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ACTINIDE RECOVERY FROM COMBUSTIBLE WASTE:
THE Ce(IV)-HNO_3 SYSTEM

FINAL REPORT

Program for the Waste Management Analysis of the
Nuclear Fuel Cycle – Oak Ridge National Laboratory

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CHEMISTRY RESEARCH AND DEVELOPMENT

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Abstract. A new method for the recovery of actinides from incinerator ash is described. Actinides in ash can be leached effectively by refluxing with Ce(IV) in HNO_3; solubilization of actinide in ash was $\geqslant$95% at ash concentrations to 30 g/ℓ in stirred leachant. Plutonium and americium were the actinides present in the ash.

Solubilized plutonium and americium were recovered from Ce(IV)-HNO_3 solution by solvent extraction. Extraction of plutonium into 30% tributyl phosphate in n-dodecane gave 99.99% recovery. The plutonium-depleted solution was then extracted with 30% dihexyl-N,N-diethylcarbamoylmethylenephosphonate (DHDECMP). Americium recovery was 99.64%.

The Ce(IV)-HNO_3 system was compared with the HF-HNO_3 system now in common use. Advantages of the former include less equipment corrosion, no volatilization of silica, safe oxidation of carbon residues, minimal secondary waste (Ce is recycled), and better solubilization of actinide in the initial contact. However, additional contacts do not significantly improve solubilization, and a small fraction of actinide is not solubilized with Ce(IV)-HNO_3 that can be solubilized by HF-HNO_3.

The effect of the fission product ruthenium on the dissolution of actinides in the Ce(IV)-HNO_3 system was investigated briefly, and a method for removing the ruthenium electrolytically was developed. Several process flowsheets were also considered. Actinide recovery requirements will suggest which of these might best be used.

INTRODUCTION

Reprocessing 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 and are either recycled or are sent 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 actinides for recycle.[3]

Because of the need for an early assessment of the partitioning transmutation concept, the program was limited to applied, rather than basic, research and development. In addition, the total program is only 3 years in length (FY 1977 through FY 1979) and only the first 2 years were to involve experimental work. The third year will be spent on the cost-risk-benefit analysis, using data obtained during the experimental phase.

One of the experimental tasks defined was actinide recovery from combustible waste. Combustible waste produced during reactor fuel fabrication and processing comprises paper, wood, plastics, rubber, cloth, spent solvent, activated carbon, and ion exchange resins. These wastes are incinerated to reduce waste volume and organic content and to facilitate actinide recovery. The incinerator effluent is a residue containing actinides and fission products. The objective of this project was to evaluate methods to recover actinides from these residues.

Previous reports have described early experimental work, including evaluation of common leaching, acid digestion, and fusion methods for dissolution of high-fired $^{239}PuO_2$ (with tracer amounts of ^{241}Am) and solubilization of actinides in incinerator ash.[1,4-6] One of the more promising methods proved to be dissolution in Ce(IV)-HNO_3 mixtures, a system that has been used by other workers to solubilize PuO_2.[7,8]

This report describes (1) evaluation of actinide dissolution in the Ce(IV)-HNO_3 system in the presence of ash, (2) recovery of solubilized actinides by solvent extraction, and (3) the effect of the fission product ruthenium on the system. Ash heels (residues left after treatment of incinerator ash) from both the Ce(IV)-HNO_3 and HF-HNO_3 systems were treated with the other leachant to determine the additional actinide dissolution attainable. The efficiency of the Ce(IV)-HNO_3 and HF-HNO_3 systems in solubilizing actinides in incinerator ash is compared. Flowsheets and partial material balances are also provided, based on tentative flowsheets provided by ORNL.[2]

EXPERIMENTAL

Materials and Equipment

Samples of ash were obtained from the fluidized bed incinerator (FBI) system and the conventional incinerator in operation at the Rocky Flats Plant (RFP). No actinide-contaminated waste has been incinerated in the FBI, so only cold FBI ash was available. The combustible wastes and both incinerator systems were described previously.[1,9,10] The composition of the FBI ash and "typical" conventional incinerator ash are shown in Table 1. The ashes differ mainly in the amount of silica, iron, aluminum, and soluble salts. Conventional incinerator ash has more silica because of RFP processes involving reduction of plutonium to metal and more iron from glove-box sweepings (which are packaged with combustibles). The high amount of aluminum in FBI ash results from the chromic oxide on alumina catalyst used in the FBI. Large amounts of sodium salts are present in FBI ash because Na_2CO_3 is the fluidized medium.

TABLE 1. Composition of Incinerator Ash

	Quantity in Ash[a]	
Component	Fluidized Bed (wt %)	Conventional (wt %)
Pu	(b)	4.6
Am	(b)	5.45×10^{-3}
SiO_2	9	48
C	26	17
Fe_2O_3	0.5	5.7
MgO	1.0	4.0
CaO	1.0	4.0
Al_2O_3	4.9	(c)
Na salts	23	(d)
Other	35	16

a. Single determination.
b. Low level; total count <10^3 dpm/g ash.
c. Negligible; large amounts in FBI ash from catalyst in afterburner.
d. Negligible; large amounts in FBI ash from Na_2CO_3 (fluidized medium).

Portions of both ashes were washed with distilled water to remove water-soluble material and/or were refluxed with 8*M* NaOH for 2 hr (liquid-to-solid ratio of 60 ml/g) to solubilize silica and enable its removal by filtration. However, once the Ce(IV) generation curves had been defined, using cold FBI incinerator ash, subsequent experiments were done on unwashed conventional incinerator ash. This change occurred because silica was not solubilized in Ce(IV)-HNO_3 leachant, and little soluble material was present in conventional ash.

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* HNO_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. Acidity then 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 950 ± 25 °C to constant weight. Analysis determined the americium concentration to be 2.27×10^{-4} g/g Pu.

Ash heel residue from the Ce(IV)-HNO_3 dissolution step was prepared (for HF-HNO_3 dissolution studies) by reacting unwashed conventional incinerator ash in 0.1*M* Ce(IV) in 4*M* HNO_3 until the actinide content was 0.0454 g Pu/g and 5.45×10^{-5} g Am/g residue.

Ash heel from the RFP HF-HNO_3 leach process[10] was obtained from the Chemical Operations Group. This ash heel was residue from the batch contacting of conventional incinerator ash with 0.1*M* F^- in 12*M* HNO_3. At 0.220 g Pu/g residue and 1.74×10^{-4} g Am/g residue, the actinide content is still well above the current discard level of 0.0034 g Pu/g residue (discard limits are based on the major element, i.e., plutonium).

The simulated fission product solution used in the experiments with ruthenium was prepared as reported in the literature.[11]

The tributyl phosphate (TBP) and n-dodecane (NDD) were technical grade. The 30% dihexyl-N,N-diethylcarbamoylmethylenephosphonate (DHDECMP) in diisopropylbenzene (DIPB) was prepared from 86% pure DHDECMP by L. D. McIsaac of Allied Chemical Company at Idaho National Engineering Laboratory. At present, DHDECMP is commercially available only in impure form (50%) from Wateree Chemical Company, Lugoff, South Carolina, and must be purified before use; methods used in purification have been described.[12] All other chemicals used were reagent grade.

The reaction vessel used in studies with electrolytically generated Ce(IV) is shown in Figure 1. The apparatus comprises a 500-ml, three-necked flask equipped with a condenser; a well with a glass frit that isolates the cathode from the system; and the anode. Platinum electrodes were used. The total surface area of each electrode was 12 cm^2.

Procedure

Ce(IV) Production and Actinide Solubilization

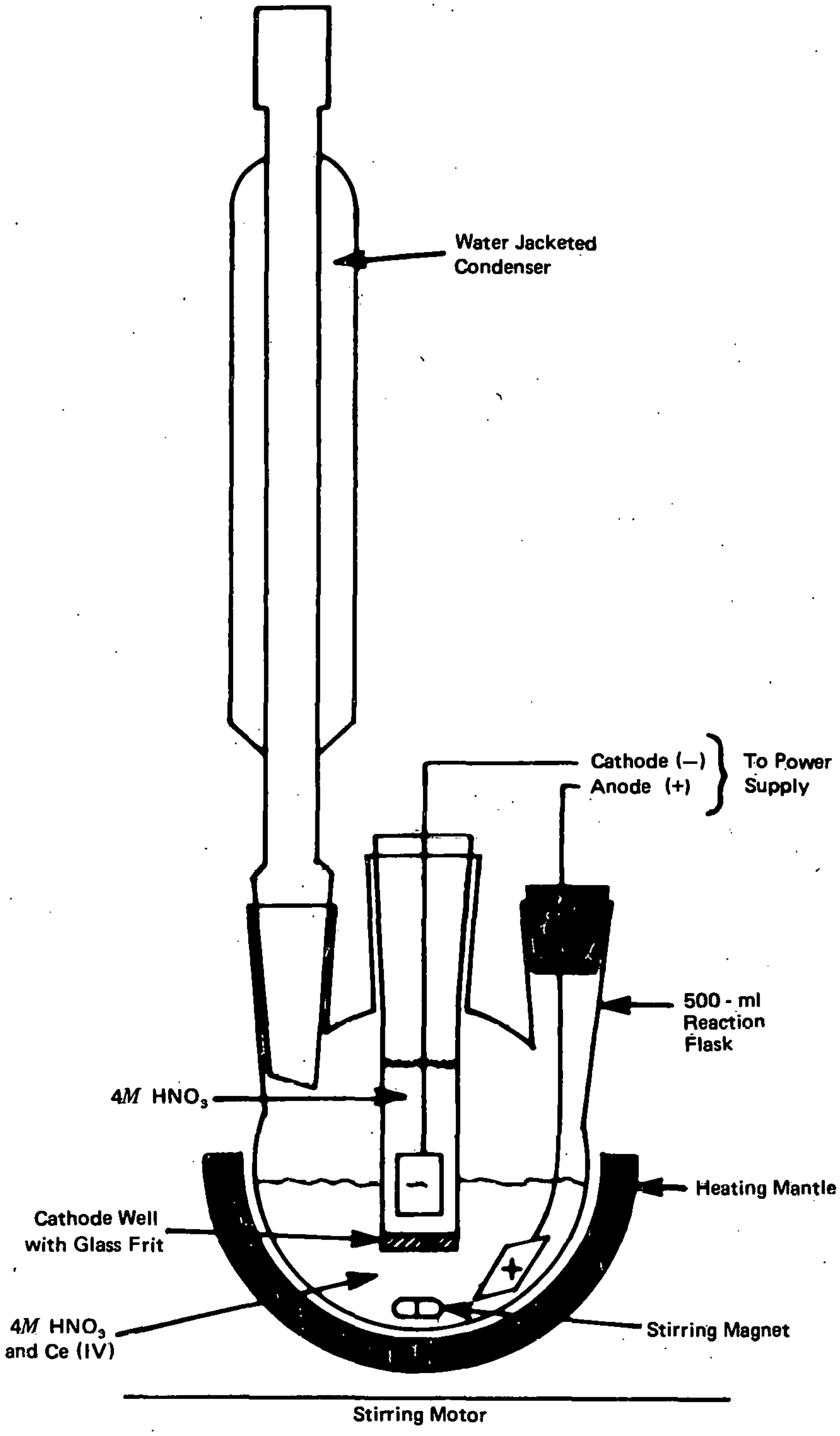
In studies of the rate of Ce(IV) generation, a known amount of cerous nitrate was dissolved in 250 ml of 4*M* HNO_3 and heated to boiling in the 500-ml flask. A constant current was then applied to the system. The reaction was kept at reflux temperature with a heating mantle. Cerium [Ce(IV)] generation was monitored by microtitration against a standardized Fe(II) solution with a ferrous-phenanthroline complex indicator. Samples were withdrawn and analyzed at regular intervals.

When the Ce(IV) concentration equalled the initial Ce(III) concentration, 1 g of ash (either untreated, water washed, or refluxed in NaOH) was added (liquid-to-solid ratio of 250 ml/g). Electrolysis was continued until a constant Ce(IV) concentration was regained.

In preliminary studies of actinide solubilization, 1 g of ash was added directly to 250 ml of 0.1*M* Ce(III) solution and the mantle was turned on. When the contents of the flask reached boiling, a current of 1.0 A was applied. Actinide concentration was monitored at regular intervals by alpha counting of 0.010-ml aliquots. Electrolysis was continued until a constant actinide level was reached.

Residues from this reaction were recovered by filtration through filters rated for removal of particulates ⩾0.2 μm. These residues were refluxed for 2 hr in 0.1*M* F^- in 12*M* HNO_3. The reflux residues were fused with a 9:1 Na_2CO_3-$NaNO_3$ flux at 900 °C for 2 hr, with subsequent actinide solubilization in 4*M* HNO_3.

FIGURE 1. Apparatus for Actinide Solubilization With Electrolytically Generated Cerium



Multiple contact studies were also done by contacting the residue from one cerium reaction again with fresh cerium solution. No attempt was made to readjust the liquid-to-solid ratio.

Additional experiments were done to determine the amount of ash that could be efficiently solubilized before a solution change became necessary. Ash was added batchwise to the 250 ml of 0.1*M* Ce(III) solution; 5-, 7.5-, 10-, and 15-g samples were added, giving corresponding concentrations of 20-, 30-, 40-, and 60-g ash/ℓ of dissolvent. The mantle was then turned on and the procedure just cited was repeated.

The actinides were recovered from the Ce-HNO_3 dissolver solution by solvent extraction. The solution was heated almost to boiling, and solid oxalic acid was slowly added to reduce Ce(IV) to Ce(III) and thus prevent Ce(IV) extraction. The end point of this titration was determined by loss of the characteristic Ce(IV) color. Plutonium was batch-extracted into 30% TBP in n-dodecane. Cerium and americium were batch-extracted into 30% DHDECMP in DIPB. Seven batch extractions were done with an aqueous-to-organic (A/O) ratio of one with both TBP and DHDECMP. A vortex mixer ensured vigorous agitation during the 2-min extractions.

Comparison of the Ce(IV)-HNO_3 and HF-HNO_3 Systems

One-gram samples of conventional incinerator ash were refluxed with 0.1*M* F^- in 12*M* HNO_3 for 2 hr or with 0.1*M* Ce(IV) in 4*M* HNO_3 for 5 to 7 hr. The residues were contacted with fresh solution under the same conditions to determine the amount of actinide solubilized by subsequent contacts.

A considerable amount of ash heel remains after conventional incinerator ash is refluxed in 0.1*M* F^- in 12*M* HNO_3. One-gram samples of the Chemical Operations material were also refluxed in 0.1*M* Ce(IV) in 4*M* HNO_3 for 6 hr to determine the degree of actinide solubilization.

Additional experimental work was done to determine if an optimum liquid-to-solid (L/S) ratio exists for the recovery of actinide from ash residue with 0.1*M* F^- in 12*M* HNO_3. Liquid-to-solid ratios of 25, 38, 50, and 75 ml of 0.1*M* F^- in 12*M* HNO_3 per gram of residue were tested, with reflux times of 2 to 6 hr. After refluxing, the sample was filtered and the filtrate sampled for actinide analysis. Residues were dried, weighed, and fused in $K_2S_2O_7$ (flux-to-solid ratio of 20). The melt was solubilized in 250 ml of 4*M* HNO_3, filtered, and the filtrate sampled for analysis. The residue from this step was also submitted for analysis of actinide content.

Removal of Ruthenium by Electrolysis

Fission product ruthenium is expected to be present in some fuel reprocessing solutions. The bulk of the ruthenium will report to the dissolver solids in head-end processing or to the high-level waste during (Purex) solvent extraction, but small amounts may be present in combustible waste. It is not expected that this will be a problem. Other workers, however, have shown that ruthenium interferes with the Ce(IV)-HNO_3 dissolution of PuO_2; the mechanism postulated was oxidation of ruthenium to RuO_4, evolution of RuO_4, condensation of RuO_4, and reduction to RuO_2 with subsequent return to the solution and repetition of the cycle.[8] Although ruthenium can be at least partially removed as RuO_4 by sparging the acidic solution, several preliminary electrolysis experiments were done to determine if ruthenium could be removed by electroplating.

The current and time required to remove 17.8 mg of ruthenium from 250 ml of 4*M* HNO_3 were determined by solubilizing 44 mg of $RuCl_3 \cdot (1\text{-}3)H_2O$ in the acid and electrolyzing at various currents. The electrodes were weighed and the solution was analyzed at the end of each period of electrolysis.

A simulated fission product solution was prepared as described in the literature.[11] However, solids did form in this solution before it was used; these solids were removed by filtration. In the experiments, 10 ml of this standard fission product solution was added to 240 ml of 4*M* HNO_3 and the mixture was electrolyzed. Samples of the feed and final solution were analyzed. The experiments were repeated with 0.1*M* Ce(IV) present.

TABLE 2. Actinide Solubilization With $0.05M$ $(NH_4)_2Ce(NO_3)_6$ in $4M$ HNO_3

Temperature: Reflux

Liquid-to-Solid Ratio: 1250 ml/g (Oxide)
125 ml/g (Ash)

Ash Pretreatment: Refluxed in $8M$ NaOH

Time: 5 hours (Oxide)
7 hours (Ash)

Sample	Actinide Solubilization in Ce(IV) Pu (wt %)	Am (wt %)	Residue Remaining After Listed Operation 8*M* NaOH (wt %)	Ce(IV)-HNO_3 (wt %)	$0.1M$ F^- in $12M$ HNO_3 (wt %)
Oxide, 0.2 g	>99.9	>99.9	(a)	–	–
FBI Ash-oxide 1.8-g ash + 0.2-g oxide	98	98	44	53	0.4
Conventional ash, 2.0 g	97 ± 1.7[b]	98 ± 1.5	69 ± 0.30	26 ± 1.3	4.1 ± 0.53

a. Not measured.
b. Mean ± standard deviation for duplicate analyses.

In a final experiment, an electrode with 17.4 mg of ruthenium plated on it was used as the anode in an attempt to oxidize $0.1M$ Ce(III) to $0.1M$ Ce(IV) in 250 ml of $4M$ HNO_3 and solubilize the actinides in 1 g of conventional incinerator ash.

RESULTS AND DISCUSSION

Ce(IV) Production and Actinide Recovery

In preliminary experiments, Ce(IV) was introduced as ceric ammonium nitrate. Results of attempts to solubilize ash and oxide samples are shown in Table 2. Excellent actinide dissolution was achieved with the system; thus, work on actinide solubilization by carbonate-nitrate fusion was preempted to permit optimization of the Ce(IV)-HNO_3 system.

Since large amounts of ceric ammonium nitrate were needed just to oxidize the carbon, and NH_4^+ would be added to the waste stream, it was decided to generate the Ce(IV) electrolytically.

Other workers have shown that PuO_2 dissolution is optimum in $0.1M$ Ce(IV) in $4M$ HNO_3.[7, 8] No work was done in this program to determine the effect of HNO_3 concentration, but the rate of Ce(IV) generation was studied as a function of different cerium concentrations and currents. The results of varying amounts of cerium are shown in Figure 2. The maximum Ce(IV) concentration was attained in about 2 hr.

At 2 hr, the ash was added, Ce(IV) was immediately reduced to Ce(III), and the cycle of cerium oxidation and reduction continued until the carbon was destroyed. At this time, the Ce(IV) concentration began to increase again but at a slower rate (especially for $0.05M$ Ce). As one would expect, carbon was more rapidly depleted when higher Ce(IV) concentrations were present initially. However, higher concentrations of cerium are not necessary for solubilization so $0.1M$ Ce(IV) was chosen.

The effect of different currents is shown in Figure 3. The process was too slow at 0.4 A, and above 1.2 A, gassing due to boiling and electrolysis caused fluctuations in current, leading to cell inefficiency. A current of 1.0 A was chosen for subsequent work.

Later experiments used only unwashed conventional incinerator ash since ORNL had decided to plan for

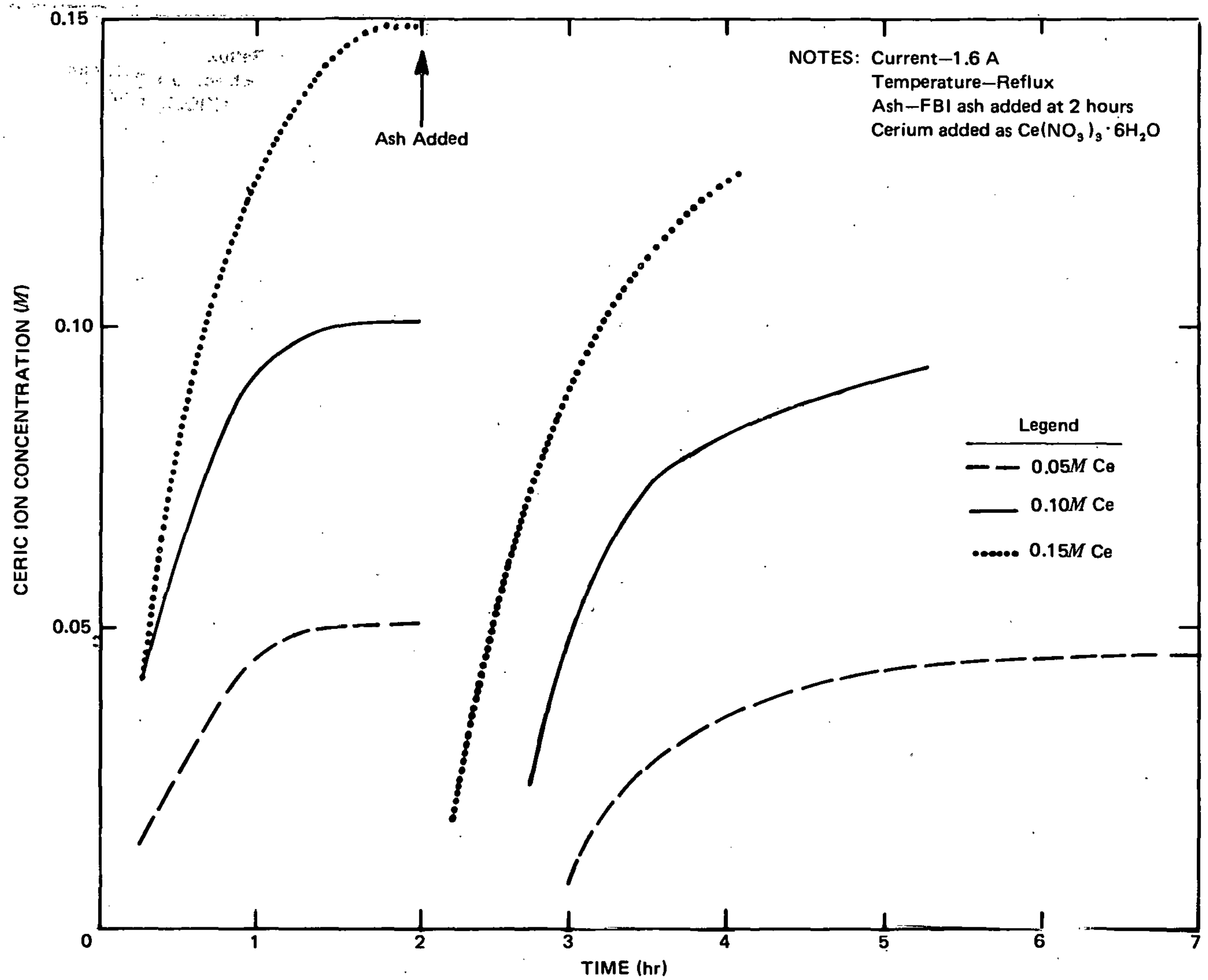


FIGURE 2. Rate of Ce(IV) Generation

conventional incineration in the fuel processing system. Preliminary washing was unnecessary then since negligible water-soluble material was present. Furthermore, refluxing with NaOH was omitted since silica is not solubilized in the Ce(IV)-HNO_3 system. The amounts of actinide solubilized by the Ce(IV)-HNO_3 system, by subsequent refluxing of residue with 0.1*M* F^- in 12*M* HNO_3, and by fusion in90 wt % Na_2CO_3-10 wt % $NaNO_3$ are shown in Table 3. Without the 8*M* NaOH pretreatment step, actinide solubilization is reduced by 2 to 4%. The mechanism by which silica retains the actinide is unknown; possible mechanisms include actinide encapsulation, adsorption, or presence of a synthetic mineral. It is unlikely that recovery of an additional 2 to 4% of the actinide would justify the NaOH pretreatment step.

Results of multiple batch contacts, shown in Table 4, suggest that such contacts would not be worth the effort for actinide recovery. Additional actinide recovery resulting from refluxing in 0.1*M* F^- in 12*M* HNO_3 again suggests that actinide is retained in some way by silica. The carbonate-nitrate fusion step, which completely solubilizes silica, completed the actinide dissolution process.

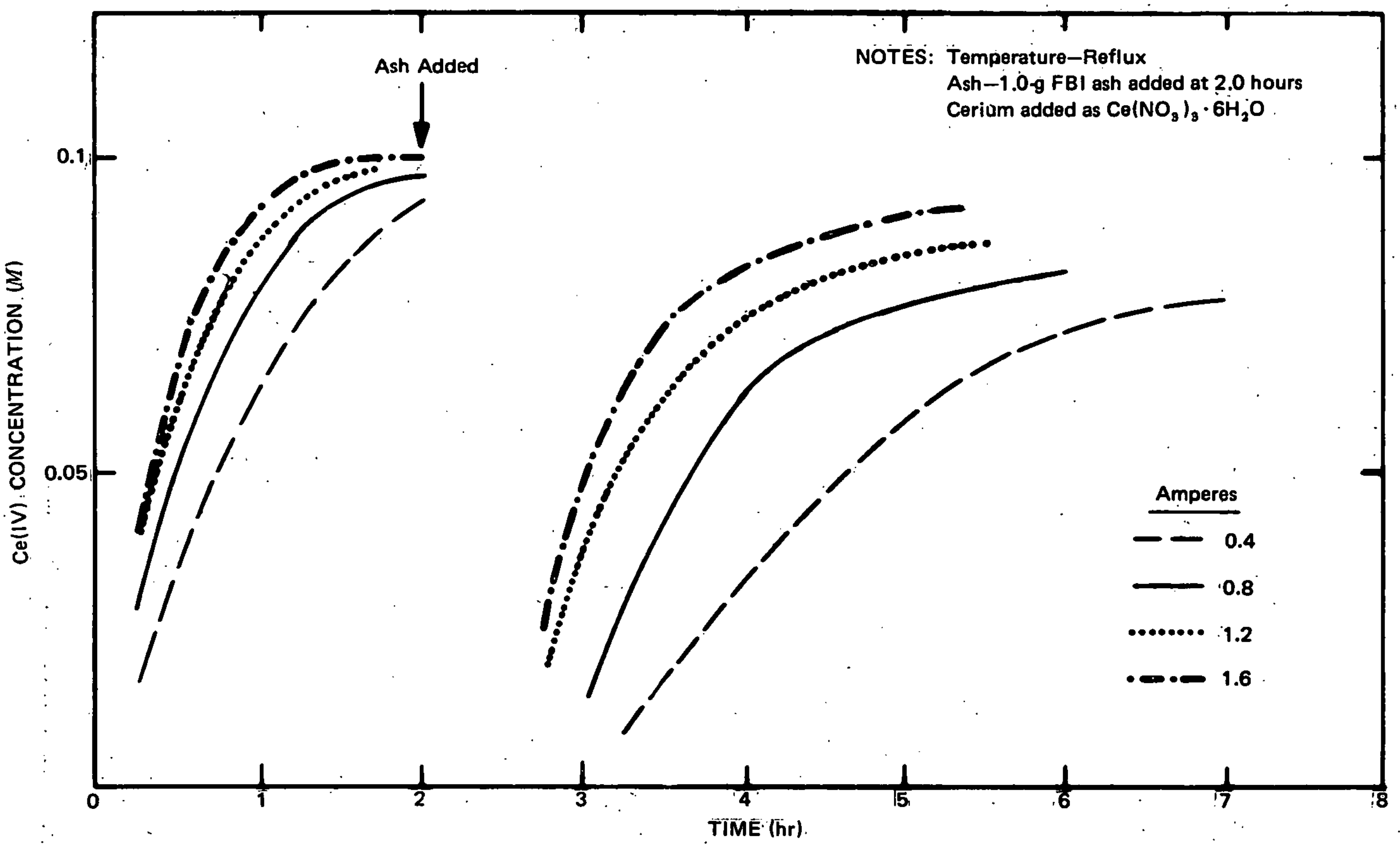


FIGURE 3. Ce(IV) Generation as a Function of Current and Time

TABLE 3. Solubilization of Actinide Contained in Untreated Conventional Incinerator Ash

Sample: 1.0 g ash

Method	Reagent	Time (hr)	Temperature (°C)	Actinide Solubilized[a] Pu (wt %)	Actinide Solubilized[a] Am (wt %)
Dissolution	$0.1M$ Ce(IV)-$4M$ HNO_3[b]	5	reflux	95.0 ± 0.58	94.0 ± 2.9
Dissolution	$0.1M$ F^- in $12M$ HNO_3[c]	2	reflux	3.7 ± 0.68	4.3 ± 0.3
Fusion	90 wt % Na_2CO_3-10 wt % $NaNO_3$[d]	2	900	1.0 ± 0.58	1.8 ± 0.8

---

a. Mean ± standard deviation for four runs.

b. Liquid-to-solid ratio = 250 ml/g.

c. Residue refluxed in 100 ml reagent.

d. Residue refluxed in $8M$ NaOH for 2 hours to solubilize SiO_2, filtered, washed with distilled water, dried, and fused in 10 g of reagent.

Results of tests to determine the maximum amount of ash per liter that can be processed and still give 95% actinide solubilization are shown in Table 5. The maximum concentration for the line-generated incinerator ash with 95% solubilization was 30 g/l. It is probable that ash of other composition would give different results, but as a first approximation, 30 g/l seems a reasonable value.

TABLE 4. Solubilization of Actinide Contained in Untreated Conventional Incinerator Ash – Multiple Batch Contact

Sample: 1.0-g ash

Method	Reagent	Time (hr)	Temperature (°C)	Actinide Solubilization (mean ± standard deviation) Pu (wt %)	Am (wt %)
Dissolution (1st contact)[a]	0.1*M* Ce(IV)-4*M* HNO_3	5	reflux	95.0 ± 0.58	94.0 ± 2.9
Dissolution (2nd contact)[b]	0.1*M* Ce(IV)-4*M* HNO_3	7	reflux	1.0 ± 0.35	3.4 ± 1.9
Dissolution (3rd contact)[b]	0.1*M* Ce(IV)-4*M* HNO_3	7	reflux	0.3[c]	0.3[c]
Dissolution	0.1*M* F^- in 12*M* HNO_3[d]	2	reflux	3.0 ± 2.5	3.1 ± 2.5
Fusion	90 wt % Na_2CO_3-10 wt % $NaNO_3$[e]	2	900	1.1 ± 0.18	1.8 ± 1.4

---

a. Liquid-to-solid ratio = 250 ml/g (values from Table 3).
b. Residue in 250-ml reagent (duplicate samples except for 3rd contact).
c. Single determination.
d. Residue in 100-ml reagent (duplicate samples).
e. Residue fused in 10-g reagent (no NaOH pretreatment); duplicate samples.

TABLE 5. Solubilization of Actinide Contained in Untreated Conventional Incinerator Ash as a Function of Ash Concentration

Dissolvent: 0.1*M* Ce(IV) in 4*M* HNO_3
Temperature: Reflux
Time: 16 hours

Concentration (g/l)	Actinide Solubilization[a] Pu (wt %)	Am (wt %)
4	96 ± 5.3	101 ± 0.9
20	96 ± 3.5	101 ± 11
30	95 ± 0.27	93 ± 6.5
40	78[b]	78[b]
60	66 ± 12	68 ± 9.7
80	60 ± 8.7	62 ± 10

---

a. Mean ± standard deviation for duplicate tests except where otherwise specified.
b. Single determination.

TABLE 6. Comparison of the Ce(IV)-HNO_3 and HF-HNO_3 Systems for Solubilization of Actinide Contained in Untreated Conventional Incinerator Ash

Sample: 1.0-g ash
Temperature: Reflux

Initial liquid-to-solid ratio = 250 ml/g; Ce(IV)-HNO_3 system
100 ml/g, HF-HNO_3 system

	0.1*M* Ce(IV)-4*M* HNO_3			0.1*M* F^- in 12*M* HNO_3		
		Actinide Solubilized[a]			Actinide Solubilized[b]	
Contact	Time (hr)	Pu (wt %)	Am (wt %)	Time (hr)	Pu (wt %)	Am (wt %)
1	5	95.0 ± 0.58	94.0 ± 2.9	2	89.0	89.0
2	7	1.2 ± 0.35	3.4 ± 1.9	2	7.1	9.3
3	7	0.3	0.3	2	2.2	1.9
4	(c)	(c)	(c)	2	<0.6	<0.9
5	(c)	(c)	(c)	2	<0.6	<0.8

---

a. From Table 3.
b. Single determination.
c. Not determined.

Therefore, 30 g/l was used in the flowsheet preparation.

The TBP-NDD and DHDECMP-DIPB extractions of the Ce-HNO_3 dissolver solution recovered 99.991 ± 0.006% (mean ± standard deviation for five runs) of the plutonium and 99.64 ± 0.09% (mean ± standard deviation for three runs) of the americium, respectively.

Comparison of the Ce(IV)-HNO_3 Systems

Table 6 shows the results of experiments done to compare 0.1*M* Ce(IV) in 4*M* HNO_3 with the 0.1*M* F^- in 12*M* HNO_3 system currently used at Rocky Flats to solubilize actinides in incinerator ash. Actinide solubilization by the HF-HNO_3 system is compared with results of three batch contacts involving one gram of conventional incinerator ash.

The data show that although actinide solubilization is higher for the Ce(IV)-HNO_3 system in the first contact, better solubilization by the HF-HNO_3 system in the second contact gives comparable results after two contacts. Also, the third HF-HNO_3 contact still solubilizes actinide whereas the third Ce(IV)-HNO_3 contact does little. The efficiency of the HF-HNO_3 system can probably be attributed to the solubilization of silica, which frees retained actinide.

Table 7 presents results of experiments designed to determine if an optimum liquid-to-solid (L/S) ratio exists for solubilization of actinide by refluxing ash heel [from the Ce(IV)-HNO_3 dissolution] in 0.1*M* F^- in 12*M* HNO_3.

The data show large standard deviations for actinide solubilization by refluxing for 2 hr. The solubilization after 6 hr refluxing is more meaningful and the trend (an increase in recovery with L/S ratio) is discernible. However, even at L/S = 75 ml/g, only half of the actinide is solubilized. Although additional dissolution might be attained by increasing either or both the L/S ratio and the reflux time, it would seem that this is a slow and tedious process. Such systems also have corrosion and off-gas problems.

TABLE 7. Actinide Solubilization by Leaching Ash Heel in 0.1*M* F^- in 12*M* HNO_3

Feed: Ash heel from Ce(IV)-HNO_3 dissolution
Actinide Content: 2.55 mg Pu/g heel; 5.96 μg Am/g heel

	Actinide Solubilized[a]			
	2-hr Reflux		6-hr Reflux	
Liquid-to-Solid Ratio (ml/g)[b]	Pu (wt %)	Am (wt %)	Pu (wt %)	Am (wt %)
25	12 ± 4.4	10 ± 9.7	10 ± 0.0	14 ± 0.9
38	15 ± 3.6	18 ± 8.9	12 ± 1.4	12 ± 3.3
50	16 ± 2.0	14 ± 10	36 ± 6.6	39 ± 1.8
75	23 ± 8.9	24 ± 11	50 ± 5.3	48 ± 2.7

a. Mean ± standard deviation for duplicate samples.
b. Milliliters of 0.1*M* F^- in 12*M* HNO_3 per gram ash heel.

One viable solution is refluxing the ash or ash residue in ⩾6*M* NaOH for 3 hr. This solubilizes the silica as silicates. The caustic silicate solution could then be filtered or centrifuged and the solids washed to remove excess caustic; dissolution in the Ce(IV)-HNO_3 system would follow.

Only two experiments with Chemical Operations ash heel from the HF-HNO_3 process were done. The Ce(IV)-HNO_3 system gave 75 ± 8.6% (mean ± standard deviation) solubilization of actinide.

Removal of Ruthenium by Electrolysis

Early attempts to electrolyze solutions containing ruthenium, in the apparatus shown in Figure 1, were not successful. Placing both electrodes in the solution rather than using the fritted-glass well facilitated the process.

Electrode weighing and solution analysis showed that no ruthenium was removed by electrolyzing the solution of 44 mg $RuCl_3 \cdot (1\text{-}3)H_2O$ in 250 ml 4*M* HNO_3 for 16 hr at 0.4 A. Electrolysis at 2 A for 8 hr gave no measurable amount of ruthenium removal. After 17 hr at 4 A, 14.2 mg of ruthenium had plated out on the cathode, reducing the original 40 ppm in the solution to 29; an additional 6 hr at 6 A gave a total of 17.4 mg of ruthenium plated, with 1 ppm of ruthenium left in the solution. There is some question as to the original amount of ruthenium in solution because of the variation in the formula $RuCl_3 \cdot (1\text{-}3)H_2O$; 17.4 mg corresponds to $RuCl_3 \cdot 2.3\ H_2O$ if the material balance (based on analysis) is correct. This would correspond to 97.6% removal of the ruthenium.

Experiments were performed with 10 ml of simulated fission product in 240 ml of 4*M* HNO_3. Results showed that removal was poor from solution from which chloride had been completely removed by the AgCl precipitation technique. (This technique was used in preparation of the simulated fission product solution.[11]) Only 28% of the ruthenium was removed after 17 hr electrolysis at 6 A. However, when this solution was spiked with additional $RuCl_3 \cdot (1\text{-}3)H_2O$ and electrolyzed, ruthenium did plate out. No explanation for this is offered and these preliminary experiments were not repeated since a complete study on ruthenium removal was outside the scope of this study. It was demonstrated, however, that no ruthenium was removed from the simulated fission product solution by electrolysis when 0.1*M* Ce was present.

A final experiment used the electrode plated with 17.4 mg of ruthenium, as just described, as the anode, with 0.1*M* Ce(III) in 4*M* HNO_3. The solution was electrolyzed at 1.2 A for 5 hr. The ruthenium metal on the electrode was oxidized and evolved from the boiling solution as RuO_4, condensing on the walls of the flask and the condenser. The maximum Ce(IV) concentration attained after 6 hr was 0.073*M*; under like conditions but without ruthenium, this value was reached in 1 hr. After

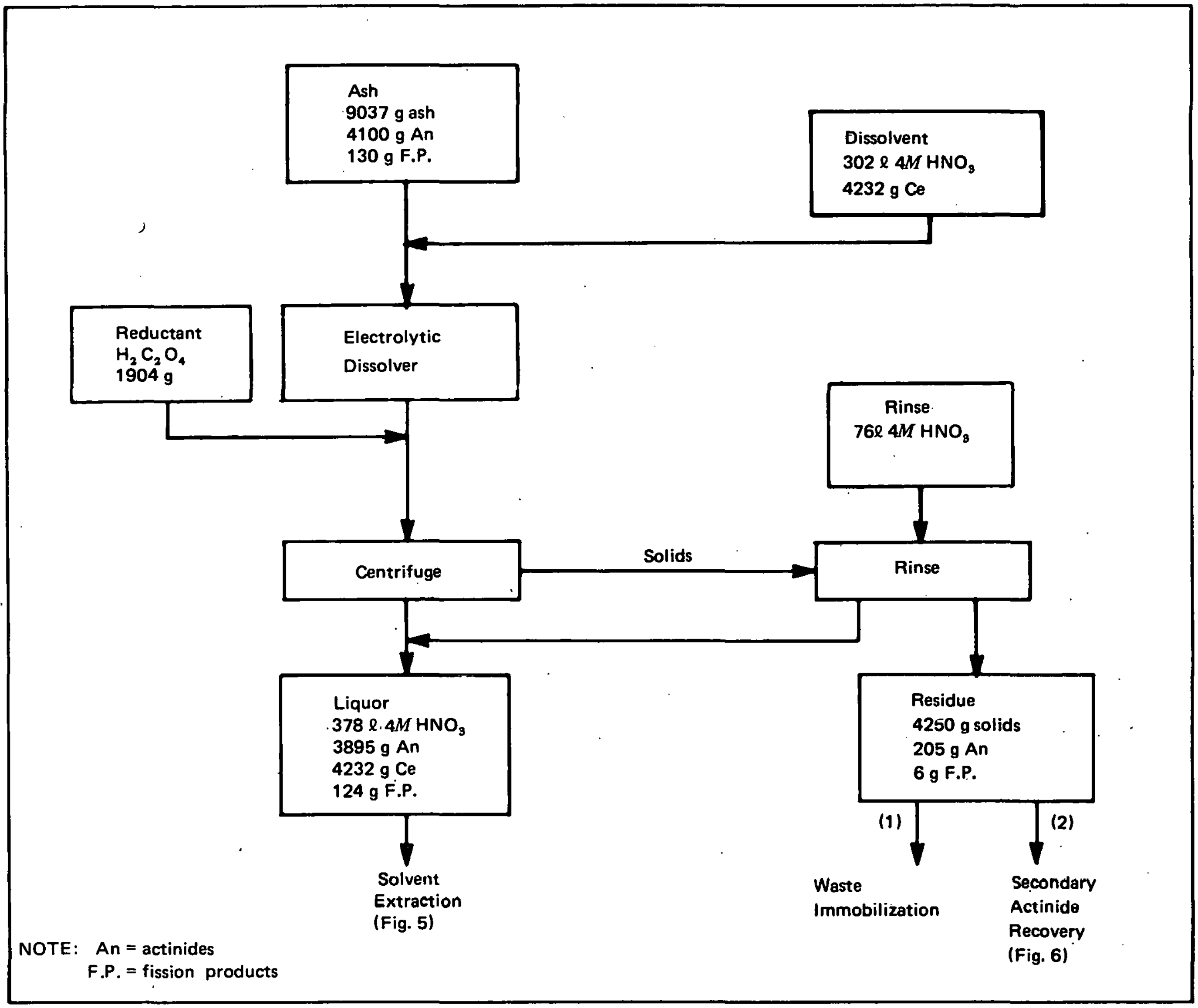


FIGURE 4. Conceptual Flowsheet for Solubilization of Actinide in Incinerator Ash

5 hr, actinide recovery was 94% compared to 95% recovery after 2.5 hr without ruthenium. Thus, solubilization of actinides was complete but took twice as long with ruthenium present.

FLOWSHEET DEVELOPMENT

Flowsheet development is based partly on conceptual flowsheets provided by ORNL[2] and partly on the process and data developed at RFP. The former have changed considerably since their initial development, and the latter have been based only on amounts of solution and residues arising from laboratory-scale experimental work. Liquids and solids from RFP-proposed processes will be combined with similar materials from other portions of the conceptual plant flowsheet for subsequent processing; consequently, no attempt has been made to determine the impact of RFP-proposed processes on flowsheets of other plant processes, nor are intermediate steps which may be required (e.g. evaporation) included.

The flowsheet proposed as a result of this work is shown in Figure 4. The amount of ash and its actinide and fission product content is based on an ORNL flowsheet.[2] Solubilization of this material, assuming an ash concentration of 30 g/l, would require 302 ℓ of 0.1*M* Ce(IV) in 4*M* HNO_3 in the electrolytic dissolver. A worst case of 50% solubilization of ash with 95% solubilization of actinide was assumed. (This is considered the worst case in that reprocessing and fuel fabrication plant incinerator ash will have approximately 20% silica, not 50%, so solubilization will be more complete, and less silica retention of actinide will exist. Also, the spent fuel is expected to contain approximately 99% uranium, and uranium oxide is easier to solubilize than plutonium oxide. These two factors should combine to give actinide dissolution in excess of 95%.)

Dissolution would be followed by slow addition of solid oxalic acid to reduce Ce(IV) to Ce(III); oxalic acid could be added in solution if dilution were desirable. Reduction before discharge from the dissolver would remove the need for subsequent reheating and would eliminate the need for corrosion-resistant equipment downstream. The slurry would then be centrifuged, washed with acid, and the combined centrifugate and wash liquors would be sent to solvent extraction. The solids could be sent to either secondary actinide recovery or to waste immobilization (fixation in concrete).

The conceptual solvent extraction flowsheet is shown in Figure 5. Although TBP-NDD recovery of plutonium and DHDECMP-DIPB recovery of americium was demonstrated in this work, the split of actinides and fission products is not defined in this flowsheet for two reasons. First, the actinide composition will differ greatly from the composition used in this work, containing approximately 99% uranium, less than 1% plutonium, and only traces of other elements such as americium, curium, and neptunium.[2] Second, actinide recovery in an efficient solvent extraction unit (e.g., a mixer-settler) should improve recovery over the laboratory-scale batch extractions reported here. Recovery of solubilized actinides by special solvent extraction and ion exchange methods is addressed by other tasks in the program.[2]

Qualitatively, the process will comprise TBP-NDD extraction of most of the uranium, plutonium, and neptunium. These actinides will be stripped from the TBP-NDD with 0.05*M* hydroxylamine nitrate (HAN) in 0.5*M* HNO_3. This stream becomes part of the fuel reprocessing plant (FRP) product; the organic stream is sent to a purification (scrubbing) step, then recycled.

The raffinate from TBP-NDD extraction contains the trivalent actinides, the cerium (from the electrolytic dissolution process), and fission products. The actinides, cerium, and any fission product lanthanides are extracted into DHDECMP-DIPB; the raffinate is sent to salt waste recovery or immobilization. Back-stripping of the actinides, cerium, and fission product lanthanides is done with 0.05*M* $H_2C_2O_4$ in 0.01*M* HNO_3. Most (90%) of this stream will be recycled to the electrolytic dissolver; the remainder will be sent to cation exchange chromatography. The DHDECMP-DIPB will be purified for recycle.

A conceptual flowsheet for secondary actinide recovery is shown in Figure 6. Residue from the electrolytic dissolver is mainly silica with entrained actinide. Silica can be solubilized by refluxing in 8*M* NaOH.[5] The amount of 8*M* NaOH needed to solubilize a given amount of silica has not been determined. (This would depend on desired reaction time and the viscosity required for handling.) Qualitatively, the dissolution of silica in residue would leave the actinides and most fission products as solids. These solids would be removed from the caustic silicate solution by centrifugation, washed with dilute caustic to reduce sodium and hydroxide ion concentrations, and recycled to the electrolytic dissolver. The caustic waste would be sent to salt waste recovery or waste immobilization depending on remaining actinide levels.

Alternative Flowsheet

There are modifications to the proposed flowsheet that could prove to be beneficial if 95% recovery is judged to be inadequate, or if organic materials other than carbon are present.

Low-temperature ashing of incinerator ash in the presence of air will remove organics that are not

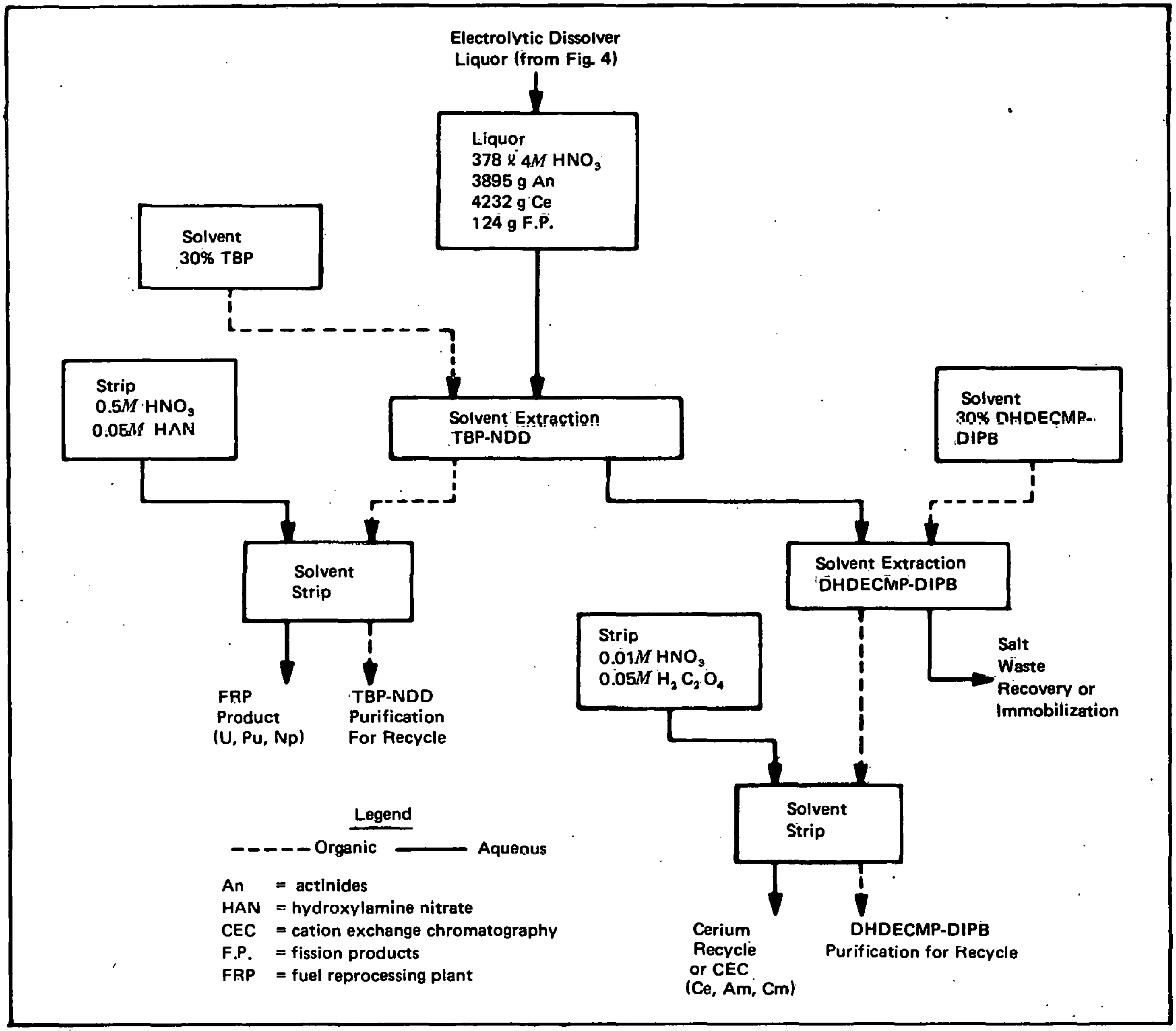


FIGURE 5. Conceptual Flowsheet for Actinide Recovery From Incinerator Ash Liquor

oxidized by the Ce(IV)-HNO_3 system. The residue could then be refluxed in 8*M* NaOH to solubilize silica. After centrifugation and washing with 0.05*M* NaOH, refluxing the residue in the Ce(IV)-HNO_3 system would result in >95% actinide recovery. This would eliminate recycling residue to the dissolver. (It is assumed some insolubles, e.g., aluminosilicates, might remain but these should contain little actinide and thus be ready for discard.)

CONCLUSIONS

This work has shown that solubilization of actinide in incinerator ash, using the Ce(IV)-HNO_3 system, is technically feasible. Ash concentrations of 30 g/l can be processed while maintaining 95% actinide solubilization; the solubilized actinides can be recovered by proven solvent extraction methods; and cerium can be recovered and recycled. Although

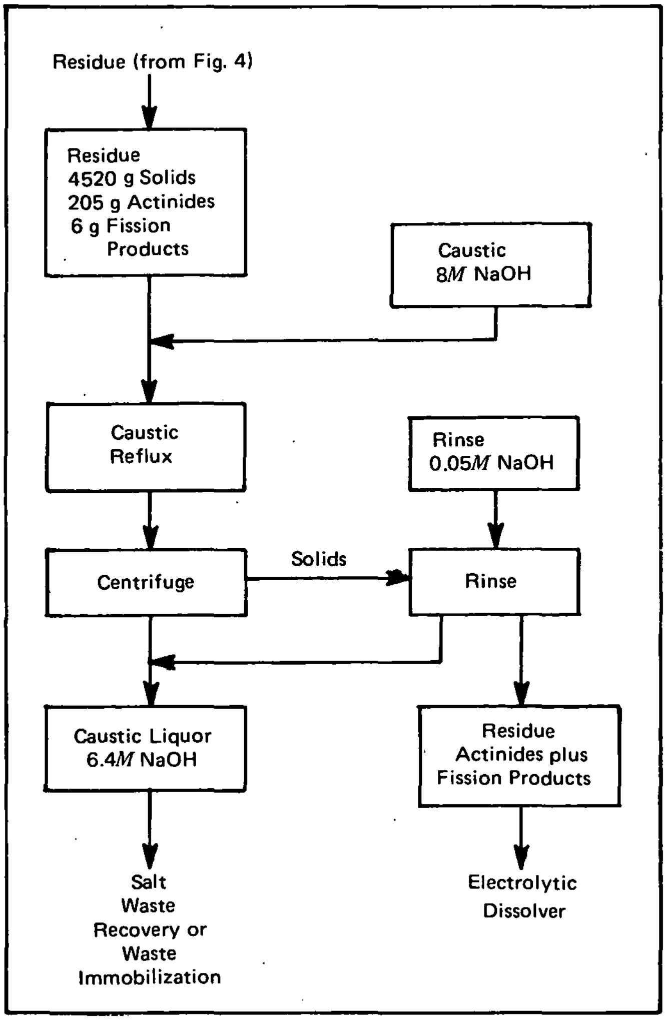


FIGURE 6. Conceptual Flowsheet for Secondary Actinide Recovery From Dissolver Residues

experimental work with ruthenium was limited, it was demonstrated that actinide dissolution will take place (though more slowly) even if ruthenium is present; moreover, ruthenium can be removed electrolytically from fission product solutions if this proves to be necessary.

Obviously a great deal of laboratory and pilot-plant-scale work remains to be done. Actinides other than plutonium and americium need to be investigated. Other contaminated ashes from different (preferably low temperature) incinerators should be tested. Scale-up of actinide solubilization and recovery systems would facilitate implementation of the Ce(IV)-HNO_3 systems, which does have definite advantages over fusion and HF-HNO_3 systems.

Advantages of the Ce(IV)-HNO_3 system over methods involving fusion of ash are (1) the system is a low-temperature process; (2) less salt waste is formed; (3) cerium can be recycled; (4) fewer corrosion problems will exist; and (5) silica is neither volatilized (causing offgas problems) nor solubilized (causing waste handling problems or re-adsorption of solubilized actinides). An additional advantage to the system is that gadolinium could be added as a neutron poison. The process could then be carried out in equipment that would ordinarily be unsafe with respect to nuclear criticality. Gadolinium would be extracted and recycled with cerium.

Advantages of the Ce(IV)-HNO_3 system over the HF-HNO_3 system are (1) cerium can be recycled whereas HF-HNO_3 must be replaced frequently; (2) corrosion and offgas problems are less severe; and (3) silica is neither solubilized nor volatilized.

The main disadvantage of the Ce(IV)-HNO_3 system (which basic fusion systems and the HF-HNO_3 system do not have) is that silica is not solubilized. Thus, one of the advantages of the system also seems to be its main disadvantage because for actinide recovery from high-fired incinerator ash to be complete, silica apparently will have to be removed. Whether this is to be done or not is a decision that will have to be deferred until "acceptable" or "adequate" recovery is defined.

A second disadvantage is the buildup of actinide and lanthanide elements that will occur in the Ce(IV)-HNO_3 system since these elements will be extracted into the DHDECMP and be recycled with cerium. This can be handled either by a bleed-off stream (with concurrent replenishment of cerium) or by allowing actinide and lanthanide to build up to the maximum concentrations allowable (to be defined) and then replacing the saturated dissolvent with fresh Ce(IV)-HNO_3 solution. Separation by cation exchange would follow, and cerium would be recycled.

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