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EXTRACTION METALLURGY DIVISION

Mines Branch Investigation Report IR 72-61

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SUMMARY

A complex bulk sulphide concentrate from Brunswick Tin Mines Limited, which would not respond to physical separation of bismuth and molybdenum, was leached to selectively extract the bismuth to give a residue for the recovery of molybdenum and tungsten.

The concentrate was leached with hydrochloric acid at concentrations ranging from 124 g/l to 300 g/l, at temperatures between 50 and 100°C, for retention times of 1 to 24 hours, and at stirring rates of 300 to 900 rpm. Under the optimum leaching conditions - 5 hours at 900 rpm with a solution containing 124 g/l HCl and 0.8 g/l HNO_3 at 100°C - more than 90% of the bismuth was extracted. The acid consumption was 260 lbs 100% HCl per ton of ore, or 7 lbs 100% HCl per lb of bismuth extracted.

The addition of the small amount of HNO_3 as an oxidizing agent made possible the use of less HCl to leach most of the bismuth. Only finely divided metallic bismuth remained, disseminated through the residue. The bulk of the other valuable metals, molybdenum, tungsten, indium, zinc, copper, and tin remained in the residue, as did most of the iron and arsenic.

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INTRODUCTION

The Mineral Processing Division of the Department of Energy, Mines and Resources produced a bulk sulphide flotation concentrate at one stage of the processing of a complex sulphide ore from Brunswick Tin Mines Limited. This concentrate, which constituted about 2.5% (by weight) of the original ore, contained the major part of the bismuth and molybdenum. Difficulty was encountered in the physical separation of the minerals of these two metals. The Mineral Processing Division requested the Extraction Metallurgy Division to leach the bismuth from the concentrate and then to return the leach residue. By further processing, a molybdenite concentrate could be produced from the leach residue.

The average analysis of several bulk concentrates is shown in Table 1.

TABLE 1

Chemical Analysis of Feed Material

Element	Per Cent
Bi	2.17
Mo	4.0
W	0.92
In	0.040
Zn	14.0
Cu	1.20
Pb	6.4
Fe	9.9
As	8.9
Sn	0.64
Total S	17.0

A study of the mineralogy of the concentrate showed that the major minerals were sphalerite (ZnS), molybdenite (MoS_2), and arsenopyrite (FeAsS); intermediate minerals were chalcopyrite ($CuFeS_2$), galena (PbS), and quartz. Minor minerals were stannite, (Cu_2FeSnS_4), tennantite $(Cu, Fe)_{12}\ As_4\ S_{13}$), bismuthenite ($Bi_2S_3$), pyrite ($FeS_2$) wolframite (Fe, Mn) WO_4, rutile (TiO_2), and cassiterite (SnO_2). Metallic bismuth and a trace amount of graphite were also present. The occurrence, mineralogy, and amenability to mineral beneficiation of the original ore deposit have been described (1).

EXPERIMENTAL

The results of previous experimental work (2) and opinions expressed in literature indicated that the most promising approach was to leach with hydrochloric acid. Accordingly, an experimental programme was undertaken in which the variables studied were acid concentration, temperature, retention time, oxidizing agent, and stirring rate.

APPARATUS AND PROCEDURE

The apparatus used in the leaching experiments is illustrated in Figure 1. In each test, 100 grams of dry concentrate was slurried in a 1 litre reaction flask which was enclosed by a heating mantle. The temperature of the slurry was regulated by a controller attached to a thermometer inserted into the slurry. The slurry was agitated by a glass stirrer, driven by a motor, at 900 rpm. A reflux condenser was attached to the gas outlet of the reactor flask lid.

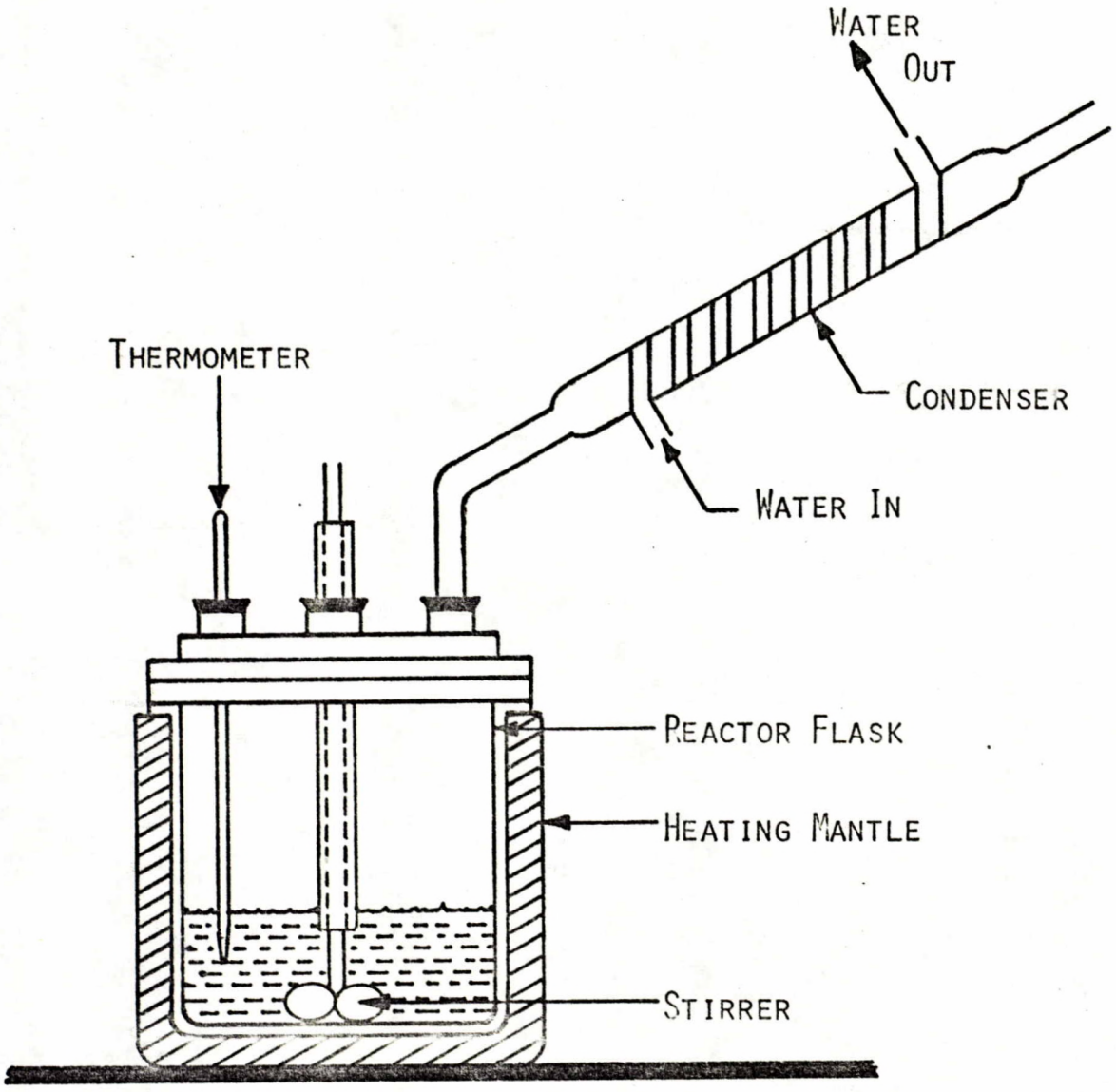

FIG. 1 APPARATUS FOR LEACHING TESTS

In the tests, the desired amount of 37% HCl was added to sufficient water to make a total volume of 500 ml. The slurry was brought to the specified temperature, oxidizing agent, if so desired, was added. After the needed retention time, the slurry was filtered and the filtrate was analysed.

RESULTS AND OBSERVATIONS

Effect of Acid Concentration

The effect of acid concentration on the extraction of bismuth is shown in Table 2 and Figure 2. It was observed that increased concentration of acid of the leaching solution resulted in increased extraction of bismuth. The increase of acid concentration was more effective at low temperatures than at high temperatures. For example, after leaching for 5 hours at 100°C the extraction of bismuth was about 62% with 124 g/l HCl and about 86% with 300 g/l HCl. At 50°C, however, after 5 hours of leaching, the extraction of bismuth was about 10% with 124 g/l HCl, and increased to over 80% with 300 g/l HCl.

TABLE 2

Effect of HCl Concentration on Bismuth Extraction

Leaching Conditions				Weight Loss %	Percent Extraction Bi
HCl Concentration g/l	HNO_3 g/l	Temp °C	Retention Time (hr)		
300	Nil	100	5	26	86
212	Nil	100	5	20	76
124	Nil	100	5	20	62
300	Nil	75	5	37	88
212	Nil	75	5	26	63
124	Nil	75	5	12	24
300	Nil	50	5	36	83
300	Nil	50	24	38	83
212	Nil	50	5	13	32
124	Nil	50	5	12	10

TABLE 3

Effect of Temperature on Bismuth Extraction

Leaching Conditions				Weight Loss %	Percent Extraction Bi
HCl Concentration g/l	HNO_3 g/l	Temp °C	Retention Time (hr)		
300	Nil	100	5	26	86
300	Nil	75	5	37	88
300	Nil	50	5	35	83
300	Nil	25	5	30	45
212	Nil	100	5	20	76
212	Nil	75	5	26	63
212	Nil	50	5	13	32
124	Nil	100	5	20	62
124	Nil	75	5	12	24
124	Nil	50	5	12	11

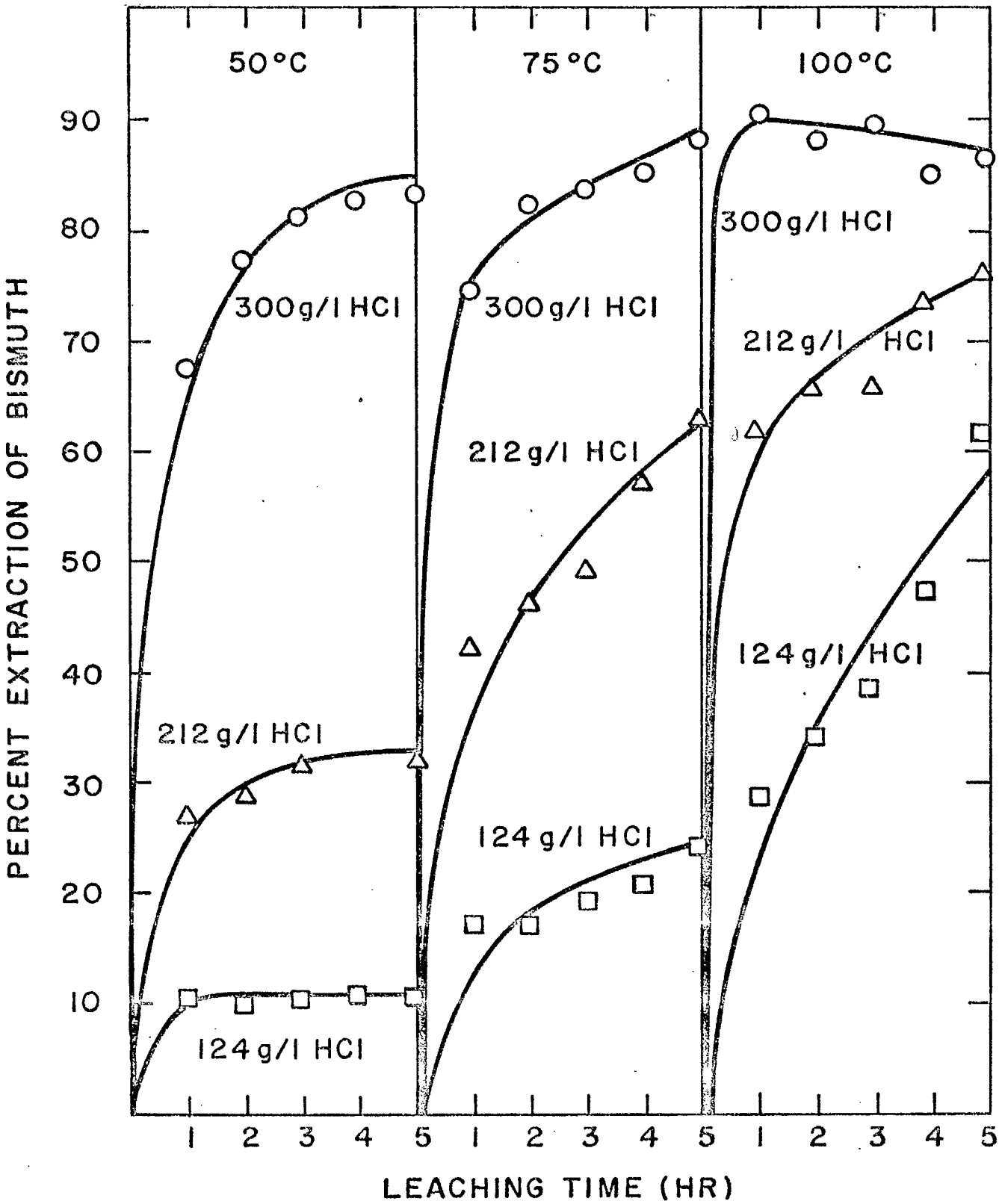

FIG. 2 EFFECT OF HCl CONCENTRATION ON THE EXTRACTION OF BISMUTH

Effect of Temperature

The effect of temperature on the extraction of bismuth, shown in Table 3 and Figure 3, was more pronounced with the weaker acid concentrations - 124 g/l and 212 g/l - than with 300 g/l HCl. This is illustrated in the following examples of 5 hour leach tests. With 124 g/l HCl, at 50°C, 11% of the bismuth was extracted, compared with 60% at 100°C. With 212 g/l HCl, bismuth extraction was 32% at 50°C compared with 76% at 100°C. With 300 g/l HCl, bismuth extractions were 45% at 25°C, approximately 80% at 50°C, and about 85% at 100°C. When 300 g/l HCl was used the extractable bismuth was leached in 1 hour at 100°C; at lower temperatures the bismuth was leached gradually during a 5 hour retention period.

Effect of Oxidizing Agent

The effects of adding an oxidizing agent are shown in Table 4 and Figure 4. The chosen oxidizing agent, nitric acid, was added in concentrations of 0.4 g/l and 0.8 g/l. The latter was the maximum amount of which could be added to the slurry without the emission of NO and NO_2 fumes. When excess nitric acid equivalent to 6.0 g/l was added to the slurry, copious quantities of brown fumes evolved.

With 300 g/l HCl, at 50°C, 75°C and 100°C the addition of nitric acid had only a slight effect on the extraction of bismuth. Likewise, at 50°C and 75°C with 124 g/l HCl, the nitric acid had only a slight effect. At 100°C with 124 g/l HCl, the addition of 0.8 g/l HNO_3 had a marked effect, and the extraction of bismuth increased from 62% to 90%.

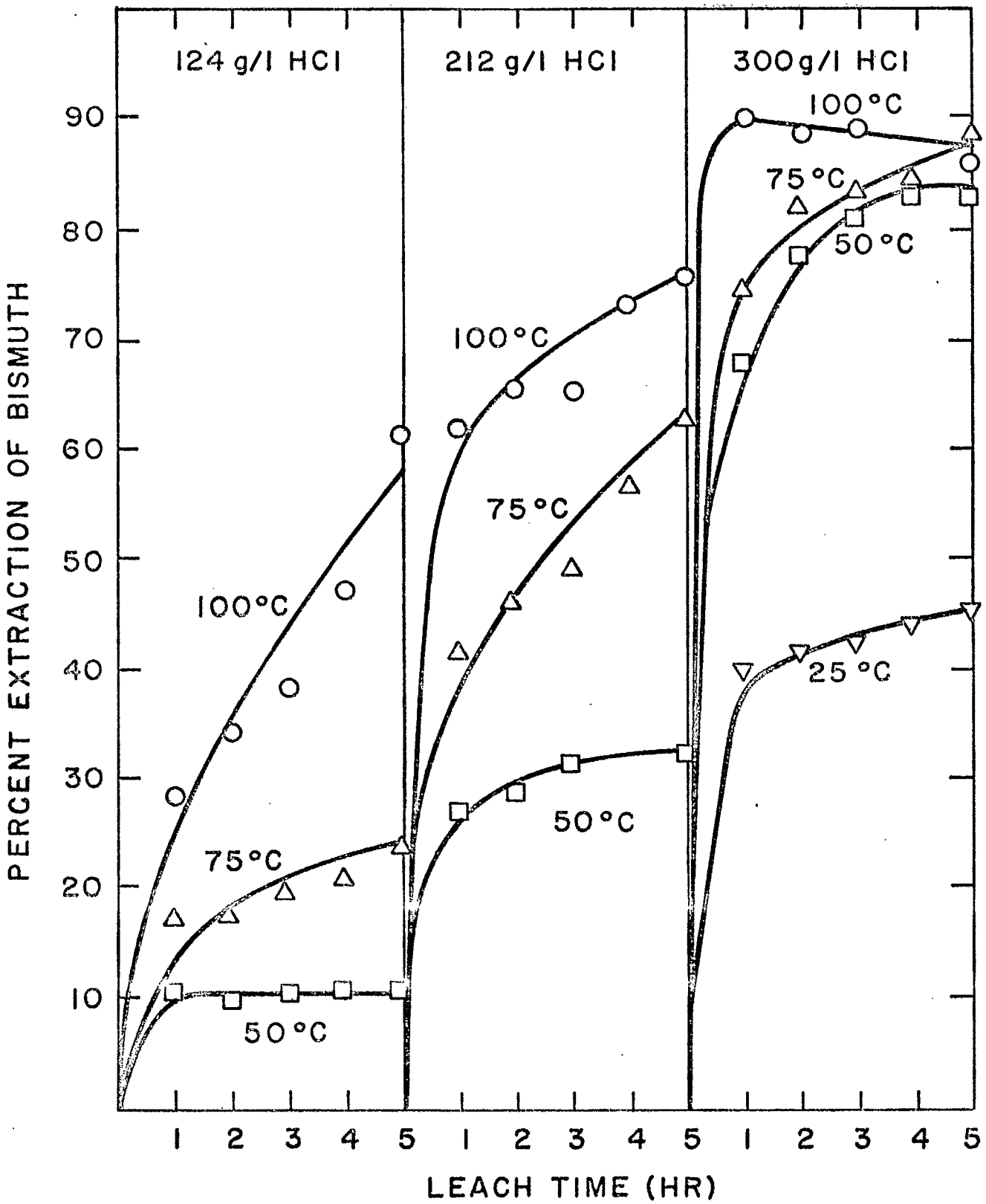

FIG. 3 EFFECT OF TEMPERATURE ON THE EXTRACTION OF BISMUTH

The effects of acid concentration, temperature and oxidizing agent are shown in Figure 4.

TABLE 4

Effect of Oxidizing Agent on Bismuth Extraction

Leaching Conditions					
HCl Concentration g/l	HNO g/l	Temp °C	Leach Time (hr)	Weight Loss %	Percent Extraction Bi
300	Nil	100	5	25	86
300	0.4	100	5	28	87
300	0.8	100	5	29	86
300	Nil	75	5	37	88
300	0.4	75	5	37	90
300	6.0	75	5	38	93
300	Nil	50	5	35	83
300	0.4	50	5	36	83
300	0.8	50	5	36	81
124	Nil	100	5	20	62
124	0.8	100	5	20	90
124	Nil	75	5	12	24
124	0.4	75	5	31	33
124	Nil	50	5	12	10
124	0.4	50	5	9	17
124	0.8	50	5	10	11

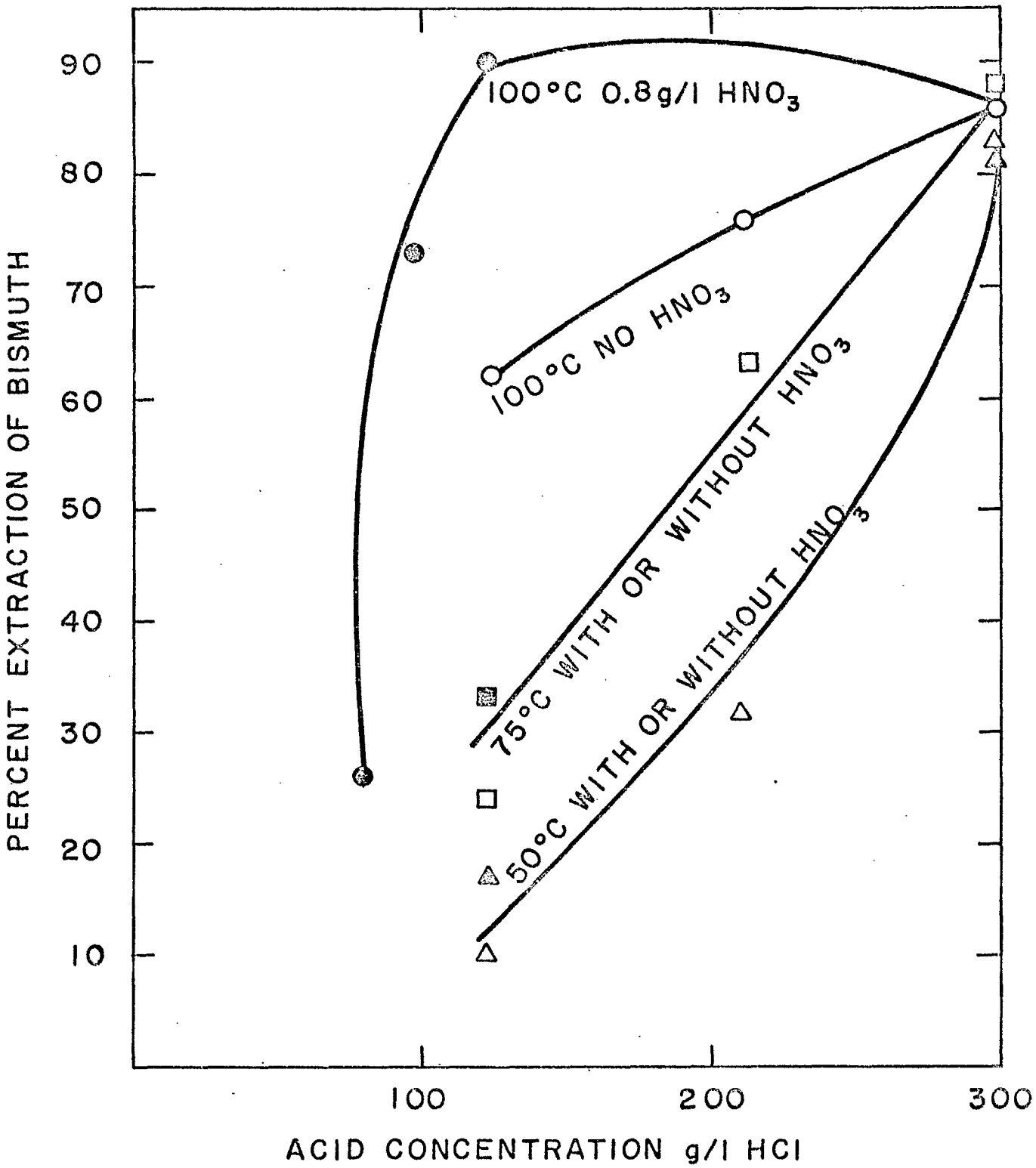

FIG. 4 EXTRACTION OF BISMUTH AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURES

Effect of Stirring Rate

The effect of the stirring rate on the extraction of bismuth is shown in Table 5. At the slow stirring rate of about 300-350 rpm, only about 54% of the bismuth was extracted. Stirring more rapidly, at a rate of about 550 rpm, resulted in a large increase in the extraction of bismuth to about 85%. A further increase of about 4% was gained by stirring at 900 rpm.

TABLE 5

Effect of Stirring Rate on Bismuth Extraction

Leaching Conditions					
HCl g/l	HNO_3 g/l	Temp °C	Retention Time (hr)	Stirring Rate rpm	Percent Extraction Bi
124	0.8	100	5	300-350	54
124	0.8	100	5	500-550	85
124	0.8	100	5	800-900	89

Extraction of Other Metals

The response of other metals to the leaching conditions is of interest. The leaching conditions under which the highest and lowest extractions were obtained are listed in Table 6. Also shown are the concentrations and percent extractions obtained with an excess of oxidizing agent. As is shown by the table, bismuth extraction varied from 10% to 90%. Only slight amounts of molybdenum and tungsten were leached under the conditions used. The extraction of zinc varied widely, from over 90% with strong acid to about 1% with weak acid; indium extraction varied from 42% to 1%. Between 40% and 25% of the iron

TABLE 6

Concentration in Solution and Percent Extraction of the Metals

Metal	Values obtained with 5 hours retention time	g/l	% Extraction	Leaching Conditions HCl g/l	HNO_3 g/l	Temp °C
Bismuth	Highest	3.90	90.0	124	0.8	100
	Lowest	0.44	10.5	124	Nil	50
	Excess HNO_3	4.06	96.6	300	6.0	75
Molybdenum	Highest	0.007	0.10	300	0-0.4	100
	Lowest	<0.001	-	300	Nil	75
	Excess HNO_3	0.008	0.11	300	6.0	75
Tungsten	Highest	<0.05	<2	-	-	-
	Lowest	<0.05	<2	-	-	-
	Excess HNO_3	<0.05	<2	300	6.0	75
Zinc	Highest	25.4	92.5	300	Nil	75
	Lowest	0.31	1.1	124	Nil	50
	Excess HNO_3	24.9	90.7	300	6.0	75
Indium	Highest	0.032	41.6	300	Nil	75
	Lowest	0.001	1.3	124	Nil	50
	Excess HNO_3	0.035	45.5	300	6.0	75
Arsenic	Highest	0.40	2.4	300	Nil	75
	Lowest	0.004	0.02	124	Nil	50
	Excess HNO_3	1.29	7.8	300	6.0	75
Copper	Highest	0.15	6.7	300	0.4	100
	Lowest	0.0002	0.009	124	Nil	50
	Excess HNO_3	0.21	9.4	300	6.0	75
Tin	Highest	0.034	3.3	300	0.8	100
	Lowest	0.006	0.6	124	Nil	50
	Excess HNO_3	0.077	6.6	300	6.0	75
Iron	Highest	3.35	40.0	300	0.4	100
	Lowest	2.10	24.7	124	Nil	50
	Excess HNO_3	4.25	50.0	300	6.0	75

dissolved. Less than 10% of the arsenic, copper and tin were extracted from the ore. The excess of nitric acid had only slight effect in increasing the extraction of bismuth, zinc and indium, but doubled that of tin from 3% to 6%, and increased the extraction of arsenic four-fold, from 2% to 8%. Copper extraction increased only slightly from 7% to 9% under the influence of excess nitric acid. It was observed that as the filtered pregnant liquors cooled, white crystals of lead chloride were deposited during a period of about a week.

Solution and Residue Analysis

The chemical analysis of the solution produced under the optium conditions of 124 g/l HCl, 0.8 g/l HNO_3 and 100°C, is shown in Table 7, and the residue analysis in Table 8. The mineralogy of the leach residue is compared with that of the concentrate in Table 8.

TABLE 7

Analysis of Solution Produced Under Optimum Leach Conditions

Leaching Conditions			Leach Liquor									
HCl	HNO_3	Temp.	Bi	Zn	Mo	In	W	Cu	Fe	As	Sn	HCl
g/l	g/l	°C	g/l	g/l	g/l	g/l	g/l	g/l	g/l	g/l	g/l	g/l
124	0.8	100	3.91	1.11	0.004	0.002	0.014	0.10	2.64	0.20	0.011	98

Retention time = 5 hours

TABLE 8

Comparison of Leach Residue* and Bulk Concentrate

Chemical Analysis

	Bi %	Zn	In	Mo	Cu	Fe	Sn	W	As
Concentrate	2.17	14.0	0.040	4.0	1.20	9.9	0.64	0.92	8.9
Residue	0.48	17.0	0.045	5.07	1.28	10.4	0.58	1.15	10.3

*Leach Residue obtained by leaching with 124 g/l HCl and 0.8 g/l HNO_3

Mineralogy**

	Bulk Sulphide Concentrate	Leach Residue
Major	Sphalerite (ZnS)	Sphalerite
	Molybdenite (MoS_2)	Arsenopyrite
	Arsenopyrite (FeAsS)	Molybdenite
Intermediate	Chalcopyrite ($CuFeS_2$)	Chalcopyrite
	Galena PbS	Tennantite
	Quartz	
Minor	Stannite (Cu_2FeSnS_4)	Wolframite
	Tennantite $(Cu,Fe)_{12}As_4S_{13}$	Rutile
	Bismuthinite Bi_2S_3	Cassiterite
	Pyrite FeS	
	Wolframite (Fe,Mm)WO_4	
	Rutile TiO_2	
	Cassiterite(SnO_2)	
	Bismuth Bi	
Trace	Graphite	Graphite

**Petruk, W. (4)

Acid Consumption

The amounts of acid consumed and the bismuth extracted, at various acid strengths, are shown in Table 9. The amount of acid consumed per ton of ore treated decreased with decrease in its initial concentration in the leach solution. However, the minimum acid consumption per lb of bismuth extracted was with 124 g/l HCl. More acid was consumed for each lb of bismuth extracted when the initial acid concentration was more than, or less than, 124 g/l HCl.

TABLE 9

Acid Consumption for Extraction of Bismuth

Acid Strength g/l HCl		Acid Consumed 100% HCl		Bismuth Extraction	
Leach Solution	Leach Liquor	lb/ton Ore	lb/lb Bi Ext'd	lb/ton	%
300	222	780	20	38	88
212	156	560	17	33	76
124	98	260	7	39	90
100	72	260	8	32	73
80	56	240	21	11	26

Discussion

The results of the experiments show that a minimum HCl cost, HCl acid consumption per pound of bismuth extracted, was achieved with a leach solution containing 124 g/l HCl and 0.80 g/l nitric acid, at a temperature of 100°C for a retention time of 5 hours.

Of the hydrochloric acid added at the beginning of the leach, 79% remained in the leach liquor, and 21% was consumed. If the bismuth is recovered from solution by the formation of

BiOCl by dilution, then the hydrochloric acid in the leach liquor is not recovered, and the whole amount must be calculated as reagent cost. On a tonnage basis, this amounts to approximately 3350 lb of 37% HCl for each ton of concentrate treated. This is roughly $77.00 per ton of concentrate, or about $2.00 per pound of bismuth extracted.

In the examination of other methods of recovering bismuth from solution, cementation by iron proved to be satisfactory (3). Since only a small amount of acid was consumed during cementation, the bismuth-free solution could be recycled and the overall acid consumption thereby greatly reduced.

A flowsheet entailing recycling of the solution after cementation is shown in Figure 5. To satisfy the volume balance, a "bleed" of approximately 77 gallons per ton of solids must be removed from the circuit. This bleed would contain about 75 pounds of HCl, which of necessity would be neutralized before disposal of the solution as waste. Thus, the acid consumed in the reaction, plus the acid discarded in the bleed would amount to about 900 pounds of 37% HCl to be added to the circuit as "make-up" acid. This would restore the leach solution to the strength of 124 g/l HCl. This "make-up" acid would cost about $21.00 per ton of concentrate treated, or about $0.55 per pound of bismuth extracted. Thus, with recycling after iron cementation a savings in acid cost is achieved of about $56.00 per ton of concentrate treated, or $1.45 per pound of bismuth extracted.

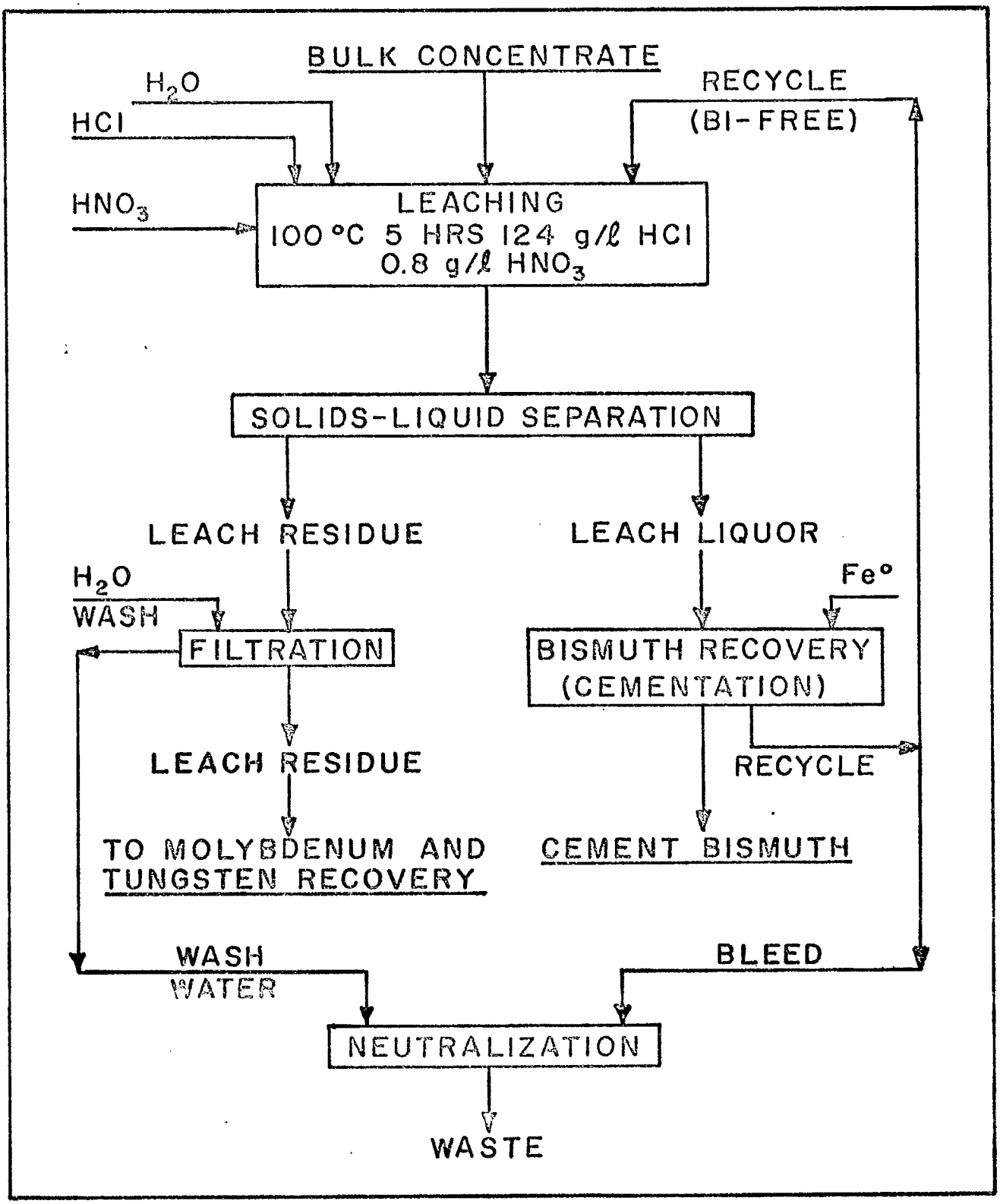

FIG.5 FLOWSHEET FOR EXTRACTION AND RECOVERY OF BISMUTH

CONCLUSIONS

1. The optimum conditions for leaching bismuth from the bulk sulphide flotation concentrate are: acid concentration 124 g/l HCl; temperature 100°C; oxiding agent (HNO_3) 0.80 g/l; retention time 5 hours. Under these conditions extraction of the bismuth from the concentrate is about 90%.
2. Under these conditions the acid consumption is 260 lbs 100% HCl per ton of ore treated, or 7 lbs 100% HCl per lb of bismuth extracted.

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