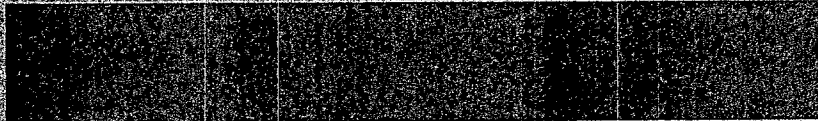


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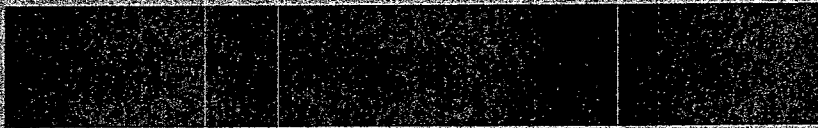
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TBP AND DBBP SOLVENT EXTRACTION  
RECOVERY AND PURIFICATION OF  $\text{Bi}(\text{NO}_3)_3$   
DECEMBER 1968



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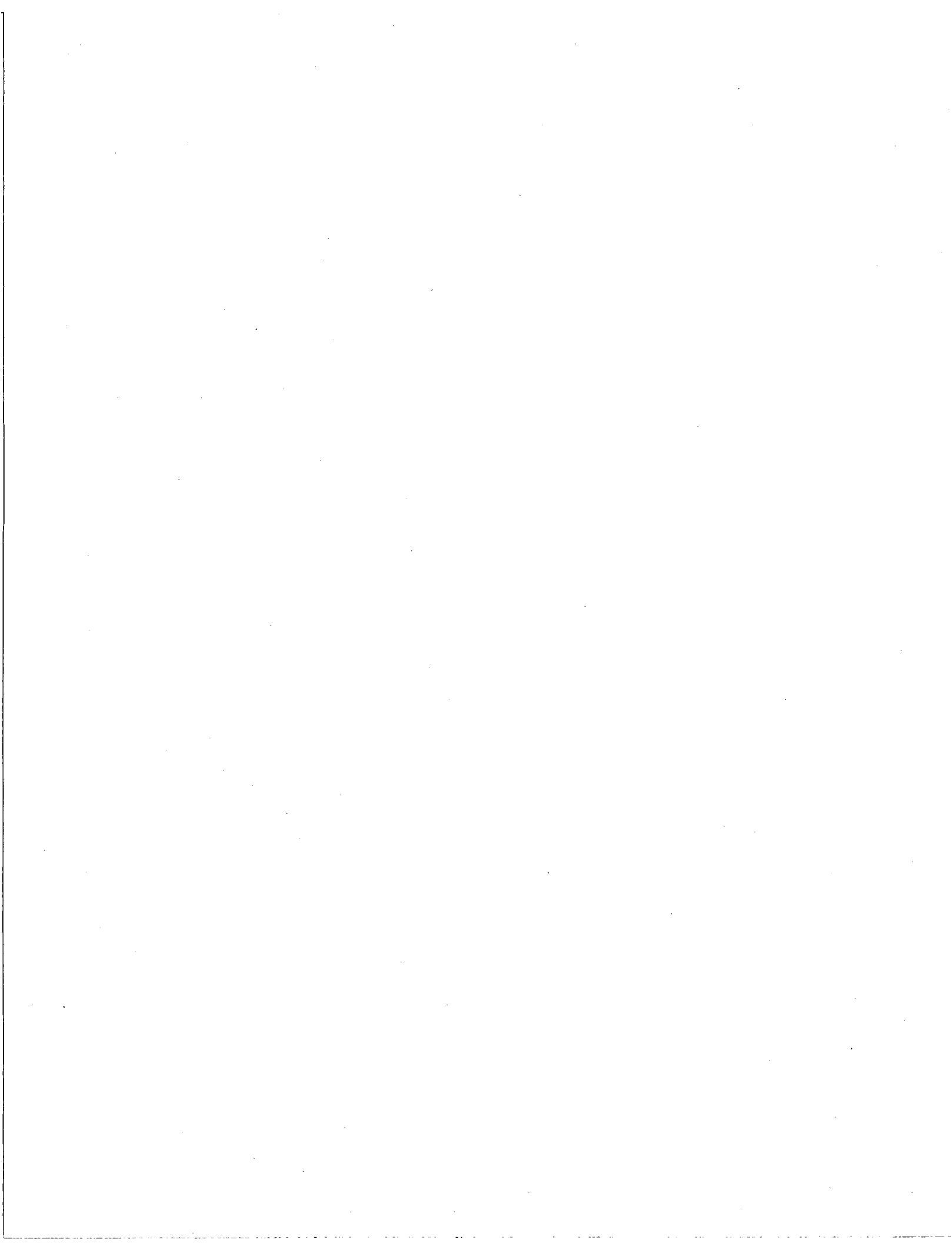
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TBP AND DBBP SOLVENT EXTRACTION RECOVERY  
AND PURIFICATION OF  $\text{Bi}(\text{NO}_3)_3$

By

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TBP AND DBBP SOLVENT EXTRACTION RECOVERY AND PURIFICATION OF  $\text{Bi}(\text{NO}_3)_3$ ABSTRACT

Equilibrium data are presented for extraction of bismuth from nitric acid solutions into dibutylbutyl phosphonate and tributyl phosphate solutions. These data were used to construct a study flowsheet for a solvent extraction process that should be capable of producing high-purity bismuth solutions. This extraction process appears well suited for recovery of bismuth used in production of  $\text{Po}^{210}$  by neutron irradiation.

TABLE OF CONTENTS

	<u>Page No.</u>
LIST OF FIGURES . . . . .	iv
LIST OF TABLES . . . . .	iv
INTRODUCTION . . . . .	1
SUMMARY . . . . .	1
EXPERIMENTAL . . . . .	2
RESULTS AND DISCUSSION . . . . .	2
Equilibrium Distribution Ratio Data . . . . .	2
Correlation of Laboratory Distribution Data . . . . .	9
Study Flowsheet for TBP Extraction of Bismuth . . . . .	12
Decontamination of Bismuth from Impurities . . . . .	14
ACKNOWLEDGEMENT . . . . .	17
REFERENCES . . . . .	17



LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	Conceptual Flowsheet for Bismuth Solvent Extraction . . . . .	3
2	Bismuth Distribution Ratios in 30% DBBP . . . . .	8
3	Bismuth Equilibrium Data Correlation . . . . .	10
4	Nitric Acid Equilibrium Data Correlation . . . . .	10
5	Bismuth Solubility in the $\text{HNO}_3$ -ANN- $\text{H}_2\text{O}$ System . . . . .	11
6	Bismuth Operating Diagram - 1A Column . . . . .	12
7	Nitric Acid Operating Diagram - 1A Column . . . . .	13
8	Bismuth Operating Diagram - 1C Column . . . . .	13
9	Nitric Acid Operating Diagram - 1C Column . . . . .	14

LIST OF TABLES

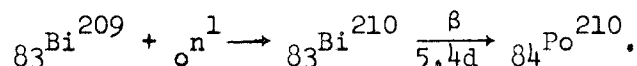
I	DBBP Extraction of $\text{Bi}(\text{NO}_3)_3$ and $\text{HNO}_3$ at 25 °C . . . . .	4
II	DBBP Extraction of $\text{Bi}(\text{NO}_3)_3$ and $\text{HNO}_3$ at 50 °C . . . . .	5
III	TBP Extraction of $\text{Bi}(\text{NO}_3)_3$ and $\text{HNO}_3$ at 25 °C . . . . .	6
IV	TBP Extraction of $\text{Bi}(\text{NO}_3)_3$ and $\text{HNO}_3$ at 50 °C . . . . .	7
V	Effects of ANN Concentration on Extraction of $\text{Bi}(\text{NO}_3)_3$ and $\text{HNO}_3$ . . . . .	7
VI	Effects of ANN Concentration on Extraction of $\text{Bi}(\text{NO}_3)_3$ into 30% TBP . . . . .	7
VII	Activation of Impurities in Bismuth Target Elements . . . . .	15
VIII	Extraction of Miscellaneous Nitrates into TBP Solutions . . . . .	15

TBP AND DBBP SOLVENT EXTRACTION RECOVERY AND PURIFICATION OF  $\text{Bi}(\text{NO}_3)_3$ 

G. L. Richardson  
W. W. Schulz

INTRODUCTION

Neutron irradiation of bismuth produces  $\text{Po}^{210}$  according to the reactions:



In the process presently used<sup>(1)</sup> for the separation and recovery of polonium from irradiated bismuth, the bismuth fraction is discarded. If polonium production increases significantly, economic considerations dictate that the bismuth be recovered and reused. Satisfactory recycle of the bismuth requires, however, that it be treated to remove neutron-activated impurities which, because of their high radiation dose rate, would complicate target fabrication and handling.

Bismuth nitrate is extractable by several common solvents.<sup>(2)</sup> Accordingly, a liquid-liquid solvent extraction process has been proposed in which the desired bismuth purification would be accomplished by extracting it away from the activated impurities. This process would be compatible with and complementary to the dibutyl carbitol extraction process proposed for large scale polonium production.<sup>(3)</sup> Two solvents, dibutylbutyl phosphonate (DBBP) and tributyl phosphate (TBP), appear to have special merit for this application; both have been investigated in laboratory equilibration studies. The results of these experiments and a conceptual flowsheet for a TBP bismuth extraction process are the subjects of this report.

SUMMARY

Equilibrium data presented show that either DBBP or TBP, diluted 2 to 5-fold with an inert diluent, can be used to extract bismuth quantitatively from nitric acid solutions. The organic-to-aqueous distribution ratios ( $E_a^o$ 's) are directly proportional to the solvent concentration in the organic phase and inversely proportional to the nitric acid concentration in the aqueous phase. At a given solvent concentration, the bismuth  $E_a^o$ 's in DBBP are several fold higher than in TBP; however, addition of a salting agent such as aluminum nitrate (ANN) to the TBP equilibrium system yields bismuth distribution ratios nearly equivalent to those obtained in the salt-free DBBP system.

Suitable bismuth extraction process flowsheets can be prepared for either solvent. In the preferred process, however, the extractant is a solution of TBP (30 vol%) in a normal paraffin hydrocarbon (NPH)

diluent. A TBP extraction process has the advantage over a DBBP process in that bismuth can be recovered from the solvent by stripping with more dilute nitric acid solutions. Also, the properties and reactions of TBP are better known than those of DBBP because of the many years it has been used as an extractant in the atomic energy industry.

A conceptual flowsheet for the TBP extraction process is shown in Figure 1. The feed (in this case, the aqueous raffinate resulting from dibutyl carbitol extraction of polonium) is adjusted to 1M ANN and fed to the center of a dual-purpose solvent extraction column. The bismuth is extracted into the organic phase and proceeds up the column countercurrent to a low-acid 1M ANN scrub stream which removes any weakly extracted metal ions from the solvent. The bismuth-containing solvent passes into a stripping column where the bismuth is stripped into a 1M HNO<sub>3</sub> aqueous phase. The aqueous raffinate from the extraction column is concentrated and recycled to the feed stream to provide the necessary ANN salting strength. Excess ANN, equivalent to the amount added to the scrub, is discarded. Although judged feasible by McCabe-Thiele operating diagrams, the process has not yet been demonstrated under countercurrent conditions.

#### EXPERIMENTAL

Aqueous solutions containing Bi(NO<sub>3</sub>)<sub>3</sub>, HNO<sub>3</sub>, and ANN were prepared from reagent grade chemicals. Portions of these solutions were contacted (mechanical stirring) for 10 min at either 25 or 50 °C with an equal volume of the appropriate extractant.

Extractants were prepared by diluting as-received DBBP (Virginia Carolina Chemical Co.) and TBP (Commercial Solvents Co.) to the desired volume percent with NPH\*. Extractants were washed with 3 vol% Na<sub>2</sub>CO<sub>3</sub> and water prior to use.

Bismuth in aqueous and organic phases was determined spectrophotometrically after extraction of the yellow diethyldithiocarbonate complex into isoamyl alcohol. Nitric acid in aqueous and organic solutions which contained bismuth was determined, after addition of sodium tartrate to complex the bismuth, by titration with standard aqueous NaOH using the derivative mode of an automatic recording titrator. This titration gives the sum of the HNO<sub>3</sub> and bismuth; the HNO<sub>3</sub> concentration is found by subtracting twice the bismuth molarity.

#### RESULTS AND DISCUSSION

##### EQUILIBRIUM DISTRIBUTION RATIO DATA

Equilibrium data for the extraction of bismuth and nitric acid into 20, 30, 40, and 50% DBBP and TBP solvents are presented in Tables I through VI. These data show that DBBP is a much stronger extractant for

\*NPH is the Hanford designation for a mixture of normal paraffin hydrocarbons, principally C<sub>10</sub> through C<sub>14</sub>.

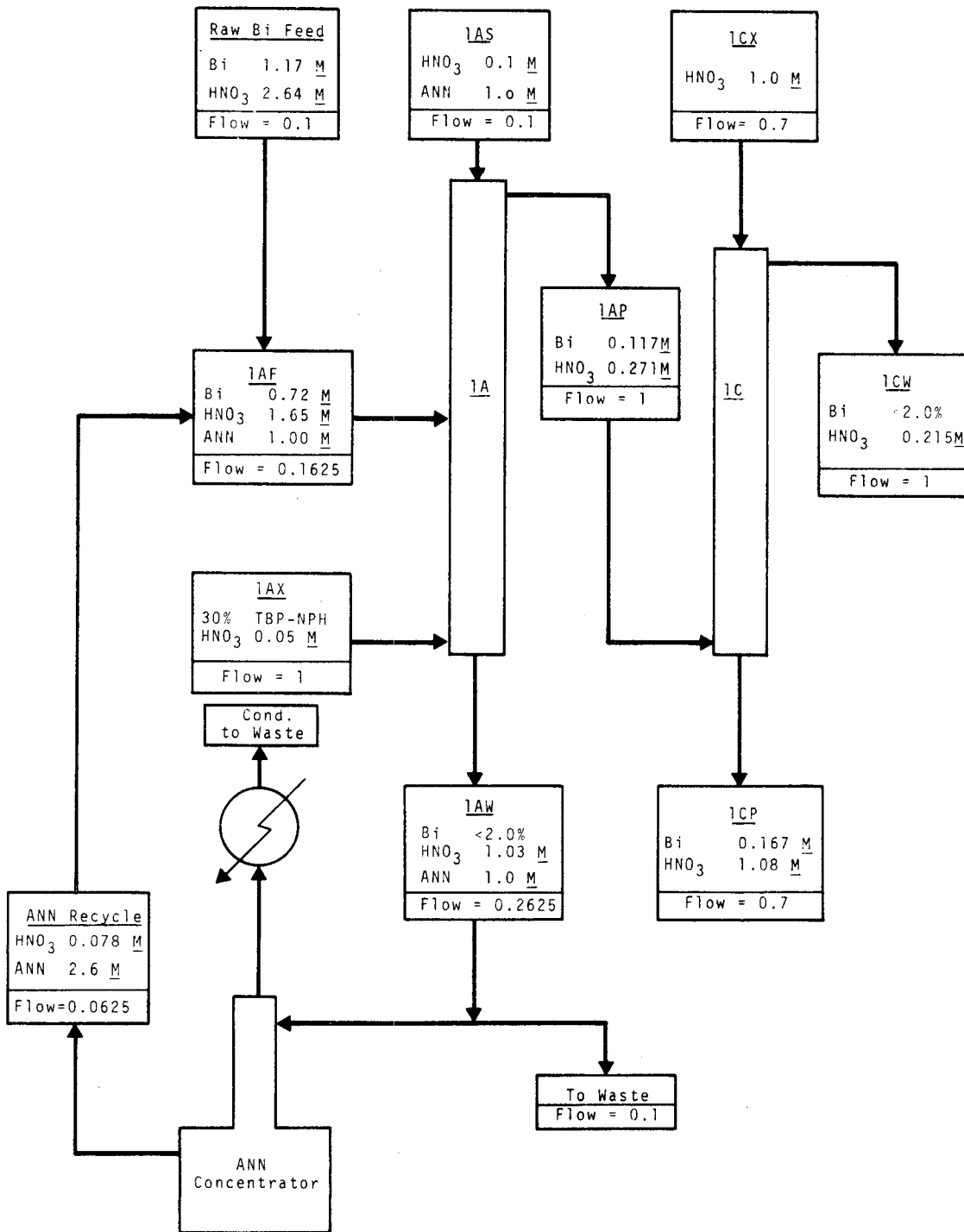


FIGURE 1  
Conceptual Flowsheet for Bismuth Solvent Extraction  
25 °C

TABLE I

DBBP EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  AND  $\text{HNO}_3$  AT 25 °CInitial aqueous: 0.5 and 1 M Bi, 1 to 6 M  $\text{HNO}_3$ 

## A. 20 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.894	0.368	0.042	0.178	0.047	0.484
1.75	0.386	0.174	0.161	0.099	0.417
2.59	0.446	0.292	0.141	0.113	0.316
3.51	0.473	0.429	0.108	0.122	0.228
4.66	0.460	0.554	0.081	0.119	0.176
5.70	0.511	0.631	0.055	0.111	0.108
0.918	0.856	0.051	0.200	0.056	0.234
1.72	0.932	0.166	0.189	0.097	0.203
2.59	0.986	0.328	0.141	0.127	0.143
3.59	0.951	0.463	0.106	0.129	0.111
4.41	1.011	0.570	0.076	0.129	0.071
5.46	-	0.601	0.078	0.110	-

## B. 30 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.832	0.309	0.085	0.242	0.102	0.783
1.69	0.325	0.251	0.226	0.149	0.695
2.50	0.378	0.435	0.189	0.174	0.500
3.41	0.397	0.633	0.143	0.186	0.361
4.23	0.453	0.816	0.101	0.193	0.223
5.13	0.491	0.963	0.058	0.188	0.118
0.848	0.766	0.110	0.290	0.130	0.379
1.81	0.758	0.299	0.246	0.165	0.325
2.55	0.864	0.468	0.203	0.184	0.235
3.49	0.852	0.666	0.149	0.191	0.175
4.35	0.914	0.815	0.114	0.187	0.125
5.18	0.979	0.958	0.080	0.185	0.082

## C. 40 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.848	0.211	0.144	0.299	0.170	1.42
1.59	0.274	0.344	0.274	0.216	1.00
2.40	0.318	0.578	0.233	0.241	0.733
3.25	0.340	0.816	0.185	0.251	0.544
4.12	0.385	1.01	0.136	0.245	0.353
4.93	0.454	1.21	0.092	0.245	0.203
0.874	0.643	0.121	0.383	0.138	0.596
1.40	-	0.324	0.336	0.231	0.462 <sup>(a)</sup>
2.36	0.831	0.466	0.299	0.197	0.360
3.32	0.801	0.790	0.228	0.238	0.285
4.19	0.848	1.02	0.161	0.242	0.190
4.96	0.944	1.19	0.122	0.240	0.129

## D. 50 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.642	-	-	0.381	-	2.51 <sup>(a)</sup>
1.62	0.176	0.423	0.328	0.261	1.86
2.45	0.220	0.694	0.280	0.283	1.27
3.22	0.261	0.927	0.240	0.288	0.920
3.97	0.325	1.20	-	0.303	0.662 <sup>(b)</sup>
4.67	0.408	1.16	-	0.249	-
0.876	0.557	0.182	0.453	0.208	0.813
1.67	0.591	0.376	0.424	0.225	0.717
2.37	0.682	0.655	0.359	0.267	0.526
3.27	0.681	0.868	0.313	0.265	0.460
3.99	0.787	1.14	0.248	0.286	0.315
4.72	0.864	1.36	0.191	0.288	0.221

(a) Calculated from initial aqueous and equilibrium organic analyses.

(b) Calculated from initial aqueous and equilibrium aqueous analyses.

TABLE II

DBBP EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  AND  $\text{HNO}_3$  AT 50 °CInitial aqueous: 0.5 and 1 M Bi, 1 to 6 M  $\text{HNO}_3$ 

## A. 20 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.855	0.398	0.163	0.108	0.184	0.271
1.67	0.484	-	0.103	0.186(a)	0.213
2.65	0.438	0.471	0.056	0.178	0.128
3.59	0.461	0.601	0.033	0.167	0.072
4.54	0.477	0.674	0.017	0.148	0.036
5.52	0.477	0.735	0.011	0.133	0.023
0.893	0.882	-	0.153	-	0.173
1.86	0.881	0.311	0.117	0.167	0.133
2.66	0.936	0.474	0.079	0.178	0.084
3.57	0.951	0.600	0.046	0.168	0.048
4.45	1.01	0.682	0.031	0.153	0.031
5.53	0.953	0.729	0.019	0.132	0.020

## B. 30 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
0.945	0.312	0.205	0.178	0.217	0.571
1.75	0.334	0.388	0.153	0.222	0.458
2.58	0.388	0.603	0.114	0.234	0.294(a)
3.28	0.426	-	-	0.232(a)	0.174(a)
4.26	0.427	0.872	-	0.205	0.144(a)
5.23	0.450	1.04	0.028	0.199	0.060
0.841	0.791	0.180	0.237	0.214	0.300
1.67	0.831	0.401	0.194	0.240	0.233
2.56	0.881	0.600	0.147	0.234	0.167
3.37	0.905	0.790	0.104	0.234	0.115
4.25	0.947	0.946	0.066	0.223	0.070
5.22	0.952	1.05	0.044	0.201	0.046

## C. 40 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
-	0.254	0.207	0.240	0.275	0.945
1.68	0.282	0.458	0.211	0.273	0.748
2.48	0.315	0.713	0.169	0.287	0.537
3.24	0.375	0.911	0.127	0.281	0.339
4.14	0.388	1.14	0.086	0.274	0.222
4.96	0.429	1.28	0.058	0.258	0.135
0.956	0.633	0.228	0.324	0.238	0.512
1.67	0.728	0.425	0.290	0.255	0.398
2.52	-	0.984	-	0.391	-
3.24	0.859	1.17	-	0.362	0.217(a)
4.12	0.979	1.14	0.118	0.278	0.134
4.87	0.952	1.29	0.085	0.264	0.089

## D. 50 Volume % DBBP-NPH

Equilibrium Aqueous		Equilibrium Organic		Distribution Ratio, $E_a$	
$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi	$\text{HNO}_3$	Bi
M	M	M	M	$\text{HNO}_3$	Bi
-	0.198	0.261	0.289	0.297	1.46
1.62	0.220	0.533	0.267	0.329	1.21
2.34	0.264	0.834	0.230	0.356	0.871
3.09	0.331	1.09	0.179	0.352	0.541
3.86	0.372	1.35	0.119	0.349	0.320
4.64	0.455	1.56	0.082	0.355	0.180
0.813	0.621	0.235	0.406	0.287	0.654
1.56	0.656	0.507	0.360	0.325	0.549
2.33	0.724	0.789	0.292	0.342	0.403
3.04	0.785	1.05	0.241	0.345	0.307
3.87	0.870	1.33	0.173	0.343	0.199
4.72	0.902	1.54	0.127	0.326	0.141

(a) Calculated from initial aqueous and equilibrium aqueous analyses.

TABLE III

TBP EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  AND  $\text{HNO}_3$  AT 25 °CA. 30 Volume % TBP-NPH

Feed			Equilibrium Aqueous		Equilibrium Organic		$E_a^\circ$	
$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{Al}(\text{NO}_3)_3$	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	Bi
<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>		
0.2	0.103	1.0	0.087	0.021	0.113	0.085	1.30	4.05
0.3	0.096	1.0	0.123	0.023	0.177	0.070	1.44	3.04
0.3	0.095	1.0	-	0.021	-	0.076	-	3.62
0.3	0.323	1.0	0.121	0.150	0.179	0.141	1.48	0.904
0.3	0.293	1.0	0.149	0.143	0.151	0.148	1.01	1.04
0.5	0.103	1.0	0.244	0.033	0.256	0.072	1.05	2.18
0.5	0.311	1.0	0.264	0.166	0.236	0.136	0.894	0.819
0.5	0.510	1.0	0.286	0.340	0.214	0.169	0.784	0.497
0.5	0.698	1.0	0.260	0.524	0.240	0.178	0.923	0.340
0.5	0.958	1.0	0.276	0.827	0.224	0.218	0.811	0.258
0.75	0.093	1.0	0.336	0.043	0.414	0.0507	1.23	1.18
0.75	0.295	1.0	0.378	0.187	0.372	0.113	0.984	0.604
0.75	0.460	1.0	0.384	0.361	0.366	0.151	0.953	0.418
0.75	0.710	1.0	0.410	0.530	0.340	0.171	0.829	0.323
0.5	0.093	0.0	0.387	0.079	0.041	0.036	0.106	0.456
1.0	0.110	0.0	0.920	0.079	0.189	0.018	0.205	0.228
1.0	0.296	0.0	0.885	0.253	0.180	0.063	0.203	0.249
1.0	0.509	0.0	0.930	0.414	0.213	0.078	0.229	0.188
1.0	0.689	0.0	0.911	0.606	0.213	0.103	0.234	0.170
1.0	1.00	0.0	1.01	0.844	0.209	0.137	0.206	0.162
1.75	0.109	0.0	1.38	0.0742	0.324	0.0202	0.235	0.272
1.75	0.300	0.0	1.44	0.245	0.307	0.0566	0.213	0.229
1.75	0.667	0.0	1.63	0.600	0.337	0.104	0.207	0.173

B. 50 Volume % TBP-NPH

0.961	0.533	0.0	0.837	0.320	0.316	0.132	0.378	0.413
1.98	0.519	0.0	1.69	0.311	0.560	0.121	0.332	0.389
3.04	0.492	0.0	2.40	0.356	0.856	0.085	0.356	0.239
4.04	0.500	0.0	3.12	0.419	1.03	0.073	0.329	0.174
4.97	0.540	0.0	3.95	0.463	1.29	0.046	0.327	0.099
5.99	0.528	0.0	4.80	0.478	1.47	0.028	0.307	0.059
1.08	1.007	0.0	0.839	0.768	0.304	0.242	0.362	0.315
2.02	1.064	0.0	1.57	0.789	0.542	0.215	0.345	0.269
2.92	1.086	0.0	2.35	0.844	0.843	0.161	0.359	0.191
4.01	1.045	0.0	3.10	0.881	1.10	0.114	0.356	0.129
5.07	0.956	0.0	3.98	0.914	1.33	0.073	0.334	0.080
5.90	1.093	0.0	4.77	0.979	1.50	0.050	0.316	0.051

TABLE IV

TBP EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  AND  $\text{HNO}_3$  AT 50 °C

50 Volume % TBP in NPH

Initial Aqueous		Equilibrium Aqueous		Equilibrium Organic		$E_a^\circ$	
$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	Bi
M	M	M	M	M	M		
0.533	0.961	0.921	0.357	0.297	0.116	0.322	0.325
0.519	1.98	1.51	0.421	0.589	0.103	0.389	0.245
0.492	3.04	2.38	0.390	0.864	0.082	0.363	0.210
0.500	4.04	3.17	0.412	1.15	0.055	0.363	0.133
0.540	4.97	4.01	0.444	1.35	0.036	0.336	0.081
0.528	5.99	4.77	0.502	1.52	0.023	0.318	0.046
1.007	1.08	0.749	0.827	0.352	0.193	0.470	0.233
1.064	2.02	1.49	0.878	0.643	0.163	0.430	0.186
1.086	2.92	2.25	0.903	0.919	0.128	0.409	0.142
1.045	4.01	2.94	0.989	1.19	0.087	0.406	0.088
0.956	5.07	3.81	1.01	1.41	0.052	0.370	0.051
1.093	5.90	4.75	0.992	1.57	0.032	0.331	0.032

TABLE V

EFFECT OF TBP CONCENTRATION ON EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  AND  $\text{HNO}_3$ 25 °C; Initial Aqueous: 1M  $\text{HNO}_3$ , 0.5 and 1M  $\text{Bi}(\text{NO}_3)_3$ 

TBP Vol%	Equilibrium Aqueous		Equilibrium Organic		$E_a^\circ$	
	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	Bi
	M	M	M	M		
20	0.942	0.431	0.133	0.053	0.141	0.128
30	0.862	0.401	0.181	0.087	0.210	0.217
40	0.881	0.350	0.226	0.123	0.257	0.343
50	0.837	0.320	0.334	0.132	0.399	0.413
20	0.824	0.934	0.155	0.084	0.188	0.090
30	0.899	0.828	0.191	0.142	0.212	0.171
40	0.851	0.783	0.210	0.201	0.247	0.257
50	0.839	0.768	0.304	0.242	0.362	0.315

TABLE VI

EFFECT OF ANN CONCENTRATION ON EXTRACTION OF  $\text{Bi}(\text{NO}_3)_3$  INTO 30% TBP, 25 °C

Initial Aqueous			Equilibrium Aqueous	Equilibrium Organic	$E_a^\circ$
ANN	$\text{Bi}(\text{NO}_3)_3$	$\text{HNO}_3$	Bi	Bi	
M	M	M	M	M	
0.0	0.51	1.0	0.414	0.078	0.188
0.50	0.50	1.0	0.411	0.123	0.299
0.75	0.50	1.0	0.378	0.127	0.336
1.0	0.50	1.0	0.395	0.143	0.362
0.50	0.52	0.75	0.385	0.138	0.358
0.75	0.52	0.75	0.378	0.154	0.407
1.0	0.51	0.75	0.351	0.155	0.442



bismuth than TBP. Under the same conditions, the bismuth distribution ratios ranged from 2.5 to 15-fold higher with DBBP than with TBP, the lower figure being obtained at high bismuth and nitric acid concentrations. On the other hand, nitric acid extraction was slightly greater into TBP than into DBBP in the presence of bismuth, apparently reflecting the increased competition with bismuth in the DBBP system.

At the macro concentrations of bismuth used in most of these experiments, the bismuth distribution ratios increased proportionately to the 1.5 to 1.8 power of the solvent concentration for both DBBP and TBP. Nitric acid distribution ratios increased linearly with the solvent concentration. Bismuth distribution ratios at 50 °C were 30 to 40% lower than those at 25 °C. Under similar conditions, however, nitric acid distribution ratios increased with temperature. Similar temperature effects are observed in uranium-nitric acid-TBP-diluent systems. The inverse temperature effect on bismuth extraction can be used to minimize the volume of stripping solution required to remove bismuth from the solvent phase.

A characteristic and important feature of extraction of bismuth by both TBP and DBBP extractants is that bismuth distribution ratios decrease with increased aqueous phase nitric acid concentration. [In more familiar case, e.g., TBP or DBBP extraction of  $UO_2(NO_3)_2$ , just the opposite behavior is observed.] The inverse dependency of bismuth extraction on aqueous phase acidity is illustrated, for the DBBP system, by the data plotted in Figure 2, and, for the TBP system, by the results in Table III.

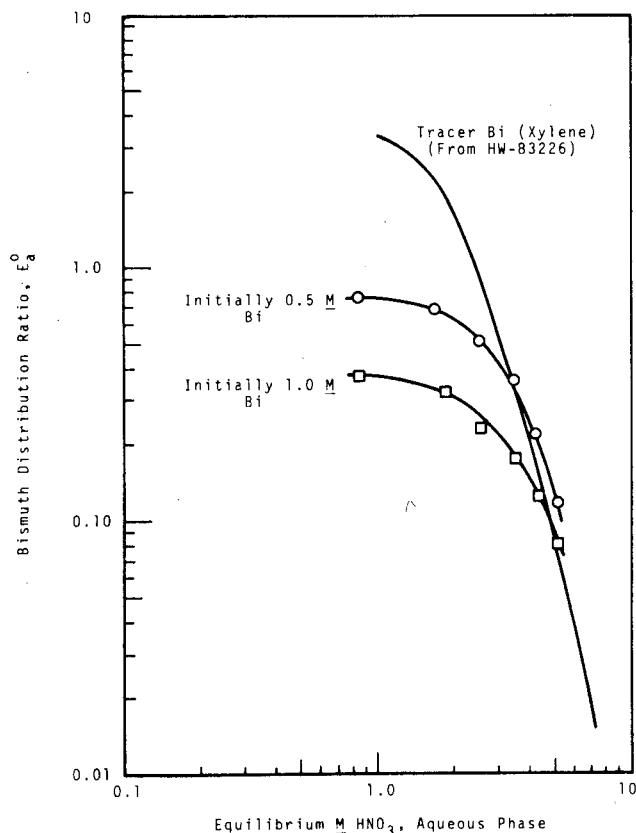


FIGURE 2  
Bismuth Distribution Ratios in 30% DBBP  
25 °C

The limited data in Table III indicate that the bismuth distribution ratios continue to increase as the aqueous phase acidity is lowered to 0.4M HNO<sub>3</sub>.

The inverse acid dependency effect was a major reason for using the TBP system to illustrate the flowsheet development described in the following sections. A final solvent extraction product solution high in bismuth and low in nitric acid concentrations is highly desirable for the succeeding conversion to bismuth metal (or oxide). This can be achieved most readily in the TBP system. From Figure 2, it is evident that 4M HNO<sub>3</sub> is required to lower the bismuth distribution ratio below 0.25 in the 30% DBBP system; whereas only 1M HNO<sub>3</sub> is required in the 30% TBP system (Table III).

Nitric acid alone does not provide sufficient salting strength in the TBP system, but bismuth distribution ratios approaching those obtained with DBBP can be obtained by the addition of ANN. The effect of aluminum nitrate salting is illustrated in Tables III and VI. Most of the development work was done with 1M ANN, but lower concentrations can probably be used with little loss in efficiency.

One of the major advantages of an ANN-salted flowsheet is the ability to operate at low nitric acid concentrations without precipitating BiONO<sub>3</sub>, as discussed in the following section. Low-acid operation permits attainment of bismuth distribution ratios 5 to 10-fold higher than those obtained with 1M HNO<sub>3</sub> in either the ANN salted or unsalted system. Since ANN greatly increases the nitric acid distribution ratios, attainment of a low-acid system is not at all difficult--even with feeds containing more acid than bismuth.

#### CORRELATION OF LABORATORY DISTRIBUTION DATA

The limited amount of equilibrium data obtained in the laboratory confirmed the feasibility of the DBBP and TBP extraction processes, but a method for extrapolating and smoothing the data was desired for flowsheet x-y diagram stage calculations. Accordingly, for the preferred 30% TBP system, empirical equations were developed which correlate the experimental data reasonably well over the range of conditions studied.

The empirical equations are based on the observation that plots of the bismuth and nitric acid distribution ratios versus the equilibrium nitrate concentration in the aqueous phase (neglecting the nitrate contribution of ANN) are straight lines on logarithmic paper. Such plots are shown in Figures 3 and 4. The empirical equations derived from these plots are listed below, together with the estimated range of conditions over which they are applicable:

#### No ANN Present:

Applicable range: 0.08 to 0.8M Bi(NO<sub>3</sub>)<sub>3</sub>  
0.4 to 1.6M HNO<sub>3</sub>

$$\text{Bi } E_a^{\circ} = \frac{0.31}{[(\text{M HNO}_3)_{\text{aq}} + 3 (\text{M Bi})_{\text{aq}}]^{0.5}} \quad (1)$$

$$\text{HNO}_3 E_a^{\circ} = 0.21 \text{ (apparently unaffected by presence of bismuth)} \quad (2)$$

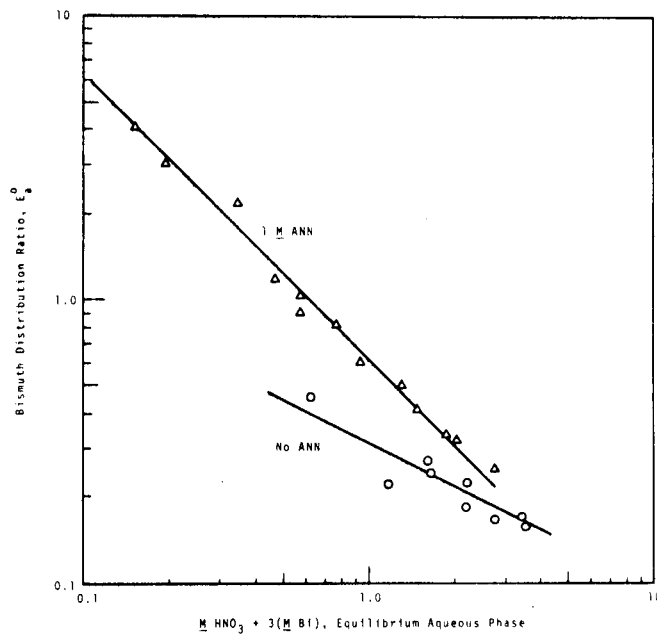


FIGURE 3  
Bismuth Equilibrium Data Correlation  
30% TBP in NPH  
25 °C

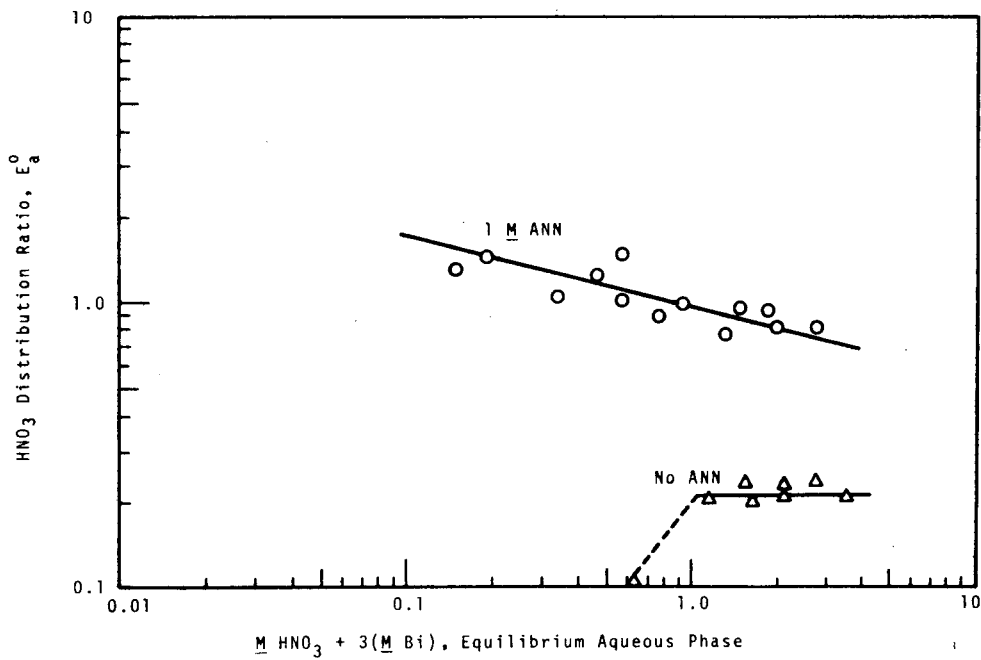


FIGURE 4  
Nitric Acid Equilibrium Data Correlation  
30% TBP in NPH  
25 °C

1M ANN System:

Applicable range: 0.02 to 0.8M Bi(NO<sub>3</sub>)<sub>3</sub>  
0.09 to 0.4M HNO<sub>3</sub>

$$\text{Bi } E_a^{\circ} = \frac{0.61}{(\text{M HNO}_3)_{\text{aq}} + 3(\text{M Bi})_{\text{aq}}} \quad (3)$$

$$\text{HNO}_3 E_a^{\circ} = \frac{0.965}{[(\text{M HNO}_3)_{\text{aq}} + 3(\text{M Bi})_{\text{aq}}]^{0.25}} \quad (4)$$

The subscript aq in these equations refers to the equilibrium aqueous phase.

In addition to the ranges of bismuth and nitric acid concentrations shown, the practical operating limits for these equations are also dependent on the aqueous solubility of bismuth at low acidities. The solubility of bismuth in nitric acid has been presented in Reference 2 and is repeated in Figure 5, along with the bismuth solubility estimated for the 1M ANN-HNO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>3</sub> system. The latter curve is based on the assumption that the bismuth solubility is dependent primarily on the pH, which is lowered considerably by the addition of ANN. Thus, the solubility curve is drawn for the ANN system on the assumption that precipitation occurs in both systems at the same pH. The pH data for the ANN system were obtained from the Reactor Handbook<sup>(4)</sup>; the effect of bismuth on the pH was ignored. Data points from the equilibration experiments, in which no precipitation was observed, are included in this plot and tend to confirm the estimation procedure.

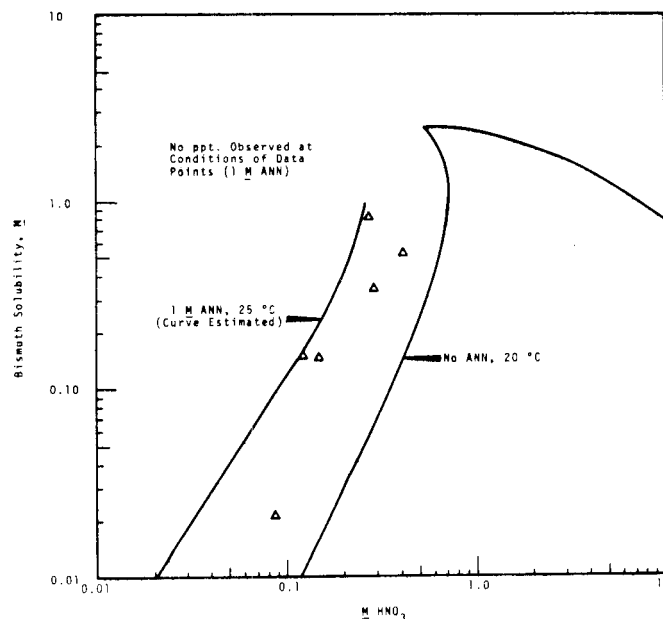


FIGURE 5  
Bismuth Solubility in the HNO<sub>3</sub>-ANN-H<sub>2</sub>O System

### STUDY FLOWSHEET FOR TBP EXTRACTION OF BISMUTH

A study flowsheet is shown in Figure 1 for the TBP bismuth extraction process. The "raw" feed composition is representative of the bismuth raffinate from the dibutyl carbitol polonium extraction process. A 1M ANN salt strength was chosen for the extraction (1A) column to permit relatively high solvent loading and to minimize bismuth reflux in the scrub section. The bismuth is stripped from the solvent in the 1C column with 1M HNO<sub>3</sub>. Higher acidities would be more effective but would increase the problem of removing the acid in subsequent metal conversion steps. A small amount of acid is added to both the 1AX and 1AS streams to assure sufficient acidity to avoid bismuth subnitrate precipitation.

Bismuth and nitric acid operating diagrams based on these parameters are shown in Figures 6, 7, 8, and 9. The equilibrium data on which these diagrams are based were obtained by the correlation method presented earlier. The operating diagrams show that three to four stages of counter-current contact should be sufficient to reduce the bismuth losses to less than 2% in the raffinate streams of both columns. Note that both nitric acid and bismuth stages must be stepped off simultaneously. Since both constituents are present in macro amounts and extract simultaneously, the equilibrium profile of each of these in the column will affect the equilibrium profile of the other.

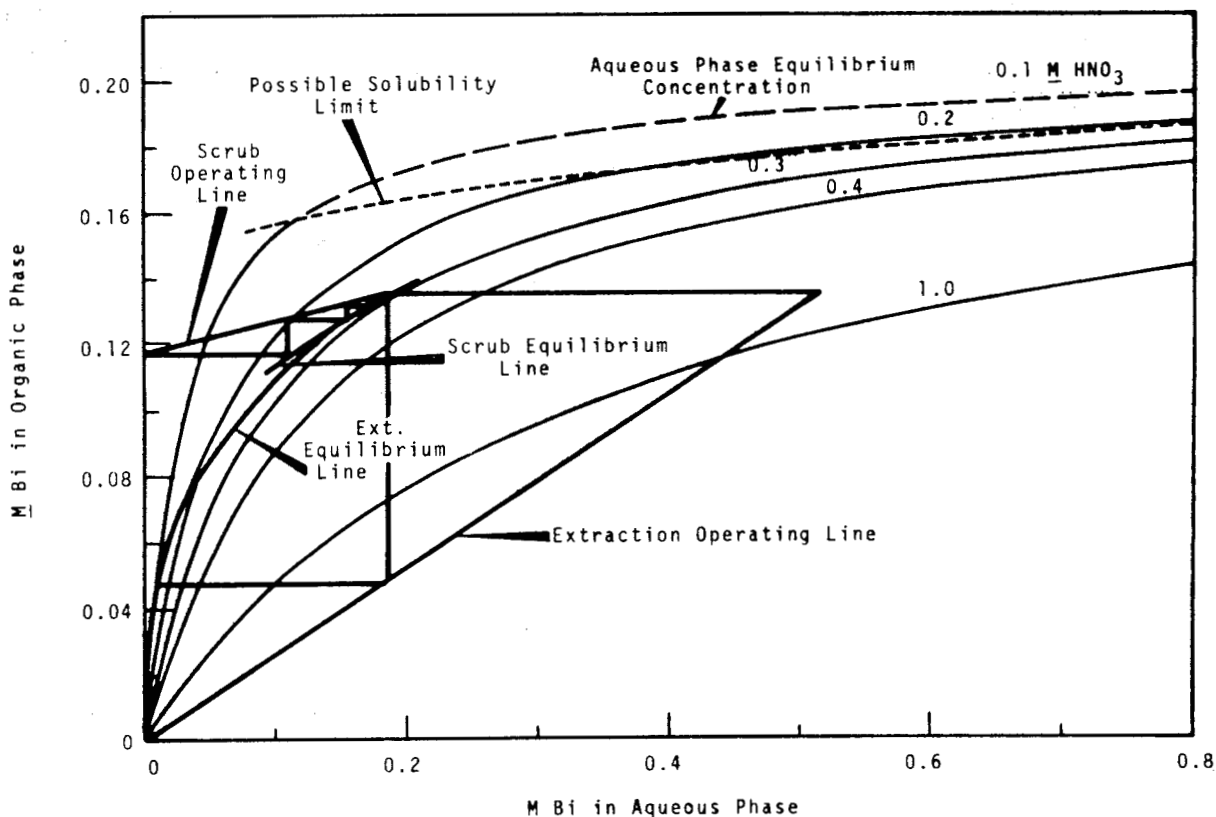


FIGURE 6  
Bismuth Operating Diagram - 1A Column  
25 °C, 1M ANN

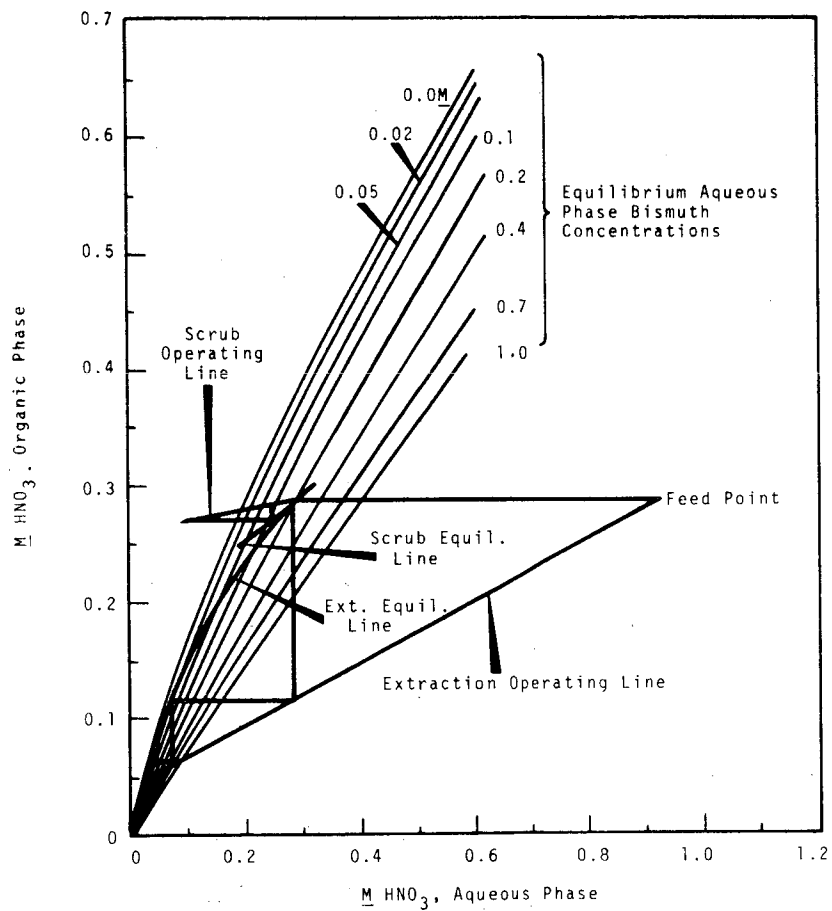


FIGURE 7  
Nitric Acid Operating Diagram  
1A Column  
25 °C, 1M ANN

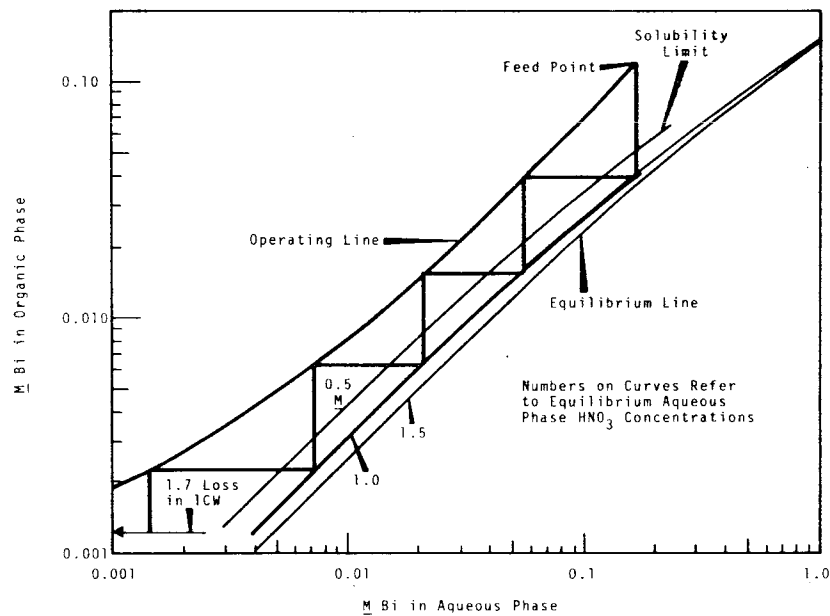


FIGURE 8  
Bismuth Operating Diagram  
1C Column  
25 °C, No ANN

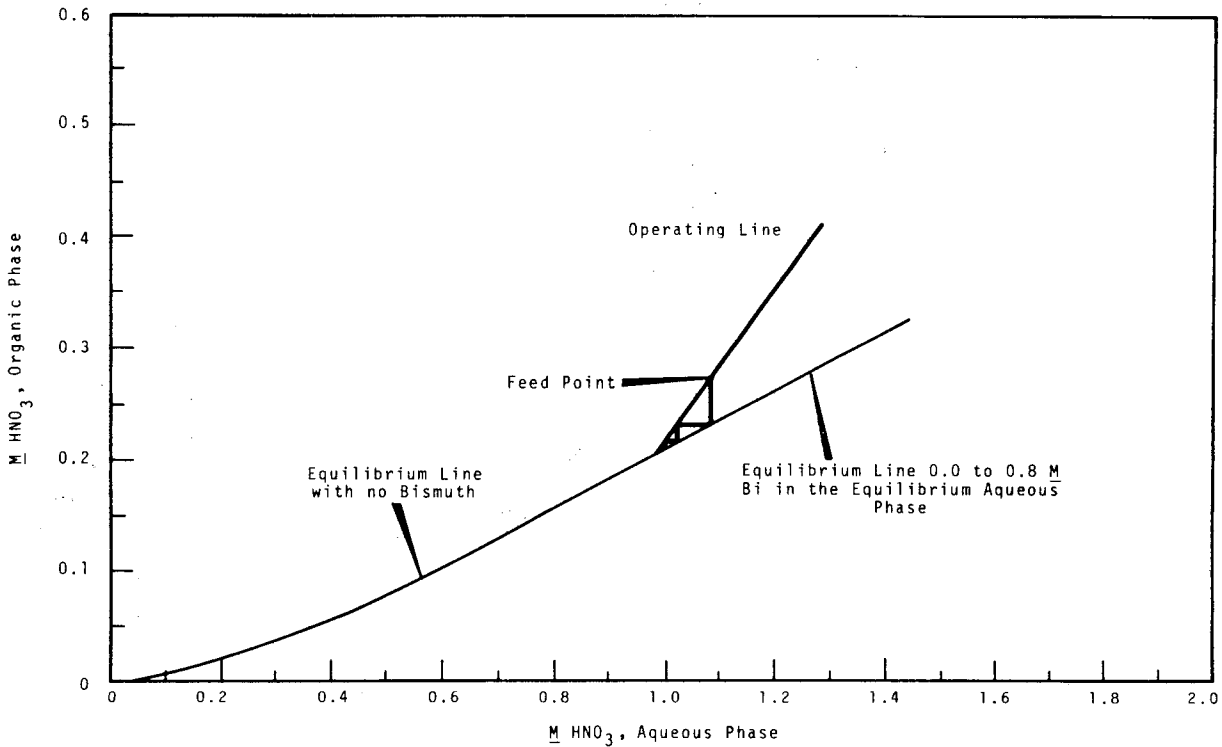


FIGURE 9  
Nitric Acid Operating Diagram - 1C Column  
25 °C, No ANN

#### DECONTAMINATION OF BISMUTH FROM IMPURITIES

The impurities of most concern in the recycle of bismuth are those that, when neutron activated, contribute to high radiation dose rates. Van Tuyl<sup>(5)</sup> has calculated the concentration of impurities that yield dose rates of 100 mR/hr at the surface of the irradiated target element as a function of cooling time after reactor discharge. His data are tabulated in Table VII. The radiation history was not specified, but the results are indicative of the impurity levels that are tolerable.

The extraction of trace impurities in the bismuth-TBP system has not been studied, but certain inferences can be made from the known behavior of metal nitrates in TBP extraction systems. In general, metallic ions in the plus four and plus six valence states are quite extractable in TBP. Most of the actinide elements fall into this category. Most trivalent metal ions are not extractable, with the notable exception of bismuth and the rare earths which are extractable in low acid systems with ANN salting. Mono and divalent ions are essentially nonextractable. Data illustrating the extractability of various metal nitrates is presented in Table VIII.<sup>(6)</sup>

TABLE VII

ACTIVATION OF IMPURITIES IN BISMUTH TARGET ELEMENTS

(Parts Per Million Which Result in 100 mR/hr Surface Dose Rate at Cooling Times Shown)

<u>Element</u>	<u>5 days</u>	<u>10 days</u>	<u>30 days</u>	<u>60 days</u>	<u>90 days</u>
Co	0.0012	0.0012	0.0012	0.0013	0.0013
Ta	0.0074	0.0085	0.011	0.013	0.016
Sb	0.0081	0.0097	0.013	0.018	0.025
Ag	0.021	0.021	0.022	0.024	0.026
Zn	0.26	0.26	0.28	0.30	0.33
Fe	1.6	1.7	2.0	2.5	3.1
Cr	2.1	2.4	4.0	8.5	18.
Cd	0.97	3.5	18.	29.	47.
Cu	20.	120.*	130.*	140.*	150.*
As	0.17	3.9	**	**	**
W	0.29	9.3	**	**	**
Mo	9.8	35.	**	**	**
Na	0.36	92.	**	**	**

Mg, Al, Ti, Mn, Ni: greater than 1000 ppm.

\* Limit due to Zn<sup>65</sup> radiation; otherwise limit is greater than 1000 ppm.

\*\* More than 1000 ppm required for 100 mR/hr surface dose rate.

TABLE VIII

EXTRACTION OF MISCELLANEOUS NITRATES INTO TBP SOLUTIONS

<u>Ion</u>	<u>Aqueous-Phase Composition</u>	<u>TBP vol%</u>	<u>Distribution Ratio, (g/liter org.)/(g/liter ag.)</u>
Al <sup>+3</sup>	4.7M HNO <sub>3</sub> , 7.2 g/liter Al	15.	0.0003
Ca <sup>+2</sup>	4.7M HNO <sub>3</sub> , 7.5 g/liter Ca	15.	0.0003
Ca <sup>+2</sup>	1M Ca(NO <sub>3</sub> ) <sub>2</sub>	30.	0.008
Co <sup>+2</sup>	2.14M Co(NO <sub>3</sub> ) <sub>2</sub>	60.	0.0002
Cr <sup>+3</sup>	3M HNO <sub>3</sub> , 1.0M Cr(NO <sub>3</sub> ) <sub>3</sub>	100.	0.0001
Cr <sup>+3</sup>	3M HNO <sub>3</sub> , 1.9M Cr(NO <sub>3</sub> ) <sub>3</sub>	100.	0.0001
Cu <sup>+2</sup>	3M HNO <sub>3</sub> , 0.8M Cu(NO <sub>3</sub> ) <sub>2</sub>	100.	0.0004
Fe <sup>+2</sup>	4.7M HNO <sub>3</sub> , 0.7 g/liter Fe	15.	0.005
Fe <sup>+2</sup> , Fe <sup>+3</sup>	2M HNO <sub>3</sub> , 2.8 g/liter Fe	12.5	0.0003
Mg <sup>+2</sup>	4.7M HNO <sub>3</sub> , 2M Mg(NO <sub>3</sub> ) <sub>2</sub>	15.	0.0003
Na <sup>+</sup>	3M HNO <sub>3</sub> , ca. 0.2M UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> 4 g/liter Na	30.	0.0003
Na <sup>+</sup>	2M HNO <sub>3</sub> , 0.18M NaNO <sub>3</sub>	12.5	0.003
Ni <sup>+2</sup>	3M HNO <sub>3</sub> , 0.90M Ni(NO <sub>3</sub> ) <sub>2</sub>	100.	0.00006
Ni <sup>+2</sup>	3M HNO <sub>3</sub> , 1.7M Ni(NO <sub>3</sub> ) <sub>2</sub>	100.	0.00006
Zn <sup>+2</sup>	2M Zn(NO <sub>3</sub> ) <sub>2</sub>	12.5	0.0001



A more general study<sup>(7)</sup> using 100% TBP and tracer elements showed that, of those impurities of interest to bismuth recycle, only silver ( $E_a^o = 0.02$ ), arsenic ( $E_a^o = 0.2$ ), tungsten ( $E_a^o = 30$ ) and molybdenum ( $E_a^o = 0.02$ ) appear to have distribution ratios high enough to be of concern. Under the same conditions ( $1M HNO_3$ ), the bismuth distribution ratio was about 2. Assuming the same relative distribution ratios hold in the ANN-salted, 30% TBP system, greater than 99% of all of these impurities except arsenic and tungsten should be removed with 3 stages of scrubbing in the 1A column. Polonium, if present, should follow the bismuth. Further decontamination from many of the impurities may be obtained during the conversion of the bismuth nitrate solution to bismuth metal, particularly if the bismuth is first precipitated as  $BiONO_3$ .<sup>(3)</sup>

ACKNOWLEDGEMENT

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