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AEC RESEARCH AND DEVELOPMENT REPORT

RECOVERY OF ACTINIDES PRODUCED BY A NUCLEAR DETONATION IN VOLCANIC TUFF OR DESERT ALLUVIUM

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Peaceful Applications
(TID-4500)

RECOVERY OF ACTINIDES PRODUCED BY A NUCLEAR DETONATION IN VOLCANIC TUFF OR DESERT ALLUVIUM

by

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ABSTRACT

A process was developed to recover transplutonium elements from the debris of a thermonuclear device detonated underground at the Nevada Test Site of the AEC.

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INTRODUCTION

A major scientific objective of the Plowshare Program(1) is the production of transplutonium isotopes by the contained detonation of a special thermonuclear device. Heavy isotopes are produced by irradiation of a target element, such as uranium, in the intense neutron flux ($\sim 10^{26}$ neutrons/cm^2) produced by the detonation of the device; successive neutron captures on the target element result in the production of heavy isotopes that would normally require years of reactor irradiation.(2)

Recovery of the products requires mining the shot debris, and processing the debris to recover the actinides. The choice of the medium for the detonation strongly influences the chemical process; salt, limestone, dolomite, granite, tuff, and alluvium are all possible. Salt is the most convenient for aqueous chemical processing;(3) but others, such as tuff and alluvium, are the major underground strata at the Nevada Test Site, and the extra expense of processing this material might be considerably less than the cost of land acquisition and establishment of nuclear testing areas.

This report describes the development of a chemical process for recovery of actinides from tuff and alluvium debris from the Nevada Test Site. Both tuff and alluvium are essentially potassium/sodium aluminum silicates. Tuff is a porous rock of volcanic origin; alluvium is a sedimentary deposit produced by the weathering of tuff. A representative chemical analysis of both materials is shown in Table I.

TABLE I

Composition of Tuff and Alluvium Debris

	Fraction of Tuff, wt %	Fraction of Alluvium, wt %
SiO_2(a)	61	65
Al_2O_3	11.1	12.7
K_2O	3.6	2.7
Na_2O	3.3	1.8
Fe	1.0	2.0
CaO	0.2	0.4
MgO	0.1	1.5
TiO_2	0.1	0.5
H_2O(b)	20	13

(a) Estimated from weight loss during treatment with HF.
(b) Data from Reference(4).

For chemical processing, the high silica content is a serious problem because dissolution of a major portion of the debris is necessary to permit recovery of a substantial fraction of the actinides. Silicates are normally difficult to dissolve; moreover hydrated silica often precipitates in an erratic fashion from solutions containing dissolved or colloidal silica. In designing the process, removal of the silica from the debris at the earliest practical stage was considered advisable. With silica eliminated, chemical processing of the debris could then be carried out routinely by existing processes.(3)

Several chemical methods are frequently employed for removal of silica: (1) fuming with aqueous HF or treatment at a high temperature with gaseous HF to remove silica as volatile SiF_4; (2) fusion with sodium carbonate, and boiling the fused mass with strong nitric acid to precipitate silica; (3) leaching the debris with a strong acid, and precipitation of colloidal silica either with gelatin or by boiling with strong acid. Treatment of pulverized debris with HF gas at high temperatures was considered to be the most attractive of these methods because of the simpler equipment required and the ease of adaption to large-scale operation.

SUMMARY

The chemical process developed for recovery of heavy actinides from the debris of nuclear detonations in tuff and alluvium consists of three major steps:

(1) Destruction of silicates by treating the debris with gaseous HF to evolve SiF_4.

(2) Dissolution of the hydrofluorinated residue in boiling $Al(NO_3)_3$-HNO_3 solution.

(3) Separation of actinide isotopes from the dissolved debris by solvent extraction with 30% tributyl phosphate (TBP).

The process was demonstrated with 30 grams of debris from the Nevada Test Site. Loss of actinide isotopes to waste fractions amounted to 11%, due to incomplete hydrofluorination of the debris. Solvent extraction recovery of ^{244}Cm from the dissolver solution adjusted to 5M NO_3^--0.1M HNO_3 was 99% efficient in six simulated contactor stages.

DISCUSSION

PROCESS DESCRIPTION

Because of the high silicate content of tuff and alluvium, the recovery process depends on the initial removal of silicates from the debris to avoid the problems associated with the dissolution and aqueous processing of siliceous material. The process flowsheet for this initial treatment is given in Figure 1.

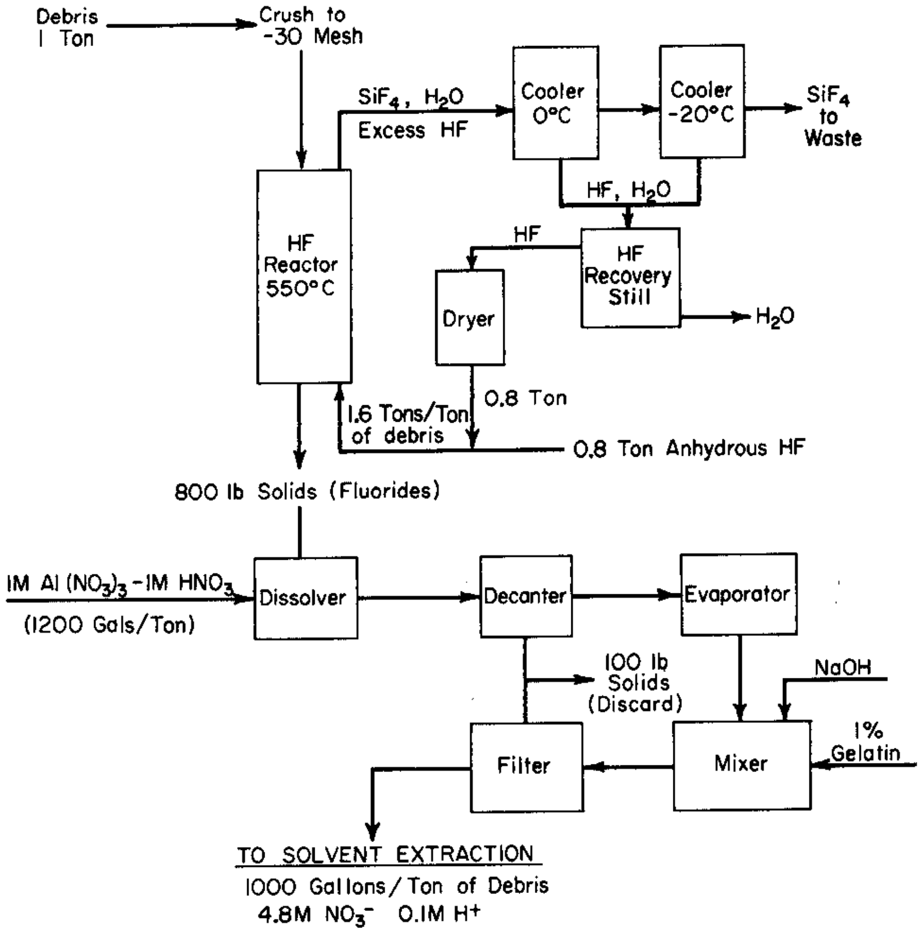

FIG. 1 RECOVERY OF ACTINIDES FROM TUFF AND ALLUVIUM-DEBRIS TREATMENT FLOWSHEET

Destruction of the silicates is accomplished by crushing the mined debris to -30 mesh, and treating at 500 to 550°C with an excess of gaseous HF; this converts the silicates to metal fluorides, volatile SiF_4, and steam. The excess HF and steam are condensed from the gas stream in a series of coolers, and fractionally distilled to recover the HF. Most of the SiF_4 passes through the coolers and is discarded.

The residue from the HF treatment contains the metallic elements in the debris as a mixture of fluorides and oxides. A boiling solution of 1M $Al(NO_3)_3$-1M HNO_3 readily dissolves approximately 85% of this residue and 85 to 90% of the actinide elements in the residue. The undissolved solids after this treatment consist mainly of unreacted silicates. Increasing the hydrofluorination efficiency by further reducing the particle size of the debris would decrease the amount of insoluble residue.

The undissolved solids and the dissolved silica must be removed from the solution to avoid the formation of emulsions during the subsequent solvent extraction steps. The solids that settle rapidly are removed by decantation of the turbid supernate, then rinsed and discarded with an attendant loss of about 10% of the actinides in the debris. The decanted solution and rinse are evaporated and partially neutralized with concentrated NaOH to 5.0M NO_3^--1M HNO_3. The suspended solids are coagulated by digestion with gelatin, then filtered and discarded. The filtrate from this step is sufficiently clarified for feed to the solvent extraction process.

This extensive clarification procedure is necessary because of the colloidal nature of part of the undissolved solids. Since removal of all of the solids by filtration may be impractical in large-scale operations, most of the solids are separated by decantation of the supernate; however the settling rate of the colloidal solids is probably too slow for practical processing. Also, during neutralization of the excess HNO_3, dissolved silica precipitates from the solution. The suspended solids and the precipitated silica should be coagulated and removed at the same time.

The solvent extraction procedure for purifying and concentrating the actinides from the clarified dissolver solution is the same as that developed for use with the debris of nuclear explosions in salt.(3) The process, shown in Figure 2, requires a clarified feed solution containing approximately 5M NO_3^- and a maximum of 0.15M HNO_3. Lower nitrate concentrations do not give sufficient salting strength for extraction of Cm^{3+}, Bk^{3+}, and Cf^{3+} and hence produce high losses; higher nitrate concentrations give too much salting and cause coextraction of other cations, such as Fe^{3+}. Too much HNO_3 in the feed results in poor actinide extraction because of "back-salting" from the organic phase by the extracted HNO_3.

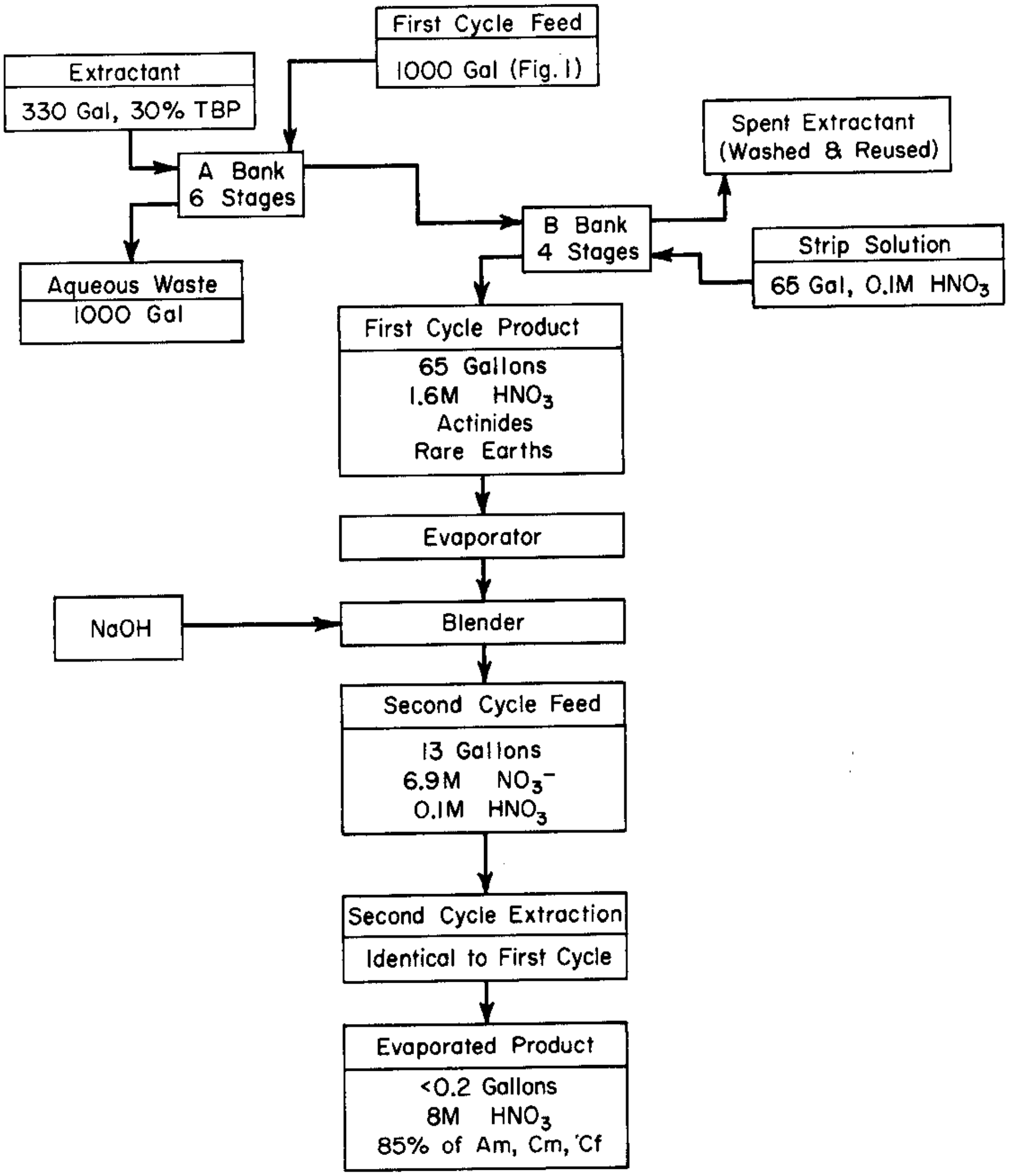

FIG. 2 RECOVERY OF ACTINIDES FROM TUFF AND ALLUVIUM-SOLVENT EXTRACTION FLOWSHEET

Two cycles of alternating solvent extraction and evaporation concentrate the actinide solutions to less than 200 gallons per kiloton of debris. In each cycle the feed solution is extracted with 30% TBP in n-dodecane in a six-stage mixer-settler. The organic raffinate from the first mixer-settler bank is stripped with a dilute HNO_3 solution in a second, four-stage mixer-settler. The aqueous product solution from the first cycle is evaporated, and the excess HNO_3 is neutralized to prepare a 6 to 7M NO_3^- -0.1M HNO_3 feed solution for the second cycle of solvent extraction.*

SILICA VOLATILIZATION TESTS

The major effort in this investigation was the development of the method for removing silica from the debris by volatilization as SiF_4. The effects of particle size, temperature, and HF flow were explored; and two methods of treating the powdered debris were tested. This study established that (1) a minimum particle size reacts most efficiently with HF, (2) 400°C is the minimum temperature for an effective HF treatment, and (3) 100% stoichiometric excess of HF is sufficient to remove >95% of the SiO_2. Tests of two arrangements for exposing the powdered debris to HF gas demonstrated that a system in which the HF gas flowed through a bed of crushed debris is more efficient than a system in which the HF flowed over a bed of powdered debris.

Hydrofluorination tests were carried out in the apparatus illustrated in Figure 3, which was constructed of nickel pipe joined with copper tubing. The apparatus was evacuated, and then flushed with nitrogen gas. The reaction chamber was positioned in a horizontal tube furnace in which it could be heated to 1000°C. Reaction temperatures were measured by a thermocouple in a nickel well positioned above the sample boat. A smaller reaction chamber (a 6-inch section of 1-inch ID nickel pipe) was wrapped with heating tape, fitted with a sample basket of 100-mesh nickel screen, and closed with a threaded nickel cap. This smaller chamber was mounted vertically and replaced the horizontal chamber shown in Figure 3. The same gas inlet system and product gas collection system were used with both reaction chambers.

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* Higher NO_3^- concentration is required in the second cycle because $NaNO_3$ is a poorer salting agent than $Al(NO_3)_3$.

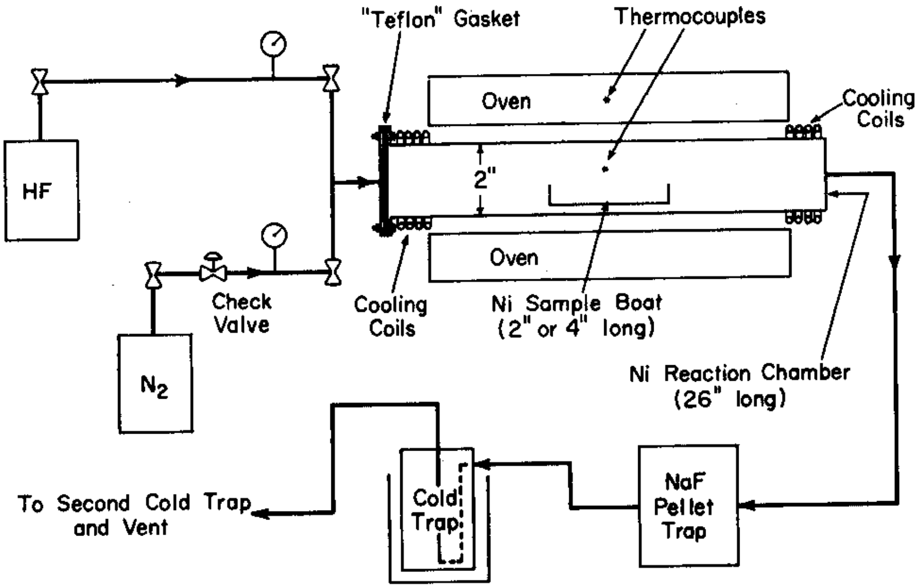

FIG. 3 HYDROFLUORINATION APPARATUS

When a sample of debris was being treated with HF, an auxiliary N_2 stream flowed at equal rate through the chamber to sweep the excess HF and the reaction products into a collection system - a chemical trap and two cold traps. The chemical trap held two cartridges filled with pellets of NaF, which removed part of the HF and H_2O from the stream. The remainder of the HF and H_2O was condensed from the stream by cooling the cold traps with a dry ice-trichloroethylene bath. The time cited below for a given experiment was the time during which HF flowed into the reaction chamber.

The flow of anhydrous HF to the reaction chamber was approximately 90 ml (STP)/min in each experiment. The gas pressure in the reaction chamber was maintained at one atmosphere during treatment of the debris.

The temperature inside the reaction chambers could not be controlled closely during treatment of a debris sample with HF. A fluctuation of about ±50°C was noted in most runs, and the reaction temperatures therefore are reported with this degree of uncertainty. Usually, the chamber temperature began rising sharply about 10 to 15 minutes after the start of the flow of HF into the chamber. The rise in temperature resulted from the heat of reaction of HF with the debris. Automatic, as well as manual, control of the oven power prevented higher temperature excursions.

The reaction temperature also varied across the length of the large chamber, as shown by the profile in Figure 4. However, the variation across a 2-inch reaction boat in the center of the chamber was only ~10°C. The profile was measured with a movable thermocouple inside a nickel well that extended the full length of the chamber interior.

The hydrofluorination reaction is not very sensitive to temperature above 400°C. As shown in Figure 5, the reaction of debris with HF was incomplete below 400°C in a series of 25-minute tests. However, at temperatures above 400°C, the reaction was very nearly complete — more than 90% of the residue from the HF treatment dissolved in the Al^{3+}-HNO_3 solution in the subsequent process step.

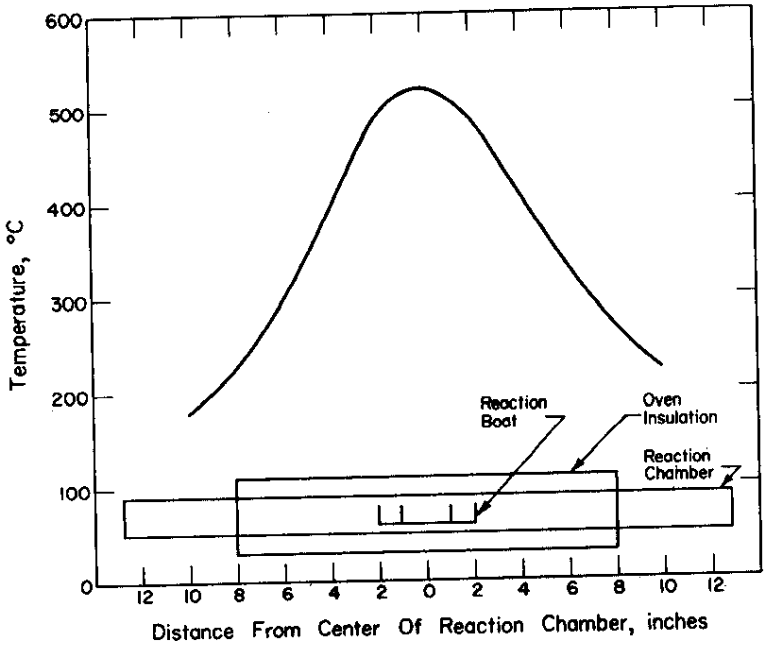

FIG. 4 TEMPERATURE PROFILE IN THE REACTION CHAMBER

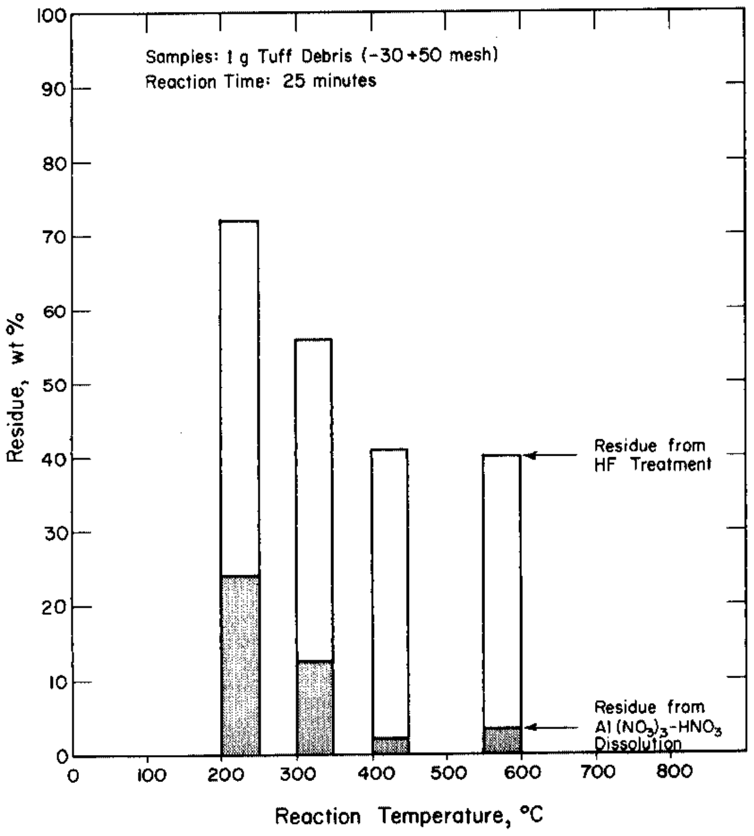

FIG. 5 EFFECT OF TEMPERATURE ON HYDROFLUORINATION

As expected, the particle size of the debris is of major importance in obtaining acceptable hydrofluorination efficiency and consequently in recovering actinides from the debris. Test results (Table II) show that for each particle size there is a corresponding amount of sample that remains unaffected, irrespective of the time of exposure to HF. Apparently, HF does not diffuse rapidly through the fluorides formed initially on the outer shell of each particle to react with the inner kernel of silicates. The results indicate that -30+50 mesh is an acceptable particle size for the debris.

TABLE II

Effect of Particle Size on SiO_2 Removal by HF

(Conditions: 1 to 2 hours at 500 to 600°C)

	Tuff, wt % of original charge		Alluvium, wt % of original charge	
Mesh	HF Residue	Insoluble*	HF Residue	Insoluble*
Lump	48	19	73	52
-30 +50	40	3.5	39	7.4
-50 +100	41	2.2	38	2.3
-100 +200	39	<2.2	39	0.7

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* In 1M $Al(NO_3)_3$-1M HNO_3.

A 15 to 20-minute treatment at 550°C with HF flowing at 90 ml/min was adequate to remove >95% of the SiO_2 from a series of 1-gram samples of -30+50 mesh debris. These samples were treated for various times in the vertical reaction chamber; however reaction times longer than 20 minutes produced no significantly greater reduction in residue. The results are shown in Figures 6 and 7.

The small laboratory equipment used in the development tests on this process restricted the extent to which the engineering problems could be explored. However, limited conclusions were inferred. Of the two hydrofluorination chambers tested, the vertical arrangement is the more efficient. In the vertical arrangement the debris presents a constant cross section to the flow of HF with little opportunity for channeling of the gas. Also, the excess of HF required for the vertical chamber is less than that for the horizontal chamber, in which HF diffusion to the bottom of the debris in the reaction boat is necessary.

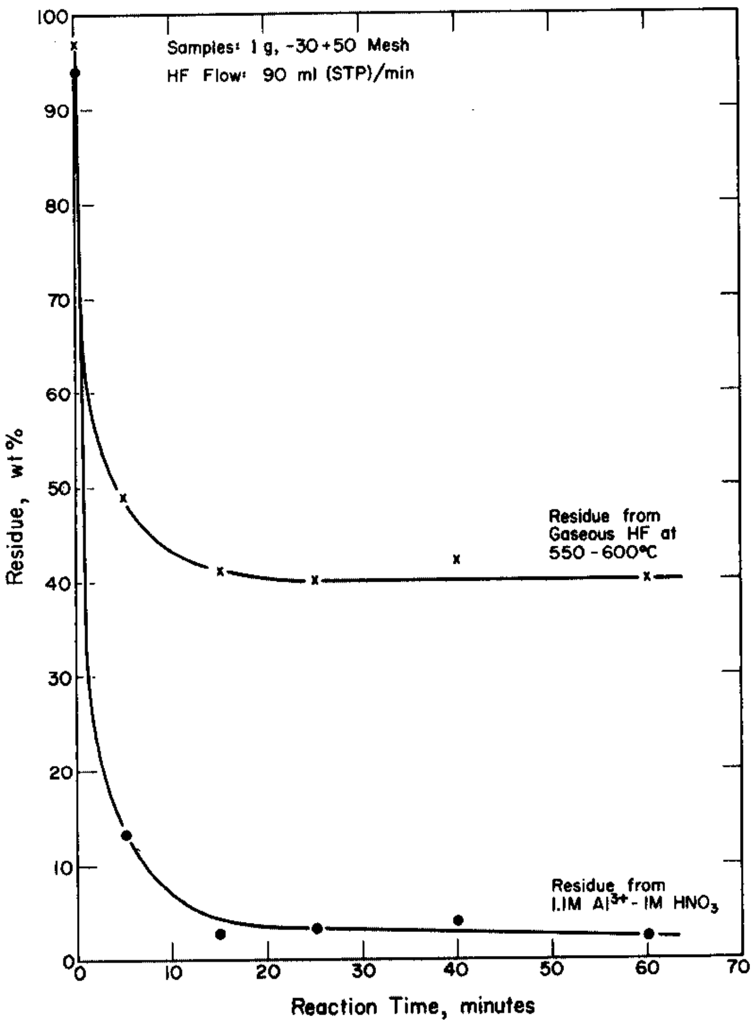

FIG. 6 SiO_2 VOLATILIZATION FROM TUFF AND DISSOLUTION OF RESIDUE

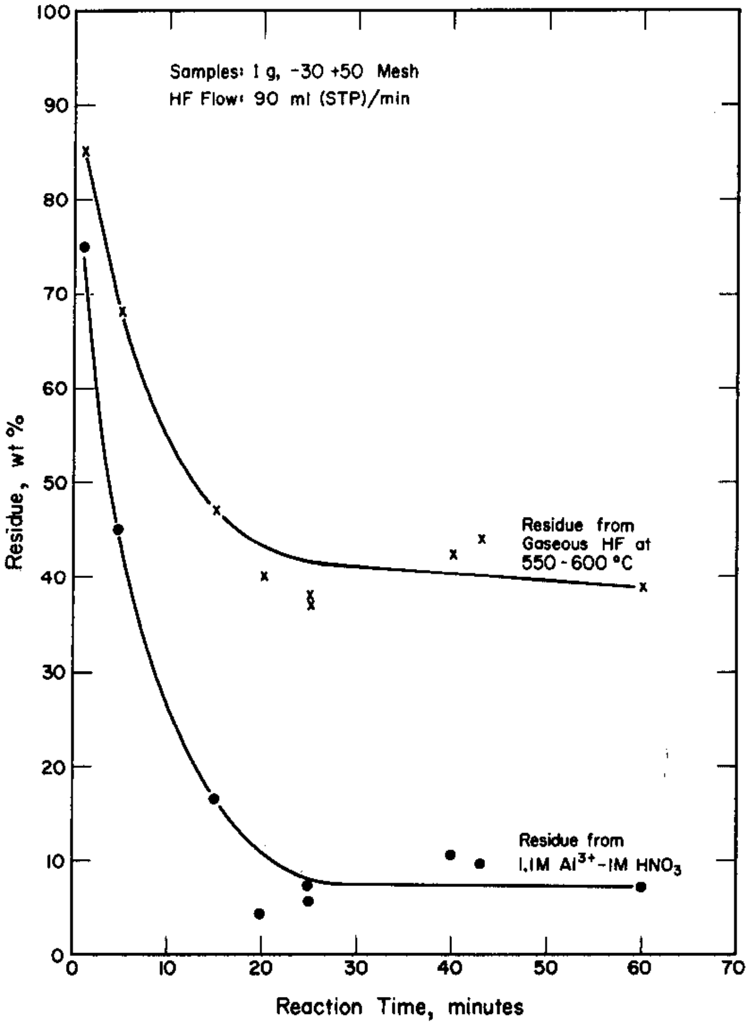

FIG. 7 SiO_2 VOLATILIZATION FROM ALLUVIUM AND DISSOLUTION OF RESIDUE

DISSOLVING TESTS

The optimum solution composition for dissolving the HF-treated debris was 1M Al^{3+}-1M HNO_3. Several variations in dissolver solution were tested, as shown in Table III. Test samples were refluxed for 2 hours. With solutions containing less than 1M Al^{3+}, the amount of debris dissolved decreased significantly. In each test shown in Table III the samples had been treated with an excess of HF in the larger reaction chamber; subsequent treatment of the insoluble residues indicated that 90 to 95% dissolution was the maximum that could be achieved. Analysis of the insoluble residues showed SiO_2, plus traces of Fe and Al.

TABLE III

Effect of Solution Concentration on Residue Dissolution

Dissolvent/Residue Ratio, ml/g	Composition of Dissolvent[(a)]		HF-Treated Residue[(b)] Dissolved, %	
	Al^{3+}, M	HNO_3, M	Tuff	Alluvium
10	0	6.0	34	24
10	0.3	1.0	42	46
10	1.0	3.5	91	89
10	1.2	1.0	93	91
50	1.1	1.0	94	89

(a) HF-treated samples refluxed in dissolvent for two hours.
(b) Debris samples treated with HF at 500-600°C for one hour.

A minimum ratio of 10 ml of dissolver solution per gram of HF-treated residue was used in these tests. With lower ratios the undissolved solids were increasingly more difficult to remove from the solution. Although centrifugation aided in removing suspended solids from the more concentrated solutions, coagulation of the dissolved silica with gelatin was less effective; and the resulting feed solutions formed emulsions during solvent extraction with TBP. In tests of the 1-gram samples that had been treated with HF in the smaller reaction chamber, the large ratio of 50 ml/g was used to ensure complete dissolution of the soluble constituents of the residue.

The aluminum content of the debris was determined from special samples of HF-treated residue that were dissolved in a boiling solution of 0.4M H_3BO_3-4M HNO_3. About 95% of these residues dissolved during the one-hour treatment. No other tests were made with H_3BO_3 as a dissolvent.

PROCESS DEMONSTRATION

Following the preliminary investigations of process variables, an integrated test was made of the proposed debris treatment flowsheet (Figure 1) with the largest sample of debris that could be efficiently treated in the experimental hydrofluorination apparatus. The test procedure is detailed in Figure 8. A

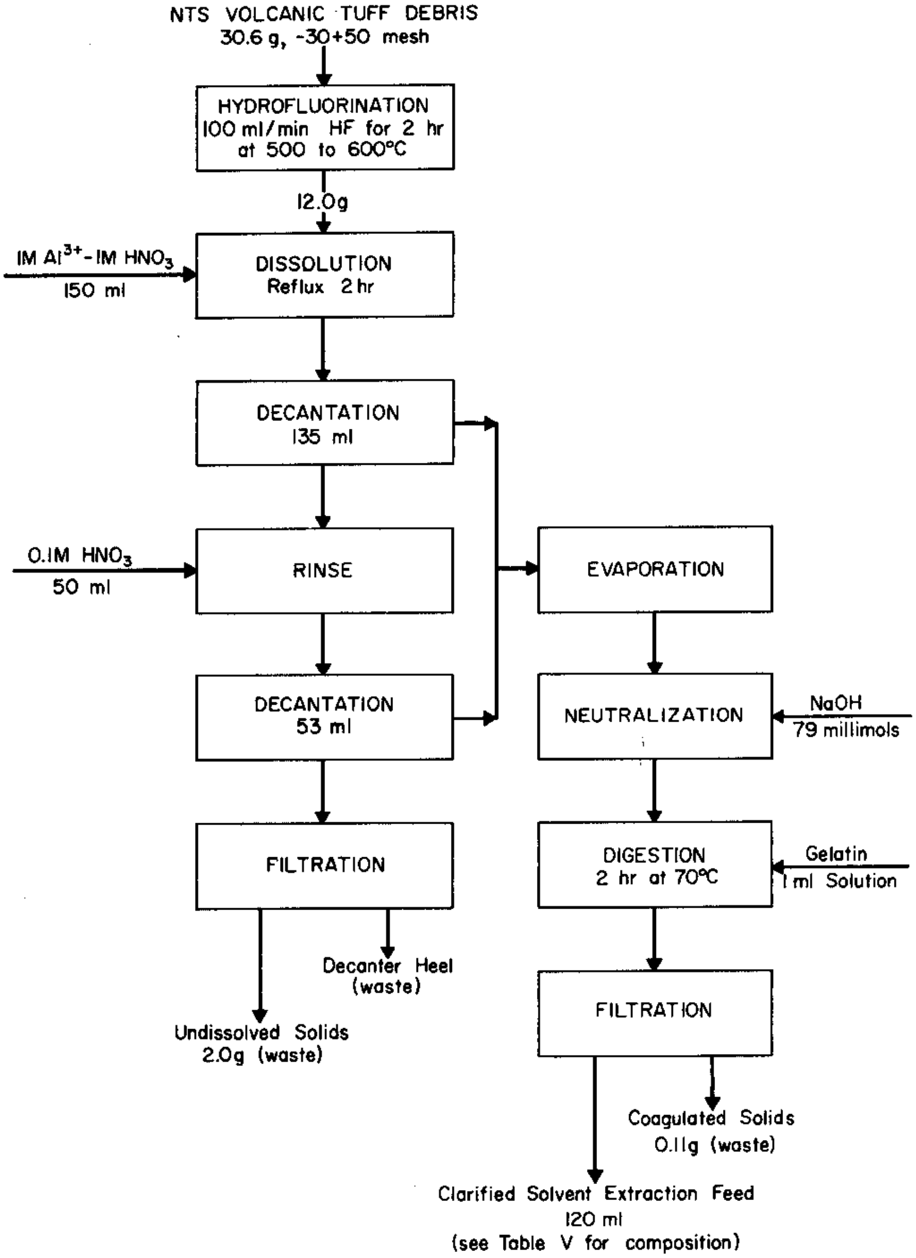

FIG. 8 PROCESS DEMONSTRATION FLOWSHEET

30.6-gram, -30+50 mesh sample of NTS tuff debris was heated at 500 to 600°C in the horizontal reaction chamber for 2 hours in a stream of anhydrous HF and N_2. The hydrofluorinated solids, amounting to 39% of the initial sample weight, were refluxed for 2 hours in 150 ml of 1.0M $Al(NO_3)_3$-1.0M HNO_3 solution. The heavy fraction of the undissolved solids in the resulting slurry settled at a rate of 1.2 inches/hr. About 135 ml of turbid, brown supernate was decanted after 24 hours. The solids were then rinsed with 0.1M HNO_3, and settled at about the same rate. The rinse solution (53 ml) was decanted; and the "heel" of solids was analyzed. This and later analyses of the decanted solution showed that 7% of the original sample containing ~11% of the actinides remained undissolved. About 10 ml of rinse solution, containing only 0.2% of the actinides, was retained by the solids in the "decanter heel." These results are shown in Table IV.

TABLE IV

Process Demonstration Test

Fraction	Weight g	Weight %	α d/m Gross	α d/m %	α d/m Cm
Tuff debris	30.6	100	2.7×10^6	100	8.3×10^4
Undissolved solids	2.0	6.5	2.7×10^5	10	7×10^3
Coagulated solids	0.11	0.4	2.0×10^4	0.8	--
Decanter heel	--	--	4×10^3	0.2	--
Clarified solvent extraction feed	--	--	2.4×10^6	89	7.2×10^4

The decanted solution and the rinse were mixed and evaporated to 99 ml to coagulate the suspended solids further. The HNO_3 concentration was next reduced to 0.10M with concentrated NaOH solution. Gelatin was added to 100 ppm, and the solution was stirred at 70°C for two hours, according to the procedure of Groh,(5) to complete the coagulation of the silica. As the solution cooled, most of the coagulated solids settled out; the solution was then filtered.

A series of tests was made to determine the suitability of the filtrate as a feed solution for solvent extraction. The solution gave a barely detectable Tyndall beam effect, indicating only a trace of suspended solids. When a sample was mixed with 30% TBP solution, no permanent emulsion formed and the organic-aqueous interface appeared clean after the emulsion had broken. The breaking time of the transient emulsion was the same (~23 seconds) as that for an emulsion of 30% TBP with a solution of $Al(NO_3)_3$-HNO_3-$NaNO_3$ with the same specific gravity (1.34). A complete analysis of the feed solution is given in Table V.

TABLE V

Composition of Clarified Feed Solution

(from 30.6g NTS Tuff Debris)

1.8M Al^{3+}
0.94M Na^+
0.036M Fe^{3+}
0.018M Mg^{2+}
0.001M Ca^{2+}

5.4M NO_3^-
0.95M F^-
0.10M HNO_3
43 ppm SiO_2

Gross α = 2.0×10^4 d/m/ml
^{239}Pu = 3.0×10^3 d/m/ml
Cm = 6×10^2 d/m/ml

To simplify analyses, the feed was adjusted to approximately 10^6 d ^{244}Cm/(min)(ml), and the solvent extraction of trivalent actinides from the feed was tested by successively contacting a single sample of the ^{244}Cm-spiked feed solution with six equal-volume portions of 30% TBP-70% n-dodecane-0.3M HNO_3. The concentration of HNO_3 in the organic phase approximated that for a continuous mixer-settler bank with a feed-to-extractant flow rate ratio of 3.(3) The results, shown in Figure 9, indicate an extraction coefficient for ^{244}Cm of 3.5, and a recovery efficiency >99% for the ^{244}Cm.

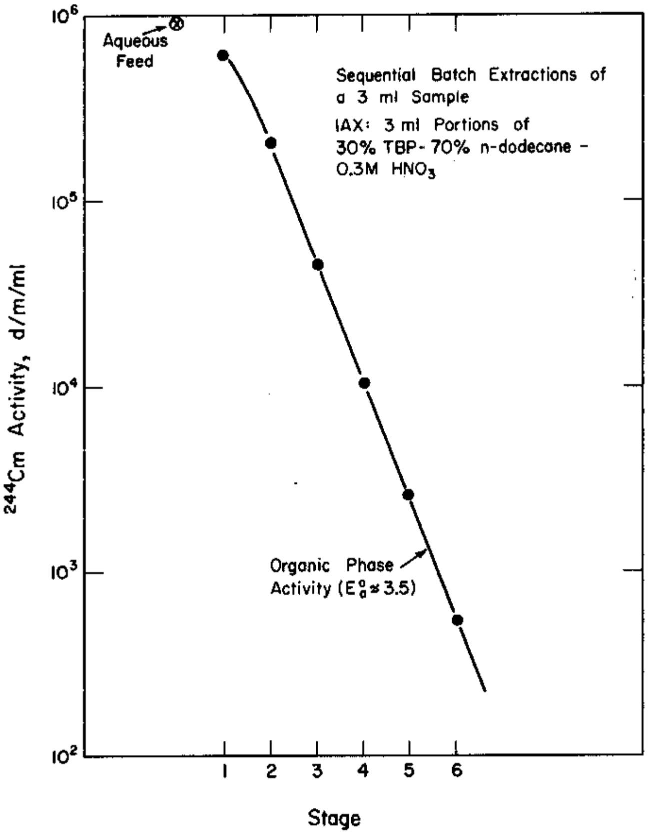

FIG. 9 ^{244}Cm EXTRACTION FROM DISSOLVED TUFF DEBRIS

Since the transplutonium elements in the solvent extraction feed are expected to be in the 3+ oxidation state, extraction tests for Cm^{3+} provide adequate indication for the recovery efficiency for these elements. If recovery of Pu and Np is also required, appropriate treatments to the solvent extraction feed solution would be necessary to divert them from the aqueous waste stream of the extraction bank and from the organic waste stream of the stripping bank.

CORROSION PROBLEMS IN PLANT-SCALE PROCESSING

The scope of this project included only the laboratory development and demonstration of a chemical process for actinide recovery from a silicate debris. Additional problems would be incurred in the scale-up to a plant that could process several tons of debris per day. One serious problem is the corrosion of equipment exposed to fluorides, both in solution and as HF gas.

Previous experience of industrial plants in handling large volumes of hot HF gas in chemical processes has demonstrated that HF can be handled with adequate protection to personnel and with reasonable equipment lifetime. For example, HF is made commercially by heating CaF_2 (fluorspar) with H_2SO_4 in vessels of cast iron, steel, brass, or alloys of nickel.(6) The Volatility Pilot Plant at ORNL uses a gaseous HF process at temperatures up to 650°C to recover uranium from zirconium- and Zircaloy-2-clad fuel elements.(7) For this service, the hydrofluorinator at ORNL is 1/4"-thick INOR-8 (71% Ni, 16% Mo, 7% Cr, 5% Fe). After 40 process runs, measurements indicated that the vessel was capable of at least 28 additional runs.

Corrosion problems in other process equipment are not as severe as in the hydrofluorination chamber because of lower operating temperatures. Also, the dissolver, feed preparation vessels, and mixer-settlers can be protected from fluoride corrosion by complexing the fluoride ion with excess aluminum. Under these conditions stainless steel is a satisfactory material of construction. The system of recovering and recycling excess HF from the hydrofluorinator should be a combination of materials, compatible with the temperature of the gas. INOR-8 or "Monel"* would probably be required for the inlet piping, the tubes in the first cooler, and the bottom of the HF recovery still. Less expensive materials, such as iron, copper, or their alloys, could be used(8) for the secondary and subsequent coolers in the waste gas line, the condenser for the recovery still, and the HF dryer.

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