

## Review

## Incorporating technetium in minerals and other solids: A review



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## HIGHLIGHTS

- This paper covers synthesis methods for technetium-containing solids.
- Synthesis routes summarized cover a variety of temperatures and chemistries.
- Many synthetic routes have not yet been demonstrated with technetium.
- $\text{Fe}(\text{OH})_2$   $\text{SnO}_2$  and others show potential to capture  $\text{Tc}^{7+}$  from aqueous solution into stable waste forms.

## ARTICLE INFO

## Article history:

Received 21 May 2015

Received in revised form

27 August 2015

Accepted 28 August 2015

Available online 29 August 2015

## Keywords:

Technetium  
Immobilization  
Waste form  
Vitrification  
Spinel  
Sodalite  
Rutile  
Perovskite  
Pyrochlore

## ABSTRACT

Technetium (Tc) can be incorporated into a number of different solids including spinel, sodalite, rutile, tin dioxide, pyrochlore, perovskite, goethite, layered double hydroxides, cements, and alloys. Synthetic routes are possible for each of these phases, ranging from high-temperature ceramic sintering to ball-milling of constituent oxides. However, in practice, Tc has only been incorporated into solid materials by a limited number of the possible syntheses. A review of the diverse ways in which Tc-immobilizing materials can be made shows the wide range of options available. Special consideration is given to hypothetical application to the Hanford Tank Waste and Vitrification Plant, such as adding a Tc-bearing mineral to waste glass melter feed. A full survey of solid Tc waste forms, the common synthesis routes to those waste forms, and their potential for application to vitrification processes are presented. The use of tin dioxide or ferrite spinel precursors to reduce  $\text{Tc}(\text{VII})$  out of solution and into a durable form are shown to be of especially high potential.

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## 1. Introduction

Some 56 million gallons of waste were produced at the Hanford Site in Washington State as part of the production of plutonium during the last century. This waste currently resides in carbon steel tanks on the Hanford Site [1]. Technetium makes up 6% of the fission products from the use of uranium in the production reactors, and is thus a large part of the legacy waste that must be dealt with. Technetium is long-lived (half-life =  $2.13 \times 10^5$  y) and environmentally mobile in its oxidized form ( $\text{TcO}_4^-$ ) [2,3]. These properties add to the U.S. Department of Energy's urgency in immobilizing Hanford tank waste before leaking tanks become an environmental problem. Long-term immobilization of Tc is critical, as Tc is the dominant source of radioactivity in high-level wastes in the range of ten to hundreds of thousands of years [4] (see Fig. 1).

The current plan to treat the contents of Hanford tanks is to separate the wastes into a large-volume, low-activity waste (LAW) and a small-volume, high-level waste (HLW) fractions at the Hanford Tank Waste Treatment and Immobilization Plant (WTP), which currently is under construction at the Hanford Site. The LAW and

HLW fractions will be vitrified in separate facilities within the WTP. Glass-forming additives and various components of the tank waste will be fed into waste-glass melters operating at temperatures of  $1150^\circ\text{C}$  to vitrify the waste. One challenge to this approach is that Tc species, such as  $\text{TcO}_4^-$ , are volatile at temperatures below  $900^\circ\text{C}$  [5,6], and this volatility is accentuated by the high temperatures found in vitrification melters. Volatiles from the melters, including Tc, will be captured in off-gas scrubbing systems that divert Tc, sulfur, and other waste-glass components to a dilute aqueous solution. The volatility of Tc makes it one of the more challenging elements to capture and store safely in glass.

Alternatives to vitrification have been either proposed or are already underway for managing Tc wastes. In some places, Tc was simply released into the ocean [7]. Transmutation of metallic Tc into ruthenium has been attempted by the French with some success [8]. Other approaches include the formation of low-temperature waste forms for Tc-containing LAW such as cementitious waste forms [9–11], ceramicrete [10], and products of fluidized bed steam reforming [12].

Another approach to Tc immobilization is to remove the  $\text{TcO}_4^-$  from waste so it can be incorporated into a separate waste form. This can be achieved via ion exchange or with Tc-getters [13,14]. Qafoku et al. [15] recently investigated materials that could be used to remove  $\text{TcO}_4^-$  from solutions via reduction. The Tc then would be immobilized in a separate waste form such as Cast Stone [15].

The final approach discussed here is incorporation of Tc into a mineral lattice that would inhibit its volatility from the melter. If the Tc could be captured in a form that restrains volatility, such a material could transport the technetium into the bulk of the melt where it would be incorporated into the glass and where it would be less able to escape as a volatile gas during vitrification. If the  $\text{TcO}_4^-$  expected to be in the waste could be bound in a mineral structure, early experiments [16] show that this approach has the potential to increase Tc retention in the glass.

Technetium is present in nature in very small amounts as a result of natural uranium fission [17] and more recent human activities involving nuclear fission. Many different host mineral phases have been synthesized to include Tc in the mineral structure. These include spinel [18], sodalite [12], pyrochlore [19,20], perovskites [20], rutile [21], goethite [22,23], and layered double hydroxides [15,24,25]. Additionally, Tc-containing metal alloys have been studied as waste forms for immobilizing Tc [26,27].

The attributes of these mineral phases such as particle size, Tc loading, stability in waste melters, and hazards of reagents for synthesis are important when considering each mineral form. Large-sized mineral particles will present less surface area-to-volume and relatively high stability, thus limiting the interaction between the melt and any incorporated Tc. Thus, particle size over a

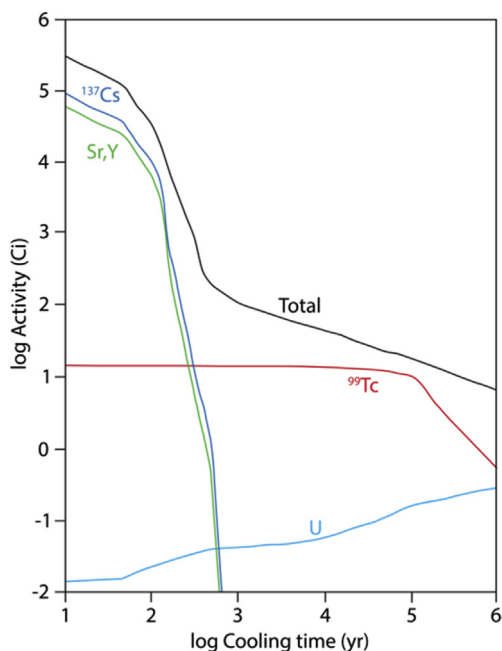


Fig. 1. Log/log plot of the activity (in Ci) of major radionuclides in high-level nuclear waste vs. time (in years) [4].

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