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RECLAMATION OF PLUTONIUM FROM PYROCHEMICAL PROCESSING RESIDUES

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ABSTRACT

Savannah River Laboratory (SRL), Savannah River Plant (SRP), and Rocky Flats Plant (RFP) have jointly developed a process to recover plutonium from molten salt extraction residues. These NaCl, KCl, and $MgCl_2$ residues, which are generated in the pyrochemical extraction of ^{241}Am from aged plutonium metal, contain up to 25 wt % dissolved plutonium and up to 2 wt % americium. The overall objective was to develop a process to convert these residues to a pure plutonium metal product and discardable waste. To meet this objective a combination of pyrochemical and aqueous unit operations was used. The first step was to scrub the salt residue with a molten metal (aluminum and magnesium) to form a heterogeneous "scrub alloy" containing nominally 25 wt % plutonium. This unit operation, performed at RFP, effectively separated the actinides from the bulk of the chloride salts. After packaging in aluminum cans, the "scrub alloy" was then dissolved in a nitric acid - hydrofluoric acid - mercuric nitrate solution at SRP. Residual chloride was separated from the dissolver solution by precipitation with $Hg_2(NO_3)_2$ followed by centrifuging. Plutonium was then separated from the aluminum, americium and magnesium using the Purex solvent extraction system. The ^{241}Am was diverted to the waste tank farm, but could be recovered if desired.

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INTRODUCTION

Currently, the primary plutonium-americium separation process at the U.S. Department of Energy's Rocky Flats Plant (RFP) is molten salt extraction (MSE).[1-3] In this pyrochemical process americium-bearing (approximately 2,000 ppm) plutonium is contacted with a 35 mole % NaCl - 35 mole % KCl - 30 mole % $MgCl_2$ salt in a two-stage, countercurrent extraction mode. This operation generates a plutonium metal product containing less than 200 ppm ^{241}Am and a spent salt residue that contains up to 25 wt % plutonium and 1 to 2 wt % americium. Plutonium must be recovered from the spent salt residue so that the salt will be a discardable waste. For many years RFP used an aqueous process to recover both the plutonium and the americium from these MSE residues.[3] This operation was slow compared to the MSE operation, was highly corrosive to stainless steel processing equipment and glove boxes, and resulted in high radiation exposure to personnel.[3]

To minimize these problems RFP proposed a joint process development program with Savannah River. Working together, a conceptual process was proposed; the development effort resulted in a viable combined pyrochemical-aqueous chemistry flowsheet for the recovery of plutonium from the MSE residues.

SUMMARY

Savannah River Laboratory (SRL), Savannah River Plant (SRP), and Rocky Flats Plant (RFP) have jointly developed a process to recover plutonium from molten salt extraction (MSE) residues. These NaCl, KCl, and $MgCl_2$ residues, which are generated in the pyrochemical extraction of ^{241}Am from aged plutonium metal, contain up to 25 wt % dissolved plutonium and up to 2 wt % americium. The overall objective was to develop a process to convert these residues to a pure plutonium metal product and discardable waste. To meet this objective a combination of pyrochemical and aqueous unit operations was used.

The proof-of-principal of a pyrochemical scrubbing technique was first demonstrated in the RFP development laboratories.[3] Collaborative efforts between RFP, SRP, and SRL resulted in an idealized "scrub alloy" button composition. This ideal "scrub alloy" button was defined as a homogeneous alloy containing 60 wt % aluminum, 38 wt % plutonium, and 2 wt % americium. Entrained or occluded salts would result in a total chloride content of less than 1,000 ppm.

At Savannah River the buttons produced in the RFP development laboratory were first physically and chemically characterized. The dissolution characteristics, as related to nuclear criticality concerns during the dissolution cycle, were determined. Procedures then were demonstrated to provide acceptable dissolution of the "scrub alloy" buttons in canyon equipment followed by removal of chloride from the dissolver solutions to levels acceptable for downstream processing of the solutions.

The simplified aqueous flowsheet for dissolving and processing the "scrub alloy" buttons consisted of the following unit operations. Aluminum cans were dissolved in HNO_3 using $Hg(NO_3)_2$ as a catalyst. Upon breaching the aluminum cans, the "scrub alloy" buttons were dissolved using a solution of HNO_3 and HF. To minimize the total amount of both mercury and fluoride necessary, several charges of "scrub alloy" were made to the same solution. After dissolution the residual chloride contained within the "scrub alloy" buttons was precipitated by adding $Hg_2(NO_3)_2$ and then removed by centrifuging. The plutonium was then extracted and purified by the SRP Purex process. The purified plutonium was finished by the SRP finishing operations of precipitation as PuF_3, oxidation to a mixture of PuF_4 and PuO_2 followed by reduction to plutonium metal with calcium.

In this pilot program ^{241}Am was diverted to the solvent extraction waste stream and then to the waste tank farm. However, it would be possible to recover the americium from the waste stream using a combination of evaporation, formic acid denitration, and batch extraction into 50 vol % tributyl phosphate. Americium would be stripped into $<0.1M$ HNO_3, concentrated by evaporation, precipitated as the oxalate, and finished as the oxide.[10-17]

BACKGROUND

At RFP americium is separated from plutonium by a liquid-liquid extraction process involving immiscible molten salt and molten plutonium metal phases (Figure 1). The molten salt extraction process[2] is based upon equilibrium partitioning of both americium and plutonium between the molten chloride salt and molten plutonium metal phases. To obtain the necessary americium decontamination, RFP uses a two-stage countercurrent extraction operation. Typical plutonium recovery is 97%.

The amount of plutonium transferred to the salt is significant (approximately 3% of the feed mass) and must be removed before the salts can be discarded to waste. A typical spent-salt composition from the 30 mole % $MgCl_2$ - 35 mole % NaCl - 35 mole % KCl feed salt is approximately 25 wt % plutonium and 1 to 2 wt % americium.

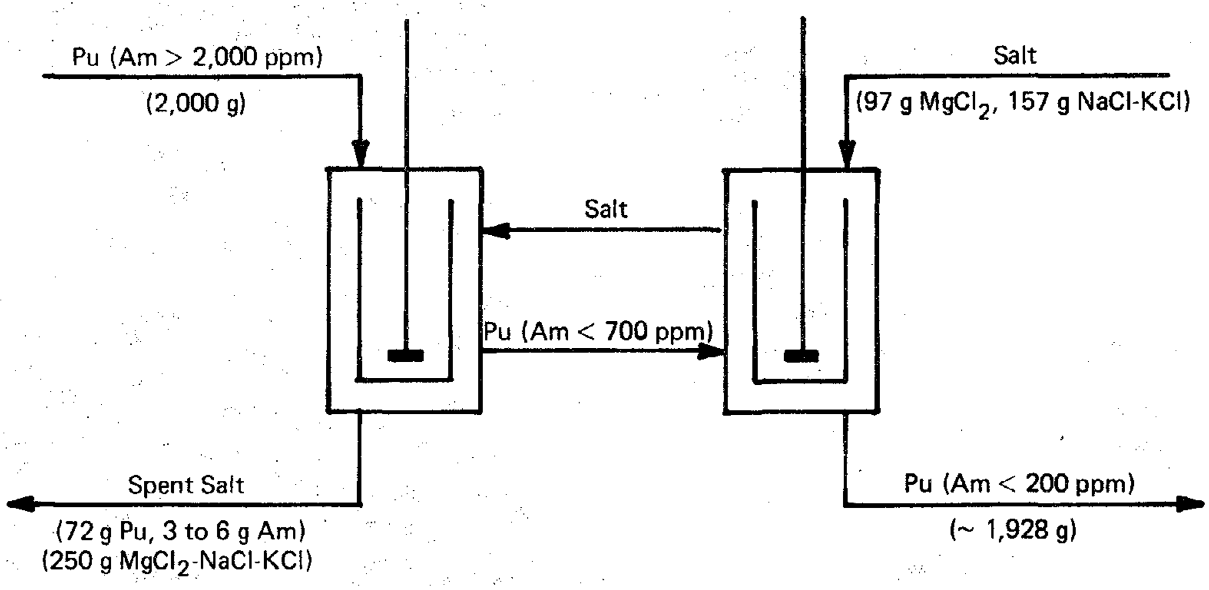


FIGURE 1. RFP Molten Salt Extraction (MSE) Flowsheet

Rocky Flats has used aqueous dissolution followed by a combination of ion exchange techniques to recovery both americium and plutonium from these spent salts.[2] However, aqueous solutions of chloride salts are highly corrosive to stainless steel processing equipment. By extracting the plutonium and americium into an alloy form, the chloride burden to an aqueous process could be decreased.

Rocky Flats proposed a joint development program with Savannah River to demonstrate a combined pyrochemical-aqueous flowsheet that would allow recovery of plutonium values from the spent MSE salts. The conceptual flowsheet resulting from joint discussions is given in Figure 2. The overall objectives of the various groups involved is given in Table 1.

DISCUSSION

RFP Pyrochemical Flowsheet Development[3]

In 1982 RFP initiated a development project to determine the feasibility of using an aluminum-magnesium "scrub alloy" process to remove plutonium and americium from 35 mole % NaCl - 35 mole % of KCl - 30 mole % $MgCl_2$ spent salts used in the molten salt extraction process. Initial investigation resulted in an alloy that yielded satisfactory phase-disengagement characteristics and discardable spent salts; this alloy's approximate composition was 26 wt % aluminum, 58 wt % magnesium, and 16 wt % actinide (plutonium plus americium). From a logistical viewpoint at both SRP and RFP, it was desirable to have an alloy with higher plutonium content.

In an attempt to double the plutonium content of the product alloy, magnesium was decreased to approximately the stoichiometric amount needed to reduce the actinides from the (III) to the (0) oxidation state. This change yielded an aluminum-plutonium button acceptable to both sites.

The primary reaction for the process is the following redox reaction:

$$\begin{aligned} PuCl_3 \text{ (salt)} + 3/2\ Mg \text{ (liquid)} = \\ Pu \text{ (liquid)} + 3/2\ MgCl_2 \text{ (salt)} \end{aligned}$$

The plutonium metal formed reacts with the solvent metal, aluminum, to form a high-melting intermetallic compound $PuAl_4$ according to the reaction:

$$Pu \text{ (liquid)} + 4\ Al \text{ (liquid)} = PuAl_4 \text{ (solid)}$$

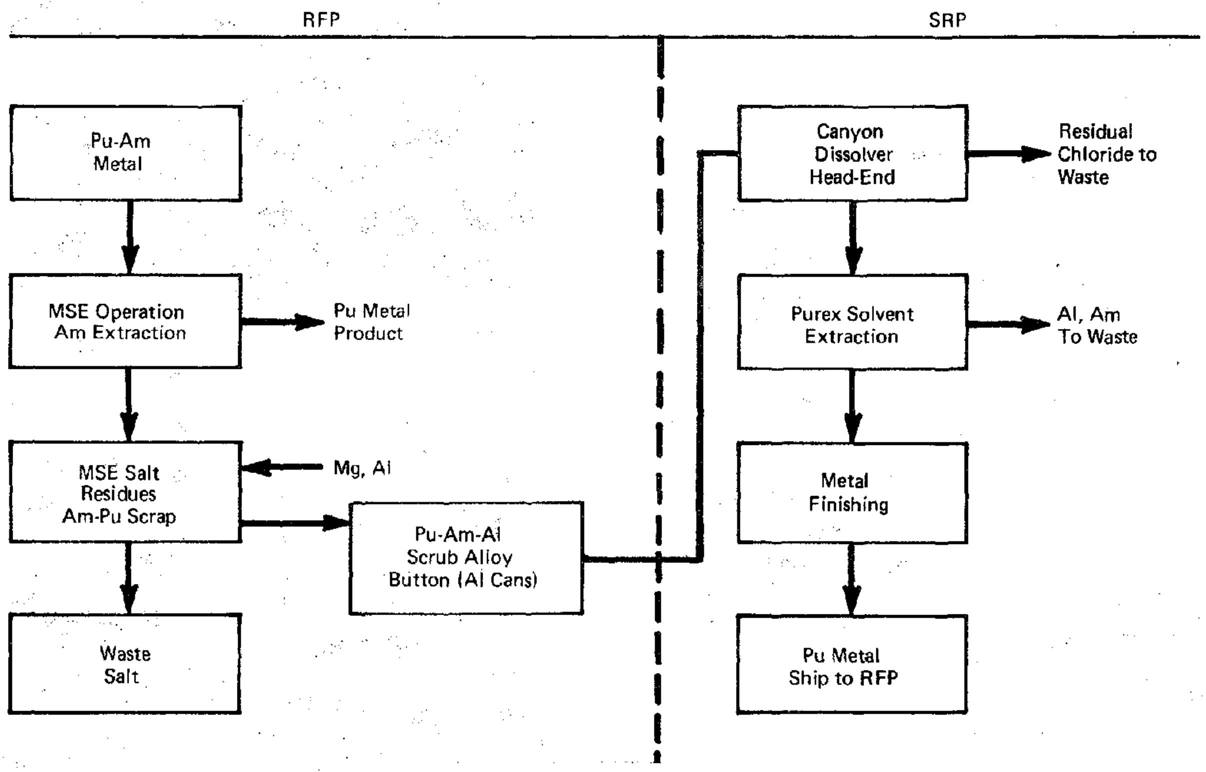


FIGURE 2. Conceptual "Scrub Alloy" Plutonium Recovery Flowsheet

TABLE 1

Plutonium Recovery from MSE Residues

RFP Objectives

- Remove Plutonium-Americium from MSE Residues
- Produce Discardable Salts
- Produce Salt-Free Alloy Buttons
- Reduce Drum Storage

SRL Objectives

- Characterize RFP Alloy Product
- Develop and Demonstrate Dissolving Flowsheet

SRP Objectives

- Dissolve Alloy Buttons Using Canyon Equipment
- Remove Residual Chloride
- Separate Plutonium-Americium (Purex)
- Divert ^{241}Am to Waste Tanks
- Produce Pure Plutonium Metal

Smooth, near salt-free buttons were formed with alloy compositions between 20 and 45 wt % actinide (plutonium plus americium). At 50 wt % actinide, the button was bowl-shaped with a considerable amount of surface salt adhered to the button. At temperatures available in the RFP furnaces, the phase-disengagement characteristics of the alloy begin to break down at about 45 wt % actinide. As a production process, strictly from a phase-disengagement standpoint, the alloy must contain ~20 to 40 wt % actinide. Discardable spent salts were produced throughout this alloy composition range.

To measure the degree of nonuniformity of plutonium and americium in the product alloy, a uniformity factor was defined as:

$$\text{Plutonium uniformity factor} = \frac{(\text{wt \% Pu button bottom})}{(\text{wt \% Pu button top})}$$

$$\text{Plutonium uniformity factor} = 2.5 \pm 1.1$$

$$\text{Americium uniformity factor} = 2.3 \pm 0.88$$

Selected raw data (showing some of the extremes) are given in Table 2.

TABLE 2

Plutonium-Americium Uniformity (Drill Samples of Selected Buttons)

Button Number	Button Surface	Solvent Alloy	% Pu	% Am	Pu/Am	Uniformity Factor Pu	Uniformity Factor Am
A30-1M	Top	Al-Mg	1.61	0.01	208	17.4	218.6
	Bottom		28.07	1.68	16.7		
A30-4M	Top	Al	17.72	0.79	22.5	1.8	1.8
	Bottom		32.60	1.43	22.9		
A30-5M	Top	Al	13.42	0.98	13.6	2.4	2.1
	Bottom		32.00	2.03	15.8		

Excess magnesium (above the stoichiometric requirements) had little effect on the product occluded-salt assay, actinide recovery, and phase disengagement. However, plutonium and americium concentrations became increasingly nonuniform with magnesium excesses above 50%. Below 50% excess only a slight increase in plutonium nonuniformity was observed. At 50% excess magnesium less adhered surface salt was apparent when qualitatively compared to the other excess values. Use of a 50% excess in the production operations also provides for a margin of error in the plutonium value of the feed salt, while not greatly affecting the actinide uniformity of the product alloy. The idealized RFP "scrub-alloy" flowsheet is given in Figure 3.

Chloride contained within salt occlusions could cause major corrosion of the stainless steel process equipment at SRP. Therefore, a preliminary estimate of salt content was made at RFP. To obtain this estimate the difference between the actual button weight and the projected button weight was attributed to salt occlusions. Although this is only a rough estimate, it was shown that buttons generally containing from 1 to 10 wt % salt ($NaCl$, KCl, $MgCl_2$) could be prepared. An example of occluded salt is shown in the picture of button A30-7M cut through the center (Figure 4).

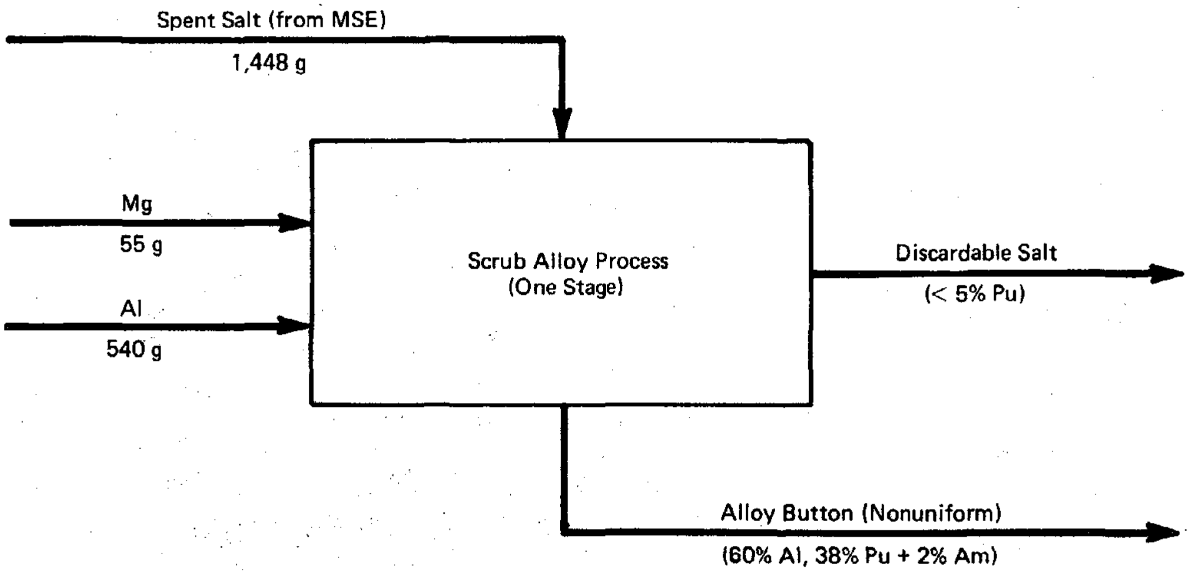
Savannah River Aqueous Flowsheet Development

Physical Characteristics

These high aluminum-plutonium "scrub alloy" buttons were approximated by a right circular cylinder, 4 in. in diameter and 0.5 to 3.0 in. high. The nominal button volume was approximately 19 $in.^3$ (310 cc), and the nominal surface area was 44 $in.^2$ (300 cm^2). The surface-to-volume ratio was approximately 2.3 $in.^{-1}$. As the total mass of the buttons was approximately 900 g, the calculated density was about 2.9 g/cc. A photograph of button A30-5M (one of the final set of developmental buttons) is shown in Figure 5.

Initial Button Dissolution Experiments

The laboratory dissolver was a standard 3-L glass kettle. The top was fitted with a ground-glass cover containing three ground-glass joints. These openings were used for chemical additions, temperature measurement, and a reflux condenser. A stainless steel basket was fabricated from expanded metal; this allowed the buttons to be both lowered into the dissolver and retrieved as needed.



1) $AmCl_3 + 3/2\ Mg = Am + 3/2\ MgCl_2$

2) $PuCl_3 + 3/2\ Mg = Pu + 3/2\ MgCl_2$

FIGURE 3. Ideal High Aluminum "Scrub Alloy" Flowsheet

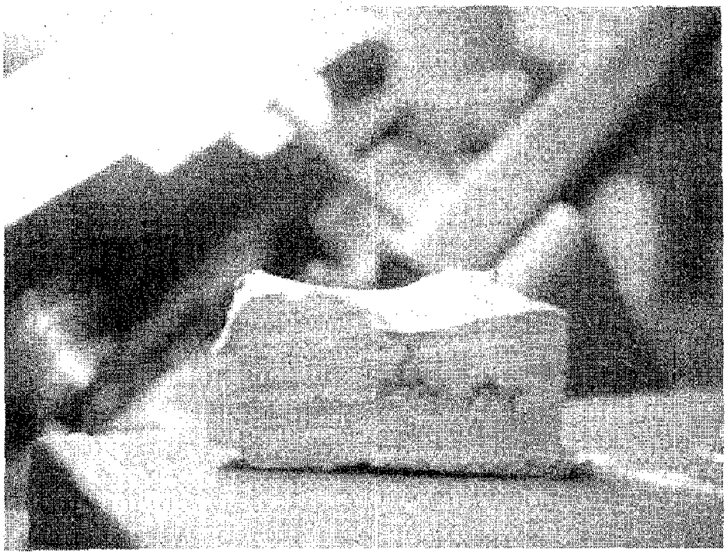


FIGURE 4. Salt Occlusions in Button A30-7M

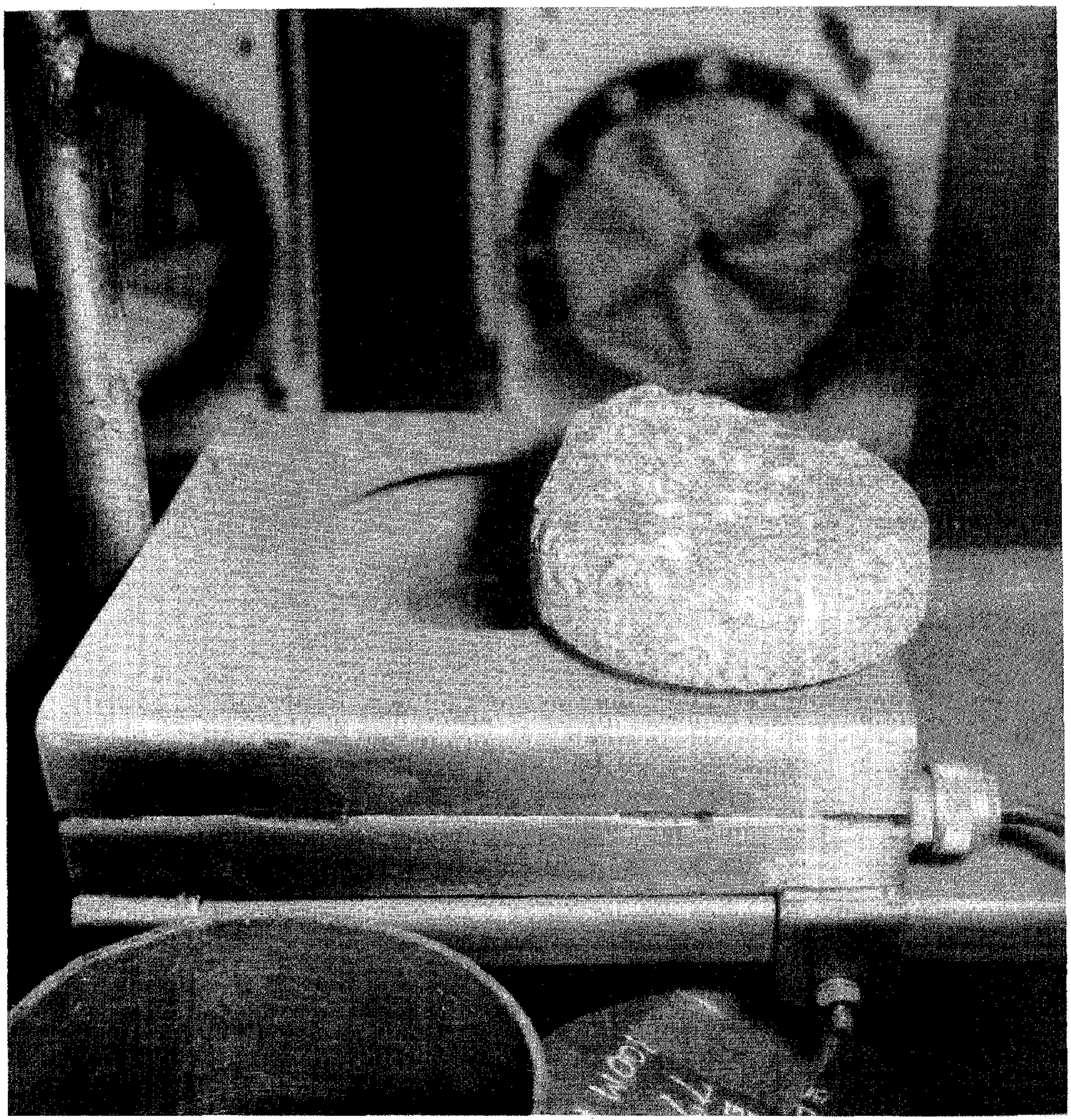


FIGURE 5. Button A30-7M (RFP Photograph)

The conceptual SRP flowsheet (Figure 6) called for buttons to be charged to the canyon dissolvers packaged in aluminum cans. As canyon dissolvers are not of a geometrically favorable design, criticality control dictates that a co-dissolution procedure be used. Practically then, the dissolvent must be a HNO_3-$Hg(NO_3)_2$-HF solution. As an aid in dissolution, a low concentration of fluoride is permitted. However, for corrosion control, fluoride must be kept to a minimum.

Initial dissolution experiments were performed using 4M HNO_3 with $Hg(NO_3)_2$ added at a slow constant rate. The button itself was placed into the basket and lowered into a dry dissolver. The top of the dissolver was assembled and nitric acid addition begun. Dissolution began on solution contact with the button. The temperature rapidly increased to >100°C as a result of the exothermic dissolution reaction. Mercury addition began when the temperature reached 90°C, but was stopped when it became evident that the reaction was too rapid. The mercury concentration at the time was ~0.001M. The self-heating reaction proceeded until the acid was depleted. Although only a small portion of the button had dissolved, a large quantity of PuO_2 sludge had formed. The experiment was repeated, without the addition of mercury, with the same result.

At this point it was evident that: (1) the buttons would react rapidly with nitric acid without the addition of $Hg(NO_3)_2$; (2) a larger dissolver would be needed to continue experiments with whole buttons; and (3) fluoride addition would be necessary to prevent the formation of PuO_2 sludge.

Full-Scale Laboratory Dissolution Experiments

The larger dissolver was also constructed of glass. A standard 3-L glass kettle was cut at about the 2-L mark, and tops and bottoms were cut from standard 4-L beakers. The pieces were rejoined in the order: bottom of kettle, 4-L beaker, 4-L beaker, and top of kettle. This gave the rounded bottom and a ground-glass joint at the top. The total volume was about 8 L. The ground-glass covers were then interchangeable between the 3-L and 8-L dissolvers.

Due to the rapid dissolution and steam-generated foaming, sufficient solution could not be added to either dissolver at one time to complete the dissolution. Dissolvent was therefore added in increments; when the reaction had sufficiently subsided, another increment of acid was added. When the reaction subsided and the temperature dropped below 100°C, the basket and button were removed. After removing the button an equal amount of acid was added to prevent polymerization of dissolved plutonium. After

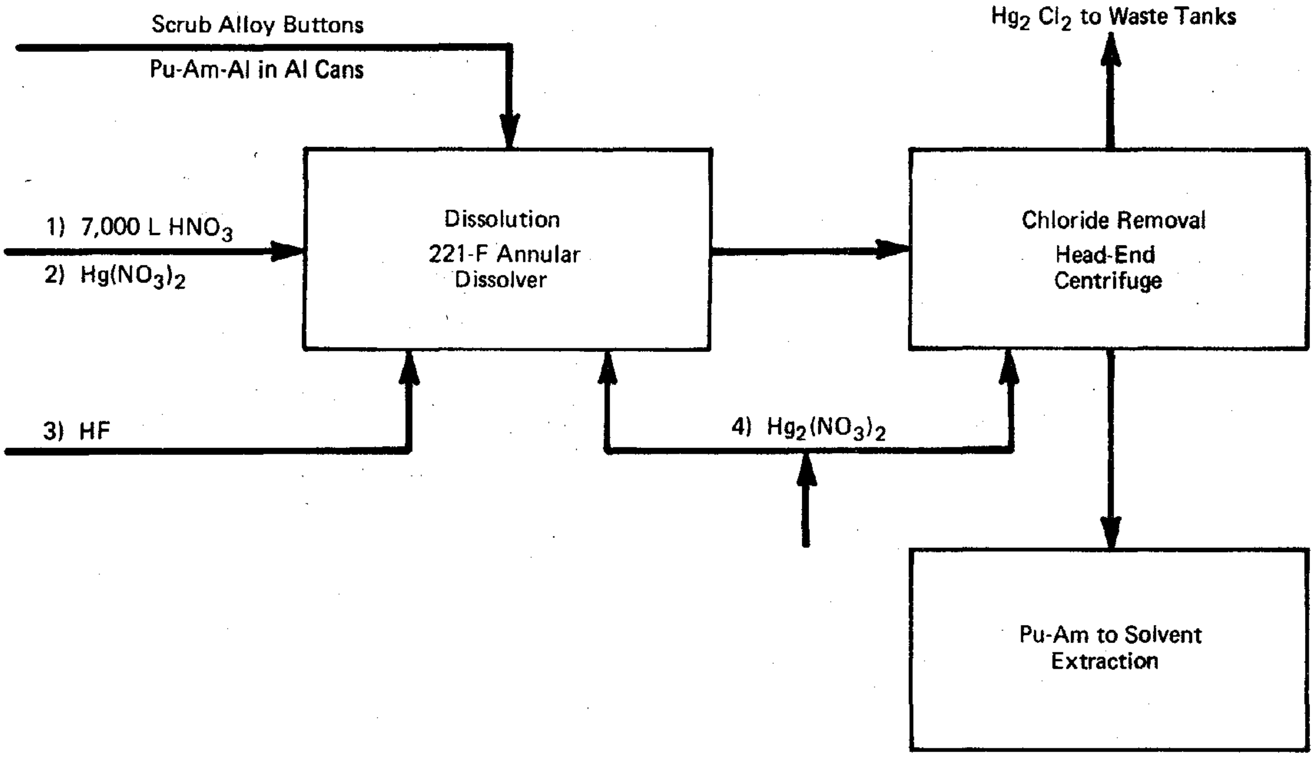


FIGURE 6. Aqueous Plutonium-Americium Feed Preparation from "Scrub Alloy" Buttons

removing the dissolver solution, button and basket were returned to the dissolver and the dissolution cycle repeated.

Dissolver solutions were transferred (by slight pressure) from a 4-L graduated cylinder directly into the dissolver located within the intermediate-level master-slave manipulator cell. Typical transfer rate was about 2 mL/sec. Typically, about 1 minute was necessary to transfer sufficient solution into the kettle for the acid to submerge the bottom edge of the button. Within 5 minutes of beginning the acid transfer, the foam-solution volume was approximately twice the actual solution volume and the temperature had risen to 109-110°C. The foam-solution volume would continue to increase to a maximum of about four to five times the actual solution volume. The first charge of acid was therefore limited to 1,000 to 1,500 mL; otherwise, the solution would foam out from the kettle.

Analytical Methods

Samples of the first few dissolution experiments were pulled directly from the dissolver analyzed for plutonium via thenoyltrifluoroacetone (TTA) extraction and alpha counting. However, due to the free acid concentration being so low (the solutions were actually acid-deficient), results were inconsistent. Two changes were made for the remaining analyses. First, an equal volume of 8M HNO_3 was added to the dissolver to raise the free acid concentration to 2 to 4M HNO_3. The second change was to determine plutonium content both by standard TTA extraction - alpha counting and by coulometry.

A standard gamma mount was prepared and ^{241}Am content determined by gamma spectrometry.

Chloride was determined by first precipitating the chloride as AgCl. The precipitate was dissolved in ammonia and silver content determined by atomic absorption. Chloride content was then back-calculated.

Cation impurities, except potassium, were determined by inductively coupled plasma spectrometry. Potassium was determined by atomic absorption techniques.

Dissolution Experimental Results

Average Chemical Composition

The original intent was to prepare buttons for shipment to SRP containing ~60 wt % Al - 40 wt % actinide (i.e., plutonium plus americium). Early scouting work at RFP had indicated that the chloride content of the buttons may be as high as 10 wt % due to occlusion of sodium, potassium, and magnesium-chloride salts. The plutonium, americium, and chloride data for the six buttons dissolved in the laboratory are given in Table 3. The plutonium content averaged 25.75 (σ 3.4) wt %; the americium content averaged 2.35 (σ 0.79) wt %. The chloride content varied from 0.25 to 4.95 wt % with an average of 2.93 (σ 1.78) wt %.

TABLE 3

"Scrub Alloy" Analytical Data

Button Number	Total Mass, g	Plutonium		Americium		Chloride	
		Grams	wt %	Grams	wt %	Grams	wt %
A30-4M	349	82.94	23.77	5.08	1.46	10.02	2.87
A30-5M	900	261.34	29.04	14.55	1.62	16.47	1.83
A30-17M	1102	247.65	22.47	22.47	3.21	2.73	0.25
A30-19M	1014	256.20	25.26	32.36	3.19	48.36	4.77
A30-29M	950	290.38	30.57	16.48	1.73	47.04	4.95
A30-30M	970	222.35	22.92	20.25	2.09	28.31	2.92

The plutonium found in the first six RFP R&D-produced buttons was about 85% of the stated amount. After these buttons were produced, RFP upgraded the NDA instrumentation used to determine plutonium in the MSE residues. RFP first determines the plutonium and ^{241}Am in the MSE residue, then scrubs the MSE residue with molten aluminum and magnesium to form the "scrub alloy" button, and again determines the plutonium and americium in the residue. The difference between the two determinations is reported as the plutonium and americium content of the button.

After NDA upgrades, two MSE residues were transferred from RFP to SRL and dissolved. Subsequent analysis of dissolved MSE residues at SRL was well within 3% of the RFP NDA analysis. In addition, approximately 120 buttons have been produced at RFP, shipped to SRP, and dissolved. Analyses of the dissolved "scrub alloy" buttons were well within the error bars of the respective analyses.

The ^{241}Am found in the six buttons dissolved in the laboratory was about 114% of the stated amount. As the expected error of analyses is about 10%, the ^{241}Am found is within the error bar.

The chloride content was found to average 2.93 (σ 1.78) wt %; it varied from as low as 0.25 wt % to as high as 4.95 wt %.

Magnesium was found to be about 2 wt %; sodium and potassium were about 1%. In general, if it is assumed that both sodium and potassium were present as chloride salts, only about 10% of the magnesium could be assumed to be present as the chloride salt. The excess magnesium is assumed to be present as magnesium-aluminum alloy.

Plutonium Distribution

Although plutonium content of "scrub alloy" buttons averaged about 26 wt %, the buttons were not homogeneous. Photographs of button A30-5M made at points throughout dissolution procedure are shown in Figures 7 through 12. The solvent metal (an aluminum-magnesium alloy) dissolves much more rapidly than the precipitated intermetallic compound, $PuAl_4$. Drill samples of the solvent metal indicate the plutonium content varies from about 1 wt % to perhaps 20 wt %. As this solvent metal dissolves, the average bulk plutonium content increases until essentially only the intermetallic compound $PuAl_4$ remains to be dissolved. The theoretical maximum plutonium is then 69 wt %.

In laboratory experiments it was evident when most of the solvent metal had dissolved as self-heating of the solution became insufficient to maintain the temperature above about 100°C. It was then necessary to heat the solutions to dissolve the remaining $PuAl_4$ intermetallic.

Laboratory Dissolution Time

Laboratory dissolution time was a function both of the nitric acid concentration used and the acid addition rate. The rate of acid addition was controlled to prevent boil over in the 8-L laboratory dissolver. Typically about 8 to 12 hours of actual dissolution time was necessary.

In plant operations, however, the acid volume was sufficient so that its concentration is not deleteriously reduced. Therefore, dissolution times were expected to be 6 hours or less. However, since buttons charged to the plant dissolvers were double-canned, the actual plant dissolution time is a combination of the time necessary to breach both cans and to completely dissolve the cans and the buttons. This was expected to require a total of 8 to 12 hours.

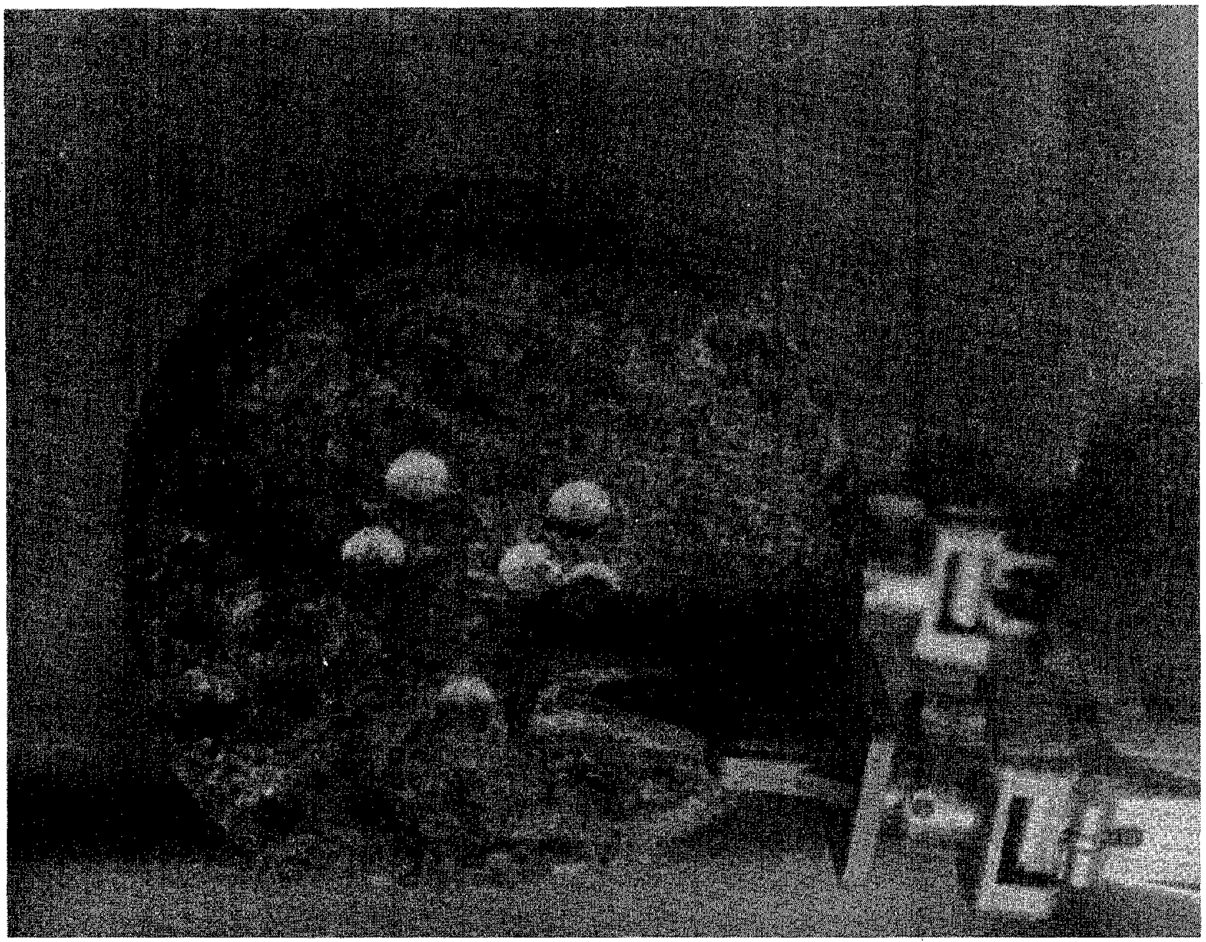


FIGURE 7. Top View Button A30-5M before Dissolution

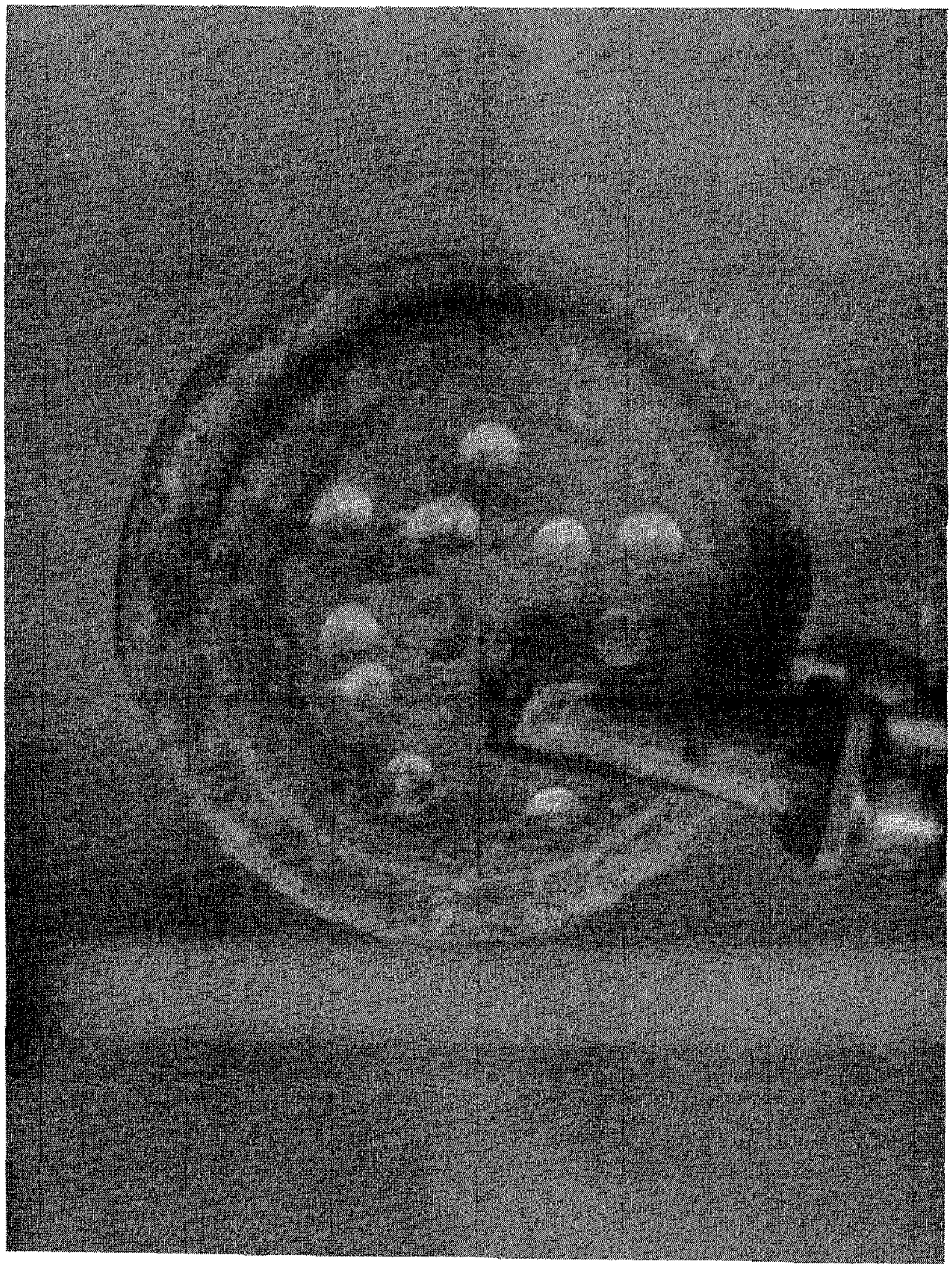


FIGURE 8. Bottom View Button A30-5M before Dissolution

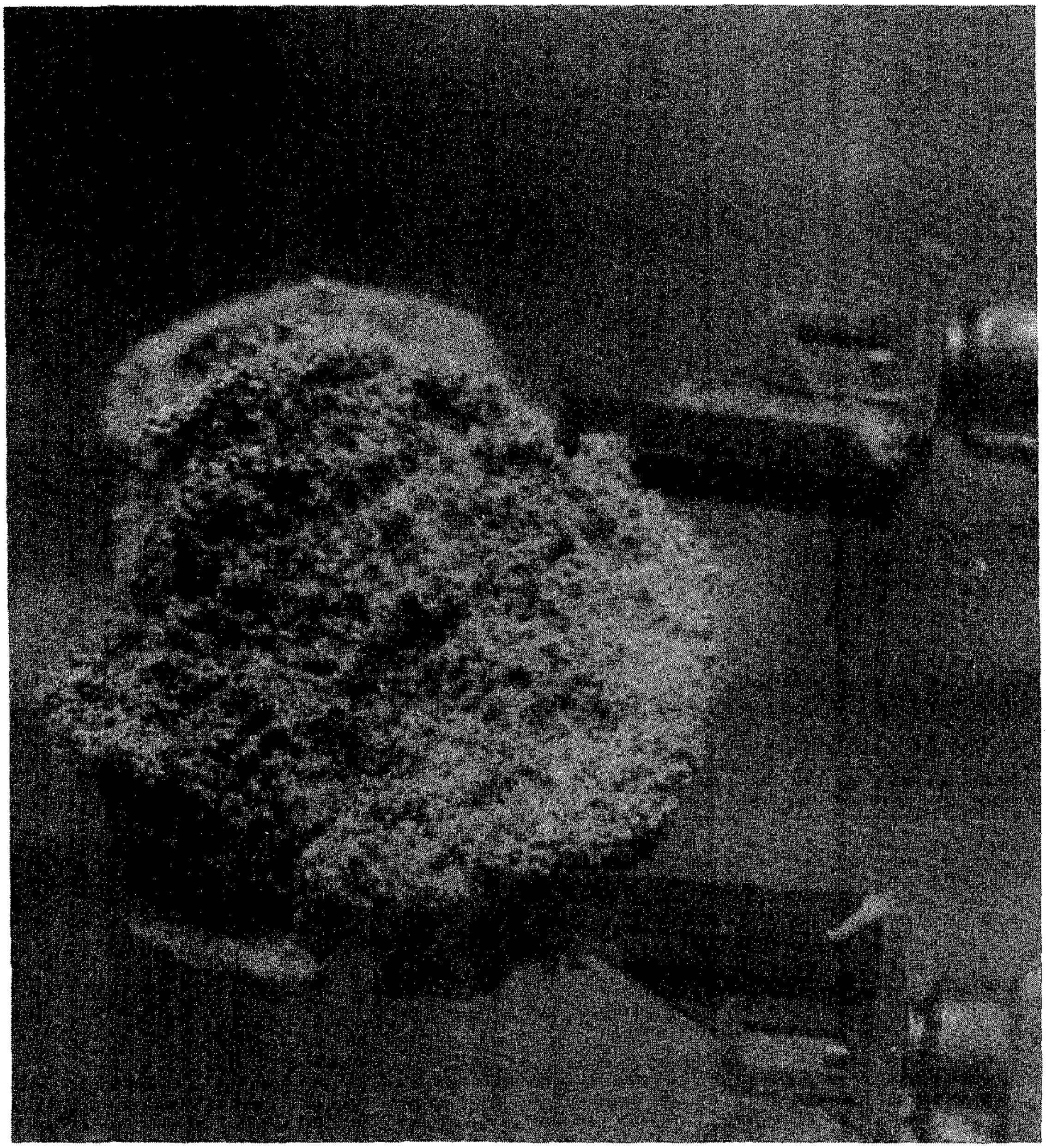


FIGURE 9. Top View Button A30-5M after First Dissolving Cut

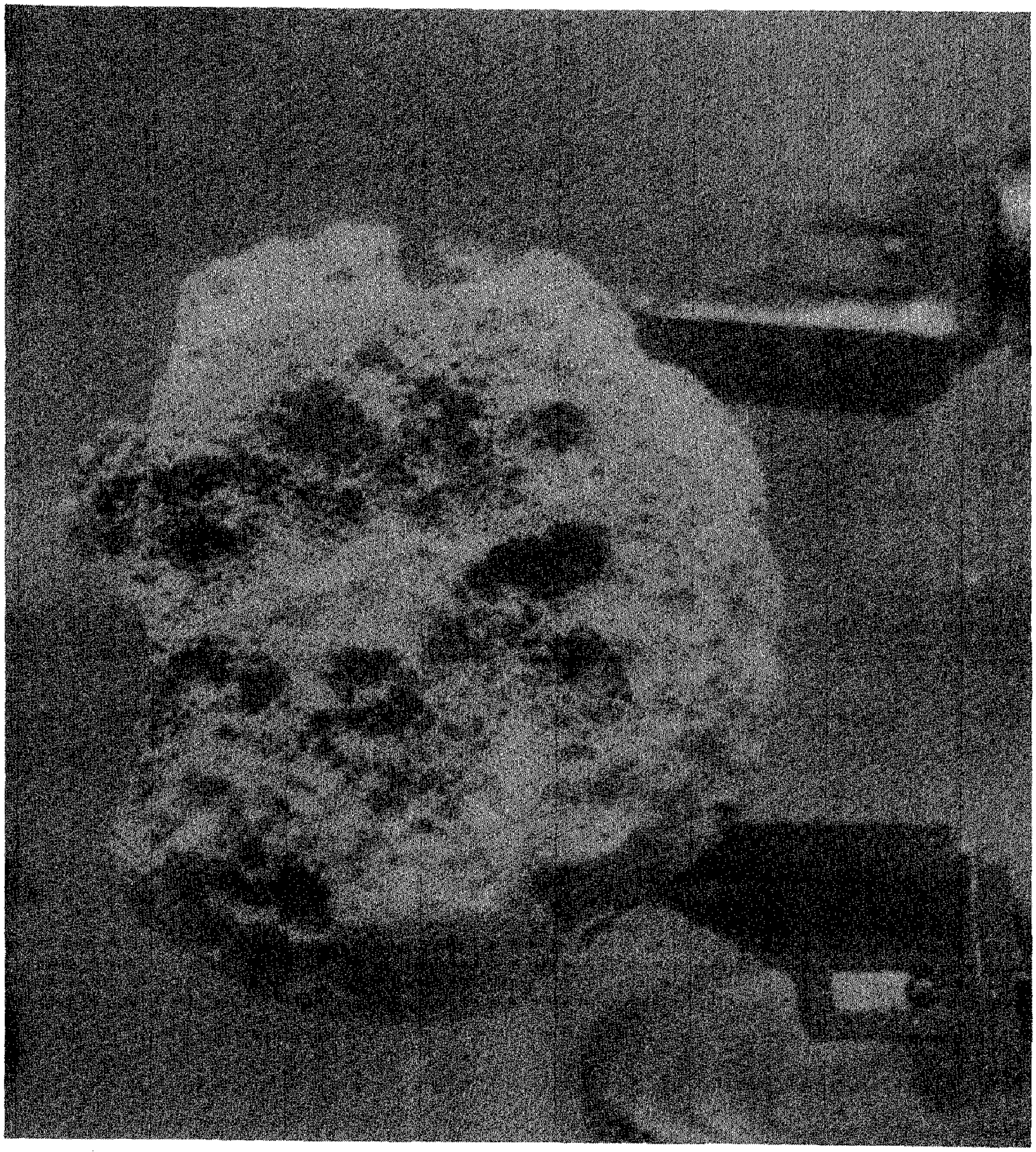


FIGURE 10. Bottom View Button A30-5M after First Dissolving Cut

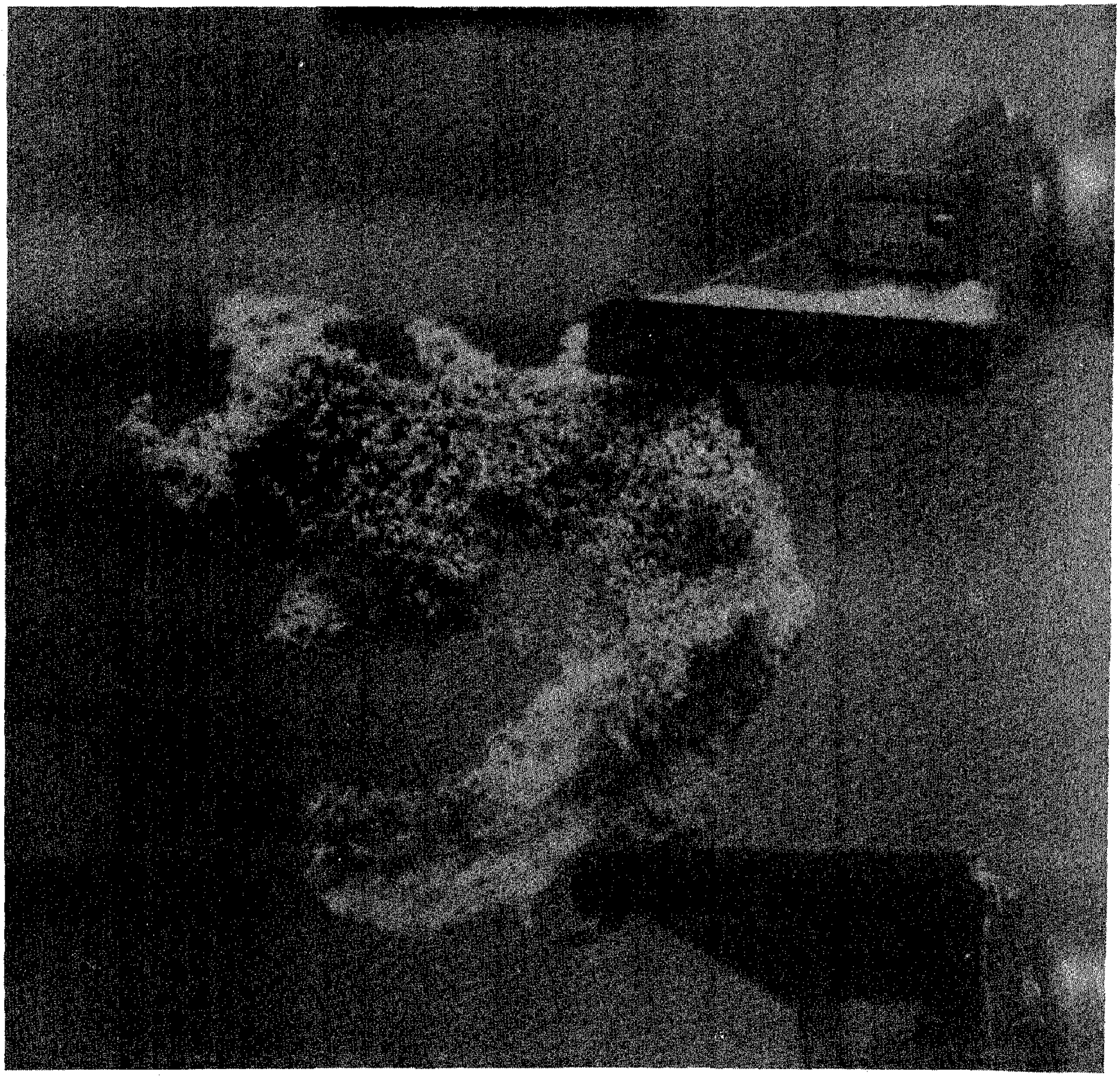


FIGURE 11. Top View Button A30-5M after Second Dissolving Cut

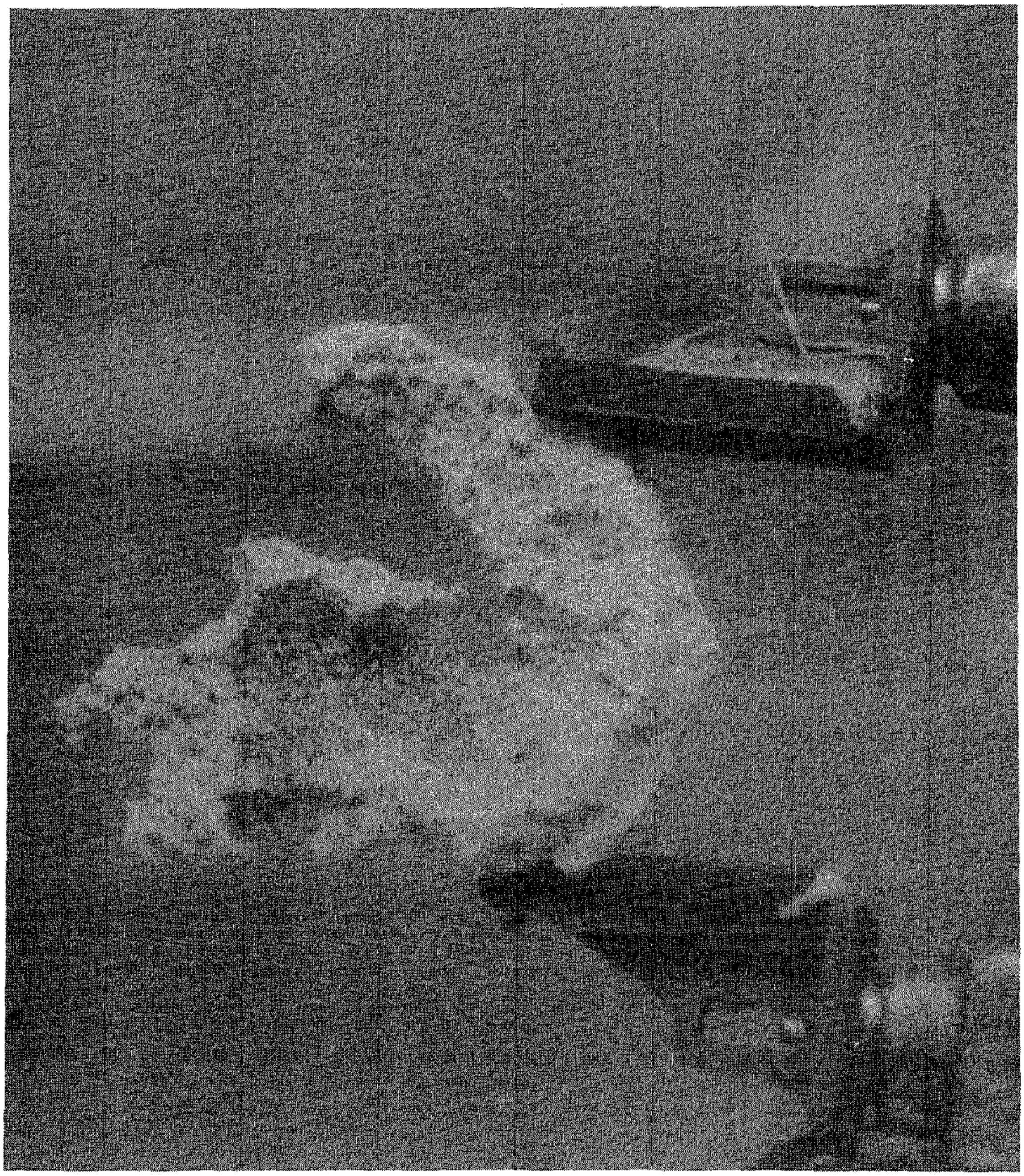


FIGURE 12. Bottom View Button A30-5M after Second Dissolving Cut

Removal of Chloride from Dissolver Solution

The insoluble chlorides ordinarily encountered in aqueous systems are those of Ag(I), Hg(I), and Pb(II). Lead chloride was omitted from laboratory testing because of its relatively high solubility vs. those of the Ag(I) and Hg(I) salts. Relative cost of the silver nitrate and mercurous nitrate is a minor processing consideration.

Based on processing assumptions, simulated dissolver solutions were prepared (Table 4). Chloride levels in this solution were reduced to less than 10 ppm using Ag(I) as the precipitant (Table 5). Chloride levels could not be analytically determined in solutions treated with Hg(I). However, mercurous chloride with a K_{sp} less than that of silver chloride should yield comparable chloride levels in solution. Chloride removal was therefore indirectly determined by analyzing precipitates for the cation therein and relying on equivalent stoichiometry to calculate the chloride content of the precipitate and initial solution. Chloride removal from simulated dissolver solutions was found to be quantitative by this method.

To recover plutonium effectively from the dissolved alloy, losses to the precipitated and centrifuged chloride solids must be minimal. Carrying of plutonium in its +3, +4, and +6 oxidation states, or as the Pu(IV) hexanitrato complex, by both Ag(I) and Hg(I) chlorides was determined. In every case greater than 99% of the plutonium remained in solution (Table 5). Analysis of the chloride solids showed less than 0.05% of the total plutonium initially present in solution (Table 6).

TABLE 4

Simulated Dissolver Solution

Component	Molarity
$Al(NO_3)_3$	0.09
HF	0.014
HCl	0.0230
$Mg(NO_3)_2$	0.16
HNO_3	3.1
$Hg(NO_3)_2$	0.009
$Fe(NO_3)_3$	0.004
$Fe_2(SO_4)_3$	0.004
Na_2SO_4	0.011
Pu	0.016

TABLE 5

Analysis of Supernates from Precipitation Tests

	Using Ag(I) as Precipitant		Using Hg(I) as Precipitant	
Plutonium Ionic Form	% Pu Remaining*	Cl^-, ppm**	% Pu Remaining*	Cl^-, ppm**
Without Adjustment	100	<10	101	***
Pu^{+3}	100	<10	102	***
Pu^{+4}	101	<10	101	***
PuO_2^{+2}	103	<10	102	***
$Pu(NO_3)_6^{-2}$	102	<10	100	***

* Originally 19.6 mg plutonium in each sample aliquot. Results are averages of duplicate test.

** By selective ion electrode. Original sample aliquot contained 816 ppm chloride.

*** Unable to analyze due to Hg(I) interference.

TABLE 6

Plutonium Carrying by AgCl and Hg_2Cl_2

	Precipitate			
	Hg_2Cl_2		AgCl	
Total mg Pu	Aliquot 1	Aliquot 2	Aliquot 1	Aliquot 2
Initially before precipitation	19.63	19.63	19.63	19.63
In supernate over precipitate	18.97	19.26	19.48	19.56
In combined washes	0.11	0.11	0.098	0.160
In dissolved precipitate (% of initial Pu)	0.0011 (0.006)	0.0014 (0.007)	0.0081 (0.04)	0.0008 (0.004)
Plutonium material balance, % of Pu initially present accounted for	97.2	98.7	99.8	100.4

Proposed Plant Dissolution Flowsheet

A simplified aqueous flowsheet for dissolving and processing the "scrub alloy" buttons is given in Figure 3. Aluminum cans were dissolved in HNO_3 using $Hg(NO_3)_2$ as a catalyst. Upon breaching the aluminum cans, the "scrub alloy" buttons were dissolved using a solution of HNO_3 and HF. To minimize the total amount of both mercury and fluoride necessary, several charges of "scrub alloy" were made to the same solution. After dissolution the residual chloride contained within the "scrub alloy" buttons was precipitated by adding $Hg_2(NO_3)_2$ and then removed by centrifuging. The plutonium was then extracted and purified by the SRP Purex process. The purified plutonium was finished by the SRP finishing operations of precipitation as PuF_3, oxidation to a mixture of PuF_4 and PuO_2, followed by reduction to plutonium metal with calcium.

Actual Plant Experience - First Campaign

Rocky Flats "scrub alloy" buttons were placed inside double sealed aluminum cans and loaded into 30-gal 6M shipping containers for shipment to SRP. The 6M containers were unloaded in Building 221-F hot crane maintenance area and the aluminum cans, (radiation rates 1 in. from the outer aluminum cans ranged between 3 and 7 rem/hr - 75% gamma/25% neutron) loaded into general purpose aluminum bundles ($<$4.0 kg Pu per bundle). These four bundles were then charged one each to the four charging ports of the annular dissolver (Figures 13 and 14). New three well inserts (Figure 15), designed for the annular dissolver, and boron addition to the dissolver solution were used to ensure nuclear safety control while dissolving the "scrub alloy." Nitric acid with mercuric nitrate catalyst and fluoride ion were used to co-dissolve the aluminum cans and the alloy in the annular dissolver (6.4D). The dissolvent concentration was 2 to 5M HNO_3, 0.006M $Hg(NO_3)_2$, 2.1 to 2.4 g/L B, 0.10M KF. The fluoride was masked with aluminum to reduce corrosion (ratio ~1 mole F to 5 to 10 moles Al).

Dissolution of all three charges of "scrub alloy" buttons went smoothly. Analyses indicated all the alloy, aluminum bundles, and cans were in solution following 10 hours of simmering at 80 to 85°C. Probing of the dissolver insert confirmed no fragments (less than 4 in.) remained after each 10-hour simmer. Analyses also confirmed all boron and fluoride added to the dissolver remained in solution. During dissolving, the air sparge was operated at 25 to 50 cfm to ensure adequate solution mixing. The dissolving reaction was controlled and no evidence of foaming was noted during processing. Total personnel radiation exposure during unloading of all 32 6M shipping containers was 40 mrads (15 mrems neutron exposure and 25 mRs gamma exposure).

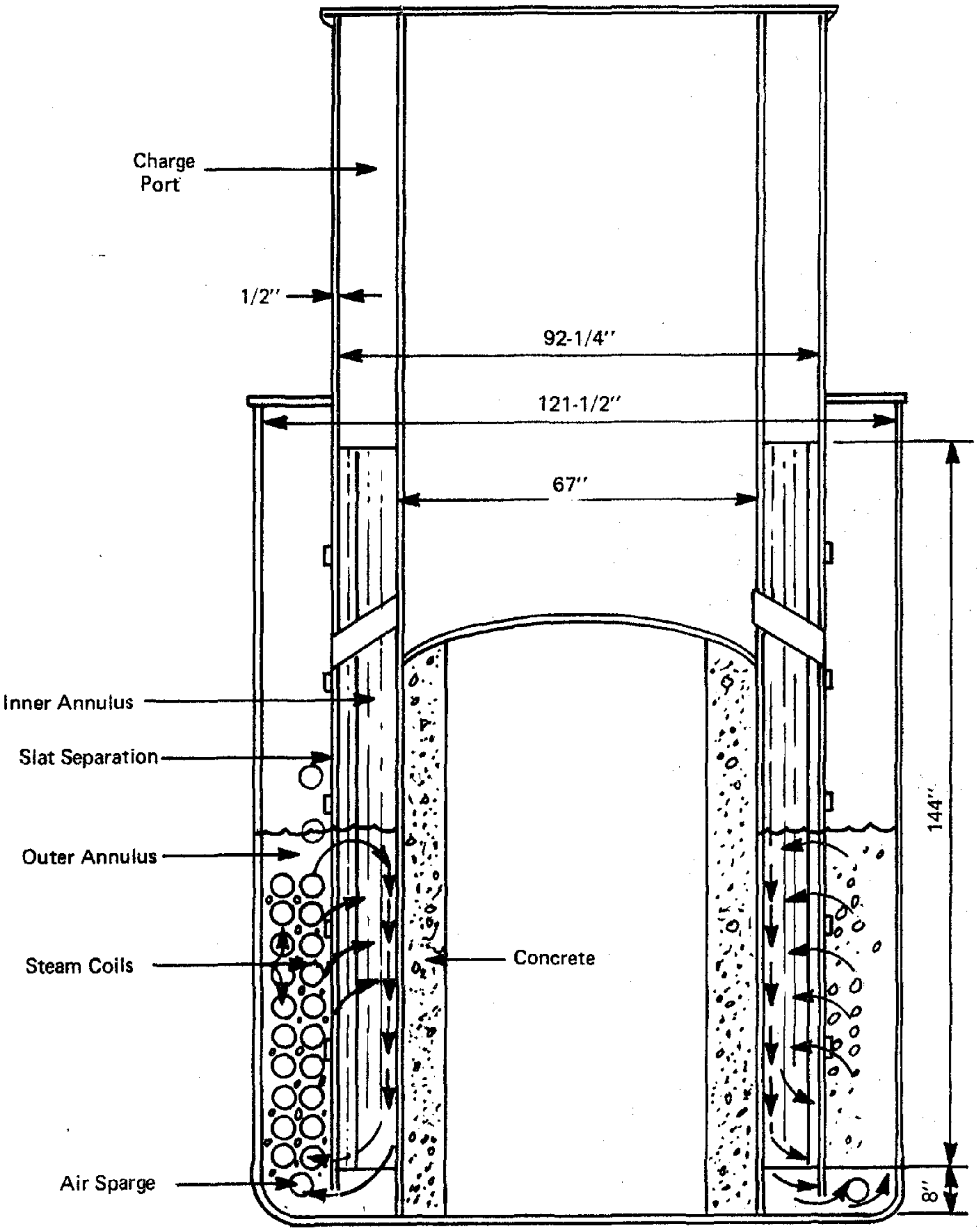


FIGURE 13. Cross Section of 6.4D Dissolver

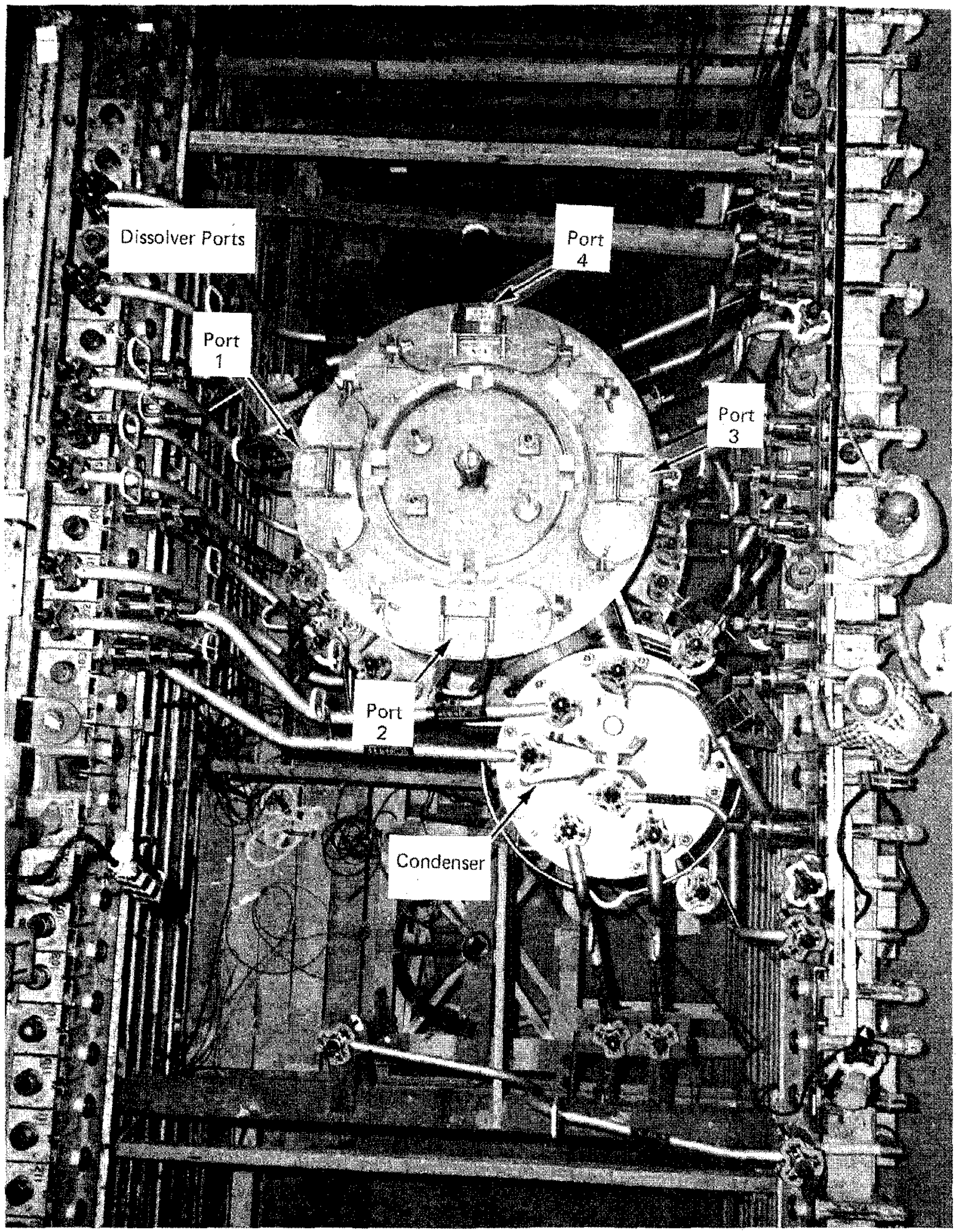


FIGURE 14. Top View of Dissolver Taken during Mockup

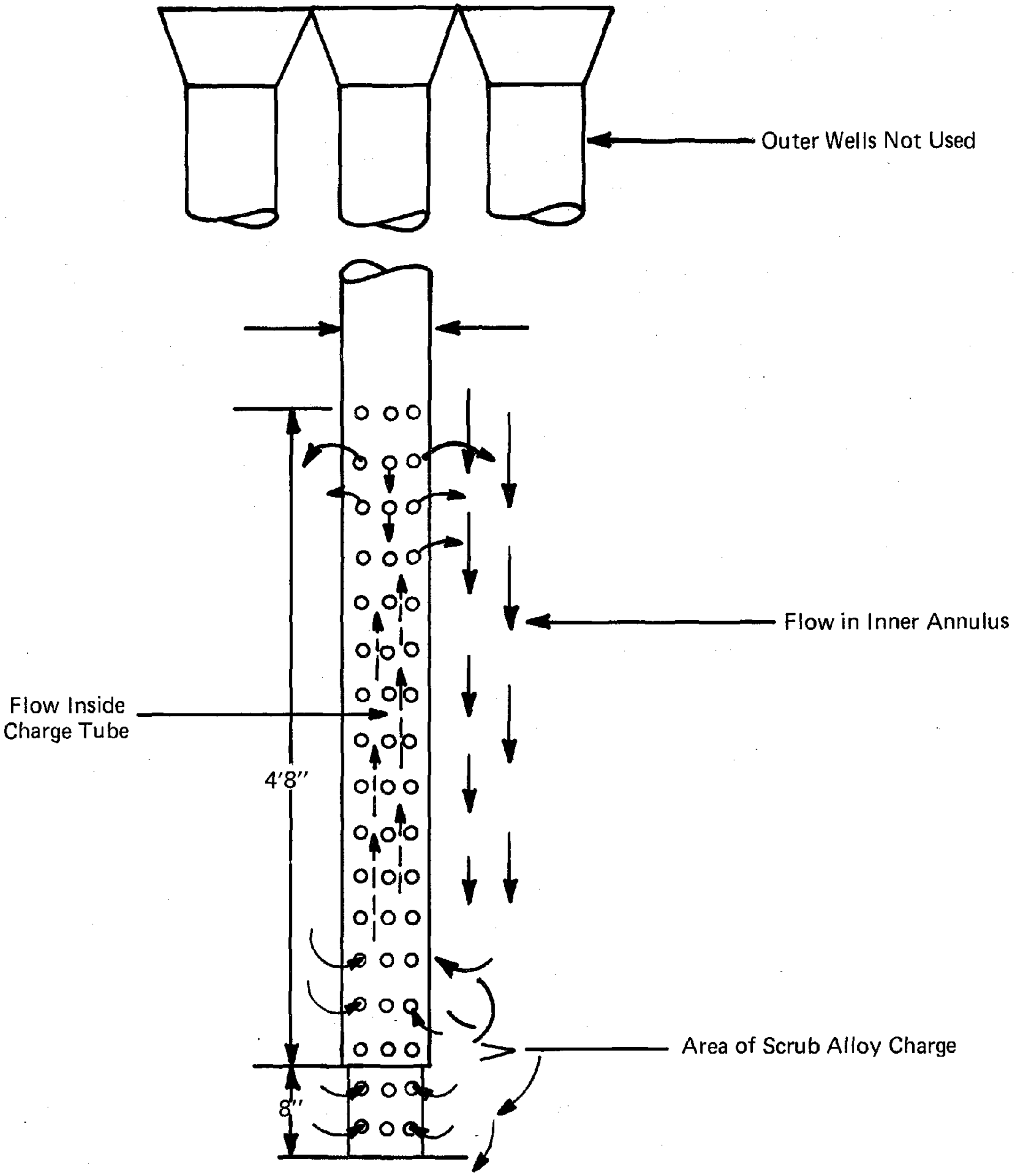


FIGURE 15. 6.4D Three-Well Insert with Flow Pattern Shown for "Scrub Alloy" Charge

After completion of the dissolving cycle, the "scrub alloy" dissolver solution was transferred to the accountability tank and sampled. This tank had been recalibrated in place in the hot canyon and equipped with a Ruska electromanometer gage to measure liquid level in preparation for the "scrub alloy" campaign. The amount of plutonium recovered was 34.9 ±0.5 kg (95% CL) based on the accountability tank volume measurements and plutonium analyses (coulometry method) of the solution. Rocky Flats had estimated the alloy contained 32.2 ±3 kg (95% CL). Analyses also indicated the alloy contained 1.86 kg ^{241}Am compared to an estimated 1.90 kg; all ^{241}Am were diverted to waste (1AW) during processing and discarded with neutralized high activity waste to the waste tank farm.

After completing accountability measurements, plutonium in the "scrub alloy" dissolver solution was valence-adjusted by addition of ferrous sulfamate and sodium nitrite to give greater than 90% Pu(IV). A gelatin strike was made to remove silica. Mercurous nitrate was added to remove chloride from solution as mercurous chloride precipitate. (Chloride removal was required to prevent excessive corrosion to the second stage high activity waste evaporator and the acid recovery unit.) Chloride content of the dissolver solution as measured in the accountability tank was 0.037M (782 parts chloride per million parts solution). Analyses of solution following addition of mercurous nitrate and centrifugation showed a chloride concentration of 0.003M (92 ppm). Excluding reduction in chloride content due to simple dilution, the chloride decontamination factor (DF) was 6.3. A second mercurous nitrate strike and centrifugation failed to remove additional chloride. As the Hg(II) concentration was twice the final chloride concentration, most of the residual chloride was assumed to exist in solution as the covalent complex ion $HgCl_n^{2-n}$. Corrosion studies indicate 100 ppm chloride will not give excessive corrosion during high activity waste evaporation or in the acid recovery unit.

During this campaign an estimated 190 lb of mercury were discarded in waste solutions sent to the waste tank farm. Ninety percent of the mercury was used to remove chloride in head end operations; about 10% was used during dissolving. The amount used was 42% less than had been expected to be required for the campaign. This reduction was achieved by adding mercurous nitrate to the "scrub alloy" dissolver solution as a single batch instead of blending "scrub alloy" solution together with Purex solution and then removing the chloride.

In summary, the overall operating experience was excellent. Recovery of plutonium and americium from the MSE residues actually exceeded predictions from laboratory experiments. The dissolution proceeded to completion in less than 10 hours in a manner consistent with maintaining critically safe configurations of all solids, fragments, and fines. Slightly better chloride decontamination was experienced in the laboratory than in the plant operation, but removal was sufficient to mitigate corrosion concerns.

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