Microbiological Transformations of Low- and Intermediate-Level Radioactive Wastes

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Low-level and intermediate-level radioactive wastes (LILW) contain a variety of organic compounds (cellulose, chelating agents, plastics, ion exchange resins), inorganic compounds such as nitrate and sulfate. Microbial degradation of the organic constituents of the waste can result the production of gases such as CO_2, CH_4 and others [1]. Radiolysis of plastics and rubber materials may not only result in the production of volatile toxic organic compounds but render the plastics more susceptible for biodegradation. An increase in microbial activity under appropriate conditions can alter the chemical speciation, solubility and sorption properties and thus could increase or decrease the concentrations of radionuclides in solution and affect their bioavailability and mobility in the environment. Although the physical, chemical, and geochemical processes affecting dissolution, precipitation, and mobilization of radionuclides have been extensively investigated, we have only limited information on the effects of microbial activity and the biochemical mechanisms which affect the stability and mobility of radionuclides. This study describes the various mechanisms of microbial transformations of U, Pu, Tc, Cs, Sr, I, ^{14}C and ^{3}H in wastes.

Microbial population distribution in radioactive wastes and related sites. Microorganisms have been detected in low-level radioactive wastes, TRU wastes, Pu-contaminated soils, backfill materials, natural analogue and waste-repository sites. Low-level wastes disposed of at the shallow-land burial grounds contain several aerobic and anaerobic bacteria including *Bacillus* sp., *Pseudomonas* sp., *Citrobacter* sp. and *Clostridium* sp. Viable, metabolically active microbes were detected in Los Alamos (LANL) TRU waste burial site, and in waste repository site environments such as Waste Isolation Pilot Plant (WIPP), Yucca Mountain repository, Nevada Test Site, Aspo Hard Rock Lab (Sweden), and Grimsel Test site (Switzerland) [2,3].

Radioactive gases from waste degradation. Radioactive gases such as CH_3T. HTO, H_3, other tritiated hydrocarbons, ^{85}Kr, ^{222}Rn, $^{14}CH_4$, and other ^{14}C-hydrocarbons have been identified emanating from the burial trenches from West Valley NY, disposal site. Methane bacteria were detected in leachate from the Maxey Flats low-level waste site and significant amounts of tritiated and $^{14}CH_4$ were generated from mixed methanogenic culture from the leachate [2].

The Waste Isolation Pilot Plant (WIPP), located in a salt bed in southern New Mexico, is designed by U.S. Department of Energy for permanent disposal of transuranic wastes. In this hyper saline environment, microbes present in the repository are dominated by halophilic or halotolerent bacteria. The brine from the underground workings contains 10^4 – 10^6 bacterial cells/mL. Microbes detected in the WIPP include denitrifiers, fermenters, sulfate reducers, and methanogens. WIPP can be categorized as an organic carbon-rich repository. Significant aerobic and anaerobic microbial activity is expected in the waste because of the presence of electron donors and acceptors. There is a concern for the long-term performance assessment of the repository with a potential CO_2 generation from biodegradation of organic materials. The generation of CO_2 can potentially impact the mobility of actinides. Microbial gas generation studies performed with simulated cellulose materials show the amount of CO_2 accumulated in nitrate-amended samples was higher than that in samples without excess nitrate amendment, demonstrating the dependence of cellulose biodegradation on the availability of electron acceptors and nutrients [1].

Biodegradation of organic constituents of the waste can result in gas generation and pressurization of containment areas, waste volume reduction, and subsidence in the repository. Microbial corrosion of the waste canisters can compromise waste integrity.

Dissolution and immobilization of radionuclides. Radionuclides of concern are the actinides (U, Pu, Am, Np, Cm), and the fission products (I, Cs, Sr, Tc). The radionuclides released may be present in various forms such as elemental, oxide, coprecipitates, ionic, inorganic-, and organic-complexes. Dissolution or immobilization of the radionuclides is brought about by the direct enzymatic action or indirect non-enzymatic action of microorganisms. These include (i) oxidation-reduction reactions, (ii) changes in pH and Eh, (iii) chelation or production of specific sequestering agents, (iv) bioaccumulation by biomass, (v) biocolloid formation, (vi) bioprecipitation, (vi) biotransformation of radionuclide-organic and -inorganic complexes, and (vii) production of volatile compounds by biomethylation.

Biotransformation of Uranium. Both aerobic and anaerobic microorganisms are involved in the mobilization and immobilization of various chemical forms of uranium. Dissolution of uranium by autotrophic sulfur- and iron-oxidizing bacteria due to production of ferric iron and sulfuric acid and by heterotorphic bacteria and by fungi due to production of

organic acids and chelating agents. The direct implication of microorganisms in the biotransformation of uranium including those complexed with organic ligands is of considerable interest because of its potential application in bioremediation of contaminated sites, in pre-treating radioactive wastes, and in processes critical to the performance of nuclear waste repositories.

Fate uranium associated with organic ligands. Biotransformation of the complexed uranium should result in its precipitation and retard migration. Biodegradation of the uranium-organic complexes is dependent on the type of complex being formed. While bidentate metal citrate complexes are readily biodegraded, the tridentate and binuclear complexes are recalcitrant showing the structure and function relationship between the uranium/organic ligand complexes and their biodegradability [3, 4].

***Immobilization of uranium*.** The immobilization of uranium is brought about by bioaccumulation, bioreduction and bioprecipitation reactions. Uranium is reduced by a wide variety of facultative and strict anaerobic bacteria under anaerobic conditions in the presence of suitable electron donor. Consequently, the potential exists for the use of anaerobic bacteria to concentrate, contain and stabilize uranium in contaminated groundwater and in waste with concurrent reduction in waste volume [3, 4].

Biotransformation of Plutonium. Plutonium (IV) is the predominant form found in contaminated soils. Plutonium can simultaneously coexist as Pu(IV), Pu(V), and Pu(VI) in oxic environments. Pu generally is considered to be relatively immobile; however, the transport of Pu, albeit at very low concentrations, was observed at several DOE sites (Rocky Flats, LANL, and NTS). Chemical characterization of Pu at contaminated sites shows that its environmental form varies according to site, and depends on the waste stream. For example, at Rocky Flats, CO, the predominant form appears to be PuO_2(s), and organic colloids; at the NTS, Pu was found to be associated with mineral colloids [5, 6].

Enzymatic reduction of Pu(VI) and Pu(V) to Pu(IV) by cell suspension of *Shewanella putrefaciens*, *S. oneidensis*, and *Geobacter metallireducens* have been reported. Reductive dissolution of Pu(IV) to Pu(III) by the strict anaerobic bacterium *Clostridium* sp has been shown and the Pu(III) oxidation state was confirmed by x-ray absorption near edge spectroscopy (XANES) [4].

Biotransformation of Technetium. Microorganisms affect the precipitation of Tc by oxidation-reduction reactions and by complexation with organic by-products. Chemolithotrophic, haloalkaliphlic, aerobic, facultative, and anaerobic (fermentative and sulfate-reducing) bacteria reduced pertechnetate ion to an insoluble form.

Biotransformation of Cesium and Strontium. Bioaccumulation of Sr and Cs (structural analogues for Ca and K, respectively), has been reported for several microorganisms. Consequently, there is considerable interest in using microorganisms to remove radioactive Sr and Cs from waste streams and contaminated sites [3, 4].

Transformation of Iodine. The predominant aqueous chemical forms of iodine (I_2), iodide (I^-) and iodate (IO_3^-) are highly soluble and mobile in the environment. Microorganisms affect the chemical behavior of iodine through processes such as volatilization (CH_3I), oxidation of I^- to I_2, reduction of IO_3^- to I^-, and bioaccumulation by bacterial cells both intracellularly and extracelluarly. Microbial volatilization of organic iodine was observed in soil slurries and seawater samples by aerobic bacteria through methylation of iodide (I^-) to form methyl iodide (CH_3I). The volatilization of iodide was also found in iodide-rich natural brine water. In addition to the organic iodine compounds, a significant amount of molecular iodine (I_2) was produced [4].

Conclusions. Fundamental understanding of the mechanisms of microbial transformations of several chemical forms of the radionuclides in the presence of electron donors and acceptors under various environmental conditions will be useful in assessing the microbial impact on the long-term behavior of radionuclides released from nuclear fuel cycle and in developing appropriate management and remediation strategies for contaminated sites.

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