



# Assessment of lead tellurite glass for immobilizing electrochemical salt wastes from used nuclear fuel reprocessing



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## ARTICLE INFO

### Article history:

Received 13 April 2017

Received in revised form

25 August 2017

Accepted 28 August 2017

Available online 30 August 2017

### Keywords:

Tellurite glass

Strontium chloride

Pyroprocessing

Oxide reduction

## ABSTRACT

This paper provides an overview of research evaluating the use of lead tellurite glass as a waste form for salt wastes from electrochemical reprocessing of used nuclear fuel. The efficacy of using lead tellurite glass to immobilize three different salt compositions was evaluated: a LiCl-Li<sub>2</sub>O oxide reduction salt containing fission products from oxide fuel, a LiCl-KCl eutectic salt containing fission products from metallic fuel, and SrCl<sub>2</sub>. Physical and chemical properties of glasses made with these salts were characterized with X-ray diffraction, bulk density measurements, differential thermal analysis, chemical durability tests, scanning and transmission electron microscopies, and energy-dispersive X-ray spectroscopy. These glasses were found to accommodate high salt concentrations and have high densities, but further development is needed to improve chemical durability.

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## 1. Introduction

Pyroprocessing is one of the options for recycling the usable actinide fraction remaining in used nuclear fuel (UNF) back into the fuel cycle. Pyroprocessing is a technique where UNF is dissolved in molten salt within an electrorefiner and the uranium, or uranium and plutonium, are electrolytically reduced and recovered at the cathode [1]. Different salts are used for the reduction of oxide fuel and electrorefining operations: a LiCl-Li<sub>2</sub>O oxide reduction (OR) salt is used to reduce oxide fuel prior to electrorefining and a eutectic mixture of LiCl-KCl (60%–40% by mole, respectively) is used as the electrorefining (ER) salt. Metallic fuel is placed directly into the LiCl-KCl eutectic salt for electrorefining. When the salt composition becomes unsuitable for efficient operation, a portion of the used salt is removed from the electrorefiner and replaced with new or recycled salt. Actinides and lanthanides can be removed from the waste salt to be discarded (drawn-down) and the decontaminated salt placed back in the electrorefiner. Then, the unused portion of

the salt requires disposal or immobilization in a waste form.

A few options have been identified that can be used for immobilizing the salt waste and one of those is the glass-bonded sodalite ceramic waste form (CWF) [2]. Sodalite has the general formula  $M_8^{1+}(AlSiO_4)_6A_2^{1-}$  [ $M = Na^+, Li^+, K^+, A = Cl^-, I^-, OH^-$ ], which is ideal for waste salt containing both alkali and halides and it can be made by mixing salt with zeolites, with aqueous solutions (e.g., NaAlO<sub>2</sub>, colloidal silica), through nepheline precursors, or solvent-alkoxide solutions using hydrothermal, sol-gel, and room-temperature synthesis routes [2–7]. In the CWF, a glass binder is used to both encapsulate the sodalite and immobilize the fission products that are not incorporated in the sodalite crystal structure (e.g., rare earths, actinides, alkaline earths, and a portion of the alkali metals).

Another waste form option is glass. While borosilicate glasses have been demonstrated as viable hosts for the wide range of radionuclides present in defense wastes [8,9], halides are only slightly soluble in borosilicates and retentions are low at the high processing temperatures required to process these glasses [10]. Recently, tellurite glasses have been evaluated for mixed-salt immobilization due to the much higher halite solubilities and lower processing temperatures [11,12]. Tellurite glasses have higher loading capacities for mixed-chloride salts than any waste glass

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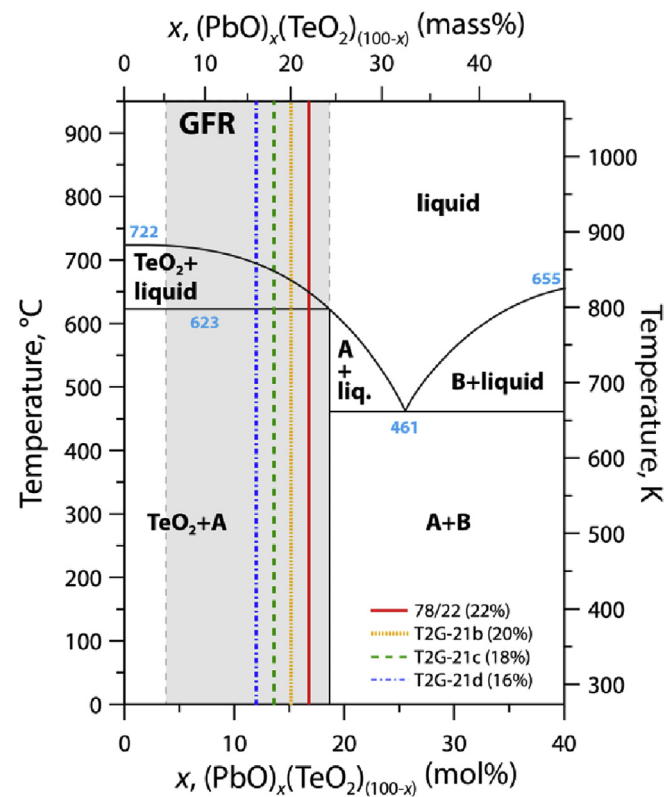
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evaluated to date (that the authors are aware of). The primary drawback to tellurite glass is that  $\text{TeO}_2$  is very rare in the earth's crust and expensive.

Early scoping studies [12,13] evaluating the use of tellurite glass to immobilize electrochemical salts were aimed at identifying simple binary or ternary systems that could be made into glass. For the initial study,  $\text{TeO}_2$  was mixed with the following additives:  $\text{PbO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3+\text{B}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Fe}_2\text{O}_3$ . The most promising systems were selected based on homogeneity, meltability, and low volatility during melting.

The five tellurite glass systems chosen for further study were:  $\text{PbO}$ ,  $\text{Al}_2\text{O}_3+\text{B}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{P}_2\text{O}_5$ , and  $\text{ZnO}$  based on available glass-formation regions [14–18] and favorable properties during glass fabrication and characterization described in more detail elsewhere [13]. These were studied further by making glasses with 10 mass% of a surrogate waste salt representing  $\text{LiCl-KCl}$  eutectic salt containing fission products from the processing of multiple fuel batches, which we refer to as ER salt. Glasses made with and without the surrogate ER salt were subjected to the ASTM C1285 [19] product consistency test (PCT-B) method to assess the chemical durability. The results from that study indicated that the  $\text{TeO}_2$ - $\text{PbO}$  system was the most promising based on low normalized releases of chloride ( $NL_{\text{Cl}} = 0.528 \text{ g m}^{-2}$ ) after a 7-day test at  $90^\circ\text{C}$  in a Teflon™ vessel [12,13].

Additionally, a series of binary  $\text{TeO}_2$ - $\text{PbO}$  glasses were made with 16–22 mass%  $\text{PbO}$  to determine the optimal glass-forming

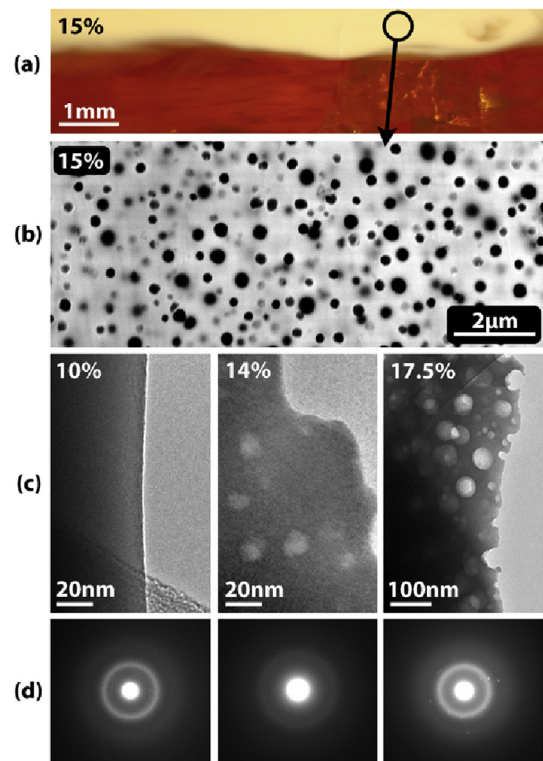


**Fig. 1.**  $\text{TeO}_2$ - $\text{PbO}$  phase diagram showing the glass-formation region (GFR) as the shaded gray area (after Paul [20]). Here, “A” denotes  $\text{Te}_4\text{PbO}_9$  and “B” denotes  $\text{Te}_3\text{Pb}_2\text{O}_8$ . Temperatures at critical locations on the diagram are listed in blue. The binary  $\text{TeO}_2$ - $\text{PbO}$  glass used in this study (78% $\text{TeO}_2$ -22% $\text{PbO}$ , by mass) as well as those made by the authors in previous studies [11,21] are shown as vertical lines including T2G-21d (16%  $\text{PbO}$ ), T2G-21c (18% $\text{PbO}$ ), and T2G-21b (20%  $\text{PbO}$ ) (values listed in mass %). Characteristic temperatures at key locations are provided in blue text in  $^\circ\text{C}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

region (see Fig. 1 [11,20,21]) and salt loading limits. A number of characterization techniques were applied to evaluate the structure, chemistry, microstructure, and chemical durability of the  $\text{TeO}_2$ - $\text{PbO}$  glasses made with different ER salt loadings [11]. Glasses made with <22 mass%  $\text{PbO}$  (>78 mass%  $\text{TeO}_2$ ) were highly crystalline and volatilization was observed during the melting process. Thus, to minimize the salt volatility during processing, the baseline composition of 22 mass% (13.78 mol%)  $\text{PbO}$  in  $\text{TeO}_2$  was used for future studies (henceforth referred to as the 78% $\text{TeO}_2$ -22% $\text{PbO}$  glass composition).

A variety of microstructures were observed at different ER salt loadings in this 78% $\text{TeO}_2$ -22% $\text{PbO}$  glass system using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). In glasses made with 14 and 15 mass% salt loadings, phase separation was observed at the nano- and macro-scales, respectively, leading to the appearance of a milky yellow-white phase (Fig. 2). The glass made with 10 mass% ER salt remained homogeneous at TEM resolutions, but phase separation was observed at the  $\sim 10$ -nm scale in the glass made with 14 mass% ER salt. The size of the phase-separated regions continued to increase with higher salt loadings (Fig. 2c) [11].

The work presented here includes studies to investigate the solubilities of  $\text{SrCl}_2$ , OR salt, and a different ER salt [ER(SF)] than what was used in previous studies pertaining to 78% $\text{TeO}_2$ -22% $\text{PbO}$  glasses. The salt-loading capacities of each system were evaluated by characterizing the microstructures, and, for glasses made with ER(SF) and OR salts, by measuring the chemical durabilities.



**Fig. 2.** (a) Optical micrograph of 15 mass% ER salt 78% $\text{TeO}_2$ -22% $\text{PbO}$  glass. (b) SEM micrograph of the same glass taken from the milky yellow-white phase-separated region on the top of the glass shown in (a). (c) TEM micrographs of 78% $\text{TeO}_2$ -22% $\text{PbO}$  glasses containing 10, 14, and 17.5 mass% ER salt. (d) Selected area diffraction patterns of samples shown in (c). Note that these micrographs were taken from McCloy et al. [11] and are included here with permission from the American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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