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Pertechnetate immobilization with amorphous iron sulfide

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Summary. The reduction of pertechnetate (TcO_4^-) with freshly prepared amorphous iron sulfide was investigated. The amorphous iron sulfide (FeS) was shown to have an elemental composition of $FeS_{0.97}$ for all of the size fractions and a point of zero charge of $pH_{pzc} = 7.4$. Solubility studies of FeS in various buffers indicated that in the pH range 6.1–9.0, the concentrations of dissociated Fe^{2+} and S^{2-} were negligible. The reductive immobilization of TcO_4^- with FeS was shown to be accelerated by increasing ionic strength and strongly pH dependent. At pH values below the pH_{pzc}, the positively charged FeS surface reacted much faster with TcO_4^- and had higher immobilization yields relative to the negatively charged FeS surface at pH values above pH_{pzc}. The TcO_4^--FeS reaction is consistent with a surface mediated reaction through ligand exchange. The TcO_4^--FeS reductive immobilization reaction product was characterized by X-ray absorption near edge spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS), Fourier transform infrared spectroscopy (FT-IR), and energy dispersive X-ray spectroscopy (EDS) and found to be predominantly TcO_2. Studies on the reductive capacity of the FeS and the long term stability of the TcO_4^--FeS reaction product under both anaerobic and aerobic environments shows the potential utility of the *in situ* gaseous (hydrogen sulfide gas) immobilization technology in solidification of TcO_4^- by creating a FeS permeable reaction barrier in the vadose zone.

Introduction

The Department of Energy Hanford Site in eastern Washington State is the largest nuclear waste storage site in the United States, with 54 million gallons of radioactive waste contained underground in storage tanks [1–3]. The first tank leak, reported in 1956, was a result of corrosion, with about 67 tanks believed to have leaked about 0.75–1.5 million gallons of radioactive waste into the soil, resulting in the contamination of the vadose zone [4].

Among the 46 radionuclides in the waste tanks [5], technetium-99 (Tc-99) is of considerable interest due to the quantities present, its long half-life ($t_{1/2} = 2.13 \times 10^5$ years), and its diverse chemistry [6–8]. Various remediation methods for technetium contamination in the vadose zone from tank leakage at the Hanford Site have been considered [9–14]. The gas-phase approach using hydrogen sulfide (H_2S) gas, which is specifically designed for vadose zone treatment, is attractive due to Tc-99 contaminated soil. The relatively easy introduction of the H_2S gas to the vadose zone, the control of H_2S delivery, and the efficient removal of H_2S gas after completion of the treatment all add to the potential utility of the *in situ* H_2S gaseous remediation method to both laboratory and real field applications [15–17].

The concentration of TcO_4^- in the tanks was at the 10^{-5} M level, indicating the TcO_4^- concentration in the vadose zone would be lower than this. Once the H_2S gas, in large excess, is introduced into the vadose zone, the fraction of H_2S that reacts with TcO_4^- and the rate of oxidation of H_2S in the gas phase would be insignificant [2, 18]. As a result, the main pathway for excess H_2S consumption in the vadose zone would involve reactions with minerals.

Iron oxides are the major constitutes of the soil in the vadose zone [19, 20] and they have been reported to effectively remove H_2S from the gas stream through a gas–solid reaction, to a theoretical maximum of 0.6 g H_2S/g Fe-oxide(s) [21]. This indicates that significant amounts of H_2S would be consumed by iron oxides present in the vadose zone during *in situ* gaseous immobilization to generate significant quantities of iron sulfide (FeS) [22, 23]. FeS might also be generated from dissimilatory sulfate reduction by bacteria present in the soil [24, 25] with no difference in the FeS product [26, 27].

Amorphous FeS is a highly reactive phase and has been widely used to reduce mobile non-radioactive metal oxyanions to insoluble species [28–30]. The interaction between iron sulfide and TcO_4^- showed that TcO_4^- in aqueous solution could be effectively reduced and coprecipitated with FeS [31–34], with a TcS_2-like product identified by X-ray absorption spectroscopy [35–37]. Further studies on the reoxidation of the FeS host with aging showed that rather than being oxidized back to TcO_4^-, a TcO_2-like phase formed, indicating that long term immobilization might be achieved [36, 37]. Based on these results, it may be possible to inject H_2S gas into the vadose zone to reduce the iron oxides to FeS, creating a permeable reactive barrier of FeS for preventing the migration of TcO_4^-. However, the FeS-TcO_4^- reaction is not well understood regarding the stoichiometry of the reaction, factors influencing the reaction, the reaction capacity, or the product characterization. The objectives of this study were to (1) study the basic chemistry between FeS and TcO_4^- in aqueous solution under anaer-

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