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CHEMICAL RESEARCH AT ROCKY FLATS

FEBRUARY 27, 1978

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**CHEMISTRY RESEARCH AND DEVELOPMENT
CHEMICAL RESEARCH**

**ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
Rocky Flats Plant
Golden, Colorado**

KWIC Index

Americium	Plutonium Recovery
Calorimeter	Precipitation
Chromatography	Separation Processes
Ion Exchange	Soils
Plutonium	Solvent Extraction
	Thermodynamics

**SEMINAR TALK FOR PRESENTATION AT THE UNIVERSITY OF DENVER, MARCH 27, AND AT THE
UNIVERSITY OF NEW MEXICO, MARCH 31, 1978**

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ABSTRACT

An overview of the research projects in the Chemical Research group will be given. The work involves actinide waste and processing chemistry, separations chemistry, radiation studies, and calorimetry and thermodynamics. Details will be given of the actinide separations research, including work with macroreticular anion exchangers and bidentate organophosphorus extractants.

Chemical Research is a 14 member group in the Chemistry Research and Development organization at Rocky Flats. Our primary responsibility is to further develop a fundamental understanding of all chemistry-related operations at Rocky Flats and 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.

Chemical Research has a team structure as shown in the first slide. The respective team leaders for the first three teams are Dr. Armen Kazanjian, Dr. Gary Thompson, and Dr. Frank Oetting. I am acting team leader for the soil and separation teams.

The Processing Chemistry team support R&D programs to improve several production processes, such as plutonium residue dissolution, anion exchange purification of plutonium, and peroxide precipitation. An outline of the dissolution process is shown in the second slide. Impure plutonium residues are dissolved in nitric and hydrofluoric acids. Dissolution process improvements have included optimization of the dissolution process and evaluation of new dissolvents. The impure plutonium nitrate solution is then purified by an anion exchange process.

The anion exchange process is shown in the third slide. Very few elements form anions in strong nitric acid solutions, thus anion exchange is a very effective procedure for purifying plutonium. The plutonium hexanitrate 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. Purification process improvements have included optimization of the process and investigation of better performing anion exchange resins. I will discuss the resin evaluation work in detail when I talk about the separations team. Planned work in this area includes investigation of photochemical valence stabilization methods for plutonium.

Plutonium peroxide precipitation is used at Rocky Flats to convert the purified plutonium nitrate solution to a solid. The next slide⁽⁴⁾ shows the process description. Plutonium nitrate solution is mixed with a solution of hydrogen peroxide to form an insoluble plutonium peroxide precipitate. Precipitation process improvement include development of new methods for operation of the process and optimization of the process. The chemistry of plutonium peroxide precipitation process was also investigated.

A by-product in the plutonium recovery stream is americium from the decay of plutonium-241. Rocky Flats separates the americium from plutonium and purifies the americium for the Department of Energy Isotope Pool. The next slide⁽⁵⁾ describes the americium recovery process (verbally describe). Process improvements and development of new processes include evaluation of better performing ion exchange resins, optimization of the process, investigation of new precipitants for americium and evaluation of solvent extraction techniques. The latter topic will be discussed in more detail later.

The Processing Chemistry team is also 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 Rocky Flats was investigated. The materials include ion exchange resins, solvents, solvent extractants, machining oils, and plastics. The radiation chemistry of nitric acid and plutonium nitrate solutions have also been studied.

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 processes.

Our newly developed process, secondary actinide recovery, is shown in the next slide⁽⁷⁾. The purpose of the process is to recover additional quantities of actinides from process waste streams. Again the evaluation of anion exchangers and the development of solvent extraction methods will be discussed later.

The team has also been involved in part of an Oak Ridge National Laboratory waste partitioning program. The program mandate is to determine the feasibility of removing all actinides (long-lived radioactive elements) from synthetic reactor fuel reprocessing wastes so the wastes would contain only shorter-lived radioactive elements. The recovered actinides could then be either recycled

to the fuel cycle or to reactors for transmutation to shorter-lived radionuclides.

Reverse osmosis, adsorption, and solvent extraction methods were evaluated for actinide removal from solution. Nitric-hydrofluoric acid dissolution and salt-fusion methods were evaluated for solid dissolution and actinide recovery.

Soil decontamination studies are also underway at Rocky Flats. The objective of this program is to develop and demonstrate a soil decontamination (volume reduction) process for plutonium and americium. The process will be used to decontaminate approximately three acres of Rocky Flats soil presently covered by an asphalt pad.

The next slide⁽⁸⁾ shows a conceptual flow sheet of the primary volume reduction process. The process consists of a wet-screening operation which separates the soil into a decontaminated fraction (>2.4 mm) and a contaminated fraction (<2.4 mm). The screening process is very effective because the plutonium is associated with the small soil particles. Tests have shown that the waste water can be filtered and re-used at least once.

The contaminated soil fraction will then be decontaminated further as shown in the next slide⁽⁹⁾. Candidate secondary processes include attrition scrubbing in the presence of a dispersing agent (such as Calgon or oxalic acid) and wet-screening. Desliming flotation, and density techniques will also be

investigated.

The calorimetry and thermodynamics team support the chemical thermodynamic needs of Rocky Flats. Several calorimeters have been utilized in these studies.

An isothermal calorimeter (slide ¹⁰) has been used to determine the half-lives of U-233, Pu-239, Pu-240, and Am-241. It has also been used to develop non-destructive plutonium assay techniques. A drop calorimeter, shown on the next slide (¹¹), has been used to measure the high-temperature enthalpy of UC, U_2C_3 , UC_2 , PuC, Pu_2C_3 , UN, PuN, and PuO_2 . A solution calorimeter (slide ¹²) has been used to determine the enthalpy of formation of beryllium sulfate and its hydrates, and the heat of solution of actinide metals. An adiabatic calorimeter is under construction to add to our thermodynamic capabilities.

A critical assessment and compilation of the thermodynamic properties of all actinide elements and compounds is in progress (slide ¹³). The compilation is being published by the International Atomic Energy Agency, and consists of 12 parts.

The separations development team investigates new techniques and improves those currently being used for separating actinides from each other as well as from non-actinides. I will describe the resin evaluation and solvent extraction studies accomplished by this team.

THE MACRORETICULAR AND GEL RESINS WERE COMPARED TO DOWEX 1-X4 USING CONVENTIONAL PLUTONIUM PURIFICATION TECHNIQUES. THE RESINS WERE LOADED SIMULTANEOUSLY WITH PLUTONIUM FROM A 7M HNO_3 FEED SOLUTION, WASHED WITH 7M HNO_3 , AND THE PLUTONIUM ELUTED WITH 0.35M HNO_3 . FRACTIONS OF THE EFFLUENT STREAMS WERE THEN ANALYZED FOR PLUTONIUM.

SLIDE 14 SHOWS PLUTONIUM LOADING BREAKTHROUGH CURVES FOR SEVERAL RESINS. THE ORDINATE AXIS IS THE RATIO OF THE CONCENTRATION OF THE ION COLUMN EFFLUENT TO THE FEED CONCENTRATION AND THE ABSCISSA IS THE MILLIGRAMS OF PLUTONIUM FED TO THE ONE CENTIMETRE DIAMETER BY 15 CENTIMETRE DEEP RESIN BEDS. THE SLIDE SHOWS THAT BREAKTHROUGH OCCURRED IN THE FOLLOWING ORDER OF RESINS: DOWEX 1-X4 (20-50 MESH) < AMBERLITE IRA-402 < DOWEX 1-X4 (50-80 MESH) < DOWEX 11. LATER, I WILL COMPARE THE BREAKTHROUGH OF OTHER RESINS AT 1% BREAKTHROUGH CAPACITY.

SLIDE 15 SHOWS PLUTONIUM ELUTION CURVES FOR THE SAME FOUR RESINS. THE PLOT IS PERCENT PLUTONIUM ELUTED VERSUS MILLILITRE OF 0.35M HNO_3 PASSED. THE DATA SHOW THAT ELUTION KINETICS INCREASED IN THE FOLLOWING ORDER: DOWEX 1-X4 (20-50

MESH) < DOWEX 1-X4 (50-80 MESH) < AMBERLITE IRA-402 < DOWEX 11.
IN THE NEXT SLIDE, I WILL COMPARE ELUTION DATA AT THE 90%
ELUTION LEVEL.

SLIDE 16 SHOWS THE COMPARISON OF RESIN PERFORMANCE PARAMETERS FOR THE RESINS TESTED. LOADING KINETICS WERE DETERMINED BY JACK RYAN AT BATTELLE NORTHWEST AND HIS RESULTS (MG PU PER GRAM RESIN PER HR) SHOW THAT THE FASTEST KINETICS OCCURRED ON THE GEL ACRYLIC IRA-458 RESIN AND THE MACRORETICULAR RESINS (AN AVERAGE OF 7 INCLUDING DOWEX MSA-1, AND AMBERLITE IRA-93 AND 900). OF THE GEL POLYSTYRENE TYPE RESINS, DOWEX 11 GAVE THE FASTEST KINETICS FOLLOWED BY DOWEX 1-X4 50-80 MESH. FIVE OTHER GEL RESINS AVERAGED 58 MG PLUTONIUM PER GRAM RESIN PER HOUR. LARGE BEAD DOWEX 1-X4 SHOWED VERY POOR LOADING KINETICS.

THE ELUTION KINETICS WERE, IN GENERAL, THE SAME ORDER AS THE LOADING KINETICS EXCEPT SEVERAL OTHER GEL RESINS GAVE BETTER KINETICS THAN DOWEX 11 AND 1-X4 TO LOWER THE AVERAGE LITRE OF 0.35M HNO_3 PASSED TO ELUTE 90% OF THE PLUTONIUM TO 0.1. NOTE, HOWEVER, THAT DOWEX 11 GAVE BETTER ELUTION KINETICS THAN SMALL BEAD DOWEX 1-X4.

SLIDE 16 ALSO SHOWS THE EFFECT OF FEED CONCENTRATION ON BREAK-THROUGH CAPACITY. THE BREAKTHROUGH CAPACITY (G PU FED TO COLUMNS

AT 1% BREAKTHROUGH) FOR THE GEL RESINS, DOWEX 11 AND 1-X4, WAS FAIRLY INDEPENDENT OF FEED CONCENTRATION WHEREAS THE MACRORETICULAR RESINS AND ACRYLIC IRA-458 RESIN HAVE A LOWER CAPACITY AT LOWER FEED CONCENTRATIONS. THE TRACE DISTRIBUTION COEFFICIENTS WERE DETERMINED AND FOUND TO BE COMPARABLE FOR BOTH TYPES OF RESINS, BUT AS THE MACRORETICULAR RESINS LOAD, THE K_D 'S DROP AND THE CAPACITY IS LOWERED; THIS DOES NOT HAPPEN WITH THE GEL RESINS WHICH SHRINK ON LOADING.

IN SUMMARY, THE MACRORETICULAR RESINS HAVE SHOWN FASTER KINETICS, BUT LOWER BREAKTHROUGH CAPACITIES AT LOWER FEED CONCENTRATIONS. THE MACRORETICULAR RESINS WOULD HAVE LITTLE PRACTICAL VALUE FOR PLUTONIUM(IV) AND NEPTUNIUM(IV) SCAVENGING AND CONCENTRATING, BUT WOULD BE USEFUL WHEN HIGH FEED (>4 G/L) CONCENTRATIONS ARE USED. DOWEX 11 (20-50 MESH) WAS CHOSEN AS A TENTATIVE REPLACEMENT FOR DOWEX 1-X4 (50-80 MESH) BECAUSE OF THE FAVORABLE KINETICS, BREAKTHROUGH CAPACITY AND LOWER RESIN COST.

PRELIMINARY SOLVENT EXTRACTION STUDIES

Slide 17 shows the nomenclature and structure of the two bidentate organophosphorus extractants tested for americium and plutonium extraction. DHDECMP and DBDECMP were obtained from Wateree Chemical Company, Lugoff, South Carolina, on a custom synthesis basis. Presently, Wateree is the only U.S. supplier of these extractants. The extractants were technical grade and both contained percentage amounts of the corresponding dialkyl esters of phosphoric acid. Caustic scrubbing was not sufficient to remove these impurities, but acid hydrolysis or contact with Amberlyst A-26[®] (OH form) resin was sufficient to remove them. Distillation could also be used to purify the DBDECMP, but DHDECMP decomposed under vacuum distillation. Percentage amounts of other bidentate organophosphorus extractants were detected in the extractants by gas chromatography-mass spectroscopy techniques after the dialkyl esters were removed, but these did not alter our extraction coefficients (E_a°) significantly. (E_a° = concentration of solute in the organic phase divided by the concentration of the solute in the aqueous phase at equilibrium.) The dialkyl esters needed removing since they caused difficult back extraction or stripping of the americium from the loaded organic.

Slide 18 shows extraction coefficients for americium in 100% DHDECMP. The DHDECMP was hydrolyzed with HCl and then washed with sodium hydroxide solution whereas the unpurified DHDECMP was only caustic washed. The results show that back extraction or stripping of americium with dilute acid is possible with the purified extractant whereas back extraction is very difficult with the unpurified DHDECMP. The same results were observed with DBDECMP. Americium and plutonium extraction coefficients for both extractants increased with nitric acid concentration to about 7M HNO_3 , then decreased.

Extraction coefficients were determined for other elements and are shown in Slide 19. Ion column effluent and wash solutions were spiked with additional impurities and equilibrated with 100% DHDECMP and DBDECMP for the determination of the extraction coefficients. In general, the extractants showed strong extraction for the actinides; moderate extraction for zirconium, vanadium, and cerium; and weak extraction for 33 other ions tested. The extraction coefficients for most of the other 33 ions were less than 0.1.

EXTRACTION CHROMATOGRAPHY

A research program is presently in progress to evaluate various support materials to sorb DHDECMP. DHDECMP was selected for the extraction chromatography stationary phase since its solubility in 7M HNO_3 is much less than DBDECMP.

Slide 20 shows the capacity results for several supports. Over 30 support materials were tested. Since a capacity of 1 gram/millilitre was desired only the materials with the highest capacities are shown in the slide. All the other materials had a capacity of 0.15 gram/millilitre or less. The data were obtained by rinsing each support with 15ml of CCl_4 followed by 30ml of water. The supports were then equilibrated with 7^MHNO_3 , washed with 30ml of water and allowed to dry at 60°C under vacuum for three days. Next the columns of support material were tared and equilibrated with a 50 volume percent DHDECMP- CCl_4 solution for 3 days. Excess extractant was removed under vacuum and the DHDECMP loaded support washed with 7^MHNO_3 until no visible extractant was observed in the wash. Finally the residual 7^MHNO_3 was removed by washing with water and the DHDECMP loaded support was dried and weighed. The capacity of the support for DHDECMP was taken as the grams of DHDECMP sorbed on a millilitre of dried, loaded material. Each result is the average and standard deviation of three determinations. Amberlite XAD-4 had the highest capacity.

Seven of the supports exhibited a high enough capacity to warrant further testing and thus were tested for extractant losses (by solubility). The results are shown in slide 20. The extractant losses were determined by passing 300 column volumes of 7^MHNO_3 over the DHDECMP loaded material. The residual 7^MHNO_3 was removed by washing with water and the DHDECMP loaded support material was dried and weighed. The extractant losses from the support materials were reported as the percent decrease in the DHDECMP capacity. Amberlite XAD-4 has the lowest extractant losses.

Amberlite XAD-4 macroreticular sorbent was tentatively chosen for further testing because of the favorable DHDECMP capacity and low extractant losses. The support was tested for americium breakthrough capacity. The support material loaded with a known amount of DHDECMP was contained in 0.6 cm bore columns with a wet support bed height of 10 cm. The flow rate was controlled at approximately two ml/min.

Each experiment consisted of loading the column with a synthetic americium feed. Fractions (5 ml) of the column effluent were collected and analyzed for americium. The americium loading breakthrough results are shown in slide 21. The ordinate axis is the ratio of the concentration of americium in the ion column effluent to the concentration in the feed (c/c_0) and the abscissa is the milligrams of americium fed to the support bed $\times 10^{-4}$. The americium breakthrough capacity was 1 mg Am/ml support at 1% breakthrough.

The americium elution behavior of DHDECMP loaded Amberlite XAD-4 was studied. The columns were eluted with 0.35M HNO_3 . Fractions (15 ml) were collected and analyzed for americium. The results of these experiments are presented in Slide 22. The plot is fraction americium eluted versus millilitre of elutriant passed.

The elution of americium is very slow and creates too much waste solution. Although the capacity and retention of DHDECMP on Amberlite XAD-4 was good, the poor elution is a definite disadvantage. Other eluting reagents will be tested, as well as smaller bead supports, to improve the americium elution kinetics.

CHEMICAL RESEARCH TEAMS

PROCESSING CHEMISTRY - A. R. KAZANJIAN

WASTE CHEMISTRY - G. H. THOMPSON

CALORIMETRY AND THERMODYNAMICS - F. L. OETTING

SOIL DECONTAMINATION - J. D. NAVRATIL (ACTING)

SEPARATIONS DEVELOPMENT - J. D. NAVRATIL

PLUTONIUM RESIDUE DISSOLUTION

PURIFICATION OF PLUTONIUM BY ANION EXCHANGE

PROCESS DESCRIPTION

Am RECOVERY PROCESS

SECONDARY RECOVERY PROCESSES

CONCEPTUAL PRIMARY PROCESS

CANDIDATE SECONDARY PROCESSES

SLIDE 11

PART 2
The Actinide Aqueous Ions

J. FUGER
 F. L. OETTING

INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA 1976

*The
 Chemical
 Thermodynamic
 of Actinide
 Elements
 and Compounds*

PART 1
The Actinide Elements

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

INTERNATIONAL ATOMIC ENERGY AGENCY

PLUTONIUM BREAKTHROUGH ON SEVERAL RESINS

- DOWEX I-X4 (50-80 MESH)
- DOWEX I-X4 (20-50 MESH)
- △ DOWEX II
- ▽ IRA-402

PLUTONIUM ELUTION CHARACTERISTICS OF SEVERAL RESINS

PERCENT PLUTONIUM ELUTED

- DOWEX I-X4 (50-80)
- DOWEX I-X4 (20-50)
- △ DOWEX II
- ▽ AMBERLITE IRA-402

COMPARISON OF RESIN PERFORMANCE PARAMETERS

Resin	Loading Kinetics (mg Pu g ⁻¹ hr ⁻¹)	Elution Kinetics (l 0.35 M HNO ₃ @ 90%)	Breakthrough Capacity (g Pu @ 1%)	
			2 g/l Pu Feed	0.5 g/l Pu Feed
Amberlite RA-458	175	0.04	0.38	0.06
7 Macroreticular Resins	126	0.09	0.20	0.14
Dowex 11	68	0.14	0.45	0.38
Dowex 1-X4 (50-80)	60	0.21	0.42	0.41
5 Gel Resins	58	0.10	0.13	—
Dowex 1-X4 (20-50)	52	0.34	0.18	0.16

SLIDE 16

DIALKYL N,N-DIETHYLCARBAMYL METHYLENEPHOSPHONATES

R = $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

DHDECMP

R = $-CH_2-CH_2-CH_2-CH_3$

DBDECMP

EXTRACTION COEFFICIENTS OF VARIOUS IONS IN 7M HNO₃
WITH 100% EXTRACTANTS

<u>Ion</u>	<u>Ea° (DHDECMP)</u>	<u>Ea° (DBDECMP)</u>
U	570	---
Pu	300	200
Am	60	110
Zr	3	10
V	2	2
Ce	2	2
33 others	<1	<1

SLIDE DHDECMP Capacity of Various Support Materials

<u>Support Material</u>	<u>DHDECMP Capacity (g/ml)</u>	<u>Decrease in Capacity After Washing (%)</u>
Amberlite [®] XAD-4	0.34 ±0.03	18
Amberlite XAD-7	0.32 ±0.04	59
Poly M Phenyl Ether Chromosorb [®]	0.29 ±0.01	37
Amberlite XAD-1	0.24 ±0.04	39
Bio-Rad [®] SM-2	0.24 ±0.02	31
Amberlite IRA-93	0.22 ±0.02	52
Amberlite XAD-2	0.22 ±0.02	40

*80 to 100 mesh beads; all others 20 to 50 mesh beads.

Am Breakthrough of XAD-4

Am Elution of XAD-4