

Synthesis of rhenium-doped tin dioxide for technetium radioactive waste immobilization

Mumtaz Khan ^a, Wooyong Um ^{a, b, *}, Won-Seok Kim ^a, Jong Heo ^{a, c}, HyunJu Kim ^a,
Seun Chang ^a

^a Division of Advanced Nuclear Engineering (DANE), Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-Gu, Pohang, Gyeongbuk, 790-784, Republic of Korea

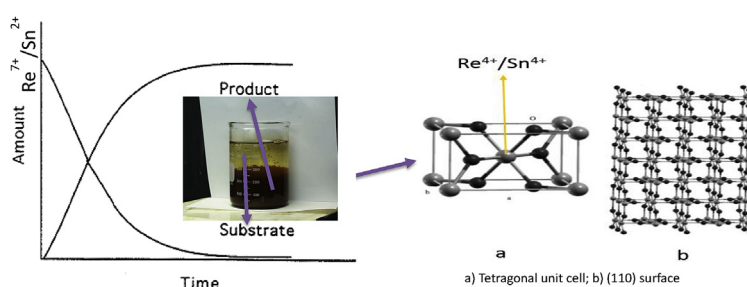
^b Division of Environmental Science and Engineering (DESE), Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-Gu, Pohang, Gyeongbuk, 790-784, Republic of Korea

^c RIST 3277, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-Gu, Pohang, Gyeongbuk, 790-784, Republic of Korea

HIGHLIGHTS

- Re^{4+} was incorporated into SnO_2 particles, called $\text{Re}(\text{SnO}_2)$.
- $\text{Re}(\text{SnO}_2)$ showed limited re-oxidation and less solubility than ReO_2 .
- Re^{1+} , Re^{2+} , Re^{4+} , and Re^{7+} species were found on $\text{Re}(\text{SnO}_2)$ surface.
- $^{99}\text{Tc}(\text{SnO}_2)$ can be synthesized like $\text{Re}(\text{SnO}_2)$ for ^{99}Tc immobilization.

GRAPHICAL ABSTRACT



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ABSTRACT

As an analog of technetium (^{99}Tc), rhenium (Re) was incorporated into the tin oxide (SnO_2) lattice structure to produce a stable phase. This new bi-metallic oxide consisting of Re^{4+} and Sn^{4+} was formed from perrhenate (ReO_4^-) reduction by tin (Sn^{2+}) and could reduce re-oxidation. After the precipitate was characterized by various techniques, the precipitate morphology and XRD patterns were found to resemble those of cassiterite (SnO_2) with narrow crystallite size ($D_{\text{average}} = \sim 1.47$ nm). The local structure of the precipitate was characterized as $\text{Re}-\text{O}$ (~ 2.02 nm), $\text{Re}-\text{Sn}$ (~ 3.15 nm), and $\text{Re}-\text{Sn}$ (~ 3.70 nm) in the first, second, and third coordination shells, respectively. As Re^{4+} was doped into the cassiterite phase, the precipitate was much less soluble than $\alpha\text{-ReO}_2$ (dissolved $\text{Re} = \sim 0.10$ mg L^{-1} vs. ~ 45.20 mg L^{-1}). The precipitate resisted re-oxidation, and the dissolved Re species were re-precipitated after 23 h. A major portion of Re dissolved during the solubility and re-oxidation tests was assigned to the species of Re^{+1} (12%), Re^{2+} (47.42%), Re^{4+} (28.48%), and Re^{7+} (12.18%) on the surface of precipitate, while Re^{+1} (1.05%), Re^{2+} (15.35%), Re^{5+} (27.77%), and Re^{7+} (55.82%) species were found on the $\alpha\text{-ReO}_2$ surface. These findings suggest that low-temperature reductive co-precipitation can incorporate ^{99}Tc (or Re) into the SnO_2 structure which limit the ^{99}Tc (or Re) re-oxidation and solubility.

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* Corresponding author. Division of Advanced Nuclear Engineering (DANE), Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-Gu, Pohang, Gyeongbuk, 790, Republic of Korea.

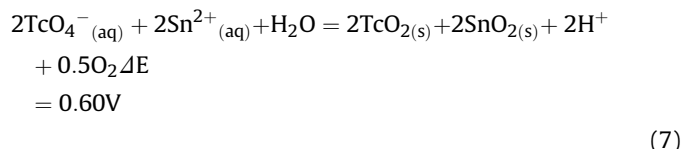
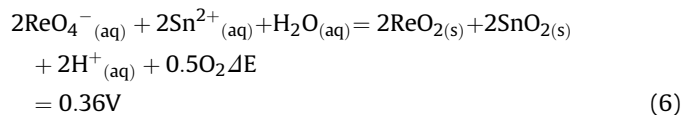
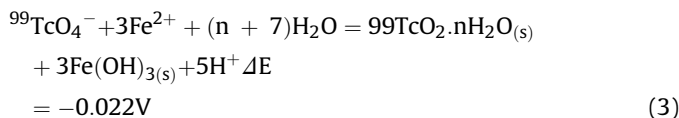
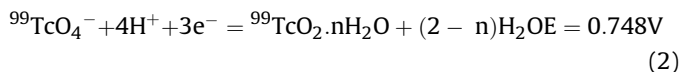
E-mail addresses: mumtazkhan03@postech.ac.kr (M. Khan), mumtazk36@gmail.com (M. Khan), wooyongum@postech.ac.kr (W. Um), wkim23@postech.ac.kr (W.-S. Kim), jheo@postech.ac.kr (J. Heo), hyunju1157@postech.ac.kr (H. Kim), seun@postech.ac.kr (S. Chang).

1. Introduction

The purex process, which reprocesses spent nuclear fuel, extracts technetium (^{99}Tc) along with uranium (U) [1]. During the final conversion stages of U–UF₆, a portion of ^{99}Tc is converted to the gaseous contaminant $^{99}\text{TcF}_6$ [1] and another significant portion (which cannot be treated by any current methods) is released as liquid waste into the environment [2]. For example, significant ^{99}Tc radioactivity ($^{99}\text{Tc} = \sim 1.85 \times 10^{13}$ Bq) was leaked into the environment at the Hanford Site (Washington, USA) [3]. The storage sites at Oak Ridge (Tennessee, USA) have discharged 3.52–1147 Bq. g⁻¹ ^{99}Tc into neighboring sediments and subsurface water [4] and the presence of many other isotopes was also reported. The Sellafield site in the UK, which lacks a long-term immobilization methodology, has also discharged significant ^{99}Tc into the ocean [2,5,6]. Spent fuel reprocessing in Asian countries will increase the ^{99}Tc pollution due to the unavailability of an appropriate treatment procedure [7]. Therefore, there is an urgent demand of immobilization methods that effectively sequester ^{99}Tc radioactive waste.

Perrhenate (ReO_4^-) is a commonly used surrogate of $^{99}\text{TcO}_4^-$ [8]. The two species have similar hydration energy (-2.4 eV for $^{99}\text{TcO}_4^-$ and -2.5 eV for ReO_4^-) and bond length ($^{99}\text{Tc}-\text{O} = 1.71$ Å; $\text{Re}-\text{O} = 1.74$ Å) [8]. Furthermore, the ionic radii of $^{99}\text{Tc}^{4+}$ and Re^{4+} are 0.78 and 0.77 Å, respectively, whereas those of $^{99}\text{Tc}^{7+}$ and Re^{7+} are 0.70 and 0.67 Å, respectively [9]. Similarities between $^{99}\text{Tc}^{7+}$ and Re^{7+} oxides have been confirmed under high pH (>10) and E_h conditions (>0.5 V) [10,11]. However, ^{99}Tc and Re oxide species with low oxidation states under low E_h (<0.5 V) and pH (<10) conditions may form different compounds. In particular, Re forms ReO_2 , ReO_3 , Re_2O_3 , and ReS_2 , whereas ^{99}Tc exists as $^{99}\text{Tc}(\text{OH})_2$, $^{99}\text{Tc}_3\text{O}_4$, $^{99}\text{TcO}_2$, and $^{99}\text{TcS}_2$ (or $^{99}\text{Tc}_2\text{S}_7$) [10,11]. These different species are attributable to the different reduction potentials of the $\text{Tc}^{7+}/\text{Tc}^{4+}$ [12] and $\text{Re}^{7+}/\text{Re}^{4+}$ [13] couples ($E = 0.510$ and 0.748 V, respectively). Despite these differences and similarities (as described above), Re is the only suitable surrogate element for ^{99}Tc .

$^{99}\text{Tc}/\text{Re}$ can be sequestered by chemical modification and incorporation of $^{99}\text{Tc}/\text{Re}$ into different metal–oxide lattice (MO_x) structures. Historically, ^{99}Tc has been incorporated into other minerals, for example, tremolite, ^{99}Tc spinel, sodalite, rutile, pyrochlore, perovskite, goethite, and layered double hydroxide [14]. Although ^{99}Tc has been incorporated into many iron oxides such as Fe_2O_3 and Fe_3O_4 [14–16] to reduce its mobility, ^{99}Tc incorporation mechanism into SnO_2 has not been extensively studied yet. As shown in Eqs. (1)–(7), Sn^{2+} is a stronger reducing agent than Fe^{2+} [11,12]. In Eqs. (3) and (7), $^{99}\text{TcO}_4^-$ is reduced by aqueous Fe^{2+} . However, reduction by Sn^{2+} is more appropriate [16–18] because Sn^{2+} reactions are spontaneous with relatively high thermodynamic drive in the forward direction. Quantitatively, the ΔE values of $\text{Re}^{7+}/\text{Sn}^{2+}$ and $^{99}\text{Tc}^{7+}/\text{Sn}^{2+}$ (0.36 and 0.60 V, respectively) are higher than that of $^{99}\text{Tc}^{7+}/\text{Fe}^{2+}$ ($\Delta E = -0.022$ V). [12,13].



Most methods of $^{99}\text{Tc}/\text{Re}$ incorporation into MO_x require high temperature (~ 1200 – 1400 °C) [14], which is unsuitable because $^{99}\text{TcO}_2$ sublimates around 900 °C and $^{99}\text{Tc}_2\text{O}_7$ boils at 311 °C [15]. The incorporation of $^{99}\text{Tc}/\text{Re}$ into SnO_2 has been suggested by previous authors [14]; however, no studies have proven how $\text{Re}/^{99}\text{Tc}$ is chemically incorporated into the SnO_2 lattice [14,19–21]. To fill this knowledge gap, this study investigates the immobilization/incorporation of Re into the SnO_2 lattice by reductive co-precipitation.

2. Experimental

2.1. Instrumentation

X-ray absorption spectroscopy [XAS] measurements were taken at 8C beamline of the Pohang accelerator laboratory (PAL). The PAL is running at 3.0 GeV with 32 beamlines. Measurements were made at x-ray incidence angle of 45° with respect to the sample. Ionization chambers in transmission as well as fluorescence mode were used to collect spectra. Data analysis was performed with Athena and Artemis software. Data normalization was done by Athena, and Atom was used to make model cluster. Single scattering paths fitted in this study were calculated by FEFF employed in Artemis. The model was developed supposing Re and Sn substituted each other position in the tetragonal cassiterite.

Inductively coupled plasma mass spectrometry [ICP-MS] (Nexion 300D) was used for Re/Sn analysis in aqueous solutions and solids digests. Surface analysis was performed with X-ray photoelectron spectroscopy [XPS] (Thermo Scientific K-Alpha™ with an Al (mono type) X-ray source). It has energy step up to 3.0 meV with energy range up to 1486.6 eV. XPS data analysis and peak fittings were performed with OriginPro 8 package. All peaks were fitted to Gaussian shape after background removal. Energy-dispersive X-ray spectroscopy [EDX] (OXFORD INCA energy system) was used for elemental analysis; whereas scanning electron microscope (SEM, JEOL-6480 LV) was used for surface morphology. X-ray diffraction [XRD] (RIGAKU D/MAX-2500 V) patterns were collected with step size of 0.01–0.06 and $2\theta = \sim 5$ – 120° . The XRD peaks were fitted with pseudo voigt function of JADE 6.0.

Oxidation-Reduction potential [ORP] and dissolved oxygen [DO] were measured using multi-channel meter (Laqua Act Horiba Scientific, model D-75G, Japan). Redox potentials were corrected to standard hydrogen electrode [SHE] values by adding +194 mV to the measured values at 30 °C. Solution pH was measured by pH meter (Orion start A211, Thermo-Scientific). Total dissolved solids [TDS] and electrical conductivity [EC] for solutions were measured by multi-channel meter (HI8732, Hanna Instrument Company). All aqueous samples were centrifuged using Eppendorf centrifuge®

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