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Potential interferences on the pertechnetate-sulfide immobilization reaction

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Summary. The potential interference from competing inorganic anions, chelating agents, and low molecular weight organic acids (LMWOAs), and the potential surface effects of selected minerals on the TcO_4^--sulfide immobilization reaction (to form Tc_2S_7) were investigated. The presence of the common inorganic anions, such as nitrate, studied did not affect the TcO_4^--sulfide immobilization process even though their concentrations were 20 times higher than that of sulfide. The chelating agents relevant to nuclear waste sites (*e.g.*, ethylenediaminetetraacetic acid) did not compete with the TcO_4^--sulfide reaction even in high excess. Of the ten selected LMWOAs investigated, only maleic acid and fumaric acid were able to inhibit the immobilization process by forming anionic water-soluble complexes with pertechnetate at concentrations significantly higher than found in the environment. None of the non-reducing minerals (*e.g.*, goethite) investigated interfered with the immobilization reaction. X-ray absorption spectroscopy showed that the product obtained in the presence of the selected co-existing species was predominantly Tc_2S_7.

1. Introduction

The Hanford Site in southeastern Washington State is the location of the largest nuclear waste storage site in the United States. Between its establishment in 1943 and deactivation in 1987, approximately 110 000 tons of nuclear fuel were processed [1].

The production of nuclear fuel generated millions of gallons of highly radioactive waste, as well as non-radioactive hazardous waste and mixed waste. About 50% of the radioactive waste is contained underground in storage tanks. These tanks contain various inorganic compounds, chelating agents, and organic solvents [2, 3], and as such have caused corrosion and leakage resulting in the infiltration of mixed waste into the vadose zone (the portion of the earth between the land surface and the zone of saturation [4]), and even the groundwater [5] making clean-up very difficult.

Forty six radionuclides are reported to be in the waste tanks [4], and among these, technetium-99 (Tc-99) is of considerable interest due to the quantities present and its long half-life ($T_{1/2} = 2.13 \times 10^5$ years), although its activity is only a small fraction of the total at this time [6]. Technetium may be present in oxidation states -1 to $+7$ in the environment [7–9], however, under non-reducing conditions, Tc-99 is generally present as the highly stable and mobile pertechnetate anion (TcO_4^-).

Various remediation methods have been considered for TcO_4^- contamination in the vadose zone at the Hanford Site [10–15]. However, *in-situ* gaseous immobilization technology using hydrogen sulfide (H_2S) is attractive for Tc-99 contaminated soil because of its ease of introduction into the vadose zone, control of the gas delivery, its efficient removal after completion of the treatment, and its successful use [16–18]. We have previously reported on the kinetics and stoichiometry of the TcO_4^--sulfide immobilization reaction in aqueous solution, with Tc_2S_7 identified as the product of this reaction [19]. The vadose zone below the leaking tanks and the groundwater potentially contain various inorganic anions such as nitrate, chelating agents such as ethylenediaminetetraacetic acid (EDTA), and low molecular weight organic acids (LMWOAs) such as acetic acid. Reduction of pertechnetate (TcO_4^-) in the presence of many of these coexisting species may result in complexes in lower oxidation states such as Tc(IV) or Tc(V) under certain conditions, for example, a Tc-EDTA complex [20–23]. Pertechnetate may also be reduced directly to the insoluble Tc(IV) species $TcO_2 \cdot xH_2O$ [24]. During the infiltration and migration of TcO_4^- from the tanks to the vadose zone, the minerals present in the soil may also affect the chemical behavior of TcO_4^- and sulfide. In addition, the coexisting species might interfere with the pertechnetate-sulfide immobilization process by retarding the reaction kinetics or lowering the yield.

In order to apply the *in-situ* gaseous immobilization technology to the vadose zone in real field applications, the potential interference from the concomitant species on the TcO_4^--sulfide reaction must be understood. The objectives of this work were to (1) systematically study the effects of selected common anions, chelating agents and LMWOAs present during the immobilization process by simulating their potential concentrations in the "real site", (2) characterize any products generated in the reactions, and (3) inves-

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