

Materials for Tc Capture to Increase Tc Retention in Glass Waste Form – A Review – 15553

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ABSTRACT

⁹⁹Techneium is a long-lived fission product found in the tank waste at the Hanford site in Washington State. In its heptavalent species, it is volatile at the temperatures used in Hanford Tank Waste Treatment and Immobilization Plant vitrification melters, and thus is challenging to incorporate into waste glass. In order to decrease volatility and thereby increase retention, technetium can be converted into more thermally stable species. Several mineral phases, such as spinel, are able to incorporate tetravalent technetium in a chemically durable and thermally stable lattice, and these hosts may promote the decreased volatility that is desired. In order to be usefully implemented, there must be a synthetic route to these phases that is compatible with both technetium chemistry and current Hanford Tank Waste Treatment and Immobilization Plant design. Synthetic routes for spinel and other potential host phases are examined.

INTRODUCTION

Some 56 million gallons of waste were produced at Hanford, Washington in the production of plutonium during the last century [1]. Technetium (Tc) makes up 6% of the fission products from the use of uranium as a nuclear fuel, and is thus a large part of the legacy waste that must be dealt with. It is long-lived, environmentally mobile, and quickly volatilizes at temperatures found in vitrification melters, making technetium one of the most challenging elements to capture and store safely. Technetium is the dominant source of radioactivity in spent nuclear fuel in the range of ten to hundreds of thousands of years, making it a critical part of waste immobilization [2].

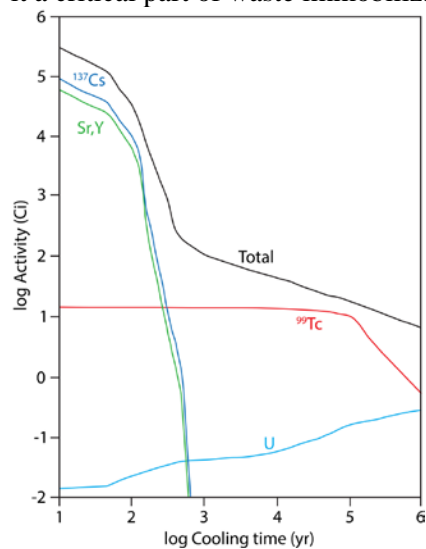


Fig. 1. Activity of high-level nuclear waste components.

Vitrification offers many solutions to the challenges of nuclear waste storage. The Hanford Tank Waste

Treatment and Immobilization Plant (WTP) currently under construction at the Hanford site will transform the complicated mix of radionuclides and harsh chemicals found in Hanford's underground tanks into glass. This is done at temperatures over 1000°C, melting the waste and added glass-forming chemicals (called 'feed') into masses of glass, which will inter the waste for thousands of years [3].

Problems with technetium arise with the pertechnetate ion, TcO_4^- , a heptavalent species and the most stable form of technetium in the Hanford waste liquids [4]. The pertechnetate form of technetium is soluble in water and very environmentally mobile [5]. Pertechnetate, and other heptavalent technetium species, volatilizes well below the temperature of the melters [3]. Melter redox is variable with batching composition and melting progress, but tends to oxidize Tc to Tc^{7+} [6] unless reducing agents, such as Fe^{2+} Oxalate, are included in the batching [7]. This means that much of the technetium in the waste evaporates from the glass melt and never incorporates into it. Repeated recycle of off-gas steams can incorporate more Tc into the glass, but also recycles in halides and sulfur, which is highly detrimental to waste-loading [7]. Controlling the form of technetium in the waste feed could prevent this low-temperature evaporation and allow increased retention in the melters, making vitrification more efficient.

One approach to increasing technetium's retention in the glass melters is by trapping the technetium in a solid refractory form that is less volatile than the pertechnetate. Such a material could transport the technetium into the bulk of the melt where it would be more readily incorporated into the glass. In this approach, vitrification would continue without the need for secondary waste forms to immobilize technetium. The reduced Tc^{4+} species is what is found in most technetium-bearing solid phases, such as spinel [8], meaning that incorporation of Tc into these phases will generally require a reduction of the Tc^{7+} found in Hanford waste to Tc^{4+} .

Magnetite, trevorite and goethite bearing ~1wt% Tc have been melted in crucible tests of waste-glass simulants [9]. Increased retention of Tc over a heating profile was demonstrated, showing the concept is sound. Rhenium-bearing sodalite, an analogy to Tc-sodalite, has also been demonstrated to increase Re retention in crucible tests in soon-to-be-published work by these authors.

In the past 50 years that it has been available for study, many different phases have been synthesized that contain technetium. Spinel, pyrochlore, perovskite, rutile, and sodalite have all been demonstrated and are potential candidates. To be useful for carrying technetium into glass melt, the phase chosen must be stable at very high temperatures and able to withstand the conditions of boiling feed. Larger micrometer-sized particle sizes are preferable to nano-sized ones. In order to be easily integrated into the WTP flowsheet, there must be an energetically inexpensive and safe way to synthesize the material. These twin issues, which material to choose and how to synthesize it, form the crux of the question at hand.

MATERIAL FORMS FOR TECHNETIUM CAPTURE

Spinel

Many species of spinel, AB_2O_4 , are formed from divalent metals and either Fe^{3+} or Ti^{4+} . The ionic radius of Tc^{4+} is similar to each of these, and charge balancing with vacancies allows Tc^{4+} to incorporate into a wide range of spinel structures [8]. A wide range of synthetic methods are used to make spinel, but most have never been demonstrated with Tc.

In 1964, Muller's seminal work described many new forms of technetium spinel, pyrochlore, and perovskite phases [8]. High temperature syntheses of several phases were described and provided a foundation for subsequent Tc work. The technique involves sintering finely mixed oxides under inert

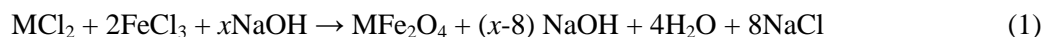
atmosphere in sealed Pt vessels at temperatures at or just above 1200°C for several hours to days. This method has been used with very little variation by Muller, Khalil, Thorogood, and Exter to study Tc-bearing phases [8, 10-12]. Pure products were reported in all cases except Co_2TcO_4 , CoNiTcO_4 , and NiCdTcO_4 , where impurities were detected by XRD. Unsuccessful syntheses were also reported; these include Cu_2TcO_4 , Ni_2TcO_4 , NiTc_2O_4 , Fe_2TcO_4 , FeTc_2O_4 , and Zn_2TcO_4 . In later research, Hartmann was able to use similar steps to synthesize Tc pyrochlore and perovskite [13, 14].

Titanate spinel of the form Zn_2TiO_4 can be sintered with TiO_2 to create a solid solution, up to a $\text{TiO}_2:\text{Zn}_2\text{TiO}_4$ ratio of 0.28 [15]. This creates a single phase product that has increased occupancy of Ti^{4+} into octahedral sites and Zn^{2+} vacancies in tetrahedral sites. TiO_2 is introduced as rutile and sintered at 950°C for this process. Technetium forms a TcO_2 oxide similar to TiO_2 and would possibly be able to combine with Zn_2TiO_4 spinel via an analogous method [16]. In normal spinel, half of the octahedral sites remain empty. If TcO_2 could fill these vacancies, higher waste loading in spinel would be possible.

Challenges of the high temperature synthesis are mainly engineering demands. The method is straightforward and can produce pure products with no flux or catalysts in most cases, with near 100% completion. Furthermore, this synthetic route has been shown to synthesize many different spinel with simple chemistry. The high temperatures and control of oxygen needed require energy and either vacuum systems or inert gases and the ability to counter the gases pressure at high temperatures. Since technetium can become volatile at higher temperatures, contamination is likely if the fidelity of the containment is broken.

Besides the high-temperature work related to Muller's paper, technetium has been incorporated into spinel by an aqueous method from Lukens [17]. This method contrasts to Muller's method in temperature (90°C instead of 1200°C), particle size (nano instead of micron), Tc-loading (4% instead of 40%), and starting material (pertechnetate ions instead of TcO_2). Lower temperature of reaction allows for higher energy efficiency and less concern for Tc volatility. Starting the reaction from an aqueous TcO_4^- ion lends flexibility when adapting the synthesis to the aqueous conditions of Hanford waste. FeCl_2 and an additional divalent metal chloride (nickel, manganese, or cobalt), and pertechnetate are dissolved in anoxic water. NaNO_3 is added as an oxidant while NaOH is added to raise the pH and precipitate out the metal ions. The reduction of Tc^{7+} to Tc^{4+} is driven by the oxidation of Fe^{2+} to Fe^{3+} , accommodated by a deficit of NaNO_3 . Reportedly, 99% of technetium is removed from solution by these methods, and spinel as the major product [17]. This represents only one method of precipitating spinel from aqueous solutions, although it is currently the only one to do so with technetium.

The basic procedure for aqueous precipitation involves combining divalent and trivalent metal salts in solution, and mineralizing with a strong base. The reaction is generally given as



where $x \gg 8$ and M represents a divalent metal cation [18]. Salts other than chlorides can be used, and include nitrates [19], sulfates [20], and organic ligands [21, 22]. Bases that are used include NaOH [18], KOH [20], or NH_4OH [23]. This is the most straight-forward aqueous synthesis, and variations including micro-emulsions and hydrothermal methods borrow from or add on to its basic foundation.

Micro-emulsion is a form of coprecipitation where particle growth is inhibited by virtue of the reacting solution being contained in discrete bubbles within an organic liquid. This is a common technique, and is used to limit the amount of reagents that can interact, thereby limiting potential particle size. While

limiting particle size is not an aim of synthesizing a Tc host-phase, much of the literature is dedicated to creating nano-sized particles, and therefore not likely to be applicable to the current challenge. Furthermore, emulsion methods often require sintering of product to promote crystallinity [19, 21, 24-27], which Lukens' method avoids. Sol-gel methods similarly mix precursors together so that crystallinity can be achieved at lower temperatures of sintering. Ethylene glycol [28], ethanol [21] or even aloe vera [29] can be used as solvents combined with metal in nitrates or organic complexes. High temperature reflux uses high-boiling point liquids to decompose metal acetates [30-32] or acetylacetonates [33] to spinel without sintering.

Hydrothermal methods use high pressure reactor vessels, temperatures and pressures of aqueous reactions can be raised well above standard temperatures and pressures [28]. The largest spinel produced by aqueous methods were from hydrothermal syntheses, making their potential usefulness high. No literature has examined hydrothermal methods with Tc chemistry. Xing simplifies the process down to one step for a zinc ferrite $ZnFe_2O_4$ [34]. $Zn(OAc)_2$ and Fe_3O_4 are dissolved in water with stirring. Concentrated hydrazine is added, and the solution is autoclaved at 180°C for 14 hours, giving hundreds of nanometer sized particles. Other methods use emulsions of metal nitrates and organic solvents, heating to 120°C for 30h, but yielding nano-sized product [35]. Conversion of $Ni(OH)_2$ and Fe_2O_3 to trevorite spinel at pH 14 and in the presence of 0.5M NaCl [36] in a non-oxidizing method that may be amenable to reduced Tc^{4+} species. Other studies have shown that microwave heating after ultrasonic treatment gave the fastest reaction times for hydrothermal spinel syntheses. Larger particle sizes are achievable through hydrothermal synthesis. Acetates dissolved in ammonia grew to 10 μ m agglomerates of 60-nm particles after one hour at 210°C [37], and iron hydroxide and amorphous NiO grew to 1 μ m for individual particles.

Molten salt synthesis is a well-known industrial process that makes use of liquid salt flux to partially dissolve oxides [38]. The oxides' mobility is thus increased compared to high temperature sintering, and reactions similar to high temperature sintering can occur at faster kinetics and lower temperatures [39]. Several hours at 900°C, or months at 400°C, are sufficient to produce homogenous μ m crystals [40]. Molten salt is a widely used industrial process but requires temperatures that would produce Tc volatility, and would be incompatible with pertechnetate.

Self-propagating high-temperature synthesis, or SHS, is a novel method proposed by Laverov [41, 42]. Metallic Ti or Zr and oxides such as MoO_3 , Fe_2O_3 , or Tc_2O_7 , are combined and ignited. The metals act as redox pairs, and exchange oxidation states in extremely quick and exothermic reactions, yielding pyrochlore, perovskite, rutile or even metal alloys. This reaction is similar to the reaction between aluminum and iron oxide powders in thermite. The redox of the reaction, and extent of oxidation of the final products, can be controlled by the ratio of starting materials. Molybdenum is used by the author as a surrogate for technetium, and rutile phases formed by SHS are found to contain the most Mo, followed by perovskite, then pyrochlore. The high temperatures that these reactions occur at obviously present a challenge to technetium applications, due to technetium's volatility. Similar difficulties are overcome in the case of Cs_2O , which sublimates at 400°C. In one experiment, Cs is incorporated into an aluminosilicate using SHS. When Cs was added to the SHS starting materials sorbed onto a silica gel, the loss of Cs was as low as 10%. Both Tc and Cs are vulnerable to volatility at high temperatures, and the demonstration of this fraction of Cs lost indicates that a similar process may be possible without higher losses of Tc.

Current research by has shown that magnetite and trevorite spinel can be formed in aqueous solution from

$\text{Fe}(\text{OH})_2$ [9]. The oxidation of Fe^{2+} to Fe^{3+} is able to concurrently reduce pertechnetate from the solution and incorporate it into the solid. The solutions used for this synthesis of spinel are formulated to be analogies of the actual WTP off-gas stream, where pertechnetate volatilized from the melters will be captured. While this research is still underway, such a method to remove Tc from the off-gas and simultaneously sequester it in a durable solid offers a promising route to recycle the Tc back into the melters.

More esoteric synthetic routes include ball-milling, ignition and liquid nitrogen atomizing. When $\text{Mn}(\text{NO}_3)_3$ and $\text{Mn}(\text{OH})_2$ are combined with a pH 11 LiOH solution, solids can be atomized into liquid nitrogen and freeze-dried into Mn_3O_4 spinel [43]. Ball-milling involves producing spinel nano-particles from oxides in a high-energy mill, often milling at ten times the acceleration of gravity and days on end [44-48]. This again would require processing Tc into TcO_2 or similar as a starting reagent, and would present an opportunity for Tc to disperse in fine airborne particles, but is a method that does not require any special chemistry that might otherwise preclude its application to Tc. Oxides are simply smashed together and allowed to reorder in a spinel lattice. Ignition method, on the other hand, is unlikely to be tolerant to the easily oxidizing Tc: Metal nitrates are combined in glycine and ignited in air. The heat of combustion prompts the decomposition of the nitrates and the reordering of the metals into spinel [49]. Tc is easily oxidized to Tc^{7+} in air, and would likely not incorporate into spinel lattice under these conditions.

Sodalite

Sodalite is an aluminosilicate that is able to incorporate a range of anions in an aluminosilicate network. Sodalite can be formulated to contain either TcO_4^- or its analogue ReO_4^- , and is durable in glass melts. Synthesis of sodalite is possible in low temperature aqueous precipitations. Mattigod produced rhenium-bearing sodalite by a hydrothermal method at 175°C for a day [50], and Missimer used a similar method for Tc-bearing sodalite [51]. Dickson, reports making a technetium sodalite by combining pertechnetate with zeolite A and sodium hydroxide and heating to 90°C for four days [52]. The use of pertechnetate as a starting material is advantageous, since pertechnetate will be the principle form of technetium in the off-gas stream. An encumbrance to sodalite synthesis in the off-gas stream is the concentrations of chlorides, sulfides, and other anions relative to pertechnetate. These have been shown to out-compete for sites in the sodalite, and would make technetium-incorporation impossible if they were not removed somehow [51].

Tin Oxide

Sintered SnO_2 doped with Sb^{3+} or Sb^{5+} is able to selectively sorb pertechnetate out of solutions, reducing it in the process [53]. This is not an ionic exchange, but an incorporation of Tc in lattice vacancies, even in the presence of competing ions such as chloride, nitrate, calcium, and ammonia [54]. Tc-doped tin dioxide has been shown to be a suitable host-phase for Tc, with high chemical durability and can be heated in air without loss of Tc [55]. These properties combined indicate that SnO_2 may be a suitable material to remove Tc from the off-gas stream and retain it in the melters. Doing this in one material and without additional chemical separation or processing of Tc would be minimally disruptive to current WTP processes.

CONCLUSIONS

Technetium can be incorporated into a number of durable materials that may serve to decrease its volatility from a waste glass melter. Magnetite and goethite, sodalite analogies have been tested and show early promise. In order to fully take advantage of the performance of these materials, a facile synthetic route that is compatible with WTP operations must be possible. The best method to recycle Tc back into melters and inhibit further volatility will be developed from a direct method that removes Tc from

solution and directly into a durable host phase. Current research into $\text{Fe}(\text{OH})_2$ shows promise as a way to remove Tc from off-gas directly into a durable host-phase, and SnO_2 is theorized to show similar results. Sodalite suffers from the need to pre-separate Tc from the off-gas, as do more conventional synthetic routes such as high-temperature sintering, ball-milling, or molten salt synthesis. Taking advantage of creative synthetic routes and Tc's unique chemistry, operations of WTP in terms of off-gas recycle can be vastly and economically improved.

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