Progress in Nuclear Energy 110 (2019) 13–23

Contents lists available at ScienceDirect

Progress in Nuclear Energy

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

Laboratory-scale quartz crucible melter tests for vitrifying a high-MoO_3 raffinate waste simulant

Brian J. Riley[a,*], Jarrod V. Crum[a], William C. Buchmiller[a], Bennett T. Rieck[b], Michael J. Schweiger[a], John D. Vienna[a]

[a] Pacific Northwest National Laboratory, Richland, WA 99354, United States
[b] AECOM, Richland, WA 99354, United States

ARTICLE INFO

Keywords:
Laboratory-scale melter
Glass
Nuclear waste immobilization

ABSTRACT

This paper details the results from two laboratory-scale (~1 L) melter experiments where the processability was evaluated for vitrifying a simulated high-MoO_3 raffinate waste from reprocessing of used commercial nuclear fuel. The target glass (CSLNTM-C-2.5) contained roughly 18 mass% waste loading (2.5 mass% MoO_3). A homogeneous glass product was produced after process optimizations. Following the experiments, condensates present in the experimental apparatus were analyzed and found to be primarily composed of SiO_2, Al_2O_3, Zr-O, rare earth, molybdate, and nitrate phases. The composition of the glassy product resulting from the second melter experiment was very similar to that of the target composition with variations noted for Al, Mo, and Zr.

1. Introduction

The US Department of Energy is investigating sustainable nuclear fuel cycles that maximize energy generation, improve uranium resource utilization, minimize waste generation, limit proliferation risk, and improve safety (DOE, 2010; Todd and Vienna, 2012). Vitrification is being evaluated as a technology to immobilize the high-level waste (HLW) raffinates that would be generated by aqueous reprocessing of used nuclear fuel (UNF) (Vienna et al., 2015). The composition of an example HLW raffinate is given in Table 1 and was the focus of the current study. For this study, the primary goal was to immobilize this waste stream into a single-phase glass without crystallinity (excluding noble metals) or phase separation. This work was a continuation of a previous study to assess maximum waste loadings prior to crystallization or phase separation and that was obtained at 18 mass% with CSLNTM-C-2.5 (Crum et al., 2009).

Alternatively, if the desire is to allow for at least some crystallization, the glass-forming additives can be carefully selected so that, after processing and during cooling, the components limiting waste loading (e.g., lanthanides, Mo) can be selectively crystallized into chemically-durable phases such as oxyapatite [i.e., $AE_2RE_8(SiO_4)_6O_2$] and powellite [i.e., $AEMoO_4$], where AE and RE denote alkaline earths and rare earths, respectively, to create a glass-ceramic waste form with upwards of 50 mass% waste loading. This alternative approach to single-phase glass was the focus of work presented elsewhere (Crum et al., 2012, 2014, 2016).

An initial reference glass was formulated for this waste stream to support flowsheet testing (Crum et al., 2009). The glass was designed to melt at temperatures below 1250 °C with a viscosity between 2 and 8 Pa s, have a liquidus temperature below 1050 °C, not form a separated molybdate-rich salt phase either at melt temperature or during slow cooling (determined by visual inspection and powder X-ray diffraction, or P-XRD, analysis), exceed the US HLW glass product consistency test response requirements by roughly an order of magnitude for both quenched and slow cooled glass, and have a reasonably high waste loading (15–20 mass%) (Crum et al., 2009). Test glasses with 3 and 3.5 mass% MoO_3 formed molybdate-rich salt phases on slow (canister centerline) cooling, and thus did not meet the requirements (Crum et al., 2009). Thus, the CSLNTM-C-2.5 glass with 2.5 mass% of MoO_3 had the highest MoO_3 loading of the test glasses that met all target properties (Table 2). The measured properties of the CSLNTM-C-2.5 glass were reported previously (Crum et al., 2009) using documented procedures (ASTM C 1285-08, 2014; ASTM C 1720-11, 2011), and are presented in Table 3 for convenience.

2. Background

2.1. Waste feed preparation

The waste composition, listed in Table 1, was adjusted to generate a

* Corresponding author.
E-mail address: brian.riley@pnnl.gov (B.J. Riley).

https://doi.org/10.1016/j.pnucene.2018.08.022
Received 22 November 2017; Received in revised form 29 August 2018; Accepted 31 August 2018

Table 1
Composition of the HLW raffinate.

Parameter/additive	Composition	Renormalized to 1-L volume
Volume (L)	101.1	1
H^+ (moles)	294.72	2.915
Actinides (mass, g)	8.89E-02	8.793E-04
Lanthanides (mass, g)	21.8	2.156E-01
Alkalis (mass, g)	4.98	4.926E-02
Alkaline earths (mass, g)	6.67	6.597E-02
Transition metals (mass, g)	10.8	1.068E-01
Noble metals (mass, g)	4.42E-01	4.372E-03
Total mass (g)	44.7	4.421E-01

Table 2
CSLNTM-C-2.5 glass composition (in mass% oxide) from Crum et al. (2009). [(a)]Glass-forming additives (not found in the waste) include Al_2O_3, B_2O_3, CaO, Li_2O, Na_2O, and SiO_2 and all others are considered waste components.

Oxide	CSLNTM-C-2.5
Ag_2O	0.07
Al_2O_3[(a)]	5.95
B_2O_3[(a)]	5.00
BaO	1.41
CaO[(a)]	7.00
CdO	0.07
Ce_2O_3	1.98
Cs_2O	1.84
Eu_2O_3	0.11
Gd_2O_3	0.10
La_2O_3	1.01
Li_2O[(a)]	4.02
MoO_3	2.50
Na_2O[(a)]	7.00
Nd_2O_3	3.36
PdO	0.01
Pr_2O_3	0.93
Rb_2O	0.27
RhO_2	0.05
RuO_2	0.13
SeO_2	0.05
SiO_2[(a)]	53.03
Sm_2O_3	0.69
SnO_2	0.04
SrO	0.63
TeO_2	0.42
Y_2O_3	0.40
ZrO_2	1.91
Waste Loading[(a)]	18.01

"waste feed" composition for testing; this was done to simplify the process and to save on the cost of raw materials. The Nd was substituted for the total actinide content on a molar basis and Tc, Ru, and Pd were omitted. Each of the components were added as nitrates, oxides (i.e., MoO_3), or oxynitrides [i.e., $ZrO(NO_3)_2$], mostly in hydrated forms; the free acid (H^+) concentration was 2.915 M (Table 4). Table 4 lists the waste feed components and amounts necessary to obtain these target concentrations.

For reference, the target concentration was on the order of 300–500 g L^{-1} (mass of glass per L of feed). However, at 2.915 M HNO_3, the solids loading is low, i.e., ~11 g of solids in 10 L. This low concentration is not ideal for a melter feed, and a pre-concentration step is necessary to allow for efficient melting. It is also necessary to prevent putting a significant burden on the calciner (if used), the melter, and the off-gas system needed to handle the large volumes of acid, as well as other gaseous byproducts, released during actual processing. In addition, selectively removing some of the HNO_3 prior to melting provides an opportunity to recycle this component into subsequent processes.

Table 3
Selected properties of CSLNTM-C-2.5 glass (Crum et al., 2009) where T_L is the liquidus temperature (ASTM C 1720-11, 2011), the PCT is the product consistency test (ASTM C 1285-08, 2014), ρ_b is the bulk density, T_g is the glass transition temperature measured using differential thermal analysis, T_m is the melting temperature measured using differential thermal analysis, η is viscosity, and ε is the electrical conductivity. Note that the temperature validity ranges for the η and ε models are provided in parentheses.

Property	Value
Quenched crystallinity, mass%	Trace RuO_2
Slow cooled crystallinity, mass%	Trace RuO_2
Optical T_L, °C	1017
P-XRD T_L, °C	1030
Primary crystalline phase	$Ca_2Nd_8Si_6O_{26}$
Quenched PCT B, g L^{-1}	0.21
Slow cooled PCT B, g L^{-1}	0.19
ρ_b, g cm^{-3}	2.78
T_g, °C	515
T_m, °C	1233
η, Pa·s (T = 1196–1399 °C)	$\ln[\eta, \text{Pa·s}] = -8.68 + 15505/T$
ε (at T_m), S m^{-1}	20.62
ε, S m^{-1} (T = 1200–1350 °C)	$\ln[\varepsilon, \text{S m}^{-1}] = 8.42–8124/T$

Table 4
Waste stream information for 10 L of feed at a final acid concentration of 2.915 M HNO_3, where X_i, M_i, and $m_{i,a}$ denote the moles, molarity (mol L^{-1}), and mass of the i-th element, respectively, and $\boldsymbol{M}_{\mathbf{HNO_3}}$ is the molarity of HNO_3.

Element	X_i (moles)	M_i, mol L^{-1}	M_i/M_{HNO_3}	Additive	$m_{i,a}$ (g)
Ba	3.634E-02	3.595E-04	1.233E-04	$Ba(NO_3)_2$	0.940
Ce	3.606E-02	3.567E-04	1.223E-04	$Ce(NO_3)_3$•$6H_2O$	1.549
Cs	3.299E-02	3.263E-04	1.119E-04	$CsNO_3$	0.636
Eu	1.645E-03	1.627E-05	5.582E-06	$Eu(NO_3)_3$•$6H_2O$	0.073
Gd	2.228E-03	2.203E-05	7.559E-06	$Gd(NO_3)_3$•$5H_2O$	0.096
La	1.966E-02	1.944E-04	6.670E-05	$La(NO_3)_3$•$6H_2O$	0.842
Mo	6.202E-02	6.135E-04	2.104E-04	MoO_3	0.883
Nd	6.479E-02	6.409E-04	2.198E-04	$Nd(NO_3)_3$•$6H_2O$	2.809
Pr	1.806E-02	1.786E-04	6.127E-05	$Pr(NO_3)_3$•$6H_2O$	0.777
Rb	6.932E-03	6.857E-05	2.352E-05	$RbNO_3$	0.101
Sm	1.020E-02	1.009E-04	3.462E-05	$Sm(NO_3)_3$•$6H_2O$	0.449
Sr	1.911E-02	1.890E-04	6.482E-05	$Sr(NO_3)_2$	0.400
Y	9.172E-03	9.072E-05	3.112E-05	$Y(NO_3)_3$•$6H_2O$	0.348
Zr	4.144E-02	4.099E-04	1.406E-04	$ZrO(NO_3)_2$•$2H_2O$	1.095
				Total Solids:	10.996

For the current experiments, a melter feed simulant with lower [NO_3^-] was prepared starting with the waste composition used to formulate CSLNTM-C-2.5, while excluding the minor components and noble metals (Table 5). For simplicity, the feed composition was formulated by first removing organics, minor components, and the excess HNO_3.

2.2. HNO_3 recovery or destruction

Some techniques have been discussed in the literature for managing HNO_3 including vacuum distillation (Smith et al., 1999) and thermochemical denitration, which is also referred to as chemical reduction (Bray, 1963). If a solution of HNO_3 is heated to 63 °C under vacuum (i.e., ~17 kPa or ~125 Torr), HNO_3 can be distilled without substantial decomposition. During this process, water can be removed up to the azeotropic point (~16 M or 68%), at which point the HNO_3 can be evolved. Thermochemical denitration can be done using a reductant, e.g., sucrose or $C_{12}H_{22}O_{11}$. The reactions of sucrose with HNO_3 result in byproducts such as CO_x, NO_x, and H_2O as shown in Reactions (1)–(4) from Bray (1963):

$$12\ HNO_3 + C_{12}H_{22}O_{11} \rightarrow 12\ CO + 6\ N_2O_3 + 17\ H_2O \quad (1)$$