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Liaison Activities with the Institute of Physical Chemistry, Russian Academy of Sciences: FY 1997

C. H. Delegard

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Executive Summary

The Institute of Physical Chemistry of the Russian Academy of Sciences is conducting a program of fundamental and applied research into the chemistry of the actinides and technetium in alkaline media such as are present in the Hanford Site underground waste storage tanks. This work is being coordinated and the results disseminated through a technical liaison maintained at the Pacific Northwest National Laboratory. The technical liaison also is performing laboratory studies on plutonium chemistry in alkaline media. The activities at the Institute of Physical Chemistry and through the liaison are pursued to improve understanding of the chemical behavior of key long-lived radioactive elements under current operating and proposed tank waste processing conditions. Both activities are supported by the Efficient Separations and Processing Crosscutting Program under the Office of Science and Technology of the U.S. Department of Energy.

The products of the Institute of Physical Chemistry research completed in FY 1997 are reports, published through the liaison, on

- removal of sodium nitrate from radioactive tank waste by fractional crystallization

- plutonium(V) stability in alkaline media

- removal of neptunium and plutonium from alkaline solution by coprecipitation

- application of catalysis to oxidation of organic waste components and to reduction of neptunium(V) in alkaline solution

- removal of technetium from alkaline solution by coprecipitation and by deposition on active metals.

A separate study on the effects of waste composition on plutonium compound solubility in pH 10 to 13 solutions was conducted by the liaison. Results of the Institute of Physical Chemistry and liaison FY 1997 activities are summarized in this report.

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1.0 Introduction

The Institute of Physical Chemistry (IPC) Liaison task is a program being conducted in fiscal year (FY) 1997 with the support of the U.S. Department of Energy (DOE) Office of Science and Technology, Efficient Separations and Processing (ESP) Crosscutting Program under the technical task plan RL37C344. Under this task, a technical liaison is being maintained with the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC/RAS) in Moscow, and their DOE-sponsored investigations into the fundamental and applied chemistry of the transuranium elements (primarily neptunium, plutonium, and americium) and technetium in alkaline media (e.g., Hanford Site tank waste).

The liaison operates at the Hanford Site in the interest of tank waste issues. It provides publications, materials, and guidance to the IPC/RAS scientists; reviews, edits, publishes, and distributes the IPC/RAS reports; and verifies and broadens IPC/RAS findings through supporting literature and laboratory studies. The IPC/RAS program and the liaison have been under way since 1994. Through FY 1996, five major tasks have been completed by the IPC/RAS with comprehensive reports issued through the liaison:

1. Review of the chemistry of the transuranium elements (TRU) and technetium (Tc) in alkaline media (Peretrukhin et al. 1995)

2. Investigation of effective oxidants and reductants for TRU and Tc in alkali (Shilov et al. 1996)

3. Study of TRU and Tc gamma radiolysis reactions in alkali (Pikaev et al. 1996)

4. Determination of TRU and Tc hydroxo compound solubility in alkali (Peretrukhin et al. 1996)

5. Investigation of TRU homogeneous coprecipitation in alkali (Krot et al. 1996).

These reports also have been published on the Internet (http://www.hanford.gov/twrs/tech/tech.htm; "Pretreatment" section).

Five tasks have been completed by the IPC/RAS since the beginning of FY 1997. Reports on these tasks have been edited and published as Pacific Northwest National Laboratory (PNNL)[a] documents. The tasks and principal investigators follow.

1. Crystallization of sodium nitrate from radioactive waste - a review of previous USSR and Russian investigations - Professor A. K. Pikaev.

2. Expanded investigation of neptunium and plutonium coprecipitation to determine effects of waste components - Dr. A. A. Bessonov

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3. Investigation of catalysts to achieve organic oxidation and neptunium(V) reduction reactions in alkali - Professor V. P. Shilov

4. Determination of plutonium(V) stability in alkali - Dr. N. A. Budantseva

5. Pertechnetate removal from alkaline solution - Professor V. F. Peretrukhin

The liaison task and principal investigator, C. H. Delegard, were transferred to PNNL from Westinghouse Hanford Company at the beginning of FY 1997.

2.0 Applicability and Accomplishments of IPC/RAS Research

Research being conducted at the IPC/RAS relates to the chemistry of the transuranium elements and technetium in alkaline media and to the processing of Hanford Site and other alkaline radioactive tank wastes under alkaline conditions. The IPC/RAS research provides understanding of the fundamental chemistry of these elements in the sparsely studied alkaline regime and offers alkaline-side process alternatives for waste pretreatment. It is useful to consider the contributions of the IPC/RAS research program in light of the envisioned tank waste pretreatment requirements and approaches.

2.1 Hanford Site Tank Waste Pretreatment

Hanford Site tank waste pretreatment ideally would separate the waste into two fractions:

- A small-volume, high-level fraction containing all the radioactive materials but no bulk waste components

- A large-volume, low-activity fraction containing no radioactive materials but all the bulk waste components.

The separated fractions then would be processed for long-term storage and isolation from the biosphere. Current plans call for the high-level wastes to be vitrified, encapsulated, and stored in a permanent geological repository. Despite the ideal goals, the low activity fraction is expected to contain residual radioactivity. Therefore, plans also call for vitrification of this waste and its storage onsite as cullets (irregular pieces) in large-capacity bins. The Clean Salt processing alternative (Herting 1996) offers the potential to produce a low activity fraction that will not require expensive vitrification. The predominantly sodium nitrate salt product would be available for beneficial uses or, at minimum, be stored indefinitely.

The baseline pretreatment processing envisioned to achieve the high/low split has several steps:

1. decantation of waste liquors

2. dilute alkali dissolution of waste salts

3. heated strong alkali digestion of residual waste sludge to

    - dissolve $Al(OH)_3$ and $AlOOH$, forming $Al(OH)_4^-$

    - metathesize phosphate compounds, forming PO_4^{3-}.

Each of these steps involves a solid/liquid separation with the solid fraction passing to the succeeding step. The remaining undissolved sludge would constitute part of the high level fraction because of its contained radioactivity (primarily from strontium, rare earths, and the actinides plutonium and americium). The waste liquors and solutions derived from salt dissolution and solids digestion would be processed by ion exchange to remove soluble radioactive cesium and by another process (ion exchange or solvent extraction) to remove technetium present as pertechnetate. The separated radioactive materials would become part of the high-level waste, while the decontaminated solutions would constitute the low-activity waste.

Complications arise, however, in the simple application of the pretreatment flowsheet because of the presence of undesired components in the final solution and solid phases. In the solution phase, certain radioactive components are present as species that do not partition to the high-level fraction by the baseline processing:

1. Strontium and americium, made soluble by chelating agents such as EDTA (Delegard and Gallagher 1983), do not report to alkali-insoluble sludge.

2. A significant fraction of technetium is present in tank waste solution in form(s) not amenable to ion exchange or other processes designed for pertechnetate removal (Blanchard et al. 1997; Schroeder et al. 1996).

3. Neptunium exists as stable soluble Np(V) hydroxo complexes in alkaline solution (Peretrukhin et al. 1996).

In the residual solid phase, some nonradioactive components remain that are not readily incorporated into the high-level glass. The glass volume must be increased to accommodate (dissolve) such components. This increases the load on the vitrification plant and the required capacity in the geologic repository. Chromium is a sludge component that has a large impact on increasing high-level glass volume (Lumetta et al. 1997).

Most methods being considered to address the problem components involve oxidation under strongly alkaline aqueous conditions. Oxidation would destroy organic chelating agents responsible for enhancing strontium and americium solubility (see, for example, Delegard et al. 1993), convert all dissolved technetium to pertechnetate so that it is available for subsequent removal steps (Blanchard et al. 1997; Schroeder et al. 1996), and dissolve chromium compounds from sludge by conversion to soluble chromate so that it will not become part of the high-level waste (Rapko et al. 1997).

Oxidation of the waste, however, can change the disposition of other elements having higher available oxidation states. Among those elements are the multivalent neptunium, plutonium, and americium. For example, oxidation and dissolution of plutonium from Tank 241-SY-101 waste sludge has been observed by ozonation (Delegard et al. 1993).

Plutonium itself provokes unique concern in tank waste storage and processing because of its ability to undergo nuclear criticality reactions. Criticality can occur when plutonium is present in sufficiently high concentration, with favorable compact geometry, and in the deficit of neutron poisons that can avert a self-sustaining nuclear chain reaction (Whyatt et al. 1996). To ensure safety, knowledge of the behavior of this key radioactive element under assorted waste processing conditions is essential.

It must be emphasized that the goals of pretreatment are ambitious, involving a diverse waste matrix, emerging problems (such as non-pertechnetate technetium), and evolving process options and requirements. Because of this, pretreatment flowsheets are by no means finalized. Prudence dictates that safe and successful engineering decisions be made based on comprehensive technical understanding of the waste chemistry and by wide-ranging consideration of the process options.

2.2 Research Topics at the IPC/RAS

The DOE-sponsored IPC/RAS research provides chemical insight and offers alternative process options relevant to Hanford Site tank waste pretreatment. Past, present, and future IPC/RAS research thus touch on a number of topics central to achieving safe and successful tank waste pretreatment.

Because of the special expertise of IPC/RAS scientists in the chemistry of transuranium elements and technetium in alkaline media, their contributions have been focused in this area. However, IPC/RAS contributions in process alternatives also arise because of perspectives gained in the former Soviet and Russian radioactive waste management programs.

The IPC/RAS research topics have been selected because they provide technical understanding of tank waste chemistry, particularly for the TRU and technetium, and because they support pretreatment processing objectives through novel alternative approaches. The extensive and continuing work on coprecipitation is noteworthy because it offers the possibility to remove the TRU elements and technetium by solid/liquid separations already required in any waste processing option. Research topics undertaken by the IPC/RAS under DOE-sponsorship are listed here with their published topical reports:

Chemistry of Np, Pu, Am, and Tc in alkaline media:

- Literature review (Peretrukhin et al. 1995)
- Solubility (Peretrukhin et al. 1996)
- Oxidation/reduction reagents and reactions (Shilov et al. 1996 and 1997)
- Gamma radiolysis reactions (Pikaev et al. 1996)
- Stability of Pu(V) (Budantseva et al. 1997)
- Plutonium disposition in waste sludge and solution (research being conducted by Krot and Fedoseev for publication in 1998).

Pretreatment process alternatives:

- Coprecipitation removal of Np, Pu, and Tc from solution (Krot et al. 1996; Bessonov et al. 1997; Peretrukhin et al. 1997) (research is under way by Peretrukhin for 1998 publication)
- Electroless deposition removal of Tc, Np, and Pu from solution (Peretrukhin et al. 1997)
- Chemical oxidation of organic complexing agents (Shilov et al. 1997)
- Sodium nitrate crystallization from waste; Clean Salt (Krapukhin et al. 1997).

3.0 Work Elements

The following three work elements were identified and described in the technical task plan:

1.　　Direction. Give guidance to the IPC/RAS principal investigators in the creation and performance of their tasks. This work element also includes provision of difficult-to-obtain DOE contractor documents and information on the Hanford Site tank waste properties and system and supply of essential laboratory equipment and materials.

2.　　Dissemination. Publish and distribute DOE-funded IPC/RAS findings to DOE Site technical personnel. Present IPC/RAS findings at seminars and at technical and · scientific meetings.

3.　　Verification. Confirm IPC/RAS findings by comparison with data from other sources and with laboratory tests.

Accomplishments in the three work elements are summarized in Sections 4, 5, and 6.

4.0 Direction Subtask

Activities under the Direction subtask include review and critique of tasks proposed by the IPC/RAS for DOE support in FY 1997, provision of technical literature to the IPC/RAS, technical dialogues, and provision of equipment and materials.

4.1 Task Review and Selection

The IPC/RAS prepared nine proposals for work in FY 1997. The proposals, received in October–December 1996, are listed below with the lead scientists followed by the laboratory head:

1. Study of americium solubility in alkaline wastes as functions of aging and solid phase (Tananaev/Krot)

2. Studies of interactions between Pu(IV,VI) (hydr)oxide compounds and d-elements to forecast phase composition and Pu distribution in alkaline waste (Fedoseev/Krot)

3. Solid state transformation of Pu(IV) precipitates in alkaline waste with aging and solution composition (Tananaev/Krot)

4. Application of electrochemical techniques to separate and concentrate Pu, Np, Tc, Sr, Cs (Fedoseev and Tananaev/Krot)

5. Study of rates of transuranic element precipitation under influence of acoustic fields (Shilov/Krot)

6. Investigation of sorption of Np, Pu, and Am from alkaline solution by chitin materials (Ershov/Krot)

7. Investigation of electrodeposition of Tc, U, Np, Pu from alkaline wastes (Peretrukhin)

8. Investigation of thermochemical processes of Tc in the thermal processing of Hanford Site tank waste (Kryutchkov/Grigoriev; both laboratory heads)

9. Investigation of removal of transuranium elements and technetium by coprecipitation (Peretrukhin/Krot; both laboratory heads).

Proposals #2 and #3 arose from suggestions by the liaison made in light of the uncertainties of plutonium disposition in tank sludge and the importance of plutonium in criticality safety and in establishing high/low-activity waste (Delegard 1996).

Comments and requests for further information were provided to the IPC/RAS on these proposals, and follow-up descriptions were requested to include experimental approach, preliminary schedules, and funding requirements. For most tasks, requested funding was about $75,000. The proposal to study technetium chemistry in thermal processing (#8) was dropped because of the remote probability of high-temperature waste pretreatment.

Recommendations were made to the DOE and to Dr. Jack Watson, the Program Coordinator for International Programs, about which tasks to support. The three most favored tasks were #2 (plutonium interactions with sludge), #3 (plutonium solid phase aging in tank waste), and #9 (further development of coprecipitation and inclusion of technetium).

Guidance from International Programs showed FY 1997 funding to the IPC/RAS would be limited to $80,000; previous annual funding levels to the IPC/RAS had been around $150,000 to support four tasks. With the decreased support, it was thought reasonable to support only two tasks (#2 and #3) at somewhat below their requested levels. Interest in continuing the promising work in coprecipitation remains high because coprecipitation is a pretreatment approach that does not require construction of radioactive material processing facilities beyond those already required for solid/liquid separations. Promising results to extend coprecipitation to technetium gave added incentive to support this work. Thus, a transfer of $40,000 to the IPC/RAS from the liaison funding was made to support this work.

Based on these considerations, Statements of Work (SOW) were drafted by the IPC/RAS for tasks #2, #3, and #9. Suggested revisions to the SOWs were made by the liaison and agreed by IPC/RAS. Conclusion of contract negotiations occurred in July 1997 through the offices of Thomas Albert and Associates, Palm Harbor, Florida.

4.2 Technical Dialogue

Technical dialogues have taken place by Fax between the IPC/RAS and the liaison in the preparation of reports on sodium nitrate crystallization from radioactive waste and the stability of plutonium(V) in alkaline media. Results of these dialogues yielded greater detail in the reports. General findings given in these reports, and findings in the other three FY 1996 IPC/RAS tasks, are summarized in Section 6.

4.3 Technical Literature and Information

The liaison provided technical reports to the IPC/RAS scientists to communicate the status of related research in the DOE and world technical community, to inform them of the composition and properties of Hanford Site tank waste, and to supply information on waste processing plans. Reports furnished in FY 1997 are listed.

- Eriksen TE, P Ndalamba, D Cui, J Bruno, M Caceci, and K Spahiu. 1993. *Solubility of the Redox-Sensitive Radionuclides ^{99}Tc and ^{237}Np Under Reducing Conditions in Neutral to Alkaline Solutions.* SKB-TR--93-18, Svensk Kärnbränslehantering AB, Stockholm, Sweden.

- Herting DL. 1996. *Clean Salt Process Final Report.* WHC-EP-0915, Westinghouse Hanford Company, Richland, Washington.

- Pederson LR and SA Bryan. 1996. *Status and Integration of Studies of Gas Generation in Hanford Wastes.* PNNL-11297, Pacific Northwest National Laboratory, Richland, Washington.

- Whyatt GA, RJ Serne, SV Mattigod, Y Onishi, MR Powell, JH Westsik Jr, LM Liljegren, GR Golcar, KP Recknagle, PM Doctor, VG Zhirnov, and J Dixon. 1996. *Potential for Criticality in Hanford Tanks Resulting from Retrieval of Tank Wastes.* PNL-11304, Pacific Northwest National Laboratory, Richland, Washington.

- Lin CC. 1996. *Radiochemistry in Nuclear Power Reactors*. NAS-NS-3119, National Academy of Sciences, National Academy Press, Washington, D.C.

- Delegard CH. 1987. *Solubility of PuO₂· xH₂O in PUREX Plant Metathesis Solutions*. RHO-RE-ST-53 P, Rockwell Hanford Operations, Richland, Washington.

- Delegard CH. 1996. *Liaison Activities with the Institute of Physical Chemistry, Russian Academy of Sciences: FY 1996*. WHC-SP-1186, Westinghouse Hanford Company, Richland, Washington.

- Blanchard DL, GN Brown, SD Conradson, SK Fadeff, GR Golcar, NJ Hess, GS Klinger, and DE Kurath. 1997. *Technetium in Alkaline, High-Salt, Radioactive Tank Waste Supernate: Preliminary Characterization and Removal*. PNNL-11386, Pacific Northwest National Laboratory, Richland, Washington.

- Schroeder NC, S Radzinski, J Ball, K Ashley, SL Cobb, B Cutrell, JM Adams, C Johnson, and GD Whitener. 1995. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using Reillex-HPQ Resin*. LA-UR-95-4440, Los Alamos National Laboratory, Los Alamos, New Mexico.

Back issues (volumes 61 to 75, 1993 to 1996) and 1997 and 1998 subscriptions (volumes 76 to 83) to the journal *Radiochimica Acta* were also provided. Cutbacks in funding from the Russian Academy of Sciences in 1993 forced the IPC/RAS to drop their subscriptions to many journals, including this very essential one.

Two books also were provided:

- *Radiochemistry and Nuclear Chemistry*. 2nd edition. G Choppin, JO Liljenzin, and J Rydberg. Butterworth-Heinemann, Oxford, UK (1995).

- *The Merck Index*. 12th edition. Merck & Co., Inc., Whitehouse Station, New Jersey (1996).

4.4 Planned IPC/RAS Scientist Visit to the U.S.

Plans were made to bring Professor Vladimir F. Peretrukhin to the United States for a 24-day agenda of technical discussions, seminars, and teaching in February and March 1997. Included on his itinerary were seminar presentations at Washington State University (WSU) at its Tri-Cities (Richland) and Pullman campuses, the Hanford Site, and the Lawrence Berkeley Laboratory (hosted by Dr. Norman Edelstein). A graduate level, one semester hour, chemistry course, "Chemistry of Actinides and Technetium in Alkaline Media," was scheduled to be offered at Washington State University, Tri-Cities, in the period 3 to 13 March 1997. Interest in the course was high with enrollment exceeding 20 students. Professor Peretrukhin was to be the primary lecturer.

Unfortunately, a serious illness forced Professor Peretrukhin to cancel his visit. Because of extensive commitments, the visit (including WSU Tri-Cities chemistry course) could not be rescheduled until spring 1998. Support for this visit is part of the planned FY 1998 liaison task. Plans are under way to offer this class in late February and early March 1998.

4.5 Equipment Provided to the IPC/RAS

Original plans for the liaison task did not include the provision of major items of scientific equipment to the IPC/RAS. Those plans changed with the news of the failure, in March 1997, of the IPC/RAS x-ray diffractometer. This instrument, manufactured in the 1970s, is central to the planned work on solids characterization in studies of plutonium disposition in sludge matrices (tasks #2 and #3 described in Section 4.1).

Market investigations by IPC/RAS personnel found that a suitably sensitive new diffractometer, delivered in Moscow, would cost more than $100,000. However, rebuilding the existing diffractometer, using about $30,000 in replacement parts (Guinier camera, monochromator, x-ray tube, and various shielding and adapter hardware), could be performed. Funding has been transferred by the liaison to support up to $30,000 in costs of replacement hardware to restore x-ray diffraction capability to the IPC/RAS.

5.0 Dissemination Subtask

The Dissemination subtask includes editing, publication, and distribution of IPC/RAS reports and presentation of DOE-funded IPC/RAS research.

5.1 Publications

Five technical reports from the IPC/RAS were drafted. These reports were reviewed and technically edited by the liaison, and were stylistically edited and published as PNNL documents.

1. *Crystallization of Sodium Nitrate from Radioactive Waste*, PNNL-11616. VB Krapukhin, EP Krasavina, and AK Pikaev.

2. *Investigation on Application of Homogeneous and Heterogeneous Catalysis for Alkaline Waste Treatment*, PNNL-11623. VP Shilov, AA Bessonov, A Yu Garnov, AV Gelis, AV Gogolev, NN Krot, IA Charushnikova, VP Perminov, and LN Astafurova.

3. *Investigation on Behavior of Plutonium(V) in Alkaline Media*, PNNL-11624. NA Budantseva, IG Tananaev, AM Fedoseev, AA Bessonov, and CH Delegard.

4. *Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solution by the Method of Appearing Reagents: Study of the Effects of Waste Components on Decontamination from Np(IV) and Pu(IV)*, PNNL-11625. AA Bessonov, NA Budantseva, AV Gelis, MV Nikonov, and VP Shilov.

5. *Decontamination of Alkaline Solution from Technetium and Other Fission Products and from Some Actinides by Reductive Coprecipitation and Sorption on Metals*, PNNL-11626. VP Peretrukhin, VI Silin, IG Tananaev, AV Kareta, and VE Trushina.

The paper, *Chemical Species of Plutonium in Hanford Radioactive Tank Waste*, has been drafted with Dr. G. S. Barney for publication in a proceedings from an American Chemical Society symposium, "Experimental and Modeling Studies of Radionuclide Speciation in Real Systems." The paper, a review of the technical literature and Hanford-specific documents on the topic area, contains many references to the IPC/RAS work and is being peer reviewed. The proceedings will be issued by Plenum Publishing.

By initiative not under the liaison, the IPC/RAS also has begun publishing results of their DOE-supported work in scientific journals.

1. Gogolev AV, VP Shilov, and AK Pikaev. 1996. "The Formation of a Neptunium(V) Peroxo Complex upon Gamma Radiolysis of Aqueous Alkaline Solutions of Neptunium Ions." *Mendeleev Communications* 6(4):127-128.

2. Gogolev AV, VP Shilov, and AK Pikaev. 1997. "Specific Oscillation Processes upon Gamma Radiolysis of Alkaline Aqueous Solutions of Neptunium and Plutonium Ions." *Mendeleev Communications* 7(1):8-9.

Additional publications of DOE-supported IPC/RAS work in the *Journal of Alloys and Compounds* are under way. The liaison participated in preparing the following manuscripts:

1.	Tananaev IG, NA Budantseva, AM Fedoseev, and CH Delegard. "Investigation on Behavior of Plutonium(V) in Alkaline Media."

2.	Budantseva N, A Bessonov, I Tananaev, A Fedoseev, and C Delegard. "Capture of Pu(V), Np(V), and Pu(VI) from Alkaline Solutions by Hydroxides of Pu(IV), Th(IV), and La(III)."

5.2 Presentations

The planned visit of Professor VF Peretrukhin to the United States included presentations at the Hanford Site, at Washington State University, and at the Lawrence Berkeley Laboratory. Professor Peretrukhin also would have presented 16 hours of classroom lecture on the chemistry of the actinides and technetium in alkaline media at WSU Tri-Cities. Unfortunately, as described in Section 4.4, that visit was postponed until the spring of 1998.

The paper, "Stability of Double Carbonate of Ammonium and Plutonyl: $NH_4PuO_2CO_3$," by IG Tananaev, NA Budantseva, and AM Fedoseev, was presented by Dr. Fedoseev at the conference "27th Journees des Actinides - 1997," April 26–29, 1997, at Dijon, France.

Other IPC/RAS findings were presented at the conference "Actinides '97" in Baden-Baden, Germany, September 21–26, 1997. The conference proceedings (papers) will be published in a special edition of the *Journal of Alloys and Compounds*. IPC/RAS scientists have prepared five papers for this conference:

1.	"The Study of Np, Pu, and Am Hydroxocompounds Solubility in Alkaline Solutions" - VF Peretrukhin and IG Tananaev (oral)

2.	"Investigation of Behavior of Plutonium(V) in Alkaline Solutions" - IG Tananaev, NA Budantseva, AM Fedoseev, and CH Delegard (poster)

3.	"Capture of Pu(V), Np(V), Pu(VI) from Alkaline Solutions by Hydroxides of Pu(IV), Th(IV), La(III)" - NA Budantseva, IG Tananaev, AM Fedoseev, and CH Delegard (poster)

4.	"The Interaction of Np(V), Pu(VI), and Tc(VII) with Some Metals in Alkaline Solutions" - VI Silin, VF Peretrukhin, and AV Kareta (poster)

5.	"Gamma Radiolysis of Alkaline Aqueous Solutions of Neptunium and Plutonium Ions" - AK Pikaev, AV Gogolev, and VP Shilov (poster).

Funds to support the speakers (listed first) in the first four papers were provided by the liaison. Funding for Professor Pikaev was made available to him by other sources.

The paper, "Chemical Factors Affecting Plutonium Compound Solubility in Hanford Site Radioactive Tank Wastes," by CH Delegard, RJ Elovich, GS Barney, and VF Peretrukhin was presented at the American Chemical Society national meeting on September 9, 1997.

6.0 IPC/RAS Results and the Verification Subtask

Verifications of the findings obtained by the IPC/RAS scientists in their FY 1996 tasks are undertaken by comparing their results with published results from independent laboratories and with previously unpublished results obtained through the liaison. The IPC/RAS data are currently being prepared for publication as PNNL documents. Results of the IPC/RAS FY 1996 tasks are summarized and compared, where possible, with other findings. Supporting laboratory investigations were conducted by the liaison to support FY 1997 IPC/RAS work.

6.1 Sodium Nitrate Crystallization

A technology review on the crystallization of sodium nitrate from radioactive wastes has been prepared by VB Krapukhin, EP Krasavina, and AK Pikaev of the IPC/RAS (Krapukhin et al. 1997). This report recounts IPC/RAS experience from the 1940s through the 1980s in the development of methods to recover sodium nitrate and sodium acetate from radioactive waste by fractional crystallization. Acetate also was separated from the waste by acidification and distillation of acetic acid.

6.1.1 IPC/RAS Findings

Early Soviet reprocessing flowsheets generated neutralized radioactive wastes containing roughly equivalent concentrations of sodium nitrate (from metal fuel dissolution) and sodium acetate (from the sodium uranyl acetate coprecipitation process used). Methods were developed to fractionally crystallize first one salt, then the other (the first being the one in abundance) under closed cyclic conditions. Therefore, extensive studies of the CH_3COONa-$NaNO_3$-H_2O phase diagram were performed. Sodium acetate generally was crystallized at about 20°C as its trihydrate. Sodium nitrate solutions were concentrated to reach a 120°C boiling point and were cooled to 70°C for crystallization. Recycle of the mother solutions and blending with fresh feed allowed nearly 100% recovery of both sodium nitrate and acetate. Decontamination factors of 30 to 50 from radioactive components were obtained for both salts over the single crystallization steps employed.

Several approaches were attempted to attain better decontamination factors from product impurities. Impurities included both radioactive components (ruthenium, strontium, cesium) and bulk chemical waste components which affected crystallization and could carry radionuclides with the salt product (e.g., chromium, aluminum, carbonate, surfactants). Thus, barium was added to precipitate the chromate and carry radiostrontium. Radiocesium was removed by coprecipitation with ferrocyanide. All these decontamination steps were performed at neutral to alkaline conditions. The partially decontaminated solution then was acidified and acetic acid removed by distillation.

However, unprecipitated ferrocyanide would carry to the acid-side evaporators, partially decompose to form hydrogen cyanide gas and partially form ferric ferrocyanide solids which would be retained, with captured fission products, in the crystallized sodium nitrate. Alternative flowsheets were developed which began with acidification and distillation of acetic acid. With this approach, chromate was reduced to Cr(III) and nonsorbing ruthenium complexes were partially destroyed. The nitrate-rich residue then was neutralized with fresh alkaline waste solution to produce a precipitate in which chromium(III) hydroxide captured aluminum and silicon, the radioactive strontium, and part of the ruthenium. By this sequence, the barium addition (to precipitate $BaCrO_4$) could be avoided.

Cesium removal became more imperative as operating efficiencies increased, waste volumes decreased (per unit uranium processed), and fission product concentrations rose. Cesium was removed by addition of preformed iron and nickel ferrocyanide to the alkaline waste mixture; process conditions (pH, temperature, time) were optimized. Because excess dissolved ferrocyanide was not present in solution, problems with hydrogen cyanide generation and ferric ferrocyanide post precipitation in acid also were eliminated. Centrifuge filters and jet-spray crystal washers were developed to remove the various decontamination solids from the process solutions and product solids, respectively.

Bulk waste components accumulated in the waste solutions as the solutions were stripped of acetate and sodium nitrate. Sodium sulfate was one such component. The influence of sodium sulfate on process conditions was, if anything, positive because it inhibited nitric acid codistillation with the acetic acid. If not removed by alkaline-side calcium precipitation, sulfate ultimately precipitated as the sodium salt with the sodium nitrate product. Because sodium sulfate did not carry radionuclides, it did not radioactively contaminate the product salt.

Other bulk waste components included carbonate, oxalate and other organics, fluoride, chloride, and potassium. The deleterious effects of carbonate (because of the poor filtration of the carbonate solids, carbonate complexation of zirconium and niobium radionuclides, and carbonate solids' contamination of sodium nitrate product) could be avoided by acidification. Oxalate also could contaminate sodium nitrate product. However, process conditions such as alkaline-side precipitation with calcium and oxidation in hot nitric acid [especially if catalyzed by manganese(II)] eliminated oxalate from the sodium nitrate crystallization solutions and the product salt. Other organics (lactic acid, thiourea, trihydroxyglutaric acid) similarly were oxidized by heating of the acidified nitrate solution. Fluoride was eliminated by alkaline-side precipitation with calcium (if calcium were present) and was partially removed by distillation. However, as with potassium and chloride, most of the fluoride was present in the sodium nitrate product as a component of the interstitial liquor.

A single recrystallization step was used for further purification of sodium nitrate salt product in more recent process improvements for wastes containing no acetate. The recrystallization achieved decontamination by removing solid and interstitial contaminants. Generally, further decontaminations of strontium, ruthenium, cesium, and plutonium radioactivity were achieved by sorption on ferrocyanide, alkaline sulfide precipitation, and sorption on pyrolusite (MnO_2).

A detergent salt, sodium dodecylbenzenesulfonate (called Sulfonol in Russia), present in more recent wastes, proved to be the most difficult contaminant in sodium nitrate crystallization. Alkaline-side precipitation of the anion with calcium or iron did not completely remove this colloidal material. Acid-side evaporation did not fully decompose Sulfonol. Filtration was marginally successful, but the solids compressed and rapidly blocked the filter. Only by a combination of these approaches could some success be achieved.

6.1.2 Comparison with Clean Salt Findings

Results of the IPC/RAS technology development in sodium nitrate crystallization can be compared with results obtained in Clean Salt process development for radioactive Hanford Site wastes. The Clean Salt process uses multiple fractional crystallizations of sodium nitrate to produce decontaminated salt product. In tests with a genuine waste from Tank 241-AW-101, a stage-to-stage decontamination factor (DF) of 21 (average over the five stages) was obtained from [137]Cs (Herting 1996). No separate decontamination approach (such as sorption or ion exchange) was used except filtration of the initial pH 2 acidified waste feed to remove undissolved solids. This DF is slightly lower than the DFs achieved through the single crystallization stages observed in the IPC/RAS work.

As in the IPC/RAS findings, salt contaminants found in the Clean Salt tests mostly were carried in the interstitial liquor and could be decreased by more extensive washing. The IPC/RAS work showed that soluble crystalline salts ultimately will build up in the process solutions and cocrystallize in the sodium nitrate product. For the Clean Salt tests with Tank 241-AW-101 wastes, potassium nitrate, sodium sulfate, and aluminum nitrate were expected to crystallize over an equilibrium process. Other salts may form for wastes of different composition.

6.2 Plutonium(V) Behavior in Alkaline Solutions

Experimental data in previous studies on plutonium compound solubility, oxidation/reduction reactions, and coprecipitation have been complicated by the apparent instability of plutonium(V) (Peretrukhin et al. 1996; Shilov et al. 1996; Krot et al. 1996). IPC/RAS researchers (NA Budantseva, IG Tananaev, AM Fedoseev, and AA Bessonov) have investigated the stability of Pu(V) in alkaline solution as functions of time, temperature, sodium hydroxide concentration, and solution composition (including other Hanford Site waste components). A report has been published describing these FY 1996 studies (Budantseva et al. 1997). The results are summarized in the following sections.

6.2.1 IPC/RAS Findings

As a first step, the studies of Pu(V) stability in alkaline solution required preparation and characterization of plutonium starting materials and gathering the spectra of dissolved Pu(VI) and Pu(V). Plutonium(IV) precipitated too rapidly and completely in alkali to allow measurement of an absorption spectrum. Preparation of Pu(VI) was performed by standard acid-side Pu(IV) oxidation in fuming perchloric acid. The Pu(VI) could then be made alkaline to prepare stock solutions. Spectral measurements showed an unstable Pu(VI) species formed below 2 $\underline{M}$ NaOH. Above 2 $\underline{M}$ NaOH, Pu(VI) solutions displayed spectra which did not change with NaOH concentration (implying a limiting hydroxide complex was formed) and whose absorbances were proportional to concentration.

However, subsequent alkaline-side preparation of Pu(V) solutions was not so direct. Various chemical reductants were tested to convert Pu(VI) to Pu(V). Uncertainties in stoichiometry for all agents and slow kinetics for some agents made this approach undesirable. Electrochemical reduction also was tested but obvious contamination by Pu(IV) was observed. Plutonium(V) ultimately was prepared for experimental tests in the form of the salt $NH_4PuO_2CO_3$. The salt, found to be reasonably stable when stored dry, contained no Pu(IV) and about 2% Pu(VI).

Tests were performed in which the Pu(V) salt was added to NaOH solutions of different concentrations and at different temperatures. Disproportionation occurred almost instantly and completely in 1 $\underline{M}$ NaOH to give green precipitated Pu(IV) hydrous oxide solids and dissolved Pu(VI). In contrast, at NaOH concentrations exceeding 8 M, Pu(V) was stable in solution for days. Plutonium(V) stability increased with increasing NaOH concentration and decreasing temperature. Disproportionation equilibrium constants were calculated for these data using spectrophotometric measurement of the dissolved Pu(VI) and Pu(V).

The reverse reaction, reproportionation of freshly precipitated Pu(IV) hydrous oxide with Pu(VI) to form dissolved Pu(V), was tested as a function of NaOH concentration. As expected, reproportionation increased with increasing NaOH concentration. Interestingly, however, the reproportionation equilibrium constants for a particular NaOH concentration did not have the expected exact inverse relationship with the corresponding disproportionation constants.

Subsequent tests showed that adsorption of Pu(V) on the Pu(IV) hydrous oxide solid phase occurs, complicating the interactions of the various plutonium oxidation states and accounting for the disparity between the disproportionation and reproportionation results. Preliminary tests, performed by introducing Pu(V) to suspensions having Pu(IV) solids, proved adsorption occurred. Additional tests using Np(V) as a surrogate for Pu(V) revealed that Np(V) [and, presumably, Pu(V)] sorption initially occurs according to a well-known coprecipitation isotherm indicating monolayer chemisorption. With time, however, some release of the Np(V) occurs, presumably by increased ordering of the Pu(IV) solids.

The disproportionation equilibrium data and the known electrode potential for the Pu(VI)/Pu(V) couple allowed prediction of the Pu(V)/Pu(IV) hydrous oxide reduction potential. At 20°C and 1 $\underline{M}$ NaOH, the reduction potential was about 0.4 V; at 4 $\underline{M}$ NaOH, the potential was about 0.2 V.

The stability of Pu(V) also was found to increase with increasing salt concentration. Tests were performed using varied NaOH concentrations in simulated Hanford Site tank waste solutions (containing nitrate, nitrite, aluminate, carbonate, sulfate, fluoride, EDTA,[a] HEDTA,[b] citrate, glycolate, and acetate). Plutonium(V) was stable indefinitely in 4 $\underline{M}$ NaOH solutions of simulated waste but disproportionated in 4 $\underline{M}$ NaOH containing no additional salt. Further tests showed Pu(VI) was rapidly reduced in NaOH solutions of HEDTA as well as in the full waste simulant (containing all waste components). No other single waste component in NaOH accelerated Pu(VI) reduction.

6.2.2 Comparison with Other Findings

Only limited experiments have been reported on the stability of Pu(V) in alkaline media. In one study, electrochemical measurements show Pu(V) is stable to disproportionation over the range 0.1 to 14.1 $\underline{M}$ NaOH (Peretrukhin and Alekseeva 1974). These results, however, run counter to the observation of increasing Pu(V) disproportionation as NaOH concentrations decrease below about 8 $\underline{M}$. The disparity of these findings, and the importance of plutonium in Hanford Site waste processing, motivated support of this research.

Reproportionation of freshly precipitated Pu(IV) hydrous oxide with Pu(VI) has been tested at 4 and 6 $\underline{M}$ NaOH. Based on these findings, and the measured Pu(VI)/Pu(V) reduction potential, the potential for the couple Pu(V)/Pu(IV) was calculated to be 0.44 V at 4 $\underline{M}$ NaOH (Bourges 1972) versus about 0.2 V estimated by disproportionation tests in the recent IPC/RAS work. These estimates agree well with each other especially when compared with the electrochemical measurements of about -0.8 V in 4 $\underline{M}$ NaOH (Peretrukhin and Alekseeva 1974). A critique of the electrochemical research is presented in the IPC/RAS report (Budantseva et al. 1997).

The increasing stability of Pu(V) with NaOH concentration is also consistent with comparisons of Pu(IV) hydrous oxide solubility in NaOH solution in oxidizing (aerated) and reducing (hydrazine) conditions. This comparison is shown in Figure 6.1. The solubilities are identical below about 6 $\underline{M}$ NaOH. Thus, Pu(IV) is the likely dissolved oxidation state at lower NaOH concentrations since hydrazine certainly reduces dissolved plutonium to the (IV) state (Shilov et al. 1996). Above 6 $\underline{M}$ NaOH, the solubility observations diverge. Plutonium(V) is observed by spectrophotometry in the aerated solutions whereas the dissolved plutonium is retained in the (IV) state for the tests with

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(a) EDTA is ethylenediaminetetraacetate.

(b) HEDTA is *N*-2-hydroxyethylethylenediaminetriacetate.
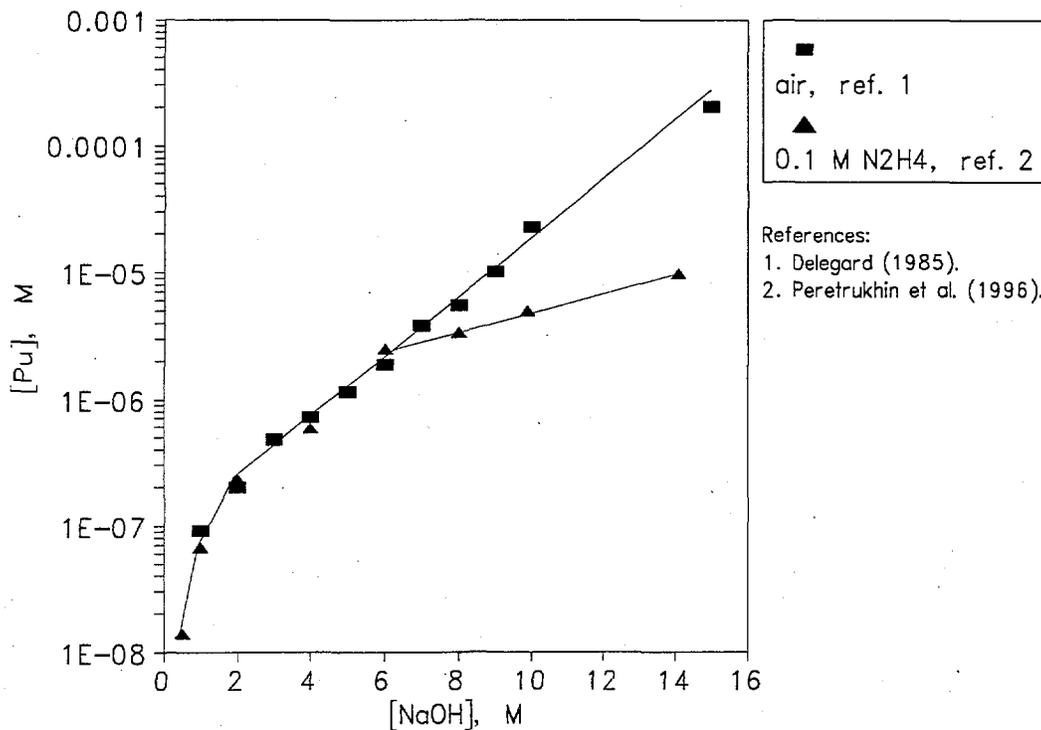
Figure 6.1. Solubility of Pu(IV) Hydrous Oxide in Aerated and Hydrazine NaOH Solutions

hydrazine. The divergence at about 6 $\underline{M}$ NaOH gives evidence that Pu(V) is stabilized above about 6 $\underline{M}$ NaOH, in agreement with the present IPC/RAS findings.

6.3 Np and Pu Coprecipitation from Alkaline Solution

Continued testing of coprecipitation removal of neptunium and plutonium from alkaline solution was performed in FY 1996 by IPC/RAS researchers (AA Bessonov, NA Budantseva, AV Gelis, MV Nikonov, and VP Shilov) and results reported (Bessonov et al. 1997).

Coprecipitation was implemented by the Method of Appearing Reagents, a technique utilizing homogeneous carrier precipitation caused by hydrolytic, reductive, or catalytic decomposition reactions of soluble precursor reactants. Carriers included hydroxides of chromium, manganese, iron, and cobalt; manganese oxide; and sodium diuranate. The research had three objectives: optimization of neptunium removal by effective use of reductants, confirmation of plutonium removal at concentrations below Pu(IV) solubility limits, and determination of the effects of individual tank waste components on coprecipitation removal using various agents.

6.3.1 Improving Neptunium Removal

Generally poor decontamination factors (DFs) were achieved for neptunium in previously reported tests (Krot et al. 1996). The lone exception was for sodium diuranate. It was anticipated that higher DFs could be achieved for the more desirable transition metal (hydr)oxide precipitating agents if reduction of the soluble and stable Np(V) to the less soluble Np(IV) could be achieved.

Scouting tests showed reducing agents most effective for Np(V) reduction were hydrazine (N_2H_4), vanadyl sulfate (VO_2SO_4), and sodium dithionite ($Na_2S_2O_4$). Hydroxylamine also achieved reduction but inordinately high concentrations (0.5 $\underline{M}$) were required. Coprecipitation with $Cr(OH)_3$ carrier was tested for the three optimum reductants as functions of time, NaOH concentration, and temperature. The best temperature for this carrier was 80°C. Hydrazine and dithionite were slightly more rapid than vanadyl, but all required about 2 to 3 hours to reach equilibrium as shown by constant DF. Decontamination factors exceeded 100 for hydrazine up to 4 $\underline{M}$ NaOH, for dithionite up to 2 $\underline{M}$ NaOH, and for vanadyl only up to 1 $\underline{M}$ NaOH. These data show that acceptable neptunium DFs can be obtained with transition metal precipitants if effective Np(V) reductants are used.

6.3.2 Removal of Dilute Pu(IV)

Tests performed previously showed plutonium, when present as Pu(V) or (VI) at about 10^{-4} $\underline{M}$, could be coprecipitated from solution (Krot et al. 1996). However, this concentration is well above the solubility of Pu(IV) itself in alkaline media (Figure 6.1). Therefore, the earlier tests may have been unduly influenced by the precipitation of the Pu(IV) hydrous oxide and not adequately measured coprecipitation effects. Additional tests were performed using the candidate coprecipitating agents $Co(OH)_3$, MnO_2, $Mn(OH)_2$, $Cr(OH)_3$, and $Fe(OH)_3$ with NaOH solutions having 5×10^{-7} $\underline{M}$ initial Pu(IV).

General trends observed in previous tests were observed here. For example, DFs decreased with increasing NaOH concentration and increased with precipitating agent concentration. Coprecipitation of plutonium by MnO_2 remained poor (DF of 40 from 2 $\underline{M}$ NaOH), as observed previously. Similarly, coprecipitation by $Mn(OH)_2$ also was low (DF of 50 at 2 $\underline{M}$ NaOH). For a given precipitating agent, and under otherwise similar conditions, somewhat lower DFs were observed in the tests using 5×10^{-7} $\underline{M}$ Pu(IV) than were observed previously at 10^{-4} $\underline{M}$ Pu(V) or (VI). However, DFs exceeding 100 from 2 $\underline{M}$ NaOH still were observed, increasing in the order $Cr(OH)_3$, $Co(OH)_3$, and $Fe(OH)_3$.

The effect of Pu(IV) aging on coprecipitation removal also was investigated. Tests were performed with 5×10^{-7} $\underline{M}$ Pu(IV) hydrous oxide aged for 1 to 30 days in 0.5 to 8 $\underline{M}$ NaOH. The tests showed that coprecipitation efficiencies (DFs) are different at the various NaOH concentrations but are unaffected by aging over this time range. Cobalt(III) and chromium(III) hydroxide carriers were tested.

6.3.3 Effects of Waste Components on Coprecipitation

Components present in Hanford Site tank waste may affect precipitation reactions by interacting with Np, Pu, or the precipitating reagents. Therefore, tests were conducted to determine the effects of hydroxide, nitrate, nitrite, carbonate, aluminate, EDTA, HEDTA, citrate, and glycolate on the decontamination of 5×10^{-7} $\underline{M}$ Pu(IV) solutions by the precipitating agents $Cr(OH)_3$, $Fe(OH)_3$, $Co(OH)_3$, and Na_2UO_4. These agents were derived from $Cr(NO_3)_3$, $Na_2[Fe(CN)_5NO]$, $Co(NH_3)_6Cl_3$, and $Li_4[UO_2(O_2)_3]$ precursors, respectively. Selected test results are summarized in Figure 6.2.

1 M OH / 0.1 M Glycolate

1 M OH / 0.05 M Citrate

1 M OH / 0.05 M EDTA

1 M OH / 0.1 M HEDTA
No precipitate

1 M OH / 0.5 M AlO2

1 M OH / 1 M CO3

1 M OH / 2 M NO2

1 M OH / 2 M NO3

4 M OH

1 M OH

Na2UO4
Fe(OH)3
Cr(OH)3
Co(OH)3

0   100   200   300   400   500
Pu(IV) Decontamination Factor
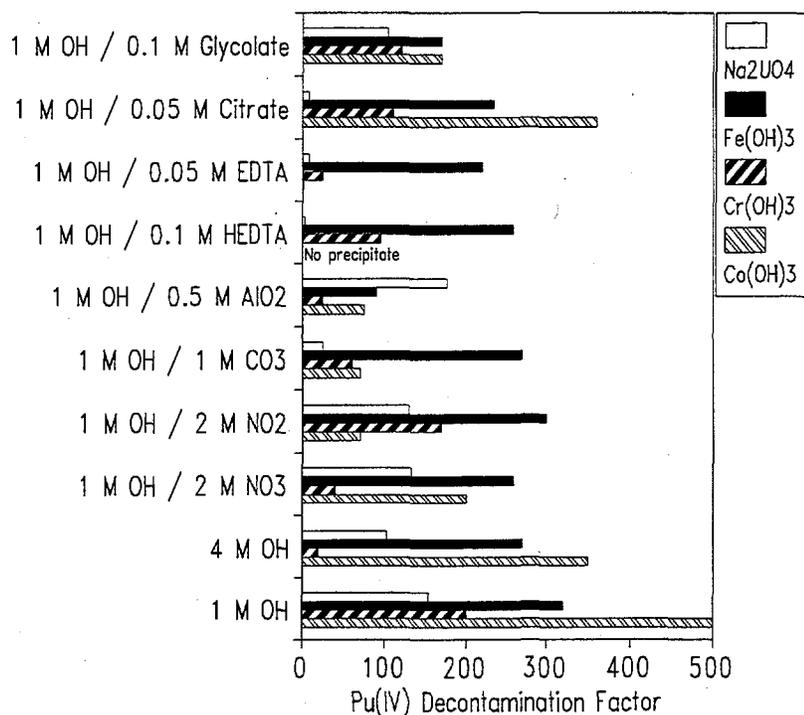
Figure 6.2. Effects of Waste Components on Solution Decontamination from Pu(IV)

These results show, for all carriers, the previously described decrease in DFs with increasing NaOH concentration. Most striking, however, are the sharply decreased DFs observed for some carriers in the presence of the chelating agents HEDTA and EDTA. The effect was sufficiently strong that $Co(OH)_3$ simply did not precipitate in the presence of 0.1 $\underline{M}$ HEDTA. Sodium uranate precipitation also was sharply inhibited. The precipitating agent showing the widest range of effectiveness was $Fe(OH)_3$. For this robust agent, DFs were 90 or higher for all tested solutions.

The effects of 0.01 $\underline{M}$ fluoride, phosphate, and sulfate on Pu(IV) coprecipitation also were tested. At these concentrations, none of the three inorganic species measurably affected DF.

6.4 Application of Catalysis for Reduction and Oxidation in Alkaline Waste Treatment

Removal of neptunium from alkaline solutions by coprecipitation is low, and the solubility of neptunium itself in alkaline media is high, because of the stability and relatively solubility of Np(V) hydroxo complexes (Krot et al. 1996; Peretrukhin et al. 1996). Reduction of Np(V) to Np(IV) would decrease the solubility and increase the degree of (co)precipitation of neptunium. Recent studies from the IPC/RAS estimate the Np(V)/Np(IV) reduction potential to be 0.13 V at 1 $\underline{M}$ NaOH (Shilov and Yusov 1997). Investigation of reagents, and catalysts, to achieve Np(V) reduction were performed and reported by IPC/RAS researchers (VP Shilov, AA Bessonov, A Yu Garnov, AV Gelis, AV Gogolev, NN Krot, IA Charushnikova, VP Perminov, and LN Astafurova).

Under the same task, the IPC/RAS scientists also studied oxidants and catalysts to destroy organic complexing agents in alkaline solution. Complexing agents, such as EDTA and HEDTA, sharply inhibit coprecipitation reactions as shown in the previous section. Complexing agents also strongly increase the solubilities of di- and trivalent radioelements (strontium, cobalt, americium) in waste solution (Delegard and Gallagher 1983). Destruction of the complexing agents would lower radioelement concentrations in waste solutions through increased (co)precipitation and deposition of the radionuclides to the high-activity sludge.

Organic destruction has been investigated previously for Hanford Site tank wastes. Methods included thermal reactions at ambient tank conditions, higher-temperature reactions limited by atmospheric boiling with native tank waste oxidants (nitrate and nitrite), pressurized hydrothermal reactions (200 to 350°C; with and without added air oxidation), and furnace temperatures (850°C). Electrochemical and ozone oxidation also have been tested. However, no systematic investigations of the efficacy of dissolved chemical oxidants on destruction of organic complexing agents at tank waste temperatures have been performed. The results of the IPC/RAS work on Np(V) reduction and organic oxidations in alkaline media have been published (Shilov et al. 1997).

6.4.1 Neptunium(V) Reduction

Further tests on reduction of Np(V) by hydrazine were conducted with various hydrazine compounds ($N_2H_4 \cdot H_2O$, $N_2H_4 \cdot HNO_3$, $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot H_2SO_4$, and $N_2H_4 \cdot CH_3COOH$). Surprisingly, except for $N_2H_4 \cdot HNO_3$, all tested compounds were ineffective Np(V) reductants. Alkaline mixtures of $N_2H_4 \cdot H_2O$ and $NaNO_3$ also were ineffective. Thus it was concluded that a decomposition product generated in the $N_2H_4 \cdot HNO_3$ was the active reductant. Tests showed that hydrazoic acid, HN_3, was present in the $N_2H_4 \cdot HNO_3$. However, addition of azide (N_3^-) salts to alkaline Np(V) solution failed to reduce the neptunium. The active reductant remains unknown. Experiments to test possible transition element salts [Co(II), Cu(II), Pd(II), and Pt(IV)] as Np(V) reduction catalysts were conducted. None of these catalysts had any effect on the rate or extent of Np(V) reduction. Research from the previous year showed enhanced reduction could be accomplished with hydrazine by increasing temperature and lowering NaOH concentration (Shilov et al. 1996).

A new reductant tested for Np(V) reduction was vanadyl [the electrode reduction potential of V(V)/V(IV) is -0.93 volts]. Reduction of Np(V) by vanadyl was tested as a function of NaOH concentration, V(IV) concentration (introduced as $VOSO_4$), and temperature. Again, higher temperatures and lower NaOH concentrations enhanced Np(V) reduction. The hydrolysis and precipitation of the V(IV) salt likely carries part of the Np(V). Catalysts were not tested with vanadyl. Up to 98% reduction of Np(V) was observed in 1 $\underline{M}$ NaOH and at 80°C.

Catalyzed and uncatalyzed reduction of Np(V) by formate was tested based on the estimated potential of the CO_3^{2-}/HCO_2^- couple of about -1 V. In the absence of catalysts, no Np(V) reduction was observed in 1 $\underline{M}$ formate with 1 to 5 $\underline{M}$ NaOH and with heating from 60 to 90°C. However, addition of 10^{-3} $\underline{M}$ Pd(II) or Pt(IV) salts caused Np(V) reduction. From 90 to 95% reduction was observed at 90°C in 1 to 5 $\underline{M}$ NaOH with the Pd(II) catalyst; the Pt(IV) catalyst was less effective. The formate apparently reduced the Pd(II) to metal, as tests with dispersed palladium metal showed. Palladium or platinum metal, deposited on anion exchange resin, also could mediate formate reduction of Np(V) in 2 to 5 $\underline{M}$ NaOH; about 80% reduction was observed.

6.4.2 Organic Oxidation

Destruction of organic complexing agents in alkaline solution was tested using chemical oxidation. The oxidants tested, peroxide, persulfate, and hypochlorite, have oxidation potentials of about 0.9, 2.0, and 0.9 V, respectively. The effects of various catalysts on these oxidants also were investigated.

Like hydrogen peroxide in acid, the hydroperoxide anion, HO_2^-, in alkaline solution can act both as an oxidant and as a reductant; i.e., it can disproportionate. In NaOH solution, it was found that hydroperoxide by itself had no effect on EDTA, HEDTA, or citrate at temperatures up to 80°C. Various transition metal ions [Co(II), Ni(II), Cu(II), Fe(III), Mn(II), Cr(III), V(V), Mo(VI), and $Fe(CN)_6^{3-}$], as well as Pb(II) and Bi(III), were tested as potential catalysts to mediate oxidation by hydroperoxide in 0.5 to 5 $\underline{M}$ NaOH. Though vigorous generation of oxygen occurred by hydroperoxide disproportionation, no decrease in EDTA concentration was found at 25 to 40°C. These results also indicate that oxidation by oxygen bubbling does not significantly decrease EDTA concentration at these conditions.

In the presence of Co(II) and at 80°C, however, hydroperoxide oxidizes HEDTA and EDTA (but not citrate). Oxidations are improved by stepwise addition of hydroperoxide (introduced as H_2O_2 solution) so that autocatalytic disproportionation is decreased. Higher temperatures, higher Co(II) concentrations, and lower NaOH concentrations favor oxidation. It was demonstrated that the active oxidant is Co(III); thus hydroperoxide oxidizes Co(II) to (III). Evidently, the oxidation involves formation of a Co(III)/organic complex. Tests also showed that nitrite, a ubiquitous waste component and potential sink for any added oxidant, has no effect on EDTA oxidation but decreases HEDTA oxidation.

Persulfate was found to be a vigorous oxidant for all organic compounds tested (EDTA, HEDTA, citrate, glycolate, even oxalate). The effectiveness of persulfate was improved with increasing NaOH concentration and greatly improved by increasing temperature to 80 or 90°C. The effect of NaOH concentration is illustrated in Figure 6.3 for EDTA. Catalysts [Ag(I) and $Fe(CN)_6^{2-}$] also enhance the effectiveness of persulfate by decreasing its induction time; other potential catalysts [V(V), Mn(II), Ni(II), Cu(II), Fe(III), Pd(II), Co(II), Mo(VI), Bi(III)] were not effective. Nitrite causes parasitic loss of persulfate.

The complexants EDTA and HEDTA also can be destroyed by hypochlorite oxidation, HEDTA somewhat better than EDTA. Catalysts [Ni(II), Cu(II), Co(II), Mn(II), V(V), Fe(III), Cr(III), and Mo(VI)] had no effect on the extent of the oxidation reaction. Increasing NaOH concentrations increased EDTA and HEDTA destruction by hypochlorite.

6.5 Isolation of Technetium from Alkaline Solutions

The goal of this task was to investigate the removal of technetium, present as pertechnetate, from alkaline solutions by coprecipitation and by deposition on active metals. Pertechnetate removal from alkaline solution by electrodeposition, solvent extraction, and ion exchange has been and continues to be examined by other researchers in the DOE complex. Therefore, investigations by the IPC/RAS researchers (VF Peretrukhin, VI Silin, IG Tananaev, AV Kareta, and VE Trushina) did not proceed along these avenues. Associated investigations also were performed on coprecipitation removal of strontium and cesium and removal of neptunium and plutonium by sorption on active metals. The results of this task have been published (Peretrukhin et al. 1997).
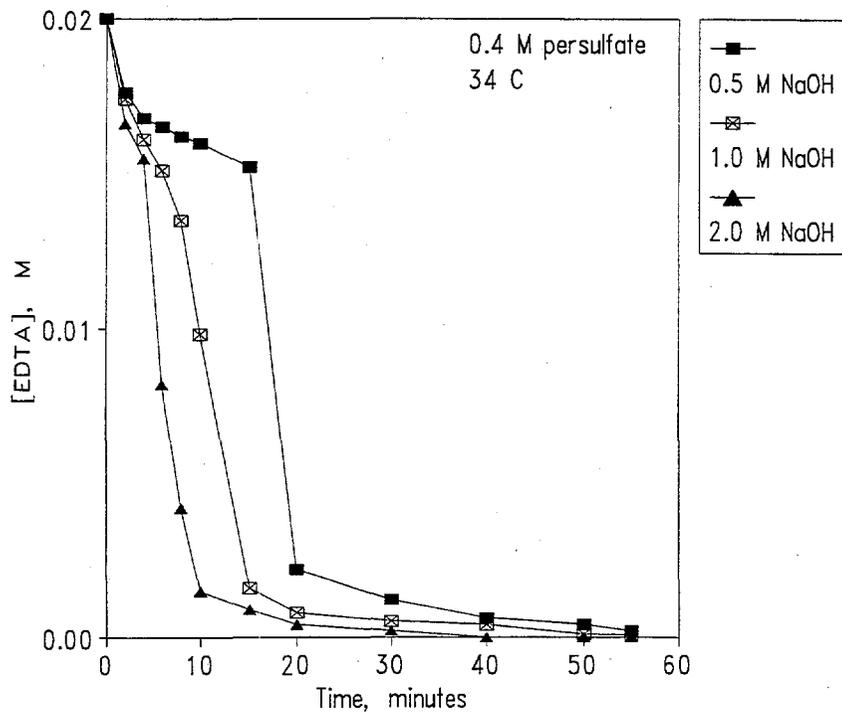
Figure 6.3. Oxidation of EDTA by Persulfate

6.5.1 Deposition on Active Metals

Deposition of technetium from alkaline solution onto active metals, caused by contact reduction of pertechnetate to low solubility Tc(IV) or (V) species, has been tested on a number of metals (lead, zinc, tin, lead/tin, lead/tin/antimony, and chromium). The metals must satisfy two criteria to achieve contact reduction: have a potential below that of pertechnetate reduction and not undergo passivation at the metal surface. The selected metals meet these criteria; other metals (aluminum and iron) have been investigated by other researchers and were not tested. Tests also were performed using neptunium and plutonium to determine whether these electroactive radioelements could be removed by contact reduction.

Decontamination factors for technetium from simple NaOH solutions onto zinc metal increase from about 1.4 to 5.7 as the NaOH concentration increases from 0.5 to 3.5 $\underline{M}$. Other metals showed lower sorption. The DFs found for neptunium and plutonium in similar conditions decrease with increasing NaOH concentration; plutonium is also sorbed better and at a higher rate than neptunium on all studied metals. In tests with simulated wastes containing nitrate, nitrite, organic agents, and chromate, much lower DFs are observed. Chromate has the largest effect on electroless deposition because reduction to Cr(III) and precipitation of the corresponding hydroxide fouls the active metal surface.

6.5.2 Technetium Coprecipitation

Tests of pertechnetate coprecipitation were performed with agents and conditions found most effective for neptunium and plutonium removal from alkaline solution by homogeneous coprecipitation by decomposition of alkali-soluble precursors (Method of Appearing Reagents; Krot et al. 1996).

6.10

Decontamination factors did not exceed 7 for pertechnetate removal from NaOH solution using the carriers $Cr(OH)_3$, $Mn(OH)_2$, $Co(OH)_2$, $Co(OH)_3$, and Na_2UO_4 under conditions that provide DFs in the hundreds for plutonium. These results are not surprising for carriers produced in the absence of chemical reductants but are disappointing for those requiring reductants and their expected formation of less soluble technetium(V).

Removal of cesium and strontium from NaOH solution by homogeneous coprecipitation also was tested. Cesium removal by the transition metal carriers was insignificant and removal by Na_2UO_4 was no more than 13%. Strontium DFs were 20 to about 150 using Na_2UO_4 carrier and lower for the transition metal carriers. The strontium could be readily leached from $Fe(OH)_3$ and $Co(OH)_3$ precipitates using mixed 0.05 $\underline{M}$ NaOH and 0.05 $\underline{M}$ EDTA solution illustrating the susceptibility of strontium to complexation.

More encouraging coprecipitation results were obtained for iron compound precursors not examined previously at the IPC/RAS for neptunium and plutonium removal. One precursor was ferrous ammonium sulfate solution. Upon introduction to the alkaline test solution, the iron(II) readily oxidizes to the (III) state and then precipitates as amorphous $Fe(OH)_3$. Because of the speed of the oxidation and precipitation, homogeneous coprecipitation is not achieved and removal efficiencies cannot be optimum.

However, the iron(II) evidently reduces pertechnetate. With this Fe(II) agent, pertechnetate DFs from 300 to 25 are found in 1 to 4 $\underline{M}$ NaOH. Combined iron(III) salt and hydrazine gives slower and less complete reductive coprecipitation. Lower DFs also are obtained with simulant wastes containing mixtures of inorganic and organic salts found in Hanford Site tank wastes. Chromate is the most disruptive because of its ready consumption of the Fe(II) reducing capacity. Reduction of highly soluble Cr(VI) to poorly soluble Cr(III) also is undesirable in itself because of the deleterious effects of chromium on high-level waste glass.

Parallel tests of technetium and plutonium capture by reductive coprecipitation by iron(II), sometimes abetted by hydrazine reductant, were performed using a comprehensive simulant waste containing hydroxide, nitrate, nitrite, carbonate, aluminate, phosphate, fluoride, chloride, chromate, EDTA, glycolate, and citrate. Plutonium removal was nearly complete and was much higher than that of technetium. Removals of both plutonium and technetium increased with increasing reductant concentration. Chromate, followed by the organic complexing agents, again was found to have the most deleterious effects on reductive coprecipitation.

6.6 Laboratory Testing at PNNL

Laboratory tests were conducted at PNNL to examine the effects of chemical components on the solubility of plutonium in low-alkalinity simulated Hanford Site tank wastes. Besides adding to the knowledge of plutonium behavior in tank waste, these studies were performed to support work at the IPC/RAS initiated in June 1997 on the behavior of plutonium under sludge-forming conditions. Previous studies examined this question in highly alkaline waste ranging from 1 to 4 $\underline{M}$ NaOH (Delegard and Gallagher 1983) and at higher hydroxide concentrations (Delegard 1985). In the present studies, tests were performed in the range pH 10 to pH 13 (0.1 $\underline{M}$ NaOH). Many sludge-bearing tanks contain wastes in this pH range. Soluble waste components investigated in the low alkaline range were sodium salts of nitrate, nitrite, (bi)carbonate, phosphate, fluoride, sulfate, and EDTA.

A statistical test design was employed to identify which of the listed components significantly affects plutonium solution concentration. Because of the large number of variables (components) being examined, a balanced two-level fractional factorial experimental design was used involving 16

experiments and four replicate experiments at the design center point (Murphy 1977). The concentrations of the solution components (or pH) were varied widely over values observed in genuine tank waste within the constraints of component concentration imposed by precipitation of low solubility double salts (e.g., phosphate and fluoride established by $Na_7F(PO_4)_2 \cdot 19 H_2O$; Herting 1996) or by unidentified salts in high ionic-strength sodium salt solutions (nitrate, nitrite, carbonate, and sulfate) (Barney 1976).

6.6.1 Experimental Materials and Methods

Purified plutonium stock solution, test solutions containing varying concentrations of Hanford Site tank waste components, and experimental and analytical techniques were required in this study. The experimental materials and methods used for these tests are described below.

Plutonium

Plutonium stock in nitric acid solution was purified of contaminants by anion exchange. The plutonium was eluted from the anion exchange column with dilute nitric acid; reductants were not used. The eluate was made 6 $\underline{M}$ in HNO_3 and residual Pu(VI) (formed by disproportionation) adjusted to the (III) and (IV) state by addition of H_2O_2 solution. Gamma energy analyses of the plutonium showed it to be 0.0274% [238]Pu, 94.36% [239]Pu, 5.22% [240]Pu, and 0.396% [241]Pu (all in atom%). No direct measurement of [242]Pu is possible by gamma energy analysis, but its contribution to the plutonium chemical concentration and alpha activity is low. The valence- and acid-adjusted stock solution was about 25 g Pu/L.

Aliquots of the mixed Pu(III)/(IV) solution (10 mg Pu each) then were delivered to 15-mL capped polycarbonate centrifuge test tubes. Sodium hydroxide solution (1 $\underline{M}$) was added slowly, with stirring, to each plutonium aliquot. The plutonium precipitated; the Pu(III) also rapidly oxidized in the alkaline solution so that the solids were bright green characteristic of Pu(IV) hydrous oxide. The plutonium precipitate was centrifuged, the supernate discarded, and the solids washed twice with distilled/deionized water (by mixing, centrifugation, and decantation).

Solutions for Parametric Tests

Test solutions were prepared from distilled/deionized water and reagent chemicals ($NaNO_3$, $NaNO_2$, $NaHCO_3$, Na_2HPO_4, NaF, Na_2SO_4, $Na_4EDTA \cdot H_2O$, and $NaOH$). The 17 compositions for the statistically designed parametric tests, given in Table 6.1, were completely dissolved in these room temperature experiments. The components' high and low concentrations ranged over a factor of 100 for nitrate, (bi)carbonate, phosphate, fluoride, sulfate, and EDTA. Because of the possible action of nitrite to control plutonium valence, the concentration range studied for this component was 10,000 so that the low concentration (0.0002 $\underline{M}$) was expected to be below that required to electrochemically buffer the solution. The pH range (10 to 13; a factor of 1,000) reflects the pH of many sludge-bearing tanks and expands the alkalinity range (1 to 15 $\underline{M}$ NaOH) examined in previous plutonium solubility studies (Delegard and Gallagher 1983; Delegard 1985). The pH 10 solutions were adjusted using a calibrated pH meter and by addition of NaOH or HNO_3 solutions, as required. The pH 13 solutions were prepared by making the tests 0.1 $\underline{M}$ in NaOH. The effect of aluminate was studied in previous studies but was not investigated in the present tests because of its low solubility in pH 10 to 13 solution.

To each aliquot of washed Pu(IV) hydrous oxide were added 5000 μL of test solution (i.e., about 8.4×10^{-3} $\underline{M}$ total plutonium was present in each test). Green solid plutonium residue remained in all tests. The suspensions were agitated periodically by vortex stirring.

Table 6.1. Solution Composition Test Matrix

| Test | Component Concentration, $\underline{M}$ | | | | | | | pH |
	NO_3^-	NO_2^-	$(H)CO_3^{(-)2-}$	$(H)PO_4^{(2-)3-}$	F^-	SO_4^{2-}	EDTA	
1	0.02	0.0002	0.005	0.0004	0.0002	0.0001	0.001	10
2	2	0.0002	0.005	0.0004	0.02	0.0001	0.1	13
3	0.02	2	0.005	0.0004	0.02	0.01	0.1	10
4	2	2	0.005	0.0004	0.0002	0.01	0.001	13
5	0.02	0.0002	0.5	0.0004	0.02	0.01	0.001	13
6	2	0.0002	0.5	0.0004	0.0002	0.01	0.1	10
7	0.02	2	0.5	0.0004	0.0002	0.0001	0.1	13
8	2	2	0.5	0.0004	0.02	0.0001	0.001	10
9	0.02	0.0002	0.005	0.04	0.0002	0.01	0.1	13
10	2	0.0002	0.005	0.04	0.02	0.01	0.001	10
11	0.02	2	0.005	0.04	0.02	0.0001	0.001	13
12	2	2	0.005	0.04	0.0002	0.0001	0.1	10
13	0.02	0.0002	0.5	0.04	0.02	0.0001	0.1	10
14	2	0.0002	0.5	0.04	0.0002	0.0001	0.001	13
15	0.02	2	0.5	0.04	0.0002	0.01	0.001	10
16	2	2	0.5	0.04	0.02	0.01	0.1	13
17 to 20	0.2	0.02	0.05	0.004	0.002	0.001	0.01	11.5

Sampling and Analysis

Plutonium concentrations were determined by alpha spectrometry using liquid scintillation analysis. The instrument was a Packard model 2500 TR/AB (Packard Instrument Company, Inc., Meriden CT). The liquid scintillation cocktail was Ultima Gold XR (also Packard Instrument Company, Inc.).

Several tests were performed to calibrate and check the performance of the scintillation analyzer. First, an alpha "window" was set to separate the alpha spectrum from the significant beta activity peak arising at low energies from decay of [241]Pu. The alpha detection efficiency above 100 counts per minute was 97±1%, based on comparing the gamma energy analysis with the liquid scintillation results for aliquots of the gamma energy analyzed acidic plutonium stock. Because this is within the analytical error in the gamma energy analysis, the liquid scintillation counting efficiency was taken to be 100%. The background-corrected rates showed linearity at least between 80 and 800,000 disintegrations per minute.

Tests showed alpha detection efficiencies were unaffected by added sodium salts (test solution number 16) to at least 2.5 millimoles sodium (at least 500 μL sample). However, it was found that with a few hours' time, nitrite interacted with the scintillation cocktail to produce a yellow color that broadened the alpha peak and shifted it to lower energies. The nitrite interference was removed by adding nitric acid, destroying the produced nitrous acid (and nitrite) by disproportionation. The scintillation cocktail was then added and the samples counted. The cocktails with sample were clear (not turbid) in all cases.

The test solutions were sampled periodically beginning at one-day's contact time. The test solution aliquots for analysis (generally 100 or 200 μL) were clarified of plutonium solids by filtration through Microfilterfuge centrifuge filters, model 7016-028 (Rainin Instrument Co., Woburn, MA). The filter membranes (30,000 nominal molecular weight pore size) are constructed of alkali-resistant polysulfone in polypropylene centrifuge cones and caps. Filtration of test solution #17 with similar filters of other pore sizes (10,000, 100,000, and 300,000 molecular weight; models 7016-027, -029 and 030, respectively) gave results experimentally indistinguishable from those obtained with the 30,000 molecular weight filter. A single analysis of solution #8 using a 0.45 μm pore-size nylon filter (Microfilterfuge model 7016-022) also gave results matching those obtained with the 30,000 molecular weight filter.

Visible absorption spectra of filtered solutions were obtained with a Spectral CCD Array UV-Vis spectrophotometer (Spectral Instruments Inc., Tucson, AZ). The crystallinity and identity of the plutonium solid phase was determined with a Scintag X-ray diffractometer. The solid sample for x-ray diffraction analysis was first stripped of mother liquor using the centrifuge filter. The solids were not washed (to prevent possible alteration of the solid phase) and were suspended in an amyl acetate solution of collodion. The suspension was pipetted onto a specially prepared glass slide and the amyl acetate allowed to evaporate. The residual collodion fixed the radioactive plutonium to the slide to prevent contamination of the diffractometer.

6.6.2 Results and Discussion

The plutonium concentration and pH data, the statistical analysis, and discussion of test results are summarized.

Plutonium Concentration and pH Data

The plutonium concentrations determined for the 20 samples as a function of time are given in Table 6.2. Also given are the measured pHs. The pH was adjusted with concentrated NaOH solution for four test solutions (5, 7, 14, and 16) at three days' contact when it was discovered they were inadvertently below the target pH 13. The plutonium concentrations in the samples taken after the pH adjustment decreased about a factor of 100 from their previous values.

The plutonium concentrations as a function of time are given for selected test solutions in Figure 6.4. The concentrations seem to be near equilibrium for most tests, as shown by the asymptotic approach to horizontal slopes. But the data for tests 17 to 20, which are run at the concentration geometric midpoints for all components, still seem to be rising. The pH values for tests 1 and 17 to 20 are decreasing with time. These five tests have relatively low concentrations of pH-buffering or -maintaining components [hydroxide, (bi)carbonate, EDTA] and thus are more susceptible to pH drift possibly caused by absorption of atmospheric carbon dioxide. The data for tests at lower concentrations (tests #4 and #11) are more scattered, reflecting approach to analytical detection limits.

Table 6.2. Plutonium Concentrations and pHs in Test Solutions

Test	[Pu], μM							pH		
	1 day	3 days	7 days	14 days	28 days	60 days	70 days	3 days	28 days	78 days
1	0.411	0.362	0.561	1.86	3.20	2.17	1.79	9.89	8.70	8.24
2	0.0699	0.0893	0.114	0.127	0.157	0.285	0.430	12.62	12.60	12.49
3	0.700	0.741	1.11	1.61	2.52	5.48	7.31	10.11	10.11	9.71
4	0.0154	0.00243	0.00211	0.00613	0.00424	0.00536	0.0225	12.56	12.62	12.53
5	44.3	53.7	0.343	0.289	0.239	0.219	0.298	10.10, 13.03	13.09	12.98
6	40.4	52.2	65.0	81.3	104	150	163	9.99	10.01	9.99
7	45.2	67.2	0.241	0.0802	0.0869	0.20 [a]	0.449	8.88, 13.23	13.33	13.26
8	43.6	59.8	85.9	117	161	241	267 [b]	9.89	9.27	9.33
9	0.120	0.134	0.144	0.171	0.210	0.336	0.412	12.61	12.56	12.43
10	0.313	0.201	0.211	0.215	0.228	0.292	0.398	9.90	9.81	9.46
11	0.103	0.00138	0.00211	0.00124	0.00087	0.00306	0.0106	12.36	12.38	12.28
12	1.09	1.08	1.06	1.16	1.56	2.84	3.70	10.06	10.17	9.92
13	27.4	20.2	37.8	50.2	60.3	80.7	87.9	9.91	9.92	9.86
14	44.3	48.8	0.683	0.713	0.702	0.710	0.970	8.69, 13.16	13.20	13.13
15	23.2	27.7	33.8	37.2	39.1	47.4	51.5	9.87	9.91	9.85
16	32.9	48.9	0.401	0.129	0.459	0.61 [a]	0.806	8.90, 13.16	13.32	13.23
17	0.147	0.149	0.211	0.314	0.570	1.91	2.77	11.59	11.33	10.71
18	0.576	0.102	0.160	0.252	0.398	0.835	1.54	11.58	11.36	10.73
19	0.150	0.130	0.194	0.294	0.548	1.97	2.95	11.58	11.31	10.71
20	0.130	0.119	0.175	0.255	0.524	1.64	2.81	11.59	11.23	10.62

(a) Estimate.
(b) 287 μM Pu at 77 days.

Statistical Data Interpretation

The solution concentration data were interpreted for each sampling time, seven days and later (i.e., when pH corresponded to the target values), by the statistical analysis technique forming the basis of the test design (Murphy 1977). The analysis determined the influences on plutonium concentration of varying concentrations of the seven waste components and the pH. Because these parameters were
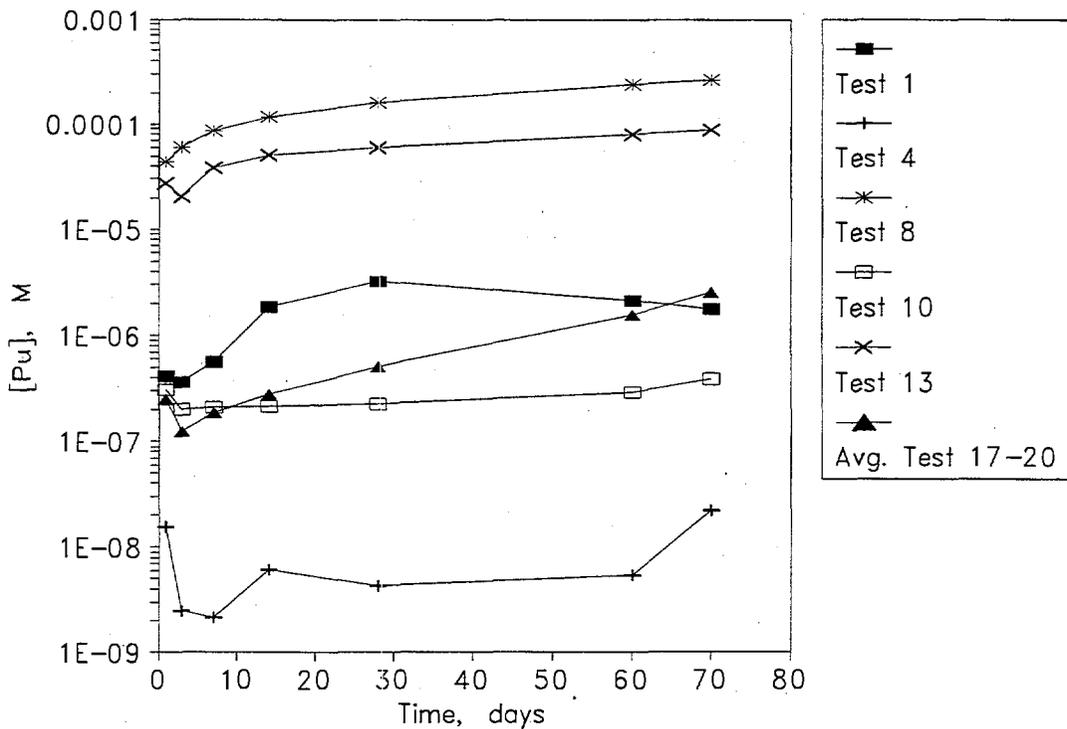
Figure 6.4. Plutonium Concentrations in Selected Tests as a Function of Time

varied on a logarithmic basis, the interpretation was based on the logarithms of the plutonium concentrations. The test matrix and statistical method can be understood better by reference to the test and analysis design given in Table 6.3. The + and - symbols indicate whether the component was at its high (+) or low (-) value for the particular test.

The effect of a component on plutonium concentration was determined by adding the logarithms of plutonium concentrations found for tests having the component at its high value, subtracting the sum of the log plutonium concentration for tests having the component at its low value, and dividing by 8 (16 tests/2). This value, called the factor effect, thus is the average impact of increasing the concentration (or pH) from its low to its high level. Because the test matrix design is balanced, the influences of all the other components are cancelled (i.e., are at high levels for four tests, and at low levels for four tests, for each of the positive and negative sums used to calculate the factor effect of the component of interest). The factor effects calculated for each component are called assigned factor effects.

Table 6.3. Test Matrix and Data for 70-Day Tests

Test	log[Pu], $\underline{M}$	Components / Assigned Factors								Unassigned Factors						
		NO_3^-	NO_2^-	$(H)CO_3^{(-)2-}$	$(H)PO_4^{(2-)3-}$	F^-	SO_4^{2-}	EDTA	pH	x	x_2	x_3	$_1x_4$	x_5	x_6	x_7
1	-5.747	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+
2	-6.366	+	-	-	-	+	-	+	+	-	-	-	-	+	+	+
3	-5.136	-	+	-	-	+	+	+	-	-	-	+	+	-	-	+
4	-7.650	+	+	-	-	-	+	-	+	+	+	-	-	-	-	+
5	-6.526	-	-	+	-	+	+	-	+	-	+	-	+	-	+	-
6	-3.788	+	-	+	-	-	+	+	-	+	-	+	-	-	+	-
7	-6.348	-	+	+	-	-	-	+	+	+	-	-	+	+	-	-
8	-3.573	+	+	+	-	+	-	-	-	-	+	+	-	+	-	-
9	-6.386	-	-	-	+	-	+	+	+	-	+	+	-	+	-	-
10	-6.401	+	-	-	+	+	+	-	-	+	-	-	+	+	-	-
11	-7.979	-	+	-	+	+	-	-	+	+	-	+	-	-	+	-
12	-5.432	+	+	-	+	-	-	+	-	-	+	-	+	-	+	-
13	-4.056	-	-	+	+	+	-	+	-	+	+	-	-	-	-	+
14	-6.014	+	-	+	+	-	-	-	+	-	-	+	+	-	-	+
15	-4.288	-	+	+	+	-	+	-	-	-	-	-	-	+	+	+
16	-6.094	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Factor Effects		0.143	-0.151	1.30	-0.189	-0.060	-0.094	0.571	-1.87	-0.542	0.106	0.294	-0.452	0.171	-0.082	0.134
Pooled Standard Deviation										0.305						

To determine the significance of the assigned factor effects, similar calculations were performed for the unassigned factors (Table 6.3). In this 16-experiment test matrix with eight assigned factors (components), there are seven unassigned factors. The unassigned factor effects are balanced for each component, representing (for each component) as many high as low levels for the positive and negative log[Pu] sums. A pooled standard deviation was then calculated as the root mean square of the unassigned factor effects. A sample calculation is shown in Table 6.3 for the data from the 70-day test.

As shown in Table 6.3, the factor effect found for nitrate was 0.143. This means that the plutonium concentration increased, on average, a factor of $10^{0.143} = 1.39$ by increasing the nitrate concentration 100-fold from 0.02 to 2 $\underline{M}$. This factor effect is less than the pooled standard deviation, 0.305 (based on the unassigned factors), and clearly is not significant. For the 70-day results, factor effects greater than the pooled standard deviation are found for (bi)carbonate (1.30), EDTA (0.571), and pH (-1.87). Thus, increasing (bi)carbonate concentration 100-fold from 0.005 to 0.5 $\underline{M}$ increased plutonium concentration a factor of $10^{1.30}$ or 20-fold; increasing pH to 13 decreased plutonium concentration to $10^{-1.87} = 0.013$ or 1/74 of its value at pH 10.

The statistical significance of the assigned factor effects can be determined better by comparing the observed factor effects with the product of the pooled standard deviation and the Student's t statistic (for seven degrees of freedom of the unassigned factors). The factor effects for the waste components at the 7- to 70-day samplings, and evaluations of their statistical significance, are given in Table 6.4.

The statistical evaluation shows the results to be consistent from sampling to sampling. The statistical test matrix variabilities (pooled standard deviations) are similar (about 0.33; $10^{0.33} \approx$ a factor of 2) at all sampling times.

The factor effects for the individual components also are similar across the 10 weeks of sampling. The effects on plutonium concentration of changing nitrate, phosphate, fluoride, and sulfate concentrations 100-fold are insignificant (less than one standard deviation) at all sampling times. Higher nitrite concentrations (2 $\underline{M}$ instead of 0.0002 $\underline{M}$) seem to correlate with lower plutonium concentration but the effect (a 2- to 3-fold decrease in plutonium concentration) is significant only at 80% or lower confidence interval. Increasing EDTA concentration increases plutonium concentrations about 3- to 4-fold at about the 80% confidence interval.

Clearly, pH and (bi)carbonate concentration have the strongest influence on plutonium compound solubility at all test intervals. The factor effect for (bi)carbonate (about 1.5 on average) is significant at about the 99.5% confidence interval. Increasing (bi)carbonate concentration 100-fold from 0.005 to 0.5 $\underline{M}$ thus increases plutonium concentration about $10^{1.5} \approx$ 30-fold averaged over all experiments. Increasing pH from 10 to 13 decreases plutonium concentration. The factor effect for the pH increase averages about -2.0 (10^{-2} or 100-fold decrease in plutonium concentration) and is significant at greater than the 99.9% confidence interval.

The statistical evaluation shows that varying the concentrations of nitrate, phosphate, fluoride, sulfate, and, to a large extent, nitrite does not significantly affect plutonium concentration. These variables thus may be neglected and the test data analyzed solely in terms of pH and the EDTA and (bi)carbonate concentrations. The 70-day plutonium concentration data (from Table 6.4) are plotted versus (bi)carbonate concentration in Figure 6.5. These data are compared with plutonium concentrations observed in potassium (bi)carbonate solutions (also containing 0.0005 $\underline{M}$ NaNO$_2$) at pH 9 to 10 and at pH 12 or 13 (Yamaguchi et al. 1994).

Table 6.4. Statistical Results and Interpretation

Component	Factor Effects (Standard Deviations)				
	7 days	14 days	28 days	60 days	70 days
NO_3^-	0.08 (0.26)	0.10 (0.29)	0.16 (0.43)	0.16 (0.36)	0.14 (0.47)
NO_2^-	-0.36 (-1.23)	-0.51 (-1.50)[a]	-0.48 (-1.32)	-0.35 (-0.90)	-0.15 (-0.50)
$(H)CO_3^{(-)2-}$	1.65 (5.63)[c]	1.44 (4.23)[b]	1.48 (4.08)[b]	1.47 (4.04)[b]	1.30 (4.27)[b]
$(H)PO_4^{(2-)3-}$	-0.06 (-0.20)	-0.22 (-0.65)	-0.20 (-0.54)	-0.13 (-0.47)	-0.19 (-0.62)
F^-	-0.05 (-0.18)	-0.19 (-0.56)	-0.14 (-0.38)	-0.03 (-0.18)	-0.06 (-0.20)
SO_4^{2-}	-0.07 (-0.24)	-0.06 (-0.16)	-0.03 (-0.08)	-0.06 (-0.26)	-0.09 (-0.31)
EDTA	0.51 (1.75)[a]	0.35 (1.03)	0.51 (1.39)	0.60 (1.83)[a]	0.57 (1.87)[a]
pH	-1.85 (-6.30)[c]	-2.07 (-6.11)[c]	-2.14 (-5.88)[c]	-2.12 (-5.99)[c]	-1.87 (-6.13)[c]
Pooled Standard Deviation	0.293	0.339	0.364	0.370	0.305

(a) Significant at 80% confidence interval (1.415 standard deviations).
(b) Significant at 99.5% confidence interval (4.029 standard deviations).
(c) Significant at 99.9% confidence interval (5.405 standard deviations).

The graph clearly shows the increase in plutonium concentration occurring with increasing (bi)carbonate concentration and with decreasing pH. With the graph, the effect of EDTA on plutonium concentration also becomes clear. At 0.5 M (bi)carbonate, increasing EDTA concentration from 0.001 to 0.1 M has no discernible effect. Under these conditions, carbonate evidently is a better ligand than EDTA for plutonium and EDTA does not appreciably increase plutonium dissolution. The plutonium concentrations at 0.5 M (bi)carbonate also correspond, within experimental error (a factor of two) with concentrations observed or extrapolated from published data (Yamaguchi et al. 1994).

In contrast, at 0.005 M (bi)carbonate, increasing EDTA concentration 100-fold from 0.001 to 0.1 M has a significant effect on plutonium concentration, increasing it about a factor of 10. The effect is greater at pH 13 than at pH 10. In addition, the plutonium concentrations at 0.005 M (bi)carbonate and 0.001 M EDTA (plus varying concentrations of nitrate, nitrite, phosphate, fluoride, and sulfate) at pH 10 and 13 are 30- to 100-times higher than observed for (bi)carbonate solutions in the absence of other complexants (Yamaguchi et al. 1994). In summary, EDTA, at concentrations observed in Hanford Site tank waste, appears to increase plutonium concentrations significantly in low (bi)carbonate solutions. The effect of EDTA is not noticeable at 0.5 M (bi)carbonate, but it is significant at 0.005 M (bi)carbonate.
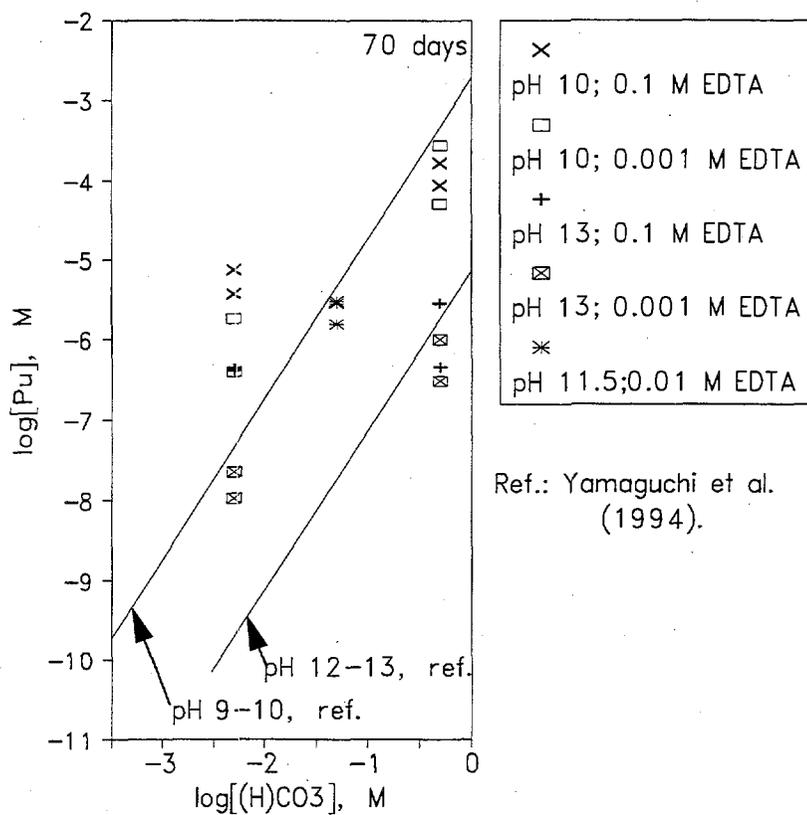
70 days

X
pH 10; 0.1 M EDTA
□
pH 10; 0.001 M EDTA
+
pH 13; 0.1 M EDTA
⊠
pH 13; 0.001 M EDTA
✳
pH 11.5;0.01 M EDTA

Ref.: Yamaguchi et al.
(1994).

pH 12-13, ref.

pH 9-10, ref.

log[Pu], M

log[(H)CO3], M

Figure 6.5. Plutonium Concentrations at 70 Days' Contact

The solid and solution phases were analyzed for the test giving the highest plutonium concentration, test solution 8. The solution was separated at 77 days' contact and found to contain 2.87×10^{-4} $\underline{M}$ plutonium by liquid scintillation spectrometry. The visible spectrum of the filtered solution, given in Figure 6.6, corresponds to Pu(IV) spectra observed by other researchers in sodium bicarbonate solution (Wester and Sullivan 1983; Capdevila et al. 1996) and shows no indication of Pu(VI). The molar extinction coefficient of the prominent peak at 486 nm is about 70 L/mol-cm, corresponding with that reported in recent research (Capdevila et al. 1996). The spectrum has been attributed to the pentacarbonato Pu(IV) complex, $Pu(CO_3)_5^{6-}$ (Capdevila et al. 1996).

Solids separated from test 8 were found to give a broad x-ray diffraction pattern corresponding to PuO_2. The broad pattern indicates the crystallites are small or poorly crystallized and likely incorporate solution water. Because the green plutonium solids were not washed before x-ray analysis, the diffraction pattern also showed that small amounts of entrained $NaNO_3$ and $NaNO_2$ were present.

The solubility and speciation data indicate that in pH 10, 0.5 $\underline{M}$ carbonate solution, plutonium precipitates as $PuO_2 \cdot xH_2O$ and the solution species is $Pu(CO_3)_5^{6-}$. Thus, the dissolution reaction should be

$$PuO_2 \cdot xH_2O + 5\ CO_3^{2-} + (2-x)\ H_2O \rightleftharpoons Pu(CO_3)_5^{6-} + 4\ OH^-$$
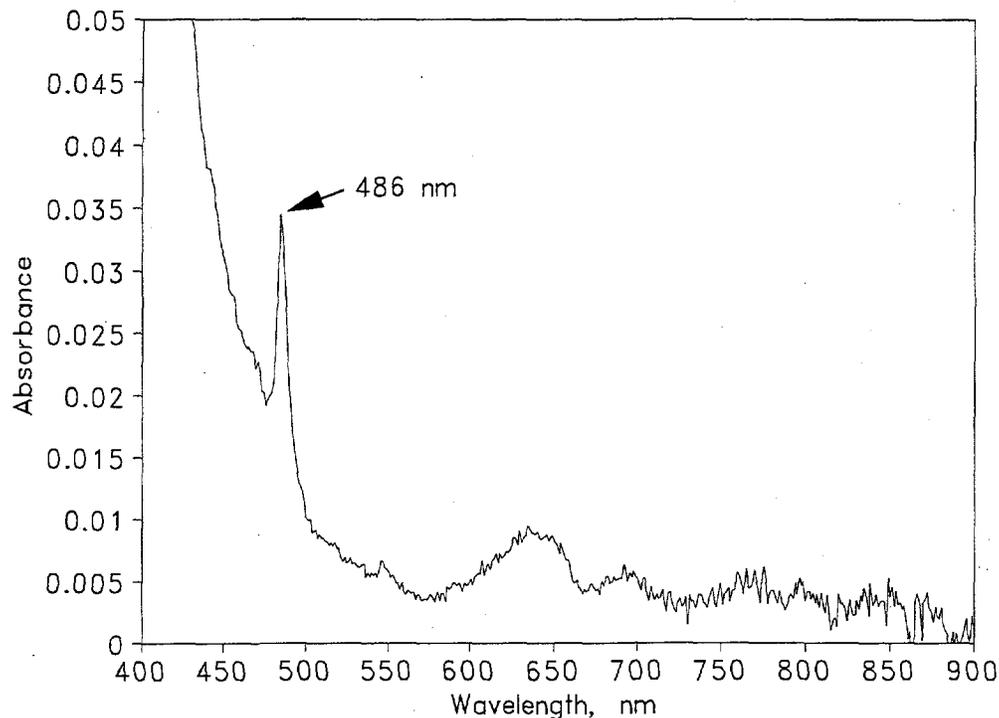
6.20
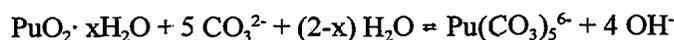
Figure 6.6. Absorption Spectrum of 2.87 x 10^{-4} M Plutonium from Test 8

If this reaction is occurring, however, at a given pH the plutonium solubility should increase with the 5th power of the carbonate concentration. The plutonium concentration dependence on (bi)carbonate, shown in the statistical tests (containing six other components), is only to about the 1st power, while the dependence shown in the work of Yamaguchi et al. (1994) is the 2nd power [the dissolved species $Pu(OH)_2(CO_3)_2^{2-}$ and $Pu(OH)_4(CO_3)_2^{4-}$ are postulated around pH 10 and pH 13, respectively]. Clearly, more investigation of the important plutonium-carbonate system is required to reconcile this divergence in plutonium concentration dependence on (bi)carbonate.

6.6.3 Review of the Effects of Carbonate on Plutonium Concentrations in Genuine Tank Waste

The effects of high concentrations of carbonate on plutonium concentration in mildly and strongly alkaline media were examined by review and comparison of technical literature data and tank waste solution analyses. The findings of Yamaguchi et al. (1994) at pH 12 and 13 have been compared with plutonium solubility tests in carbonate solutions containing 3 to 5 $\underline{M}$ NaOH and with genuine waste solutions containing molar hydroxide concentrations (Delegard 1996). The comparison now has been extended to the findings of Yamaguchi et al. (1994) at pH 9 to 10, to other studies at lower pH in concentrated bicarbonate solutions (Cunningham 1954), and to additional genuine tank waste supernatant solution analyses at high pH.

The various data are presented in Figure 6.7. The data from the diverse scientific publications seem to be consistent. Furthermore, the scientific data at higher pH compare well with analyses of genuine tank waste solution samples. The waste solutions were drawn from Tanks 241-AN-102, 241-AN-107, 241-AY-101, 241-AY-102, and 241-C-106 (Bratzel 1985; Herting 1994; Castaing 1993). These samples all were associated with solid phases with higher concentrations of plutonium (i.e., the solutions could be saturated) and had high pH or contained measurable hydroxide concentrations.
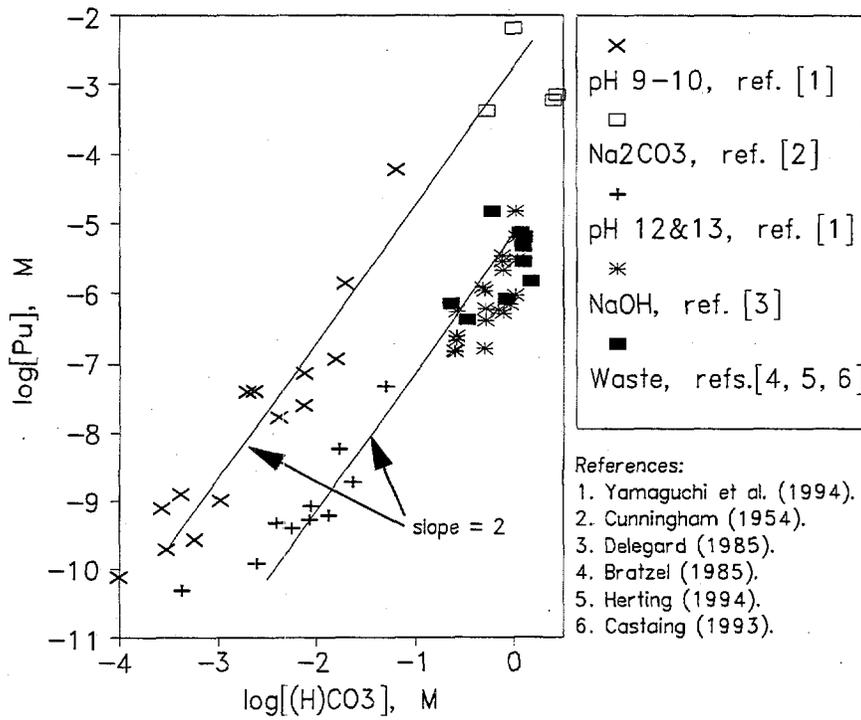

Figure 6.7. Plutonium Concentration as a Function of (Bi)carbonate Concentration

8.0 References

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