RFP - 3036

CONF-800303--3

MASTER

CHEMICAL RESEARCH STUDIES FOR THE RECOVERY OF AMERICIUM AT ROCKY FLATS

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Paper prepared for presentation at the 179th
National Meeting of the American Chemical
Society, Houston, Texas, March 23-28, 1980

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ABSTRACT

Americium is recovered from plutonium and pyrochemical waste salts at Rocky Flats by an aqueous chemical process. The process is a five-step operation: dissolution of the chloride salt, conversion from the chloride to the nitrate system by cation exchange, separation of plutonium by anion exchange, evaporation of the anion column effluent, and precipitation of americium as the oxalate. Recent research will be discussed that shows the process can be improved through procedural modifications; for example: 1) by diluting the feed stream the selective sorption of the actinides by cation resin is increased, 2) by rinsing the cation resin with 1.5N nitric acid the carryover of impurities with the actinides is reduced, and 3) by lowering the molarity of the oxalate ion concentration and adding a small amount of chloride ion, during the oxalate precipitation step, the coprecipitation of lead impurity is reduced.

MSE WASTE SALT PROCESSING

As a result of the natural beta decay of plutonium-241 to americium-241, plutonium metal that has been in storage for some time must be processed for americium removal. The method used at Rocky Flats is a molten salt-molten metal process. For process operation, the plutonium metal is heated in an inert atmosphere furnace to the molten phase with a sodium-potassium-magnesium salt mixture and stirred for one hour. During this period, the americium, together with some of the plutonium, is extracted into the salt phase. The products of this operation are a purified plutonium metal button and a molten salt extraction (MSE) waste salt which contains the americium and some plutonium.

The subsequent recovery of americium from the plutonium and pyrochemical waste salts is an aqueous chemical process. The process is a five-step operation: dissolution of the chloride salt, conversion from the chloride to the nitrate system by cation exchange, separation of plutonium by anion exchange, evaporation of the anion column effluent, and precipitation of americium as the oxalate.

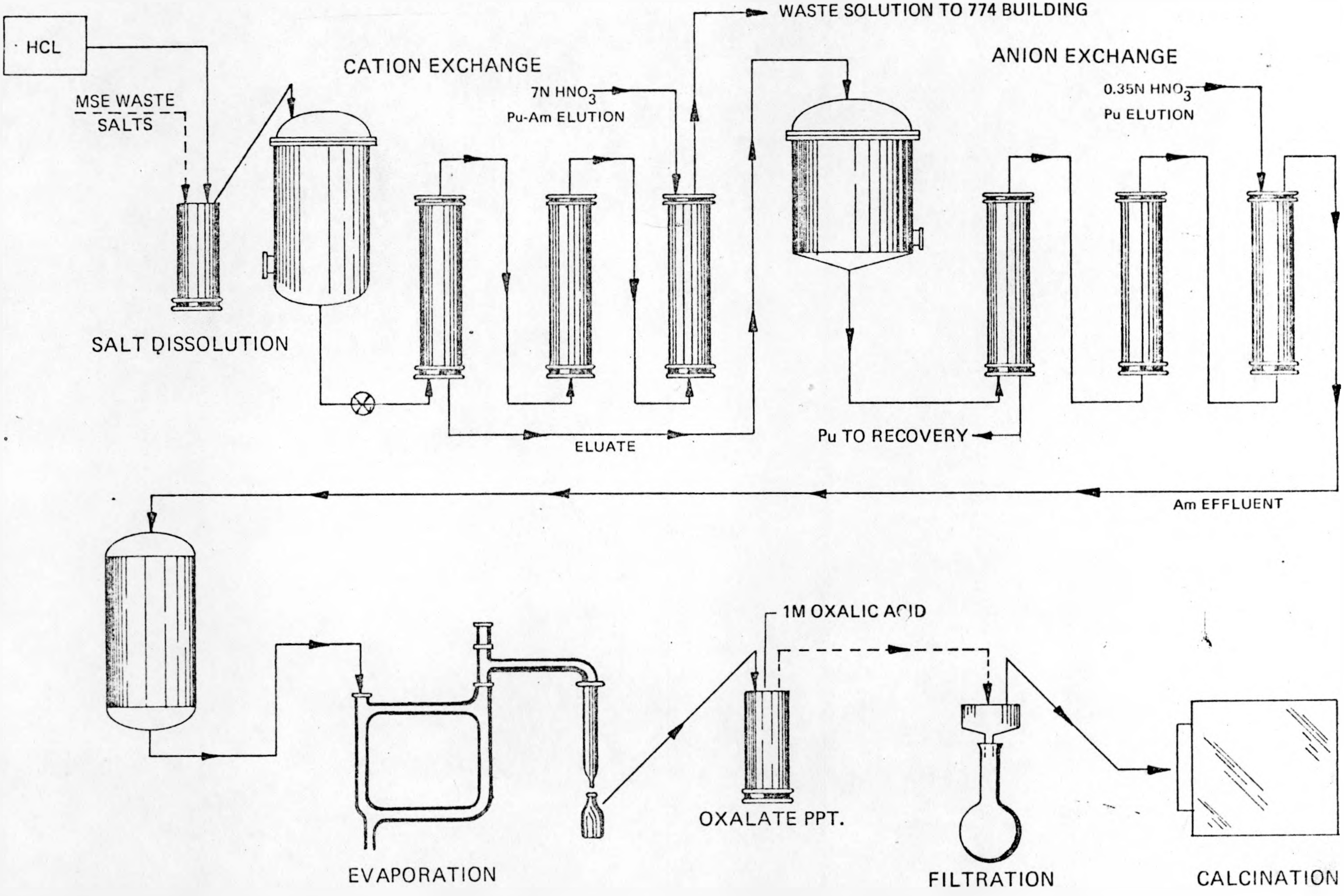
A flow diagram of the process is shown in the first slide. For process operations, approximately 1.5 kilograms of waste salt is dissolved in three litres of a heated solution of 0.5N hydrochloric acid and 0.04M hydroxlamine hydrochloride. Following dissolution, the solution is transferred to a holding tank where it is diluted with water until the chloride concentration is reduced to less than 50 grams per litre. This is done to prevent the formation of an anionic plutonium chloride complex.

From the holding tank, the solution is passed with up-flow loading onto three columns of cation exchange resin connected in series. Since sorption favors trivalent and tetravalent ions, the plutonium and americium are retained on the column and most of the monovalent and divalent cations are passed on through with the effluent. After the loading cycle, the columns are washed with 0.35N nitric acid to remove residual chloride ions. The cations are then eluted from the column by displacement with 7N nitric acid.

The plutonium is separated from the eluate by anion exchange. The acidity of the solution is first adjusted to about 7N which converts the plutonium to an anionic complex. The solution is then pumped with up-flow loading onto the column of anion exchange resin. The effluent from the columns, which contains the americium and some of the MSE salt cations is transferred into a holding tank. After the columns are loaded, the plutonium is eluted from the columns with down-flow elution using 0.35N nitric acid. The plutonium is then sent to subsequent recovery and purification operations.

Slide 1.

BUILDING 771
AMERICIUM RECOVERY PROCESS



HCL

MSE WASTE SALTS

CATION EXCHANGE

7N HNO_3

Pu-Am ELUTION

WASTE SOLUTION TO 774 BUILDING

ANION EXCHANGE

0.35N HNO_3

Pu ELUTION

SALT DISSOLUTION

ELUATE

Pu TO RECOVERY

Am EFFLUENT

1M OXALIC ACID

EVAPORATION

OXALATE PPT.

FILTRATION

CALCINATION

The americium effluent in the holding tank is concentrated by passing the solution through a thermosiphon loop-type evaporator. This solution then becomes the feed for the subsequent oxalate precipitation process.

In preparation for oxalate precipitation, the feed solution is first diluted with water until the acidity is less than 0.5N. A feed volume of ten litres is then pulled into a glass column, and a solution of oxalic acid is added until the solution is 0.1M in oxalate ion.* The resultant precipitate slurry is stirred by air sparging for about 20 minutes, and the solids filtered from solution by vacuum filtration onto a glass frit. The precipitate is then washed with water and air dried until it has a powder-like consistency.

Following the crying cycle, the precipitate is transferred to a crucible and calcined in a muffle furnace at 650°C for six hours. During this period, the americium oxalate is converted from $Am_2(C_2O_4)_3$ to an americium oxide product, AmO_2.

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*As a result of recent research to improve product purity, the oxalate ion concentration has been reduced to 0.05M, and the solution is made 0.03M in chloride ion.

CHEMICAL RESEARCH FOR RECOVERY AND PURIFICATION OF AMERICIUM

Although MSE waste salt processing has been in effect at Rocky Flats for some time, production yields and product purity have been a problem. The main problem has been that the cation exchange process is not sufficiently selective, and therefore allows considerable carryover of the MSE salt constituents and impurities with the plutonium and americium. The problem is not as serious with plutonium since plutonium can be subsequently purified by anion exchange. For americium, however, the subsequent recovery process is oxalate precipitation which is not as selective, and therefore carries some of the impurities into the final product.

Originally, selective separation by cation exchange was to have taken place because of large differences in the distribution values between those of the actinides and those of the MSE salt constituents. The problem with this assumption is dependency of the distribution value (or selectivity coefficient) upon factors such as temperature, pressure, complexing ions, and ionic strength. The differences in selectivity due to temperature, pressure, and complexation are probably slight compared to ionic strength. Ionic strength is extremely important in separating ions of different valencies.

Other considerations for selective separation are related to the basic principles of ion exchange. For example, cation displacement should proceeed until the column is loaded to capacity with plutonium and americium.

If this procedure is not employed, the excess resin simply sorbs the displaced cations (i.e., Mg, Na, K, etc.), and then they are rejoined with the actinides during the elution cycle. In addition to displacement, there is an advantage in using a column washing cycle. Cations can be separated by washing with an ion of the same form as the resin; however, unlike selective loading, the concentration of the washing solution should be stronger.

To determine if the cation exchange process can be improved, a chemical research investigation was made on the effects of ionic strength and column washing procedures.

IMPROVING SEPARATION BY CATION EXCHANGE

These studies have shown that through slight modifications in process procedures, the breakthrough capacity of the resin can be increased by as much as 100%, and the carryover of impurities with the actinides can be reduced to minimal quantities. First, the ionic strength of the feed solution needs to be lowered. Dilution of the feed stream allows for ion selectivity, which, therefore, results in an increased capacity of the resin for plutonium and americium and a greater separation of the actinides from impurities. In test runs, as is shown in the next slide, when the salt solution is passed on to the resin in a concentration strength similar to production operations (2.7M), the plutonium band migrated about 25 cm or 86% of the column length. In contrast, when the feed was diluted by a factor of five (to ∿0.9M) using 0.5M HCl, the plutonium band migrated to only 13 cm or 45% of the column length.

After the column is loaded, the second suggested modification is to wash the column in two steps. The first wash is with 0.35N HNO_3 which removes the residual chloride ion and prevents polymerization of plutonium. The second wash is with 1.5N HNO_3 which displaces most of the residual cosorbed impurity cations. In test runs, as is shown in the next slide, when the column is washed with 0.35N HNO_3, only a small percentage of the impurity cations are removed. In contrast, when the column is washed with 1.0, 1.5, or 2.0N HNO_3, relatively high percentages of the cations are removed. Washing with nitric acid does cause some displacement of plutonium, especially at the 2N level. However, since this solution will be free of chloride and will contain few impurities, it can be returned to the plutonium secondary recovery process where the impurities can be easily separated.

Slide 2.

MIGRATION OF PLUTONIUM THROUGH DOWEX 50W X8 CATION EXCHANGE RESIN

RUN NO.	DILUTION FACTOR	PU MIGRATION, CC	% COLUMN LOADED
1	0	26.0	86.7
2	0	24.5	85.8
3	5	14.5	48.3
4	5	12.5	41.7

Slide 3.

ELEMENTAL SEPARATION BY CATION EXCHANGE

RUN	ELEMENT	SECOND WASH % IN EFF.
Dil: 5 2nd Wash: 0.35N	Pu	<0.1
	Am	<0.1
	Ca	12.4
	Mg	10.3
	Pb	1.2
	K	17.1
Dil: 5 2nd Wash: 1.0N	Pu	<0.1
	Am	<0.1
	Ca	59.8
	Mg	40.2
	Pb	24.9
	K	22.9
Dil: 5 2nd Wash: 1.5N	Pu	0.4
	Am	<0.1
	Ca	80.0
	Mg	45.2
	Pb	53.2
	K	30.8
Dil: 5 2nd Wash: 2.0N	Pu	7.0
	Am	2.2
	Ca	87.6
	Mg	48.4
	Pb	66.4
	K	31.3

SEPARATION OF LEAD FROM AMERICIUM BY OXALATE PRECIPITATION

Since many metal ions form oxide compounds, and the steps preceding oxalate precipitation afford only a partial purification, a persistent problem is the production of an americium oxide product that does not meet purity specifications. The most troublesome impurity, in this respect, has been lead.

Although lead is not involved in the production chemistry ot plutonium and americium, it is continually present in the feed stream. The most probable source of the lead contamination is from the shielding material used inside the gloveboxes.

The objective of this research work was to determine the optimal conditions for oxalate precipitation which would effect maximum solubility of lead with a minimal loss of americium. To accomplish this goal, studies were made to determine the effects of nitric acid concentration, oxalate concentration, and digestion time. Also investigated was the addition of a complexing agent (Cl^-) to solubilize lead.

As shown in the next slide, both americium and lead are increasingly soluble with increasing nitric acid concentration; however, lead is more soluble than the americium. The americium oxalate is fairly insoluble until the hydrogen ion approaches $0.5\underline{N}$; whereas, about 50% of the lead is solubilized at this acidity.

For the study in which the solubility of americium and lead were determined as a function of oxalate ion concentration, the results as shown in the next slide show the common ion effect is much greater for lead than it is for americium. In runs in which the oxalate concentration was varied from 0.4 to $0.04\underline{M}$, the solubility of americium was unaffected; whereas, the solubility of lead increased with decreasing oxalate concentration. Limiting the oxalate concentration to $0.04\underline{M}$ maximizes the lead solubility without affecting the americium solubility.

Also, during these studies it was found that the lead solubility could be increased by adding chloride as a lead complexing agent. A small amount of chloride increases the solubility of lead; however, since americium does not form complexes with chloride under these conditions, its solubility is unaffected. The increase, rather than total solubilization, is probably due to the relatively weak lead-chloride complex. These results are shown in the following slide.

Slide 4.

SOLUBILITY OF AM AND PB AS A FUNCTION OF NITRIC ACID CONCENTRATION

HNO_3, N	AM IN FILTRATE		PB IN FILTRATE	
	MG/L	% SOLUBILIZED	MG/L	% SOLUBILIZED
0.1	2.4	0.4	9	7
0.3	5.7	0.9	42	33
0.5	12.2	1.9	61	48
0.7	32.0	5.0	66	52
0.9	66.2	10.3	70	55

*RESULTS ARE BASED ON SINGLE DETERMINATION

Slide 5.

SOLUBILITY OF AM AND PB AS A FUNCTION OF OXALATE CONCENTRATION*

$H_2C_2O_4$, M	AM IN FILTRATE		PB IN FILTRATE	
	MG/L	% SOLUBILIZED	MG/L	% SOLUBILIZED
0.4	4.7	0.7	10	7.8
0.2	3.6	0.6	7	5.5
0.15	3.4	0.5	16	12.5
0.10	3.9	0.6	22	17.2
0.08	4.5	0.7	19	14.5
0.06	4.1	0.6	32	25.0
0.05	4.6	0.7	58	45.3
0.04	5.4	0.8	65	50.8
0.02	9.4	1.5	78	60.9

*RESULTS BASED ON SINGLE DETERMINATION

Slide 6.

SOLUBILITY OF Am AND Pb AS A FUNCTION OF CHLORIDE*

Cl^-, M	Am in Filtrate		Pb in Filtrate	
	Mg/L	% Solubilized	mg/L	% Solubilized
0.00	5.7	0.9	42	33
0.05	4.3	0.7	81	63
0.10	4.1	0.6	74	58
0.15	4.8	0.7	82	64

*RESULTS BASED ON SINGLE DETERMINATION

Studies with an americium oxide contaminated with 3.2% lead was processed on a laboratory scale to show the differences between the current operating conditions and those found more favorable. The results, as shown in the following slide, show that very little, if any, lead is separated when the precipitation takes place under the current operating conditions of 0.1M. If, however, the oxalate concentration is reduced to 0.04M, then the lead in the americium product is reduced to about 2.6%. If chloride ion is added as a complexing agent for the lead, for solutions 0.1M oxalate, the lead in the americium product is reduced to 1.7%, and for solutions 0.04M oxalate, the lead is reduced to about 0.9%.

Slide 7.

SEPARATION OF LEAD FROM AMERICIUM BY OXALATE PRECIPITATION

(Original Oxide Contained About 3.2% Lead)

Run No.	Precipitation Conditions	w/w % Pb in Oxide Product
1.	$0.1M\ H_2C_2O_4$	3.18
2.	$0.1M\ H_2C_2O_4$	3.21
3.	$0.04M\ H_2C_2O_4$	2.60
4.	$0.04M\ H_2C_2O_4$	2.65
5.	$0.1M\ H_2C_2O_4 + 0.03M\ Cl^-$	1.65
6.	$0.1M\ H_2C_2O_4 + 0.03M\ Cl^-$	1.62
7.	$0.04M\ H_2C_2O_4 + 0.03M\ Cl^-$	0.91
8.	$0.04M\ H_2C_2O_4 + 0.03M\ Cl^-$	0.97

These studies, therefore, show the recovery of americium from plutonium and pyrochemical waste salts can be improved through procedural modifications: 1) by diluting the feed stream the select sorption of the actinides by cation resin is increased, 2) by rinsing the cation resin with 1.5N nitric acid the carryover of impurities with the actinides is reduced, and 3) by lowering the molarity of the oxalate ion concentration and adding a small amount of chloride ion, during the oxalate precipitation step, the coprecipitation of lead impurity is reduced.