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Technical Liaison with the Institute of Physical Chemistry (Russian Academy of Science)

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse
Hanford Company Richland, Washington

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TECHNICAL LIAISON WITH THE INSTITUTE OF PHYSICAL CHEMISTRY (RUSSIAN ACADEMY OF SCIENCE)

Task Description

The Institute of Physical Chemistry of the Russian Academy of Science (IPC/RAS) is engaged by the DOE to conduct studies of the fundamental and applied chemistry of the transuranium elements (TRU; primarily neptunium, plutonium, and americium; Np, Pu, Am) and technetium (Tc) in alkaline media. This work is being supported by the DOE because the radioactive wastes stored in underground tanks at DOE sites (Hanford, Savannah River, and Oak Ridge) contain TRU and Tc, are alkaline, and the chemistries of TRU and Tc are not well developed in this system. Previous studies at the IPC/RAS centered on the fundamental chemistry and on coprecipitation. Work continuing in FY 1996 will focus more on the applied chemistry of the TRU and Tc in alkaline media and continue effort on the coprecipitation task.

The technical liaison at Westinghouse Hanford Company (WHC) was established to provide information to the IPC/RAS on the Hanford Site waste system, to define and refine the work scope, to help publish IPC/RAS reports in public-release documents and presentations, to compare IPC/RAS results with results from other sources, and to test chemical reactions or processes proposed by the IPC/RAS with genuine Hanford Site tank waste.

Technology Needs

EM Focus Area: High-level waste tank remediation

Knowledge of the chemistry of TRU and Tc in alkaline media is vital because isolation of the TRU and Tc to a low-volume high-level waste fraction is a primary goal of Hanford Site tank waste processing (pretreatment). Current knowledge of the chemistry does not reliably predict the TRU and Tc behaviors and distributions (to the solid or solution phases) under existing Hanford Site tank conditions and particularly under possible alkaline waste processing options. Methods must be developed to process tank waste and to separate TRU and Tc from waste and waste process solutions.

Scientific Background

The TRU (Np, Pu, Am) and Tc are elements which have multiple oxidation states available in aqueous solution. In general, the (IV) oxidation states of these elements form oxides or hydrous oxides of low solubility while the higher oxidation states [(V), (VI), or (VII) for the TRU and (VII) for Tc] give oxyanions of appreciable solubility, especially in highly alkaline solution.

In the absence of complexing agents, chemically reducing conditions decrease the solubility of these elements while oxidizing conditions favor their dissolution. The accessibility of the higher oxidation states increases in the order Am < Pu < Np < Tc. The solubilities of these elements in alkaline media (i.e., their distributions to the solid and solution phases) is a function of their solid phase oxidation state and crystallinity, complexation, possible redox reactions, radiolytic reactions (which can produce oxidants and reductants), and coprecipitation reactions (with bulk waste components).

Technical Approach

Laboratory-scale studies at the IPC/RAS initially focussed on the solubility, redox reactions, radiolysis effects, and coprecipitation of the TRU and Tc in highly alkaline media. Subsequent studies will continue the investigation of coprecipitation and other methods to remove these radioelements from alkaline waste. The tests and processes performed at the IPC/RAS with simple alkaline systems (simulant wastes) are designed in consultation with the Hanford Site liaison. The processes designed by the IPC/RAS must be verified with genuine wastes available at the Hanford Site. Results from the IPC/RAS and Hanford Site studies will be disseminated in technical publications and presentations.

Accomplishments

In 1994, the IPC/RAS prepared a technical literature review of the chemistry of the TRU and Tc in alkaline media. This review was edited and published by the liaison as a WHC document in May 1995. Eleven tasks to investigate the chemistry of the TRU and Tc were proposed by the IPC/RAS; four were selected by the DOE for FY 1995 support:

- oxidation and reduction reactions and reagents for Np, Pu, Am, and Tc
- solubilities of Np, Pu, Am, and Tc as functions of oxidation states, hydroxide concentration, and presence of other bulk waste components
- reactions and reagents suitable to coprecipitate Np and Pu in the (V) and (VI) oxidation states
- gamma radiolysis reactions of Np, Pu, and Tc.

Draft technical reports on the four tasks received in September 1995 and January 1996 are being edited for publication as contractor documents.

The studies showed that the strongly reducing conditions necessary to produce tetravalent TRU and Tc increase in the order Am < Pu < Np < Tc. Thus, only hydrazine was found to reduce Tc(VII) to Tc(IV) whereas hydrazine or dithionite reduce Np(V) and Pu(V) to the (IV) state and Am(V) to the (III) state. Other reductants studied (hydroxylamine, sulfite, ascorbate, hydroquinone, thiourea dioxide) were less effective.

Oxidations of Np, Pu, and Tc solids in the (IV) and (V) oxidation states by atmospheric oxygen were studied. Negligible oxidation of Pu(IV) was observed; Np oxidized to the (V) state and Tc to the (VII) state. Other oxidants studied (though not for all radioelements) were ozone, hypochlorite, hypobromite, nitrate, nitrite, persulfate, permanganate, ferrate(VI), chromate, and ferricyanide.

The solubilities of Np(IV) and Pu(IV) hydrous oxides (in the presence of hydrazine) were 10^{-6} to 10^{-5} M for Np and 10^{-7} to $10^{-5.5}$ M for Pu as NaOH concentration increased from 2 to 14 M. The solubilities of pentavalent Np, Pu, and Am were similar above 6 M NaOH increasing from $10^{-3.7}$ to $10^{-3.5}$ M at 14 M NaOH. Technetium(IV) and (V) solubility measurements are very sensitive to air oxidation; in the presence of hydrazine, solubilities range from $10^{-5.3}$ to $10^{-3.3}$ M. Electrodeposited $TcO_2 \cdot nH_2O$ has a solubility of $10^{-6.2}$ M in 4 M NaOH.

Coprecipitation by the method of arising reagents (MAR) was studied for Np and Pu in the (V) and (VI) oxidations states. The MAR uses precipitating agents which initially are soluble in the alkaline solution. Decomposition of the soluble agent to form the precipitating solid then takes place by reduction or thermal means and carrier precipitation of the trace radionuclides occurs. Carriers studied included reduced hydroxides or hydrous oxides of chromium, manganese, iron, and cobalt introduced to solution as soluble complexes or oxidized species. Plutonium solution coprecipitation was satisfactory for most reagents (decontamination factor, DF, up to 1000) whereas Np removal was unsatisfactory (DF of 5 to 20). Further tests to remove solubilized Np by other agents are promising.

Final results of gamma radiolysis studies are not yet reported. Initial results show gamma radiolysis strongly influences redox reactions. The course of the redox reactions can be altered by reagents that themselves are radiolytically active or act as radiolytic scavenging agents.

Benefits

Fundamental knowledge of the chemical behavior of the TRU and Tc in alkaline media is essential to the successful design and operation of the pretreatment processes used to segregate the low- and high-level fractions of the Hanford Site tank wastes. Current and future studies to design radionuclide removal processes for the soluble and long-lived Np and Tc radioelements are particularly important to pretreatment and are a central part of the IPC/RAS task.

Results to date from the IPC/RAS show the solubilities of the TRU and Tc are strongly dependent on oxidation state and can be successfully altered by various common chemical oxidants and reductants. Solution decontamination by the MAR for Pu has been shown to be promising; similar results are possible for Np.

Technology Transfer/Collaborations

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Keywords

americium, neptunium, plutonium, technetium, alkaline, sodium hydroxide, solubility, coprecipitation, radiolysis, oxidation, reduction, redox, TWRS, pretreatment, Hanford Site, tank waste

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