that are likely due to sample inhomogeneity.
- The $K(Re,Tc)O_4$ phase was identified in condensate samples except Cases 4 (no sulfate) and 6 (pre-melted glass).
- Current test methods seem to have a high efficiency of collecting volatile Re and Tc.
- Crucible scale tests showed that feed with no sulfate had noticeably reduced Re/Tc volatilization compared to the baseline feed. Although removal of sulfate is not directly applicable for process enhancement, the information gained from these test is valuable for understanding Tc volatilization to point to other possible process enhancements such as controlling the BV operational parameters to minimize the sulfate layer formation.
- It was confirmed that a reduced state can be maintained during melting process up to 1200°C by adding sucrose and carbon to slurry feed.
- Feeds with reduced nitrates, either by reductants or using reduced Re/Tc without nitrates, do not reduce Re/Tc volatilization.
- Significant volatilization of Re and Tc occurs from the pre-melted glass sample, although this rate is much slower than the rate observed in the melting feed.

Preliminary conclusions on Tc volatilization and related mechanisms can be summarized as follows:

- Re and Tc are the components with highest volatility among volatile species investigated in this study. Volatilization of Re and Tc occurs at a fairly high rate even from a glass where the Re and Tc were already incorporated. Based on the data presented in this report, the order of volatilization from both a pre-melted glass and melting feed is $Re \approx Tc > Cl > F > S > K > B \approx Na$.
- The plausible explanations for higher volatilization of Re and Tc from the melting feed compared to the pre-melted glass are
  - low viscosity of initial glass-forming melt due to slow dissolution of refractory components (e.g., quartz from soil and ZrO_2) into glass melt

  - enhanced mixing by reaction gas generation and higher surface area of foamy and bubbly melt (roughly at T <1000°C).

- The sulfate in the feed promotes the volatilization of Re and Tc through
  - formation of a salt layer concentrated with Re and Tc from which volatilization of Re and Tc is much higher than from the glass
  - enhanced mixing by sulfate bubble transport at high temperatures (roughly at T >1000°C).

The present results from crucible feed melting tests suggest that certain operational adjustments can be made to reduce Tc volatilization, such as decreasing the holding time at the end of the process run and using a cold cap as much as possible during the process. The present results may warrant the following additional crucible studies:

- Effect of concentration of other highly volatile species such as Cl and F on the Tc volatilization.
- Effect of glass composition on the Tc volatilization in terms of K and B concentrations, sulfate solubility (thermodynamic) and sulfate retention (kinetic), and viscosity of the glass melt.
- Effect of raw materials, e.g., choice of soil and additives such as using silica sand partially replacing soil and using zircon ($ZrSiO_4$) replacing ZrO_2, on the melting reactions and Tc volatilization. The choice of raw materials including different particle size affects the viscosity of initial glass-forming melt and temperature range of gas bubble and foam generation, which are expected to influence volatilization of Tc.

9.0 Conclusions

Several potential methods of reducing the Tc(VII) contained in a tank waste simulant and keeping it in a less volatile, reduced state were proposed and tested including: finely divided metallic iron, dithionite, and borohydride. None of the initially proposed reductants were successful. Finely divided iron (25-nm particles) did not reduce pertechnetate in a tank waste simulant. Neither dithionite nor borohydride reduced pertechnetate under basic conditions of the tank waste simulant. Furthermore, when $TcO_2 \cdot nH_2O$ (the reduced form of technetium) was added to tank waste simulant, it was quickly oxidized back to TcO_4^- by the waste simulant even when air was excluded.

A broader set of screening experiments were conducted to determine the feasibility of reducing technetium in caustic waste streams considered for bulk vitrification (BV). A long list of potential reducing agents was tested using a simplified simulant spiked with orders of magnitude more Re than that expected for Tc in tank waste. The high Re concentrations allowed quick Raman screening analyses to be conducted to determine the reductant's ability to effectively reduce Re(VII) and keep it in a reduced state for an extended time. $SnCl_2$ was found to be an effective, although temporary reducing agent for Re in simulated LAW feeds. Stable reduction was demonstrated by removing water with addition of anhydrite ($CaSO_4$). Results with other binders, including bentonite clay and poly acrylic acid were inconclusive. Several additional water binders and reductants remain to be investigated.

Thermal sucrose denitration of a simulated Hanford LAW was investigated as a pretreatment step to reduce the thermal oxidizing potential of Hanford wastes during vitrification using thermogravimetric analysis (TGA), differential thermal analysis (DTA), and nitrate/nitrite analysis of residual solids. The results of these thermal sucrose denitration studies indicate that Hanford LAW can be effectively denitrated at 400°C. It was shown that this process is an effective approach for removing nitrate and nitrite from Hanford LAW.

A feed melting reduction study found that adding sucrose at a carbon to nitrogen ratio (C/N) of 1 and carbocite at a C/N of 0.5 provided reducing conditions sufficient to keep the melt at a relatively reduced state up to high temperatures. These additions were selected for use in the crucible feed melting tests for Tc volatilization under reducing glass melt conditions. However, crucible scale tests showed that keeping the melt in a reduced state did not reduce Tc/Re volatilization. This was true even when feed without nitrates and spiked with reduced Tc and Re were used. Crucible scale tests showed that feed with no sulfate had noticeably reduced Tc/Re volatilization compared to the baseline feed. Although removal of sulfate is not directly applicable for process enhancement, the information gained from these tests is valuable for understanding Tc volatilization and may point to other possible process enhancements such as controlling the BV operational parameters to minimize the sulfate layer formation. It was also found that significant volatilization of Tc and Re occurs from a pre-melted glass sample, although the volatilization rate from glass is much lower than the rate from melting glass feed materials.

The added understanding of Tc volatilization and related mechanisms obtained from the crucible melt studies includes:

- Re and Tc behave similarly and both readily volatilize from both glass and melting feed.

- Tc/Re volatilization from melting feed is higher than pre-melted glass and is likely a result of the low viscosity of the initial glass-forming melt, enhanced mixing by reaction gases generated during melting, and the higher surface area of the foamy/bubbly melt that exist at temperatures below ~1000°C.
- The sulfate in the feed promotes volatilization through formation of a salt layer concentrated with Re and Tc. Volatilization of Re and Tc is much higher from the salt layer than from the glass. Enhanced sulfate bubble transport at high temperatures may also play a role at higher temperatures.

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Appendix A

Pure Simulant Salts: Melting, Decomposition, and Boiling Temperatures of the Simulant Components

Appendix A: Pure Simulant Salts: Melting, Decomposition, and Boiling Temperatures of the Simulant Components

Compound	M.P., °C	Decomp., °C	B.P., °C
[1]$Na_2C_2O_4$	250-270	250-270	……
[2]CH_3COONa	120	324	……
[3]$NaNO_3$	308		380
[4]KNO_3	333	400	400
[5]NaOH	318		1389
[6]$Al(NO_3)_3{\cdot}9H_2O$	73	135	135
[7]Na_2CO_3	851		1600
[8, 8a]Na_2SO_4 Anhydrous	844		…..
[9]Na_2CrO_4	792	>792	…..
[10]$Na_3PO_4{\cdot}12H_2O$ Anhydrous	73-77 1340	…..	…..
[11]NaCl	1040	…..	1413
[12]NaF	980	…..	1700
[13]$NaNO_2$	271	320	…..
[14]$CsNO_3$	414	…	…..

1) http://www.jtbaker.com/msds/englishhtml/s4586.htm
2) http://www.jtbaker.com/msds/englishhtml/s2666.htm
3) http://www.jtbaker.com/msds/englishhtml/s4442.htm
4) http://www.jtbaker.com/msds/englishhtml/P5950.htm
5) http://www.jtbaker.com/msds/englishhtml/S4034.htm
6) http://www.jtbaker.com/msds/englishhtml/a2832.htm
7) http://www.atmos.umd.edu/~russ/MSDS/sodium_carbonate_anhydrous.htm
8) http://www.jtbaker.com/msds/englishhtml/s5022.htm
8a) Na_2SO_4—Na_2S exists as a eutectoid mixture at a temperature of 730°C and about 23 wt% of sodium-sulfide. Therefore, the complete conversion of sodium-sulfate will be prevented. The effect of caustic on the reaction has not been studied.
9) http://www.jtbaker.com/msds/englishhtml/s5022.htm
10) http://www.jtbaker.com/msds/englishhtml/s4757.htm
11) http://ptcl.chem.ox.ac.uk/MSDS/SO/sodium_chloride.html
12) http://www.jtbaker.com/msds/englishhtml/S3722.htm
13) http://www.jtbaker.com/msds/englishhtml/s4466.htm
14) http://physchem.ox.ac.uk/MSDS/CA/caesium_nitrate.html

Appendix B

Analytical Data: Residual Anions Analysis by Ion Chromatography

Appendix B: Analytical Data: Residual Anions Analysis by Ion Chromatography

Submitted under ASR # 7071

Quality Control Discussion

The IC performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001. **The QC has been evaluated ONLY for the analytes of interest specified on the ASR; i.e., nitrite and nitrate.**

Processing Blank: No processing of the samples was performed before analysis. The diluent blank and the IC System QC (i.e., calibration verification blanks) is used to assess potential contamination and quality of the dilution media. Low concentrations of nitrate were detected above the method detection limite (MDL) in the dilution blanks. The dilution blank results have been normalized to the dilutions used for reporting the sample results. The dilution blank nitrate results are less than the estimated quantitation limit (EQL); thus, they meet the QC plan acceptance criteria. However, it should be noted that the blank contributes significantly to many of the sample results, which have concentrations near the EQL.

Duplicate (Precision): Sample SSC49-10 was analyzed in replicate. The relative percent difference for nitrite and nitrate were well within the QA plan criterion of <21.7.

Laboratory Control Sample/Blank Spike (LCS/BS): An LCS/BSs was analyzed with each run, and the nitrate and nitrate LCS results (99 to 103 recovery) were within the acceptance criterion of 80 to 120.

Matrix Spike (MS) (Accuracy): A matrix spike was prepared by adding a known concentration of mid-range concentration multi-mix standard, “ICV040703.” The nitrate and nitrite results of 97 and 100, respectively, were within the acceptance criterion of 75 to 125.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run. For all data reported, all IC System QC bounding the sample analyses produced results within the acceptance criterion of the ASO’s QA Plan (i.e., 90 to 110 recovery for verification standards and results <EQL for verification blanks).

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- The MDL is set at the concentration of the lowest calibrations standard divided by 10. The EQL is defined as the concentration of the lowest calibration standards times the sample dilution factors (processing and analysis) and assumes non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, if requested.
- Routine precision and bias are typically ±15 or better for non-complex aqueous samples that are free of interference.

Codes for Data Flagging

U = The analyte was undetected. For NO_2, NO_3, PO_4, SO_4, and C_2O_4, the MDL was 0.25 µg/mL. For F and Br, the MDL was 0.13 µg/mL, and for Cl, the MDL was 0.12 µg/mL.

J = Samples were analyzed using standard ASO methods and reagents by the ASO-trained analyst. The first set of analytical data were diluted by a factor of 200, and this dilution factor proved too high. The results from the second data set were obtained on the undiluted leachates. The second table is considered more reliable. But a sense of the reproducibility of the data, and in particular the U and J flagged data, can be appreciated by comparisons of both data sets.

RPL Number	Sample ID	F MDL ug/mL	F Result ug/mL	Cl MDL ug/mL	Cl Result ug/mL	NO2 MDL ug/mL	NO2 Result ug/mL	Br MDL ug/mL	Br Result ug/mL	NO3 MDL ug/mL	NO3 Result ug/mL	PO4 MDL ug/mL	PO4 Result ug/mL	SO4 MDL ug/mL	SO4 Result ug/mL	C2O4 MDL ug/mL	C2O4 Result ug/mL
9/12-13/04																	
04-01727 DB	Dil Blk @Instrument	0.013	0.013 U	0.012	0.10 J	0.025	0.025 U	0.013	0.013 U	0.025	0.025 U	0.025	0.025 U	0.025	0.10 J	0.025	0.025 U
04-01727 DB	Dil Blk @Sample Dilution	1.3	1.3 U	1.2	10 J	2.5	2.5 U	1.3	1.3 U	2.5	2.5 U	2.5	2.5 U	2.5	10 J	2.5	2.5 U
04-01727	SSC42-1	1.3	12 J	1.2	42.6	2.5	5.4 J	1.3	1.3 U	2.5	20 J	2.5	81.6	2.5	182	2.5	2.5 U
04-01728	SSC43-1	1.3	17.0	1.2	57.8	2.5	2.5 U	1.3	1.3 U	2.5	8.3 J	2.5	108	2.5	277	2.5	2.5 U
04-01729	SSC44-10	1.3	9.6 J	1.2	34.4	2.5	2.5 U	1.3	1.3 U	2.5	3.6 J	2.5	51.7	2.5	51.0	2.5	2.5 U
04-01730	SSC45-10	1.3	4.4 J	1.2	45.8	2.5	2.5 U	1.3	1.3 U	2.5	5.8 J	2.5	58.1	2.5	53.6	2.5	2.5 U
04-01731	SSC46-20	1.3	23.6	1.2	35.5	2.5	2.5 U	1.3	1.3 U	2.5	9.0 J	2.5	46.9	2.5	164	2.5	2.5 U
04-01732	SSC47-20	1.3	24.3	1.2	29.5	2.5	2.5 U	1.3	1.3 U	2.5	3.9 J	2.5	51.3	2.5	116	2.5	32.6
04-01733	SSC48-1	1.3	46.4	1.2	159	2.5	96.4	1.3	1.3 U	2.5	82.6	2.5	67.9	2.5	914	2.5	2.5 U
04-01734	SSC49-10	1.3	26.9	1.2	54.9	2.5	50.7	1.3	1.3 U	2.5	8.3 J	2.5	47.3	2.5	330	2.5	2.5 U
04-01734 Dup	SSC49-10 Duplicate	1.3	20.4	1.2	41.4	2.5	49.1	1.3	22.1	2.5	9.4 J	2.5	47.3	2.5	232	2.5	2.5 U
RPD (%)			27		28		3		n/a		n/a		0		35		n/a
QC Samples																	
04-01727 MS(200	Matrix Spike (% Rec)		92		96		97		103		100		99		102		102
LCS 040912	Lab Control Sample (% Rec)		102		101		101		105		103		102		103		102

RPL Number	Sample ID	F MDL ug/mL	F Result ug/mL	Cl MDL ug/mL	Cl Result ug/mL	NO2 MDL ug/mL	NO2 Result ug/mL	Br MDL ug/mL	Br Result ug/mL	NO3 MDL ug/mL	NO3 Result ug/mL	PO4 MDL ug/mL	PO4 Result ug/mL	SO4 MDL ug/mL	SO4 Result ug/mL	C2O4 MDL ug/mL	C2O4 Result ug/mL
9/21/04																	
04-01727 DB	Dil Blk @Instrument	0.013	0.013 U	0.012	0.081 J	0.025	0.025 U	0.013	0.013 U	0.025	0.058 J	0.025	0.025 U	0.025	0.13 J	0.025	0.025 U
04-01727 DB	Dil Blk @Sample Dilution	0.13	0.13 U	0.12	0.81 J	0.25	0.25 U	0.13	0.13 U	0.25	0.58 J	0.25	0.25 U	0.25	1.30 J	0.25	0.25 U
04-01727	SSC42-1	0.13	8.17	0.12	37.2	0.25	6.39	0.13	0.13 U	0.25	17.9	0.25	82.8	0.25	181	0.25	0.25 U
04-01728	SSC43-1	0.13	6.24	0.12	65.4	0.25	0.25 U	0.13	0.13 U	0.25	8.59	0.25	103	0.25	286	0.25	0.25 U
04-01729	SSC44-10	0.13	5.73	0.12	30.9	0.25	0.25 U	0.13	0.13 U	0.25	0.85 J	0.25	47.8	0.25	43.5	0.25	0.25 U
04-01730	SSC45-10	0.13	5.17	0.12	43.5	0.25	0.25 U	0.13	0.13 U	0.25	1.2 J	0.25	55.9	0.25	43.9	0.25	0.25 U
04-01731	SSC46-20	0.13	16.3	0.12	25.6	0.25	0.25 U	0.13	0.13 U	0.25	6.22	0.25	43.6	0.25	161	0.25	9.10
04-01732	SSC47-20	0.13	18.5	0.12	21.6	0.25	0.25 U	0.13	0.13 U	0.25	3.62	0.25	48.7	0.25	105	0.25	27.2
04-01733	SSC48-1	0.13	0.13 U	0.12	189	0.25	87.7	0.13	0.13 U	0.25	81.3	0.25	0.25 U	0.25	1,010	0.25	1.8 J
04-01734	SSC49-10	0.13	18.5	0.12	41.6	0.25	41.1	0.13	0.13 U	0.25	7.52	0.25	44.0	0.25	239	0.25	2.0 J
04-01734 Dup	SSC49-10 Duplicate	0.13	18.5	0.12	41.4	0.25	41.2	0.13	0.13 U	0.25	7.25	0.25	44.6	0.25	240	0.25	1.9 J
RPD (%)			0		0		0		n/a		4		1		0		n/a
QC Samples																	
LCS 040912	Lab Control Sample (% Rec)		97		100		99		102		102		100		101		102

Shaded results: Values exceed upper calibration range.

Comparison of Original Anions Composition to the Final Composition after Thermochemical Reaction with Sucrose

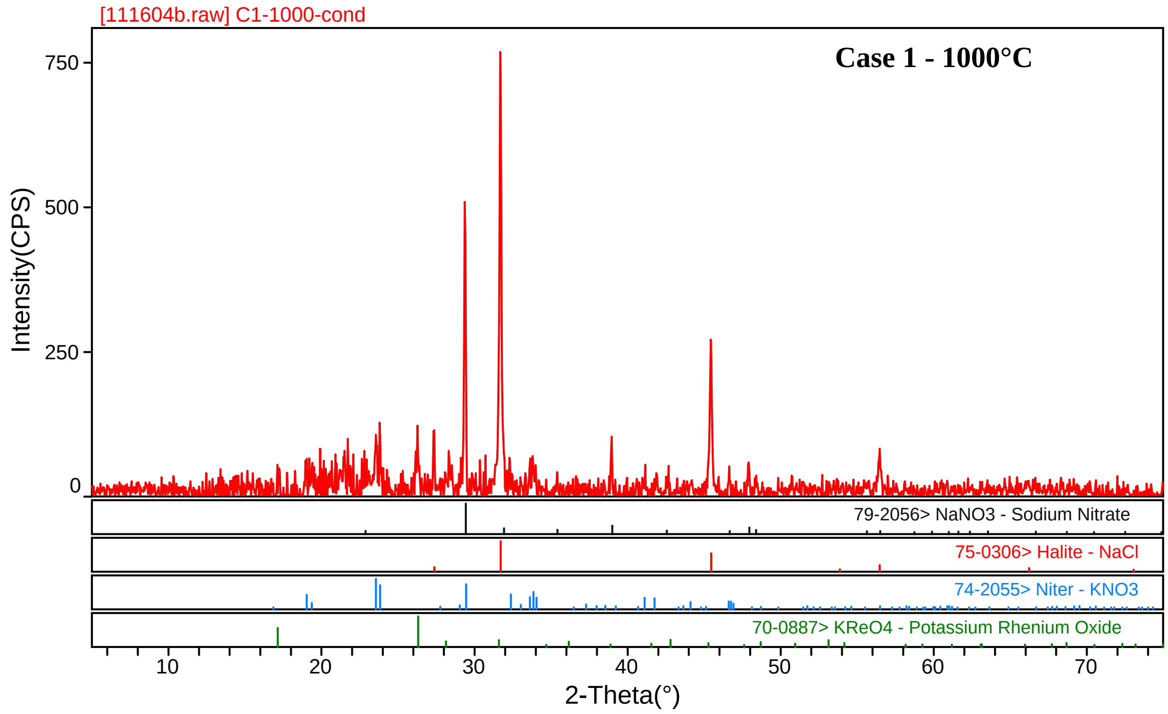
Cl^-			F^-			SO_4^{2-}			PO_4^{3-}	
Final ug/mL	% Change	Original ug/mL	Final ug/mL	% Change	Original ug/mL	Final ug/mL	% Change	Original ug/mL	Final ug/mL	% Change
37.20	93.67545	30.01171	8.17	72.8	2.88E+02	182	36.9	1.82E+02	82.8	5.44E+01
57.80	98.79752	49.18084	6.24	87.3	4.72E+02	286	39.5	2.98E+02	103	6.54E+01
159.00	97.75163	133.8576	0	100.0	1.29E+03	914	28.9	8.10E+02	0	1.00E+02
34.40	100.8563	29.87998	5.73	80.8	2.87E+02	51	82.2	1.81E+02	47.8	7.36E+01
43.50	82.68013	30.97485	5.17	83.3	2.98E+02	53.6	82.0	1.87E+02	55.9	7.02E+01
41.60	97.15631	34.80833	18.5	46.9	3.34E+02	330	1.3	2.11E+02	44	7.91E+01
25.60	93.79857	20.68006	16.3	21.2	1.99E+02	164	17.4	1.25E+02	43.6	6.52E+01
21.60	90.08103	16.75725	18.5	-10.4	1.61E+02	116	27.9	1.01E+02	48.7	5.20E+01

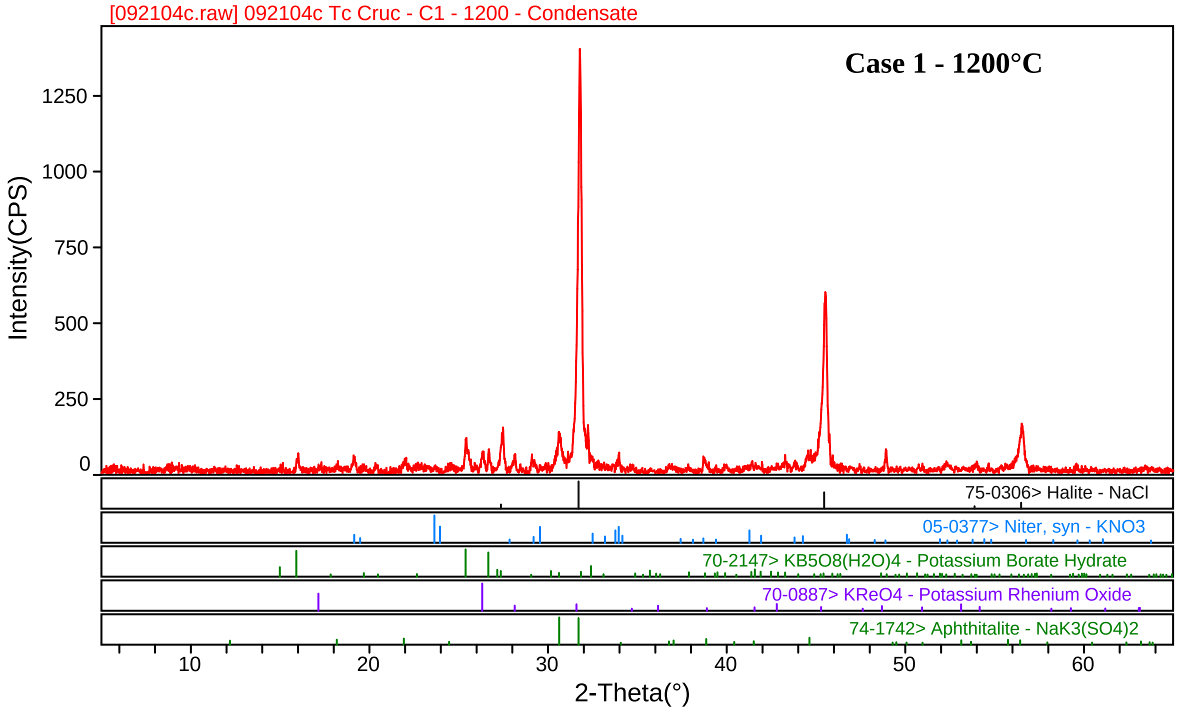
NO_3^-			NO_2^-			$C_2O_4^{2-}$	
Final ug/mL	% Change	Original ug/mL	Final ug/mL	% Change	Original ug/mL	Final ug/mL	% Change
17.9	99.59536	446.1796	6.39	98.56784	35.64066	0	100
8.59	99.88151	731.1641	j	j	58.40512	0	100
81.3	99.58795	1990.042	87.7	95.59306	158.9638	j	j
j	j	444.2244	j	j	35.48448	0	100
j	j	460.5019	j	j	36.78472	0	100
7.52	99.85348	517.494	41.1	92.05788	41.33723	j	j
6.22	99.79595	307.4519	j	j	24.55915	9.1	62.9466
3.62	99.85344	249.1312	j	j	19.90051	27.2	-36.67992

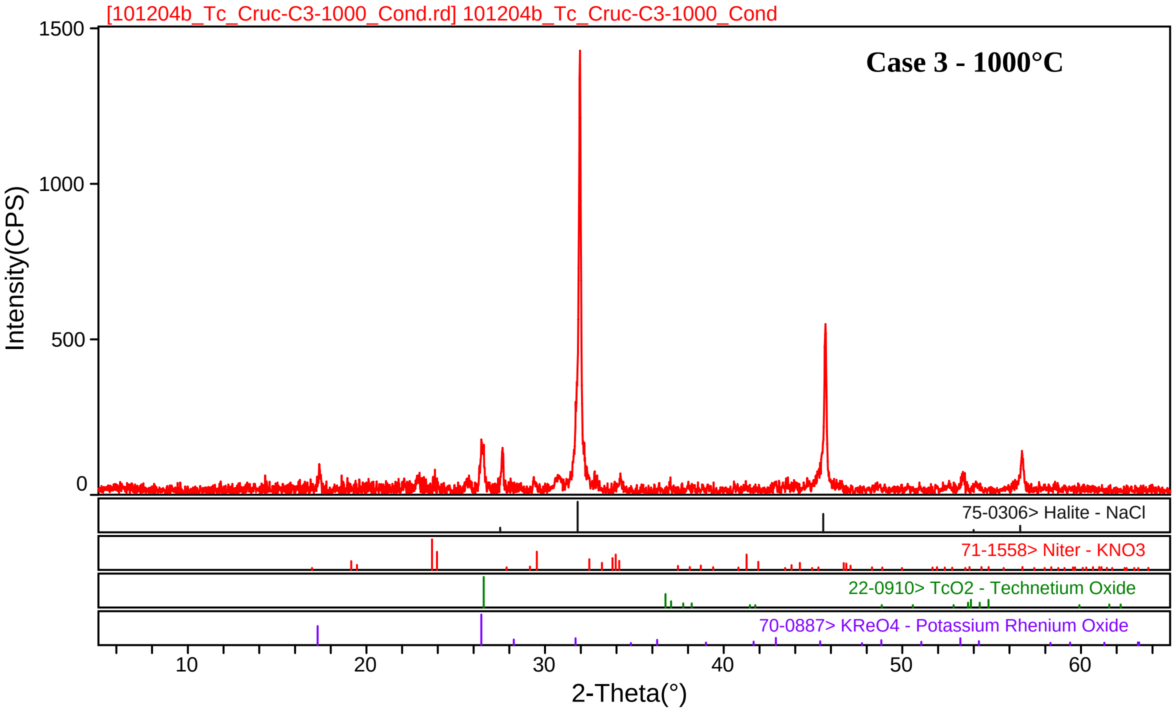
Appendix C

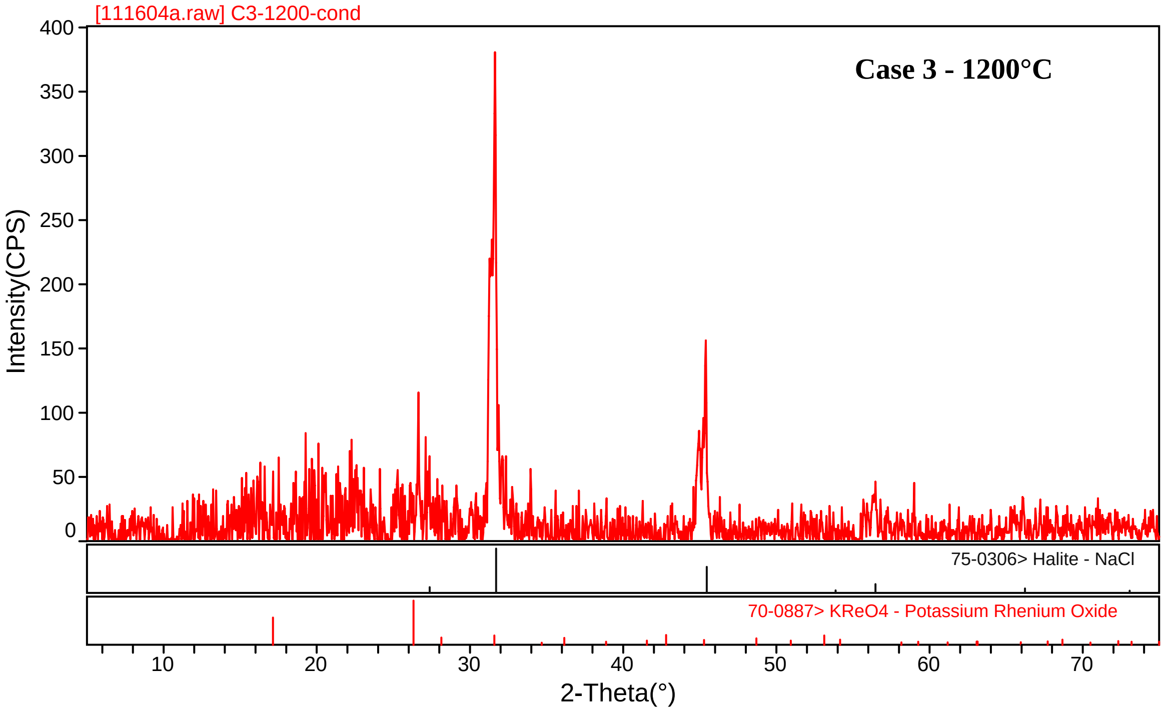
XRD Patterns on Condensate Samples

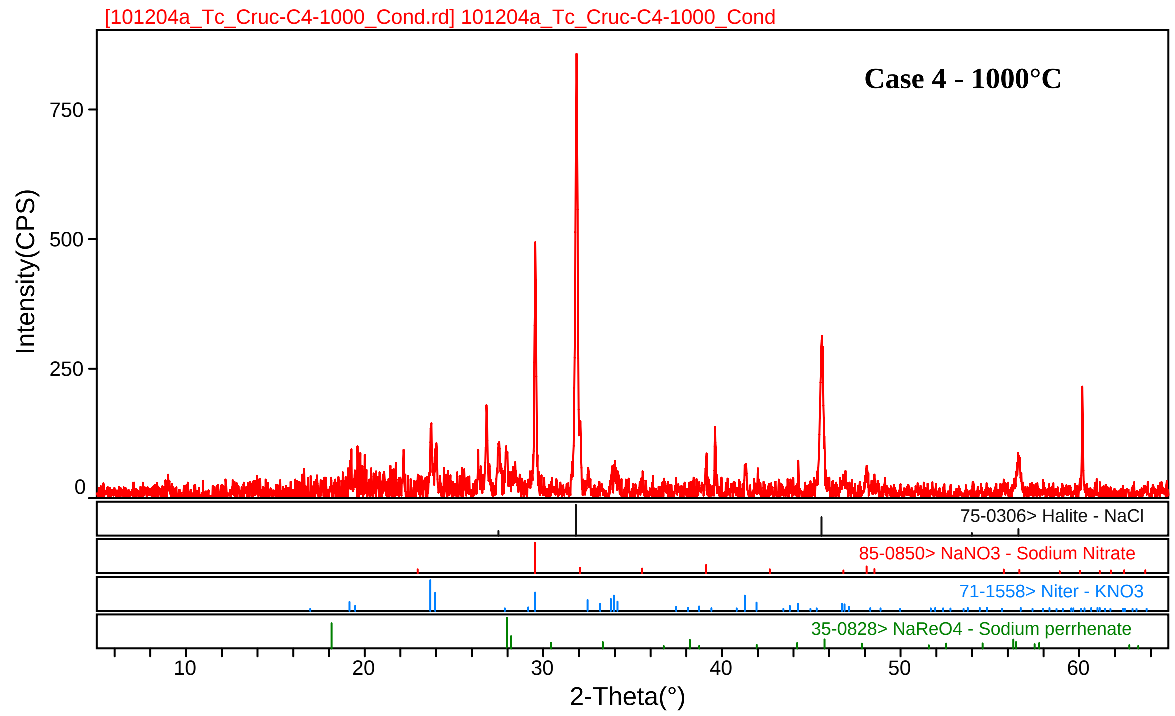
Appendix C: XRD Patterns on Condensate Samples

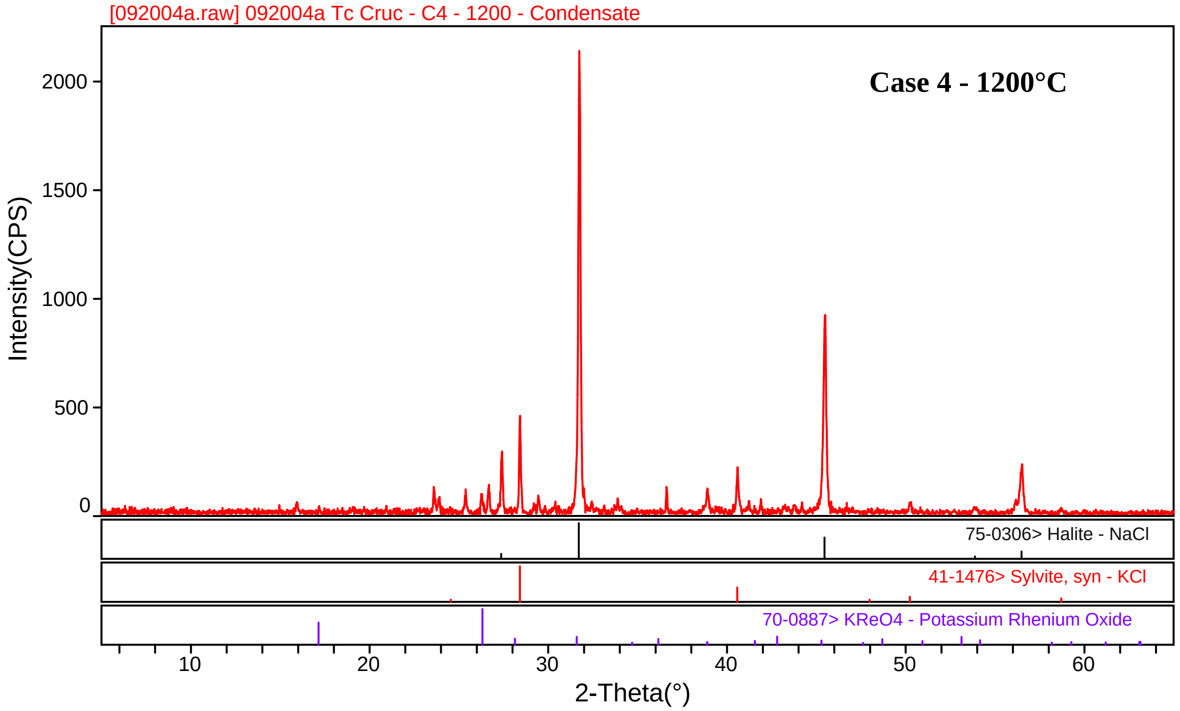


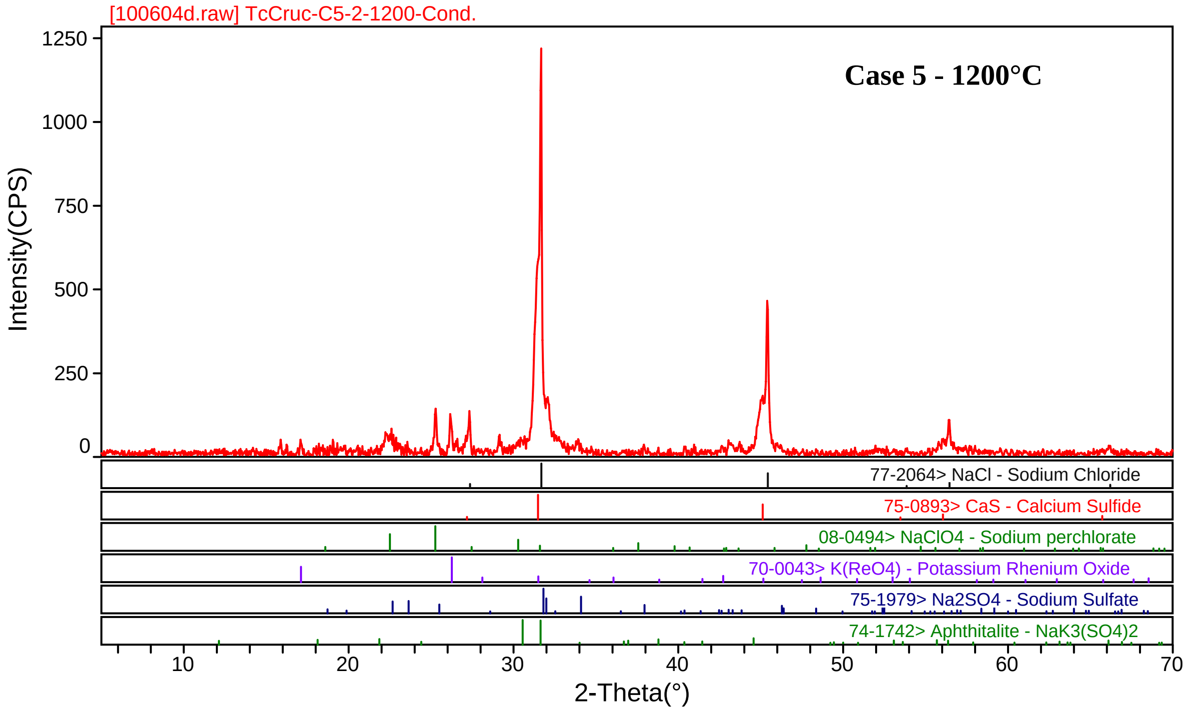


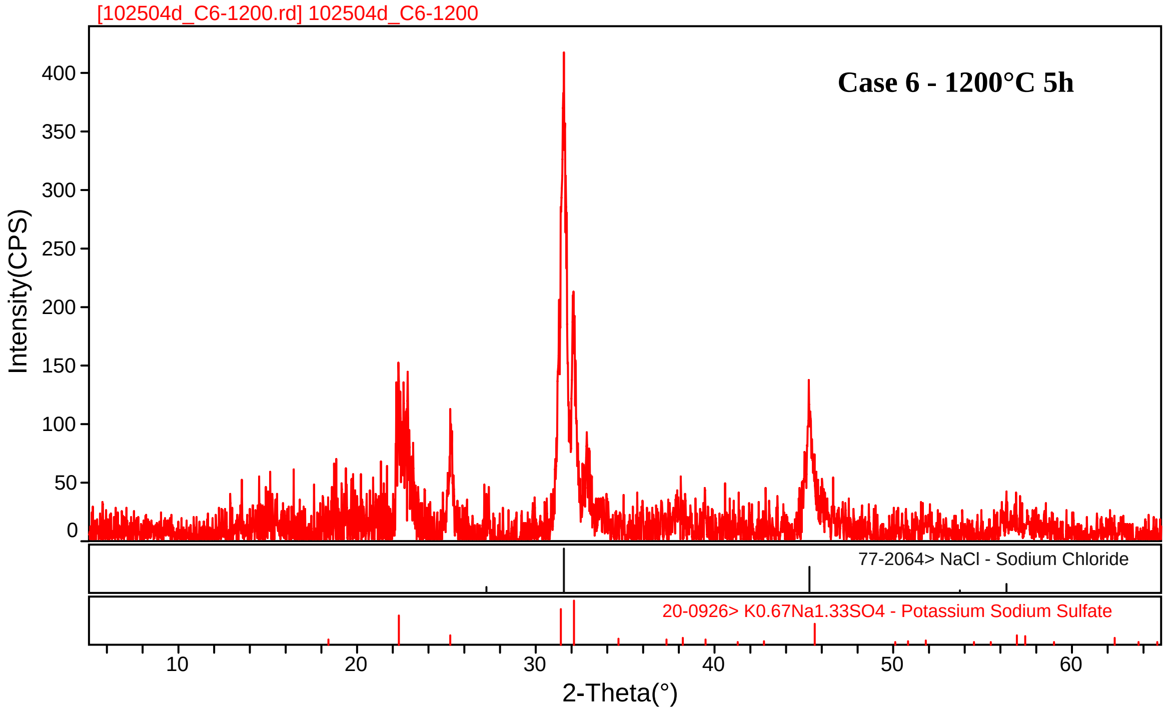

[101204b_Tc_Cruc-C3-1000_Cond.rd] 101204b_Tc_Cruc-C3-1000_Cond
Case 3 - 1000°C
Intensity(CPS)
1500
1000
500
0
75-0306> Halite - NaCl
71-1558> Niter - KNO3
22-0910> TcO2 - Technetium Oxide
70-0887> KReO4 - Potassium Rhenium Oxide
10
20
30
40
50
60
2-Theta(°)


[111604a.raw] C3-1200-cond
Case 3 - 1200°C
Intensity(CPS)
400
350
300
250
200
150
100
50
0
75-0306> Halite - NaCl
70-0887> KReO4 - Potassium Rhenium Oxide
10
20
30
40
50
60
70
2-Theta(°)


[101204a_Tc_Cruc-C4-1000_Cond.rd] 101204a_Tc_Cruc-C4-1000_Cond
Case 4 - 1000°C
Intensity(CPS)
750
500
250
0
75-0306> Halite - NaCl
85-0850> NaNO3 - Sodium Nitrate
71-1558> Niter - KNO3
35-0828> NaReO4 - Sodium perrhenate
10
20
30
40
50
60
2-Theta(°)


[092004a.raw] 092004a Tc Cruc - C4 - 1200 - Condensate
Case 4 - 1200°C
Intensity(CPS)
2000
1500
1000
500
0
75-0306> Halite - NaCl
41-1476> Sylvite, syn - KCl
70-0887> KReO4 - Potassium Rhenium Oxide
10
20
30
40
50
60
2-Theta(°)


[100604d.raw] TcCruc-C5-2-1200-Cond.
Case 5 - 1200°C
Intensity(CPS)
1250
1000
750
500
250
0
77-2064> NaCl - Sodium Chloride
75-0893> CaS - Calcium Sulfide
08-0494> NaClO4 - Sodium perchlorate
70-0043> K(ReO4) - Potassium Rhenium Oxide
75-1979> Na2SO4 - Sodium Sulfate
74-1742> Aphthitalite - NaK3(SO4)2
10
20
30
40
50
60
70
2-Theta(°)


[102504d_C6-1200.rd] 102504d_C6-1200
Case 6 - 1200°C 5h
Intensity(CPS)
400
350
300
250
200
150
100
50
0
77-2064> NaCl - Sodium Chloride
20-0926> K0.67Na1.33SO4 - Potassium Sodium Sulfate
10
20
30
40
50
60
2-Theta(°)

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