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Studies of the Chemistry of Transuranium Elements and Technetium at the Institute of Physical Chemistry, Russian Academy of Sciences, Supported by the U.S. Department of Energy

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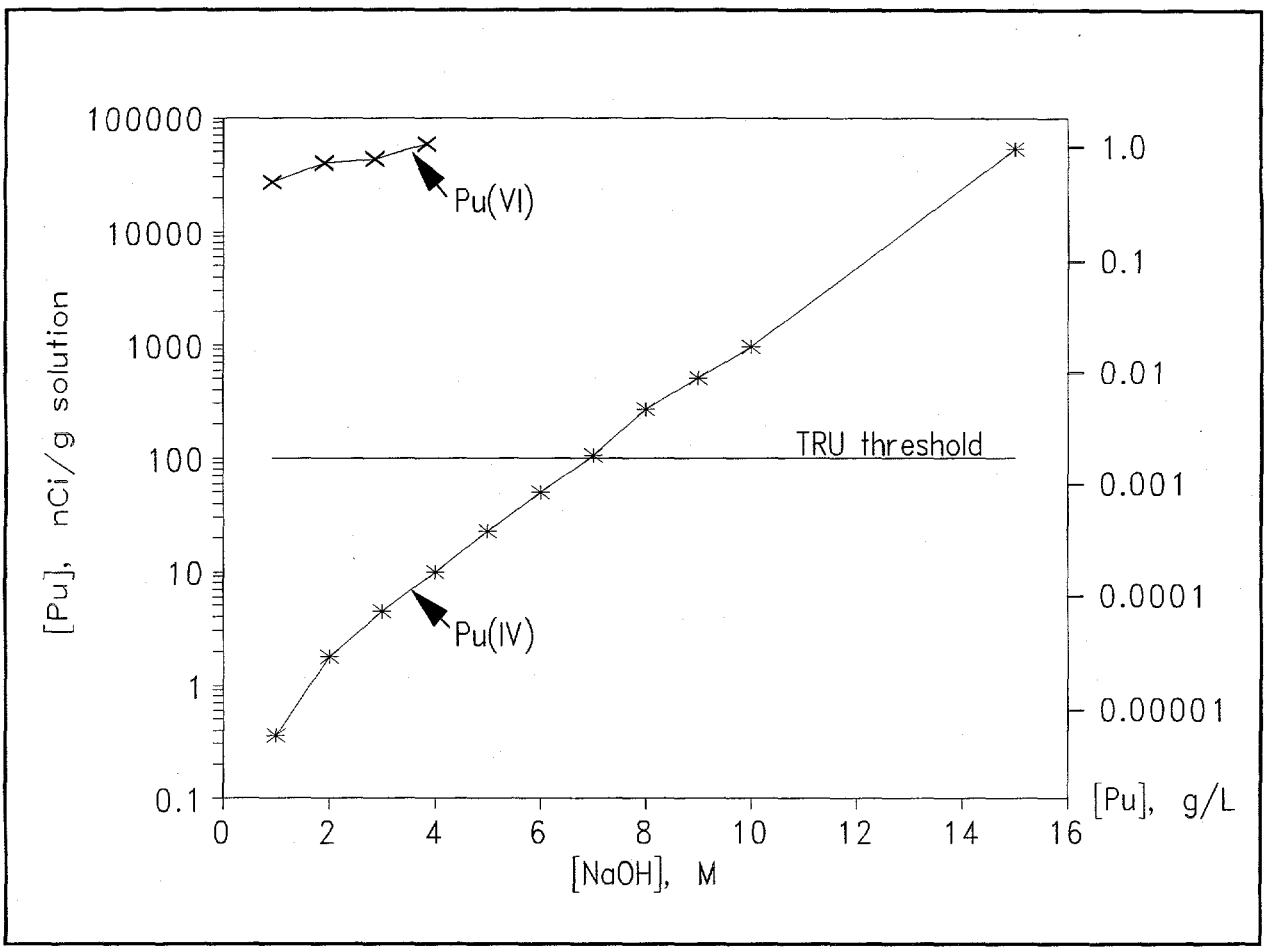
Alkaline high-level wastes produced in the separation of plutonium for defense are stored underground in reinforced concrete tanks lined with mild steel at the U.S. Department of Energy's (USDOE) Hanford and Savannah River Sites. Retrieval, treatment, and immobilization of these wastes into separate high-level and low-level forms for long-term storage is planned to occur over the next few decades. Key to the separation of the low- and high-level fractions is knowledge of the chemical behaviors of the radioactive transuranic elements (TRU; principally neptunium - Np, plutonium - Pu, and americium - Am) and technetium (Tc) in the wastes' alkaline media.

Over the past 30 years, studies of the chemistry of TRU and Tc in alkaline media have been conducted at the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC/RAS). Studies initially were motivated by the 1967 discovery, by Professors Krot and Gel'man at the IPC/RAS, of the heptavalent oxidation states of Np and Pu.[1] The Np(VII) and Pu(VII) were generated by ozonation of the respective (VI) state elements in alkaline media. The discovery of Am(VII) followed a few years later.[2] The initial studies on the heptavalent states were summarized in a comprehensive monograph.[3] In the intervening years, a large number of scientific papers have been published by researchers from the IPC/RAS describing the electrochemistry,[4] redox reactions,[5] radiation/chemical reactions,[6] speciation,[7] sorption,[8] and ion exchange[9] of TRU elements in alkaline media. Similar studies for Tc also have been undertaken.[10]

Studies conducted at the Hanford Site in the 1980s revealed the potential for actinides to form stable soluble complexes in alkaline media, thus simulating the composition of the radioactive tank waste.[11] Of particular interest was an anionic hydroxide complex of Pu(V) that formed by apparent oxidative dissolution of poorly crystalline $PuO_2 \cdot xH_2O$.[12] The study showed that plutonium(IV) hydrous oxide and Pu(VI) solubility increased with increasing hydroxide concentration (see figure on Page 2). Solubility also was found to increase by increasing ionic strength and aluminate and carbonate concentrations. Publication of these results, which cited work performed at the IPC/RAS,[13] informed the IPC/RAS researchers of the practical applicability, in the United States, of their work, and led to direct contacts between the United States and Russian researchers in 1993.



Plutonium Compound Solubility in Aqueous NaOH Solutions.

The initial discussions resulted in the production of a technical literature review of the chemistry of TRU and Tc in alkaline media, especially as it relates to alkaline waste treatment. This review, which was prepared by Professors V. F. Peretrukhin, V. P. Shilov, and A. K. Pikaev of the IPC/RAS under the support of the USDOE, addresses oxidation states, solubility, speciation, redox reactions, electrochemistry, radiation chemistry, and separations in alkaline media. The review is over 150 pages long and contains over 300 references to the technical literature.[14]

As an outgrowth of the technical review, a program of fundamental and applied chemistry studies is being conducted at the IPC/RAS under continued USDOE support. Current studies focus on four aspects of TRU and Tc chemistry in alkaline media: solubility, redox reagents, coprecipitation, and radiation-chemical reactions. The present paper dwells on the initial investigations into TRU and Tc solubility.

Solubility considerations are essential to understanding the distribution of TRU and Tc to the solid and solution phases. Initial divisions of the low- and high-level waste fractions in Hanford Site tank waste treatment will be made using solid-liquid separation techniques (settling, centrifugation, filtration) in the existing alkaline media. Because many radioelements of concern (particularly isotopes of strontium, rare earths, and the TRU) have

low solubility in the alkaline waste, and extraction from solids without prior solubilization is not possible, the insoluble waste necessarily will be high level.

For this reason, knowledge of the solubilities of the TRUs and Tc in alkaline media is required to understand the partitioning behavior of these elements to the low- and high-level fractions. A solubility task, organized along the following areas of investigation, is a primary focus of the IPC/RAS work funded by the USDOE:

- Determination of the solubilities of Np and Pu (IV) (hydr)oxide compounds in 0.5 to 14 M NaOH media. Reducing conditions will be required to maintain the (IV) states. On the basis of these studies, the amphoteric behavior of Np(IV) and Pu(IV) will be determined; i.e., their ability to form anionic species of the form $An(OH)_{4+x}^{x-}$.

- Studying the effects of complexing ions (e.g., chelating agents, oxalate, glycolate, citrate, carbonate, phosphate, and fluoride) on the solubility of Np(IV) and Pu(IV).

- Development of experimental techniques for synthesis of hydrated and dehydrated oxides of Tc(IV) and Tc(V) using different reducing agents.

- Determination of the chemical forms of Tc(IV) and (V) in 0.5 to 14 M NaOH in the presence of various reducing agents (e.g., hydrazine, nitrite, hydroxylamine, sulfite).

- Determination of the solubility of Tc(IV) and (V) in the presence of complexing ions (e.g., chelating agents, oxalate, glycolate, citrate, carbonate, phosphate, fluoride) and in the presence of oxidants (diatomic oxygen, ozone, permanganate, persulfate, hypobromite, hypochlorite).

- Study of the aging of Tc(IV) and (V) hydroxides in 0.5 to 14 M NaOH to determine the effects on solubility.

- Estimating the effects of NaOH concentration on the solubilities of $Na_3AnO_2(OH)_3$ (where An is Np, Pu, and Am). Redox controls will be imposed and possible changes in the solid phase will be studied.

This overview provides fundamental information on the Hanford Site tank waste system, the USDOE technological needs, and the IPC/RAS developments in the solubility chemistry of the TRU and Tc in alkaline waste media. This work was performed for the Office of Research and Development, U. S. Department of Energy.

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