

Project ID: **54893**

Project Title: **Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes**

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## I. Kinetics of the Oxidation of Pu(IV) by Manganese Dioxide (A. Morgenstern)

This research is investigating the kinetics of the oxidation of plutonium(IV) by manganese dioxide. Manganese dioxide is a component in some stored radioactive wastes where it may influence the oxidation state distribution of plutonium. Manganese dioxide is also present in many natural waters and may contribute to the oxidation of plutonium(IV) to higher oxidation states in such waters. In this study, the oxidation of Pu(IV) by manganese dioxide is being investigated by solvent extraction at an ionic strength of 1.0 m (NaCl) over a range of pH values.

A sample of manganese dioxide has been prepared according to a standard literature procedure [Kee '84]. Its BET surface area has been determined as 164 m<sup>2</sup>/g. A stock solution of tetravalent <sup>238</sup>Pu was prepared electrochemically immediately before the start of the experiment [Neb '61]. The oxidation state purity of the stock solution has been determined by solvent extraction.

An experimental procedure has been developed to analyze the oxidation state distribution of plutonium in contact with the manganese dioxide solid phase. The experiments have been designed as batch experiments. At appropriate time points plutonium is leached from the solid phase by lowering the sample pH. Appropriate leaching conditions have been established using <sup>230</sup>Th(IV), <sup>237</sup>Np(V) and <sup>233</sup>U(VI) as oxidation state analogs for Pu(IV), (V) and (VI). The leachate is passed through an ultrafiltration unit to remove polymeric species of Pu(IV). The oxidation state distribution of plutonium in the filtrate is analyzed by solvent extraction using a solution of TTA in cyclohexane and HDEHP in heptane as extractants from aqueous phases of pH 0.5 and 1.5, respectively.

Blank runs without addition of manganese showed no oxidation of Pu(IV) within the time frame of the experiments. Experiments with a concentration of manganese dioxide of 0.5 m<sup>2</sup>/l and 5.0 m<sup>2</sup>/l indicate a very fast oxidation of Pu(IV) to pentavalent and hexavalent plutonium.

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## II. Kinetics of Oxidation of Pu (V) by Hypochlorite (A. E. Irwin)

For aqueous systems, in which NaCl is present, radiolysis reactions lead to the production of HClO. Dissociation of HClO may lead to the formation of ClO<sup>-</sup> with both species being strong oxidizing agents. Such reactions then lead to changes in plutonium oxidation state due to the presence of the oxidants HClO, ClO<sup>-</sup> and H<sub>2</sub>O<sub>2</sub>. Therefore, studies of the effect of both NaOCl and H<sub>2</sub>O<sub>2</sub> are essential.

Pu (V) is prepared as the <sup>238</sup>PuO<sub>2</sub><sup>+</sup> species following the method of Saito et al. [Sai '85]. Pu (V) produced in this way is back extracted into a saline aqueous phase at pH 4.5 and isolated. The appropriate amount of stock solution is added to a NaCl solution to give a final solution concentration of 10<sup>-10</sup> M plutonium. This Pu/NaCl solution is added to buffer solutions to achieve stock solutions for the batch experiments.

The effect of NaOCl on Pu (V) in 4 M NaCl at a pH of 8.0 is being studied. DBM (dibenzoylmethane) is used as the extracting agent to remove Pu (VI) & (III) (if present) from Pu (V) & (IV) [Sai '83]. Following extraction, the aqueous phase is contacted with

pre-treated CaCO<sub>3</sub> to adsorb the Pu (V) present [Kob '88]. This study is still in progress.

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### III. An(IV)-EDTA Stability Constants in Chloride Media (D. R. Peterman)

The goal of this investigation is the determination of the stability constant values for An(IV)-EDTA (EDTA = ethylenediaminetetraacetic acid) complexes as a function of ionic strength. Reliable values for the An(IV)-EDTA complexation constants in dilute media are available in the literature [Mar '78]. Within the DOE complex many actinide containing waste streams are comprised of high ionic strength media [Ril '92] for which reliable stability constant data are not available. In this study, Th(IV) is used as a representative An(IV) species and competitive equilibria involving citric acid are exploited for the Th-EDTA stability constant determinations. The stability constant of the Th-EDTA complex is determined relative to the known stability constant of the Th(Cit)<sub>3</sub> (Cit = citric acid) complex. The required Th(Cit)<sub>n</sub> (n = 1 – 3) stability constants are determined by potentiometric titration at several ionic strengths. The experimentally determined values of the Th(CIT)<sub>n</sub> stability constants as a function of ionic strength are listed in Table 1.

Table 1. Stability constants of Th(Cit)<sub>n</sub> complexes at 25 °C.

Ionic Strength	logβ <sub>102</sub>	logβ <sub>112</sub>	logβ <sub>103</sub>	logβ <sub>113</sub>	logβ <sub>ThEDTA</sub>
0.1 m NaCl	20.89±0.18	23.80±0.18	26.26±0.18	30.53±0.19	24.7 ± 0.4
0.3 m NaCl	20.36±0.02	22.56±0.04	25.45±0.06	29.39±0.07	23.6 ± 0.4
0.5 m NaCl	19.19±0.02	21.42±0.04	24.32±0.04	28.43±0.05	22.4 ± 0.3
1.0 m NaCl	19.12±0.01	21.70±0.01	24.12±0.03	28.50±0.02	21.8 ± 0.3

The competitive equilibria between citric acid and EDTA for thorium complexation are monitored by <sup>1</sup>H NMR spectroscopy and the stability constant of the Th-EDTA complex is calculated from the integrated <sup>1</sup>H NMR spectrum. The experimental values for the Th-EDTA stability constants as a function of ionic strength are also listed in Table 1.

Experiments are currently being conducted which extend the Th-EDTA and Th(Cit)<sub>n</sub> stability constant determination to higher ionic strength media (up to 5 m NaCl). After these determinations are complete, the stability constants will be modeled using Pitzer theory.

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