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Integration of Advanced Nuclear Materials Separation Processes

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Abstract

This is the final report of a two-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). This project has examined the fundamental chemistry of plutonium that effects the integration of hydrothermal technology into nuclear materials processing operations. Chemical reactions in high temperature water allow new avenues for waste treatment and radionuclide separation. Successful implementation of hydrothermal technology offers the potential to effectively treat many types of radioactive waste, reduce the storage hazards and disposal costs, and minimize the generation of secondary waste streams. The focus has been on the chemistry of plutonium(VI) in solution with carbonate since these are expected to be important species in the effluent from hydrothermal oxidation of Pu-containing organic wastes. We investigated the structure, solubility, and stability of the key plutonium complexes. Installation and testing of flow and batch hydrothermal reactors in the Plutonium Facility was accomplished. Preliminary testing with Pu-contaminated organic solutions gave effluent solutions that readily met discard requirements. A new effort in FY 1998 will build on these promising initial results.

Background and Research Objectives

This project has examined the fundamental chemistry of plutonium that effects the integration of new separation technology into nuclear materials processing operations. Chemical reactions in high temperature water (hydrothermal processing) allow new avenues for effective waste treatment and radionuclide separation. Successful implementation of hydrothermal technologies offers the potential to effectively treat many types of radioactive waste and reduce the storage hazards and the disposal costs, while minimizing the generation of secondary waste streams.[1-7] A major category of radioactive wastes includes combustible material such as organic solvents, rags, plastics, and paper that are contaminated with transuranic (TRU) elements. Some of these wastes also contain strong oxidizers such as nitrates. In some cases these wastes are an acute safety hazard because of the production of flammable gases from organic decomposition initiated by

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*Principal Investigator, e-mail: gjarvinen@lanl.gov radioactive decay. Experiments at a laboratory scale have demonstrated that hydrothermal processing can reduce the volume and oxidize the organic and nitrate components with high efficiency (>99.999%) of most of the common combustible wastes generated by the nuclear industry. Understanding the speciation and solubility of actinides during and after hydrothermal treatment is crucial for the design of post-processing effluent separations, and ultimately for the deployment of this technology for TRU waste reduction and residue stabilization.

Hydrothermal processing employs water at high temperature and pressure as an efficient reaction medium. A substrate is mixed with water and reagents, pressurized, heated, and held at reaction temperature for a time sufficient to complete the desired chemical processes (e.g., oxidation, reduction, and dissolution). The mixture is then cooled and depressurized, and the solid, liquid, and gaseous products are separated for disposal or further treatment. Under oxidizing conditions (e.g., addition of hydrogen peroxide), the organic components of the waste substrates are oxidized to carbon dioxide by reaction with the water and oxidant. Nitrate contaminants also react with the organic material and are converted to nitrogen gas. Heteroatoms such as chlorine, sulfur, and phosphorus are oxidized and converted to acids or salts depending on the pH of the solution. Reaction temperatures and pressures are typically 540 °C and 6000 psi. At temperatures above 500°C, reactions are rapid, and greater than 99% conversion efficiencies can be achieved in seconds.

For actinide disposition, the focus has been on the chemistry of plutonium(VI) in solution with carbonate since these are expected to be important species in the effluent from hydrothermal oxidation of Pu-containing organic wastes. The strongly oxidizing environment during hydrothermal processing will generate plutonium(VI); and upon destruction of organics, hydrothermal reactor effluent solutions will likely contain substantial concentrations of carbonate. Depending upon the pH, salts present, and total Pu(VI) and carbonate concentration in the process effluent, a number of solution and solid state species may be present. The structure, solubility, and stability of these species was investigated in this project.[8]

Scientific Approach and Accomplishments

Spectrophotometric titration data were collected on the plutonium(VI) carbonate system to identify the complexes present in solution. Based upon a preliminary fit of these data the calculated formation constants for the tris- and biscarbonato complexes are $\log \beta_{130} = 17.7$ and $\log \beta_{120} = 13.6$, respectively. These values are in excellent agreement with those calculated from the solubility of plutonium(VI) carbonate in $NaClO_4$, log β_{130} = 17.4 and log β_{120} = 13.4.[9] The tris- and biscarbonato species have much smaller formation constants than the analogous uranyl species, log β_{130} = 21.8 and log β_{360} = 48.6.[10] These formation constants indicate that under conditions relevant to the hydrothermal process effluent, $PuO_2CO_{3(aq)}$ is the predominant species over a large pH range. Thus, experiments were set up to measure the solubility of the corresponding solid plutonyl carbonate, PuO_2CO_3.

The plutonyl carbonate compound, PuO_2CO_3, was prepared and characterized, and powder x-ray diffraction data and EXAFS analysis verified that it was isostructural with UO_2CO_3. The solubility product of PuO_2CO_3 was determined to be log Ksp = -12.9 in 0.1 M NaCl (Figure 1). This value compares well with the solubility product determined for UO_2CO_3, log Ksp = -13.3 in 0.1 M NaCl[11] and the two literature values for the solubility product of PuO_2CO_3 in 0.1 M $NaClO_4$, log Ksp = -13.4[9] and -13.98.[12] The solubility product of plutonyl carbonate was also determined at higher concentrations of NaCl. Based upon our results and the few data available in the literature, the plutonyl carbonate was found to be significantly more soluble in NaCl than in $NaClO_4$. This difference is due to the formation of chloro complexes $PuO_2Cl_x^{2-x}$.

Solutions from the solubility experiments showed that Pu(VI) was reduced to Pu(V), which in turn disproportionated to yield polymeric Pu(IV) hydroxide. These oxidation-reduction reactions were monitored using optical absorbance spectroscopy. The solid phase changed from an initial tan color to green after aging for several months. Characterization of the aged solid by diffuse reflectance spectroscopy showed that it is a mixture of the starting PuO_2CO_3 solid and polymeric Pu(IV) hydroxide (Figure 2). The rate of the transformation depends on the chloride concentration. At low NaCl concentrations Pu(VI) is reduced within hours in the absence of an oxidizing agent; whereas in concentrated NaCl (5.6 M) Pu(VI) is stable for several days. Concentrated NaCl appears to stabilize the higher oxidation state via chloro complexation and radiolytic production of hypochlorite.

Installation and testing of the flow hydrothermal reactor in the Plutonium Facility required a formal DOE Readiness Assessment that was concluded late in FY 1997. A schematic of the flow reactor is shown in Figure 3. Liquid wastes can be pumped in directly, but solid wastes must be size-reduced to fit through the pump openings and slurried with an aqueous solution. Usually, the slurry solution contains a small amount of a thickening agent to increase the viscosity of the aqueous solution to improve the pumping efficiency. The liquid waste or slurry is pumped into the reactor along with sufficient 30% hydrogen peroxide solution to give complete oxidation. The flow rate determines the average residence time of material in the reactor. Typically, a 60-second residence time is sufficient to oxidize organics to levels below the detection limit for total organic carbon.

A set of batch reactors was also built to allow rapid, small-scale studies of reactions under hydrothermal conditions. These reactors heat a small volume (2-3 mL) of reactants in a closed vessel up to hydrothermal conditions. The reactors also underwent a formal safety review and testing process before installation in the Plutonium Facility.

Both flow and batch hydrothermal reactors were used in an extensive series of laboratory tests with nonradioactive materials. These tests showed that a wide variety of glovebox waste items, including ion exchange resins, gloves, tape, paper, cloth and organic liquids, could be treated by hydrothermal processing. In all these studies, the organic content in the effluents was <2 ppm. The likely redox state of plutonium after hydrothermal processing was examined using chromium. If chromium(III) was added, it was oxidized to chromium(VI), indicating that plutonium should be oxidized to plutonium(VI) since it is more readily oxidized than chromium. As shown by the solubility and speciation work reported above, Pu(VI) is not stable indefinitely under the final solution conditions that often result from hydrothermal processing of organics. The information we have gathered will allow us to design a flexible hydrothermal process that simplifies the separation of the small amounts of plutonium and other actinides from the bulk of the effluent.

In initial tests with radioactive material, two organic solutions contaminated with plutonium and americium were processed. The summary results of these studies are given in Table 1. The first run processed 50 ml of contaminated pump oil that was received by operations personnel at the Plutonium Facility. The second experiment processed a sample of a liquid scintillation cocktail that was spiked with a known amount of americium. Samples were collected throughout the run to quantify the volume of the hydrothermal equipment. The activity of the radionuclides in the effluent was monitored. In both tests, the effluent was a clear colorless solution with a pH of 4. The effluents from both experiments readily met discard limits to the Los Alamos Waste Treatment Facility. The total organic carbon (TOC) in the effluents was reduced more than 99.99% in these initial studies. The preliminary alpha counting results on the effluent solutions indicate that the radionuclides appear to be forming both solution and colloidal phases, but some of the activity in the effluent originates from the plutonium glovebox environment. This prevents us from making definitive conclusions at this time about colloid formation. Further tests are planned on a variety of higher-activity, actinide-containing organic wastes.

In summary, experiments with non-radioactive materials have shown that hydrothermal reactions can dissolve, oxidize, and separate metals, reformulate solids, and destroy organics and nitrates in simulants of TRU wastes. Preliminary results with actual wastes were quite promising. We have gathered the fundamental data on plutonium speciation that we need to develop flexible processing options for the effluent from hydrothermal processing. A new effort starting in FY 1998 will build on these promising initial results and develop engineering data needed for implementation in future processing operations.

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Table 1. Summary of Actinide-Contaminated Organic Waste Treatment Studies

Waste Type	**Composition**	**Reaction Conditions**	**Results**
Vacuum pump oil	Olefin: $(CH_2)_n$, where $20<n<40$; Pu content 0.5 µCi/L	550°C, 44 MPa, 60 seconds, 30 wt.% H_2O_2	25,000 ppm TOC reduced to 2 ppm; Pu content <0.3 µCi/L pH~4.0
Liquid Scintillation Cocktail (Ultima Gold)	long chain alkylbenzenes, diphenyloxazole ; Am content 8 µCi/L	550°C, 44 MPa, 60 seconds, 30 wt.% H_2O_2	25,000 ppm TOC reduced to 2 ppm; Am content <0.2 µCi/L pH~4.0

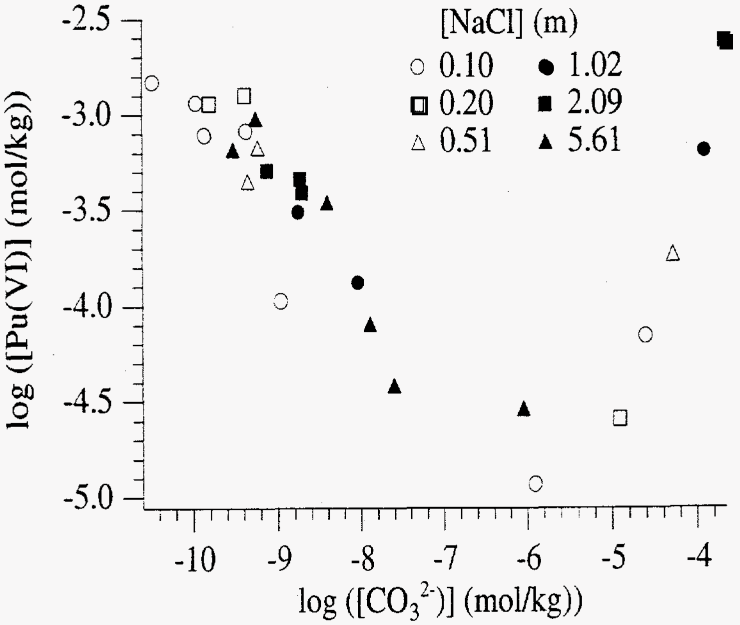

Figure 1. Solubility of Pu(VI) in NaCl solution as a function of free carbonate concentration.

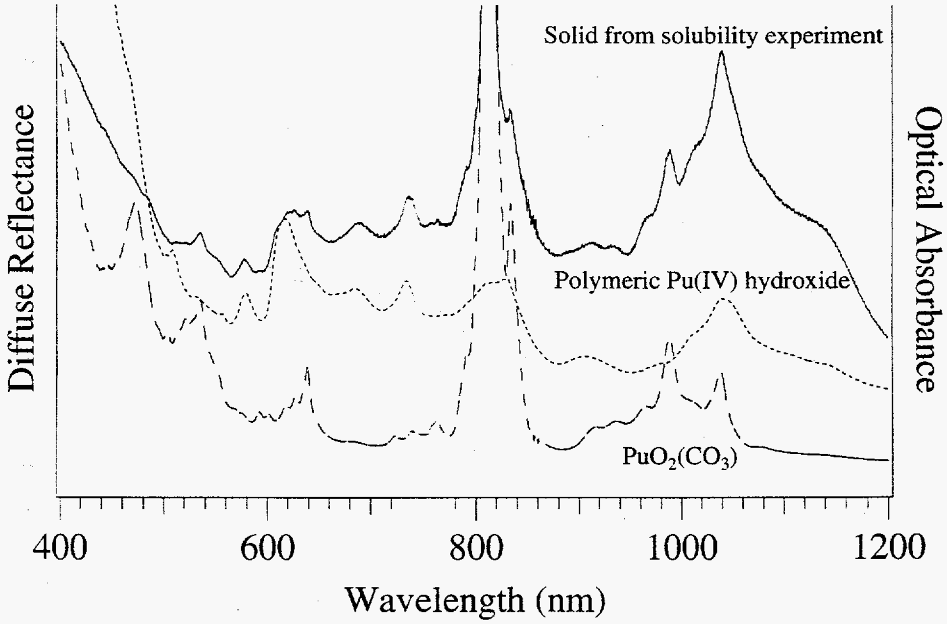

Figure 2. Diffuse reflectance spectrum of PuO_2CO_3 solid aged in 0.1 M NaCl for 4 months compared to diffuse reflectance spectrum of pure PuO_2CO_3 solid and optical absorbance spectrum of polymeric Pu(IV) hydroxide.

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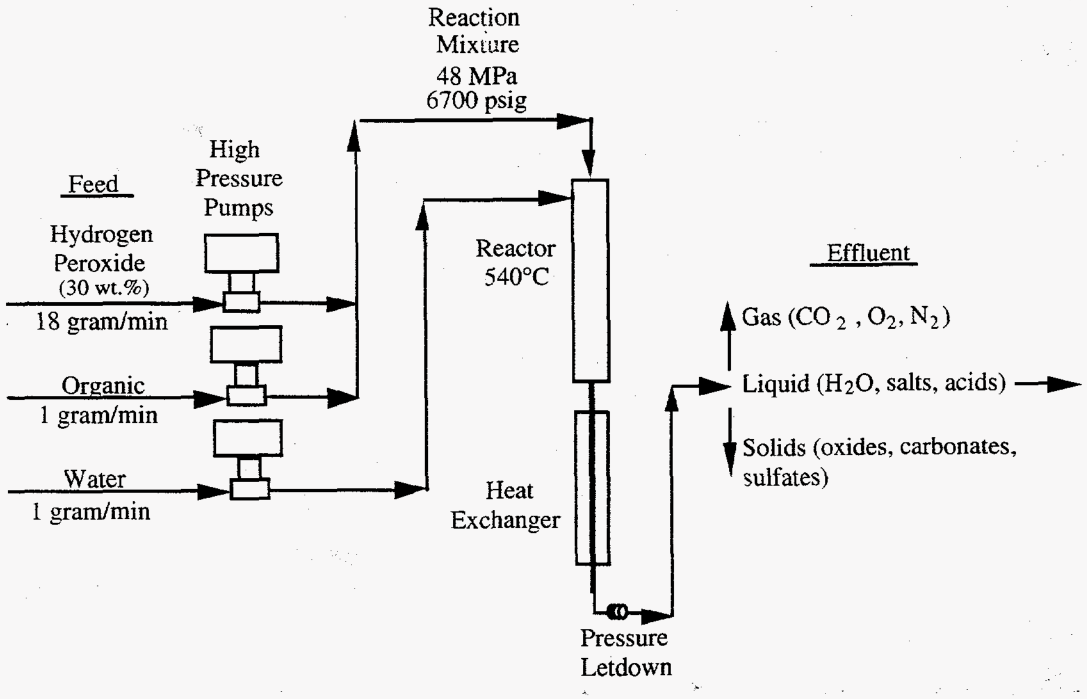

Figure 3. Schematic of hydrothermal processing.