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WASTE MANAGEMENT ANALYSIS FOR THE
NUCLEAR FUEL CYCLE - ACTINIDE RECOVERY FROM COMBUSTIBLE WASTE
OCTOBER 1977 - MARCH 1978

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**WASTE MANAGEMENT ANALYSIS FOR THE
NUCLEAR FUEL CYCLE - ACTINIDE RECOVERY FROM COMBUSTIBLE WASTE
OCTOBER 1977 - MARCH 1978**

G. H. Thompson, C. M. Smith, E. L. Childs, and R. L. Kochen

Abstract. Evaluation of the Ce(IV)-HNO₃ system for recovery of actinides from incinerator ash is continuing. High-fired americium-traced plutonium oxide was completely solubilized in this system and recovery of actinides from incinerator ash was $\geq 95\%$.

Recovery of solubilized plutonium was done by solvent extraction using tributyl phosphate. Trivalent actinides will be recovered by a bidentate organophosphorus solvent extractant.

The Ce(IV)-HNO₃ system was compared with the F⁻-HNO₃ system now in common use. Advantages of the former include less equipment corrosion, no volatilization of silica, and better recovery of actinide in the initial contact. However, additional contacts do not significantly improve recovery (because silica is not solubilized), and the system requires a large liquid/solid ratio for efficient actinide recovery. Additional work is in progress.

INTRODUCTION

Combustible waste produced during reactor fuel fabrication and reprocessing includes paper, wood, plastics, rubber, cloth, spent solvent, activated carbon, and ion exchange resins. These wastes are incinerated or acid digested to reduce waste volume and organic content and to facilitate actinide recovery. The product is residue containing actinides and fission products. The objective of 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 offgas, not materially increase final waste volumes, or adversely affect glass or concrete waste forms.

During the first reporting period, a preliminary literature survey was completed.^{(1)*} A preliminary evaluation of common leaching and fusion methods showed that fusion with commonly used reagents dissolves $>60\%$ of the ash from the fluidized bed incinerator (FBI) process and leaching with concentrated nitric dissolves 40 to 60% of the same ash. Preparation of plutonium-contaminated FBI ash was attempted.

During the second reporting period, evaluation of leaching and solubilization methods was continued using ²⁴¹Am-traced high-fired PuO₂.⁽²⁾ It was shown that fusion with commonly used fluxes solubilizes $\geq 96\%$ of high-fired plutonium-americium oxide. Acid digestion with 95 volume percent H₂SO₄-5 volume percent HNO₃ (concentrated acids) also solubilized the high-fired oxide, but lengthy refluxing was required.

A third report described additional evaluation of promising actinide recovery methods using mixtures of ²⁴¹Am-traced high-fired PuO₂ with FBI ash, and conventional incinerator ash.⁽³⁾ Methods evaluated further included the fusion methods described above and ash dissolution (60 to 70% solubilized) in the Ce(IV)-HNO₃ system.^(4, 5) The design of the lab-scale FBI system for combustion of plutonium-contaminated waste was also included.

This report describes additional evaluation of ash dissolution in the Ce(IV)-HNO₃ system. Mixtures of FBI ash and ²⁴¹Am-traced high-fired PuO₂, and conventional incinerator ash were reacted with electrolytically-generated Ce(IV) in HNO₃ to remove carbon in the ash as carbon dioxide and solubilize actinides. Subsequent actinide recovery involved solvent extraction into 30% tributyl phosphate (TBP) in n-dodecane (NDD).

*Numbers in parentheses refer to references at end of text.

TABLE 1. Composition of Incinerator Ash

Component	Quantity in Ash, wt %	
	Fluidized Bed	Conventional
Pu	— ^a	5.3
Am	— ^a	5.8×10^{-3}
SiO ₂	9	48
C	26	22
Fe ₂ O ₃	0.5	5.7
MgO	1.0	4.0
CaO	1.0	4.0
Al ₂ O ₃	4.9	— ^b
Na Salts	23	— ^c
Other	35	11

a. Low level; total count $<10^3$ dpm/g ash

b. Negligible; large amounts in FBI ash from catalyst in afterburner

c. Negligible; large amounts in FBI ash from Na₂CO₃ (fluidized medium)

EXPERIMENTAL

Materials and Equipment

Samples of ash were obtained from the FBI system and the conventional incinerator. The combustible wastes and both incinerator systems were described previously.^(1, 6) The composition of the FBI ash and "typical" conventional incinerator ash are shown in Table 1; additional analyses of the ashes are in progress.

Portions of both ashes were washed with distilled water to remove water-soluble material and/or refluxed with 8M NaOH for two hours (liquid/solid ratio of 60) to solubilize silica and enable its removal by filtration. Still other portions were left untreated.

The preparation of the ²⁴¹Am-traced high-fired PuO₂ has been previously described.⁽²⁾ Analysis determined the americium content to be 2.27×10^{-4} gram per gram of Pu.

FIGURE 1. Electrolysis Reaction Apparatus for Actinide Recovery With Electrolytically Generated Cerium

All other chemicals used were reagent grade. The reaction vessel used in studies of electrolytically-generated Ce(IV) is shown in Figure 1. The glass-fritted well isolates the cathode and its electrolysis products from the reaction system.

TABLE 2. Actinide Recovery by Dissolution With $0.05N(NH_4)_2Ce(NO_3)_6$ in $4M HNO_3$

Sample	Actinide Recovery in Ce(IV), wt %		Residue Remaining After Listed Operation, wt %		
	Pu	Am	8M NaOH	Ce(IV)- HNO_3	0.1M F^- -12M HNO_3
Oxide, 0.2 g	>99.9	>99.9	— ^a	—	—
FBI ash-oxide; 1.8 g ash + 0.2 g oxide	98	98	44	5.3	0.4
Conventional ash, 2.0 g	97 ± 1.7	98 ± 1.5 ^b	69 ± 0.30	26 ± 1.3	4.1 ± 0.53

Notes: Temperature: Reflux

Liquid/Solid Ratio: 1250 (Oxide)
125 (Ash)

Ash Pretreatment: Refluxed in 8M NaOH

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

a. Not measured.

b. Mean % ± standard deviation for duplicate analyses.

Procedure

Ce(IV) Production. In studies of the rate of Ce(IV) generation, a known amount of cerous nitrate was dissolved in 250 ml of 4M HNO_3 and heated to boiling in the 500-ml flask, then a constant current was applied to the system. The reaction was kept at reflux temperature with a heating mantle. Ce(IV) generation was monitored by redox titration of aliquots withdrawn from the molten vessel at regular intervals.

When the Ce(IV) concentration equaled the initial Ce(III) concentration, one gram of ash (either untreated, water washed, or refluxed in NaOH) was added (liquid/solid ratio of 250). Electrolysis was continued until a constant Ce(IV) concentration was regained.

Actinide Recovery. In studies of actinide recovery, 1 gram of ash was added directly to 250 ml of 0.1M Ce(III) solution and the mantle was turned on. When the contents of the flask reached boiling, a current of 1.0 amp 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 and refluxed for 2 hours in 0.1M F^- in 12M HNO_3 . The reflux-residues were then fused with a 9:1 Na_2CO_3 - $NaNO_3$ flux at 900 °C for 2 hours, with subsequent actinide recovery in 4M HNO_3 .

In multiple batch studies, the residue from one cerium reaction was contacted again with fresh cerium solution. No attempt was made to readjust the liquid to solid ratio.

In recycle studies, the original cerium solution was repeatedly reacted with fresh quantities of ash, after the plutonium had been extracted with two contacts of 30%-tributyl phosphate (TBP) in n-dodecane (NDD). Since TBP would extract Ce(IV), the Ce(IV) was reduced to Ce(III) with solid oxalic acid before extraction. Acidity and cerium concentration were readjusted to their original values at the start of each cycle.

Results

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 recovery was achieved with the system; thus, work on actinide recovery by

FIGURE 2. Rate of Ce(IV) Generation

carbonate-nitrate fusion was preempted to permit optimization of the $\text{Ce(IV)}\text{-HNO}_3$ 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 . (4, 5) 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 the same time.

At two hours, 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.

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

However, more cerium also means more waste, 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 amp, and above 1.2 amps gassing, due to boiling and electrolysis, caused fluctuations in current, leading to cell inefficiency. A current of 1.0 amp was chosen for subsequent work.

Later experiments used only unwashed conventional incinerator ash since ORNL had decided to plan for conventional incineration in the fuel processing system; and preliminary washing was unnecessary 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 recovered by the Ce(IV)- HNO_3 system and subsequent refluxing of residue with 0.1M F^- in 12M HNO_3 and fusion in 9/1 Na_2CO_3 - NaNO_3 are shown in Table 3. Without the 8M NaOH pretreatment step, actinide recovery is reduced by 2 to 4%; apparently this is the amount

of actinide either encapsulated in or adsorbed by silica. It is unlikely that recovery of an additional 2 to 4% of the actinide would justify the NaOH pretreatment step.

The results of multiple batch contacts are shown in Table 4. Although americium recovery seems to be increased by the second contact, these results suggest that multi-batch contacts would not be worth the effort for actinide recovery. However, the results of attempts to recycle the Ce(IV)- HNO_3 dissolvent, discussed below, suggest multi-batch contacts may be necessary.

Because the liquid/solid ratio of 250 used in this work is high, an effort was initiated to determine the amount of conventional incinerator ash that can be solubilized in 250 ml of recycled 0.1M Ce(IV) in 4M HNO_3 . At present, five grams of conventional incinerator ash have been solubilized in this fashion. Results are shown in Table 5. Although these results are preliminary, and the work done has been limited in scope, the data suggest that actinide solubilization

TABLE 3. Actinide Recovery From Untreated Conventional Incinerator Ash

Method	Reagent	Time (hr)	Temperature (°C)	Actinide Recovery, wt % ^a	
				Pu	Am
Dissolution	0.1M Ce(IV)-4M HNO ₃ ^b	5	reflux	95.0 ± 0.58	93.7 ± 2.9
Dissolution	0.1M F ⁻ -12M HNO ₃ ^c	2	reflux	3.7 ± 0.68	4.3 ± 0.39
Fusion	90 wt % Na ₂ CO ₃ -10 wt % NaNO ₃ ^d	2	900	1.0 ± 0.58	1.8 ± 0.83

Note: Sample: 1.0 g ash

a. Mean % ± standard deviation for four runs.

b. Liquid/solid ratio = 250.

c. Residue Refluxed in 100 ml reagent.

d. Residue refluxed in 8M NaOH for two hours to solubilize SiO₂; filtered, washed with distilled water; dried; and fused in 10 g reagent.

TABLE 4. Actinide Recovery From Untreated Conventional Incinerator Ash Using Multi-Batch Contact With Ce(IV)-HNO₃

Method	Reagent	Time (hr)	Temperature (°C)	Actinide Recovery, wt % (mean ± std. dev.)	
				Pu	Am
Dissolution	0.1M Ce(IV)-4M HNO ₃ (1st contact) ^a	5	reflux	95.0 ± 0.58	94.0 ± 2.9
Dissolution	0.1M Ce(IV)-4M HNO ₃ (2nd contact) ^b	7	reflux	1.2 ± 0.35	3.4 ± 1.9
Dissolution	0.1M Ce(IV)-4M HNO ₃ (3rd contact) ^b	7	reflux	0.3	0.3
Dissolution	0.1M F ⁻ -12M HNO ₃ ^c	2	reflux	3.0 ± 2.5	3.1 ± 2.5
Fusion	90 wt % Na ₂ CO ₃ -10 wt % NaNO ₃ ^d	2	900	1.1 ± 0.18	1.8 ± 1.4

Note: Sample: 1.0 g ash

a. Liquid/solid ratio = 250 (values from Table 2).

b. Residue in 250 ml reagent (duplicate samples except for 3rd contact).

c. Residue in 100 ml reagent (duplicate samples).

d. Residue fused in 10 g reagent (no NaOH pretreatment); duplicate samples.

efficiency decreases rapidly. If this proves to be true, batch countercurrent, multi-stage extraction may be necessary to minimize the amount of Ce(IV)-HNO₃ dissolvent needed to recover the actinides.

The amount of plutonium recovered by solvent extraction indicates a buildup of plutonium concentrations (values in Table 5 were not corrected

for plutonium remaining from previous dissolutions). However, only two batch extractions were made and an efficient, multi-stage mixer-settler system should improve this recovery.

One set of experiments was done to compare the 0.1M Ce(IV) in 4M HNO₃ system with the 0.1M F⁻ in 12M HNO₃ system currently used at Rocky Flats to recover actinides from incinerator ash. One gram

TABLE 5. Recycle of Ce-HNO₃ Dissolvent and Recovery of Actinide From Conventional Incinerator Ash

Total ^a ash, g.	Dissolution ^b time, hours	Solubilized ^c Pu, wt %	Extracted ^d Pu, wt %
1	3	96	82
2	4	80	81
3	5	72	84
4	6	82	88
5	7	100	85

a. Ash added in 1 gram increments

b. Samples taken each hour; dissolution time is hours required to attain maximum actinide concentration

c. Values adjusted for actinide encapsulated in silica (residues not fused in carbonate-nitrate)

d. Extractant: 30% TBP in NDD (two extractions); values not adjusted for amount remaining from previous solubilization

of conventional incinerator ash was refluxed with five 100-ml portions of 0.1M F⁻ in 12M HNO₃. The actinide recovery results are compared with the results of three batch contacts with one gram of conventional incinerator ash (Table 4) in Table 6.

The data show that although actinide recovery is higher for the Ce(IV)-HNO₃ system in the first contact, better recovery by the HF-HNO₃ system in the second contact gives comparable recovery after two contacts. Also, the third HF-HNO₃ contact still recovers actinide, whereas the third Ce(IV)-HNO₃ contact does little to improve recovery. The efficiency of the HF-HNO₃ system can probably be attributed to the solubilization of silica, freeing encapsulated actinide.

CONCLUSIONS

Work this period has shown that recovery of actinide from incinerator ash using the Ce(IV)-HNO₃ system is feasible. Recovery in the first contact is better with this system than with HF-HNO₃, possibly because carbon is being oxidized. Carbon tends to adsorb many elements and compounds. However, actinide recovery after the first Ce(IV)-HNO₃ contact decreases rapidly, whereas recovery with HF-HNO₃ continues. This can be attributed to the presence of silica, which is not attacked by the Ce(IV)-HNO₃ system, but is dissolved in the

TABLE 6. Comparison of the Ce(IV)-HNO₃ and HF-HNO₃ Systems for Actinide Recovery From Conventional Incinerator Ash

Contact	Time (hr)	0.1M Ce(IV)- 4M HNO ₃		0.1M F ⁻ - 12M HNO ₃	
		Actinide Recovery, wt % ^a		Actinide Recovery, wt % ^b	
		Pu	Am	Time (hr)	Pu Am
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

Notes: Sample: 1.0 g ash

Temperature: reflux

Initial liquid/solid ratio = 250; Ce(IV)-HNO₃ 100; HF-HNO₃

a. From Table 3

b. Single determination

c. Not determined

HF-HNO₃ system. Improving actinide recovery will require pretreatment of the ash to remove silica.

More disturbing is the rapid decrease in actinide recovery when the Ce(IV)-HNO₃ dissolvent is recycled. These data are preliminary and more work is needed. However, if true, these results suggest that a high liquid/solid ratio will be required. This ratio could be reduced somewhat by going to a batch countercurrent multi-stage operation, but this would impose additional problems related to the difficulties in handling and contacting solids and liquids.

FUTURE WORK

Additional work is needed to define the amount of ash which can be effectively solubilized in a given amount of Ce(IV)-HNO₃ dissolvent. Larger aliquots of ash will be solubilized and plutonium will be extracted with 30% TBP in NDD as described above. Americium will be extracted by the organophosphorus extractant dihexyl-N,N-diethylcarbamylmethylene-phosphonate (DHDECMF). The actinide-stripped cerium solution will be recycled to determine how much ash can be solubilized before process efficiency is adversely affected.

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