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**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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DIBUTYL CARBITOL SOLVENT EXTRACTION OF POLONIUM-210
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W. W. Schulz and G. L. Richardson

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.

TABLE OF CONTENTS

ABSTRACT.	v
LIST OF FIGURES	vii
LIST OF TABLES	viii
INTRODUCTION.	1
SUMMARY AND CONCLUSIONS	1
PROCESS DESCRIPTION	2
Fuel Dissolution	2
Solvent Extraction	2
PROCESS CHEMISTRY CONSIDERATIONS.	6
EXPERIMENTAL AND RESULTS.	7
Materials	7
BISMUTH DISSOLUTION STUDIES	9
Laboratory Tests	9
Pilot Plant Tests	9
DENSITIES AND SOLUBILITIES OF $\text{Bi}(\text{NO}_3)_3\text{-HNO}_3$	14
SOLUTIONS	
SOLVENT EXTRACTION TESTS.	16
Distribution Ratio Data.	16
Bismuth and HNO_3 Extraction.	25
Mixer-Settler Runs	29
Pilot Plant Column Runs.	32
Solvent Degradation Effects.	36
Solvent Washing Techniques	42
TREATMENT OF BISMUTH FRACTION	44
Removal of Residual Polonium	44
Conceptual Scheme for Preparation	44
of Metallic Bismuth	
Concentration and Acid Boiloff Studies	45
Precipitation of Bismuth	46
TREATMENT OF POLONIUM FRACTION	49
ACKNOWLEDGEMENTS	49

REFERENCES	50
APPENDIX A. PILOT PLANT RUN DATA.	A-1
APPENDIX B. X-RAY POWDER DIFFRACTION DATA	B-1
DISTRIBUTION.	Distr-1

LIST OF FIGURES

1	Dissolution of Aluminum-Clad Bismuth Elements: Process Flowsheet	3
2	Dibutyl Carbitol Extraction of ^{210}Po : Process Flowsheet	4
3	Instantaneous Bismuth Dissolution Rates in Boiling HNO_3	10
4	Effects of NaNO_3 on Bismuth Dissolution in Boiling HNO_3	11
5	Solubility of $\text{Bi}(\text{NO}_3)_3$ in HNO_3 at 20 °C	15
6	Effects of Temperature and Aqueous Phase Composition on DBC Extraction of Polonium	18
7	DBC Extraction of Polonium and Quadrivalent Actinides from HNO_3 Solutions	19
8	Comparison of Equilibrium and Nonequilibrium Extraction of ^{210}Po at 25 °C	21
9	Effects of Contact Time on DBC Extraction of Polonium from HNO_3 - $\text{Bi}(\text{NO}_3)_3$ Solutions	23
10	Effects of Contact Time on HNO_3 Stripping of ^{210}Po from DBC Solutions	24
11	DBC Extraction of Bismuth from HNO_3 -1M $\text{Bi}(\text{NO}_3)_3$ Solutions	27
12	DBC Extraction of HNO_3 from HNO_3 and HNO_3 - $\text{Bi}(\text{NO}_3)_3$ Solutions	28
13	HNO_3 Concentrations Resulting from Boildown of $\text{Bi}(\text{NO}_3)_3$ Solutions	45
14	Approximate Boiling and Freezing Points of $\text{Bi}(\text{NO}_3)_3$ - HNO_3 Solutions	45

LIST OF TABLES

I	Radioisotopes Used in This Study	8
II	Instantaneous Bismuth Dissolution Rates in Boiling Solutions	12
III	Complete Dissolution Test	13
IV	Pilot Plant Dissolution Studies	13
V	Time and Temperature Effects on Attainment of Equilibrium Polonium Species	20
VI	Mixer-Settler Runs to Demonstrate Polonium Extraction Process	30
VII	Effects on Polonium Extraction Capacity of Heating DBC-HNO ₃ Solutions at 50 °C	37
VIII	Effects on Polonium Extraction Capacity of a DBC-HNO ₃ Solution Standing at 25 °C	37
IX	Degradation of DBC by HNO ₃ -NO ₂ ⁻ Solutions	39
X	Effect of Organic Nitrogen Compounds on DBC Extraction of Polonium	40
XI	Alkaline Washes of Degraded DBC	42
XII	Washing of Degraded DBC with HNO ₃ -KMnO ₄ Solutions	43
XIII	Precipitation of Bismuth-Decontamination Studies	48
A-1	Feed Stream Compositions for Pilot Plant Runs	A-1
A-2	Pilot Plant Pulse Column Run Summaries	A-2
A-3	Pilot Plant Packed Column Run Summaries	A-3
B-1	X-Ray Powder Diffraction Data	B-1

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 (1AF 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 1AF 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

pilot plant extraction tests. Extraction column feed stock for mixer-settler runs was prepared by HNO_3 dissolution of mechanically de-clad fuel elements which had been irradiated in Hanford reactors and then stored 2 to 11 months after discharge from the reactor.

Dibutyl carbitol from the Union Carbide Chemical Co. was used as received. This material contains about 5 vol% of an unidentified acidic impurity, but Sheppard⁽⁹⁾ found earlier that polonium and bismuth distribution ratios were not influenced by the presence of this contaminant.

Organic nitrogen compounds were added deliberately to the DBC in some experiments to test their effect on polonium extraction. Butyl and octyl nitrites were procured from Distillation Products Industries. Octyl nitrate and nitro-octane were prepared by E. C. Martin of this laboratory from procedures described in the literature.^(15,16)

Radioisotopes used in studies of the precipitation of $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ from $\text{Bi}(\text{NO}_3)_3 - \text{HNO}_3$ solutions are listed in Table I. ^{51}Cr was obtained from Oak Ridge National Laboratory ^{22}Na was procured from Abbott Laboratories and all other isotopes were obtained from New England Nuclear Corporation.

TABLE I. *Radioisotopes Used in This Study*

<u>Radioisotope</u>	<u>Chemical Form</u>
^{59}Fe	Fe(III) in HCl
^{51}Cr	Cr(III) in HCl
^{54}Mn	Mn(II) in HCl
^{60}Co	Co(II) in HCl
^{125}Sb	Sb(III) in HCl
^{110}Ag	Ag(I) in HNO_3
^{22}Na	NaCl in H_2O
^{182}Ta	Ta in KOH

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 3. *Instantaneous Bismuth Dissolution Rates in Boiling HNO_3*

FIGURE 4. Effect of NaNO_3 on Bismuth Dissolution

The pilot plant dissolution runs were normally started by covering the bismuth elements with water, heating to boiling, and adding 12.2M HNO_3 incrementally to maintain the acidity at about 3 to 4M. The addition rate was dictated partly by the rate of gas evolution and by foaming of the dissolver solutions. (The dissolver had about 20 in. of freeboard above the liquid surface, and the foam level in Run 2 reached within 1 in. of the top).

TABLE II. *Instantaneous Bismuth Dissolution Rates in Boiling Solutions*

Dissolvent Composition, M			Dissolution Rate, mg/min cm^2	Penetration Rate, mil/hr	Boiling Temp., $^{\circ}\text{C}$
HNO_3	NaNO_3	$\text{Al}(\text{NO}_3)_3$			
1	0	0	1.5	3.5	102
1(a)	0	0	0.9	2.1(a)	102
2	0	0	9.5	23	104
2(a)	0	0	16	39(a)	104
3(a)	0	0	65	160(a)	104
4	0	0	134	400	107
6	0	0	340	820	110
1	1	0	5.7	14	104
1	3	0	14	34	107
1	5	0	23	56	109
1	7	0	28	67	111
2	4	0	50	120	107
2	6	0	47	110	112
3	2	0	65	160	107
1	0	1	15	36	106
2	0	2	69	170	113

(a) *Test coupon was one-half of a fuel element (about 10-fold larger than other coupons).*

TABLE III. Complete Dissolution Test

Sample No.	Dissolution Time, min	<u>M HNO₃</u>		Final Bi <u>M</u>	Dissolution Rate, mg/min cm ²	Penetration Rate, mil/hr	Final Boiling Temp., °C
		Start	End				
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, <u>M</u>	Moles Acid Used per mole Bi dissolved	Average Penetration Rate mil/hr
		Start	End							
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
4	286	12.2	1.4 ^(b)	(3.8)	0.7	5.5	90	1.66	(3.7)	80 ^(c)
(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).

Run 4 was a departure from the standard procedure in that the total acid requirement was charged to the cold dissolver as 12.2M HNO_3 and heated slowly. The reaction began at 50 °C and became vigorous enough at 65 °C for the NO_2 fumes to overwhelm the off-gas scrubbing system. The reaction was slowed by diluting the acid with water to a nominal 11.1M and cooling it to 55 °C. After about an hour, the temperature was slowly raised to boiling without further incident. The reaction evidently was only slightly exothermic. While the heat to the dissolver was off, the dissolver temperature leveled off at 54 °C. The reaction during the other runs also was observed to subside quickly whenever the steam to the dissolver was shut off.

Excellent acid economy was achieved in these runs. An average of only 3.45 moles of HNO_3 was used per mole of bismuth dissolved, compared with the theoretical minimum of three for the overall reaction

The economy was achieved with a downdraft reflux condenser in which the off-gases were passed down through a packed condenser-absorber.

DENSITIES - SOLUBILITIES OF $\text{Bi}(\text{NO}_3)_3$ - HNO_3 SOLUTIONS

The densities of the $\text{Bi}(\text{NO}_3)_3$ solutions obtained in the dissolution studies just discussed were found to fit the equation

$$d_{25} \text{ } ^\circ\text{C} = 1.0012 + 0.3045(\text{M Bi}) + 0.03096(\text{M HNO}_3)$$

with an accuracy of $\pm 1.4\%$ over the range studied (see Tables III and IV).

The data in Tables III and IV, together with that of Rutten and Van Bemmelen⁽³⁾ were used to calculate $\text{Bi}(\text{NO}_3)_3$ solubilities in HNO_3 at 20 °C. The results are plotted in Figure 5. Solubilities are considerably higher in heated solutions, and concentrations as high as 4M Bi have been obtained in boiling solutions.

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

SOLVENT EXTRACTION TESTS

Distribution Ratio Data

The distribution ratio (E_a^0) is defined as the ratio of the concentration of the element of interest in the less dense organic phase to the concentration of the element in the more dense aqueous phase after equilibration of the two essentially immiscible liquids. Phases were contacted by mechanical stirring, and separated by either centrifugation or gravity settling. Temperatures were controlled to ± 0.5 °C during the contact period. Except where the effect of contact time was studied, a standard 10-min contact time was allowed for attainment of equilibrium at 50 °C while, at 25 °C and 35 °C, the standard contact time was 30 min. Unless otherwise indicated, equal volumes of aqueous and DBC solutions were used.

Polonium Extraction Studies

Equilibrium Distribution Data. Solutions of the composition 2 to 6M HNO_3 -1M $\text{Bi}(\text{NO}_3)_3$, each containing about 3 Ci per liter of ^{210}Po , were prepared by adding water or 15.6M HNO_3 to a LAF solution obtained by dissolving irradiated bismuth metal in HNO_3 . These solutions were allowed to stand for one week at 25 °C to ensure establishment of equilibrium polonium species. Each of the equilibrium solutions was contacted with DBC at both 25 and 50 °C at an aqueous-to-organic volume ratio of 0.425.

A DBC solution of the composition 1.6M HNO_3 -0.038M $\text{Bi}(\text{NO}_3)_3$ -1.0 Ci per liter ^{210}Po was contacted at 25, 35, and 50 °C with various dilute HNO_3 solutions to determine polonium extraction behavior at low $\text{Bi}(\text{NO}_3)_3$ concentrations. The DBC solution used in these experiments was prepared by contacting (for 10 min at 50 °C) one volume of DBC, previously adjusted to 1.6M HNO_3 by adding 15.6M HNO_3 , with 0.425 volumes of 2.6M HNO_3 -1.2M $\text{Bi}(\text{NO}_3)_3$ solution containing 2.3 Ci per

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 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 1M $\text{Bi}(\text{NO}_3)_3$ 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

FIGURE 6. Effects of Temperature and Aqueous Phase Composition on DBC Extraction of Polonium

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 - $\text{Bi}(\text{NO}_3)_3$ solutions is established only slowly at 25 °C. Typical data illustrating this point are listed in Table V. These distribution data indicate three days or more at 25 °C are required to establish the equilibrium species. Slow establishment of polonium equilibrium species in HNO_3 solutions at 25 °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 °C. Both sets of data represent DBC extraction of ^{210}Po (30 min contact at 25 °C) from

aqueous 2-6M HNO_3 -1M $\text{Bi}(\text{NO}_3)_3$ solutions containing about 3 Ci per liter of ^{210}Po . The acid bismuth solutions used in these experiments were prepared by addition of water or 15.6M HNO_3 to a 1AF solution obtained by HNO_3 dissolution of irradiated bismuth metal. The resulting solutions were allowed to stand one week at 25 °C before contact with DBC in one case while in another set of experiments the solutions were contacted with DBC within one to two hours after preparation. The shorter standing time was reflected in lower polonium extraction, particularly at the lower HNO_3 concentrations.

TABLE V. Time and Temperature Effects on Attainment of Equilibrium Polonium Species

Conditions: A solution of the composition 2.5M HNO_3 -1.23M $\text{Bi}(\text{NO}_3)_3$ -2.4 Ci/l ^{210}Po was prepared by adding HNO_3 to a 2.4M HNO_3 -1.67M $\text{Bi}(\text{NO}_3)_3$ -3.4 Ci/l ^{210}Po solution. Portions of the resulting solution were stored at both 25 and 50 °C, and, at intervals indicated, were contacted with DBC according to the conditions indicated.

Hours Stood	Extraction at 25 °C ^(a)		Extraction at 50 °C ^(a)	
	Solution Stored at 25 °C	Solution Stored at 50 °C	Solution Stored at 25 °C	
	Po E_a^0	Po E_a^0	Po E_a^0	
0.5	1.19	-	1.79	
1.0	-	5.32	-	
5.	-	5.43	-	
24.	1.92	5.06	-	
68.	3.78	-	-	
168.	6.19	-	2.06	
408.	6.15	-	-	

(a) 10 min contact at $A/O = 0.425$ with DBC previously adjusted to 1.6M HNO_3 .

The equilibrium polonium species in aqueous HNO_3 solutions is attained much more rapidly at 50 °C than at 25 °C. As is evident from the data in Table V, this is true both when the aqueous HNO_3 solution is allowed to stand at 50 °C and then contacted with DBC at 25 °C, and conversely.

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

solution is first established (Figure 9). However, when the equilibrium polonium species has not been established in the 1AFS, then polonium extracts considerably more slowly at 25 than at 50 °C. In the former case, contact time measurements provide information about the transfer rate of the equilibrium extractable polonium species. The transfer rate of this species is as fast at 25 as at 50 °C, attaining the equilibrium E_a^0 at both temperatures in 3 to 5 min of vigorous agitation. When the equilibrium polonium species have not been established in the 1AFS solution, however, contact with a DBC solution provides not only extraction of the extractable polonium species but a means of shifting equilibrium in the aqueous phase toward the formation of the equilibrium extractable species.

Transfer of polonium from the DBC phase to an aqueous HNO_3 solution is also about as fast at 35 as at 50 °C (Figure 10). Just as for transfer in the forward direction, the equilibrium distribution ratio for scrubbing or stripping is attained in 3 to 5 min of contact.

Care was taken in these contact time studies to use the same mechanical stirring setup and the same stirring speed. The aqueous-to-organic volume ratio was 0.425 in the forward transfer experiments (Figure 9) and was one in the reverse transfer experiments (Figure 10). The DBC solution used in the latter experiments was prepared by contact (10 min, 50 °C, A/O = 0.425) of a 1AFS solution which had stood one week at 25 °C.

Choice of Extraction Column Temperature. The extraction column is designed to operate at 50 °C in the chemical flow-sheet (Figure 2) presently favored for the DBC polonium recovery process. This temperature is specified to ensure reproducible polonium extraction behavior and transfer kinetics commensurate with phase residence times encountered in conventional pulse or packed column equipment.

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

FIGURE 10. Effects of Contact Time on HNO_3 Stripping of ^{210}Po from DBC 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

HNO_3 in the aqueous phase, and about 54 ml per mole of HNO_3 in the DBC phase. Nitric acid transfer is thus apparently accompanied by some transfer of water also to account for part of the change in phase volumes on extraction.

Inert bismuth in both aqueous and organic solutions was determined by spectrophotometric determination of the yellow diethyldithiocarbonate complex after extraction into isoamyl alcohol.⁽¹⁹⁾ Nitric acid in aqueous and organic solutions containing bismuth was, after addition of sodium tartrate to complex the bismuth, determined by titration with standard NaOH to a phenolphthalein end point. This latter titration gives the sum of the HNO_3 and bismuth; the HNO_3 concentration is found by subtracting twice the bismuth molarity.⁽²⁰⁾

At 25 °C, maximum extraction of bismuth into DBC from aqueous HNO_3 solutions occurs at about 4M HNO_3 (Figure 11). Extraction falls off rapidly below this acidity but decreases only slightly over the range 4 to 7M HNO_3 . Bismuth extracts less at 50 °C than at 25 °C, and, at both temperatures, extracts less than polonium. At flowsheet (Figure 2) extraction column conditions, 50 °C and 2.6M HNO_3 , the ratio of polonium and bismuth distribution ratios (separation factor) is about 80.

Experimental data for the distribution of HNO_3 between DBC and aqueous HNO_3 - $\text{Bi}(\text{NO}_3)_3$ solutions are shown as plotted points in Figure 12. The distribution data at 25 °C can be correlated fairly well by means of the empirical equation:

$$\text{HNO}_3 \text{ } E_a^0 = \text{HNO}_3 (E_a^0)_{0.0\text{M Bi}} + 0.167(\text{M Bi in equilibrium aqueous phase})$$

This equation was used to draw the full curves shown in Figure 12 for 0.0 to 1.0M $\text{Bi}(\text{NO}_3)_3$ in the aqueous phase. It was also used to estimate HNO_3 extraction behavior from 1.5 and 2.0M $\text{Bi}(\text{NO}_3)_3$ solutions. This extrapolation is shown as dashed curves in Figure 12.

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

FIGURE 12. DBC Extraction of HNO_3 from HNO_3 - $\text{Bi}(\text{NO}_3)_3$ 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

under either simple extraction, simple scrub, or simple strip column conditions. All 12 of the mixer-settler stages were used in each of these runs. In two experiments, composite extraction-scrub column runs were made in which the mixer-settler was operated at 50 °C with 7 extraction and 5 scrub stages. Aqueous solutions of the composition 2.6M HNO_3 -1.23M $\text{Bi}(\text{NO}_3)_3$ and 2.4M HNO_3 -1.67M $\text{Bi}(\text{NO}_3)_3$, each containing from 1 to 6 Ci per liter of ^{210}Po , were used as feeds in the simple extraction and composite extraction-scrub column runs, respectively. Sulfamic acid was added, in one run of each type, to the extraction column feed and also to the HNO_3 scrub solution.

TABLE VI. Mixer-Settler Runs to Demonstrate Polonium Extraction Process

Run Number:	1(a)	2(a)	3(a,c)	4(b)	5(b,c)
Feed ^{210}Po , Ci/l:	1.0	3.5	3.7	1.3	5.9
Po Loss, %					
Extraction Column:	0.49	0.46	0.61	1.4	1.3
Scrub Column:	4.0	92.	4.4		
Strip Column:	0.15		0.45	0.3	0.7
Bismuth DF					
Extraction Column:	18.	13	14	1250	
Scrub Column:	140.		100		
Strip Column:	1.5		1.2	1.2	
Overall:	3800		1700	1500	

(a) Simple extraction, scrub, and strip column runs.

(b) Composite extraction-scrub column runs.

(c) Feed and scrub contained 0.1 and 0.05 mole per liter sulfamic acid, respectively.

Polonium losses to the aqueous scrub stream were excessively high in Run 2. Otherwise, the mixer-settler runs adequately and successfully demonstrated the utility of the DBC solvent extraction process. Thus, typical ^{210}Po losses under simple extraction, scrub, and strip column conditions were about 0.5, 4, and 0.4%, respectively. These losses were well within desired

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

Also, in plant operation of the DBC extraction process, the organic solution from the extraction column would cascade or be pumped to the scrub column without appreciable delay. This situation corresponds to the conditions prevailing in the composite extraction-scrub column mixer-settler runs. These runs proceeded without any evidence of solvent degradation.

Pilot Plant Column Runs

Equipment and Procedures

The pilot plant facility consisted of three 3-in. diameter glass pulse columns with contacting sections ranging from 9 to 19 ft long. Each column also contained enlarged end sections made in 2 to 3-ft lengths of 4-in. diameter glass pipe for phase disengagement. Influent streams were introduced in these enlarged sections within about 2 in. of the contact section, and effluent phases were removed at the extreme ends of the columns. The phase interfaces were also located in the disengaging sections about 8 to 12 inches from the contact section.

Two types of stainless steel nozzle plate cartridges were used. The 1A and 1C columns contained 4-in. spaced plates with 3/16-in. diameter holes and 23% free area. The 1B column contained 4-in. spaced plate with 1/8-in. holes and 10% free area. The nozzles were indented about 0.04-in. beyond the face of the plate and were oriented pointing down. In addition, several scouting runs were made with packed columns containing 3/4-in. stainless steel Raschig rings. Detailed cartridge and packed heights are given in Tables A-2 and A-3 in Appendix A, along with the operating conditions used in each run.

Most of the runs were made at ambient temperature using an early version of the final elevated temperature flowsheet. Run times were generally long enough to approach steady state but, since the runs were of a scouting nature, rigorous proof of

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.

Acid in the 1A column was quite critically controlled to avoid bismuth subnitrate precipitation. This control was achieved by adding 1M HNO_3 to the DBC extractant. Acid-free DBC could be used safely at steady-state provided that the flow-sheet was properly designed to avoid excessive extraction of HNO_3 .

1S Column. The flooding capacity of the 1S column, using the 10% free-area cartridge, was the lowest obtained in these studies. With the aqueous phase continuous, the maximum stable capacity was only slightly greater than the highest volume velocity demonstrated (590 gal/hr ft^2 , sum of flows). Somewhat higher capacities were indicated by the frequencies attainable with the solvent phase continuous. Still higher capacities should be obtained with the same 23% free-area cartridge used in the other columns.

The primary efficiency of the 1S column was measured by the bismuth decontamination factors. These ranged from 230 to 920 (HTU's of 1.5 to 1.9 ft) with 0.1 to 0.2M HNO_3 in the scrub stream to 1900 to 3300 (HTU's of 1.3 and 1.4 ft) with 1M HNO_3 scrub. Insufficient runs were made to confirm the apparent improvement in efficiency with the higher acid scrubs.

Uranium and HNO_3 HTU's were also determined for several of the runs. Apparent uranium HTU's of 1 and 1.1 ft were obtained in conjunction with 1A column tests previously described, while HNO_3 HTU's appeared to be about the same as the bismuth values.

1C Column. The 1C column proved to be highly stable. Volume velocities as high as 1600 gal/hr ft^2 were readily obtained with the aqueous phase continuous, and higher capacities appeared to be possible. The high rate runs were often characterized by cyclic buildups of the dispersed organic phase, followed by coalescence and channeling of large organic droplets

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

earlier. Adding pulse energy lowered the 1C column HTU slightly, though not as much as might be inferred from the improvement in dispersion.

Two 1 O-column tests were also made using 5% Na_2CO_3 to scrub HNO_3 and impurities from the solvent. The capacity was about half that obtained in the other columns and was about 20% higher at 48 °C than at room temperature. A good dispersion was obtained, and scrubbing performance was apparently adequate.

Solvent Degradation Effects

Reaction of DBC with HNO_3 at 25 and 50 °C

As stated earlier, the high polonium loss noted in one of the mixer-settler scrub column runs prompted detailed studies of the effects and consequences of solvent degradation on polonium extraction capacity. In initial studies, DBC was equilibrated at 25 °C with 15.6M HNO_3 to yield an organic solution of 0.5 to 2.0M HNO_3 . Portions of the resulting organic solution were placed in tightly stoppered containers and maintained at 50 °C for periods of time ranging from 3 to 96 hours. Each organic solution was cooled at appropriate times to 25 °C, titrated for HNO_3 concentration, washed with an equal volume of water, and readjusted to 1.6M HNO_3 . The polonium extraction capacity of the resulting organic solution was measured by contact (10 min, 50 °C, A/O = 1/2.35) with 1AFS solution. Results of these experiments are tabulated in Table VII.

In similar studies, DBC was adjusted to 1.64M HNO_3 and contacted (10 min, 50 °C, A/O = 0.425) with 1AFS solution to produce an organic phase about 1.6M HNO_3 and 0.04M $\text{Bi}(\text{NO}_3)_3$ and containing about 1.0 Ci per liter of ^{210}Po . This organic solution was allowed to stand 336 hours at 25 °C. Portions of this organic phase were removed at certain selected intervals and

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^0
	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^0
1.7	2.46
24.7	3.92
48.7	2.87
72.7	3.67
144.7	2.87
366.	2.92

Little or no loss in polonium extraction capacity occurred when the DBC-HNO₃ solution was allowed to stand two weeks at 25 °C. However, some reaction occurred in DBC-HNO₃ solutions allowed to stand for 24 hours or longer at 50 °C in sealed containers which resulted in destruction of HNO₃ and loss of polonium extraction capacity. The extent of this reaction depended, as would be expected, on reaction time and initial HNO₃ concentration.

No gross destruction of DBC was disclosed by gas chromatographic and infrared analyses when DBC-HNO₃ solutions were allowed to stand at 50 °C. This finding was supported by the fact that all the water-washed, degraded DBC solutions extracted HNO₃ about as well as "as-received" material. These results thus showed that the loss in polonium extraction capacity could not be attributed simply to destruction of DBC by the HNO₃. Rather, consideration of the results of Susano⁽¹⁴⁾ on the role of nitrite ion in attack of DBC by HNO₃ suggested that nitrite ion could also be involved in some way with loss of polonium extraction capacity and led to the studies reported in the section immediately following.

Degradation of DBC by HNO₃-NaNO₂ Solutions

The polonium extraction capacity of DBC decreases markedly when it is contacted at 50 °C with aqueous HNO₃-NaNO₂ solutions (Table IX). Even in the absence of added nitrite, a similar decrease in polonium distribution ratio results when the aqueous HNO₃ solution contains 0.5 (or more) Ci per liter of ²¹⁰Po. In either case, addition of sulfamic acid or hydrazine to the aqueous phase before contact with the organic solution prevents degradation of the DBC extractant.

Peaks characteristic of nitrite compounds⁽²⁴⁾ were plainly evident in the ultraviolet absorption spectra of all the degraded (Table IX) DBC solutions. The adverse effect of nitrites

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 .

on extraction of ^{210}Po by DBC was also noted when either octyl or butyl nitrite was added to "as-received" DBC (Table X). Adding either nitrooctane or octyl nitrate, however, did not affect polonium extraction. While the reaction mechanism responsible for the deleterious effect of nitrites on polonium extraction is not known, reduction of Po(IV) to Po(II) in the organic phase may be involved. Alternatively, some aqueous-favoring complex between nitrites and Po(IV) may be formed.

TABLE X. Effect of Organic Nitrogen Compounds on DBC Extraction of Polonium

Conditions: DBC solutions containing indicated organic nitrogen compounds were adjusted to 1.6M HNO_3 by addition of 15.6M HNO_3 and then contacted (10 min, 50 °C, A/O = 0.425) with IAFS solution.

<u>Organic Nitrogen Compound</u>		<u>Po E_a^0</u>
<u>Type</u>	<u>Vol%</u>	
Butyl Nitrite	1	0.326
	5	0.104
Octyl Nitrite	1	0.238
	5	0.0749
Octyl Nitrate	1	1.72
Nitrooctane	1	1.74

Significantly, contact of the DBC extractant with aqueous HNO_3 - NaNO_2 solutions at 50 °C did not impair the capacity of the DBC to extract HNO_3 . Furthermore, gas chromatographic and infrared analyses of the degraded DBC solvents indicated little, if any, destruction of the DBC itself. The degradation conditions employed and encountered in this work were only sufficient, apparently, to produce small amounts of unidentified organic nitrite compounds which interfere with extraction of 10^{-6} to 10^{-5}M polonium. Presumably, prolonged contact of DBC at 50 °C with HNO_3 solutions containing nitrite would lead to the degree and kind of degradation observed by Susano,⁽¹⁴⁾ but such exposure is beyond that expected in operation of the polonium extraction process.

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 LAP 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) LAFS solution. The resulting organic solution was held (in a pot open to the air) at 50 °C for 100 hours without precipitation of solids.

At this point solid NaNO_2 was added to the organic solution to make it about 0.1M in nitrite. Large amounts of white solids precipitated within about 10 hours.

Solvent Washing Techniques

The used DBC extractant from the strip column will contain small amounts of polonium, bismuth, and HNO_3 . These contaminants can be removed by routine washing of the solvent with a dilute Na_2CO_3 or NaOH solution (Table XI).

However, alkaline washes do not restore the polonium extraction capacity of DBC degraded by exposure to HNO_3 - NaNO_2 solutions. For this purpose, HNO_3 - KMnO_4 washes are very effective as illustrated by the results shown in Table XII. Spectrophotometric and chromatographic analyses indicate the KMnO_4 oxidizes the organic nitrites in the degraded DBC to innocuous species without any appreciable attack on the DBC.

TABLE XI. *Alkaline Washes of Degraded DBC*

Conditions: Degraded DBC (48 hrs at 50°C with equal volume of 2.6M HNO_3 -0.1M NaNO_2) washed twice with water. Portions of resulting material washed (10 min, 25 °C, A/O = 1) with alkaline washes indicated. Finally, the washed DBC was adjusted to 1.6M HNO_3 and contacted (10 min, 50 °C, A/O = 1/2.35) with 1AFS solution to determine polonium extraction capacity.

<u>Wash Composition</u>	<u>Po Extraction Capacity</u>
	<u>E_a^{O}</u>
3% Na_2CO_3	0.0348
1M NaOH	0.0446
None (a)	0.0157

(a) Water washes only.

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.

Organic Code (a)	KMnO_4 M	Polonium, E_a^{O}
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.

TREATMENT OF BISMUTH FRACTION

Removal of Residual Polonium

Economic considerations require that, in any large scale application of the DBC solvent extraction process, the aqueous bismuth fraction (1AW stream) be processed to prepare metallic bismuth for further irradiation. For maximum polonium recovery, the processing of irradiated bismuth fuel elements is anticipated within 5 to 10 days after reactor discharge. Under these conditions the 1AW stream will contain an appreciable quantity of ^{210}Bi . This isotope has a half life of about 5 days and decays to ^{210}Po . Removal of this polonium is necessary to permit contact maintenance techniques in refabricating metallic bismuth fuel elements. Accordingly, it is proposed⁽²⁶⁾ to store the aqueous $\text{Bi}(\text{NO}_3)_3$ solution for about 60 days and then reprocess it again through the DBC extraction process to reduce the polonium concentration to a value considered satisfactory for further processing.

Conceptual Scheme for Preparation of Metallic Bismuth

One conceptual scheme⁽²⁷⁾ for preparation of metallic bismuth from 1AW solutions, after removal of residual ^{210}Po , involves concentration of the bismuth and boiloff of part of the HNO_3 . Formaldehyde is then added to the resulting solution at 80 to 90 °C to destroy residual HNO_3 and precipitate over 97% of the bismuth as $\text{BiONO}_3 \cdot \text{H}_2\text{O}$. After centrifugation and washing, the $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ is calcined at about 400 °C to yield Bi_2O_3 . Finally, metallic bismuth is obtained by reduction of the Bi_2O_3 at about 800 °C with CO.

Laboratory studies of the concentration and boiloff step, and of the formaldehyde treatment step, were performed as part of this investigation. Results of these studies are discussed in the two succeeding sections.

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

An unexpectedly vigorous denitration reaction occurred during the first attempt to concentrate aqueous raffinate produced in cold pilot plant extraction column runs. The reaction, which resulted in pressurization and foam-over of the concentrator, was caused by dissolved and entrained DBC in the aqueous raffinate. Subsequent laboratory measurements indicated the solubility of DBC in the aqueous raffinate to be 0.5 ± 0.05 vol% independent of $\text{Bi}(\text{NO}_3)_3$ and HNO_3 concentrations. Evolution of NO_2 from boiling raffinates occurred over the temperature range 110 to 114 °C, corresponding to HNO_3 concentrations of 3.5 to 4M.

In further tests, the reaction was readily controlled by carefully regulating the boilup rate, and was eliminated completely by steam-stripping the raffinate before it entered the concentrator.

In steam stripping studies, raffinate from solvent extraction runs was fed at 0.8 to 1 l/min to the top of an 8-in. diameter steam stripping tower packed with 4.5 ft of 1-in. stainless steel Raschig rings. The solution passed counter-current to steam derived from the concentrator while the boilup rate was set to keep the concentrator volume constant. Essentially complete DBC removal was indicated by the lack of a denitration reaction in the concentrator and by the absence of the typical rancid odor of DBC degradation products in the concentrator.

Precipitation of Bismuth

The aqueous $\text{Bi}(\text{NO}_3)_3$ raffinate produced in plant scale operations will contain various metal impurities. These impurities will be introduced as corrosion products and/or as contaminants in process chemical reagents. Certain isotopes of the likely impurities (e.g. ^{50}Cr , ^{58}Fe , ^{59}Co) are critical in the sense that they would undergo neutron activation during

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 1AW 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, 1AW 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 1AW 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.

TABLE XIII. *Precipitation of $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ -
Decontamination Studies*

Conditions: $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ precipitated from synthetic 1AW^(a) containing indicated radioisotopes and washed with water as described in text.

<u>Radioisotopes</u>	<u>Decontamination Factor^(b)</u>
^{59}Fe	16
^{51}Cr	26
^{54}Mn	18
^{22}Na	27
^{60}Co	30
^{110}Ag	5
^{182}Ta	1.3
^{125}Sb	1.3

(a) Composition was:

1.5M $\text{Bi}(\text{NO}_3)_3$	0.001M NaNO_3
4.0M HNO_3	0.002M $\text{Mn}(\text{NO}_3)_2$
0.01M $\text{Fe}(\text{NO}_3)_3$	0.001M $\text{Co}(\text{NO}_3)_2$
0.0024M $\text{Cr}(\text{NO}_3)_3$	0.001M AgNO_3
0.001M $\text{Ni}(\text{NO}_3)_2$	0.007M Mo

(b) $\frac{\text{Conc. Activity in 1AW Solution}}{\text{Conc. Activity in HNO}_3 \text{ Solution}} \propto \frac{\text{Conc. Bi in HNO}_3 \text{ Solution of ppt}}{\text{Conc. Bi in 1AW Solution}}$

The precipitation - denitration procedure outlined above yielded a dense, easily centrifugable cake. About 99% of the bismuth precipitated when 4 ml of 13.3M formaldehyde was added to 10 ml of the 1AW; the terminal acidity was about 0.8M. Bismuth recoveries were smaller (54 to 93%) when smaller amounts (2.5 to 3.5 ml) of the formaldehyde reagent were added.

The bismuth precipitate obtained by the formaldehyde treatment contained 66.2 wt% bismuth; $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ contains 68.5 wt% bismuth. The differential analysis thermogram of the bismuth precipitate was identical to that of Fisher Scientific Co. reagent grade bismuth subnitrate. However, the x-ray powder diffraction pattern (Table B-1) of the precipitated solid did not correspond to that given in the ASTM file for $\text{BiONO}_3 \cdot \text{H}_2\text{O}$.

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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BNWL-584

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)

A-1

BNWL-584

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
		1A	1S	1C	1A	1S	1C	1A	1S	1C	Normal Operation			Instability Threshold			1A	1S	Overall	Bi		HNO ₃		
											1A	1S	1C	1A	1S	1C				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

A-3

BNWL-584

BNWL-584

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.

B-1

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