**DIBUTYL CARBITOL SOLVENT
EXTRACTION OF POLONIUM-210
FROM NITRIC ACID SOLUTIONS
OF IRRADIATED BISMUTH**

BY

W. W. SCHULZ AND G. L. RICHARDSON

FEBRUARY 1968

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Chemical Development Section
Chemistry Department

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ABSTRACT

A continuous countercurrent solvent extraction process utilizing dibutyl carbitol as the extractant has been developed for separating ^{210}Po from large amounts of associated bismuth. Both laboratory and pilot plant data demonstrate the process is a suitable headend step in recovery of kilogram quantities of ^{210}Po . Typically, the extraction process recovers over 98% of the ^{210}Po , essentially free from bismuth ($\text{Bi DF} > 1500$), in a dilute HNO_3 solution suitable as a starting material for final concentration and purification steps.

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DIBUTYL CARBITOL SOLVENT EXTRACTION OF POLONIUM-210
FROM NITRIC ACID SOLUTIONS OF IRRADIATED BISMUTH

Wallace W. Schulz and Gerald L. Richardson

INTRODUCTION

Neutron irradiation of bismuth produces ^{210}Po according to the reactions

^{210}Po has a half life of about 138 days and decays by alpha emission to stable ^{206}Pb . Because of its short half life and high specific activity, ^{210}Po is a valuable isotopic power source.

Separation and purification of curie amounts of ^{210}Po have been performed for many years by the Mound Laboratory of the Monsanto Research Corporation.⁽¹⁾ The scheme used at the Mound Laboratory to separate ^{210}Po from irradiated bismuth metal involves a series of deposition and redissolution steps in which the ^{210}Po is concentrated and purified by spontaneous deposition on unirradiated bismuth powder.

This paper describes a new continuous countercurrent solvent extraction process developed as an alternative way of separating ^{210}Po from large amounts of associated bismuth. This solvent extraction process employs dibutyl carbitol [bis(2-butoxyethyl)ether] as the extractant.

SUMMARY AND CONCLUSIONS

A dibutyl carbitol (DBC) solvent extraction process for recovery and purification of ^{210}Po from HNO_3 solutions of irradiated bismuth metal is described. The process is an efficient, high capacity processing technique suitable as a headend step in recovery of kilogram quantities of ^{210}Po for subsequent uses in isotopic power sources.

The separation scheme involves selective countercurrent extraction of polonium from an aqueous $\text{HNO}_3\text{-Bi}(\text{NO}_3)_3$ feed solution containing about 4 Ci per liter of ^{210}Po into approximately a double volume portion of DBC. The resulting organic extract is scrubbed with 3M HNO_3 to provide further decontamination from bismuth. Polonium is then stripped into a 0.2M HNO_3 solution. The resulting aqueous solution is considered a suitable starting material for final concentration and purification of the ^{210}Po . Laboratory and pilot plant tests demonstrate overall bismuth decontamination factors to be typically 1500 or higher.

PROCESS DESCRIPTION

FUEL DISSOLUTION

The bismuth target elements currently irradiated in Hanford reactors are 6 in. long, 1.34 in. in diameter, and weigh 3.01 lb. They are clad in an aluminum can with a 0.035 in. wall thickness. The bismuth is irradiated to yield about 6 Ci of ^{210}Po per lb of bismuth (2.5 g of ^{210}Po per ton of bismuth).

The aluminum cans are removed by dissolution in a NaOH-NaNO_3 solution in accordance with well established techniques for decladding irradiated reactor fuel elements.⁽²⁾ The bismuth is then dissolved in boiling dilute HNO_3 to prepare extraction column feed stock (IAF solution). A satisfactory dissolution procedure is to start the dissolution reaction in a minimum volume of 4 to 6M HNO_3 and then add concentrated HNO_3 periodically over a 1 to 2-hr period. A chemical flowsheet for the decladding and dissolution operations is given in Figure 1.

SOLVENT EXTRACTION

A detailed chemical flowsheet for the DBC extraction separation of ^{210}Po from bismuth in the IAF solution is shown in Figure 2. Principal features of the extraction process are:

FIGURE 1. Dissolution of Aluminum-Clad Bismuth Elements: Process Flowsheet

FIGURE 2. Dibutyl Carbitol Extraction of ²¹⁰Po: Process Flowsheet

- ^{210}Po is preferentially (>98%) extracted by the DBC solvent in the extraction column. About 2 to 8% of the bismuth is also extracted.
- Most of the extracted bismuth is removed from the DBC phase by contacting it with a small volume of 3M HNO_3 in the scrub column. The aqueous raffinate from the scrub column is routed to the extraction column to recover the small amounts of ^{210}Po which are also scrubbed from the organic phase.
- A dilute HNO_3 solution is used in the strip column to strip the purified ^{210}Po from the organic phase. The resulting aqueous solution is considered a suitable starting material for final concentration and purification of the ^{210}Po by chemical or electrolytic deposition techniques.
- The process provides for recovery of over 98% of the ^{210}Po with an overall bismuth decontamination factor of greater than 1500.

Successful operation of the extraction process requires careful control of the HNO_3 concentration in the various aqueous and organic streams. Of particular concern is the HNO_3 concentration in the extraction column since $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ will begin to precipitate if the HNO_3 concentration falls below about 0.8M.⁽³⁾ The required control of HNO_3 concentration in the extraction column is achieved by proper adjustment of flow ratios and also by adjusting the DBC to about 1.6M HNO_3 before introducing it into the process. Control of the HNO_3 concentration in the scrub and strip columns is provided by selection of flow ratios and scrub and strip solution acidities.

Equilibrium DBC extraction of polonium from $\text{HNO}_3\text{-Bi}(\text{NO}_3)_3$ solutions is established more rapidly at 50 °C than at 25 °C. The extraction column is operated at 50 °C, therefore, to ensure both the reproducible extraction behavior and the transfer kinetics commensurate with phase residence times encountered

in conventional pulse or packed column equipment. Increase in temperature depresses equilibrium ^{210}Po distribution coefficients. To overcome this effect, a large flow of solvent is required in the extraction column. Conversely, the effect of increased temperature in lowering ^{210}Po distribution coefficients is effectively employed in the strip column to aid removal of the polonium from the organic phase.

Finally, sulfamic acid is added to the extraction column feed stock and to the scrub HNO_3 solution to react with and destroy any nitrite ion or HONO which might be present. Degradation of the DBC by reaction with HNO_3 is catalyzed by nitrite ion.

PROCESS CHEMISTRY CONSIDERATIONS

Polonium is presumed to exist in the +4 oxidation state in the dilute HNO_3 solutions used in the DBC extraction process since this is the most stable oxidation state of polonium in aqueous solution.⁽⁴⁾ Some evidence suggests that anionic nitrate complexes such as $\text{Po}(\text{NO}_3)_5^-$ and $\text{Po}(\text{NO}_3)_6^{2-}$ exist in concentrated ($>6\text{M}$) HNO_3 solutions.^(4,5)

Extraction of polonium from HNO_3 solutions by organic solvents has not been studied extensively although important contributions have been made by Matsuura and coworkers,^(6,7) by Cairo,⁽⁵⁾ and by Donnan and Zamith.⁽⁸⁾ Respectively, these workers studied extraction of polonium by methylisobutylketone, diisopropylketone, and various ethers and alcohols. The most recent studies are those of Sheppard^(9,10) who surveyed extraction of both polonium and bismuth from HNO_3 solutions by several phosphate esters and long chain amines as well as by various oxygenated solvents. The best polonium-bismuth separations were obtained with the oxygenated solvents.

Sheppard's results were instrumental in the choice of DBC as the extractant to be used in laboratory and pilot plant

development of a solvent extraction process for recovery and purification of kilogram amounts of ^{210}Po . For application in such a process, DBC has the desirable qualities of a high flash point, of being readily available on a commercial scale, and of acceptably separating ^{210}Po from bismuth. Previous plant scale use of DBC in solvent extraction schemes has included the British Butex process^(11,12) for separation of uranium and plutonium from fission products and, in the United States, for recovery of ^{235}U from various waste solutions produced in final processing of enriched uranium solutions.⁽¹³⁾

Many of the properties and reactions of DBC are fairly well known because of the early plant applications. A particularly important and undesirable property of DBC is its reaction with moderately concentrated HNO_3 , sometimes with explosive violence. Reaction of DBC with HNO_3 leads ultimately to CO_2 and water. Intermediate oxidation products include mono-n-butyl cellosolve, mono-n-butyl carbitol, and oxalic and butyric acids.⁽¹⁴⁾ The extent of the degradation reaction depends on the HNO_3 concentration and temperature. Degradation of DBC by HNO_3 is catalyzed by HONO and nitrite ion. The importance of nitrite catalysis was first established by Susano⁽¹⁴⁾ who found that the degradation reaction is not initiated in the absence of HONO or nitrite ion. Anticipating results discussed in detail later, our work has shown that a first step in the degradation reaction appears to be formation of an organic nitrite compound which interferes strongly with extraction of polonium.

EXPERIMENTAL AND RESULTS

MATERIALS

Unirradiated and unclad bismuth fuel elements were used in metal dissolution studies and in preparing feed for cold

BISMUTH DISSOLUTION STUDIES

Laboratory Tests

Laboratory dissolution tests were made to establish optimum dissolution conditions in an existing pilot plant dissolver.⁽¹⁷⁾ The tests included both instantaneous dissolution studies with wafers cut from a fuel element, and complete dissolution of one-half of a fuel element.

The results of the instantaneous tests are presented in Table II and Figures 3 and 4. (The data points are averages of at least 2 determinations agreeing within $\pm 10\%$). The data were obtained by inserting bismuth wafers into boiling HNO_3 solutions and measuring the weight loss as a function of dissolution time. Several of the acid solutions also contained either NaNO_3 or $\text{Al}(\text{NO}_3)_3$ to serve in independently determining the effect of nitrate ion on dissolution.

In the complete dissolution test, one-half of a fuel element was suspended in a reflux dissolver initially containing 500 ml of boiling 4M HNO_3 . Nitric acid was added in increments every 10 to 20 min to maintain the acidity at about $3 \pm 1\text{M}$ HNO_3 . The dimensions of the element were measured at these times and sample aliquots were withdrawn for analysis. The results of this test are shown in Table III. About 10% of the bismuth was undissolved at the end of the final dissolution period. The average HNO_3 consumption was 4 moles per mole of bismuth dissolved.

Pilot Plant Tests

Dissolution runs in the pilot plant dissolver confirmed the laboratory results. A summary of the pilot plant data is presented in Table IV.

FIGURE 4. Effect of NaNO_3 on Bismuth Dissolution

TABLE III. Complete Dissolution Test

Sample No.	Dissolution Time, min	<u>M HNO₃</u>		Final Bi M	Dissolution Rate, mg/min cm ²	Penetration Rate, mil/hr	Final Boiling Temp., °C
		<u>Start</u>	<u>End</u>				
1	12	4.0	1.90	0.62	55	130	-
2	21	3.35	1.65	0.97	27	64	104
3	16	3.77	1.94	1.30	43	103	105
4	15	3.82	2.44	1.45	54	129	106
5	14	3.94	2.78	1.59	58	140	105
6	14	4.09	3.02	1.73	61	146	108
7	16	4.21	3.05	1.81	66	158	107
8	19	4.11	3.19	1.90	66	160	-
9	25	4.17	2.97	2.02	64	153	-
10	30	3.54	3.0	2.35	54	131	-

TABLE IV. Pilot Plant Bismuth Dissolution Studies

Run No.	lbs Bi	<u>M HNO₃</u>		Avg	Acid Addition Time, hrs	Dissolution Time, hrs	% Dissolved	Final Bi, M	Moles Acid Used per mole Bi dissolved	Average Penetration Rate mil/hr
		<u>Start</u>	<u>End</u>							
1	150	4	3.2	3.2	3.3	4.0	96	1.93	3.6	130
2	288	3.9	3.3	3.4	2.6	4.1	>99	1.92	3.3	163
3	283	6.1	2.3 ^(b)	3.2	1.7	4.9	99	1.74	(3.2)	120 ^(c)
4	286	12.2	1.4 ^(b)	(3.8)	0.7	5.5	90	1.66	(3.7)	80
(a)	27	8.1	(3.0)	(3.9)	(0)	2.5	100	(1.4)	-	>90

(a) Heel from Run 4.

(b) Partially neutralized by overflow of NaOH from off-gas scrubber.

(c) Low rate due to low temperature during first 2.5 hours of the run and to partial acid neutralization during the final period of the run (see note b).

FIGURE 5. Solubility of $\text{Bi}(\text{NO}_3)_3$ in HNO_3 at 20°C

liter of ^{210}Po . The transfer of HNO_3 occurring in these and most other extraction contacts necessitated analysis of each aqueous phase for HNO_3 content. ^{210}Po in aqueous and DBC phases obtained in these and all other extraction contacts was determined by direct alpha counting of aliquots. Special pains were taken to control temperature during drying of the mounts to prevent volatilization of polonium.

The effects of temperature and aqueous phase composition on equilibrium DBC extraction of ^{210}Po from $\text{HNO}_3\text{-Bi}(\text{NO}_3)_3$ solution are well illustrated by the data plotted in Figure 6. Increased temperature depresses ^{210}Po extraction in all cases, indicating perhaps an enthalpy effect on the extraction reaction. Maximum extraction of polonium from $1\text{M Bi}(\text{NO}_3)_3$ solution occurs at about 2.6M HNO_3 while, at low $\text{Bi}(\text{NO}_3)_3$ concentration, the maximum distribution ratio is at about 4M HNO_3 . The occurrence of maximum distribution ratios at about these same HNO_3 concentrations was noted previously by Sheppard.⁽⁹⁾ The position of the maximum polonium E_a^0 appears to depend only on the aqueous phase composition and not on temperature. The 25°C distribution data shown in Figure 6 are in excellent agreement with those determined previously by Sheppard⁽⁹⁾ at a polonium concentration about 10^3 to 10^4 times lower than the concentration used in this study.

Dibutyl carbitol extraction behavior of polonium(IV) from HNO_3 solutions is compared, in Figure 7, with that of certain other quadrivalent metal ions. The data shown for the actinide elements are those reported by McKay and co-workers.⁽¹⁸⁾ The occurrence of a maximum distribution ratio for polonium is an obvious difference. According to Sheppard,⁽¹⁰⁾ the occurrence of the maximum E_a^0 suggests that the charge on the polonium(IV) nitrate complex is zero near

$4M$ HNO_3 . It is tempting, therefore, to ascribe the decrease in polonium extraction above $4M$ HNO_3 to the formation of anionic nitrate complexes. Surprisingly, however, $Pu(IV)$ and $Np(IV)$ extraction increases monotonically as a function of HNO_3 concentration even at acid concentrations where these actinides are known to form hexanitrate complexes. (19)

Non-Equilibrium Polonium Extraction. Evidence

obtained at several points in this study indicate that the equilibrium polonium specie(s) in aqueous HNO_3 - $Bi(NO_3)_3$ solutions is established only slowly at $25^\circ C$. Typical data illustrating this point are listed in Table V. These distribution data indicate three days or more at $25^\circ C$ are required to establish the equilibrium species. Slow establishment of polonium equilibrium species in HNO_3 solutions at $25^\circ C$ has also been reported by Matsuura and coworkers, (7) but at

FIGURE 7. DBC Extraction of Polonium and Quadrivalent Actinides from HNO_3 Solutions

lower polonium and HNO_3 concentrations than used in this work. What may be involved is breaking and reestablishment of oxygen to polonium bonds in a dimeric or polymeric nitrate species.

The polonium distribution data plotted in Figure 8 further demonstrate that the equilibrium polonium species is established slowly at $25^\circ C$. Both sets of data represent DBC extraction of ^{210}Po (30 min contact at $25^\circ C$) from

FIGURE 8. Comparison of Equilibrium and Nonequilibrium Extraction of ^{210}Po at 25 °C

Finally, in one experiment, a piece of irradiated bismuth metal was dissolved in boiling 7.55M HNO_3 to yield directly without dilution a solution of the composition 2.64M HNO_3 -1.23M $\text{Bi}(\text{NO}_3)_3$. This solution was cooled to 25 °C and a portion was contacted (30 min, 25 °C, A/O = 0.425) within 1 to 2 hrs with DBC previously adjusted to 1.6M HNO_3 . The ^{210}Po E_a^0 was 5.64; the expected (Figure 6) E_a^0 for extraction of the equilibrium polonium species was 6.1. Thus this experiment gave further proof of the effect of increased temperature in hastening attainment of polonium equilibrium.

Effects of Contact Time on Polonium Extraction. Polonium extracts into DBC from 1AFS solution (2.64 M HNO_3 -1.23 $\text{Bi}(\text{NO}_3)_3$ - 3 to 4 Ci/l ^{210}Po) about as fast at 25 °C as at 50 °C provided the equilibrium polonium species in the 1AFS

FIGURE 9. Effects of Contact Time on DBC Extraction of Polonium from HNO_3 - $\text{Bi}(\text{NO}_3)_3$ Solutions

Results presented in the next two sections amply demonstrate the utility of the 50 °C extraction column flowsheet. Operation of the extraction column at 50 °C rather than at 25 °C, however, does have two potential disadvantages. To compensate for the lower polonium distribution ratios at 50 °C than at 25 °C, a greater organic-to-aqueous flow ratio is required to provide the desired recovery of polonium. Secondly, the chances of nitrite-catalyzed HNO_3 degradation of the DBC are greater at 50 °C, as explained later in this report, than at 25 °C.

The slow rate of attainment of equilibrium polonium species at 25 °C, and the consequences thereof delineated earlier, are naturally a deterrent to operation of the extraction column at 25 °C. A scheme to permit operation at 25 °C may be simply to digest all entering aqueous polonium streams for an hour or two at 50 °C before introduction into the extraction column. This concept was not tested in the mixer-settler runs made in this study. It may be feasible, however, in view of the now known effects of temperature on establishment of equilibrium polonium species.

Bismuth and HNO_3 Extraction

Distribution of bismuth and HNO_3 between DBC and aqueous solutions of the composition 0.5 or 1M $\text{Bi}(\text{NO}_3)_3$ -1 to 9M HNO_3 was measured at both 25 and 50 °C. One portion of DBC was contacted five times at both temperatures with fresh portions of each $\text{Bi}(\text{NO}_3)_3$ - HNO_3 solution. Concentrations of bismuth and HNO_3 in the aqueous and organic phases from the fifth contact, which occurred without volume change, were measured. This technique obviated the large volume changes which occur when DBC is contacted with an aqueous HNO_3 solution, and permitted determination of distribution ratios at essentially constant aqueous phase bismuth concentration. In this latter connection, the volume occupied by HNO_3 is about 31 ml per mole of

FIGURE 11. DBC Extraction of Bismuth
from HNO_3 -1M $\text{Bi}(\text{NO}_3)_3$ Solutions

Mixer-Settler Runs

Tests of the DBC extraction process with feeds containing ^{210}Po were made in a 12-stage mixer-settler. This unit was a Hanford designed version of a type developed at the Knolls Atomic Power Laboratory by Coplan and others.⁽²²⁾ Mixing and settling chambers were constructed of flurothene; pump impellers were made of type 304-L stainless steel; and weirs used to control liquid level were made of glass: ^{210}Po did not deposit spontaneously on any of these materials. The mixing and settling chambers for this work were embedded in an electrically heated sand bath to permit operation at 35 and 50 °C.

In testing the chemical flowsheet, the mixer-settler was operated with the particular feed, scrub, strip, and organic solution required until a steady state in the effluent streams was reached. Flow rates of aqueous streams were maintained by a syringe-drive system. The DBC, both with and without ^{210}Po , was metered to the mixer-settler from an aspirator bottle through a glass flowmeter. Samples of the effluent streams were taken hourly and analyzed to determine when steady state was reached. Polonium losses and bismuth decontamination factors (DF) were computed from analyses of steady state effluent streams. The organic product solutions collected under steady state conditions in the extraction and scrub column runs were used as feed solutions in the succeeding scrub and strip column runs. Except as noted later, mixer-settler runs generally were of 6 to 12 hours duration, and organic solutions containing ^{210}Po stood 16 to 24 hours at 25 °C before use in a scrub or strip column run.

Mixer-settler tests results of the DBC polonium extraction process are summarized in Table VI. The flowsheet conditions shown in Figure 2, except as noted, were used in these runs. The mixer-settler was operated in the majority of runs

and specified flowsheet limits. Overall decontamination from bismuth in these runs was also satisfactorily high. Polonium losses were slightly higher and bismuth decontamination was slightly lower in the composite extraction-scrub column runs, corresponding to the fewer extraction and scrub mixer-settler stages employed.

The large polonium loss in the scrub column part of Run 2 was puzzling at first and prompted the detailed studies of solvent degradation discussed subsequently. These studies demonstrated that the excessive polonium losses occurred as the result of a particular kind of chemical degradation of the DBC extractant. For example, the DBC solution used as feed in the scrub column run was found, by distribution ratio measurements, to be almost totally lacking in polonium extraction capacity. Also, the ultraviolet absorption spectrum of the DBC solution demonstrated the presence of organic nitrite compounds. These properties are now known to be characteristic of DBC degraded by HNO_3 solutions containing nitrite ion. The extraction column part of Run 2 was atypical in that the mixer-settler was operated only 5 to 6 hours each day for a total of 4 days. The DBC product was allowed to stand during the intervening periods in a closed container, and the mixer-settler was also allowed to stand full of aqueous feed and DBC extractant. These conditions were conducive to nitrite-catalyzed HNO_3 attack of the DBC.

Addition of sulfamic acid to feed and scrub solutions is an effective way of preventing nitrite-catalyzed HNO_3 attack of the DBC extractant without affecting either recovery or decontamination performance (Runs 3 and 5). Sulfamic acid destroys HONO rapidly and efficiently according to the reaction

steady-state was usually not obtained. The columns were usually operated in a cascade series with the solvent phase overflowing from the 1A column to the 1S column, and from the 1S column to the 1C column. Aqueous raffinate from the 1S column was continuously pumped back to the top of the 1A column to blend with the feed.

Initial feeds for the runs were prepared in the pilot plant dissolver facility.⁽¹⁷⁾ For economy, several feeds were prepared by concentration of raffinates from the 1A column and by adjustment of acidity by acid boiloff. Detailed compositions of the feed and other influent streams are presented in Table A-1 in Appendix A.

Pulse Column Run Results

1A Columns. The maximum capacity demonstrated in the 1A column, 920 gal/hr ft², was apparently near the limit obtainable with the aqueous phase continuous although considerably higher capacities appeared to be feasible with the organic phase continuous. Considerable variation observed in the instability threshold frequencies may be attributable in part to the recycle of concentrated bismuth raffinate as feed. Detailed run results are shown in Table A-2 in Appendix A.

The 1A column extraction efficiency was calculated for Runs 9 and 10 by using uranium as a stand-in for polonium. The uranium HTU's (overall raffinate-film basis)* were estimated to be 1.5 to 1.6 ft with either phase continuous. These results are in line with the excellent quality of the dispersion, which was characterized by uniform, well-dispersed 1/16-in. diameter droplets. A conservative uranium distribution ratio of 3 was used in the HTU calculation while the uranium concentration in the feed was about 0.04M.

* HTU refers to the height of a transfer unit; see Reference 23 for a discussion of transfer units, their use, and methods of calculation.

to the top. At all times, the dispersion in the 1C column had a very frothy appearance due to the wide range of drop sizes ($<1/16$ to $1/4$ in.). This type of performance is typical of coalescing systems. Large drops do not necessarily lead to poor extraction performance in such systems because of the constantly renewed surfaces produced by coalescence and redispersion.

Both bismuth and HNO_3 HTU's were used to determine the efficiency of the 1C column. The most representative values were in the range of 1.2 to 1.7 ft at a volume velocity of 550 gal/hr ft² and 1.6 to 2.6 ft at 1550 gal/hr ft².

Packed Column Studies

A series of packed column runs was made to determine the feasibility of installing the DBC process in the Hanford Redox Plant, a recently deactivated solvent extraction plant used to purify uranium and plutonium by hexone extractions in packed columns. The results are presented in Table A-3.

The runs demonstrated that stable volume velocities as high as 2000, 1360, and 1610 gal/hr ft² were obtainable in the 1A, 1S, and 1C columns, respectively, at 50 °C. Capacities were about 10% lower at 25 °C.

The quality of the dispersion was excellent in the 1A column over a volume velocity range of 500 to 2000 gal/hr ft². The 1S column had a fairly good dispersion in all but the top third of the column. The 1C column had a very coarse dispersion throughout. With the notable exception of the 1A column, the performance generally obtained with the packed columns was visually inferior to that obtained with the pulse columns. This evaluation was confirmed by bismuth and HNO_3 HTU's obtained for the 1S and 1C column. These were typically about twofold higher than the HTU's obtained in the pulse column runs described

contacted (30 min 35 °C, A/O = 1) with 3.4M HNO_3 to determine polonium extraction capacity. Results of this test are given in Table VIII.

TABLE VII. Effects on Polonium Extraction Capacity of Storing DBC- HNO_3 Solutions at 50 °C

Conditions: As described in text.

Hours DBC- HNO_3 Solution stood at 50 °C	Organic Concentration		Po Extraction by Degraded DBC Po, E_a^o
	Initial M	Final M	
0	1.64	1.64	2.92
3	1.64	1.64	2.81
6	1.64	1.63	2.34
10	1.64	1.60	2.19
24	1.64	1.52	0.0860
48	1.64	1.43	0.0597
96	0.5	0.37	0.314
96	1.0	0.75	0.206
96	1.6	1.11	0.151
96	2.0	1.40	0.184

TABLE VIII. Effects on Polonium Extraction Capacity of Storing A DBC- HNO_3 Solution at 25 °C

Conditions: As described in text.

Hours DBC Solution Stood At 25 °C	Polonium Extraction Capacity Po, E_a^o
1.7	2.46
24.7	3.92
48.7	2.87
72.7	3.67
144.7	2.87
366.	2.92

TABLE IX. Degradation of DBC by $\text{HNO}_3\text{-NO}_2^-$ Solutions

Conditions: DBC stirred for time indicated at 50 °C with equal volume of indicated aqueous solution. Resulting organic phase cooled to 25 °C, washed with an equal volume of water, and adjusted to 1.6M HNO_3 by addition of 15.6M HNO_3 . The resulting organic solution was then contacted (10 min, 50 °C, A/O = 0.425) with IAFS solution.

NaNO_2 M	Aqueous Phase Composition (a)				Time at 50 °C hrs	Polonium Extraction Capacity of Degraded DBC Po E_a^0
	Sulfamic Acid M	Hydrazine M	$\text{Bi}(\text{NO}_3)_3$ M	^{210}Po Ci/l		
0.0	0.0	0.0	0.0	0.0	48	1.87
0.005	0.0	0.0	0.0	0.0	48	1.91
0.01	0.0	0.0	0.0	0.0	48	2.00
0.015	0.0	0.0	0.0	0.0	48	0.0419
0.020	0.0	0.0	0.0	0.0	48	0.0408
0.025	0.0	0.0	0.0	0.0	48	0.0263
0.05	0.0	0.0	0.0	0.0	6	0.0184
0.05	0.0	0.0	0.0	0.0	17	0.0344
0.05	0.0	0.0	0.0	0.0	48	0.0170
0.10	0.0	0.0	0.0	0.0	48	0.0157
0.0	0.0	0.0	1.62	0.54	48	0.0160
0.0	0.0	0.0	1.62	6.0	24	0.207
0.025	0.05	0.0	0.0	0.0	48	1.49
0.025	0.0	0.025	0.0	0.0	48	1.55
0.025	0.0	0.05	0.0	0.0	48	1.74
0.05	0.1	0.0	0.0	0.0	17	1.69
0.0	0.1	0.0	1.62	0.54	48	1.63
0.0	0.05	0.0	1.62	6.0	24	1.62
0.0	0.10	0.0	1.62	6.0	24	1.74
0.0	0.0	0.1	1.62	6.0	24	1.24

(a) All solutions also contain 2.6 moles per liter of HNO_3 .

Nitrite is known to be one of the radiolysis products of aqueous polonium nitrate solutions.⁽²⁵⁾ Radiolytically-generated nitrite presumably brings about the solvent degradation which occurs when DBC is contacted at 50 °C with HNO₃ solutions containing ²¹⁰Po. British workers,⁽¹¹⁾ in their investigation of the reaction between DBC and HNO₃, noted that beta and gamma radiation triggers off a reaction indistinguishable from the thermal reaction.

Precipitation of Solids from Degraded DBC Solutions

Black solids were precipitated from 1AP solutions produced in the various mixer-settler runs when such DBC solutions were allowed to stand for about two weeks in closed containers. A portion of these solids, isolated, washed with water and acetone, and air-dried, were found to contain 69.0 wt% bismuth and considerable amounts of ²¹⁰Po.

The identity of the black solids has not been established. Their x-ray powder pattern does not correspond to any of those described in the American Society for Testing Materials (ASTM) card file, nor are these solids indicated by differential thermal analysis to be BiONO₃·H₂O. It seems likely, however, that they are some hydrolysis product precipitated when HNO₃ in the DBC solution is destroyed. The black color presumably arises from the color centers produced by the intense alpha radiation from the ²¹⁰Po present.

White solids containing 64.4 wt% bismuth and having the same (Table B-1, Appendix B) x-ray powder diffraction pattern as the black solids were prepared in the absence of polonium by the following procedure. As-received DBC was adjusted to 1.6M HNO₃ by addition of 15.6M HNO₃ and then contacted (10 min, 50 °C, A/O = 0.425) with synthetic (no ²¹⁰Po) 1AFS solution. The resulting organic solution was held (in a pot open to the air) at 50 °C for 100 hours without precipitation of solids.

TABLE XII. *Washing of Degraded DBC with HNO_3 - KMnO_4 Solutions*

Conditions: DBC from sources indicated were contacted 60 min at 25 °C with an equal volume of 2M HNO_3 -0.0 to 0.2M KMnO_4 solution. Without phase separation, the aqueous phase was made 0.2M oxalic acid and phases were mixed 10 min at 50 °C. Resulting organic solution was washed twice with water (10 min, 25 °C, A/O = 1), adjusted to 1.6M HNO_3 , and contacted (10 min, 50 °C, A/O = 1/2.35) with 1AFS solution.

<u>Organic Code (a)</u>	<u>KMnO_4 M</u>	<u>Polonium, E_a^0</u>
A ^(b)	-	1.74
B ^(b)	-	0.134
B	0.1	1.52
B	0.2	1.53
C ^(b)	-	0.238
C	0.2	1.34
D	0.0	0.0238
D	0.05	0.0666
D	0.10	0.035
D	0.15	0.366
D	0.20	1.54

-
- (a) A As-received DBC
 B Degraded DBC from mixer-settler Run 2, Table VI
 C As-received DBC containing 1 vol% octyl nitrite.
 D Chemically degraded (48 hr contact at 50 °C with equal volume of 2.6M HNO_3 -0.1M NaNO_2) DBC

(b) Not washed.

Manganese dioxide, which precipitates when degraded DBC is contacted with a HNO_3 - KMnO_4 solution, accumulates at the organic-aqueous interface and makes phase separation difficult. A convenient way to circumvent this problem is to add oxalic acid to the aqueous phase before attempting phase separation. The oxalic acid reacts with, and dissolves, the MnO_2 without negating the beneficial effects of the acid KMnO_4 wash on polonium extraction capacity.

Concentration and Acid Boiloff Studies

Qualitative studies showed that HNO_3 could readily be removed from dissolver product and extraction column aqueous raffinate solutions by solution boildown. Typical results of these studies are presented in Figure 13. In the experiment illustrated, the HNO_3/Bi mole ratio was reduced from 1.6 to 0.87 by concentration to the point where bismuth crystals began to form in the boiling solution [about 4M $\text{Bi}(\text{NO}_3)_3$]. Approximate relationships between bismuth concentration and the boiling and freezing (or crystallization) points of the resulting solution are shown in Figure 14.

FIGURE 13. HNO_3 Concentrations Resulting from Boil-down of $\text{Bi}(\text{NO}_3)_3$ - HNO_3 Solutions

FIGURE 14. Approximate Boiling and Freezing Points of $\text{Bi}(\text{NO}_3)_3$ - HNO_3 Solutions

irradiation of the bismuth and become troublesome gamma and beta emitters in the bismuth during refabrication and reactor charging operations in the following cycle.

Precipitation of the bismuth from the raffinate as $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ not only provides a convenient starting material for preparation of Bi_2O_3 , but also provides a process step to achieve partial decontamination of the bismuth from metallic impurities. Determination of the extent of such decontamination was the primary purpose of the precipitation studies discussed in this section.

The exact type and concentration of impurities present in the aqueous bismuth raffinate produced in plant scale application of the DBC has not been established. The composition of the synthetic LAW solution used in these studies (Table XIII) was selected to provide what is believed to be a representative spectrum of impurities and concentrations. For convenience only, molybdenum was added as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$; antimony and tantalum were added only as radioisotopes. After addition of radioisotopes, LAW solutions were allowed to stand 5 to 7 days before precipitation of bismuth.

The results in Table XIII were obtained, in each case, by adding, at about 70 °C, 4.0 ml of 13.3M formaldehyde to 10 ml of synthetic LAW solution containing the appropriate radioisotope. The resulting mixture of liquid and $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ precipitate was digested one hour at boiling temperature, cooled to 25 °C, and centrifuged. After removal of the liquid, the precipitate was washed once at 25 °C with a volume of water equal to the volume of centrifuged precipitate (about 2 ml). The wash liquid was removed, and the precipitate was dissolved in about 10 ml of 10M HNO_3 .

The washed bismuth precipitate contained only traces of iron, chromium, manganese, cobalt, and sodium. However, decontamination from silver was slight, and essentially all the tantalum and antimony followed the bismuth.

TREATMENT OF POLONIUM FRACTION

The DBC solvent extraction process described in this paper is just one part of the overall polonium production scheme. Its function is to recover the ^{210}Po and to free it from the bulk of the associated bismuth. Further purification and treatment of the separated ^{210}Po is necessary to obtain material suitable for preparation of power sources. Technology for these latter process steps has been proposed and/or developed by various other investigators^(26,28) and is reviewed only briefly here.

One process proposed for final purification of the polonium fraction utilizes technology developed at the Mound Laboratory.⁽¹⁾ In this scheme, the dilute HNO_3 product stream from the solvent extraction process is treated with HCl and formic acid to destroy nitrate ion and convert to a chloride system. Subsequently, polonium is reduced to the metal by addition of SnCl_2 , while the bulk of the bismuth remains in the aqueous phase. If further purification is required before encapsulation, the polonium metal can be dissolved in a $\text{HCl-H}_2\text{O}_2$ solution and again precipitated by reduction with SnCl_2 . Alternative processes suggested for purification of the polonium product include a second cycle of solvent extraction and electrolytic deposition of polonium metal directly from the dilute HNO_3 product solution.

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APPENDIX A

PILOT PLANT RUN DATA

TABLE A-1. Feed Stream Compositions for Pilot Plant Runs

Run No.	1AF(a)		Sulfamic Acid, M	1AX HNO ₃ , M	1SS		1SF HNO ₃ , M	1CX		1CF HNO ₃ , M
	Bi, M	HNO ₃ , M			HNO ₃ , M	Sulfamic Acid, M		HNO ₃ , M	Oxalic Acid, M	
1	1.85	3.1	0	0.94	0.1	0	1.6	0.1	0	0.01
2	1.85	3.1	0	0.94	0.1	0	---	0.1	0	---
3	1.85	3.1	0	0.09	0.1	0	2.6	0.1	0	0.36
4	1.98	2.5	0	0.59	0.94	0	2.1	0.1	0	0.25
5	1.98	2.5	0	0.01	1.1	0	2.2	0.1	0	0.32
6	---	---	-	---	---	-	---	0	0	2.5
7	1.50	3.2	0	0	1.0	0	---	0	0	1.7
8a	1.55	2.7	0	0	1.0	0	---	0	0	1.9
8b	1.50	3.2	0	0	1.0	0	---	0	0	1.6
9	1.60	1.7	0	0.04	0.21	0	1.1	-	-	---
10	1.60	1.7	0	0.04	0.21	0	1.4	-	-	---
11a & b	---	---	-	---	---	-	---	0	0	0.07
12a	1.3	2.6	0.1	1.3	---	-	---	-	-	---
12b	1.3	2.6	0.1	2.1	---	-	---	-	-	---
13a, b, c	---	---	-	---	0.75	0.05	1.9	-	-	---
14a & b	---	---	-	---	---	-	---	0	0	0.74
16	---	---	-	---	---	-	---	0	0	2.1
17	---	---	-	---	---	-	---	0	0	2.1
18	---	---	-	---	---	-	---	0	0	2.1
19	---	---	-	---	---	-	---	0	0	2.1
20a & b	---	---	-	---	---	-	---	0	0	1.7
21a	---	---	-	---	---	-	---	0	0	0.16
21b, c, d & e	---	---	-	---	---	-	---	0	0	2.2
22a, b, c	---	---	-	---	---	-	---	0.52	0.2	1.4
23a, b, c	---	---	-	---	---	-	---	0.2	0.2	1.4

24a & b Organic = low-acid DBC; Aqueous = 0.5M Na₂CO₃.

(a) Freshly dissolved bismuth feed was used in Runs 1, 2, 3, 8a, 9, and 10. All other runs used recycled bismuth (concentrated 1AW)

TABLE A-2. Pilot Plant Pulse Column Run Summaries

Cartridge: 1A = 19.4 ft of 4-in.-spaced, 23% free area nozzle plates with 3/16-in. holes.
1S = 10.2 ft of 4-in.-spaced, 10% free area nozzle plates with 1/8 -in. holes.
1C = 9.3 ft of 4-in.-spaced, 23% free area nozzle plates with 3/16-in. holes.

Temperature: Ambient. Pulse amplitude: 1-in. except where noted. See Table A-1 for feed stream compositions. Columns operated in cascade 1A→1S→1C or 1A→1C.

Run No.	Run Length, Min	Interface Position			Volume Velocity, gal/hr ft ²			A/O Flow Ratio			Amplitude x Frequency, in./min						Bi Decontamination Factor(d)			HTU _{or} , ft				Remarks
											Normal Operation			Instability Threshold						Bi		HNO ₃		
		1A	1S	1C	1A	1S	1C	1A	1S	1C	1A	1S	1C	1A	1S	Overall	1S	1C	1S	1C				
1	260	Top	Top	Bottom	810	590	450	1.4	0.76	0.33	39	26 ^(a)	80	---	33	---	37	630	23,200	1.6	---	1.7	---	Flooding test
2	100	Top	Bottom	Bottom	810	590	450	1.4	0.76	0.33	--	---	---	≥62	≥65	≥90	--	---	----	---	---	---	---	1S freq. not recorded.
3	180	Top	Top	Bottom	860	540	530	1.3	0.43	0.42	40	---	80	---	---	---	51	920	47,200	1.5	---	---	1.7	
4	190	Top	Top	Bottom	810	570	550	1.3	0.65	0.58	40	32	88	~40 ^(c)	---	---	44	3300	144,000	1.3	---	---	(2.3)	
5	140	Top	Top	Bottom	810	570	520	1.4	0.66	0.50	40	32	88	≥40 ^(c)	---	---	52	1860	96,000	1.4	---	---	<2.4	
6	220	---	---	Bottom	---	---	570	---	----	0.75	--	---	80	---	---	85	--	---	----	---	---	---	1.2	No Bi present.
7	150	Bottom	---	Bottom	800	---	580	1.4	----	0.74	96	---	70	108 ^(c)	---	75	42	---	----	---	≤1.0	---	1.4	
8a	75	Top	---	Bottom	800	---	570	1.5	----	0.76	54	---	70	59	---	---	50	---	----	---	(1.9)	---	(3.2)	Not at steady state.
8b	90	Top	---	Bottom	800	---	570	1.5	----	0.76	52	---	85	54 ^(c)	---	85	43	---	----	---	1.3	---	---	
9	130	Top	Bottom	---	890	550	---	1.7	0.65	----	40	64	---	---	≥64	---	--	---	>340,000	---	---	<2.2	---	U HTU = 1.6 ft in 1A, 1.0 ft in 1S
10	245	Bottom	Bottom	---	920	570	---	1.7	0.66	----	96	64	---	105	≥64	---	59	230	13,000	1.9	---	<1.7	---	U HTU = 1.5 ft in 1A, 1.1 ft in 1S
21a	40	---	---	Top	---	---	1860	---	----	1.0	--	---	---	---	---	36 ^(b)	--	---	----	---	---	---	---	Cyclic instability, top half.
21b	30	---	---	Top	---	---	1860	---	----	1.0	--	---	74 ^(b)	---	---	86 ^(b)	--	---	----	---	---	---	---	
21c	60	---	---	Top	---	---	1530	---	----	1.2	--	---	63 ^(b)	---	---	---	--	---	----	---	---	---	2.1	Cyclic coalescence.
21d	20	---	---	Top	---	---	1530	---	----	1.2	--	---	---	---	---	75 ^(b)	--	---	----	---	---	---	---	Flooding run.
21e	25	---	---	Top	---	---	1530	---	----	1.2	--	---	19 ^(b)	---	---	---	--	---	----	---	---	---	1.6	Cyclic coalescence.
22a	60	---	---	Top	---	---	1590	---	----	1.1	--	---	98 ^(b)	---	---	---	--	---	----	---	---	---	2.45	
22b	10	---	---	Top	---	---	1590	---	----	1.1	--	---	98 ^(b)	---	---	110 ^(b)	--	---	----	---	---	---	---	
22c	15	---	---	Bottom	---	---	1590	---	----	1.1	--	---	92 ^(b)	---	---	---	--	---	----	---	---	---	2.6	

(a) Amplitude = 0.3 in.
(b) Amplitude = 1.15 in.
(c) Recycled bismuth (concentrated 1A column raffinate) used as feed.
(d) Defined as the ratio of the grams of bismuth per minute entering with the feed to the column (or system) to the grams per minute leaving with the "product" stream.

TABLE A-3. Pilot Plant Packed Column Run Summaries

Packing = 3/4-in. stainless steel Raschig rings
Interface = Top Pulse Amplitude (when used) = 1.0 in.
See Table A-1 for feed stream composition.

Run No.	Type of Column	Run Length, Min	Temp., °C	Packed Ht., ft	Volume Velocity gal/hr-ft ²	A/O Flow Ratio	Ampl x Freq, in./min		Bi DF	HTU _{or} , ft		Remarks
							Operating	Flood		Bi	HNO ₃	
12a	1A	160	23	19	1730	0.46	0	-----	8.1	---	---	Near flood
12b	1A	150	50	19	2010	0.41	0	-----	16.	---	---	Stable (a)
13a	1S	60	20	19	1260 ± 100	0.20	0	-----	---	---	---	Flooding test
13b	1S	30	46	19	1360	0.20	0	-----	---	---	---	Stable
13c	1S	120	50	19	1130	0.17	0	-----	>570	≤2.9	---	
11a	1C	120	22	19	1460 ± 100	0.67	0	-----	---	---	---	Flooding test
11b	1C	60	22	19	1210	1.0	0	-----	---	---	5.3	
14a	1C	60	54	19	1610	1.0	0	-----	---	---	≤3.8	
14b	1C	30	54	19	1760 ± 150	1.0	0	-----	---	---	---	Flooding test
16	1C	60	25	10	810	1.6	0	-----	---	---	3.0	
17	1C	40	25	10	1070	1.4	0	-----	---	---	3.1	
18	1C	30	25	10	1490	1.2	0	-----	---	---	3.0	Near flood
19	1C	50	50	10	1490	1.2	0	-----	---	---	2.8	
20a	1C	35	25	19	1300	1.2	-	46 ± 6	---	---	---	Flooding test
20b	1C	60	25	19	1300	1.2	40	-----	---	---	3.4	
23a	1C	55	53	19	1560	1.1	0	-----	---	---	5.5	
23b	1C	60	50	19	1560	1.1	47	-----	---	---	4.7	Cycling
23c	1C	40	50	19	1560	1.1	-	52 ± 5	---	---	---	Flooding test
24a	10	--	27	19	810 ± 110	0.58	0	-----	---	---	---	Flooding test
24b	10	--	48	19	980 ± 80	0.53	0	-----	---	---	---	Flooding test

(a) Good dispersion over operating range of 500 to 2010 gal/hr ft²

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APPENDIX B

X-RAY POWDER DIFFRACTION DATA

TABLE B-1. X-Ray Powder Diffraction Data (Cu K_α Radiation)

White Solids ^(a,b)			Black Solids ^(d,e)			Bismuth Solids from Formaldehyde Treatment ^(g)		
2θ	d spacing	Intensity ^(c)	2θ	d spacing	Intensity ^(c,f)	2θ	d spacing	Intensity ^(c)
6.5	13.6	W	15.5	5.72	M-W	6.7	13.2	VS
15.5	5.73	VS	22.2	4.00	S	11.8	7.50	S
20.9	4.25	M-S	27.3	3.26	S	13.2	6.70	S
22.2	3.99	VS	31.5	2.83	S	19.8	4.47	M
26.2	3.40	W	45.3	2.00	VS	23.6	3.77	M-S
29.4	3.03	M	52.9	1.73	M-W	25.1	3.55	M-S
30.0	2.97	S	57.1	1.61	M-W	25.7	3.47	M
30.5	2.92	W	60.6	1.53	M-W	26.4	3.37	M
31.5	2.83	VS	76.6	1.24	M-W	27.2	3.28	M-S
33.4	2.68	M	78.4	1.22	M-W	27.9	3.19	M
34.0	2.64	S				28.9	3.08	M
37.2	2.42	W				30.0	2.97	M
37.9	2.38	M				31.2	2.86	M
42.6	2.12	M				33.1	2.71	M
43.4	2.08	M				33.6	2.67	M
43.9	2.06	M				35.7	2.52	M
45.1	2.01	S				42.7	2.12	M
45.6	1.99	M-S				52.7	1.74	W
47.7	1.92	M						
48.2	1.89	M						
49.0	1.86	M-S						
50.2	1.82	M						
60.8	1.52	M						

(a) White solids obtained from synthetic IAP (see p.41)

(b) Powder pattern obtained with General Electric Co., XRD-5 diffractometer

(c) Intensity Key: VS - Very strong M - Moderate
S - Strong W - Weak

(d) Black solids obtained from mixer-settler IAP (see p.41)

(e) Powder pattern obtained with Norelco x-ray diffractometer

(f) Sample exhibited severe line broadening and only the stronger lines could be measured.

(g) See p. 48 for preparation of compound.

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