Copy 3

COMMONWEALTH OF AUSTRALIA

DEPARTMENT OF NATIONAL DEVELOPMENT
BUREAU OF MINERAL RESOURCES
GEOLOGY AND GEOPHYSICS

RECORDS:

1965/179

RECOVERY OF BISMUTH FROM CENTRAL BATTERY TAILINGS

(A.M.D.L. Report No. 256)

by

D.C. Madigan

RECOVERY OF BISMUTH FROM CENTRAL BATTERY TAILINGS

(A.M.D.L. Report No.256)

by

D.C. Madigan*

Records 1965/179

Table of Contents

---

* of the Australian Mineral Development of Laboratories, Adelaide.

Introduction

At the time this research project was sponsored there was already interest in the recovery of bismuth from ores from the Tennant Creek area. The Northern Territory Mines Branch, being about to cyanide sands from the Central Battery No.3 Dump, felt that it might be possible to recover some bismuth by a second (acid) leach of material, already being handled through leaching vats for gold recovery.

It was to examine this possibility that this project was carried out.

The report has been included in the Bureau's Record series so that it may have a wide distribution through the Bureau's "open file" system. It has not been altered in any way.

2/1/5

AMDL Report 256
June, 1963

RECOVERY OF BISMUTH FROM CENTRAL BATTERY TAILINGS

by

D. C. Madigan

to

BUREAU OF MINERAL RESOURCES

Investigated by: Metallurgy Section
Officer in Charge: P. K. Hosking

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Adelaide South Australia

CONTENTS

1. INTRODUCTION

The Northern Territory Mines Branch intends to leach the Central Battery No. 3 dump at Tennant Creek for gold in June, 1963. The gold content of the dump is stated by the Sponsor to be 5.3 dwt per ton and the bismuth content 0.37 per cent. Leaching is to be by percolation with cyanide solution, and it will be necessary for the sands and slimes of the dump to be broken up and mixed, loaded into a truck, and dumped and spread in the percolation vats. The residue after cyanidation is to be scraped out of the vats with an electrically operated scraper. It is estimated by the Mines Branch that two thirds of the treatment costs will be taken up by the acts of breaking, mixing, carting, dumping and scraping large quantities of material. The Mines Branch also considers that, with modifications to protect the vats against acid attack, the percolation plant could be used for an acid leach without any great increase in capital cost. Accordingly, if a suitable acid leaching process could be found, the recovery of bismuth, by acid leaching after cyanidation to extract the gold, might be profitable, since the greater part of the treatment cost is necessarily incurred by the gold extraction. The Bureau of Mineral Resources therefore requested an examination of the feasibility of percolation techniques for the recovery of bismuth from these tailings.

In addition to the sample of No. 3 dump sent for leaching tests, samples of two other Central Battery dumps were submitted for bismuth assay and spectrographic analysis.

2. SUMMARY

Leaching techniques were examined for the recovery of bismuth from a sample from Central Battery No. 3 dump at Tennant Creek, N.T., which contained 0.37 per cent of bismuth. Leach solutions containing sulphuric acid, sodium chloride and ferric chloride were investigated, and the results indicated that about 73 per cent of the bismuth could be extracted by percolation leaching with a solution containing:

a. 40 g of H_2SO_4 and 35 g of NaCl per litre,

or

b. 30 g of H_2SO_4 and 50 g of NaCl per litre.

The minimum quantity of solution (a) or (b) required to achieve the maximum extraction of bismuth (i.e., about 73 per cent) was 280 gallons per ton of ore, equivalent to 1.3 tons of solution (b) per ton of ore. No improvement in leaching efficiency was obtained by replacing sodium chloride with ferric chloride.

Samples of two other Central Battery dumps were sent for analysis. That marked "Central Battery Sands 1958 to 1962 including Orlando" contained 0.28 per cent of bismuth, and that marked "Central Battery Sands 1958 to 1962 excluding Orlando" contained 0.25 per cent of bismuth. Spectrographic analyses of these two samples are appended to this report.

3. MATERIAL EXAMINED

Three samples were received from Mr C. S. Muir, Acting Battery Manager, Central Battery, Tennant Creek, N. T., marked as follows:

i. Sample No. 3

ii. Central Battery Sands 1958 to 1962 including Orlando

iii. Central Battery Sands 1958 to 1962 excluding Orlando.

The bismuth content of these samples was:

	Bi %
Sample No. 3	0.37
Central Battery including Orlando	0.28
Central Battery excluding Orlando	0.25

A screen analysis of Sample No. 3 showed:

Mesh Size BSS	
+ 36	1.6
- 36 + 52	6.3
- 52 + 72	10.4
- 72 + 100	11.5
- 100 + 150	10.7
- 150 + 200	7.6
- 200 + 300	7.5
- 300	44.4
	100.0

Sample No. 3 was used for the leaching tests. The other two samples were submitted for analysis only, and the spectrographic analysis by Mr A. B. Timms is included as an appendix to this report.

4. EXPERIMENTAL PROCEDURE AND RESULTS

All percolation tests were made with 50 g portions of Sample 3 placed in a glass tube of 2.3 cm internal diameter. The tube was held vertically and the sample was supported on a disc of Whatman No. 540 paper placed on a rubber bung which was inserted into the lower end of the tube. A similar disc of filter paper was placed on top of the column of sample, and the leach solution was carefully run on to this from a pipette. The rubber bung had a hole through its centre, into which was inserted a glass drainage tube of 3 mm internal diameter, through which the percolate was collected. The depth of the sample bed in the percolation tube was approximately 3 in. The volume of liquid retained in the bed was 12.3 ml.

Leach solutions containing sodium chloride, ferric chloride and sulphuric acid were used. These were made by weighing out an appropriate quantity of salt, and adding a suitable volume of acid. The exact acid concentration was then determined by titration with standard alkali. The first series of tests, the results of which are given in Table 1, was designed to show the effect of the concentration of these reagents on bismuth extraction. The leaching time shown in Table 1 is the time from the first addition of leach solution until the last drop of effluent was collected. Flow was not always continuous during this time since, in some cases, the bed drained overnight, leaving no free liquor on top. Bismuth was determined in the effluent leach liquor and in the dried residue, and bismuth extraction has been calculated in two ways: (1) from the calculated head value, and (2) from a fixed head value of 0.37 per cent. The results of both calculations are shown in Table 1.

A second series of tests, the results of which are shown in Table 2, was made to determine the effect of contact time and volume of leach solution. The leach solution used contained 30.1 g of H_2SO_4 and 50 g of NaCl per litre. This solution was added in 12.3 ml portions to the 50 g bed of sample. No effluent was obtained from the first addition, since the volume of liquid retained in the bed was 12.3 ml. The second 12.3 ml portion of leach solution was added 1, 2, 3 and 4 days after the first in tests 21, 22, 23 and 24 respectively, and subsequently two more portions were successively added, each after the preceding portion had drained into the bed. The effluents obtained after each addition were kept separate and assayed for bismuth, as was the residue. Since the last addition remained in the bed, only three fractions were obtained, A, B and C. The bismuth extracted in each fraction was calculated as before in two ways, from calculated and fixed head values, but the difference was small and the average of these two calculations is shown in Table 2. Table 2 also shows the leaching time of each fraction, that is, the residence time of each fraction in the bed. This was calculated by assuming that, when one fraction was displaced by another, there was no mixing of the fractions, and by taking, as the end of the residence time of each fraction, the time half-way between the addition of the displacing fraction and the completion of its passage into the bed.

TABLE 1: PERCOLATION LEACHING OF SAMPLE 3 EFFECT OF REAGENT CONCENTRATION

Test No.	Leach Solution H_2SO_4 g/l	NaCl g/l	FeCl g/l	Volume of Effluent ml	Leaching Time hr	Bismuth Extraction 1(a)	2(b)
5	19.7	50	-	50	32	63.3	61.1
1	18.6	75	-	"	33	-	69.7
2	18.6	250	-	"	29	-	67.6
13	30.4	30	-	"	29	39.3	38.9
14	30.6	40	-	"	28	64.0	63.2
18	30.0	45	-	"	33	70.2	68.1
15	30.4	50	-	"	30	72.9	73.5
9	40.1	20	-	"	30.5	21.5	20.8
16	40.6	30	-	"	30	56.9	57.8
17	40.2	35	-	"	22.5	72.9	71.3
10	40.5	40	-	"	30	73.6	72.2
6	39.7	50	-	"	32	73.8	73.0
7	37.8	75	-	"	29.5	74.7	73.0
8	59.8	75	-	"	28	71.2	71.4
11	39.7	50	-	75	54.5	75.3	75.4
12	39.7	50	-	100	54.5	76.2	75.9
3	-	-	50.0	50	27.5	1.5	1.5
4	-	-	100.0	"	64	11.7	12.4
19	40.0	20	18.5	"	22	74.0	72.4
20	40.0	-	37.0	"	28.5	71.2	70.8

(a) 1. From calculated head.
(b) 2. From head = 0.37 %.

TABLE 2: PERCOLATION LEACHING OF SAMPLE 3
Effect of Contact Time and Reagent Volume

Test Number	Fraction			Total
	A	B	C	
	Bismuth Extraction, %			
21	9.8	31.5	21.3	62.6
22	7.2	33.7	17.1	58.0
23	11.3	34.4	27.1	72.8
24	4.6	34.4	30.1	69.1
	Leaching Time, hours			
21	28	7½	15	50½
22	50¼	4¾	67¾	122¾
23	77	24	24	125
24	99	6	17½	122½

5. DISCUSSION

5.1 Leaching with Sulphuric Acid and Sodium Chloride

The use of solutions of sulphuric acid plus sodium chloride for leaching a bismuth ore from Tennant Creek has been described by Woodcock[1], and his work formed the basis for the initial selection of leaching solutions (Tests 1 and 2). A plot of bismuth extraction against sodium chloride concentration at several acid strengths for a total effluent of 50 ml per 50 g of sample is shown in Figure 1, the results being taken from Table 1. As explained in Section 4, Table 1 gives the bismuth extraction based on calculated head values and on a fixed head value of 0.37 per cent Bi. The calculated head value is based on two bismuth estimations, in leach liquor and residue, and accumulates the errors of both; the use of a fixed head value on the other hand assumes even distribution of bismuth throughout the original sample; it therefore seemed best to take the average of these two values, and this has been plotted in Figure 1. It can be seen from Figure 1 that the maximum extraction of bismuth, about 73 per cent, was obtained with

(a) 40 g of H_2SO_4 + 35 g of NaCl per litre
or
(b) 30 g of H_2SO_4 + 50 g of NaCl per litre.

---

[1] Woodcock, J.T., Leaching of bismuth ore from the Jubilee mine, Tennant Creek, N.T., CSIRO Ore-Dressing Investigations, Report 615, Melbourne, June, 1961.

An increase of either constituent in (a) or (b) did not increase the extraction significantly, but a decrease reduced it.

In Tests 11 and 12 (Table 1), in which a leach solution containing 40 g of H_2SO_4 and 50 g of NaCl per litre was used, the volume of effluent per 50 g of sample was increased to 75 and 100 ml respectively, and a slightly higher extraction (75 to 76 per cent) was obtained, but it is not certain that the difference is significant. It therefore seems reasonable to take 50 ml per 50 g of sample as the upper limit to the volume of effluent required.

Woodcock (loc. cit.) reported that sulphuric acid and sodium chloride are roughly the same price, hence in the case where bore water already containing some chloride is to be used to make the leach solution, the preference is likely to be for solution (b) above. This solution was therefore used for the tests reported in Table 2, which were designed to determine the minimum volume of leach solution required, and the effect of contact time.

In these tests (Table 2), the bismuth content of the fractions showed no correlation with leaching time, and no advantage was gained by prolonging the contact of ore and leach liquor by allowing the ore bed saturated with leach liquor to stand for up to 4 days. The greater extraction in Tests 23 and 24 is due to the increased extraction in fraction C, which can hardly be ascribed to the time factor.

The second fraction B was the richest in bismuth, and contained more than 3 times the bismuth content of the first fraction A, which was the poorest. A possible explanation of this is that bismuth may be at first dissolved, but prolonged contact of the leach solution with the ore may result in some neutralisation of the acidity, with consequent precipitation of bismuth as an oxy-salt, which would readily be dissolved by a fresh portion of leach solution.

The total volume of leach solution added per 50 ml of sample in Tests 21 - 24 was 4 x 12.3 = 49.2 ml, of which 36.9 ml were collected as effluent. One further addition of 12.3 ml would have made a total effluent of 49.2 ml, very nearly the same as that of the majority of tests in Table 1. Test 15 (Table 1) may therefore be regarded as representing the final stage of these tests. Figure 2 shows a plot of bismuth extraction against effluent volume, the figures for the former being obtained from Table 2 by averaging the 4 results for each fraction, and from Test 15 of Table 1. Figure 2 shows that the minimum quantity of effluent required is about 50 ml. Hence, since the bed retains 12.3 ml, 62.3 ml of solution (b) are required per 50 g of Sample 3 to achieve maximum extraction. This is equivalent to about 280 gallons or 1.3 tons of leach solution per ton of ore, since the leach solution containing 30.1 g of H_2SO_4 and 50 g of NaCl per litre had a specific gravity of 1.0544 at 20°C.

5.2 Leaching with Ferric Chloride

The failure to extract more than about 75 per cent of the bismuth with the acid-salt mixture may be due to the presence of bismuth in a form not readily attacked by this reagent. While oxidised bismuth minerals may be expected to react readily with acids, this is not true of sulphides, and an attempt was therefore made to improve the extraction by leaching with ferric chloride which, owing to its oxidising power, has been used to leach sulphide minerals. Solutions of ferric chloride alone gave very low bismuth extraction (see Tests 3 and 4, Table 1), presumably because insufficient acid was produced by hydrolysis. In Test 19 half and in Test 20 all of the sodium chloride in the leach solution of Test 10, which contained 40 g of H_2SO_4 and 40 g of NaCl per litre, was replaced by the stoicheiometric equivalent of ferric chloride, but this made no significant difference to the extraction of bismuth. It may be concluded that it is the chloride ion that is the effective leaching agent, and the replacement of sodium by ferric ion is of no significance.

6. CONCLUSION

Bench scale percolation leaching tests indicated that about 73 per cent of its bismuth content could be extracted from the Central Battery No. 3 sample by a leach liquor containing 30 g of sulphuric acid and 50 g of sodium chloride per litre. The minimum quantity of leach liquor required was 280 gallons or 1.3 tons per ton of ore. It seems reasonable to suppose that similar results would be achieved by large-scale percolation leaching in the field.

If the bismuth recovery is considered sufficiently high to warrant percolation leaching after cyanidation, further work may be necessary on the precipitation and purification of the bismuth. The method of bismuth precipitation used will determine whether the barren leach liquor can be recycled.

It should be noted that, if acid leaching is applied after cyanide leaching for gold recovery, it will be necessary to take adequate precautions to avoid danger from liberation of hydrocyanic acid.

APPENDIX A

QUALITATIVE ANALYSIS BY EMISSION SPECTROSCOPY

%			Central Battery Sands 1958-1962	
			Including Orlando	Excluding Orlando
100	-	10	Si	Si
10	-	1	Al, Fe, Na, K	Al, Fe, Na, K
1	-	0.1	Mg, Mn, Bi, Ti	Mg, Mn, Bi, Ti
0.1	-	0.01	Zn, Cu, Mo, Rb	Zn, Cu, Mo, Rb
0.01	-	0.001	Pb, Ni, Sn, V, Ca, Li	Pb, Ni, Sn, V, Ca, Li
0.001	-	0.0001	Co, Ag, Ga, Ba, Sr, B	Co, Ag, Ga, Ba, Sr, B

As and P were not sought. Other elements were not detected at limits quoted overleaf.

Spectrographic Analysis by: A. B. Timms

Officer in Charge, Analytical Section: T.R. Frost

SPECTROGRAPHIC ANALYSES

Detection-Limit Concentrations of Elements

D. C. Arc Excitation

ELEMENT	Per cent	ppm	ELEMENT	Per cent	ppm
Ag	0.00005	0.5	Na	0.00005	0.5
Al	0.0002	2	Nb	0.003	30
As	0.01	100	Nd	0.001	10
Au	0.001	10	Ni	0.0002	2
B	0.001	10	Os	0.005	50
Ba	0.0002	2	P	0.02	200
Be	0.0005	5	Pb	0.0002	2
Bi	0.0005	5	Pd	0.001	10
Ca	0.0002	2	Pr	0.001	10
Cd	0.001	10	Pt	0.005	50
Ce	0.04	400	Rb	0.0001	1
Co	0.0002	2	Re	0.01	100
Cr	0.0001	1	Rh	0.001	10
Cs	0.0002	2	Ru	0.001	10
Cu	0.00005	0.5	Sb	0.002	20
Dy	0.001	10	Sc	0.0002	2
Er	0.001	10	Si	0.002	20
Eu	0.001	10	Sm	0.05	500
Fe	0.0005	5	Sn	0.001	10
Ga	0.0003	3	Sr	0.0001	1
Gd	0.02	200	Ta	0.01	100
Ge	0.0002	2	Tb	0.001	10
Hf	0.01	100	Te	0.02	200
Hg	0.01	100	Th	0.01	100
Ho	0.001	10	Ti	0.001	10
In	0.0001	1	Tl	0.0001	1
Ir	0.005	50	Tm	0.001	10
K	0.0002	2	U	0.02	200
La	0.001	10	V	0.0005	5
Li	0.0001	1	W	0.005	50
Lu	0.001	10	Y	0.001	10
Mg	0.0002	2	Yb	0.001	10
Mn	0.001	10	Zn	0.0025	25
Mo	0.0005	5	Zr	0.001	10

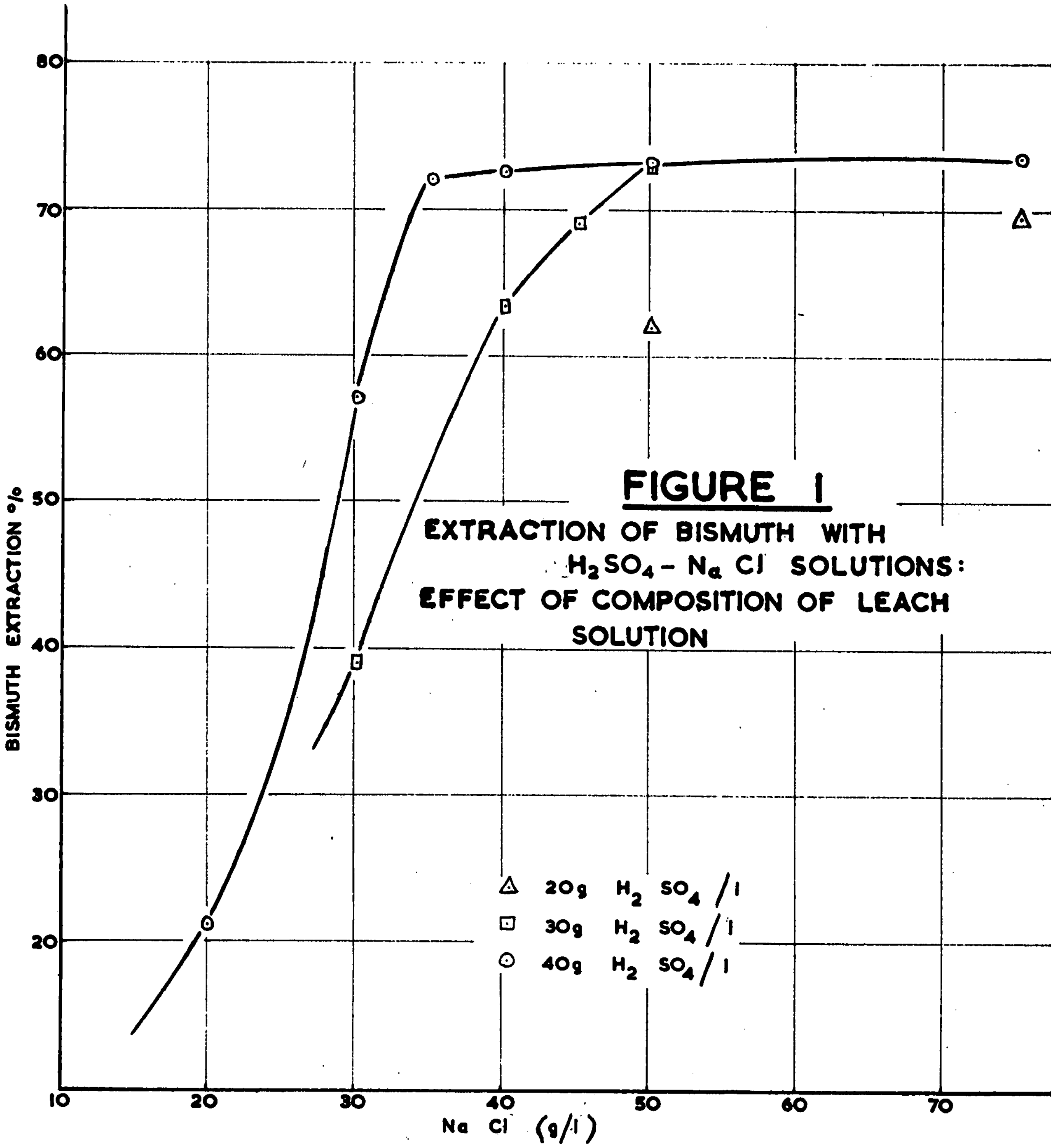

FIGURE 1

EXTRACTION OF BISMUTH WITH H_2SO_4 - NaCl SOLUTIONS: EFFECT OF COMPOSITION OF LEACH SOLUTION

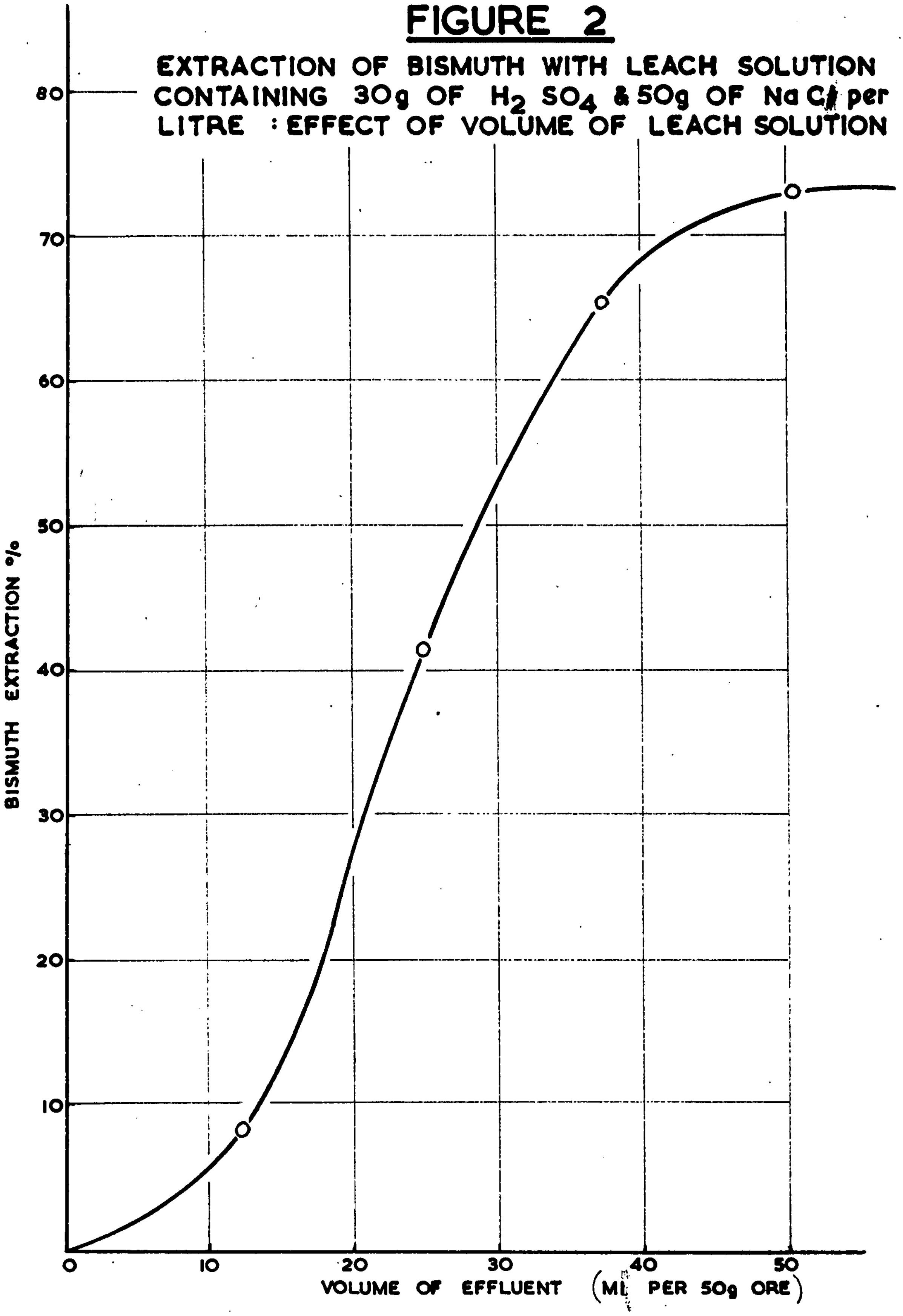

FIGURE 2

EXTRACTION OF BISMUTH WITH LEACH SOLUTION CONTAINING 30g OF H_2SO_4 & 50g OF NaCl per LITRE : EFFECT OF VOLUME OF LEACH SOLUTION