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Pertechnetate immobilization in aqueous media with hydrogen sulfide under anaerobic and aerobic environments

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Summary. The basic chemistry for the immobilization of pertechnetate (TcO_4^-) by hydrogen sulfide was investigated in aqueous solution under both aerobic and anaerobic environments. Pertechnetate immobilization was acid dependent, with accelerated rates and increased immobilization yields as the acid concentration increased. Oxygen had no effect under acidic conditions. Under anaerobic alkaline conditions, the pH, and therefore the speciation of sulfide, was the determining factor on the immobilization of pertechnetate. Only 53% of the TcO_4^- was immobilized at pH 8, while the yield increased to 83% at pH 9 as HS^- became the dominant sulfide species. The immobilization yield then decreased to 73% at pH 13. No reaction was observed between TcO_4^- and sulfide under aerobic alkaline conditions, indicating that oxygen suppressed this reaction.

Pertechnetate immobilization was found to be first order with respect to both sulfide and pertechnetate in acidic solutions, and in alkaline solution under anaerobic conditions. The results of stoichiometry studies and product analysis under alkaline anaerobic environments indicated that Tc_2S_7 was obtained at pH 9. EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) studies suggested that the samples obtained from acidic, aerobic solution and alkaline anaerobic solution were both Tc_2S_7. The stability of Tc_2S_7 is affected by O_2 with accelerated dissolution at high pH.

1. Introduction

The development of the nuclear weapons program between 1943 and 1987 resulted in the production of large quantities of nuclear waste at the Hanford Site of the U.S. Department of Energy in southeastern Washington State. About 54 million gallons of radioactive materials are stored in underground storage tanks, which include 149 single- and 28 double-shelled steel-lined concrete tanks [1]. The tanks contain a variety of radionuclides, inorganic ions and organic compounds, making this site the largest and most complex environmental cleanup project in the United States.

A recent study indicated that at least sixty-seven single-shelled tanks have leaked, resulting in significant quantities of radionuclides leaching into the vadose zone which is a portion of Earth between land surface and saturation zone, and groundwater [2]. Among the radionuclides, Tc-99 poses a special concern to the long-term risk assessments due to its relatively long half-life ($T_{1/2} = 2.1 \times 10^5$ years) and the chemical stability and solubility of its most stable form, the pertechnetate ion (TcO_4^-), under non-reducing environments [3–5]. At least 26 000 Ci of Tc-99 are stored underground with an almost equal distribution between single-shelled and double-shelled tanks [6]. In the tanks and vadose zone, Tc may exist as complexes in various oxidation states because of the complex chemical and environmental conditions present, however, significant amounts of Tc-99 exist as the chemically stable form, TcO_4^- (Tc(VII)), in aqueous media [7–9].

Many methods have been investigated for the remediation of TcO_4^-, such as ion exchange resins [10, 11], and adsorption materials [12–15], however, TcO_4^- is highly mobile and has poor adsorption properties. Additionally, there are limitations for the remediation of Tc-99 contamination in the subsurface because these methods cannot be used in the vadose zone [16]. Immobilization technologies have also been studied for the solidification of TcO_4^- to an insoluble Tc_2S_7 (Tc(VII)) species or Tc(IV) species such as TcO_2 [17–22]. A National Research Council report recently recognized that much of the contamination in the subsurface at DOE sites will not be removed by any active remediation efforts due to the high cost and technological limitations [23]. Alternatively, *in-situ* stabilization is expected to become one of the most important remediation strategies that may meet the requirements of on-site clean-up of contaminants in the vadose zone [24]. Chemical *in-situ* immobilization *via* gaseous hydrogen sulfide is very promising due to control of reactant delivery, minimal depth limitation, *etc*. [25].

The *in-situ* gaseous immobilization technology has already been used for the remediation of Cr(VI) in the subsurface [25]. The primary objective of this work was to understand the basic chemistry between pertechnetate and sulfide in order to begin determining the feasibility of using *in situ* gaseous hydrogen sulfide immobilization for use in pertechnetate contaminated soils. This study reports on the basic

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