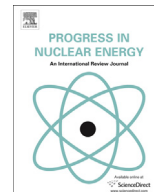




Contents lists available at ScienceDirect

## Progress in Nuclear Energy

journal homepage: [www.elsevier.com/locate/pnucene](http://www.elsevier.com/locate/pnucene)

## Waste form evaluation for RECl<sub>3</sub> and REO<sub>x</sub> fission products separated from used electrochemical salt

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## ARTICLE INFO

## Article history:

Received 13 April 2017

Received in revised form

11 August 2017

Accepted 4 September 2017

Available online xxx

## Keywords:

Electrorefiner

Tellurite glass

LABS glass

## ABSTRACT

The work presented here is based off the concept that the rare earth chloride (RECl<sub>3</sub>) fission products within the used electrorefiner (ER) salt can be selectively removed as RECl<sub>3</sub> (not yet demonstrated) or precipitated out as a mixture of REOCl and REO<sub>x</sub> through oxygen sparging (has been demonstrated). This paper presents data showing the feasibility of immobilizing a mixture of RECl<sub>3</sub>s at 10 mass% into a 78% TeO<sub>2</sub>-22%PbO glass while also showing that this same mixture of RECl<sub>3</sub>s can be oxidized to REOCl at 300 °C and then to REO<sub>x</sub> by 1200 °C, evolving Cl<sub>2(g)</sub>. When the REO<sub>x</sub> mixture is heated at temperatures >1200 °C, the ratios of REO<sub>x</sub>s change. The mixture of REO<sub>x</sub> was then immobilized in a lanthanide borosilicate (LABS) glass at a high loading of 60 mass%. Both the 78%TeO<sub>2</sub>-22%PbO glass and LABS glass systems show good chemical durability. The advantages and disadvantages of tellurite and LABS glasses are compared.

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### 1. Introduction

Pyroprocessing is one way of reprocessing used nuclear fuel (UNF). In this process, UNF is dissolved in a eutectic salt (e.g., LiCl-KCl) within an electrorefiner and the actinides are separated from the fission products by electrolytic reduction at the cathode. As the fission products get too concentrated in the salt, or to avoid criticality limits, the salt can be replaced to keep the electrorefiner running at full efficiency. At that point, the salt containing fission products can be: (1) directly disposed of in a salt repository, (2) immobilized in a single waste form such as a glass-bonded sodalite ceramic waste form (Frank et al., 2015; Riley et al., 2012a; Vance et al., 2012), tellurite glass waste form (McCloy et al., 2013; Riley et al., 2012b), or other type of waste form, or (3) partitioned with each separate fraction being treated separately for immobilization (fission products) or recycling (i.e., Li, Na, K, Cl).

The partitioning process has advantages and disadvantages. The primary disadvantage of partitioning the salt is that it increases the difficulty and cost of the process. However, the biggest advantages to partitioning the salt are that it can significantly reduce the

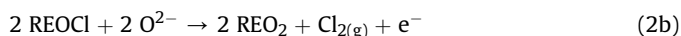
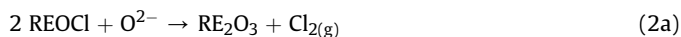
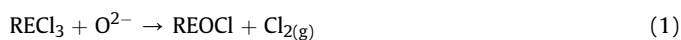
volume of waste that requires disposal and portions of the salt can be recycled into subsequent batches of ER salt. For example, simply dechlorinating the waste can reduce the mass of salt requiring disposal by more than half, such as the sol-gel approach to make the silica aluminophosphate (SAP) waste form (Park et al., 2008, 2011) where Cl<sub>2(g)</sub> is evolved and can be captured on a mordenite or other sorbent.

Another approach to partitioning the salt is to remove the RE fission products so that they can be immobilized in a separate waste form. One way to do this is to render them insoluble so that they precipitate out of solution, which can be achieved by oxygen sparging of the salt melt (Cho et al., 2009) or by precipitation in an aqueous solution by adding KOH (Leturcq et al., 2005). For the approach in the molten salt bath, the RE chlorides (RECl<sub>3</sub>) are converted to a mixture of oxides and oxychlorides as shown in Reactions (1) and (2), depending on the final oxidation state of the RE (e.g., 3+ or 4+). Data in the literature show incongruent results across the range of RECl<sub>3</sub> compounds evaluated (Castillejo et al., 2002; Cho et al., 2006, 2009; Hayashi and Minato, 2005; Katayama et al., 1995; Suh and Paik, 1992a, b) where some RECl<sub>3</sub> tend to form oxides (i.e., Y<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>) and some form oxychlorides (i.e., CeOCl, LaOCl, NdOCl, PrOCl, and SmOCl) (Castillejo et al., 2002; Cho et al., 2006; Hayashi and Minato, 2005) and the stability of each has been linked to the oxide-ion (O<sup>2-</sup>) activity

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(Katayama et al., 1995; Suh and Paik, 1992a, b) and oxobasicity of the melts (Castrillejo et al., 2002).



For the aqueous approach, after dissolving an electrochemical salt waste in water, Leturcq et al. (2005) were able to precipitate out the rare earth (RE) fission products and alkaline earth fission products as oxides (i.e.,  $\text{REO}_x$  and AEO, respectively). Then, KOH was added to the solution and the product was recovered through filtration.

The current work discusses the following: (1) an approach to immobilize a mixture of  $\text{RECl}_3$  fission products (denoted as ERF) from an electrorefiner salt in a tellurite glass waste form, (2) production of REOCl, and subsequently  $\text{REO}_x$ , by heating a mixture of  $\text{RECl}_3$  to 300 °C in air and to 1500 °C with hot-stage X-ray diffraction (HS-XRD), and (3) the production of a lanthanide borosilicate (LABS) glass using the same mixture that was used in (1) and (2). For the experiment in (1) to be feasible, this requires that the  $\text{RECl}_3$  can be selectively removed from the used salt, which has not yet been demonstrated. The approach listed for (3), could be used to immobilize  $\text{REO}_x$  at high waste loadings of >60 mass% in the event that (2) and/or oxygen sparging are successful at precipitating the  $\text{RECl}_3$  as  $\text{REO}_x$  or converting them to  $\text{REO}_x$  through heat treatment of REOCl. Using a LABS glass as a host for radionuclides is not a new concept and has been discussed previously for similar wastes and applications (Choi et al., 2014; Ebert, 2006; Marra and Ebert, 2003; Marra et al., 2006; Mohd Fadzil et al., 2016, 2015; Riley et al., 1999) but was included here for completion of the concept discussed. Characterization of these aforementioned products is also presented.

## 2. Methods

### 2.1. $\text{RECl}_3 \rightarrow \text{REOCl} \rightarrow \text{REO}_x$

#### 2.1.1. Conversion of $\text{RECl}_3$ to REOCl

The moisture content of each  $\text{RECl}_3 \cdot n\text{H}_2\text{O}$  used in this study was determined using a loss-on-drying approach where masses were recorded for each following heat treatments at 150 °C over the course of 5 d. Then, a mixture of  $\geq 99.9\%$   $\text{RECl}_3 \cdot n\text{H}_2\text{O}$  (Alfa Aesar, Ward Hill, MA), while accounting for the water content, was weighed out with a target of 20 g of dehydrated salt with the target composition shown in Table 1. The salts were combined and ground to a fine powder in a Diamonite™ mortar and pestle (MP100, Products Manufacturing) followed by a heat treatment at 150 °C overnight in a fused quartz crucible. Following this, the mixture was then ground again to a finer powder in the mortar and pestle and heated in air at 300 °C for 2 h in a fused quartz crucible.

**Table 1**  
Composition of reduced  $\text{RECl}_3$  mixture based off an electrorefiner salt discussed previously (Riley et al., 2015).

Component	Mass%
NdCl <sub>3</sub>	64.71
YCl <sub>3</sub>	16.70
LaCl <sub>3</sub>	7.24
PrCl <sub>3</sub>	6.52
SmCl <sub>3</sub>	4.83

Following the heat-treatment, the product was analyzed with powder X-ray diffraction (P-XRD) and found to be a mixture of REOCl. This powder was then stored in a vacuum desiccator to prevent rehydration.

#### 2.1.2. Conversion of REOCl to $\text{REO}_x$ (hot-stage XRD)

HS-XRD was performed on the product produced in section 2.1.1. Here, a small amount of the powdered sample was mixed with ethanol and placed onto a platinum heater strip (sample holder) using a pipet to form a thin, uniform layer. The slurry was allowed to dry on the sample holder and then was mounted in the hot-stage assembly. Compressed air was used as a purge gas, which flowed through the chamber at  $\sim 1 \text{ L min}^{-1}$  and bubbled through a flask of deionized water. Analysis was performed using a Bruker® D8 Advance (Bruker AXS Inc., Madison, WI) equipped with a Cu K $\alpha$  target at 40 kV and 40 mA. The instrument had a LynxEye™ position-sensitive detector with a range of  $3^\circ 2\theta$ . A P-XRD pattern was collected at room temperature and then the specimen was heated at  $100^\circ \text{C min}^{-1}$  in  $100^\circ \text{C}$ -increments to temperatures of 300–1200 °C and then in  $50^\circ \text{C}$ -increments from 1200 to 1500 °C, with holds of 1 h at each dwell temperature while scans were collected. Scans were collected at  $5\text{--}70^\circ 2\theta$  with increments of  $0.015^\circ$  and  $2\theta$  and a 1-s dwell per step. Bruker AXS DIFFRAC<sup>plus</sup> EVA and TOPAS software programs were used to identify and quantify the crystalline phases, respectively.

### 2.2. Tellurite glass fabrication

Twenty grams of each tellurite glass shown in Table 2 were batched using high-purity constituents ( $\geq 99\%$ , Alfa Aesar) that were milled in a Diamonite mortar and pestle. For the 78%TeO<sub>2</sub>-22% PbO glass without any other additives, two different batches were made with the same composition, one with high-purity (HP) TeO<sub>2</sub> (99.999%) and one with lower purity (LP) TeO<sub>2</sub> (technical grade) using the same processing conditions and batch sizes. The powders were loaded into a Pt/10%Rh crucible, a lid was placed on top of the crucible, and then this was placed into a furnace (Deltech, Inc., Denver, CO) for melting at various processing temperatures ( $T_m$  – see Table 2) for 20 min each. Following the melting process, they were quenched onto an Inconel® quench plate. For the 10%ERFP glass, the 10 mass% loading was chosen based on previous studies with other electrochemical salts and the HP TeO<sub>2</sub> additive was used during fabrication (McCloy et al., 2013; Riley et al., 2012b, 2015).

### 2.3. LABS glass fabrication

For the LABS glass, oxides were batched following the composition listed in Table 3. Oxides and H<sub>3</sub>BO<sub>3</sub> were mixed together in an agate milling chamber for 4 min and melted in a Pt/10%Rh crucible

**Table 2**  
Composition of lead tellurite glasses in mass%. \*Both the “LP” and “HP” glasses were batched with the same composition, just different TeO<sub>2</sub> purities.

Component	LP and HP* (0% salt)	10%ERFP
TeO <sub>2</sub>	78.00	70.20
PbO	22.00	19.80
NdCl <sub>3</sub>	0.00	6.48
YCl <sub>3</sub>	0.00	1.67
LaCl <sub>3</sub>	0.00	0.72
PrCl <sub>3</sub>	0.00	0.65
SmCl <sub>3</sub>	0.00	0.48
RECl <sub>3</sub>	0.00	10.00
$T_m$ (°C)	700	760

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