



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrsol

Letter to the editor

Incorporation and distribution of rhenium in a borosilicate glass melt heat treated in a sealed ampoule



Dongsang Kim*, Michael J. Schweiger

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA

ARTICLE INFO

Article history:

Received 24 May 2013

Received in revised form 25 July 2013

Available online xxxx

Keywords:

Rhenium;

Technetium;

Solubility;

Low-activity waste;

Borosilicate glass

ABSTRACT

We investigated a mass balance of rhenium (used as a surrogate for technetium-99) in a borosilicate glass that was mixed with excess Re source (KReO_4) beyond its solubility and heat treated in a vacuum-sealed fused silica ampoule. Distribution of Re in the bulk of the glass, in a salt phase formed on the melt surface, and in condensate material deposited on the ampoule wall was evaluated to understand the Re migration into different phases during the reaction between the molten glass and KReO_4 . The information gained from this study will contribute to an effort to understand the mechanism of technetium retention in, or escape from, glass melt during early stages of glass batch melting, which is a goal of the present series of studies.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Volatile loss of radioactive ^{99}Tc to off-gas, and hence low retention in glass, is a concern during vitrification of low-activity waste (LAW) stored at the U.S. Department of Energy's Hanford Site [1,2]. Extensive scaled melter tests with various simulated LAW glass feeds have been performed to identify the major factors that affect the retention of ^{99}Tc in glass (see Abramowitz et al. [2]). Currently, studies are underway to understand the mechanism of ^{99}Tc retention in, or escape from, glass melt during early stages of glass batch melting and eventually to help develop the strategy for ^{99}Tc management during LAW vitrification. A previous study [3] applied a vacuum-sealed fused silica ampoule setup to measure the solubility of rhenium, used as a surrogate for ^{99}Tc , in a representative LAW glass. The X-ray absorption near edge structure spectroscopy of the heat treated samples showed that Re^{7+} (fully oxidized) was the only significant species present [3]. The measured solubility of Re^{7+} was 3000 ppm mass (metal basis) at 1000 °C. Assuming the same atomic solubility for Tc^{7+} as for Re^{7+} in this glass, the solubility of technetium was estimated as ~1500 ppm mass [3]. A series of solubility tests with ^{99}Tc has also been performed using the same technique. The results are planned for publication elsewhere.

The estimated ^{99}Tc solubility is more than two orders of magnitude higher than the projected average ^{99}Tc concentration of ~3 ppm mass in LAW glass [3]. This suggests that the retention of ^{99}Tc in glass is not limited by its solubility. Partitioning of ^{99}Tc to molten salt phase, especially if sulfate is present, and subsequent volatilization from molten salt during early stages of feed melting has been suggested as one of the

mechanisms that can increase the escape of ^{99}Tc [4,5]. Therefore, it is important to understand how ^{99}Tc partitions into different phases during early stages of LAW feed melting to study the mechanism of ^{99}Tc incorporation into or escape from glass melt.

In a previous study on the Re solubility [3], the excess Re above solubility migrated to the melt surface and formed a separated salt. Characterization of the salt phase that formed on the glass surface by x-ray diffraction and scanning electron microscopy–energy dispersive x-ray spectroscopy was presented previously [6]. In this study, an additional experiment was performed for quantitative evaluation of partitioning of Re (surrogate for ^{99}Tc) in the salt phase that formed on the melt surface and the condensed phase that deposited on the fused silica ampoule.

2. Experimental

The experimental setup used in the present mass balance test was the same as was used in a previous study [3]. The baseline glass prepared without Re addition was mixed by mechanical milling with the appropriate amount of KReO_4 to prepare a 30 g batch and heat treated in a vacuum-sealed, fused silica ampoule for 2 h at 1000 °C. The target concentration of Re in glass (if 100% retained) was 6474 ppm mass. Table 1 summarizes the target and analyzed compositions of the baseline glass and the composition of the resulting final glass containing Re, calculated based on the analyzed composition of the baseline glass. Table 1 also shows the relative percent difference (RPD) between target and analyzed concentrations of the baseline glass. The RPDs for all components were less than 10% except for SO_3 , which had an unreasonably high difference. Evaluation of all source chemicals used to prepare the baseline glass revealed that hematite (source of

* Corresponding author. Tel.: +1 509 372 4611; fax: +1 509 372 5997.

E-mail address: dongsang.kim@pnl.gov (D. Kim).

Table 1
Target and analyzed compositions of a baseline glass and calculated target composition of Re-added glass (in mass fractions).

Component	Baseline glass			Re-added glass
	Target	Analyzed ^a	RPD	Target ^b
Al ₂ O ₃	0.0610	0.0633	3.8	0.0627
B ₂ O ₃	0.1000	0.0955	−4.5	0.0945
CaO	0.0207	0.0209	1.0	0.0207
Cr ₂ O ₃	0.0002	0.0002	0.0	0.0002
Fe ₂ O ₃	0.0550	0.0533	−3.1	0.0528
K ₂ O	0.0047	0.0051	8.5	0.0067
MgO	0.0148	0.0136	−8.1	0.0135
Na ₂ O	0.2100	0.2096	−0.2	0.2075
SiO ₂	0.4530	0.4598	1.5	0.4552
SO ₃	0.0016	0.0025	56.3	0.0025
TiO ₂	0.0140	0.0140	0.0	0.0139
ZnO	0.0350	0.0350	0.0	0.0346
ZrO ₂	0.0300	0.0272	−9.3	0.0269
Re ₂ O ₇	0.0000	0.0000		0.0084
Sum	1.0000	1.0000		1.0000

RPD: relative percent difference between target and analyzed concentrations.

^a Average from duplicate analyses normalized to sum to 1.

^b Calculated based on analyzed composition of a baseline glass.

Fe₂O₃) contained impurity sulfur that resulted in the higher SO₃ in the glass. This increased SO₃ in the baseline glass does not interfere with our study because the calculation of the target concentration for mass balance will be based on the analytical results.

The test ampoule containing the glass and salt was separated into two portions after allowing natural breakage along the boundary of the glass (at the meniscus of the glass melt, see Fig. 1) in the ampoule: (1) the upper ampoule wall portion with condensate deposit but without any glass (designated as *wall* material) and (2) the lower bulk glass portion attached to the ampoule wall and bottom (*glass* material). Each portion was put in a plastic bag and was broken into small pieces (roughly a few mm size on average) and moved to a 150 ml beaker.



Fig. 1. Heat treated sample remaining after the upper part of the fused silica ampoule wall is broken off along the boundary of the glass (at the meniscus of glass melt).

The broken material was ultrasonically washed twice for 1 min with ~75 ml of deionized (DI) water, decanting the solution from each wash to a collection container, and then washed two more times with ~10 ml DI water and decanted into the same collection container. The mass of *wall* wash solution was 142.23 g and that of *glass* wash solution was 149.01 g. After homogenizing the solution, approximately 20 ml of each wash sample was collected and sent for chemical analyses. The remaining solid material in each 150 ml beaker was dried for 24 h in an oven at 90 °C. The dry mass of *wall* material was 23.53 g before wash and 23.47 g after, and that of *glass* material was 38.19 g before wash and 38.00 g after. Each dried sample was ground in a tungsten carbide mill for 2 min to produce fine powder and homogenize. Approximately 1 g of sample was taken for chemical analyses. Chemical analyses were performed by Southwest Research Institute¹ using inductively coupled plasma–mass spectrometry for rhenium and inductively coupled plasma–atomic emission spectroscopy for all other elements.

3. Results and discussion

The mass of each element in each sample is calculated as:

$$m_{ij} = c_{ij}m_j \quad (1)$$

where m_{ij} is the mass of the i^{th} element in the j^{th} sample (g), c_{ij} is the concentration of the i^{th} element in the j^{th} sample (mass fraction), and m_j is the mass of the j^{th} sample (g). For solid samples, m_j is after rinsing and drying. Each sample was designated by abbreviations as follows: *ws* = *wall* solid, *gs* = *glass* solid, *ww* = *wall* wash, and *gw* = *glass* wash. The fraction analyzed in each sample is calculated as:

$$f_{ij} = m_{ij}/m_{i,t} \quad (2)$$

where f_{ij} is the fraction of the i^{th} element analyzed in the j^{th} sample and $m_{i,t}$ is the total target mass of the i^{th} element in all collected materials. The $m_{i,t}$ values were calculated from the target composition (Table 1) of 30.01 g of starting Re-containing glass and by assuming that the remaining material (31.71 g) out of all collected materials (61.72 g before wash) is pure SiO₂ (fused silica).

Table 2 summarizes the values for $m_{i,t}$, m_{ij} and f_{ij} for all elements present in the system. Table 2 shows that the f_{ij} values for all elements sum to between 93% and 101% except for Cr, showing good mass-balance closure. The worst mass-balance closure of 112% for Cr is not of concern considering its low concentration in glass at 0.02 wt.% Cr₂O₃.

As shown in Table 2, the wash samples contain four elements, Re, S, Na, and K, which are water soluble and are expected to be present in the salt. The presence of small amounts of other glass components (e.g., Al, Ca, Fe, etc.) in the *wall* solid sample (see $f_{i,ws}$) suggests that it contained a small amount of glass, potentially from fine glass powder adhered to the wall during loading into the ampoule or from glass meniscus material that separated into the *wall* portion during natural breakage. As expected, the $f_{i,ws}$ values other than silicon were negligibly small, <0.5% except for sulfur ($f_{S,ws} = 2.7\%$). The relatively high $f_{S,ws}$ is probably a result of a reaction between salt vapor in the head space and fused silica during 2 h heating at 1000 °C.

Out of the total 94% Re recovered, 42% was in the *glass* solid sample dissolved in the bulk of the glass, as shown in Fig. 2. The mass of Re in this sample ($m_{Re,gs} = 81.3$ mg) corresponds to 2710 ppm mass in the glass (81.3 mg divided by 30.01 g) disregarding minor loss of glass components to other samples. This value matches reasonably well with the Re solubility of 3000 ppm mass reported in a previous article [3]. The rest of the Re was in wash samples, 43% in *glass* wash and 9% in *wall* wash. It is believed that the 9% Re in the *wall* wash sample was

¹ Southwest Research Institute (SwRI), 6220 Culebra Rd., San Antonio, Texas 78238-5166 (<http://www.swri.org>).

Table 2

Total mass of each element (m_j), mass of element analyzed in each sample (m_{ij}), and fraction of element analyzed in each sample (f_{ij}).

Element (i)	Mass of element, mg					Fraction analyzed in sample, %				
	m_{it}	$m_{i,ws}$	$m_{i,gs}$	$m_{i,ww}$	$m_{i, gw}$	$f_{i,ws}$	$f_{i,gs}$	$f_{i,ww}$	$f_{i,gw}$	Sum
Re	194	0.188	81.3	18.2	83.7	0.10	41.9	9.4	43.1	94.4
Al	995	4.91	933			0.49	93.7			94.2
B	881		885				100.5			100.5
Ca	444	2.16	426			0.49	95.9			96.4
Cr	4.07		4.56				112.2			112.2
Fe	1108	2.30	1093			0.21	98.6			98.9
K	167		157	1.44	2.19		94.1	0.86	1.3	96.3
Mg	244	0.474	231			0.19	94.9			95.1
Na	4619	10.7	4408	2.25	12.4	0.23	95.4	0.05	0.27	96.0
Si	21,207	10,562	10,203			49.8	48.1			97.9
S	29.7	0.807	25.7	0.144	1.57	2.7	86.4	0.48	5.3	94.9
Ti	249	0.418	236			0.17	94.6			94.7
Zn	835	1.50	802			0.18	96.0			96.2
Zr	598	0.990	553			0.17	92.4			92.6

Blank represents analyzed concentration below reporting limit.

Sample identification: ws = wall solid, gs = glass solid, ww = wall wash, gw = glass wash.

present as vapor phase at 1000 °C and preferentially condensed on the ampoule wall, which was significantly cooler than the melt surface during air cooling.

Although the concentration of SO_3 in this glass is below its solubility, estimated at ~0.6 wt.% (based on the measured value in a glass with similar composition [7]), compared to 0.25 wt.% (Table 1), sulfur was present in the salt phase formed on the glass surface ($f_{s,gw} = 5.3\%$) (note that the glass without Re or with Re below its solubility did not form any salt [3] as expected). During initial heating of the glass and KReO_4 mix, the KReO_4 melts (melting point = 550 °C) and wets the glass particles. As the temperature increases, the glass particles sinter and form pores that will become filled with molten KReO_4 . The reaction between glass and liquid KReO_4 droplets progresses during heat treatment at 1000 °C, dissolving KReO_4 into the glass. The presence of sulfate salt observed in this study (see also Ref. [6]) suggests that there was an ion exchange between SO_4^{2-} and ReO_4^- during the reaction between glass and KReO_4 . If it is assumed that ReO_4^- behaves similarly to SO_4^{2-} in glass as postulated by Goel et al. [8], it is possible that these anions compete for the structural sites that can accommodate them, which means that the solubility of Re may depend on the concentration of

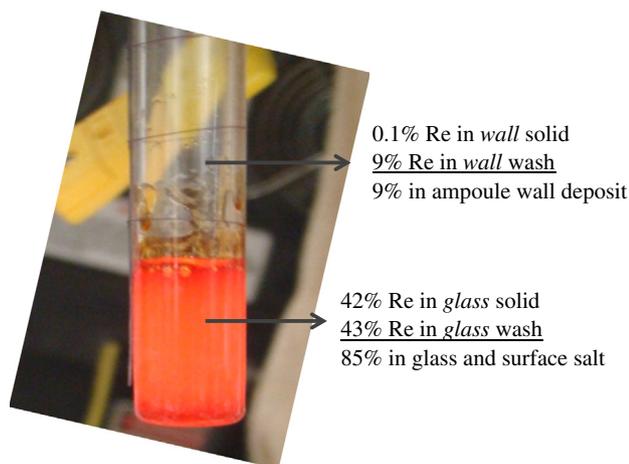


Fig. 2. Distribution of Re in each sample out of the total 94% Re recovered (image is a typical example of a fused silica ampoule containing glass immediately after removal from the furnace).

Table 3

Potassium-to-sodium and rhenium-to-sulfur mole ratios in surface salt and ampoule wall deposit samples compared to target values in glass.

Sample	K/Na	Re/S
Glass solid (target in glass)	0.02	0.5
Glass wash (surface salt)	0.10	9.2
Wall wash (ampoule wall deposit)	0.38	21.8

SO_3 already present in the glass, and possibly on the concentration of other anions. However, no additional tests were performed to support this hypothesis.

Similar to the anion exchange between SO_4^{2-} and ReO_4^- , it is apparent that there was a cation exchange between K^+ and Na^+ during the reaction between glass and KReO_4 . Table 3 summarizes the K/Na and Re/S mole ratios in wash samples compared with the mole ratios in the glass (glass solid sample). As can be seen from Table 3, the surface salt in the glass wash sample had a K/Na mole ratio of 0.10, i.e., 91% of total cations was Na and 9% was K starting from 100% K (in KReO_4 starting material) and had a Re/S mole ratio of 9.2, i.e., 10% of total anion components was S and 90% was Re starting from 100% Re. Apparently, K/Na and Re/S mole ratios were getting close to the ratios in the glass although it cannot be known whether equilibrium between the salt and the glass was reached before the salt migrated to the surface. The larger K/Na and Re/S mole ratios in the wall wash sample (ampoule wall deposit) than in the glass wash sample (surface salt) are consistent with the known information that K and Re are more volatile (i.e., have higher activity coefficients [9]) than Na and S, respectively.

4. Conclusions

A good mass balance closure was attained for all glass components including Re, with a total 94% Re recovery in four different samples. Out of 94% Re recovered, 42% was dissolved in glass, which corresponds to a Re solubility of 2710 ppm mass, and the other 52% escaped from the glass melt, resulting in a salt phase formed on the melt surface (43%) and a condensate deposited on the ampoule wall above the glass melt (9%). While Re dissolves into glass through reaction between molten glass and KReO_4 droplets, significant ion exchange progresses before the salt reaches the melt surface, resulting in enrichment of the surface salt with Na and S that were not initially present. Dissolution and ion exchange reactions similar to those observed in this simple system are expected to occur during melting of waste glass batches containing technetium but in a much more complex manner involving multiple solid, liquid and gas phases that evolve with temperature. Experimental studies to investigate the partitioning of Re (as surrogate for ^{99}Tc) into various phases during early stages of waste glass melting are underway to understand the mechanism of ^{99}Tc retention in or escape from glass melt.

Acknowledgements

This work was supported by the U.S. Department of Energy's Waste Treatment and Immobilization Plant Federal Project Office under the direction of Dr. Albert A. Kruger. The authors greatly appreciate Dr. John McCloy for his helpful suggestions. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830.

References

- [1] J.G. Darab, P.A. Smith, Chem. Mater. 8 (1996) 1004–1021.
- [2] H. Abramowitz, M. Brandys, R. Cecil, N. D'Angelo, K.S. Matlack, I.S. Muller, I.L. Pegg, R.A. Callow, I. Joseph, RPP-54130 Rev 0, Washington River Protection Solutions, Richland, WA, 2012. (<http://www.osti.gov/bridge/servlets/purl/1059435/>).

- [3] J.S. McCloy, B.J. Riley, A. Goel, M. Liezers, M.J. Schweiger, C.P. Rodriguez, P.R. Hrma, D. Kim, W.W. Lukens, A.A. Kruger, *Environ. Sci. Technol.* 46 (2012) 12616–12622.
- [4] D-S. Kim, C.Z. Soderquist, J.P. Icenhower, B.P. McGrail, R.D. Scheele, B.K. McNamara, L.M. Bagaasen, M.J. Schweiger, J.V. Crum, J.D. Yeager, J. Matyas, L.P. Darnell, H.T. Schaefer, A.T. Owen, A.E. Kozelisky, L.A. Snow, M.J. Steele, PNNL-15131, Pacific Northwest National Laboratory, Richland, WA, 2005. (http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15131.pdf).
- [5] D-S. Kim, L.M. Bagaasen, J.V. Crum, A. Fluegel, A. Gallegos, B. Martinez, J. Matyas, P. Meyer, D.R. Paulsen, B.J. Riley, M.J. Schweiger, C.W. Stewart, R.G. Swoboda, J.D. Yeager, PNNL-16267, Pacific Northwest National Laboratory, Richland, WA, 2006. (http://www.pnl.gov/main/publications/external/technical_reports/PNNL-16267.pdf).
- [6] B.J. Riley, J.S. McCloy, A. Goel, M. Liezers, M.J. Schweiger, J. Liu, C.P. Rodriguez, D. Kim, *J. Am. Ceram. Soc.* 96 (2013) 1150–1157.
- [7] I.S. Muller, I.L. Pegg, VSL-03R3460-1 Rev 0, Vitreous State Laboratory, The Catholic University of America, Washington DC, 2003.
- [8] A. Goel, J.S. McCloy, C.F. Windisch, B.J. Riley, M.J. Schweiger, C.P. Rodriguez, J.M. Ferreira, *Int. J. Appl. Glas. Sci.* 4 (2013) 42–52.
- [9] R.G.C. Beerkens, *J. Am. Ceram. Soc.* 84 (2001) 1952–1960.