

Effect of Sulfate on Rhenium Partitioning during Melting of Low-Activity-Waste Glass Feeds – 14116

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ABSTRACT

The volatile loss of technetium-99 (^{99}Tc) is a major concern for low-activity waste (LAW) vitrification at Hanford. We investigated the incorporation and volatile loss of Re (a nonradioactive surrogate for ^{99}Tc) during batch-to-glass conversion up to 1100°C. The AN-102 feed, which is one of the representative Hanford LAW feeds, containing 0.59 wt% SO_3 (in glass if 100% retained) was used. The modified sulfate-free AN-102_0S feed was also tested to investigate the effect of sulfate. For each heat-treated sample, the salts (soluble components in room temperature leaching), early glass-forming melt (soluble components in 80°C leaching), and insoluble solids were separated by a two-step leaching and the chemical compositions of each phase were quantitatively analyzed. The final rhenium retention ratios of AN-102 and AN-102_0S in glass are 32% and 63%, respectively. The presence of sulfate in the salt phase between 600 and 800°C leads to a significantly higher Re loss via volatilization from the salt layer. At $\geq 800^\circ\text{C}$, for both samples, no more Re is incorporated into the insoluble phase because for AN-102_0S there is no salt left i.e., the split into the insoluble and gas phases is complete by 800°C, and for AN-102 all the Re contained in the remaining salt phase is lost through volatilization. The present results on the effect of sulfate, although not directly applicable to LAW vitrification in the melter, will be used to understand the mechanism of Re incorporation into glass to eventually develop methods that can increase ^{99}Tc retention during LAW vitrification at Hanford.

INTRODUCTION

Vitrifying the low-activity waste (LAW) stored at the U.S. Department of Energy's Hanford site is one of the primary missions of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) currently under construction. To immobilize the hazardous waste into a stable glass waste form, the LAW, which is an aqueous solution of predominantly nitrates and nitrites with other salts/hydroxides and organics, will be mixed with additives consisting of silica, boric acid, and other chemicals/minerals, and vitrified in a Joule-heated ceramic melter [1]. One of the significant radionuclides in Hanford LAW is ^{99}Tc , which is well-known for its long half-life and high environmental mobility in the form of soluble TcO_4^- [2]. Volatilization of ^{99}Tc during batch-to-glass conversion of the waste glass feed (waste plus additives) is a concern during vitrification of Hanford LAW. Maximizing the incorporation of ^{99}Tc into glass is important for an efficient vitrification process.

Rhenium has been the preferred nonradioactive surrogate for ^{99}Tc because of similarities in chemistry, ionic size, and speciation in glass [2]. Kim et al. [3] compared the partitioning, volatilization, and retention of ^{99}Tc and Re during melting of the LAW glass feeds developed to demonstrate the bulk vitrification technology for Hanford LAWs [4]. For each composition treated under the same crucible melting conditions, Tc and Re showed the same trends in the

“oxidizing” feeds containing nominal nitrates and nitrites [3], which supports Re being a suitable surrogate for ^{99}Tc under the typical conditions that are expected during the LAW vitrification process. However, the “reducing” feeds that were modified to remove or reduce the nitrates and nitrites showed differences between ^{99}Tc and Re in their partitioning into salt phases during melting as well as in the final retention in glass [3]. This result, which is consistent with other studies that reported dissimilarities largely due to the difference in the reduction potential of $^{99}\text{Tc}^{7+}$ and Re^{7+} [2, 5], suggests that caution needs to be taken when using Re as a surrogate for ^{99}Tc under reducing conditions.

Extensive small-scale Joule-heated melter tests have been performed by Matlack et al. [6, 7] for various simulated melter feeds formulated for seven representative Hanford LAWs. The feeds were spiked with 400–850 ppm Re and approximately 0.05–0.2 ppt $^{99\text{m}}\text{Tc}$ (both metal basis). The single-pass retention ratio of $^{99\text{m}}\text{Tc}$ and Re (concentration retained in glass divided by target concentration) varied widely from 18–66% for $^{99\text{m}}\text{Tc}$ and 25–57% for Re [6]. The retention ratio of $^{99\text{m}}\text{Tc}$ showed a trend reasonably similar to that of Re [6, 7]. However, there have been no clear explanations of the mechanisms that control the retention of Tc and Re during melting process.

Recently, we launched a series of studies to understand the mechanism of ^{99}Tc retention in, or escape from, glass melt during early stages of glass batch melting, with the goal of eventually developing a method for increasing ^{99}Tc retention. Using Re as a surrogate, the initial study was performed with two representative simulated LAW glass feeds, designed to vitrify AN-102 and AZ-102, which showed the lowest (AN-102) and the highest (AZ-102) retention ratios of $^{99\text{m}}\text{Tc}$ and Re from melter tests mentioned above [6]. The results are to be published elsewhere [8]. One of the key findings was that the Re incorporates into the glass melt by $\leq 800^\circ\text{C}$ and the remaining Re volatilizes from the segregated salt, predominantly alkali sulfate, at $\geq 800^\circ\text{C}$ [8].

Sulfate has been known to be a problematic component in waste glass melting because the segregated molten sulfate salt, which is highly corrosive, can shorten the useful life of the melter [9, 10]. Kim et al. [3] first investigated the role of sulfate on the retention of ^{99}Tc and Re during melting of bulk vitrification glasses that are designed for processing at $\sim 1350^\circ\text{C}$. The present study aims to further evaluate the effect of sulfate on Re partitioning and retention in LAW glass designed for processing at 1150°C in a Joule-heated melter using the two-step leaching procedures previously developed [8]. Two AN-102 feeds with SO_3 target concentrations of 0.59 wt% and 0 wt% in glass were prepared and tested. Simulated AN-102 feed was modified by replacing Na_2SO_4 in the simulant with NaOH while keeping the concentration of Na_2O constant to formulate a glass feed with 0 wt% SO_3 (designated as AN-102_0S). The results for Re partitioning between various phases will be discussed in connection with the effect of SO_3 on the formation of the segregated sulfate and on the volatilization of Re during early stages of melting.

METHODS

Experimental Procedures

The compositions of simulated AN-102 waste, additives, and the resulting glass with a waste loading of 16.22 wt%, expressed in terms of mass% of oxides and halides, which are the same

as used by Matlack et al. [6], are shown in TABLE I,. Note that the AN-102-0S glass has the same composition as the original AN-102. The target Re concentration was 8.1 ppm mass (as of rhenium metal) in both glasses, which is a typical projected concentration in Hanford LAW glasses [3, 4]. TABLE I also includes the melter feed makeup in mass of each chemical/mineral per liter of simulated waste for the original AN-102 feed; the masses of NaOH and Na₂SO₄ for AN-102_0S feed are given in parenthesis. The makeup of AN-102 feed was also from Matlack et al. [6], but was modified based on the composition and purity of the materials used in the present study.

The mass of each chemical given in TABLE I was added to deionized water, allowing each chemical to dissolve completely before adding the next chemical, to prepare 1 L of simulated waste. This was followed by mixing with additive chemicals/minerals to make the feed slurry. The slurry was then dried at 105°C for 12 h to obtain dried glass feeds.

The dried feeds were thermally treated in a Pt crucible, heating at 5°C/min to 600, 700, 800, 900, 1000, and 1100°C. The samples were quenched in air after reaching each temperature. The mass loss measurement was performed by weighing samples before and after the heat treatment.

TABLE I Target compositions of simulated AN-102 waste, additives, and resulting AN-102 glass (in mass% of oxides and halides) and feed makeup for AN-102 and AN-102-OS glass feeds (in g per L of simulated waste)

Target glass compositions (mass%)				Feed makeup (g per L of simulated waste)	
	AN-102 waste	Additives ^a	AN-102 Glass	Chemicals	AN-102 (AN-102_OS)
Loading	16.22	83.78	100.00	Source in LAW Simulant (1 L)	
				Al(NO ₃) ₃ ·9H ₂ O	87.97
Al ₂ O ₃	6.29	5.97	6.02	H ₃ BO ₃	0.10
B ₂ O ₃	0.06	11.77	9.87	Ca(NO ₃) ₂ ·4H ₂ O	1.46
CaO	0.18	7.50	6.31	Na ₂ CrO ₄ ·4H ₂ O	2.76
Cr ₂ O ₃	0.49		0.08	KOH	7.38
Fe ₂ O ₃		6.48	5.43	NaOH	52.88 (59.68)
K ₂ O	3.33		0.54	NiO	0.09
Li ₂ O		3.78	3.17	PbO	0.09
MgO		1.78	1.49	SiO ₂	0.10
Na ₂ O	83.42		13.53	NaCl	3.72
NiO	0.06		0.01	NaF	1.97
PbO	0.06		0.01	Na ₃ PO ₄ ·12H ₂ O	7.56
SiO ₂	0.06	53.41	44.75	Na ₂ SO ₄	12.07 (0)
TiO ₂		1.65	1.38	NaNO ₂	64.80
ZnO		4.13	3.46	NaNO ₃	94.65
ZrO ₂		3.53	2.96	Na ₂ CO ₃	49.21
Cl	1.23		0.20	Sodium Formate (NaHCO ₂)	24.90
F	0.49		0.08	Sodium Oxalate (Na ₂ C ₂ O ₄)	1.44
P ₂ O ₅	0.74		0.12	Glycolic Acid (C ₂ H ₄ O ₃)	30.60
SO ₃	3.64		0.59	Citric Acid (C ₆ H ₈ O ₇)	8.98
Sum	100.00	100.00	100.00	Re ₂ O ₇	0.0121
Re (spiked)			8.1 ppm	Water (estimated in 1 L of simulant)	792.96
^a Additives contain both glass formers and glass modifiers necessary for making the glass waste form.				Additives^a	
				Kyanite (Al ₂ SiO ₅)	98.73
				Borax (H ₃ BO ₃)	200.58
				Wollastonite (CaSiO ₃)	155.51
				Hematite (Fe ₂ O ₃)	59.46
				Li ₂ CO ₃	89.87
				Olivine (Mg ₂ SiO ₄)	35.54
				SiO ₂	362.31
				Rutile (TiO ₂)	15.22
				Zincite (ZnO)	39.63
				Zircon (ZrSiO ₄)	50.83

A two-step leaching procedure was used to separate the soluble salts and early glass-forming melts¹ formed during the melting process. The as-dried and heat-treated samples were crushed until most particles were <0.425 mm (sieved by a #40 stainless steel sieve). The leaching procedure is summarized in TABLE II.

TABLE II. Leaching test procedure

Intended phases	Two-step leaching method
Salts	Leached at room temperature (RT) for 1 h. 5 g of solution was taken for analysis and 5 g of deionized water was added. Most soluble salts were expected to dissolve.
Early glass-forming melt (Early melt for short)	Continued to leach at 80°C for 24 h. 5 g of solution was taken for analysis. A fraction of “non-durable” early glass-forming melts was expected to dissolve. The mass of each element removed by a RT sample was added to the total mass dissolved. The mass of each element dissolved by RT leach was subtracted from the total mass dissolved to obtain the mass dissolved by 80°C leach.
Insoluble	The resulting sample was filtered after the 2-step leach, and the remaining solid was dried for chemical analysis.
Gases	Calculated by mass balance.

TABLE III summarizes the mass of dried feed or heat-treated samples and the volume of water used for the leach test. The ratio of the sample mass to the water volume was varied to achieve comparable concentrations of the soluble components and to avoid approaching the detection limits in the chemical analysis. For the dried feed, two separate samples were leached (2.5 g was leached at room temperature for 1 h and 5.0 g at 80°C for 24 h) instead of the continuous two-step leach that was used for all other samples; this was because the dried feed became a suspension (slurry) after RT leaching, which made it difficult to take a solution sample without filtering the suspension, resulting in the sample not being useable for the second step leach at 80°C.

TABLE III. Sample/water amount used in the leaching test

Sample	Sample mass/water volume
Dried Feed	2.5 g/100 ml (RT) or 5 g/200 ml (80°C)
600°C	5 g/200 ml
700°C	5 g/100 ml
800–1100°C	20 g/100 ml

The solution samples obtained by the RT and 80°C leaching were filtered through 8 µm filter paper (Whatman 40, Whatman Ltd., UK) and the remaining solids were dried for chemical analysis. Each sample was weighed before and after leaching to obtain the total masses of the soluble and insoluble components.

¹ A qualitative and general term used to describe the initial glassy phases with lower chemical durability (e.g., alkali borate with low concentration of SiO₂) compared to the final glass.

Chemical analyses were performed by Southwest Research Institute² according to its standard procedures. Two liquid samples from the RT and 80°C leaching and solution samples prepared from fusion and acid leaching of dried solids were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) for Re and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for all other cationic elements. Ion chromatography (IC) was used to analyze NO_3^- , NO_2^- , F^- , and Cl^- and the total inorganic carbon (TIC) method was used for CO_3^{2-} .

Mass Balance Calculation

In the AN-102 LAW glass, there are 20 elements (except oxygen): Al, B, Ca, Cr, Fe, K, Li, Mg, Na, Ni, Pb, Si, Ti, Zn, Zr, Cl, F, P, S, and Re (TABLE I). There are also NO_3^- , NO_2^- , CO_3^{2-} , and organics in the dried feed that will all be lost through evolved gases during melting. Furthermore, some lattice water is expected to be in the dried feed.

The ICP-AES, ICP-MS, and IC methods produced the raw data as element or anion concentrations. In order to achieve mass balance, the element or anion concentration was converted to the mass of oxides or halides in the analyzed sample. For example, components of the mixed salt containing NaNO_3 , NaNO_2 , Na_2CO_3 , Li_2CO_3 , Na_2SO_4 , etc. can be recovered from the masses of Na_2O , Li_2O , N_2O_5 , N_2O_3 , CO_2 , SO_3 , etc., resulting in the 23 components tracked in this study: Al_2O_3 , B_2O_3 , CaO , Cr_2O_3 , Fe_2O_3 , K_2O , Li_2O , MgO , Na_2O , NiO , PbO , SiO_2 , TiO_2 , ZnO , ZrO_2 , Cl , F , P_2O_5 , SO_3 , N_2O_5 , N_2O_3 , CO_2 and Re (Re is calculated by element).

Each dried feed or heat-treated sample can be profiled by the mass of each component for the 23 components listed above in each phase:

$$m_{Tot} = \sum_{i=1}^{23} \sum_{j=1}^4 m_{ij} \quad (\text{Eq.1})$$

where m_{ij} is the mass of the i^{th} component in the j^{th} phase (j represents *Salt*, *Early melt*, *Insoluble*, and *Gas*), m_{Tot} is the total mass of each dried feed or heat-treated sample when expressed in terms of 23 components. The m_{Tot} is obtained from the analytical results of leached solutions and solid samples for the dried feed by:

$$m_{Tot} = \sum_{i=1}^{23} m_i^0 \quad (\text{Eq.2})$$

where m_i^0 is the initial mass of the i^{th} component analyzed in the dried feed samples, i.e.,

$$m_i^0 = \sum_{j=1}^3 m_{ij}^0 = m_{i,Salt}^0 + m_{i,Early\ melt}^0 + m_{i,Insoluble}^0 \quad (\text{Eq.3})$$

where m_{ij}^0 is the initial mass of the i^{th} component in the j^{th} phase. The value of the m_{Tot} is slightly different from the starting mass of dried feed because of the likely presence of lattice

² Southwest Research Institute (SwRI), 6220 Culebra Rd., San Antonio, Texas 78238-5166 (<http://www.swri.org/>).

water that cannot be analyzed and analytical uncertainty. The mass of evolved gases in each treated sample is calculated by:

$$m_{i,Gas} = m_i^0 - m_{i,Salt} - m_{i,Early\ melt} - m_{i,Insoluble} \quad (\text{Eq.4})$$

We define three symbols to express the composition of each sample or phase:

$$f_{ij} = \frac{m_{ij}}{m_i^0} \quad (\text{Eq.5})$$

$$F_{ij} = \frac{m_{ij}}{m_{Tot}} \quad (\text{Eq.6})$$

$$w_{ij} = \frac{m_{ij}}{\sum_{i=1}^{23} m_{ij}} \quad (\text{Eq.7})$$

where f_{ij} is the mass fraction of the i^{th} component in the j^{th} phase normalized to the initial total mass of each component in the dried feed ($\sum_{j=1}^4 f_{ij} = 1$), F_{ij} is the mass fraction of the i^{th}

component in the j^{th} phase normalized to the total mass of the dried feed ($\sum_{i=1}^{23} \sum_{j=1}^4 F_{ij} = 1$), and w_{ij} is the mass fraction of the i^{th} component in the j^{th} phase normalized to the total mass of each phase (i.e., composition of each phase, $\sum_{i=1}^{23} w_{ij} = 1$).

RESULTS AND DISCUSSION

Overview of the Feed-to-Glass Conversion

During melting of LAW glass feed, the salts from the waste decompose and/or react with the additives, releasing a considerable amount of gases, primarily NO_x from nitrates/nitrites and

CO_2 from carbonates. Fig. 1 shows the mass distribution of each phase ($F_j = \sum_{i=1}^{23} F_{ij}$) in the

dried feed and heat-treated samples up to 1100°C for AN-102 and AN-102_0S feeds. The two feeds show a very similar trend, as expected from the minor difference in their feed makeup.

Approximately 9% of the total mass is lost to the evolved gases after heating to 600°C and ~15% after heating to 800°C, after which the mass fraction remains constant up to 1100°C (light green area in Fig. 1).

The soluble salt phase (dark blue in Fig. 1) is about 35% in the dried feed, originating from the salts in the simulated LAW waste and boric acid and lithium carbonate in the additives (Na_2O , Li_2O , B_2O_3 , N_2O_5 , N_2O_3 , CO_2 , and SO_3 contribute over 98% of the salt). During heating to 600–700°C, the salt phase decreases, releasing N_2O_5 , N_2O_3 , and CO_2 as gases while most of the Na_2O , Li_2O and B_2O_3 become incorporated into the insoluble glass melt. Above 800°C, the salt phase drops to less than ~0.5% and the major gas release is complete. Fig. 2 compares the total salt mass fraction (F_{Salt}) as a function of temperature in the two feeds, which shows that at $\geq 800^\circ\text{C}$ the small amount of remaining salts in AN-102 is significantly higher than that in AN-102_0S.

A small amount of early glass-forming melt phase (or a non-durable glass-forming melt) consisting mainly of B_2O_3 and Na_2O is seen at 600–700°C (light blue area), which decreases to less than 1% above 800°C and survives until 1100°C. There are ~62% insoluble solids in both of the dried feeds (SiO_2 and other additives), which increase to ~85% at 800°C and remain constant to 1100°C.

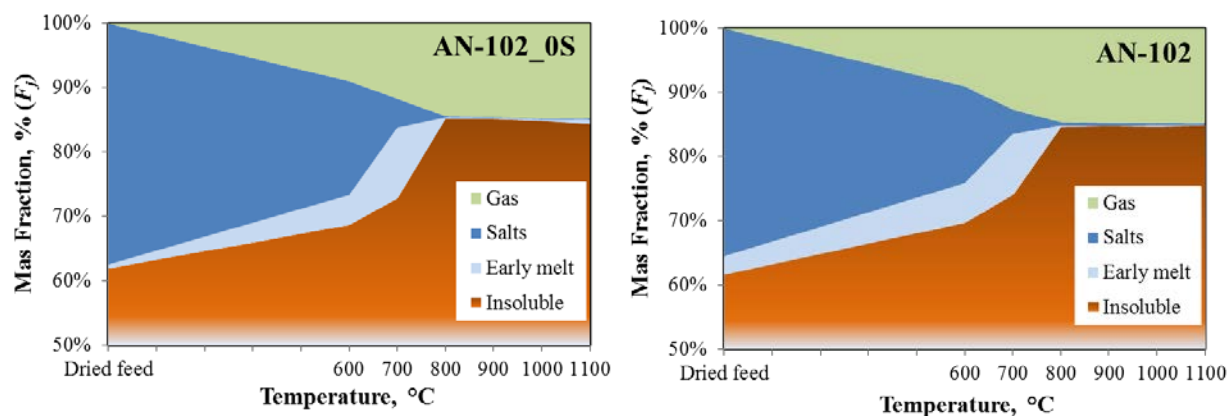


Fig. 1. Mass distribution of different phases in the dried feed and heat-treated samples.

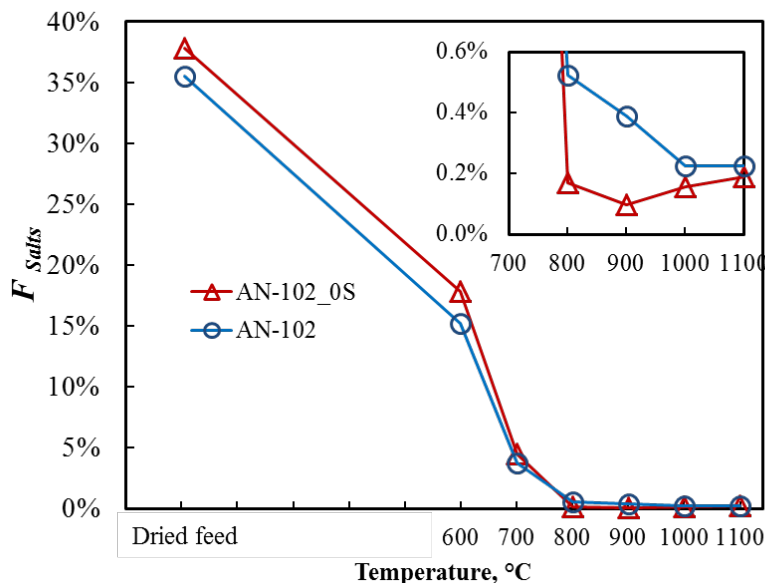


Fig. 2. Mass fractions of the salt phase out of the total mass of the dried feed.

Decomposition of the Salt Phase

The compositions of the salt phase in AN-102 and AN-102_S ($F_{i,Salt}$) are shown in Fig. 3 for the seven primary components mentioned earlier. In AN-102, SO_3 is a minor component with a target of 0.59% in the glass, which resulted in 1.5% in the salt phase of the dried feed, i.e.,

$$w_{SO_3,Salt} = 1.5\%, \text{ corresponding to } 0.56\% \text{ in the total mass of the dried feed, i.e., } F_{SO_3} = \sum_{j=1}^3 F_{SO_3,j}$$

= 0.56%. In AN-102_OS, $F_{SO_3} = 0.045\%$, which is likely from other chemical impurities.

For both feeds, after heating to 600°C, most of the N_2O_3 and CO_2 are released to the gas phase and ~70% of the N_2O_5 survives. Li_2O mostly incorporates into the insoluble phase at $\leq 600^\circ\text{C}$. From 600°C to 700°C, all components in the salt phase decrease and the total salt is less than 5% after heating to 700°C, where Na_2O and N_2O_5 contribute ~80% in the salt phase.

At 800°C, the mass fractions of the total salts (F_{Salt}) decrease to 0.5% in AN-102 and 0.2% in AN-102_OS, and the compositional differences become significant due to the different sulfate content. For AN-102_OS, the small amount sulfur from impurities was not detected in the salt phase $\geq 800^\circ\text{C}$. For AN-102, sodium sulfate is the major component of the salt phase and decreases continuously $\geq 800^\circ\text{C}$. During crucible melting, a surface segregated sulfate layer was observed on top of the molten glass in the samples heated to 800, 900, and 1000°C. B_2O_3

and a portion of $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ detected $\geq 800^\circ\text{C}$ are likely from the leaching of very fine particles produced during sample preparation.

In summary, the salt phase decreases from 35% in the dried feed to less than 0.5% after heating to 800°C . By 800°C , the major components in the salt phase (Na_2O , Li_2O , B_2O_3 , N_2O_5 , N_2O_3 , and CO_2) have mostly decomposed and partitioned into insoluble phase and evolved gases. For the AN-102 feed, a segregated sodium sulfate layer forms on the molten glass surfaces $\geq 800^\circ\text{C}$ and survives up to 1000°C . For AN-102_0S, except for a very small amount of nitrate remaining at 800°C , there are no salts remaining after the decomposition of nitrates, nitrites and carbonates $\geq 800^\circ\text{C}$.

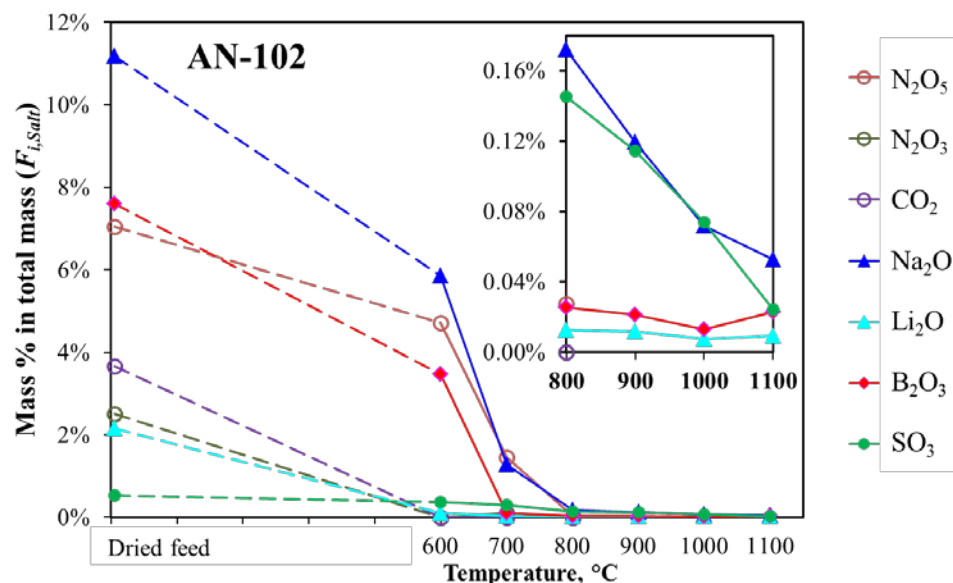
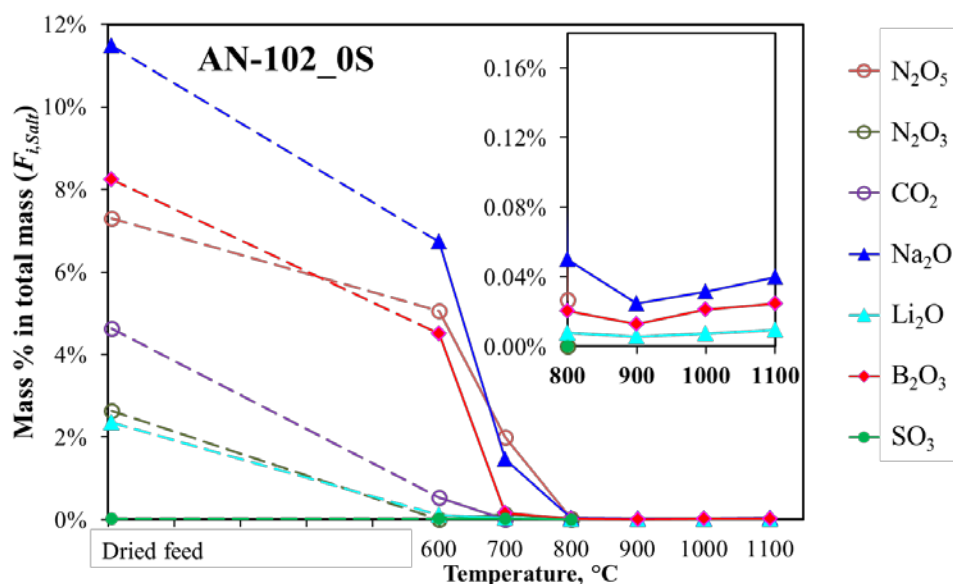


Fig. 3. Mass fractions ($F_{i,Salt}$) of the components in the salt phase out of the total mass of the dried feed.

Rhenium Incorporation and Volatilization

The chemical analysis results for Re are shown in TABLE IV.

TABLE IV. Chemical analysis results for Re in AN-102_0S and AN-102. $F_{Re,j}$, $w_{Re,j}$, and $f_{Re,j}$ were defined in Eqs. 5–7. F_{Salt} is the mass fraction of the salt phase in the total dried feed mass.

AN-102_0S		Dried feed	600°C	700°C	800°C	900°C	1000°C	1100°C
$F_{Re,j}$ (ppm)	Salt	7.55	5.78	4.55	0.54	0.05	0.02	0.02
	Early melt	0.32	0.56	0.46	0.15	0.02	0.03	0.06
	Insoluble	0.00	1.65	1.93	6.01	5.37	5.47	4.96
	Gas		0.00	0.92	1.16	2.42	2.34	2.82
F_{Salt}		37.78%	17.81%	4.45%	0.17%	0.10%	0.16%	0.19%
$w_{Re,j}$ (ppm)	Salt	19.98	32.48	102.22	321.51	56.01	13.26	11.99
	Early melt	50.49	11.90	4.16	60.09	10.80	12.53	8.34
	Insoluble	0.00	2.38	2.67	7.08	6.35	6.57	5.95
	Gas		0.00	7.92	8.05	16.69	16.15	19.42
$f_{Re,j}$	Salt	95.99%	73.56%	57.92%	6.91%	0.69%	0.26%	0.29%
	Early melt	4.01%	7.08%	5.79%	1.88%	0.21%	0.38%	0.78%
	Insoluble	0.00%	20.93%	24.57%	76.47%	68.33%	69.59%	63.05%
	Gas		0.00%	11.72%	14.73%	30.76%	29.77%	35.88%

AN-102		Dried feed	600°C	700°C	800°C	900°C	1000°C	1100°C
$F_{Re,j}$ (ppm)	Salt	7.61	5.11	5.21	2.93	0.60	0.03	0.02
	Early melt	0.62	0.65	0.18	0.35	0.02	0.02	0.00
	Insoluble	0.00	2.39	1.60	3.13	3.34	2.71	2.62
	Gas		0.08	1.24	1.82	4.27	5.48	5.59
F_{Salt}		35.54%	15.21%	3.74%	0.53%	0.39%	0.22%	0.23%
$w_{Re,j}$ (ppm)	Salt	21.41	33.60	139.53	557.08	153.50	13.35	10.87
	Early melt	21.26	10.51	1.88	151.41	44.66	5.48	5.43
	Insoluble	0.00	3.41	2.18	3.75	4.00	3.24	3.13
	Gas		0.86	9.97	12.64	29.30	37.44	38.16
$f_{Re,j}$	Salt	92.48%	62.09%	63.36%	35.55%	7.25%	0.36%	0.30%
	Early melt	7.52%	7.95%	2.15%	4.23%	0.30%	0.21%	0.05%
	Insoluble	0.00%	29.02%	19.39%	38.04%	40.59%	32.89%	31.79%
	Gas		0.94%	15.10%	22.17%	51.86%	66.54%	67.86%

The batched target concentration of Re in AN-102 glass (if 100% retained) is 8.1 ppm mass, which is ~6.6 ppm mass in the dried feed. By ICP-MS with a Re detection limit of ~0.0025 ppm we successfully tracked the changes of Re in each sample. The total Re recovered, from the analytical results for the tests with dried feed (F_{Re} , no gas involved), is 7.87 ppm in AN-102_0S feed and 8.23 ppm in AN-102 feed. The corresponding target concentrations of Re in AN-102_0S and AN-102 glasses, if 100% retained, are 9.4 ppm and 9.9 ppm, respectively, which are 16% and 23% higher than the batched target. This difference was likely caused by the difficulty of batching such a small amount of Re (as Re_2O_7) in the feed and the analytical bias or uncertainty. Here we define the retention ratio of Re in glass, R_{Re} , as the mass fraction of Re analyzed in the insoluble phase at 1100°C, $F_{Re,Insoluble}$ (1100°C), divided by the total target mass fraction in the dried feed, F_{Re} , i.e.,

$$R_{Re} = \frac{F_{Re,Insoluble}(1100^\circ C)}{F_{Re}} \quad (Eq.7)$$

From TABLE IV, the retention ratio (R_{Re}) is $4.96/7.87 = 63\%$ for AN-102_0S and $2.62/8.23 = 32\%$ for AN-102. By the definition of f_{ij} in Eq. 5, $R_{Re} = f_{Re,Insoluble}$ (1100°C), which is also given in TABLE IV.

Re distribution in the different phases is shown in Fig. 4. In the dried feed, all the Re is in the soluble phases with the large amount of salts from the waste simulant. During early melting, it is clear that Re strongly favors the salt phase. After heating to 600°C, 20–30% Re incorporated into the insoluble phase in both samples. Between 600 and 800°C, a large amount of Re incorporates into the insoluble phase in AN-102_0S, during which the nitrate/boric acid salt decomposes or reacts (Fig. 3). However, this is not the case for AN-102, i.e., there is no noticeable Re incorporation into the insoluble phase between 600 and 800°C. Over 35% of the Re is still in the remaining salt phase at 800°C, which is only 0.53% of the initial total mass, (see F_{Salt} in TABLE IV). In both feeds, the Re remaining in the salt phase becomes concentrated due to the loss of other salt components at 700–900°C (see $w_{Re,Salt}$ values in TABLE IV). Above 800°C, for both samples, there is no more incorporation of Re into the insoluble phase, probably within the overall experimental error: for AN-102_0S there is no salt left, i.e., the split into the insoluble and gas phases is complete by 800°C; for AN-102 all the Re contained in the remaining salt phase is lost through volatilization. The large amount of Re remaining in the salt phase leads to a ~30% volatile loss between 800 and 900°C for AN-102, compared to a ~6% loss for AN-102_0S.

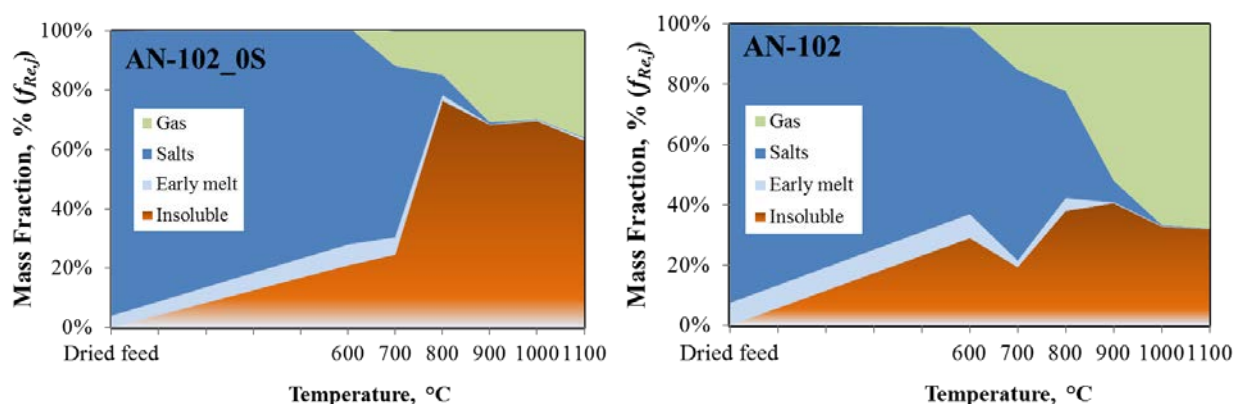


Fig. 4. Re distribution ($f_{Re,i}$) in different phases.

CONCLUSIONS

Through chemical analyses of the leach solution and solid samples obtained from two-step leaching of the heat-treated simulated LAW feeds we successfully profiled the incorporation of Re from the salt phase into molten glass. The AN-102 feed, which is one of the representative Hanford LAW melter feeds, and the modified sulfate-free AN-102_0S feed were tested to investigate the role of sulfate on Re partitioning and retention during crucible-scale melting.

The AN-102 feed had a Re retention ratio of 27% from the small-scale melter tests [6], which is close to that of 32% obtained in the present crucible tests. Changing the target SO_3 concentration in glass from 0.59 to 0 mass% increased the Re retention ratio from 32% to 63%. The presence of sulfate in the salt phase between 600 and 800°C leads to a significantly higher Re loss via volatilization from the salt layer at the surface of the melt.

The present results on the effect of sulfate cannot be applied directly to increase the ^{99}Tc retention during LAW vitrification in the melter because removing sulfate from LAW feeds is not an option during plant operation. However, the information gained from this series of studies to understand the mechanism of Re incorporation into glass during the melting process can be used to develop methods that can increase the ^{99}Tc retention.

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