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

PROGRESS REPORT FOR PERIOD APRIL 1 TO SEPTEMBER 30, 1977

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Chemistry Research and Development
CHEMICAL RESEARCH GROUP
*Pilot Plant Development Group

Work performed as part of Oak Ridge National Laboratory
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Rockwell International

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SUBJECT DESCRIPTORS

Actinide Compounds
Absorption
Americium
Ash Fusion
Dissolution
Incinerator Ash
Leaching
Nuclear Fuel Elements
Plutonium
Radioactive Waste Processing
Radioactive Wastes
Separation Processes
Solvent Extraction
Transuranium Compounds
Waste Management

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INTRODUCTION

The U. S. Energy Research and Development Administration (ERDA) initiated a major research and development program to close the light water reactor (LWR) fuel cycle; this program is being continued by the U. S. Department of Energy (DOE). The program comprises efforts by both DOE 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. A program consisting of both experimental and computational tasks for development of a cost-risk-benefit analysis of actinide partitioning and transmutation as a waste management concept was assigned to Oak Ridge National Laboratory (ORNL). The program has been defined by ORNL[1] * and a preliminary assessment has been made.[2]

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. 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 is limited to applied, rather than basic, research and development.

PART I - ACTINIDE RECOVERY AND RECYCLE PREPARATION FOR WASTE STREAMS

J. D. Navratil, L. L. Martella, and C. M. Smith

Abstract. A preliminary evaluation of methods for the salt waste and waste water streams and recycle preparation problems was completed. A feasibility study for removing actinides from synthetic salt waste showed that a bidentate organophosphorus extractant is the most efficient for actinide removal. The evaluation of adsorbents for removing detergents and anions from waste water suggests the use of a combination of a non-ionic and a strong base ion exchange resin for best results.

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

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*Numbers, unless exponents, refer to references at end of text.

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."[2]

Evaluation of methods on a laboratory scale for the salt waste and waste water streams will be the major emphasis of this subtask. Ion exchange methods will be evaluated for the salt waste streams; adsorption and membrane techniques will be evaluated for the waste streams. If the program is continued in the future, the best methods for both waste streams will be tested further to obtain process information for flow sheet analysis.

During the last reporting period,[4] a program plan was written, a preliminary literature search was made, and waste streams were defined. The testing of a bidentate organophosphorus solvent extractant for determining the feasibility of removing actinides from salt waste streams was initiated. The extractant is DHDECMP (dihexyl-N, N-diethylcarbamoylmethylene 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. In addition, the total program is only three years in length (FY 1977-1979). Furthermore, funding for the program was reduced for FY 1978. The experimental program was thus confined to 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. Nine subtasks, as follows, are in the first group: (1) Actinide recovery from solids; (2) Am-Cm recovery, using bidentate extractants; (3) Am-Cm recovery, using inorganic ion exchange media; (4) Recovery alternatives applicable 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.

Subtasks 5 and 6 have been the responsibility of Rocky Flats. Unfortunately, the reduction in funding at the end of FY 1977 caused the elimination of subtask 6. The work that was done in the last half of FY 1977 is documented in this report; the work done from January to March 1977 was reported earlier.[1, 4]

EXPERIMENTAL

Materials

The bidentate organophosphorus extractant, DHDECMP (dihexyl-N, N-diethylcarbamoylmethylene phosphonate), 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.[4] The analysis of the DHDECMP before and after purification is shown in Table 1.

A synthetic salt waste solution was prepared by combining an incineration liquor and analytical waste (Table 2) and acidifying with 7*M* HNO_3 (nitric acid). The acidification process required care because considerable foam and heat were produced. Filtration after acidification indicated that no solids were present in the waste.

Six types of granular adsorbents were evaluated for removing organics and anions from waste water: Anasorb coconut carbon, Calgon bituminous coal carbon, Amoco carbon, Amberlite® XAD-4 neutral adsorption resin, Amberlite IRA-93 anionic weak base exchange resin, and Amberlite IRA-900 anionic strong base exchange resin. Also, a nongranular adsorbent - *in situ* formed open-pore-polyurethane (OPP) - was evaluated.

All adsorbents were dry-sieved to obtain a particle size between 40 and 50 mesh. The carbon samples from Amoco and Calgon had to be ground with mortar and pestle to obtain this mesh size.

TABLE 1. Gas Chromatography - Mass Spectroscopy (GC/MS) Analysis of Impure and Purified DHDECMP[a]

Component	Impure (%)[b]	Purified (%)[b]
diethylamine	0.1	0
decane	0.3	0
undecane	0.3	0
dichloro-N, N-diethylacetamide	0.7	0.3
α, diethylamino-N, N-diethylacetamide	2.4	0.2
unidentified components	2.5	1.8
hexylchloride	2.5	0.7
chloro-N, N-diethylacetamide	3.0	0.5
dihexylphosphite	4.1	0
dihexylmethylphosphite	7.8	7.5
trihexylphosphate	27.9	26.0
dihexyl-N, N-diethylcarbamoylmethylene phosphonate	47.0	63.0

---

a. Purified by Amberlyst® A-26 Resin Treatment.

b. Relative peak area of GC/MS.

TABLE 2. Composition of Synthetic Basic Wastes Prior to Acidification

Component	Concentration
Incinerator Liquor	
Na_2CO_3	1.36*M*
Na_3PO_4	0.46*M*
NaCl	0.52*M*
Na_2SO_4	0.37*M*
$NaNO_3$	0.07*M*
Pu	0.0002*M*
Am	0.00002*M*
U	0.02*M*
Fission products (synthetic)	0.14 g/liter
Analytical Waste	
HNO_3	1.5*M*
HCl	0.1*M*
$NaNO_3$	0.005*M*
$K_2Cr_2O_7$	0.005*M*

Acidified salt waste composed of 22 vol % Incinerator Liquor, 2 vol % Analytical Waste and 76 vol % 7*M* HNO_3.

A weighed portion of adsorbent was poured into columns with an inner diameter of 0.6 cm, to give a bed height of 10 cm. Bed volume for all granular columns was 2.8 cm^3. Before use, the columns were washed with 20 bed volumes (bv) of methanol, 20 bv of 1*M* HNO_3, and finally, 200 bv of distilled de-ionized water.

The OPP columns were prepared by *in situ* polymerization of 60-40 vol % toluene-carbon tetrachloride solutions of an isocyanate and a polyol.[5] This column, 10 cm long and 0.4 mm in diameter, was rinsed with 20 ml heptane, 20 ml methanol, and 200 ml deionized-distilled water prior to use.

A 2.5-g/l Pierce laundry detergent solution, adjusted to pH 5.0, was prepared for use as the synthetic waste stream. This solution was filtered through Watman #42 paper prior to use.

Procedure

The distribution coefficients (D) were determined by equilibrating equal volumes of actinide feed solutions and extractant. After phase separation, the aqueous phase was analyzed for HNO_3 and actinide concentration. Other extraction and back-extraction (stripping) experiments were made by equilibrating aqueous and organic phases at specified aqueous-to-organic (A/O) ratios, followed by phase separation and analysis.

For the detergent breakthrough experiments, one liter quantities of the detergent solution were pumped through each column at an average flowrate of 5.0 ±0.3 ml/min. Forty-five fractions of 20 ml each were collected with an SMI drop-counting fraction collector. A selected number of fractions was analyzed for TOC (total organic carbon) and chloride ion to determine breakthrough capacities.

The elution behavior of the materials was determined by pumping methanol through the columns at 1.5 ml/min. Fractions of the eluate were collected and analyzed to determine the elution behavior.

Nitric acid concentration was determined by acid-base titration. Uranium concentration was determined by flourometric techniques, and plutonium and americium concentration by radiometric counting methods. Plutonium, in the presence of salt and americium, was determined by pulse-height radiometric analysis after isotopic dilution and solvent extraction separation.

The analysis of TOC was made with a Beckman, Model 915, Total Organic Carbon Analyzer. Chloride ion was determined by use of selective ion electrode.

RESULTS AND DISCUSSION

Salt Waste Management

Prior workwith impure DHDECMP (dihexyl-N, N-diethylcarbamoylmethylene phosphonate) showed high uranium distribution ratios (D) in dilute nitric acid.[1] These earlier determinations were repeated using a different batch of purified DHDECMP (Table 1) and an improved uranium analytical method. Figure 1, shows D values of uranium(VI) with DHDECMP versus nitric acid (HNO_3) concentration. The results show lower uranium D values at low acidities than obtained previously, indicating less uranium stripping problems.

Uranium stripping from 30 vol % DHDECMP-DiPB (diisopropylbenzene) was compared to 30 vol % TBP-dodecane using water as the stripping agent. Each extractant (100 ml) was contacted with 20 ml of 42-g/l uranium in 7*M* HNO_3. The uranium-loaded extractants were then repeatedly contacted with water using an aqueous-to-organic ratio (A/O) of five. The uranium concentration in the aqueous strip solutions was determined to construct Figure 2.

Figure 2 shows a plot of the percent uranium stripped from the two extractant systems versus the number of contacts. The results show that the TBP-dodecane system permits uranium to be stripped the fastest while the DHDECMP extraction systems retains uranium. The leveling off of uranium removal with the DHDECMP indicates the presence of an impurity in the DHDECMP which has a high affinity for uranium. Other stripping

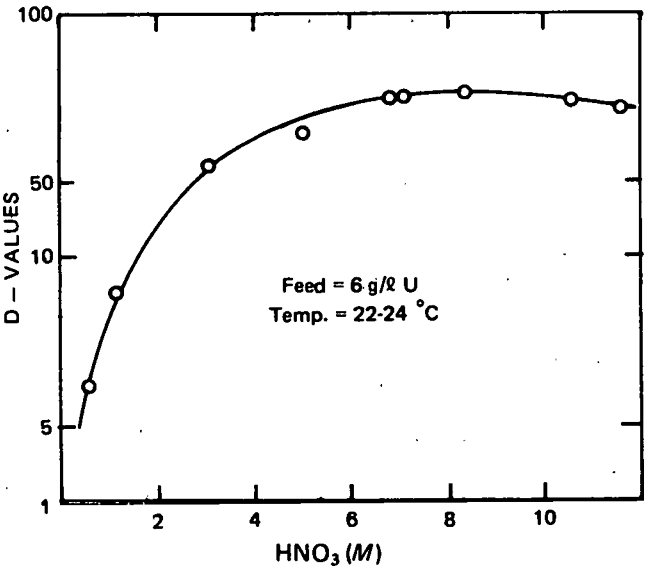
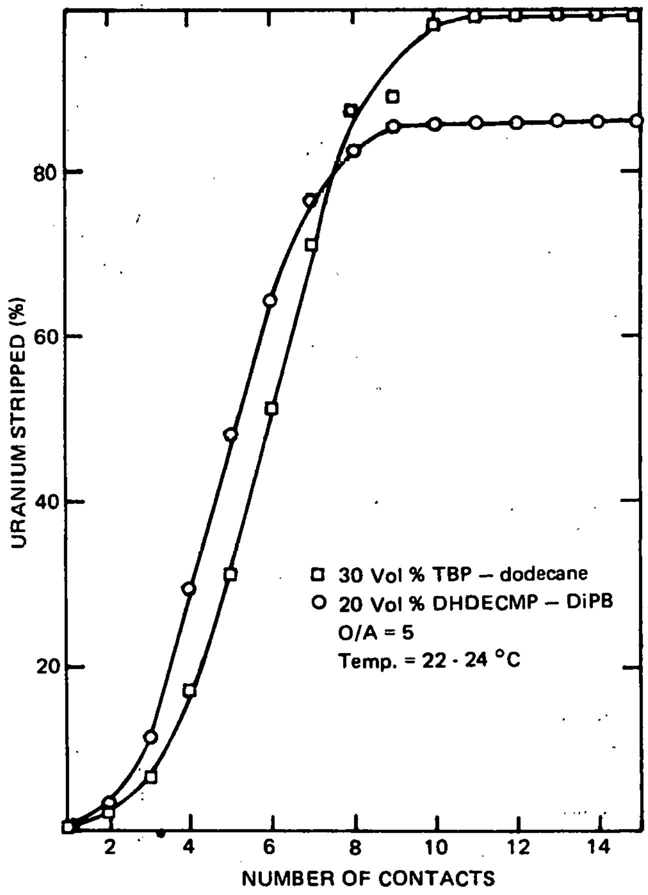


FIGURE 1. Uranium D Values Versus HNO_3 Concentration for 30 Vol % DHDECMP-CCl_4

FIGURE 2. Water Stripping of Uranium From Two Extraction Systems



agents, such as solutions of oxalic acid, acetic acid, and citric acid, did not significantly improve uranium stripping compared to water stripping.

Plutonium extraction from various acidified salt waste solutions was investigated. The synthetic waste solutions were made by adding plutonium nitrate to a basic salt waste solution.[1] This solution was then acidified with $7M$ HNO_3 to an H^+ of $6M$, then split into four batches. One batch of acidified solution was not treated and was used as a control. A second batch was boiled for one hour. A third acidified solution was boiled for one hour, adjusted to $0.1M$ Fe(II) with $3M$ ferrous sulfamate, and sodium nitrite added. A fourth batch was adjusted to $0.1M$ F^- with concentrated hydrofluoric acid, boiled for one hour, and adjusted to $0.1M$ Al^{3+} with an acidified, concentrated solution of aluminum nitrate.

The four acidified waste salt solutions were each equilibrated seven times with 20 vol % DHDECMP - 30 vol % TBP-DiPB (A/O = 5). After the fourth and seventh contact, the aqueous phase was analyzed for plutonium. The results of the plutonium analyses are shown in Table 3.

The results show no difference between the acidified salt waste and the solution which was boiled. Compared to these two solutions, more plutonium was removed from the solution in which the plutonium valency was adjusted (Fe^{2+}, NO_2^-), and significantly more plutonium was removed from the solution treated with fluoride to destroy plutonium polymer.

These and results in Table 4 indicate the following conclusions: A combined TBP-DHDECMP extraction system would be the best to remove actinides from salt waste unless purified DHDECMP (99%) alone would permit efficient uranium back extraction; the DHDECMP extraction system will remove >99.98% of the plutonium and >99.91% of the americium from the acidified salt waste.

TABLE 3. Plutonium Removal From Various Acidified Salt Waste Solutions With 20 vol % DHDECMP - 30 vol % TBP-DiPB

Acidified Waste Treatment	Plutonium Content After 4 Contacts (mg/l)	Plutonium Content After 4 Contacts (%)	Plutonium Content After 7 Contacts (mg/l)	Plutonium Content After 7 Contacts (%)
No Treatment	0.10	0.08	0.05	0.04
Boiled	0.10	0.08	0.05	0.04
Boiled; Fe^{2+}, NO_2^- Added	0.08	0.07	0.02	0.02
F^- Added; Boiled; Al^{3+} Added	0.02	0.02	---	---

Initial Plutonium Concentration: 120 mg/l
Temperature: 22-24 °C
Estimated Accuracy: ±20%

TABLE 4. Actinide Removal From Acidified Salt Waste After Consecutive Contacts With a Bidentate Extractant

Number of Contacts[a]	Percent Pu Removed[b]	Percent Am Removed[c]
2	99.89	90.90
4	99.96	98.91
6	99.97	99.60
8	99.98	99.91

---

a. Aqueous-to-organic ratio of five.
b. 20 vol % DHDECMP - 80 vol % DiPB.
c. 50 vol % DHDECMP - 50 vol % DiPB.

Waste Water Processing

The evaluation of various adsorption materials for potential use in removing detergents and anions from waste water was completed. The evaluation consisted of determining the detergent and chloride breakthrough capacities and the elution behavior of the adsorption materials.

The results of the detergent and chloride breakthrough capacities and the elution behavior of the adsorbents are shown in Table 5. Amberlite®

TABLE 5. Breakthrough and Elution Data on Adsorbent Materials

Adsorbent Materials	Breakthrough Capacity (ml det./g mat.)[a]	Breakthrough Capacity (mg Cl^-/g mat.)[b]	Elution (ml MeOH/g mat.)[c]
Anasorb	225	7	--
Amoco GX-31	240	--	>12
Calgon F 400	215	--	--
Amberlite XAD-4	250	--	1
Amberlite IRA-93	16	9	--
Amberlite IRA-900	11	47	--
OPP	100	48	8

---

a. Milliliters of detergent passed per gram of adsorbent at breakthrough of 0.30 TOC in effluent. Feed = 89 mg/l TOC. Breakthrough defined as concentration of solute in effluent divided by concentration of solute in feed.

b. Milligrams of chloride passed per gram of adsorbent at breakthrough of 0.30. Feed = 1 mg/l Cl^-.

c. Milliliters of methanol passed per gram of adsorbent at 30% TOC eluted.

XAD-4 has the highest capacity for detergent, but no ionic capacity. Amberlite IRA-900 resin and OPP have the highest capacity for chloride, but the former material would be best since the latter elutes the detergent poorly. Amberlite XAD-4 eluted the detergent the fastest. These results suggest the use of XAD-4 and IRA-900 (mixed or in separate columns) should accomplish the best removal of organics and anions from waste water.

Figure 3 shows a conceptual flowsheet for removing organics and anions from waste water employing the two suggested resin schemes. The material balance is based on the assumption that the resins selectively remove the organics and anions, with the actinides following the effluents. The correctness of these assumptions needs to be determined with actinide-containing waste water.

SUMMARY AND CONCLUSIONS

A preliminary evaluation of methods for the salt waste and waste water streams and recycle preparation problems was completed. A feasibility study was conducted for removing actinides from synthetic salt waste using the following extraction systems: (1) 30 vol % TBP-dodecane, (2) 20 vol % DHDECMP - DiPB, and (3) 20 vol % DHDECMP - 30 vol % TBP-DiPB.

The results indicate that the bidentate systems are the most efficient for actinide removal; >99.98% Pu and >99.91% Am.

The evaluation of adsorbents for removing detergents and anions from waste water was completed. The breakthrough capacities, with respect to total organics and chloride, were determined for six granular-type adsorbents. Results suggest the use of a combination of Amberlite XAD-4 (non-ionic resin for organics) and Amberlite IRA-900 (strong base resin for anions) would be an effective preparatory step in the recycle of a waste water stream.

FUTURE WORK

If this program is continued, the best methods for both waste streams will be tested further to obtain process information for flow sheet analysis.

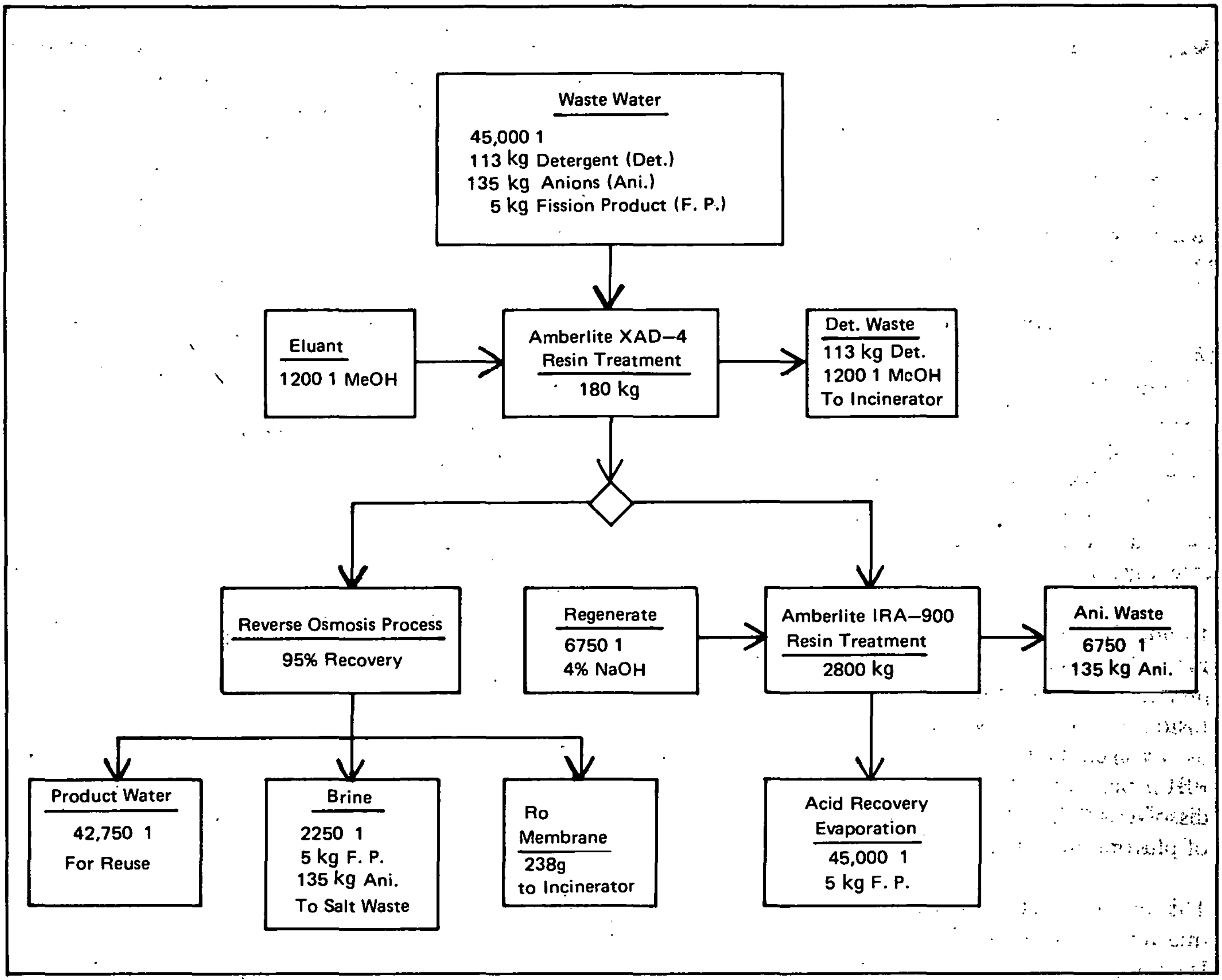


FIGURE 3. Conceptual Flow Sheet for Waste Water Treatment

PART II - ACTINIDE RECOVERY FROM COMBUSTIBLE WASTE

G. H. Thompson, D. L. Cash, E. L. Childs, and L. J. Meile

Abstract. Evaluation of leaching and dissolution methods for the recovery of actinides from combustible waste (incinerator ash) was continued. Two promising recovery methods are: (1) reaction with cerium(IV) in nitric acid to solubilize carbon and actinide oxides, and (2) fusion with carbonate-nitrate mixtures. Silica proved to be a problem. If dissolved, it interferes with subsequent actinide recovery by forming polysilicic acid upon acidification. If not solubilized, silica-encapsulated actinide oxides may not be contacted by the dissolvent. Pretreatment of ash by refluxing with $\geqslant 6M$ sodium hydroxide appears to remove silica, simplifying subsequent recovery steps.

INTRODUCTION

Combustible waste produced during reactor fuel fabrication and 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 a residue containing actinides and fission products. The objective of this project is to evaluate methods to recover actinides from these residues. 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 off-gas, not materially increase final waste volumes, or adversely affect glass or concrete waste forms.

During the first (quarterly) reporting period, a preliminary literature survey was completed.[4] A preliminary evaluation of common leaching and fusion methods showed that fusion with commonly used reagents dissolves >60% of the ash from the FBI process, and leaching with concentrated nitric dissolves 40 to 60% of the same ash. Preparation of plutonium-contaminated FBI ash was attempted.

This report describes work done in two subsequent quarters. During the first of these, evaluation of leaching and solubilization methods was continued using ^{241}Am-traced high-fired PuO_2. During the second, additional evaluation of promising actinide recovery methods was done using mixtures of the high-fired actinide oxide with FBI ash, and conventional incinerator ash (which contains both americium and plutonium). Methods evaluated further include fusion methods and ash dissolution in the cerium(IV)-nitric acid system.[6,7] The design of the lab-scale FBI system for combustion of plutonium-contaminated waste is also included.

EXPERIMENTAL

Materials

The pilot-scale FBI system currently in use at RFP and the ashes it produces were described previously.[4] This ash contains no actinides nor radioactive fission products since the system has not yet been used for contaminated waste. It does contain approximately 20 wt % carbon, 10 wt % aluminum, and 9 wt % silica. An attempt was made to prepare contaminated ash by adding plutonium nitrate in 0.35*M* nitric acid (HNO) to ash, then drying and fluidizing the ash in a quartz reactor at 550 °C. Although the amount of nitrate present was small, deflagration ocurred at approximately 325 °C. This was not unexpected (since 20% of the ash is carbon), but the outcome proved that it will be necessary to prepare contaminated ash in another way.

The conventional incinerator ash was produced in the RFP production incinerator. The production incinerator is a stationary grate incinerator which operates from about 800 to 1000 °C.[8] Combustible wastes incinerated in this facility are plastics (polyvinyl chloride and polyethylene), paper, and surgeon's gloves. Radiometric analysis of the conventional incinerator ash gave plutonium and americium concentration in ash of 0.053 g/g ash and 5.8×10^{-5} g/g ash, respectively. Additional analysis of this ash is in progress. Analysis of "typical" conventional incinerator ash produced at RFP has shown 48% SiO_2, 22 wt % C, 5.7 wt % Fe_2O_3, 4.6 wt % MgO, 4.0 wt % CaO, 2.8 wt % PuO_2, and minor constituents.[10]

Because the most difficult actinide to recover will be high-fired PuO_2 resulting from fuel fabrication operations, ORNL requested that this material be used to evaluate proposed recovery methods. However, since trivalent actinides and lanthanides will be present during fuel reprocessing, it was suggested that ^{241}Am tracer be included.

The high-fired actinide oxide used in the experiments was prepared as follows. Plutonium metal was dissolved in 12*M* HCl with cooling. The solution was adjusted to 7*M* NO_3^- and the plutonium sorbed on anion exchange resin. The column was washed with five column volumes of 7*M* HNO_3 and the plutonium eluted with 0.35*M* HNO_3. The acidity was adjusted to 0.5*M* by denitration with formic acid. A tracer amount of ^{241}Am was added, and plutonium and americium were precipitated as the oxalates. After drying, the actinide oxalates were calcined at 925 °C to constant weight. Analysis determined the americium concentration to be 2.27×10^{-4} g/g Pu.

All fusion and leaching agents were reagent grade chemicals.

Procedure

The procedure will be described in the sequence of investigation; this will best describe the manner in which the candidate recovery methods were evaluated and chosen. A procedure was developed for solubilizing only high-fired oxide at first; this procedure was then used to evaluate actinide recovery from ash. A procedure for removing silica from contaminated ash was also investigated because silica interfered with subsequent processing.

1. Actinide Oxide

a. Leaching. An attempt was made to dissolve 0.1 g of the high-fired PuO_2 in 25 ml of concentrated HNO_3 (liquid: solid ratio of 250: 1). The mixture was refluxed for 12 hours; a total reflux condenser was used to prevent liquid loss. After cooling, the mixture was filtered. The filtrate was diluted to a known volume and sampled. Undissolved PuO_2 was refluxed in a solution of 0.1*M* F^- in 12*M* HNO_3 for two hours. After filtration, the filtrate was diluted to a known volume and sampled.

b. Acid digestion. Two tests of the acid digestion method developed by Lerch and Cooley[11, 12] were made. Twenty ml of 95 vol % H_2SO_4/5 vol % HNO_3 was refluxed with 0.2 g PuO_2 for 12 hours (Test 1) and 16 hours (Test 2). Additional HNO_3 was added incrementally during this time (2-3 ml/hour). After cooling, the acid was removed by filtration and the residue was washed with 4*M* HNO_3 to solubilize plutonium and americium sulfates. Residue (undissolved oxide) was removed by filtration, then solubilized by refluxing in a solution of 0.1*M* F^- in 12*M* HNO_3, as described above.

c. Fusion. For fusion experiments, 10 grams of flux was mixed with 0.1 g PuO_2 (flux: solid ratio of 100: 1). NaOH fusions were done in both nickel and high-purity alumina crucibles. Other basic fluxes (Na_2CO_3, 90 wt % Na_2CO_3-10 wt % Na_2SO_4, 90 wt % Na_2CO_3-10 wt % $NaNO_3$, and 50 wt % Na_2CO_3-50 wt % $Na_2B_4O_7 . 10 H_2O$) were evaluated in the high-purity alumina crucibles. Acidic fusions (with $KHSO_4$ and $K_2S_2O_7$) were done in quartz crucibles. Samples were mixed and fused at the desired temperature for 2 hours. After cooling, the samples were solubilized in 4*M* HNO_3, filtered to remove any PuO_2 remaining, and the filtrate diluted to a known volume and sampled. The residues were solubilized by refluxing in solution containing 0.1*M* F^- in 12*M* HNO_3. After cooling and filtration, these solutions were also diluted to a known volume and sampled.

The effect of time was evaluated by fusion tests of 8 hours duration. The actinide recovery methods were identical to those described above.

2. Contaminated Ash

a. Fusion. For fusion experiments, 10 grams of flux was mixed with 1 g of conventional incinerator ash, or a mixture of 0.9 g FBI ash and 0.1 g of high-fired oxide (flux: solid ratio of 10: 1). Fluxes evaluated were Na_2CO_3, 90 wt % Na_2CO_3-10 wt % Na_2SO_4, 90 wt % Na_2CO_3-10 wt % $NaNO_3$, 82 wt % $Na_3PO_4 . 12 H_2O$-9 wt % Na_2CO_3-9 wt % $NaNO_3$, 90 wt % $NaH_2PO_4 \cdot 7H_2O$-10 wt % $NaNO_3$, 90 wt % $Na_2HPO_4 . 7H_2O$-10 wt % $NaNO_5$; the water in hydrated salts was considered to be eliminated during fusion, so initial weights of salt were adjusted to provide the specified wt % of "anhydrous" salt at the fusion temperature used. Most fusions were done in high-purity alumina crucibles.

Fusions with 50 wt % Na_2CO_3 -50 wt % $Na_2B_4O_7.10\ H_2O$ required platinum crucibles. Fusions with $KHSO_4$ and $K_2S_2O_7$ were done in quartz crucibles.

Samples were mixed and fused at the desired temperature for times ranging from 1-2 hours. After cooling, the samples were solubilized in 4*M* HNO_3, filtered to remove any residue, and the filtrate was diluted to a known volume and sampled. The residues were solubilized by refluxing for 2 hours in solutions containing 0.1*M* F^- in 12*M* HNO_3. After cooling and filtration, these solutions were also diluted to a known volume and sampled.

b. Dissolution with Ce(IV). For these experiments 0.15*M* Ce(IV) in 4*M* HNO_3 was reacted with samples at ambient and at reflux temperatures at a solid: liquid ratio of 125: 1 or 250: 1. Additional Ce(IV) was added as $(NH_4)_2Ce(NO_3)_6$ to replace Ce(IV) reduced by carbon. In subsequent experiments Ce(III) was reoxidized to Ce(IV) electrolytically. Solutions containing 0.05*M* Ce(IV) in 4*M* HNO_3 were reacted with samples at current-times from 6 to 15 amp-hours.

Once the carbon had been removed by oxidizing it to CO_2, the samples were filtered and the residue was washed, dried, and weighed.

c. Silica Removal. Because silica interfers with both actinide recovery methods, procedures for removing silica were tested. Cold FBI ash samples were pretreated by refluxing for 3 hours with 2, 4, 6, or 8*M* NaOH at a liquid: solid ratio of 100: 1. After cooling, the samples were filtered and the residues washed and dried. The residues were then fused with 90 wt % Na_2CO_3 -10 wt % $NaNO_3$ (flux: solid ratio of 10: 1) for 2 hours at 900 °C. After cooling, the mass was solubilized in 4*M* HNO_3 and the residue removed by filtration. The residue was then dried and weighed.

RESULTS AND DISCUSSION

Because these experiments were preliminary, designed to test many primary (dissolution) and secondary (recovery) methods, few tests were run on each method. Therefore the mean, standard deviation, and numbers of tests are shown rather than the 90% confidence level. The most promising methods will be evaluated during the coming year using conventional incinerator ash and contaminated FBI ash (Appendix A).

Actinide Oxide Solubilization Tests

1. Leaching and Acid Digestion

Results of the leaching and acid digestion experiments are shown in Table 6. Fusion experiment results are shown in Tables 6 and 7. Actinide recovery is expressed as the percent recovered of the original quantity.

Leaching with concentrated HNO_3 recovered only 0.09% and 3.5% of the plutonium and americium present, respectively. This is not surprising for PuO_2, and apparently americium (which forms more soluble oxides) was trapped within the plutonia matrix. This is suggested by the similarity in the amount of plutonium and americium recovered and this trend was consistent throughout for a given method.

The acid digestion process does solubilize the high-fired oxides. The process appears to be fairly slow and requires frequent addition of HNO_3, with resultant evolution (at the $\sim$230 °C reflux temperature) of NO_X. However, additional study is needed for adequate evaluation of this method.

The efficiency of NaOH fusion (Table 6) depended on the type of crucible used. Fusion in nickel crucibles gave much better recovery than fusion in alumina; results were reproducible. Unfortunately, fusion with NaOH at $T > 500$ °C is difficult because the molten NaOH "crawls" out of the crucible, carrying sample with it. Fusion with Na_2CO_3 or 90 wt % Na_2CO_3-10 wt % Na_2SO_4 at 900 °C is not an efficient was to recover the actinides. The most efficient flux was 90 wt %

TABLE 6. Actinide Recovery by Leaching, Digesting, and Fusion

Method	Temperature (°C)	Time (hours)	Actinide Recovery (Mean %) ± Standard Deviation	
			Pu	Am
15.7*M* HNO_3 leach[a]	(reflux)	12	0.09	3.5
H_2SO_4-HNO_3 digestion	(reflux)	12	94	84
H_2SO_4-HNO_3 digestion	(reflux)	16	97	96
NaOH fusion[b]	500	2	98 ±0.97	96 ±0.89
NaOH fusion[c]	500	2	34 ±4.6	32 ±4.0
Na_2CO_3 fusion	900	2	7.7 ±2.5	6.9 ±0.35
Na_2CO_3-Na_2SO_4 fusion	900	2	6.3 ±3.9	6.7 ±1.2
Na_2CO_3-$NaNO_3$ fusion	900	2	98 ±2.3	98 ±2.6
Na_2CO_3-$Na_2B_4O_7 \cdot 10H_2O$ fusion	900	2	96 ±2.9	92 ±0.62
$KHSO_4$ fusion	500	2	95 ±2.8	94 ±3.5
$K_2S_2O_7$ fusion	500	2	92 ±5.3	89 ±5.0

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a. single determination
b. Ni crucible
c. Alumina crucible

Leach: Solid Ratio of 250:1
Digestant: Solid Ratio of 100:1
Flux: Solid Ratio of 100:1

Sample: Am-traced PuO_2
(2.27 x 10^{-4} g Am/g Pu)
fired at 925 °C to
constant weight

TABLE 7. Actinide Recovery by Fusion

Flux	Temperature (°C)	Actinide Recovery[a] (%)	
		Pu	Am
NaOH[b]	500	96	97
NaOH[c]	500	84	84
Na_2CO_3	900	29	27
90% Na_2CO_3-10% Na_2SO_4	900	23	13
90% Na_2CO_3-10% $NaNO_3$	900	99.8 ±0.06	97.1 ±1.2
$KHSO_4$	500	97	96
$K_2S_2O_7$	500	98	96

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a. Results of single determination, except for carbonate nitrate (mean % ± standard deviation)
b. Nickel crucible
c. Alumina crucible

Flux: Solid Ratio of 100: 1
Time: 8 hours
Sample: Am-traced PuO_2
(2.27 × 10^{-4}g Am/g
Pu) fired at 925 °C
to constant weight

TABLE 8. Actinide Recovery From Fluidized Bed Incinerator Ash by Fusion, With 4*M* HNO_3 Recovery

Flux	Temperature (°C)	Actinide Recovery (%)[a]	
		Pu	Am
90 wt % Na_2CO_3 - 10 wt % $NaNO_3$	900	8.2 ±6.1	28 ±22
Na_2CO_3	900	15	15
90 wt % Na_2CO_3 - 10 wt % Na_2SO_4	900	10	24
$K_2S_2O_7$	500	97	94
$KHSO_4$	500	94	93
NaOH	500	2.4 ±0.44	15 ±5.8

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a. Results of single determination, except for carbonate, nitrate, and NaOH (mean % ± standard deviation for duplicate samples)

Flux: Solid Ratio of 10: 1
Time: 2 hours

Sample: Mixture of Am-traced PuO_2 (2.27×10^{-4} gAm/gPu) fired at 925 °C to constant weight; and FBI Ash.
90 wt % Ash - 10 wt % oxide.

Na_2CO_3-10 wt % $NaNO_3$. This mixture efficiently recovered plutonium and americium and did not attack the alumina crucible. The 50 wt % Na_2CO_3-50 wt % $Na_2B_4O_7.10H_2O$, while efficiently recovering the actinides, also severely attacked the alumina crucible. The $KHSO_4$ and $K_2S_2O_7$ fusions gave good recovery, but have the disadvantage of adding sulfate to the waste. Sulfate has an adverse effect on glass waste forms.

The effect of fusing the samples for a longer time (8 hours) is shown in Table 7. Actinide recovery was improved, especially for NaOH in alumina, Na_2CO_3, and 90 wt % Na_2CO_3-10 wt % Na_2SO_4. However, increasing reaction time does not appear to be the most efficient way to improve recovery. The fluxes effective in 2 hours are not improved to any great extent, and the ineffective fluxes, though greatly improved, are still inadequate. Increased fusion temperatures will probably be more effective.

Contaminated Ash

1. Leaching and Acid Digestion

Refluxing high-fired actinide oxide with concentrated HNO_3 did not solubilize the oxide, as shown in the previous section. Therefore the recovery of actinides from a mixture of high-fired oxide and FBI ash was not attempted. Experience at RFP has shown that recovery of actinides from conventional incinerator ash using HNO_3 only is also ineffective; usually fluoride must also be used.[9, 10]

The acid digestion process was not considered during this phase of the study, either. The reasons were the excessive amount of reaction time required; the residue, a difficult-to-handle sludge which hardens to a glassy (but soluble) material; and the adverse effect of sulfate on glass waste forms (although most of the process acid is recycled).

2. Fusion

Fusion methods evaluated the previous quarter (on the described high-fired oxide) were tested using mixtures of the oxide and FBI ash. Results of these tests are shown in Table 8. The results show that fusion with basic fluxes (carbonate-nitrate, carbonate, carbonate-sulfate, and NaOH) give poor recovery. Previously, excellent recovery (>99% Pu, 97% Am) was attained with carbonate-nitrate fusion and good recovery (>84% for both Pu and Am) was attained with NaOH fusion. The difference is attributed to the solubilization of silica in the ash by basic fusion; the silicates form polysilic acid upon acidification to recover the actinides. Polysilicic acid is difficult to filter and sorbs the solubilized actinides from solution.

Attempts to improve filterability by using gelatin strikes; flocculating agents; evaporation and dehydration of the silica gel followed by dilute acid recovery of the actinide; and aging of the heated solution failed to improve recovery.

TABLE 9. Ash Solubilization by Fusion With Phosphate, Phosphate-Nitrate, and Phosphate-Nitrate-Carbonate Mixtures

Flux	Ash Solubilized, (Mean %) ± Standard Deviation
82 wt % $Na_3PO_4.12\ H_2O$-9 wt % Na_2CO_3-9 wt % $NaNO_3$[a]	97
90 wt % $Na_3PO_4.12\ H_2O$-10 wt % $NaNO_3$[b]	96 ±1.4
90 wt % $Na_2HPO_4.7\ H_2O$-10 wt % $NaNO_3$[a]	72
$Na_2HPO_4.7\ H_2O$[c]	78 ±2.3

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a. Single determination
b. Six Samples
c. Duplicate Samples

Flux: Solid Ratio of 10: 1
Time: 2 Hours
Temperature: 980 °C

Sample: Cold FBI Ash

Since carbonate-nitrate fusion gave the best results, attempts were made to solubilize the cooled melt in 0.3*M* NaOH to enable removal of soluble silicates by filtration, followed by residue acidification to recover the actinide hydroxides. Unfortunately, substantial amounts of americium and plutonium were found in the filtrate, possibly the result of carbonate complexation in the basic solution.

Fusion of 0.1 g oxide in 1, 5, 10, and 20 g $NaNO_3$ for 2 hours at 350 °C with subsequent 4*M* HNO_3 recovery gave an average recovery of 0.32 ±0.06% for the four runs. No trend was discernible for the different flux: solid ratios. Apparently, high temperature is necessary for nitrate to be effective. (That nitrate or some radical or ion formed from it is present in carbonate melts at temperatures greater than the 380 °C $NaNO_3$ decomposition temperature is shown by the evolution of NO_X at higher temperatures - see Appendix B).

Cold FBI ash and high-fired oxide were fused (separately) at 900 °C with 50 wt % Na_2CO_3-50 wt % $Na_2B_4O_7.10H_2O$ in platinum. The flux: solid ratio was 10: 1 for ash and 100: 1 for oxide. The cold melt was solubilized in 4*M* HNO_3. Efficiency of dissolution was determined by weight of residue for the cold ash and radiometrically for solubilized actinide oxide. The mean % ± standard deviation was 97% ±3.4 (three tests) for ash solubilization; duplicate tests on oxide alone gave 96% ±2.8 recovery of actinides. This method does give good dissolution but filterability was again poor with ash because of polysilicic acid formation. The method is no better than carbonate-nitrate fusion and introduces boron into process streams.

The results of fusing cold ash with phosphate-carbonate-nitrate and phosphate-nitrate mixtures are shown in Table 9.

The results show that fusion with sodium orthophosphate-sodium nitrate mixtures solubilized the ash; the presence of carbonate did not seem to affect solubilization. Fusion with sodium monohydrogen phosphate, either with nitrate or alone, did not adequately solubilize the ash. Solutions from the orthophosphate-nitrate fusions (which were effective in solubilizing ash) were difficult to filter. Solutions from the monohydrogen phosphate fusions (ineffective in solubilizing ash) were easy to filter. Fusion with sodium dehydrogen phosphate-sodium nitrate flux gave a glossy material which was difficult to dissolve. Because the phosphate fusions offer no advantage over the carbonate-nitrate system no work on the actinide oxide was done.

Fusion of a mixture of 0.9 g FBI ash - 0.1 g oxide in 90 wt % NaOH -10 wt % $NaNO_3$ at 500 °C for 2 hours, with subsequent water recovery instead of acid was also tried, to remove silica as silicate and circumvent the carbonate complexation problem. After filtration, the residue was leached with 4*M* HNO_3. However, in four tests actinide recovery averaged only 3.4 ±2.9%. This anomalous behavior (NaOH fusion alone gives >84% recovery if no silica is present) cannot be explained. Silica should have been solubilized by fusion and removed in the water dissolution and filtration steps.

3. Dissolution with Ce(IV)

The experiments with Ce(IV) came late in this report period so only a few results are available.

The preliminary experiment [with 1 g FBI ash in 125 ml 0.15*M* Ce(IV) in 4*M* HNO_3] demonstrated rapid reduction of Ce(IV) to Ce(III) with evolution of CO_2. Additional ceric ammonium nitrate was added and the mixture was refluxed until all the carbon had been oxidized; the total amount of reagent used, including the initial dissolvent, was 0.05 moles. The white residue (mainly SiO_2) was recovered and dried. Seventy percent of the ash had been solubilized. A second experiment used only the 125 ml of 0.15*M* Ce(IV) in 4*M* HNO_3 under reflux, but included electrolysis of Ce(III) to Ce(IV). A total of 15 amp-hours was delivered at a rate of 6 amps for 1.5 hours and 3 amps for 2 hours. At the end of this time the carbon was gone and 64% of the ash had been solubilized.

In another experiment 250 ml of 0.05*M* Ce(IV) in 4*M* HNO_3 was reacted with 1 g of cold FBI ash with electrolysis and refluxing during the entire period. Two amps were delivered for 3 hours (6 amp-hours). At the end of this time, carbon had been oxidized to CO_2 and 66% of the ash had been solubilized.

Additional work on this system is in progress. Preliminary results suggest that: (1) little solubilization of oxide occurs during the early reaction stage since Ce(IV) is rapidly reduced by carbon, and (2) the solubilization of the oxide is slow even when carbon is gone under our present operating conditions [0.05-0.15*M* Ce(IV) in 4*M* HNO_3 with electrolysis at 0.5-6 amps while refluxing].

4. Removal of Silica

The results of pretreating cold ash samples by refluxing them with NaOH before fusion are shown in Figure 4. Refluxing with ⩾6*M* NaOH adequately removes silica, permitting subsequent fusion with 90 wt % Na_2CO_3-10 wt % $NaNO_3$ and actinide recovery with 4*M* HNO_3. The cold ash residues were dried and weighed to determine the wt % residue. Duplicate samples of 1 g FBI ash containing 0.1 g high-fired oxide gave 98% ±1.7 recovery of the actinides.

SUMMARY AND CONCLUSIONS

The program to determine the feasibility of actinide recovery from combustible waste is continuing. Evaluation of leaching and solubilization methods using mixtures of ^{241}Am-traced high-fired PuO_2 and fluidized bed incinerator (FBI) ash, and conventional (contaminated) incinerator ash shows that:

Refluxing with 0.15*M* cerium(IV) in 4*M* nitric acid oxidizes the carbon present in all incinerator ash and solubilizes 65% of the ash.

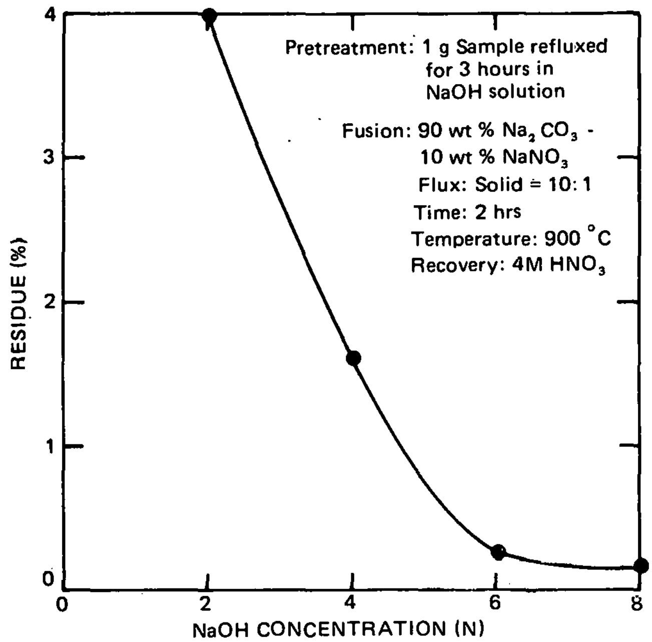

FIGURE 4. Effect of Sample Pretreatment to Remove SiO_2 on Solubilization by Fusion

Adequate actinide recovery may require dissolution of silica present in ash to free encapsulated actinide oxide so that dissolvent may contact the oxide.

Fusion with 90 wt % sodium carbonate -10 wt % sodium nitrate solubilizes both silica and actinide oxide. However, attempts to recover the actinides in 4*M* HNO_3 causes formation of polysilicic acid, which is difficult to filter and adsorbs the solubilized plutonium. Removal of silica is therefore necessary for this method.

Silica can be removed by refluxing with $\geq$6*M* sodium hydroxide. The actinides can then be solubilized and recovered without interference from silica.

The actinide recovery methods described were chosen after preliminary evaluations of several leaching and solubilization methods using ^{241}Am-traced high-fired PuO_2 only. Methods investigated which did not appear as promising were fusion with various sodium salts (carbonate, carbonate-sulfate, bisulfate, pyrosulfate, hydroxide, and phosphates); acid digestion with 95 vol % H_2SO_4 -5 vol % HNO_3; and refluxing with 12*M* HNO_3.

Attempts to prepare simulated ash by fluidized plutonium nitrate-traced ash in a quartz reactor failed because of ignition and rapid burning of the high-carbon ash. A laboratory scale fluidized bed incinerator (FBI) is being built which will burn combustible waste. Actinide recovery methods will be evaluated using the contaminated ash produced in this FBI system.

FUTURE WORK

Work has begun on recovering plutonium and americium from conventional incinerator ash and from mixtures of FBI ash and high-fired oxide. The FBI ash-PuO_2 mixture simulates contaminated FBI ash; actual contaminated FBI ash will be prepared by adding plutonium to combustible waste and burning it in a laboratory scale FBI system. This system is currently being built and completion (including preliminary testing) is scheduled early in 1978. Combustible wastes to be burned in the FBI system include general trash, ion exchange resins, and spent solvents.

The most promising actinide recovery techniques evaluated to date are fusion with carbonate-nitrate mixtures and dissolution with Ce(IV) is HNO_3. Because Cd(IV) in HNO_3 is a low temperature system and because Cd(III) can be electrolytically oxidized to Ce(IV) and recycled, this system is more appealing. FY 1978 will be spent in evaluating this primary recovery method and attendant secondary recovery methods. The carbonate-nitrate system will be evaluated only if the Ce(IV)-HNO_3 system proves to be inadequate. Pretreatment methods to remove silica will be refined if silica removal proves to be necessary for adequate actinide recovery.

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APPENDIX A

Fluidized Bed Incinerator For Plutonium Contaminated Waste

A quartz, laboratory-scale fluidized bed incineration (FBI) system has been designed for burning plutonium contaminated combustibles. The unit will be used to produce representative FBI ash samples for plutonium recovery studies. It will have the capacity to burn approximately one pound of waste per hour, which represents a heat release of about 10,000 btu/hr. Completion of assembly and testing of the quartz ware, control instrumentation, and auxiliary equipment is scheduled early in 1978.

FBI Process Description

The FBI process differs considerably from conventional incineration; consequently, a dissimilar type of ash is produced. In the fluidized bed system combustion is carried out in two separate steps. Initial combustion takes place in a bed of fluidized sodium carbonate (Na_2CO_3) granules. This bed serves a dual function, one of which is providing an active media for uniform heat transfer. This characteristic of the fluidized bed permits controlled combustion at a relatively low operating temperature of approximately 550 °C. The low combustion temperature produces a low-fired, non-refractory ash that cannot be achieved by conventional incineration methods. In addition to optimum heat transfer, the primary fluidized bed supplies Na_2CO_3 for immediate neutralization of chlorides or sulphates released during waste decomposition. This reaction converts a portion of the Na_2CO_3 bed material to sodium chloride (NaCl) and sodium sulphate (Na_2SO_4).

An air-nitrogen gas mixture is used for fluidization of the Na_2CO_3 bed. This mixture is controlled to provide only enough oxygen for the degree of combustion required to maintain an operating temperature of 550 °C. In the absence of sufficient oxygen for complete burning, a portion of the waste is pyrolyzed into gaseous hydrocarbons. Afterburning of these unburned hydrocarbons is accomplished in a bed of fluidized oxidation catalyst granules. A catalyst of chromic oxide (Cr_2O_3) on alumina (Al_2O_3) support material is used for this application. Air is used for fluidization in the catalytic afterburner, which operates at approximately 550 °C. The fluidization air also provides excess oxygen for complete combustion of the hydrocarbons entering the bed.

Dust is generated in both beds by particle abrasion during fluidization. Ash from waste combustion is also ground to a very fine powder in the fluidized beds. This fine particulate mixture made up of Na_2CO_3, NaCl, Na_2SO_4, Cr_2O_3, Al_2O_3, carbon and mineral ash is removed from the primary bed and afterburner by elutriation with the flue gas stream. The fines are removed from the flue gas by cyclone separation and sintered metal filtration. All ash is removed from the system in this manner, thus it is unnecessary to drain the beds for ash removal. Consequently, FBI ash is in the form of a fine particulate containing the sodium salts, catalyst, carbon, and mineral ash previously mentioned. The sodium salts and catalyst would not be present in conventional incinerator ash; however, the same sodium salts would be present in the aqueous wastes from conventional off-gas scrubbing systems.

Equipment Description

The laboratory scale incineration system shown in Figure Al will be installed within a glovebox for contamination containment. Modular quartz construction was selected for the incinerator and afterburner vessels to facilitate modifications during installation and cold testing and to permit visual observation of the fluidized bed process. The incinerator consists of two vessels, a lower primary

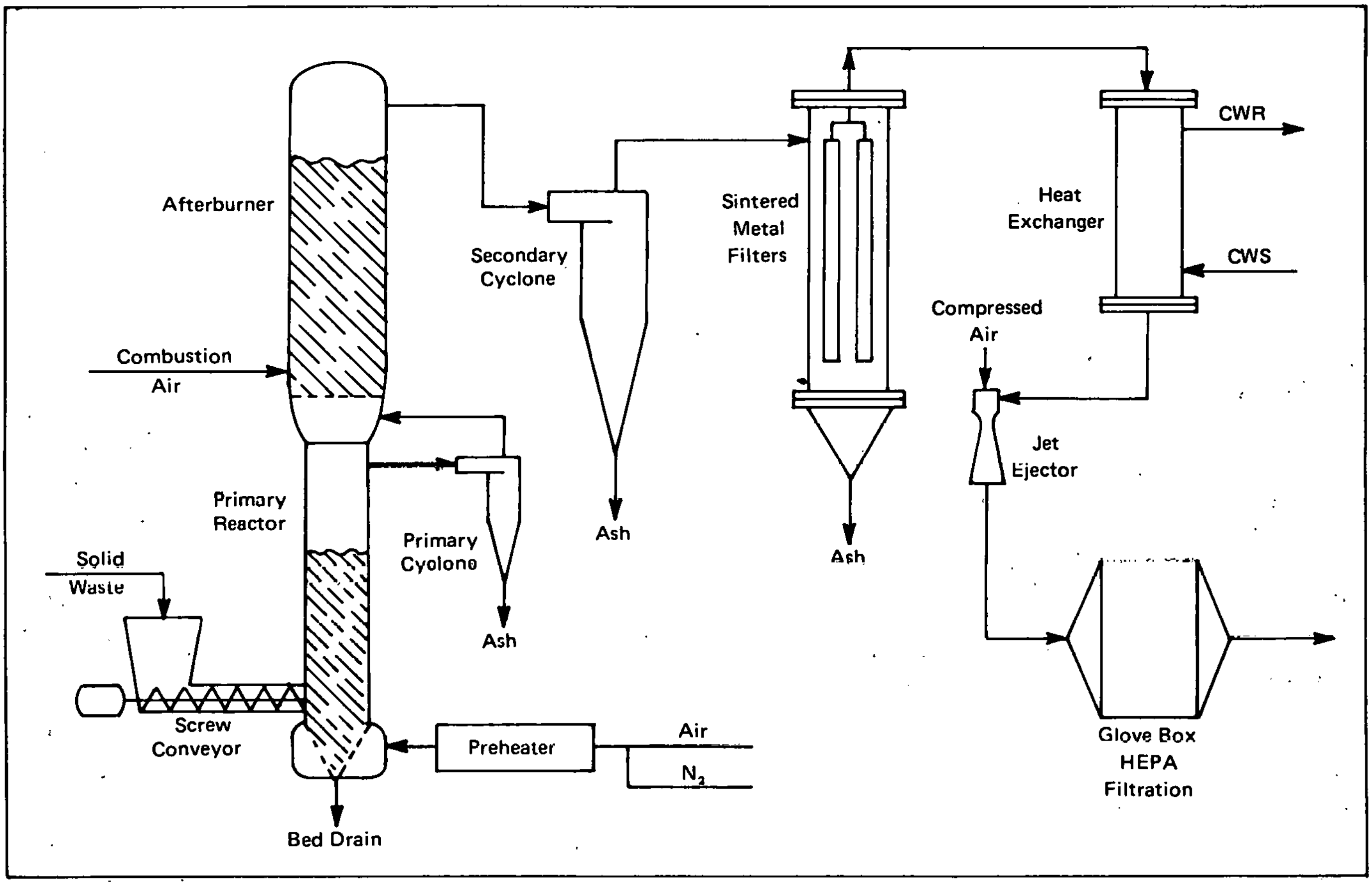

FIGURE A1. Schematic of Laboratory Scale Fluidized Bed Incineration System

reaction chamber and an upper afterburner chamber. The primary reactor is fabricated from 90-mm diameter quartz and is approximately 560 mm in length. The afterburning section is 150 mm in diameter and about 813 mm in length. The offgas from the primary reactor will pass through a quartz cyclone separator to remove most of the entrained dust from the stream before it passes through another quartz cyclone separator for dust removal prior to final filtration in the sintered metal filters. Six 38-mm diameter by 457-mm long sintered metal filters will perform this function. Clean off-gas leaving the metal filters is cooled by a water cooled heat exchanger before being exhausted into the glovebox ventilation system. Motive force for the system will be provided by a small air ejector.

Fluidization gas will be preheated during startup with a Chromolox electrical resistance heater and a tube furnace pebble bed heater. A 32-mm diameter screw conveyor will feed preshredded waste into the primary reactor. Pneumatic controls will maintain gas flow rates and any air - N_2 gas ratio that is desired for fluidization and combustion in the primary reactor. The ejector will also be pneumatically controlled to maintain a slight negative pressure throughout the system. Temperatures will be measured at various points within the system for control and data acquisition.

Planned Operating Procedure

Uncontaminated combustible waste samples of predetermined composition will be prepared and shredded outside the glovebox. Waste will then be weighed and transferred into the glovebox where it will be spiked with a predetermined amount of plutonium. Plutonium can be added in any form that might be desirable for future ash leaching tests. The incinerator will be preheated to approximately 300 °C before waste feeding is started. Waste will then be screw-conveyed into the incinerator at a rate sufficient to maintain an operating temperature of approximately 550 °C in both the primary cyclone, secondary cyclone, and sintered metal filters as is done on the larger FBI units. When a run is complete, ash and bed samples will be analyzed to compile a plutonium material balance. Work will then proceed to recover the plutonium from the ash samples.

APPENDIX B

Thermogravimetric and Mass Spectral Analysis of Volatiles Produced During Fusion Experiments

Fusion experiments have shown that Na_2CO_3 alone is not an effective flux for solubilization of ash and high-fired actinide oxides, at least not at temperatures less than 1000 °C. Fusion with 90 wt % Na_2CO_3-10 wt % $NaNO_3$ is very effective, however. Since $NaNO_3$ decomposes at 380 °C the question arose as to whether the $NaNO_3$ oxidation of ash constituents is complete at that relatively low temperature or whether NO_X species are present in the melt at higher temperatures. Thermogravimetric analyses (TGA) and mass spectral (MS) analyses were therefore made simultaneously on some fluxes and flux-ash mixtures to correlate weight loss and off-gas composition at temperatures up to 1200 °C.

The programmed heating rate was 10 °C per minute. The volatile components were carried into the mass spectrometer inlet in a stream of helium carrier gas.

The percent of weight loss and the temperature ranges in which the losses occurred are shown in Table B-1, with comments concerning the species being evolved. Table B-2 shows the composition of the gas over the sample at the specified temperature. The results suggest that the carbonate-nitrate system is successful because nitrate decomposition products (oxidizing species) are present in the melt at temperatures much higher than the 380 °C decomposition temperature of $NaNO_3$. Nitrate decomposition species are also undoubtedly present in the hydroxide-nitrate system at higher temperatures (as shown by the small amount of NO_X at 500 °C in Table B-2 and nitrate decomposition at $T > 750$ °C shown in Table B-1); however NaOH is volatile enough that at temperatures >500 °C, it wets the sides of the crucibles and "crawls out," carrying sample with it. Although we have not defined the mechanism, successful fusion with nitrate seems to require presence of a flux which inhibits nitrate decomposition and loss at lower temperatures and acts as a stabilizing medium for the effective oxidizing species which are present at higher temperatures. Comparing the phosphate-nitrate-ash results also shows the evolution of NO is much greater when ash is present; this is almost certainly the result of oxidation of carbon in the ash.

TABLE B-1. TGA/MS Results for Fusion Experiments

Sample	Temperature Range (°C)	Weight Loss (wt %)	Event
90 wt % Na_2CO_3 -	25-180	11.5	desorption of H_2O
10 wt % $NaNO_3$	180-500	0	
	500-900	9.2	nitrate and carbonate decomposition
	900-1200	20.7	carbonate decomposition, volatilization of sodium oxide resulting in attack of quartz balance components
90 wt % Na_2CO_3 -	25-160	8.91	loss of sorbed H_2O
10 wt % $NaNO_3$ +	160-300	0.18	further water loss
1 g FBI ash	320-500	1.78	carbonate decomposition.
(Flux: Solid = 10/1)	500-750	9.45	nitrate decomposition
	760-980	2.14	carbonate decomposition
90 wt % NaOH-	25-350	6.2	loss of sorbed H_2O
10 wt % $NaNO_3$	490-960	41.8	water evolved, nitrate decomposition above 800°C-- sodium hydroxide volatile attacked quartz balance components
90 wt % NaOH-	25-210	6.19	loss of sorbed H_2O
10 wt % $NaNO_3$ +	210-410	2.03	water evolved
	410-900	20.3	water, nitrate decomposition
1 g FBI Ash			above 750°C, volatilization of sodium hydroxide-attack
(Flux: Solid = 10/1) of quartz balance components.			
90 wt % $Na_3PO_4 .12\ H_2O$-[a]	25-180	41.1	loss of water of hydration
	180-250	2.84	further loss of H_2O
10 wt % $NaNO_3$	250-490	0	
	490-800	2.84	decomposition of nitrate salt (N_2, NO, O_2)
	800-1030	1.42	further decomposition, possible volatile of sodium oxide
90 wt % $Na_3PO_4 .12\ H_2O$-[a]	25-150	41.2	loss of hydrated H_2O
10 wt % $NaNO_3$ +	150-220	2.44	further loss of H_2O
	220-380	0	
1 g FBI Ash	380-660	2.82	decomposition of nitrate
(Flux: Solid = 10/1)	660-1000	0	salt (N_2, O_2, NO)

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[a] Original weight adjusted to provide specified wt % of "anhydrous" salt after water of hydration has been expelled.

TABLE B-2. Composition of Gases Evolved During Fusion Experiments

		Volumes % of Gas Over Sample								
Sample	Temperature (°C)	H_2O[a]	CO_2	NO	N_2O	O_2	N_2	H_2	Ar	H.C.[b]
90 wt % Na_2CO_3-10 wt % $NaNO_3$ + 1 g FBI Ash	900	T[c]	77.6	18.6	--	--	3.6	0.23	--	T[c]
90 wt % NaOH-10 wt % $NaNO_3$ + 1 g FBI Ash	500	34.5	--	0.54	2.0	2.4	19.5	40	0.06	1.0
90 wt % $Na_3PO_4 .12 H_2O$[d]-10 wt % $NaNO_3$	950	49	--	0.66	0.82	38.0	3.3	7.3	0.04	1.0
10 g of 90 wt % $Na_3PO_4 .12 H_2O$[d]-10 wt % $NaNO_3$ + 1 g FBI Ash	950	5.7	16.1	59.5	1.4	0.3	13.5	3.1	0.04	0.43

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a. Because the sample was evacuated prior to heating, hydrated water may have been removed to some extent. Mass Spectral valves for water are less reliable.

b. Hydrocarbon is reported as the total hydrocarbon in the volatile, including methane, ethane, propane, butane, and benzene.

c. Trace.

d. Original weight adjusted to provide the specified wt % of "anhydrous" salt after water of hydration has been expelled.