

Kinetics of Perrhenate Reduction by Stannous and Analysis of the Solid Phase Product

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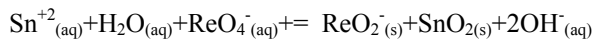
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1. Introduction

Technetium-99 contamination is a big problem in reprocessing of spent and defense nuclear fuel. At the Hanford site in Washington, 500 Ci ⁹⁹Tc has leaked to the environment¹⁻³. Similarly 95 and 31,000 pCi.g⁻¹ ⁹⁹Tc activity has been reported in sediment and water at a field research center Oak Ridge Tennessee. Perrhenate [ReO₄⁻] can be used as a surrogate of pertechnetate. These reactions are fairly possible with relatively high thermodynamic feasibility towards the forward direction because ΔE = -0.598, is fairly high for Sn⁺² than Fe⁺², so these were the reasons that Sn⁺² was selected as reducing agent. We have tried Sn⁺² to immobilize the Re(VII) to produce low solubility Re(IV) precipitates.



$$\Delta E = 0.598 \text{ eV} \quad \dots\dots\dots (1)$$

$$\text{Sn}^{+2} = \text{Sn}^{+4} + 2\text{e}^{-} \quad E = -0.15 \text{ eV} \quad \dots\dots\dots (2)$$

$$\text{ReO}_4^{-} + 3\text{e}^{-} = \text{ReO}_2 \quad E = 0.748 \text{ eV} \quad \dots\dots\dots (3)$$

2. Materials and Methods

2.1 Reduction of ReO₄⁻

NH₄ReO₄ (2 g) and SnCl₂ (1.428 g) were dissolved in 0.1 M HCl. Both solutions were mixed and final solution volume was adjusted to 214 mL in a beaker under ambient conditions. Samples were taken after regular intervals of time to monitor the removal of Re from the solution. The data confirms the presence of complete reducing conditions under ambient conditions. After completion of the reaction, a brown color precipitate was appeared. The slurry was centrifuged for 50 minutes at 4000 rpm. The precipitate was dried at 50°C overnight. Physical observation reveals that surface of the precipitate

was black whereas bulk precipitate was brown. The precipitate was again dissolved in HCl (pH 1.40) for washing, centrifuged, and dried at 50°C in oven. The supernatant was stored in refrigerator for analysis on Nexion 300 Inductively coupled plasma mass spectroscopy (ICP-OES) of unreacted Re and Sn in the solution mixture. The solid precipitate (RRS-1.34) was analyzed on Thermo Scientific K alpha⁺ x-ray photo electron spectroscopy (XPS), and Rigaku D/max-2500V x-ray diffraction (XRD). After one month, a new precipitate (RRS-1.34-2) was observed in washing solution.

2.2 Removal Efficiency, oxidation, and solubility

Equal molar ratios of Re and Sn (Re:Sn~1:1) did not removed all ReO₄⁻¹ from the solution. A significant portion of ReO₄⁻ was present in supernatant. An other Re:Sn (1:8) ratio was studied to completely remove Re from the solution under similar conditions, as used in Re:Sn~1:1.

Precipitates of both categories were oxidized in unbuffered solution having initial pH 10.74 under open air to check the release of Re. Solubility of precipitate was also checked and compared with pure ReO₂.

3. Results & Discussion

Re was removed slowly from the solution than Sn⁺². Re was also not removed completely as compared to Sn, however when Re:Sn was 1:8, whole of Re was removed along with Sn⁺² [Fig 1]. A precipitate was separated after reduction. It was analyzed by XRD. It revealed phases of both ReO₂ and SnO₂ present in precipitate [Fig 2]. XPS analysis [Fig. 3] of the same precipitate also confirmed the presence of Re(IV) that was another

clue that ReO_4^- has been reduced and stabilized as ReO_2 solid product. The precipitate was oxidized in alkali solution of pH 10.74. Release of Re was monitored [Fig. 4] The Re release was faster, reaches maximum after 45 h and then decreases and stabilized to some extent, indicating the reversing conditions in open air system. The solubility of the precipitate was also lower than pure ReO_2 solid showing more strongly bind phases than ReO_2 .

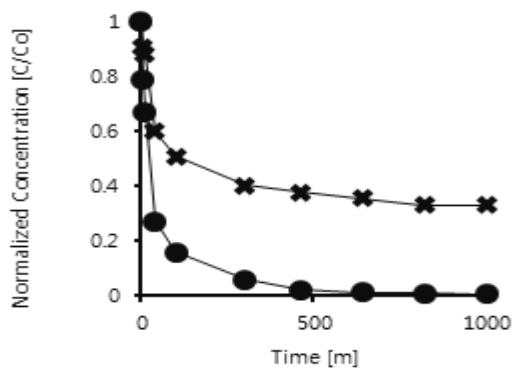


Fig. 1. Normalized ReO_4^- and Sn^{+2} removal rate from the solution. Cross marker: Re concentration; round marker: Sn concentration.

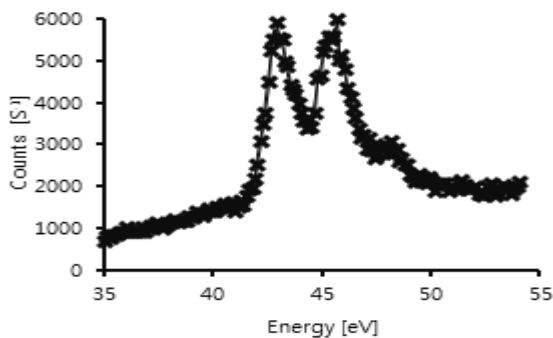


Fig. 2. XRD Spectrum of the precipitate RRS-1.34.

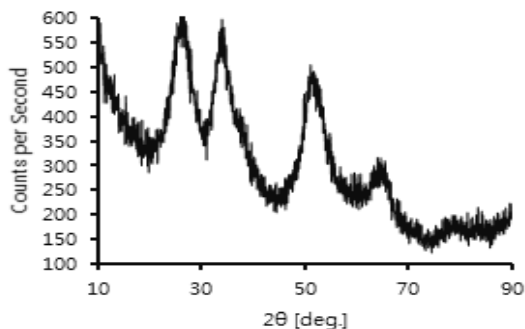


Fig. 3. Re XPS 4f scan, of precipitate RRS-1.34.

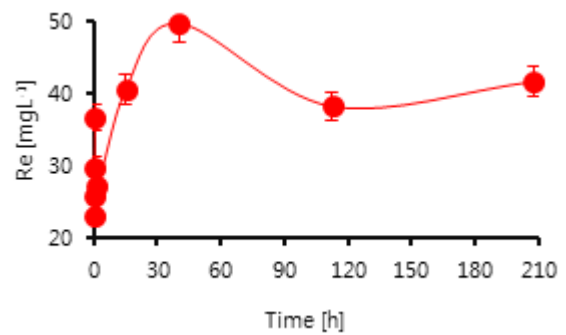


Fig. 4. Release of Re with time from the precipitate to solvent of pH 10.73.

4. Conclusion

In this research, we planned to explore the importance of Sn^{+2} as a reducing agent instead of Fe^{+2} for the reduction of ReO_4^- . It was explored that precipitate is a complex mixture of SnO_2 and ReO_2 oxides with surface impurity of Sn^{+2} , SnCl^+ , SnCl_2 , and CO_3^{-2} . The reduced precipitate, has potential application to generate a phase, which has low solubility of Re than ReO_2 . This character is important for ^{99}Tc waste management for long term stability of waste form.

5. References

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