277
0-21-77

Sh. 1509

RFP-2667
September 21, 1977

RFP-2667
September 21, 1977

WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE – PARTS I AND II

PROGRESS REPORT FOR PERIOD ENDING MARCH 31, 1977

G. H. Thompson, D. L. Cash, E. L. Childs,
J. D. Navratil, L. L. Martella, and C. E. Plock

MASTER

CHEMISTRY RESEARCH AND DEVELOPMENT
Chemical Research Group

Work performed as part of Oak Ridge National Laboratory
Program 189C No. ON 38 0 9 A

Rockwell International
Atomics International Division
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT EY-76-C-04-3533

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161
Price: Printed Copy $~~5.00~~ 4— Microfiche $3.00
Price Is Subject to Change Without Notice

Printed
September 21, 1977

RFP-2667
UC-70 NUCLEAR WASTE
MANAGEMENT
TID-4500-R65

WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE – PARTS I AND II

PROGRESS REPORT FOR PERIOD ENDING MARCH 31, 1977

G. H. Thompson, D. L. Cash, E. L. Childs,
J. D. Navratil, L. L. Martella, and C. E. Plock

CHEMISTRY RESEARCH AND DEVELOPMENT
Chemical Research Group

SUBJECT DESCRIPTORS
Actinide Compounds
Nuclear Fuel Elements
Radioactive Waste Processing
Transuranium Compounds

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P. O. BOX 464
GOLDEN, COLORADO 80401

Prepared under Contract EY-76-C-04-3533
for the
Albuquerque Operations Office
U. S. Energy Research and Development Administration

CONTENTS

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of D. L. Ziegler, L. J. Meile, and A. J. Johnson of the Pilot Plant Development group of Chemistry Research and Development, and Dr. F. J. Miner of the Chemical Research group for their assistance in this program.

WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE

INTRODUCTION

The U.S. Energy Research and Development Administration (ERDA) has initiated a major research and development program to close the light water reactor (LWR) fuel cycle. The program comprises efforts by both ERDA facilities and industry to provide the technology and design for fuel recycling facilities and to determine the economic and environmental impact of recycling.

The reprocessing of nuclear fuel elements generates liquid and solid radioactive wastes which must be converted to forms that can be transported and stored. ERDA has assigned Oak Ridge National Laboratory (ORNL) a broadly based program consisting of both experimental and computational tasks to develop a meaningful cost-risk-benefit analysis of actinide partitioning and transmutation as a waste management concept; the program has been defined by ORNL(1,2).[1]

The principal emphasis of the ORNL program will be to evaluate partitioning. In this approach, long-lived and biologically significant nuclides are recovered (partitioned) from waste streams produced within the nuclear fuel cycle. These nuclides may then either be recycled to the fuel cycle or to special reactors for transmutation and fission to shorter-lived, less biologically significant radionuclides(2). Successful partitioning could reduce the need for long-term storage of fission products to 10(3) years, as well as recover valuable actinides for recycle(3).

Because of the recognized need for an early assessment of the partitioning-transmutation concept, the program will be limited to applied, rather than basic, research and development. Only those partitioning and transmutation options which presently show promise from an engineering viewpoint will be considered under this program.

In addition, the total program is only three years in length (FY 1977-1979). The major part of the experimental program is to be completed in the first two years.

The program has been divided into three groups of tasks. One group is composed largely of experimental work concerned with separations; the other two groups are concerned with nonpartitioning aspects of the program. In the first group, there are nine subtasks as follows: (1) Actinide recovery from solids; (2) Am-Cm recovery using bidentate extractants; (3) Am-Cm recovery using inorganic ion-exhcange media; (4) Recovery alternatives appliable to waste streams; (5) Actinide recovery from combustible waste; (6) Actinide recovery and recycle preparation for waste streams; (7) Radiation effects; (8) Thermal transmutation studies; and (9) Risk-benefit analysis.

Rocky Flats has responsibility for subtasks 5 and 6. The work that has been done to date in each of these subtasks is summarized in this report. Reports will be issued periodically to document subsequent work and the results.

---

[1] Numbers in parenthesis refer to references at end of text.

PART I - ACTINIDE RECOVERY FROM COMBUSTIBLE WASTE

G. H. Thompson, D. L. Cash, E. L. Childs

ABSTRACT

Preliminary evaluation of leaching, acid digestion, and fusion methods for actinide recovery from incinerator ash was begun. Cold ash from the fluidized bed incinerator was used as a stand-in for contaminated ash being prepared. Solubilization of ash was used as the measure of method efficiency. Fusion with basic fluxes appears to be most promising both with respect to actinide recovery efficiency and minimum impact on waste volume and form.

INTRODUCTION

The Rocky Flats project, Actinide Recovery from Combustible Wastes (RAW) is a subtask of the ORNL program Waste Management Analysis for the Nuclear Fuel Cycle. Combustible waste produced during fuel reprocessing comprises paper, wood, plastics, rubber, cloth, spent solvent, activated carbon, and ion-exchange resins. These wastes are incinerated or acid digested to reduce waste volume and organic content, and to facilitate actinide recovery. The product is residue containing actinides and fission products. The objective of the RAW project is to evaluate methods to recover actinides from these residues. ORNL has explicitly stated that only currently known recovery methods are to be evaluated. For a recovery method to receive serious consideration, it must efficiently recover actinides from residues in a form suitable for recycle or transmutation, result in little actinide entrainment in the process offgas, not materially increase final waste volumes, or deleteriously affect glass or concrete waste forms.

These studies will be made on a laboratory scale. A discussion of the methods evaluated and the data obtained will be transmitted to ORNL in quarterly reports during FY 1977, 1978, and 1979. A final report will be submitted at the end of the program. The findings will be used by ERDA and ORNL to assist in determining the feasibility of partitioning ash from combustible waste.

EXPERIMENTAL

Materials

The ash being used in this initial period is from general trash combusted in the pilot-scale fluidized bed incinerator (FBI) system (Appendix A). This ash contains no actinides or radioactive fission products. Analyses of the ash from the primary cyclone, secondary cyclone, and porous stainless steel filter system are shown in Table I. All fusion and leaching agents are reagent grade chemicals.

Procedure

Actinide recovery from incinerator ash has been practiced for many years at Rocky Flats. A brief review of the methods used is given in Appenxix B.

Leaching and fusion experiments were done on ash which had been washed with distilled water to remove solubles, dried overnight at 110°C, and stored in a desiccator.

For leaching experiments, 100 ml of concentrated HNO_3 was added to 10 grams of ash (liquid:solid ratio of 10:1). The mixture was refluxed for 2 hours; a total reflux condenser was used to prevent liquid loss. After cooling, the mixture was filtered or centrifuged and the residue was washed with ∿500 ml of distilled water. The residue was dried overnight at 110°C, cooled in a desiccator, and weighed.

The acid digestion method reported by Lerch and Cooley(4,5) was also investigated. This method uses a mixture of concentrated H_2SO_4 and HNO_3 (95 and 5 volume percent, respectively). Ten grams of ash was slowly added to 500 ml of the acid mixture at ∿230°C. After all the ash had been added, additional HNO_3 was added in 2 to 3 ml increments until oxidation was complete (as evidenced by clearing of the mixture). After cooling, the acid was decanted and the residue fumed to remove residual acid. The residue was washed with ∿500 ml of distilled water, centrifuged or filtered to remove the wash, dried overnight at 110°C, cooled in a desiccator, and weighed.

For fusion experiments, 10 grams of flux was mixed with 1 gram of ash (solid:ash ratio of 10:1). Fusions with basic fluxes were done in nickel or high-purity alumina crucibles. Fusions with acidic fluxes were done in quartz crucibles. Fluxes evaluated were NaOH, Na_2O_2, Na_2CO_3, $KHSO_4$, $K_2S_2O_7$, and a mixture of 90 wt % Na_2CO_3-10 wt % Na_2SO_4. Samples were intimately mixed and fused at the desired temperature for times ranging from 0.5 to 2.0 hours. After cooling, the residue was dissolved in ∿250 ml of distilled water, filtered, and washed with another 250 ml of distilled water. After drying overnight at 110°C the residues were cooled, weighed, and stored in vials for subsequent leaching with acid or base.

RESULTS AND DISCUSSION

Results of the leaching, fusion, and firing experiments are shown in Table II. Results are expressed as percent ash destroyed since the ash in these preliminary tests did not contain radionuclides.

Leaching with concentrated HNO_3 dissolved approximately half of the ash. Although it is not possible to conclude from these results that HNO_3 leaching will not suffice (tests on contaminated ash are required), it is virtually certain that the desired recovery (≥99% of the plutonium) will not be achieved because some high fired PuO_2 nonhomogeneous mixed oxides will be present.

The acid digestion process destroys ∿75% of the ash. Carbon is oxidized by the process and apparently only inorganic residues remain. Before washing, the weight of the residue is actually greater than the original sample due to the formation of inorganic sulfates. The residue weight at this point is not too meaningful because it is a function of the time and temperature used to drive off excess H_2SO_4; the fumed residue is also very hygroscopic. The weight after washing is more meaningful and those are the weights reported in Table II.

Fusion with NaOH, Na_2O_2, Na_2CO_3, Na_2CO_3-Na_2SO_4, $KHSO_4$, or $K_2S_2O_7$ destroyed from 60 to 80% of the ash. Sodium hydroxide fusions are useful for siliceous materials(6), but are not effective on carbon; NaOH did an acceptable job at higher temperatures and longer times. Sodium peroxide is effective for both silica and carbon(7), but attacked the crucibles severely, particularly at higher temperatures. Sodium carbonate did not dissolve the ash as well; however, all washing in these preliminary tests was done with distilled water. The residues will be leached as part of the study on secondary recovery methods. It is certain that acid washing will solubilize the residues from these basic fluxes better than washing with water. Fusion with a mixture of 90 wt % Na_2CO_3 and 10 wt % Na_2SO_4 was done to simulate the molten salt combustion process developed by Atomics International(8,9). In this process, shredded waste and air are introduced below the surface of the molten salt at ~800°C. Combustion occurs with scrubbing of gaseous products by the salt; acidic gases react with the salt and are retained in the melt. Fusion of ash with this mixture did not give the desired ash dissolution; however, the reaction was more like sintering, since it did not melt at 800°C. Additional testing at higher temperatures is in progress. Fusion with $KHSO_4$ and $K_2S_2O_7$, through converting oxides to soluble sulfates(10), does have the disadvantage of adding sulfate to the waste; sulfate is deleterious to glass waste forms. NaOH, Na_2O_2, and Na_2CO_3 enter into the glass-making reaction so their use would not increase the final waste volume since addition of some such compound (usually Na_2O or Na_2CO_3) is required anyway.

SUMMARY AND CONCLUSIONS

The program to determine the feasibility of actinide recovery from combustible waste is in progress. A preliminary literature survey has been completed and the program plan has been submitted. Preliminary evaluation of common leaching and solubilization methods shows that: (1) Fusion with commonly used reagents solubilizes >60% of the ash from the fluidized bed incinerator process; (2) Leaching with concentrated HNO_3 dissolves ~50% of the same ash; and, (3) Acid digestion with a mixture of concentrated HNO_3 and H_2SO_4 dissolves ~75% of fluidized bed incinerator ash.

Plutonium- and americium-contaminated waste is being prepared in a lab-scale fluidized bed incinerator. Fusion, leaching, and acid digestion methods extant in the literature will be evaluated when this ash is available.

FUTURE WORK

Although the percent of ash dissolved should give an indication of the recoverability of the actinides, the weight method is by no means conclusive. Work is under way to prepare contaminated ash to permit radiochemical analysis. Two ashes will be used: an interim ash, prepared by contaminating cold ash with plutonium oxide and fluidizing the ash at ~550°C; and actual contaminated ash, prepared by adding plutonium to combustible waste and burning it in a lab scale FBI system. In addition to the ash now in use (from general trash), ash produced by incineration of ion exchange resins and spent solvents will be investigated.

The methods and techniques developed using cold ash will be extended to the contaminated ashes. The preliminary investigation of the leaching, acid digestion, and fusion methods will be complete once the recovery of actinides (plutonium and americium) from ash has been demonstrated. Promising primary and secondary recovery methods will be more extensively investigated until the end of FY 1977. At that time, the candidate primary and secondary recovery methods will be selected. FY 1978 will be spent in investigating and documenting the candidate recovery processes. Determination of actinide and fusion product losses to the offgas system will be made concurrently with leaching, acid digestion, and fusion experiments on contaminated ash.

PART II - ACTINIDE RECOVERY AND RECYCLE PREPARATION FOR WASTE STREAMS

J. D. Navratil, L. L. Martella, C. E. Plock

ABSTRACT

Evaluation was begun of methods and recycle preparation problems for salt waste and waste water streams. A feasibility study for removing actinides from the salt wastes with a bidentate organophosphorous extractant was initiated. The composition of these waste streams was defined and actinide extraction coefficients, using dihexyl-N, N-diethylcarbamylmethylene phosphonate as the extractant, were determined as a function of nitric acid concentration. For the waste water streams, preliminary flow sheets were developed for purifying water by reverse osmosis.

INTRODUCTION

The Rocky Flats project, Actinide Recovery and Recycle Preparation for Waste Streams, is a subtask of the ORNL program, Waste Management Analysis for the Nuclear Fuel Cycle.

The purpose of the subtask is to determine the feasibility of removing actinides from secondary aqueous waste streams likely to be produced during reactor fuel fabrication and reprocessing. The waste streams are part of two proposed flow sheets titled "Salt Waste Management" and "Acid and Waste Water Management"(11).

Evaluation of methods on a laboratory scale for the salt waste and waste water streams will be the major emphasis of this subtask. Solvent extraction and ion exchange methods will be evaluated for the salt waste streams; adsorption and membrane techniques will be evaluated for the waste water streams. The best methods for both waste streams will be tested further to obtain process information for flow sheet analysis.

These studies will be on a laboratory scale. The experimental data will be used by ORNL to determine the feasibility of the partitioning concept. The data obtained will be transmitted to ORNL by quarterly reports during FY 1977, 1978, and 1979. A final report will be submitted at the end of the program.

This is a new project at Rocky Flats, so no prior work has been done. However, other programs have been under development which are related to this project.

Rocky Flats has been working on decreasing the plutonium concentration in liquid waste streams for the past four years. Plutonium concentrations in acidic waste streams have been decreased from 10^{-3} to 10^{-5} g/l by use of evaporation techniques coupled with anion exchange. Development of a secondary americium process using a bidentate organophosphorous extractant has also been under investigation for the past year. These processes have been designed for use in a new $140-million plutonium recovery facility.

Complete water recycle will be utilized in a new water recovery facility at Rocky Flats. The water will be purified by reverse osmosis which has been under development at Rocky Flats for the past five years.

EXPERIMENTAL

Materials

The bidentate organophosphorous extractant, dihexyl-N, N-diethylcarbamylmethylene phosphonate (DHDECMP), was obtained in impure (∼50%) form from Wateree Chemical Company, Lugoff, South Carolina. The impure DHDECMP contains an impurity which prevents efficient stripping of actinides at low acidity.

The impurity was removed by an ion-exchange process adopted from a method to purify tributyl phosphate(12). The process consisted of passing 30 vol % DHDECMP-CCl_4 (carbon tetrachloride) through a bed of Amberlyst ^{R} A-26, a macroreticular, strong-base, anion-exchange resin in the hydroxide form. The impurity was sorbed on the resin. The resin was regenerated by washing with 3M HNO_3, water, 2M NaOH and water again before being dried with acetone.

The actinide feed solutions were prepared from purified stock solutions of americium, uranium, and plutonium.

Procedure

The extraction coefficients were determined by equilibrating equal volumes of actinide feed solutions and 30 vol % DHDECMP-CCl_4. After phase separation, the aqueous phase was analyzed for HNO_3 and actinide concentration.

Nitric acid concentration was determined by acid-base titration. Uranium concentration was determined by fluorometric techniques, and plutonium and americium concentration by radiometric counting methods.

RESULTS AND DISCUSSION

Evaluation of methods and recycle preparation problems for salt waste and waste water streams were begun. A program plan was written as an internal document to assist in the planning and management of the program. A preliminary literature search was made of applicable methods for use on the waste streams. The waste stream compositions were defined and research initiated.

Salt Waste Management

Figure 1 shows a conceptual flow sheet for salt waste management. Waste streams for fuel reprocessing are shown(11), but it is envisioned that the salt wastes from a fuel fabrication plant could be treated in a similar manner. The cooling water will be sent to water purification, and perhaps the tributyl phosphate (TBP) scrub will be treated by another process. An organic removal step may be needed, and investigations of organic removal processes for waste water could apply here.

Three experimental approaches are presently planned for processing salt wastes: (1) bidentate extraction; (2) combination tributyl phosphate-bidentate extraction; and (3) cation exchange. Testing of a bidentate organophosphorous solvent extractent for determining the feasibility of removing actinides from salt waste streams has been initiated. The extractant, dihexyl-N, N-diethylcarbamylmethylene phosphonate (DHDECMP), is being evaluated in a batch contractor as well as on a macroporous sorbent support using an extraction chromatography technique.

Impure (∿50%) DHDECMP contains an impurity which prevents efficient stripping of actinides at low acidity. The impurity was removed and Table III shows americium extraction coefficients of the DHDECMP before and after impurity removal. It is apparent from these values that at low HNO_3 concentrations expecially, the impurity in the DHDECMP prevents stripping americium from the organic phase.

Extraction coefficients for uranium, plutonium, and americium versus HNO_3 concentration are plotted in Figure 2. The values for uranium at 5, 7, and 9<u>M</u> HNO_3 were all $>10^3$ (and are off the top of the figure). The high uranium extraction coefficients at low acidity indicates uranium stripping reagents other than water or diluent HNO_3 will be needed. However, the DHDECMP purified by passage over Amberlyst A-26 could still contain impurities causing the high uranium extraction at low acidity.

Waste Water Management

A determination of the feasibility of using reverse osmosis (RO) for water purification has been identified. Figure 3 shows the conceptual flow sheet for the purification of waste water containing insignificant quantities of corrosive anions and low concentrations of impurities and radioactivity. This conceptual flow sheet is based on Rocky Flats experience with RO(13). It is applicable to tritiated as well as non-tritium containing water streams.

RO is capable of reducing the volume of a waste stream by as much as 95%. The reduction in volume will depend on the osmotic pressure of the impurities in the brine generated, as well as the composition of the impurities in the waste stream. If the concentration of the impurities is high, the osmotic pressure will be high, resulting in a decrease in the flux and desired water recovery. If the impurities in the waste stream are substances with low solubilities, such as silica and the salts of calcium, barium, and strontium, the possibility of scaling the membranes is increased. If scaling does take place, the flux will be reduced.

The advantages of RO are that it is a low energy-consuming process, waste water stream adjustment is minimal, and the quantity of combustible waste generated is small.

Figure 4 shows the conceptual flow sheet for the purification of waste water containing significant quantities of anions and/or detergents. The methods planned for flow sheet testing include adsorption, reverse osmosis, ultrafiltration, ion exchange, or combinations thereof. The flow sheet applies to both tritiated and non-tritiated waste streams.

Ultrafiltration (UF) methods would be used mainly for the removal of detergents and would need to be coupled with an anion removal step, such as RO. Use of UF and/or RO methods would reduce the quantities of waste materials for incineration compared to adsorption-ion exchange methods.

SUMMARY AND CONCLUSIONS

The program was initiated to determine the feasibility of removing actinides from secondary aqueous waste streams likely to be produced during reactor fuel fabrication and reprocessing. Evaluation of methods for the salt waste and waste water streams and recycle preparation problems is the major emphasis of this program.

A program plan was written, a preliminary literature search was made, and waste streams were defined. The testing of a dibentate organophosphorous solvent extractant for determining the feasibility of removing actinides from salt waste streams was initiated. The extractant is dihexyl-N, N-diethylcarbamylmethylene phosphonate. Extraction coefficients for uranium, plutonium, and americium were determined as a function of nitric acid concentration.

A program to determine the feasibility of using reverse osmosis (RO) for water purification was initiated. Conceptual flow sheets were constructed for purifying waste water. The preliminary flow sheet was based on RO experience at Rocky Flats.

FUTURE WORK

A bidentate extraction process will be evaluated for processing salt wastes. New and recycled extractants will be tested with synthetic waste to determine actinide decontamination factors. During the investigation with synthetic waste solutions, problems of acidifying and digesting the salt wastes will also be investigated.

Adsorption materials will be evaluated for removing detergents and corrosive anions from waste water streams. Conceptual flow sheets for RO, UF, and ion exchange will be evaluated.

TABLE I. Analyses of Ash Produced by Burning General Trash Constituents (Weight Percent)

Ash	Cl	C	Cr	Al	Water Insoluble
Primary Cyclone	4.2	18.2	0.42	7.4	77.2
Secondary Cyclone	5.7	16.0	3.50	14.3	88.7
Filter Fines	6.7	12.7	2.78	18.3	94.3

Presence of Cr in primary ash not explained since no catalyst is used in the fluidized incinerator bed.

All fusion and leaching agents are reagent grade chemicals.

TABLE II. Ash Destruction by Leaching, Digestion, and Fusion

Method	Temperature (^{0}C)	Time (hours)	Ash Destroyed (wt %) Primary	Ash Destroyed (wt %) Secondary	Ash Destroyed (wt %) Filter Fines
15.7<u>N</u> HNO_3 leach	(reflux)	2	57	36	51
H_2SO_4/HNO_3 digestion (95% H_2SO_4)	(reflux)	2	75	80	68
NaOH fusion	500	0.5	60	66	44
NaOH fusion	800	2	81	81	74
Na_2O_2 fusion	500	0.5	80	75	70
Na_2CO_3 fusion	500	0.5	33	51	19
Na_2CO_3-Na_2SO_4 fusion	800	2	34	57	19
$KHSO_4$ fusion	500	2	59	60	60
$K_2S_2O_7$ fusion	500	2	59	54	64

Leach: Solid Ratio of 10:1

Digestant: Solid Ratio of 50:1

Flux: Solid Ratio of 10:1

TABLE III. Effect of Purity of DHDECMP on Americium Extraction Coefficients

HNO_3 (M)	DHDECMP Purified	Am Extraction Coefficients DHDECMP[a] (vol %) 30	50	70	100
0.35	Yes	0.09	0.42	1.3	3.3
0.35	No	125	-	-	116
7.0	Yes	1.9	15	43	53
7.0	No	5.5	-	-	68

[a] Estimated accuracy ±25%.

APPENDIX A. INCINERATION AT ROCKY FLATS

A conventional stationary grate-type incinerator has been used at Rocky Flats for about 15 years to convert bulky combustible residues to an ash that can be processed to recover plutonium. The incinerator has provided a valuable service, but there are several disadvantages in its use. One disadvantage is the acidic (HCl) offgas which results from burning polyvinyl chloride (PVC) plastics; PVC accounts for approximately 40% of Rocky Flats waste(14). The HCl has caused corrosion of the incinerator shell and scrubbing equipment. A second disadvantage is the need for a caustic scrubber to remove the acidic offgases and reduce the temperature of the exiting flue gases. The scrub solution is an aqueous waste requiring processing. A third disadvantage is the short refractory life, which results from the corrosive atmosphere and high operating temperature (800-1000°C); frequency of rebricking has been about once every 6 to 12 months. A fourth disadvantage is the refractory plutonium oxide (PuO_2) formed at the operating temperature.

To overcome some of the problems associated with conventional incineration, a system was investigated in which the combustible material is burned in a bed of fluidized Na_2CO_3(14). The HCl generated by PVC combustion is neutralized by the Na_2CO_3, thus alleviating the severe corrosion problem and removing the need for a caustic scrubber with its attendant waste problem. The lower operating temperature (550-600°C produces more soluble PuO_2 and a catalytic (chromic oxide on alumina) afterburner permits flue gas combustion without refractory-lined equipment.

The data generated by laboratory-scale equipment were used to design a fluid bed pilot plant incinerator with a 10 pound/hour capacity(15). Based on data generated by the pilot plant incinerator, a demonstration unit with a capacity of 180 pounds/hour presently is being constructed for combustion of transuranic waste(16).

The fluidized bed incinerator (FBI) process produces three ashes: (1) ash from the fluidized bed (incinerator), recovered in the primary cyclone; (2) ash from the catalytic afterburner which burns the flue gas, recovered in the secondary cyclone; and (3) ash recovered from the porous stainless steel filters used to clean the gas stream prior to the HEPA filter system. These ashes are referred to as primary, secondary, and filter ash. The composition of the ash varies depending on the waste being burned. However, all the ashes contain carbon (C) and, except for the primary bed ash, all contain 2-4% chromium (Cr).

APPENDIX B. ACTINIDE RECOVERY AT ROCKY FLATS PLANT (RFP)

Many plutonium-bearing residues are generated in production operations at RFP. These residues comprise reduction slag (resulting from the bomb reduction of PuF_4 with calcium metal), glovebox sweepings, and incinerator ash (from incineration of plutonium-contaminated combustible waste). The incinerator ash is particularly difficult to process, often requiring 5 or 6 leach contacts before the plutonium content is reduced to discard level(17).

Actinide recovery at RFP has usually been done with halide-containing leachants or fluxes. Leachants investigated have included hydrobromic acid(18), hydrochloric acid (17,19), NaOH(17), and mixtures of $HF\text{-}HNO_3$(20), $CaF_2\text{-}HNO_3$(17,20,21,22), $HCl\text{-}SnCl_2\text{-}HF$(17), and $HNO_3\text{-}Al(NO_3)_3$ for incinerator ash pretreated by hydrofluorination(17). The $CaF_2\text{-}HNO_3$ system has received attention because CaF_2 is present in reduction slag and F^- addition is therefore unnecessary; obviously this system is the same as $HF\text{-}HNO_3$, since CaF_2 merely provides F^- for association with H^+ in strong HNO_3 solution. Leaching with HNO_3 only does not suffice to quantitatively dissolve the refractory plutonium oxides produced in the conventional incinerator at RFP. A report on the recovery of plutonium from incinerator ash at RFP has been issued recently. This report describes the process and equipment currently used, along with operating experiences during the last several years(23).

Fusion methods have been investigated at RFP but have not been used on a production scale. Fluxes investigated have included ammonium bifluoride (investigated at Hanford, Washington, on ash supplied by RFP)(24), LiF, NaF, KF, NaOH, $NaOH\text{-}AlCl_3$, $NaOH\text{-}SnCl_2$, $NaOH\text{-}SnCl_2\text{-}KF$(17), and $K_2S_2O_7$(17,25).

REFERENCES

1. J. D. Blomeke. "A Program to Establish the Technical Feasibility and Incentives for Partitioning," Proceedings of Nuclear Regulatory Commission Workshop on the Management of Radioactive Waste: Waste Partitioning as an Alternative. NR-CONF-001. June 1976. page 38-48.

2. J. D. Blomeke, et al. private communication, Oak Ridge National Laboratory, March 29, 1977.

3. H. C. Claiborne. Effect of Actinide Removal on the Long-Term Hazard of High-Level Wastes. USAEC Report ORNL-TM-4724. Oak Ridge National Laboratory, Oak Ridge, Tennessee, January 1975.

4. R. E. Lerch and C. R. Cooley. Treatment of Low-Level Alpha Contaminated Solid Waste by Acid Digestion. USAEC Report HEDL-TME-73-22. Westinghouse Hanford Company, Hanford Engineering Development Laboratory, Richland, Washington. April 1973.

5. C. R. Cooley and R. E. Lerch. "The Acid Digestion Process for Treatment of Combustible Wastes." Proceedings of the Seminar on the Management of Plutonium-Contaminated Solid Wastes. CONF-741026. Marcoule, France. October 14-16, 1974. page 172.

6. I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein. Quantitative Chemical Analysis. McMillan Company, Ontario, Canada, 4th edition. 1969. page 651.

7. G. L. Silver. Dissolution Methods. USERDA Report MLM-2234. Monsanto Chemical Company, Mound Laboratory, Miamisburg, Ohio. January 1976.

8. D. E. McKenzie, et. al. Disposal of Transuranic Solid Waste Using Atomics International Molten Salt Combustion Process. USERDA Report AI-ERDA-13151. Rockwell International, Atomics International Division, Canoga Park, California. May 1975.

9. L. F. Grantham, et al. Disposal of Transuranic Solid Waste Using Atomics International Molten Salt Combustion Process, II. USERDA Report AI-ERDA-13169. Rockwell International, Atomics International Division, Canoga Park, California. March 1976.

10. I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein. Quantitative Chemical Analysis. McMillan Company, Ontario, Canada, 4th edition. 1969. page 524.

11. J. O. Blomeke. private communication. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

12. W. W. Schulz. "Macroreticular Anion Exchange Cleanup of TBP Solvent." ARH-SA-129. Atlantic Richfield Hanford Company, Richland, Washington. May 15, 1972.

13. R. T. Heitzer and C. E. Plock. "Reverse Osmosis to Achieve Water Control and Recycle." Proceedings from the First Desalination Congress of the North American Continent. Mexico City, Mexico. October 24-29, 1976.

14. D. L. Ziegler, A. J. Johnson, L. J. Meile. Fluid Bed Incineration.

USAEC Report RFP-2016. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. June 1973.

15. D. L. Ziegler, et al. Pilot Plant Development of a Fluidized Bed Incineration Process. USAEC Report RFP-2271. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. October 1974.

16. D. L. Ziegler. Fluidized Bed Incineration of Radioactive Waste. USERDA Report RFP-2471. Rockwell International, Atomics International Division, Rocky Flats Plant, Golden, Colorado. May 1976.

17. D. L. Ziegler, J. W. Lindsay, and John K. Fraser. Evaluation of Methods to Recover Plutonium from Incinerator Ash. USAEC Report RFP-1723. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. August 1971.

18. J. M. Cleveland. Dissolution of Refractory Plutonium Dioxide. Journal of Inorganic and Nuclear Chemistry. 1470. 1964.

19. G. F. Molen. Dissolution of Plutonium Oxide. USAEC Report RFP-922. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. August 1967.

20. F. E. Butler, J. D. Moseley, and G. F. Molen. Recovery of Plutonium from Incinerator Ash. USAEC Report RFP-396. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. July 1964.

21. G. F. Molen and R. O. Wing. Dissolution of Plutonium-Bearing Residues in a Nitric Acid-Calcium Fluoride Solvent System. USAEC Report RFP-776. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. November 1966.

22. G. F. Molen, Effects of Acid Concentration and Feed Particle Size on the Dissolution of Plutonium-Bearing Materials. USAEC Report RFP-890. Dow Chemical Company, Rocky Flats Division, Golden, Colorado. February 1968.

23. T. C. Johnson. Recovery of Plutonium from Incinerator Ash at Rocky Flats. USERDA Report RFP-2520. Rockwell International, Atomics International Division, Rocky Flats Plant, Golden, Colorado. December 1976.

24. H. W. Crocker. Ammonium Bifluoride Fusion of Ignited Plutonium Dioxide. USAEC Report HW-68655. General Electric Company, Hanford Atomic Products Operation, Richland, Washington. February 1961.

25. J. K. Patterson. Investigation into the Dissolution and Direct Assay of High-Fired Plutonium Dioxide. USERDA Report RFP-2402. Rockwell International, Atomics International Division, Rocky Flats Plant, Golden, Colorado. April 1976.

ILLUSTRATIONS →

Figures 1 through 4

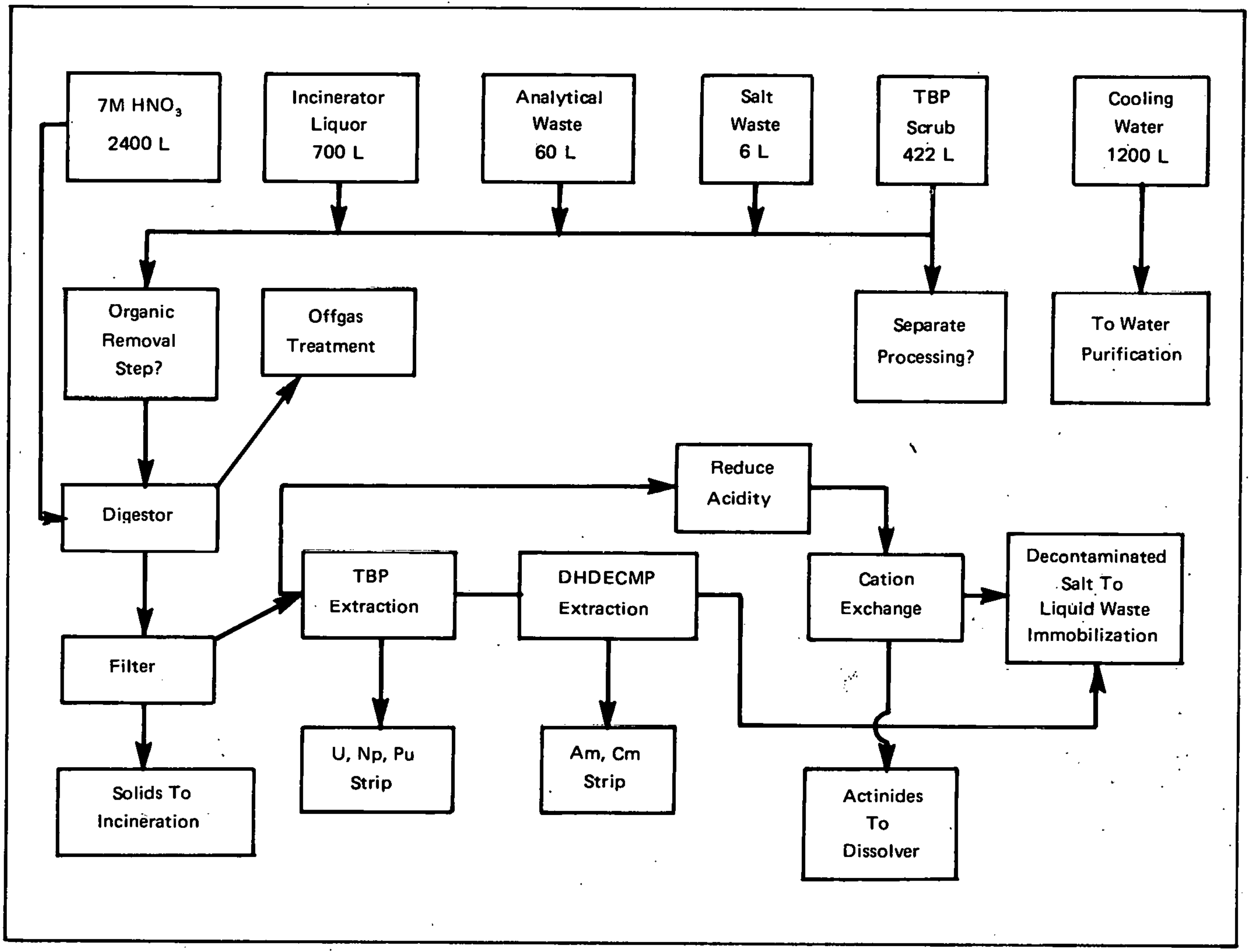

FIGURE 1. Conceptual Flow Sheet for Salt Waste Management.

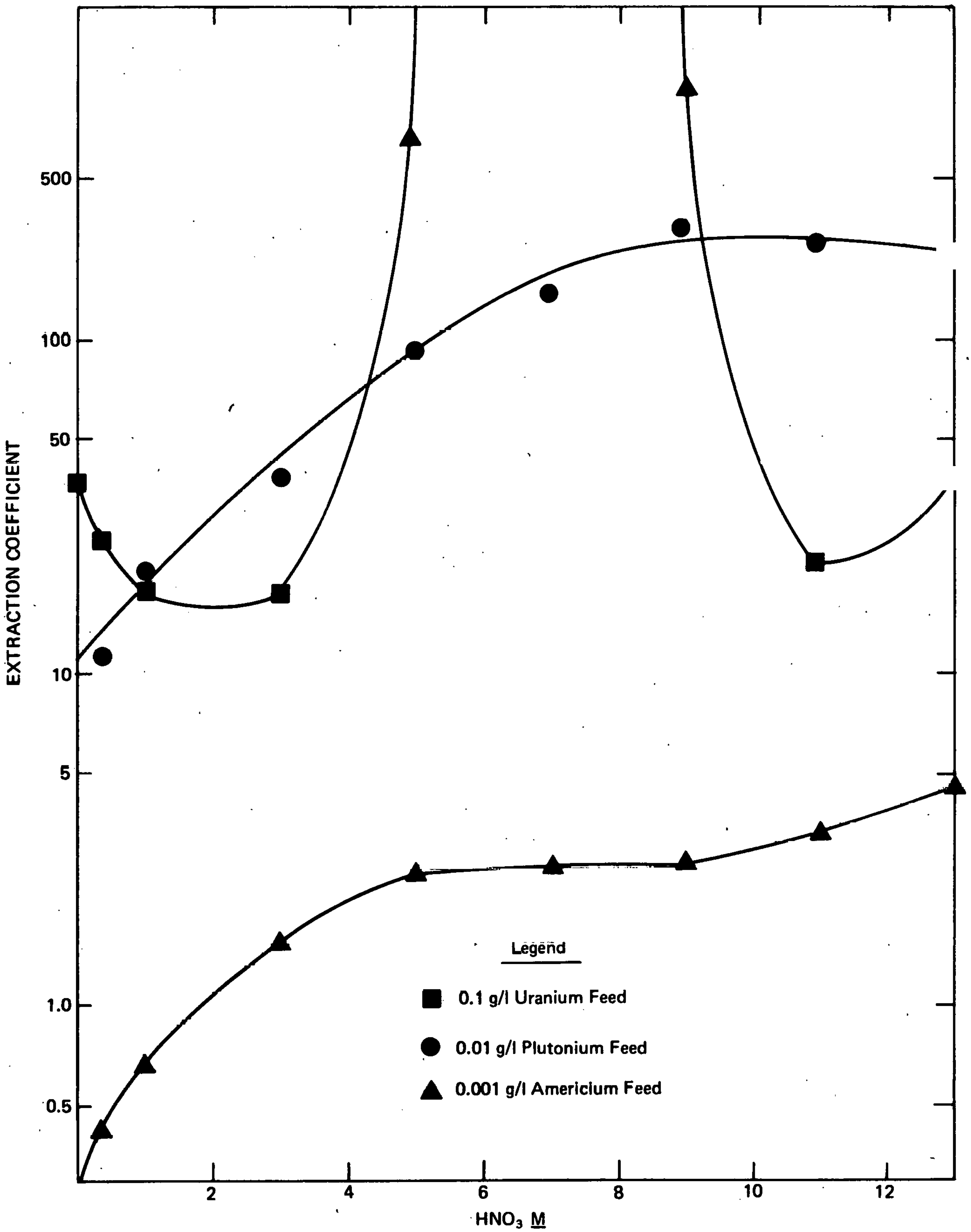

FIGURE 2. Effect of Nitric Acid Concentration on Actinide Extraction Coefficients for 30 vol % DHDECMP-CCl_4.

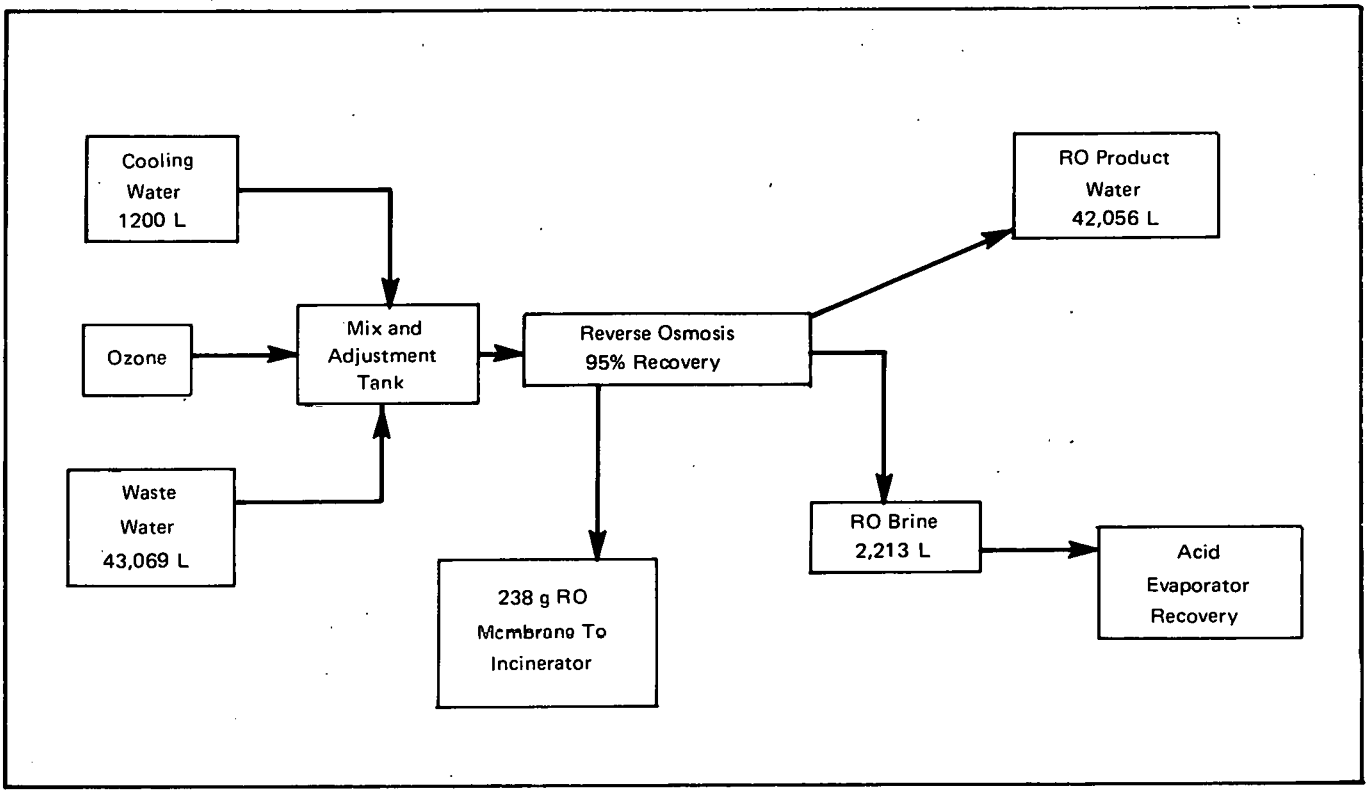

FIGURE 3. Conceptual Flow Sheet for Water Purification.

FIGURE 4. Conceptual Flow Sheet for Waste Water.