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ACTINIDE CHEMISTRY RESEARCH AT ROCKY FLATS

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Chemical Research
Chemistry Research and Development

MASTER

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ENERGY SYSTEMS GROUP
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Golden, Colorado

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Actinide
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SEMINAR TALK FOR PRESENTATION AT FLORIDA STATE UNIVERSITY, MAY 10, AND AT THE ACTINIDE WORKSHOP, AUGUSTA, GEORGIA, MAY 11, 1982.

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ABSTRACT

Actinide chemistry research in the Chemical Research group of Chemistry Research and Development will be described. The group develops new chemical processes for use in actinide purification, recovery, and waste treatment, and provides a fundamental understanding of all process chemistry related to plutonium and americium operations at Rocky Flats. The chemical research involves actinide waste and processing chemistry, separations chemistry, radiation studies, and calorimetry and thermodynamics.

INTRODUCTION

Chemical Research is an 18-member group in the Chemistry Research and Development organization at Rocky Flats (RF). The group is divided into five technical sections, as shown on the first slide. The technical leader for the Physicochemical section is Dr. Frank Oetting; the scope of the activities of this section includes the basic chemistry of pyrochemical processes and the chemical thermodynamics of processes and materials important at RF. The Process Chemistry section, led by Dr. Armen Kazanjian, investigates the chemistry involved in actinide recovery and purification processes, and develops new processes or improves the present processes. Dr. Tony Muscatello and the other members of the Separation Chemistry section investigate new techniques and materials, and improve those currently used for the recovery, separation, and purification of actinides. The Waste Chemistry section develops new processes or improves the current processes for actinide waste treatment, and studies the chemistry of these processes; the technical leader is Dr. Tom Boyd. The Chemical Development section supports the group in the area of process and separations chemistry development, maintains liaison with production and other R&D groups, and coordinates proposals for new areas of chemical research work.

The primary responsibility of the Chemical Research group is to provide fundamental chemical information to the RF organization, to further develop a fundamental understanding of all chemistry-related operations at RF, and to develop new chemical processes for use in production operations. The production operations consist mainly of plutonium and americium recovery processes. I will give an overview of the production processes which we support, as well as a description of the research programs currently underway in Chemical Research.

Actinide Recovery and Waste Treatment Processes at RF

The second slide shows a simplified flow sheet for plutonium recovery operations at RF. Impure plutonium metal is sent through a pyrochemical process to remove elemental impurities, including americium.[1] The waste chloride salt is dissolved; then the actinides are precipitated with carbonate and redissolved to convert from a chloride to a nitrate media.[2]

Impure oxide residues are dissolved in $12M\ HNO_3$-$0.1M$ HF under refluxing conditions and then purified by anion exchange. Very few elements form anions in nitric acid solutions, thus anion exchange is a very effective procedure for purifying plutonium. The hexanitrato anion is sorbed on the resin from a 7M nitric acid solution. A nitric acid wash is used to remove residual impurities from the resin. Dilute nitric acid is used to elute the purified plutonium from the resin. Plutonium is leached from other residues, such as metal and glass, and is also purified by anion exchange. The purified eluate from the anion exchange process is precipitated with hydrogen peroxide. The plutonium peroxide is calcined to the oxide, and the plutonium oxide is fluorinated. The plutonium tetrafluoride is finally reduced to the metal with calcium.

Acid waste streams are sent through a nitric acid recovery process and then to a secondary plutonium recovery process using anion exchange. Acid and basic waste streams are combined and sent to waste treatment. The actinides in the aqueous waste are removed by a hydroxide-iron carrier, flocculent precipitation process. The filtrate solution is then evaporated with a spray dryer.

Physicochemical Studies

The Physicochemical section investigates the basic chemistry of pyrochemical processes and the chemical thermodynamics of processes and materials important to RF. For the latter studies, several calorimeters have been utilized.

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[1] Americium accumulates in the plutonium-239 from the decay of the plutonium-241 present.

[2] The americium is purified by a thiocyanate ion exchange process for the Department of Energy Isotope Pool.

The third slide shows the adiabatic calorimeter used to determine the heat capacity and energies of transformations of the alpha, beta, gamma, and delta phase of plutonium metal. The same measurements have been made for delta-stabilized plutonium metal and will be made for the plutonium hydrides, $PuH_{2.0}$ and $PuH_{2.7}$.

The solution calorimeter shown in the fourth slide is an LKB calorimeter reconstructed with new integrated circuitry and logic functions to automate and improve data acquisition. Five measurements of the enthalpy of neutralization of NBS SRM 724 (TRIS) in 0.1$\underline{M}$ HCl gave the average result of (-7110.8 ± 3.3) cal mol^{-1}. This is in excellent agreement with the literature value of (-7108 ± 6) cal mol^{-1}, which demonstrated the reliability of the improved calorimetry system. The calorimeter has been used to determine enthalpy of solution of plutonium and its hydrides.

A critical assessment and compilation of the thermodynamic properties of all actinide elements and compounds is in progress (slide 5). The compilation is being published by the International Atomic Energy Agency, and consists of 14 parts.

Process and Separations Chemistry

The Processing Chemistry team is responsible for radiation studies. Our facilities are capable of irradiating materials with gamma, beta, and alpha radiation sources. The next slide (6) shows our gamma cell. The effect of high energy radiation on numerous materials exposed to the radiation environment at RF have been investigated. The materials include ion exchange resins, solvents, solvent extractants, machining oils, and plastics. Photochemical valence adjustment methods for plutonium have also been studied.

Other process chemistry and development work has been involved in the dissolution and precipitation operations (slide 7). Hydrochloric acid dissolution of difficult-to-dissolve residues is being investigated. Carbonate precipitation and cation exchange are being examined to convert the plutonium from a chloride to a nitrate system. The chemistry of the plutonium peroxide precipitation process is being studied, as well as alternative precipitation processes such as oxalate, carbonate, fluoride, and thermal denitration. Processes are being examined to process Pu/U and Pu/Np residues.

The objective of the Pu/U work is to determine the feasibility of reducing the plutonium in uranium product from the batch contacter solvent extraction process at RF, using either extraction chromatography or anion exchange techniques. A limit of 1.4 μg plutonium per gram of uranium has been established as a receiving requirement for uranium oxide shipped at Oak Ridge National Laboratory for further processing.

An extraction chromatography process has been developed involving selective adsorption of uranium onto a column of Amberlite XAD-4 resin impregnated with tributyl phosphate (TBP). Trivalent plutonium, reduced with ferrous sulfamate (FeSA) does not significantly sorb on the resin. After uranium loading, the resin is washed with $0.1\underline{M}$ FeSA in $3\underline{M}$ HNO_3 to remove residual plutonium. Uranium is then eluted from the resin with $1\underline{M}$ ammonium sulfate.

A new anion exchange resin Amberlite IRA-938 has been tested on a laboratory scale and is currently being tested on a production scale for plutonium recovery at RF. Amberlite IRA-938 had the best plutonium capacity and elution performance of the 20-50 mesh resins tested. Since the resin is extremely porous, elemental impurity separation is expected to increase. Tests so far indicate this to be the better process.

The objective of the Pu/Np work is to separate and recover plutonium from neptunium-plutonium residues to provide a plutonium product containing less than 100 μg neptunium per gram plutonium. Both anion exchange (Amberlite 938) and solvent extraction (TBP) techniques are being investigated.

Plutonium-neptunium oxide was dissolved in nitric acid and the solution adjusted to $7.2\underline{M}$ HNO_3. This feed was then passed over a 7.62 cm diameter column containing 3.4 l of Amberlite IRA-938 (20-50 mesh) anion exchange resin preconditioned with 7.2M HNO_3. After both plutonium and neptunium were loaded onto the resin, the plutonium was washed from the column with 5.4M HNO_3-0.1 FeSA (ferrous sulfamate). The neptunium was then eluted with 0.35M HNO_3. A flow rate of <2 ml min^{-1} cm^{-2} was maintained throughout the tests.

The extraction of plutonium in 4.5M HNO_3 using 30 vol % TBP (tributylphosphate) dodecane was also tested. The feed solution was adjusted to 0.01M NO_2^- with sodium nitrate prior to plutonium extraction. Nitrite oxidizes neptunium to the non-extractable pentavalent oxidation state. Residual neptunium is scrubbed from the loaded organic with 3M HNO_3-0.01M NO_2^-. Plutonium is then stripped from the organic with 0.35M HNO_3-0.1M FeSA. An aqueous-to-organic ratio of 0.5, 0.2, and 0.5 were used for the extraction, scrub, and strip steps, respectively.

Results of the preliminary tests using anion exchange and solvent extraction showed that only the former method gave a product of <100 μg neptunium per gram plutonium.

The Separations Chemistry section evaluates new techniques and materials for the separation, recovery, and purification of actinides. New anion and cation exchange resins, sorbents for extraction chromatography and waste treatment processes, and new solvent extractants are now being studied. The solvent extraction work will be described in more detail in another presentation. The next slide (9) shows the flow sheet of a combined anion exchange - extraction chromatography process for the recovery and purification of americium from Molten Salt Extraction residues. The process has been successfully demonstrated on a laboratory and pilot plant scale. The extraction chromatography process uses DHDECMP (dihexyl-N,N-diethylcarbamoylmethylenephosphonate) sorbed on Amberlite® XAD-4 resin. The process effectively separates and purifies americium from impurities such as aluminum, calcium, chloride, copper, fluoride, iron, lead, magnesium, plutonium, potassium, sodium, and zinc. A total of 100 g of americium oxide has been produced during pilot plant testing. The product oxide contained 96.5 wt % AmO_2, with 0.08 wt % Pu and less than 0.06 wt % of any individual impurity element.

Waste Chemistry

The Waste Chemistry team investigates the chemistry involved in current waste treatment and waste management processes to obtain a more complete understanding of the process. They also develop new processes and improve current waste treatment processes.

A ferrite waste treatment process is being investigated to determine if it can more effectively remove actinides from waste solution with less solid waste generation than the flocculant precipitation method presently used at RF.

Ferrite waste treatment was shown by other investigators to be very effective and economical in removing heavy metal ions and particulate matter from liquid waste at electrical generating plants. This work prompted the investigation of this technique for treatment of low-level actinide waste at RF.

Investigation of ferrite waste treatment at RF was begun in connection with the Soil Decontamination Program in FY 1980. Preliminary work showed that low levels of plutonium could be removed by adsorption on metal ferrites dispersed in steel wool or by precipitation as the plutonium ferrite compound. Ion column effluent solutions treated with ferrite showed reduction of plutonium levels from 1.5×10^{-3} g/l to 5.9×10^{-7} g/l and americium levels from 8.6×10^{-7} g/l to 1.2×10^{-9} g/l.

Ferrite was introduced into aqueous media by two techniques. With the *in situ* method, ferrite was formed within the actinide-containing solution by addition of Fe(II), Fe(III), and sodium hydroxide. With the preformed ferrite method, ferrite solids were prepared separately and added to the actinide solution.

Only ferrites containing one Pu(III) or Am(III) species per ferrite molecule were obtained. X-ray diffraction analyses showed these "ferrites" to be mixtures of γ-Fe_2O_3 and a species isomorphous with known transition metal ferrites.

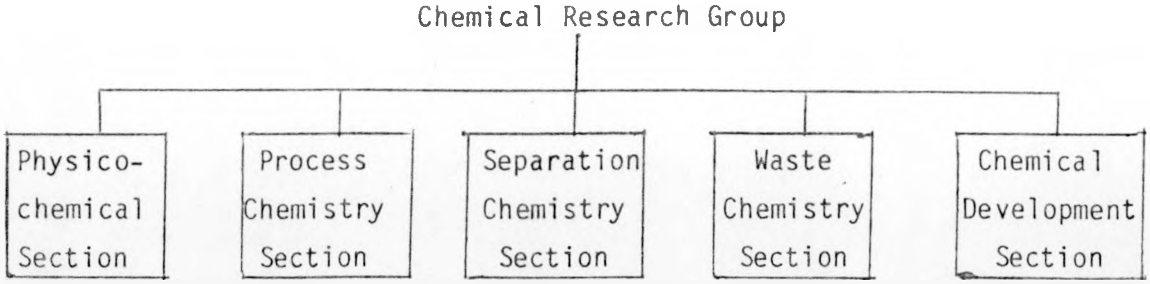
Using ferrite waste treatment, plutonium and americium concentrations in aqueous media can be lowered consistently by three to five orders of magnitude in one treatment step. No difference was observed in the level of plutonium removal irrespective of whether it was ionic Pu(III), Pu(IV), or polymeric plutonium. Maximum actinide removal was observed over a pH range of 9 to 13.

Both preformed and in situ ferrite lowered plutonium concentrations in simulated process waste from 10^{-4} g/l to 10^{-8} g/l in one treatment step. Two or three flocculant precipitations, as currently used for waste processing, were required to achieve the same result. Ferrite waste treatment produced 4.1 g/l solids, while production waste processing during the past year, using the flocculant process, produced 7.9 g/l. Beryllium was identified as a major interference in ferrite waste treatment.

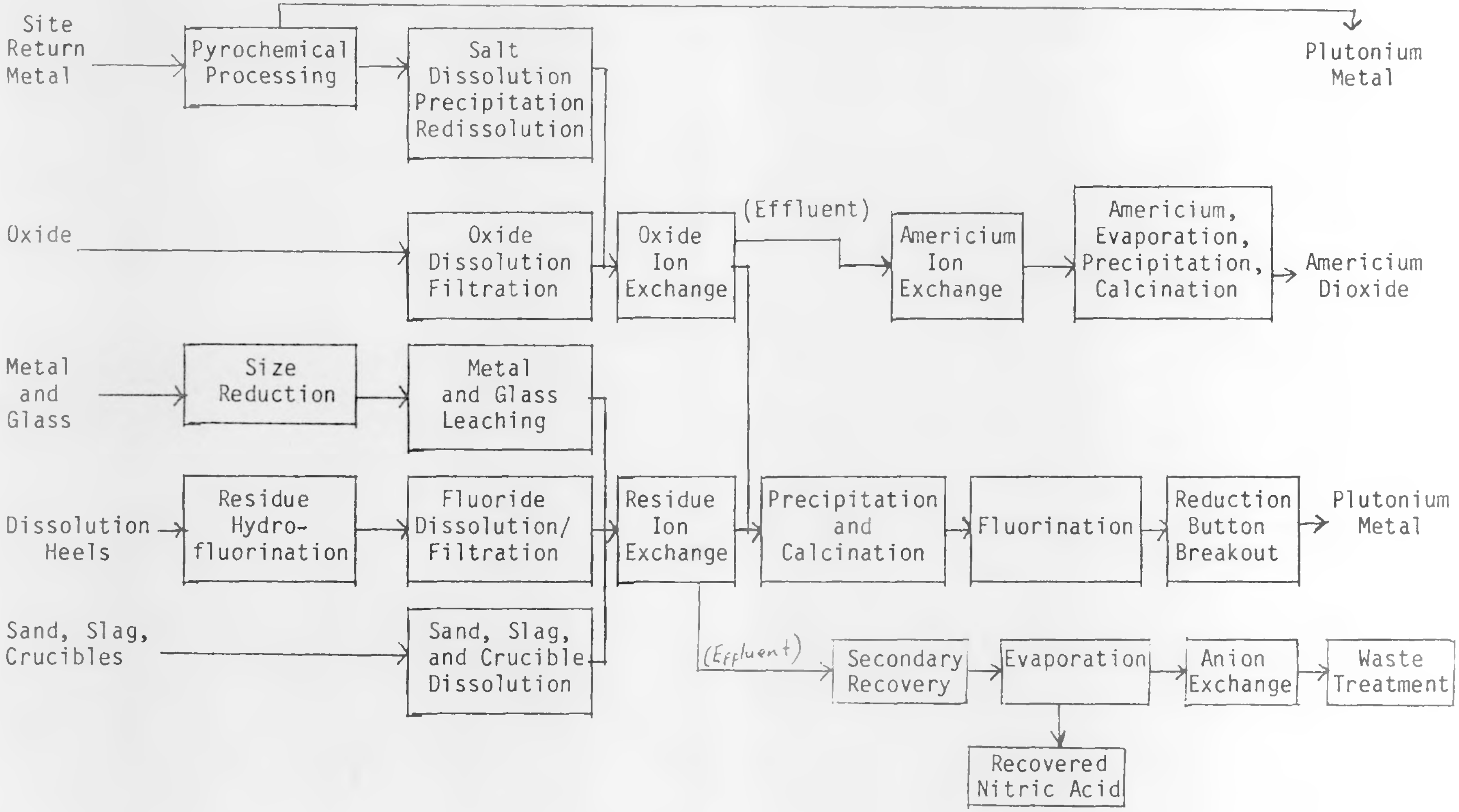
The ferrite waste treatment method will be demonstrated on a larger scale and will be applied using a continuous process. Purer actinide ferrites will be prepared for structural determination. Preliminary immobilization studies on ferrite solids will be conducted and the ferrite process will be applied to other waste media.

As I hopefully have shown, the Chemical Research group has a large variety of actinide process chemistry projects underway. The work will certainly add to our understanding of actinide chemistry and will result in actinide process improvements.

Slide 1



- Chemical Research Group
  - Physico-chemical Section
  - Process Chemistry Section
  - Separation Chemistry Section
  - Waste Chemistry Section
  - Chemical Development Section


Site Return Metal
Pyrochemical Processing
Salt Dissolution Precipitation Redissolution
Plutonium Metal

Oxide
Oxide Dissolution Filtration
Oxide Ion Exchange
(Effluent)
Americium Ion Exchange
Americium, Evaporation, Precipitation, Calcination
Americium Dioxide

Metal and Glass
Size Reduction
Metal and Glass Leaching

Dissolution Heels
Residue Hydro-fluorination
Fluoride Dissolution/ Filtration
Residue Ion Exchange
Precipitation and Calcination
Fluorination
Reduction Button Breakout
Plutonium Metal

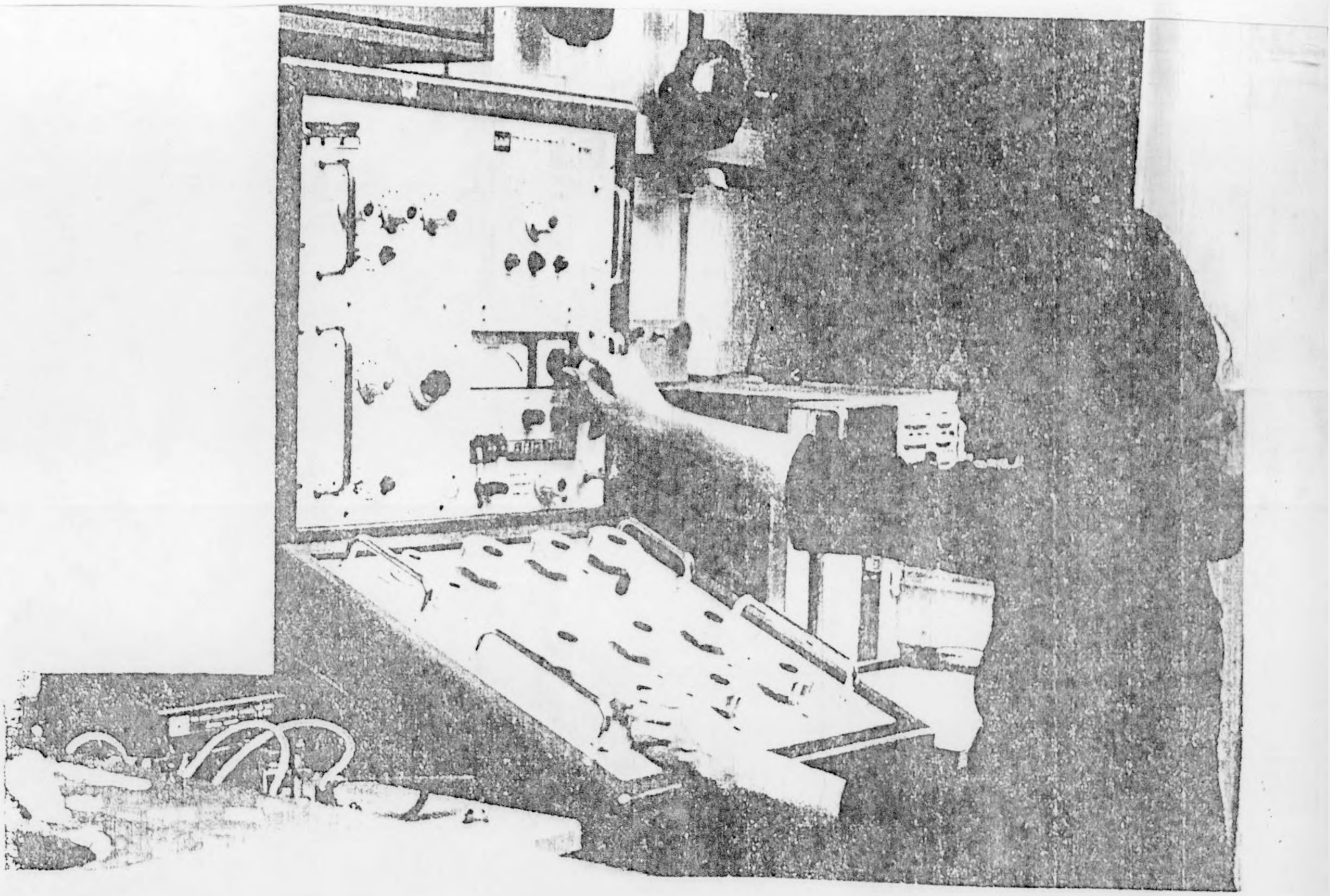
Sand, Slag, Crucibles
Sand, Slag, and Crucible Dissolution

(Effluent)
Secondary Recovery
Evaporation
Anion Exchange
Waste Treatment
Recovered Nitric Acid

Slide 2

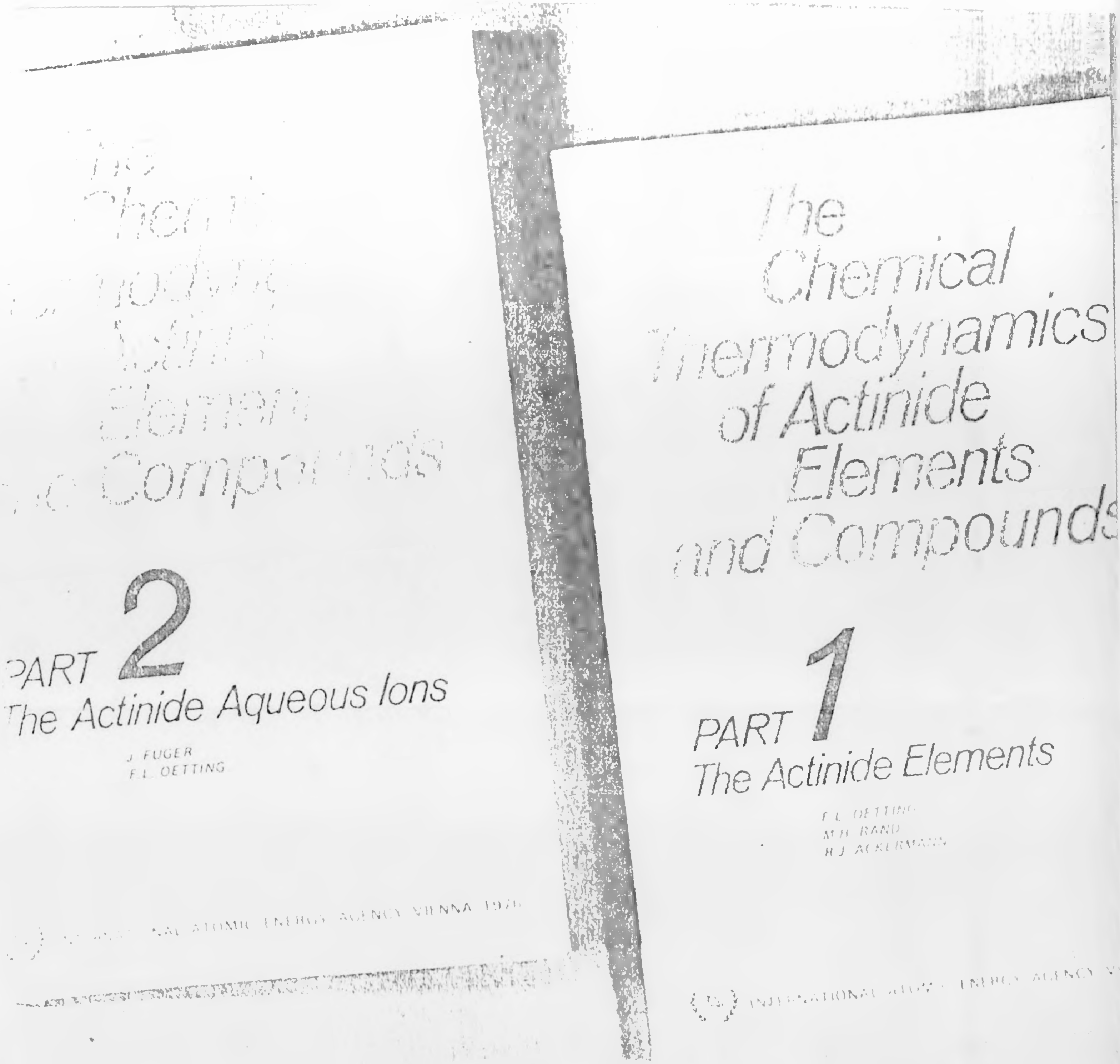
Plutonium Recovery Process

Slide 3
Adiabatic Calorimeter



Slide 4

LKB Solution Calorimeter



The Chemical Thermodynamics of Actinide Elements and Compounds

PART 2
The Actinide Aqueous Ions

J. FUGER
F.L. OETTING

INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA 1976

The Chemical Thermodynamics of Actinide Elements and Compounds

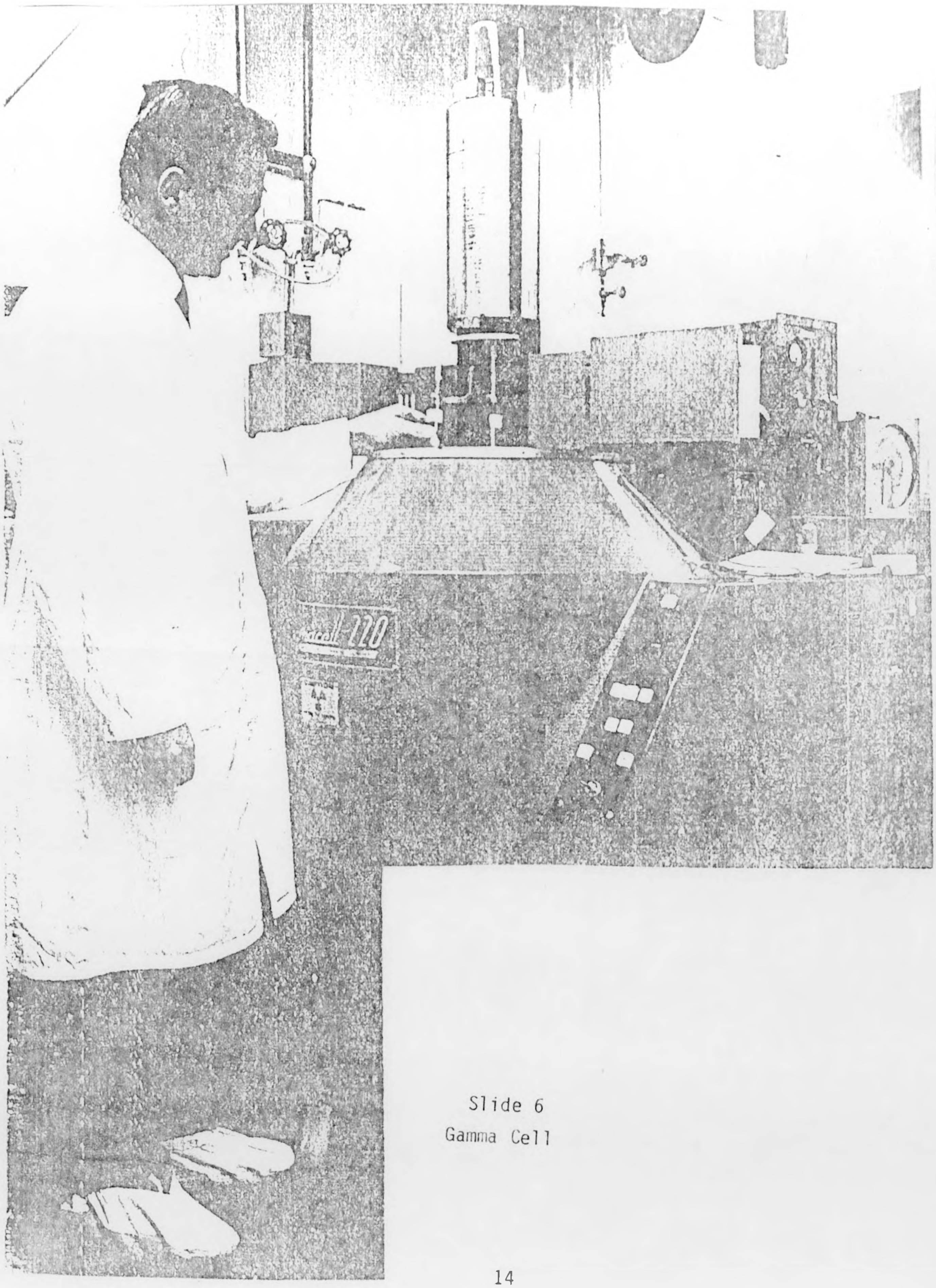
PART 1
The Actinide Elements

F.L. OETTING
M.H. RAND
R.J. ACKERMANN

INTERNATIONAL ATOMIC ENERGY AGENCY V

Slide 5

IAEA Compilation Program



Slide 6
Gamma Cell

Slide 7

Current Projects - Process Chemistry and Development

- Radiation Studies of Separation Materials
- Advanced Dissolution Methods
- Chloride-to-Nitrate Conversion
- Alternative Processes for Plutonium Precipitation
- Methods for Pu/U and Pu/Np Residues

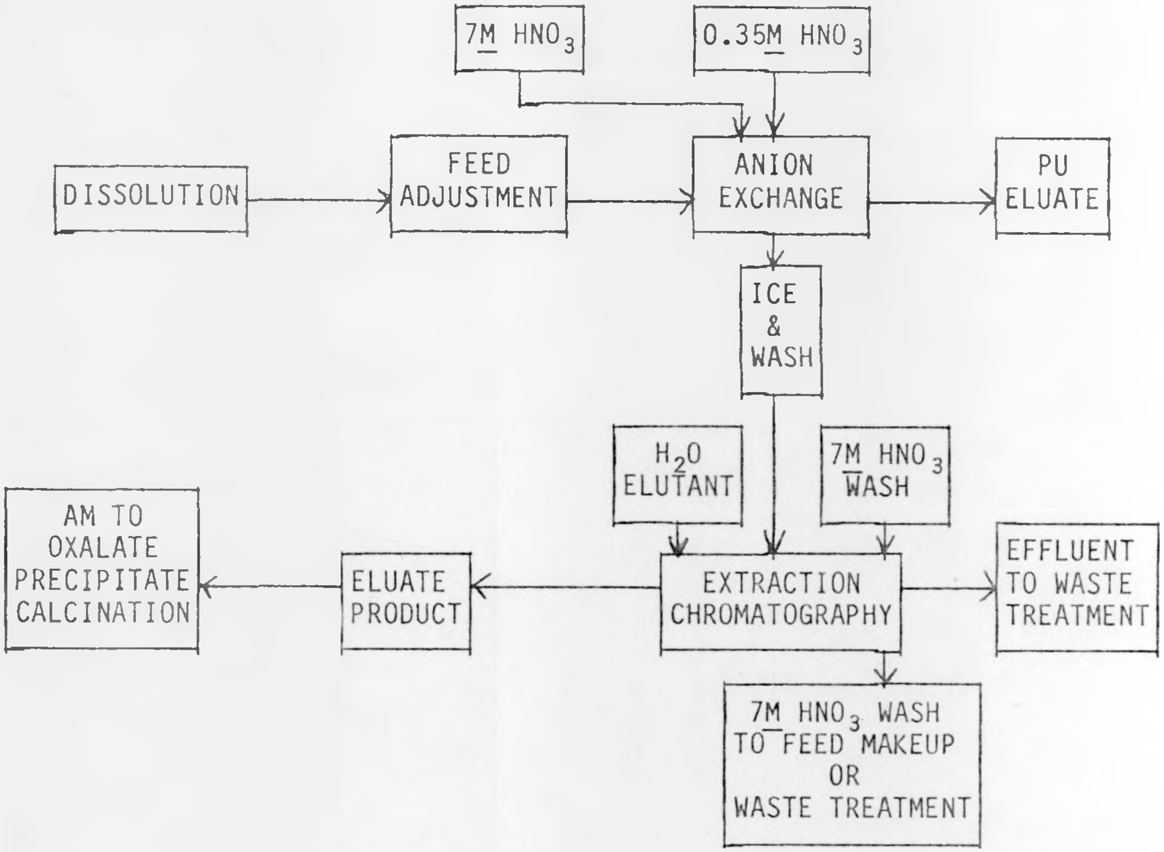
Slide 8

Current Projects - Separations Chemistry

- Evaluate New Solvent Extractants
- Evaluate New Ion Exchange Resins and Sorbents

Slide 9

Conceptual Flow Diagram



7M HNO$_3$

0.35M HNO$_3$

DISSOLUTION

FEED ADJUSTMENT

ANION EXCHANGE

PU ELUATE

ICE & WASH

H$_2$O ELUTANT

7M HNO$_3$ WASH

AM TO OXALATE PRECIPITATE CALCINATION

ELUATE PRODUCT

EXTRACTION CHROMATOGRAPHY

EFFLUENT TO WASTE TREATMENT

7M HNO$_3$ WASH TO FEED MAKEUP OR WASTE TREATMENT

Slide 10

Comparison of Waste Treatment Processes

Process	Number of Treatments	Pu Conc., g/ℓ Initial	Pu Conc., g/ℓ Final	Solids, g/ℓ
Floc ppt'n, old facility	2	10^{-3} (max)	2.2×10^{-7} (max)	7.7
Floc ppt'n, new facility	3	4.4×10^{-6}	10^{-9}	9.5
In situ ferrite	1	10^{-4}	1.1×10^{-8}	4.1
In situ ferrite	1	4.4×10^{-6}	1.6×10^{-9}	4.1
Preformed ferrite	1	10^{-4}	6.0×10^{-9}	---