

FLOTATION OF BISMUTHINITE
FROM A BISMUTH-COPPER ORE

A Thesis Submitted for the Degree of M.Phil.

in

The University of London

by

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September 1970

ABSTRACT

The thesis consists of two parts. In part 1, the study of the treatment of a bismuth-bearing copper ore from Shinhoong mine, Korea, was carried out for the purpose of obtaining from it an economically attractive copper and bismuth concentrate. The mineralization is mainly a fine dissemination of sulphides in silicates. The copper is present mainly as chalcopyrite and the bismuth, as identified by electron micro-probe analysis, as a lead-bismuth mineral, which is known to be a less important bismuth mineral. Recoveries of 93% Cu and 75% Bi were obtained with grades of 25% Cu and 3.3% Bi.

In part II, the effect of potassium ethyl, amyl and hexyl xanthate, diethyldithiocarbamate and diethyldithiophosphoric acid, and the influence of potassium dichromate with amyl xanthate on the contact angle at the bismuthinite surface have been investigated.

The behaviour of bismuthinite in water is related to its crystal structure which permits reversible development of ionic sites in alkaline solutions with complete loss of contact angle.

Potassium ethyl xanthate, diethyldithiocarbamate and diethyldithiophosphoric acid have a very low affinity for bismuthinite forming very low contact angles. Evidently those three collectors are not useful for bismuthinite.

Potassium amyl and hexyl xanthates have a very high affinity

for bismuthinite forming contact angles of 60° - 74° . 20mg per litre of potassium amyl xanthate was found to be a critical concentration which produces the maximum contact angles over the pH range 3.0 to 6.0.

It was found that potassium dichromate is an effective depressing agent in a bismuthinite-xanthate system in acid solution. The mechanism of bismuthinite depression by dichromate is suggested to be due to the easy oxidizability of bismuthinite and the formation of a hydrophilic film of $(\text{BiO})_2 \text{Cr}_2 \text{O}_7$ on its surface.

ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to Dr. O. Mellgren for his valuable guidance and encouragement throughout the course of this work; also to Professor M.G. Fleming and Drs. J.A. Kitchener and E. Cohen for their encouragement and many helpful suggestions.

He would like to thank Dr. J. Gavrilovic for his guidance and other members of the academic and technical staff of the Department of Mining and Mineral Technology for their useful suggestions and frequent assistance.

He is also indebted to the Ministry of Overseas Development and the British Council for financial support during the period of this work, and to the Korean Government and the Chon-Nam National University in Korea for leave of absence during his stay in the United Kingdom.

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P A R T I

TREATMENT OF BISMUTH-BEARING
COPPER ORE

1. INTRODUCTION

The ore sample originated from Kohoong-Koon, Chon-Nam, Korea and it was provided by the Shinhoong Mining Company. The ore body owned by this company contains predominantly sulphide copper together with bismuth mineral.

Mining operations were terminated in 1967 because difficulties arose in beneficiation of the ore. The said mining company was in need of proper mineralogical examinations of the ore to determine the compositions and liberation characteristics of sulphide minerals, and also a suitable procedure for the beneficiation of the ore to produce saleable products.

The method of concentration applied to sulphide ores of copper depends upon the associated metals, upon smelter contracts and freight rates available, rather than upon limitations imposed by concentration technology. Flotation is the basic method in all cases, and a substantially clean copper-sulphide concentrate can be made.

It has been known (57) that workable copper ores normally range from 0.8% copper upward, although few run higher than 6 to 7%. Recoveries range from 85 to 90% of the sulphide copper with the low-grade ores, and from 90 to 97 for the higher-grade feeds. Sulphide tailing on low-grade feeds ranges from 0.05 to 0.1%; or from 0.2 to 0.3% with high-grade feed. The grade of concentrate ranges from 35 to 50% Cu when chalcocite is the principal copper mineral and

iron bearing minerals are eliminated; corresponding grades for chalcopyrite are 25 to 30%. When little attempt is made to remove iron bearing minerals, either because of its saleability or because of gold content, grade run down to 10 to 15% Cu.

Little of the bismuth produced is the result of mining, concentration, and metallurgical procedures operated specifically for the recovery of this metal (8). Generally, bismuth is recovered as a by-product of the smelting operations by which tin, lead, copper and silver are produced (78)(79)(8). For example, the ore mined by Ikuno mining company (9), in Japan, contains 0.01% Bi as bismuthinite is not treated to recover the bismuth as the main product. Bismuth is, however, concentrated to about 0.1-0.2% Bi in the copper and lead concentrates by flotation, and is then recovered as a by-product of the smelting of these concentrates.

It was with these considerations that the present project was undertaken, the object of this investigation was intended to:

- (i) Establish the mineralogical and textural composition of the ore.
- (ii) Establish the liberation characteristics of the sulphide minerals and their differences in rates of comminution.
- (iii) Investigate the applicability of flotation in providing saleable mineral concentrates.

2. MINERALOGICAL ASSESSMENT OF THE ORE SAMPLE

2.1 Description of the Sample

The ore sample used in this research work was received from Sinhoong Mining Company of Korea. Sample for the study was taken from a large stock of ore covered with canvas. The exact location of the stockpile is unknown.

A total of 36 Kg of the ore was received the particle size of which was 4 to 5 inches. Some fine material was found at the bottom of the container. This presumably originated as a result of transportation (long journey) and due to the friable nature of the ore. The principal feature noted during examination was the fairly uniform distribution of most sulphides, particularly chalcopyrite.

2.2 Mineralogical Examination

In the first part of this study attempts were made to identify all valuable components of the ore as well as gangue minerals. This was followed by determination of other factors important in mineral technology such as texture, size distribution and liberation study.

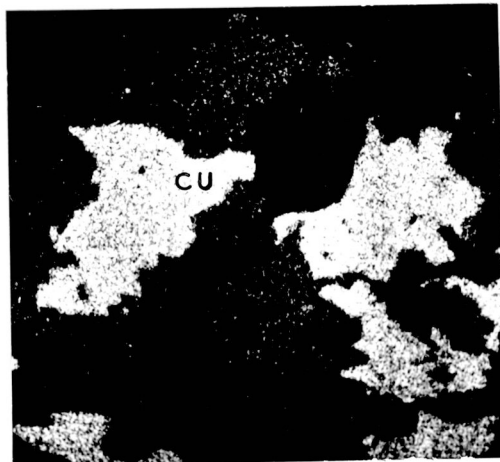
Eight lumps were chosen to represent the different constituents, structures, grain size and textures of the ore. Two slices of each lump were cut and one was used as a polished surface.

Eight polished specimens were examined by optical microscopy and, in some cases, by electron-probe micro analysis. The copper bearing mineral was found to be mainly chalcopyrite. Other sulphide minerals identified in the specimens were pyrite, arsenopyrite and

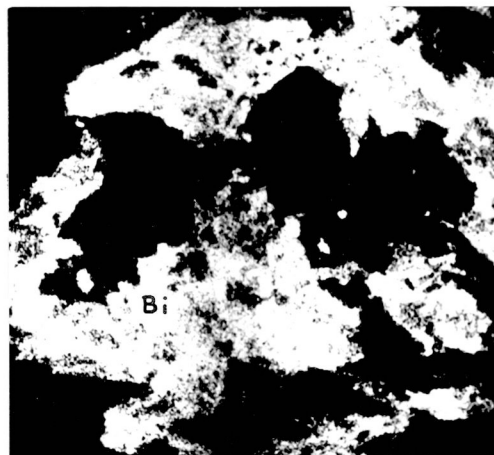
sphalerite. Of these arsenopyrite and particularly sphalerite were present in very small quantities.

Identification of lead-bismuth mineral was not easy by reflected light because of the variable polishing characteristics of that mineral. Microprobe analysis was thus used for positive identification of the Bi-Pb bearing minerals. Some of the phases in the ore shown in plate 1 and electron images of the different elements are shown in Figure 1a-f. Chemical composition of this mineral was also established on the electron probe microanalyser. A number of Pb-Bi and Pb-Cu-Bi sulphide minerals are reported in the literature (29) and some of their properties are given in Table 1. All these minerals are similar in composition and there are strong indications that the present ore contains the whole range of minerals starting from low Pb and high Bi chiviatite down to galenobismutite and possibly cosalite where the lead content is high.

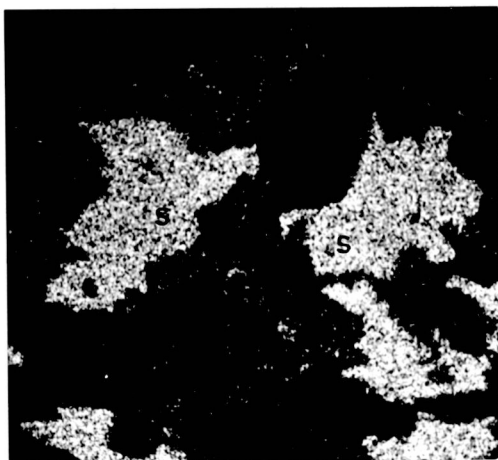
The structures and features of these minerals are shown in the following photomicrographs (plates 1 to 8). Generally, most of the photomicrographs indicate a lack of structural discontinuity at the boundaries between the different minerals, particularly in plates 1 and 2. In most of the samples Bi-Pb minerals were finely intergrown with chalcopyrite (see plates 1 and 2) and included quartz (see plates 2 and 3). The principal gangue minerals are quartz and mica. Pyrite occurs in general on grains mixed with chalcopyrite (see plates 4 and 5). Chalcopyrite is finely disseminated with Bi-Pb



(a) Cu



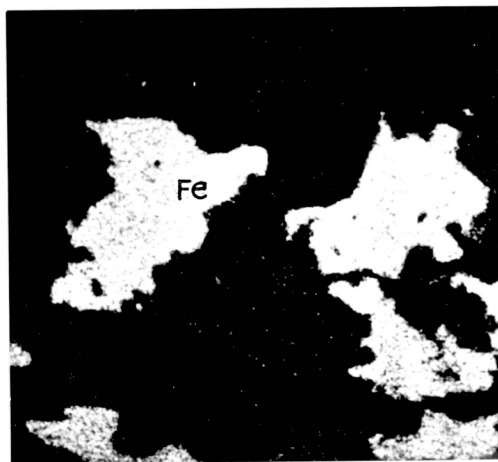
(b) Bi



(c) S



(d) Pb



(e) Fe



(f) Si

Fig. 1 Electron-probe photographs showing a section containing Cu, Bi, S, Pb, Fe and Si.

Table 1. Characteristics of Lead-Bismuth Minerals

Name and Chem. Composition	% Bi	% Pb	% S	Colour	S.G.	Hardness	Occurrence and others
Chiviatite $\text{PbS } 2\text{Bi}_2\text{S}_3$	65.95	16.35	17.70	lead grey			Foliated massive. Microscopic study of material from this locality showed it to be a mixture of bismuthinite and various copper minerals.
Platynite $\text{PbS Bi}_2\text{S}_3$	55.48	27.50	17.02	colour like graphite	7.98	2 - 3	Basal and rhombohedral cleavages Streak shining.
Galenobismutite $\text{PbS Bi}_2\text{S}_3$ Also with Ag, Cu.	55.48	27.50	17.02	Lead grey	6.90		Occurs with bismutite at Nordwark, Vermland, Sweden, where it sometimes carries gold. The seleniferous variety is from Falun, Sweden. Material from Quartzburg district, Boise Co., Idaho, yields on analysis the sample formula. However, much that has been called galenobismutite is shown on microscopic study to be a mixture of ² cos ₂ l ₂ ite, sphalerite, and bismuth.
Bismutoplagionite $5\text{PbS } 4\text{Bi}_2\text{S}_3$	51.40	31.85	16.75	faintly bluish lead-grey	5.35	2 - 8	In needle-like crystals and possibly orthorhombic. Found in Montana.
Hammarite $5\text{PbS } 3\text{Bi}_2\text{S}_3$	45.78	37.83	16.37	steel grey		3 - 4	Nonoclic. In short prisms or needles. Cleavage is good. Streak black. Found on quartz at Gladhammar, Sweden.

Table 1 (cont.)

Name and Chem. Composition	% Bi	% Pb	% S	Colour	S.G.	Hardness	Occurrence and others
Cesalite $2\text{PbS Bi}_2\text{S}_3$	42.11	41.74	16.15	lead-steel	6.39- 6.75	3	Usually massive, fibrous or radiated. Originally found in a silver mine at Casala, Mexico. In Ontario from McElory township (originally reported as galenobismutite) and from cabalt district.
Lillianite $3\text{PbS Bi}_2\text{S}_3$	33.93	50.46	15.61	steel-grey	7.0	2 - 3	Orthorhombic. Crystalline and massive.
Goongarrite $4\text{PbS Bi}_2\text{S}_3$	28.41	56.34	15.25		7.23	3	Monoclinic. Fibrous to platy. Two good cleavage.
Beegerite $6\text{PbS Bi}_2\text{S}_3$	21.44	63.76	14.80	light to dark-grey	7.27		Cubic cleavage and therefore probably isometric. In Colorado at two localities in Park Co., from Poufheepsie Gulch, Quarry Co.

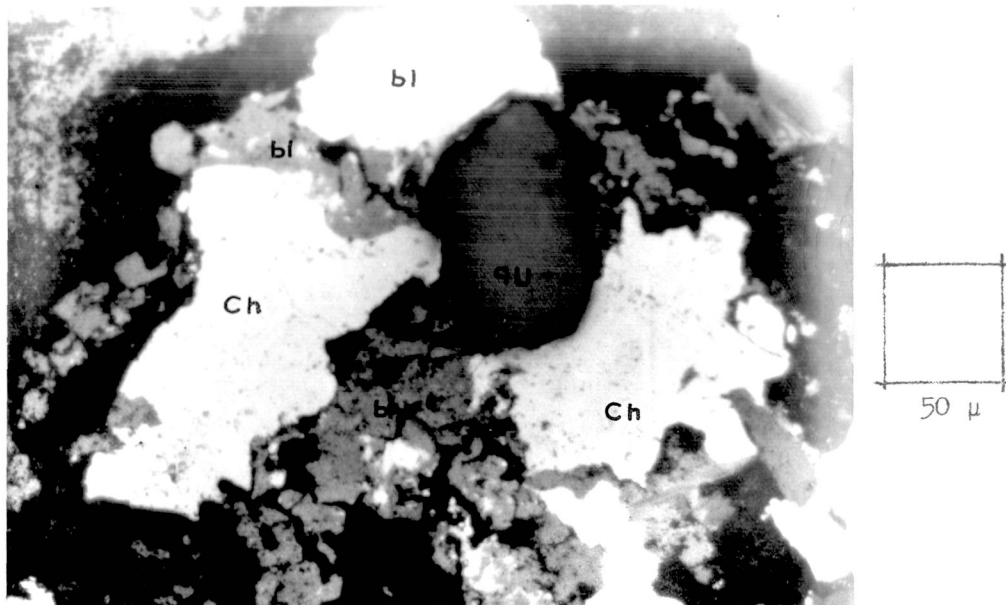


Plate 1 - (320X) A quartz (qu) grain surrounded by chalcopyrite (Ch) and Bi-Pb mineral (bl) with inclusion of quartz (qu).

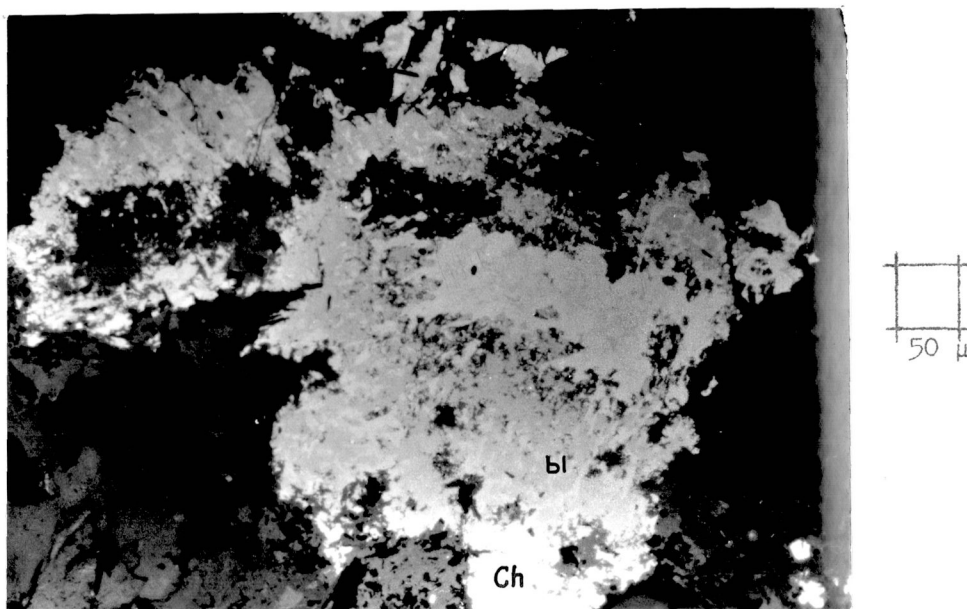


Plate 2 - (176X) Gray area of Bi-Pb mineral (bl) is disseminated with white area of chalcopyrite (Ch) against a dark background of gangue matrix.

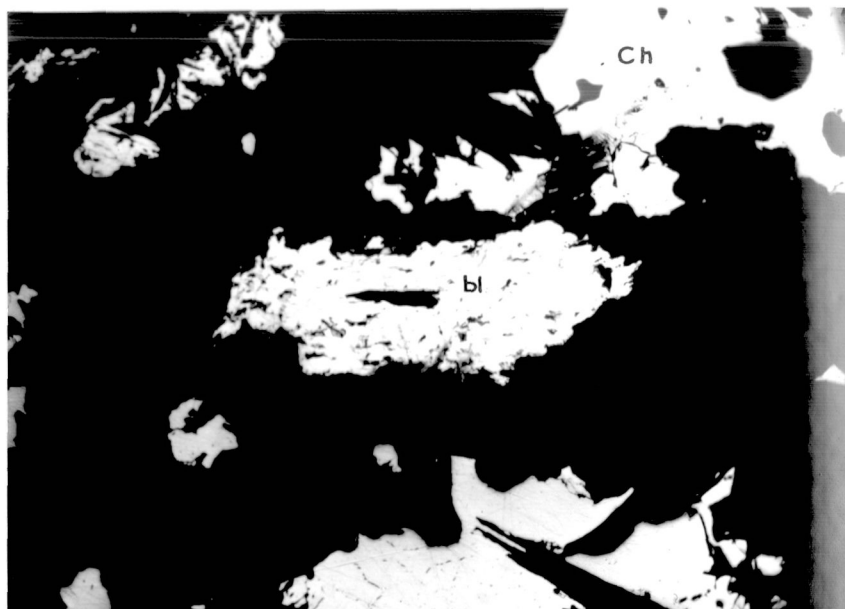


Plate 3 - (208X) White area of Bi-Pb mineral (bl) surrounded by dark area of quartz (qu) included a dark grain of quartz in centre.

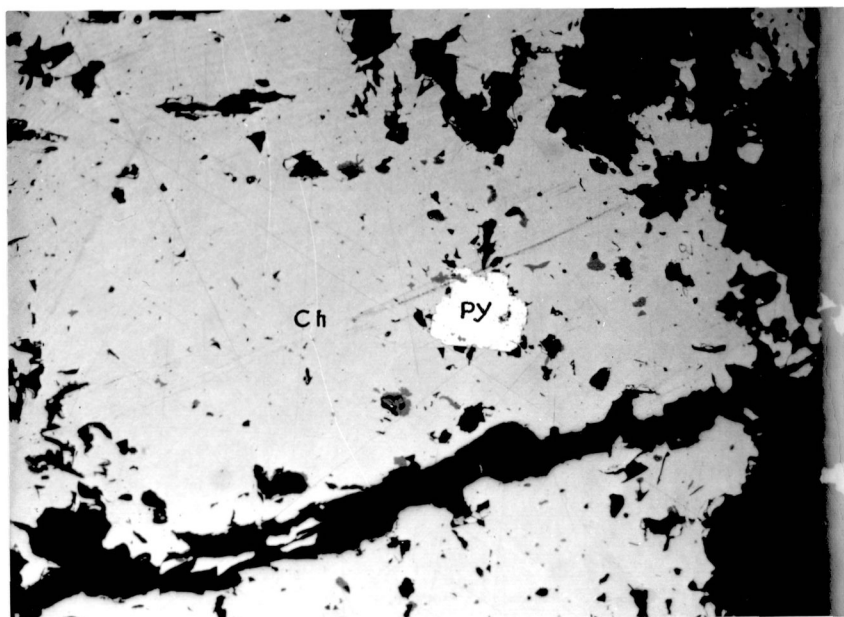


Plate 4 - (160X) A pyrite (Py) grain rimmed by chalcopyrite (Ch) with inclusion of dark area of quartz (qu).

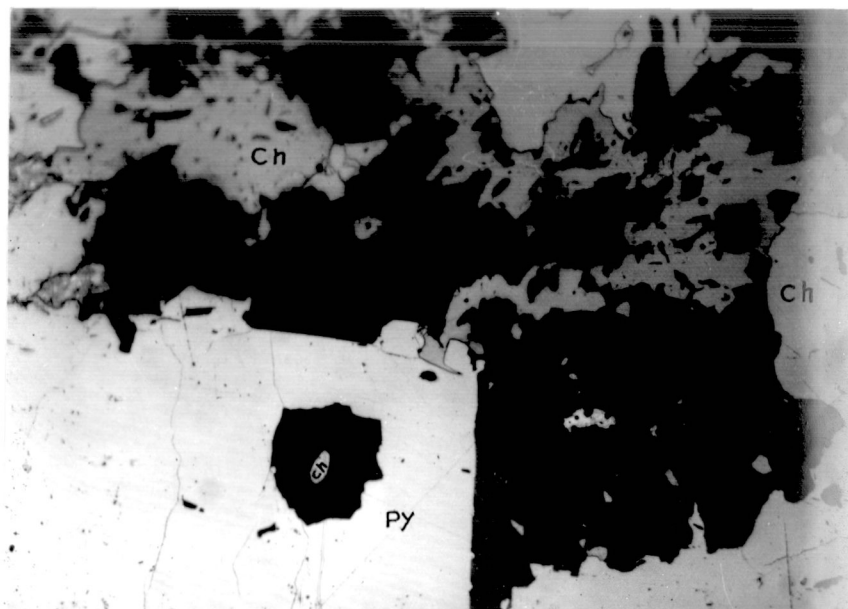


Plate 5 - (160X) Dark area of quartz (qu) rimmed by pyrite included a chalcopyrite (Ch) grain.



Plate 6 - (160X) Dark area of quartz (qu) surrounded by chalcopyrite (Ch) included a grain of chalcopyrite (Ch).

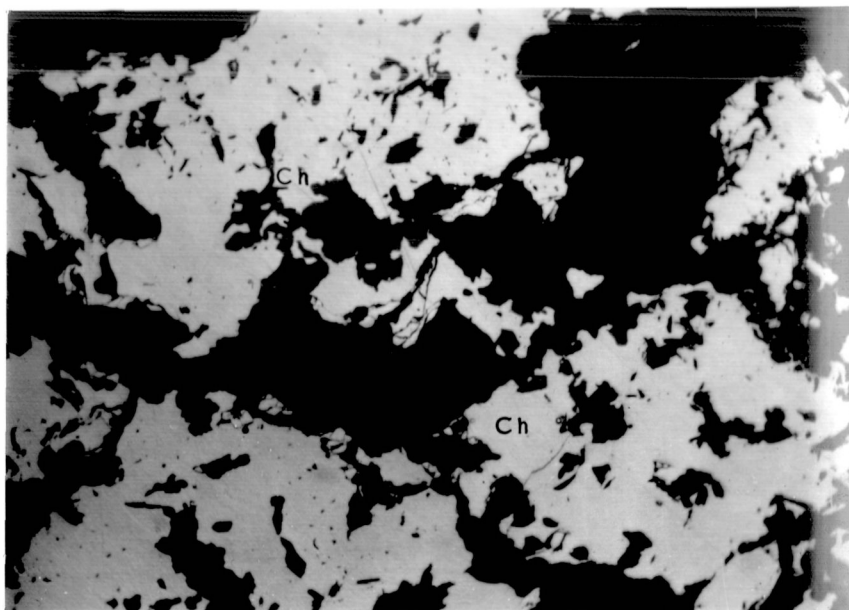


Plate 7 - (160X) Dark area of quartz (qu) disseminated with gray area of chalcopyrite (Ch) and fine inclusions of dark gray area of sphalerite (sp).

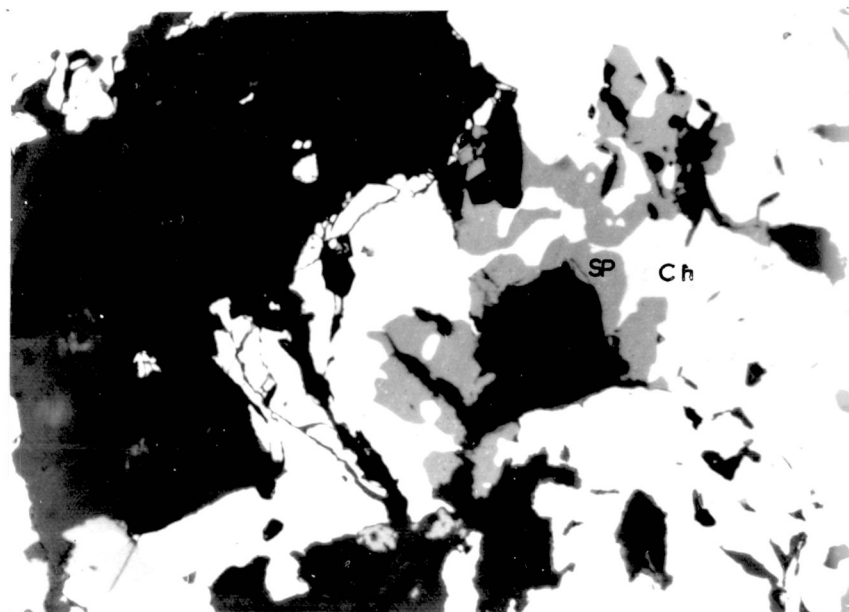


Plate 8 - (400X) The dark grey area of sphalerite (sp) is interlocked with grey area of chalcopyrite (Ch) and black area of quartz (qu).

mineral in a matrix of quartz (see plates 1 and 2). Although chalcopyrite was found almost free of association with pyrite (see plates 4 and 5), high porosity was observed (see plates 4 and 6). Small grains of chalcopyrite enclosed in quartz, which in turn is surrounded by either pyrite or chalcopyrite, were found (see plates 5 and 6). Sphalerite was found as small inclusions in chalcopyrite; it was seen in very small amounts and was always associated with quartz (see plates 7 and 8).

2.3 Sample Preparation

The original bulk of the sample as received was screened and the size distribution is shown in Table 2.

A close examination of the results obtained for plus 10 mesh particles of the ore, in each fraction, showed that all of the particles contained some sulphide. From a few selected hand specimens it was estimated that the maximum size of sulphide grains (mainly chalcopyrite) was less than 0.1-0.2 cm. Therefore it was decided to reduce the size of the ore particle down to minus $\frac{1}{4}$ inch - safely above any possible liberation size.

The sample was crushed in closed circuit in a laboratory jaw crusher set at 1 inch.

Visual inspection of the minus $\frac{1}{4}$ inch plus 7 mesh sizes showed that the gangue was still closely associated with sulphide minerals. These minus $\frac{1}{4}$ inch plus 7 mesh fractions were treated in tetrabromethane and examined. On the basis of microscopic studies and

Table 2

Size distribution of head sample

Size B.S.S. Mesh	Weight (g)	Weight (g)	Cumul. % wt, finer
-5" + 1"	32396.0	89.77	100.00
-1" + $\frac{1}{2}$ "	1581.5	4.38	10.23
- $\frac{1}{2}$ " + $\frac{1}{4}$ "	497.0	1.38	5.85
- $\frac{1}{4}$ " + $\frac{1}{8}$ "	337.0	0.93	4.47
- $\frac{1}{8}$ " + 7	139.3	0.39	3.54
-7 + 10	143.5	0.40	3.15
-10 + 14	109.3	0.30	2.75
-14 + 18	109.6	0.30	2.45
-18 + 25	115.2	0.32	2.15
-25 + 36	115.0	0.32	1.83
-36 + 52	90.1	0.25	1.51
-52 + 72	82.6	0.23	1.26
-72 + 100	74.4	0.21	1.03
-100 + 150	67.8	0.19	0.82
-150 + 200	58.7	0.16	0.63
-200	168.8	0.47	0.47
Total	36085.8		

tetrabromethane treatment (20) of these fractions, it was decided to reduce further to minus 7 mesh. The procedure of crushing used is shown in the flow diagram in Fig.2.

Crushed sample was mixed well, coned, quartered and finally it was split by means of rotating cascade sampler to approximately 500 g fractions. Each split fraction was stored in plastic bags.

Gy's sampling formula was used to determine the necessary sample weights using 0.05% as the permissible error. This indicated that 200 g was a sufficient sample weight for minus 7 mesh material.

2.4 Chemical Analysis

A 500 g representative sample ground to -200 mesh in a Tema mill was prepared for analytical purposes. Part was sent to Analytical Services of the Royal School of Mines for a qualitative elemental analysis by the X-ray fluorescence method. The elements detected and their approximate concentrations were as follows:

Major elements : Cu, Fe, K, Si, Al. ($\geq 1\%$)

Minor elements : Ba, Te, Sn, Ag, Bi, Pb, Zn, Mn, Ti, S. ($< 1\%$)

From the results of these analyses eight elements, (Cu, Bi, Pb, Zn, Fe, K, Al and Si), which are in large quantity were analysed quantitatively by the X-ray fluorescence method.

The four elements Cu, Bi, Fe, and Zn were also analysed quantitatively by atomic absorption spectroscopy.

The results of these assays are shown in the following table.

Assay method Constituents	X-ray fluorescence	Atomic absorption
Cu	3.45 %	3.35
Bi	0.73 %	0.70
Pb	0.54 %	-
Zn	0.13 %	0.14
Fe	5.90 %	4.28
K	3.00 %	-
Al	11.00 %	-
Si	38.00 %	-

Details of the analytic methods by atomic absorption spectroscopy is given in Appendix 1.

2.5 Determination of Soluble Minerals

The percentage of soluble copper minerals in the ore sample was determined by treating the sample in water, sulphuric acid and ferric sulphate solution. These copper minerals include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), Cu present as CuO and CuSiO_3 and chalcocite (Cu_2S).

Their solubilities, however, in water, sulphuric acid and ferric sulphate are different. Chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is soluble in water (27). Tenorite (CuO) and chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$) are soluble in sulphuric acid. Chalcocite (Cu_2S) is soluble in ferric sulphate (29).

This method was not very accurate because part of the dissolved copper would be precipitated by pyrite. Therefore, it

would give values for the water-soluble Cu slightly lower than the actual amount of copper sulphate present in the ore. The presence of pyrite and O_2 in leaching system with H_2SO_4 would produce some ferric sulphate which dissolves part of the chalcocite and increases the amount of acid-soluble copper. The introduction of air into the pulp was reduced by using a low rate of stirring.

The apparatus used in this experiment consisted of a 500 ml beaker and a constant speed stirrer. A sample of 100 g ground to -200 mesh (B.S.S.) with "Tema" mill was added to 450 ml of distilled water. After it was stirred for 5 minutes, the stirrer was stopped for 10 minutes to allow the solids to settle out and then a 5 ml sample of the solution was taken by a pipette and replaced by an equivalent amount of fresh distilled water. The pH of the solution was about 6.5. After five samples had been taken according to the same procedure, concentrated sulphuric acid was added ($pH\ 1.0 \pm 0.2$). After taking another five samples, 10 g of ferric sulphate, $Fe_2(SO_4)_3 \cdot 9H_2O$, was added and five samples were taken again. The samples were assayed for Cu and Bi by atomic absorption spectroscopy. Results are shown in Table 3 and Fig.3.

These results showed that about 0.9% of total copper present in the sample was in a water-soluble form, i.e. as chalcocite. 1.98% of total copper is soluble in water and sulphuric acid. Only 2.97% of total copper is soluble in ferric sulphate through water and sulphuric acid.

Bismuth was not soluble in water but soluble in the sulphuric

Table 3. Solubility of Cu and Bi

Leaching time (min.)	Solvent	Cu		Bi	
		Assay %	% of total Cu	Assay %	% of total Bi
5	H ₂ O	0.032	0.90	0.	0.
10		0.031	0.88	0.	0.
15		0.029	0.82	0.	0.
20		0.027	0.76	0.	0.
25		0.027	0.76	0.	0.
30	H ₂ SO ₄ (pH 1.0)	0.046	1.30	0.343	50.37
35		0.057	1.61	0.364	53.45
40		0.063	1.78	0.375	55.07
45		0.069	1.95	0.375	55.07
50		0.070	1.98	0.364	53.45
55	Fe ₂ (SO ₄) ₃	0.102	2.88	0.443	65.05
60		0.105	2.97	0.461	67.69
65		0.107	3.02	0.461	67.69
70		0.105	2.97	0.461	67.69
75		0.105	2.97	0.461	67.69
Insoluble		3.433	97.03	0.220	32.31
Total		3.538	100.00	0.681	100.00

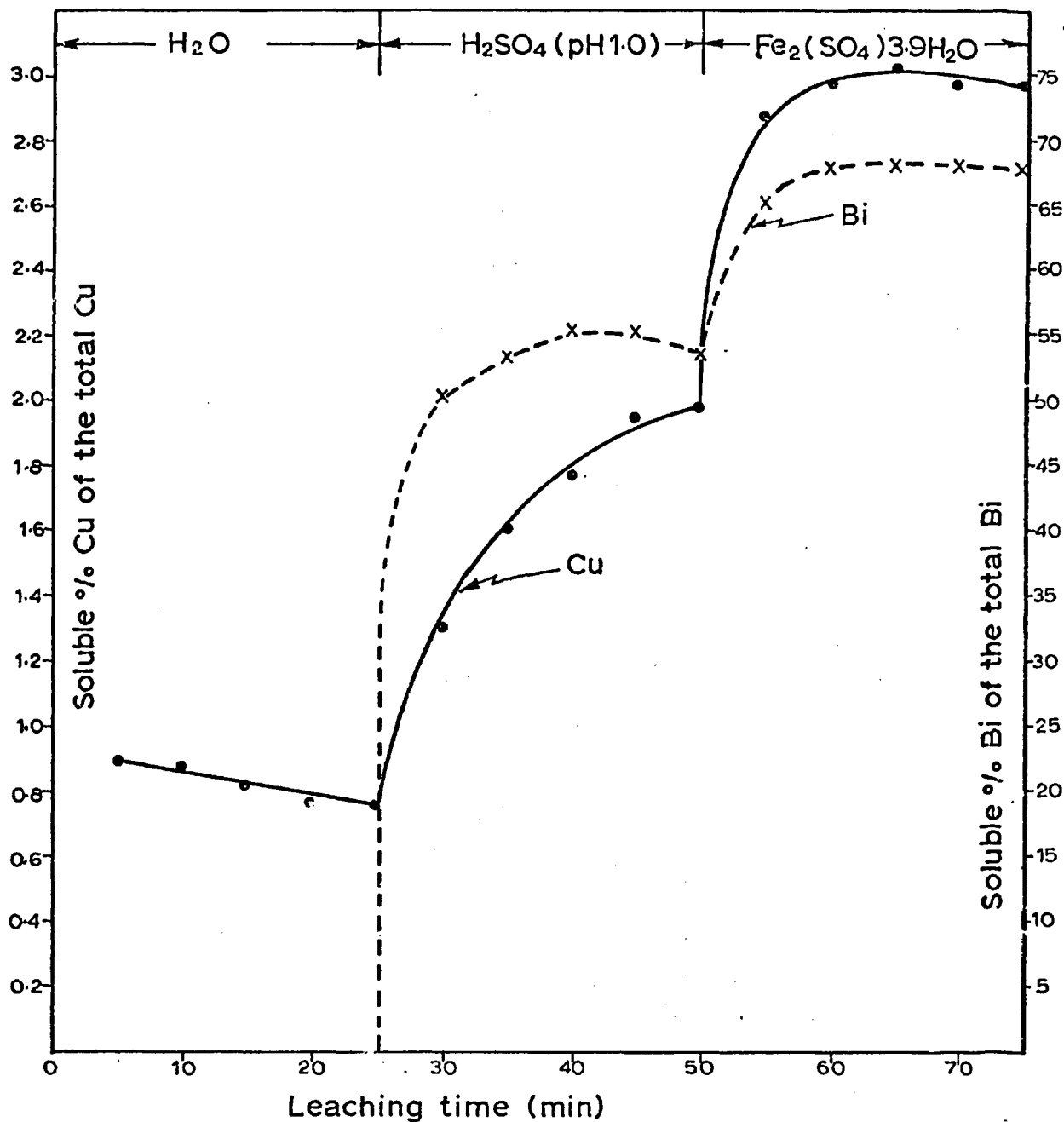
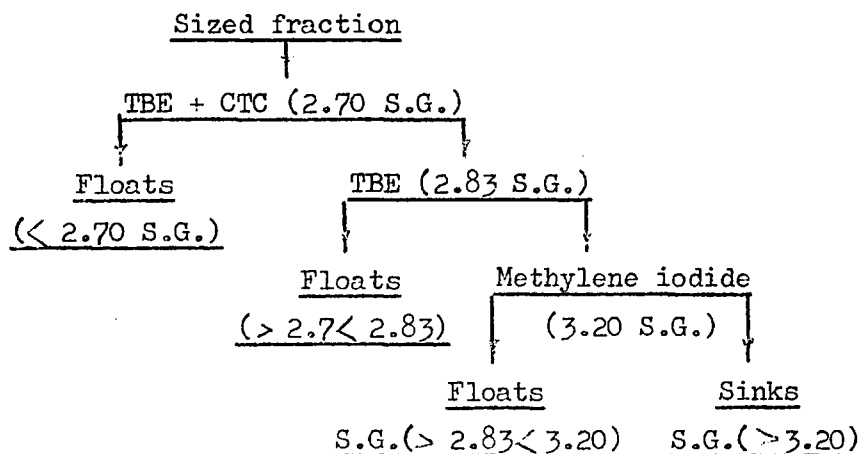


Fig. 3 Soluble of the Cu and Bi as a function of leaching time with various solvents.

acid and ferric sulphate. The results in Table 3 showed that about 67.69% of total Bi was in a soluble form in sulphuric acid and ferric sulphate.

3. LIBERATION CHARACTERISTICS

From the mineralogical examination of the ore it was obvious that the liberation of the individual sulphide minerals would occur at a fine size (about 200 mesh), and that liberation at coarser sizes would be restricted to the separation of gangue minerals from sulphide minerals. In order to investigate the possibility of pre-concentration of the coarser material, the minus $\frac{1}{4}$ inch head sample was wet-screened on a 7 mesh screen. The oversize (+7 mesh) was classified by the further screening, and heavy liquid separations were carried on the different size fractions using tetrabromethane (TBE), carbon tetrachloride (CTC) and methylene iodide (MI). The following procedure was used:



The separated fractions were assayed by atomic absorption spectroscopy.

The results are shown in Table 4.

The results in Table 4 showed that a heavy liquid separation

Table 4. Results of Heavy Liquid Separation of Minus $\frac{1}{4}$ inch Material

Feed								
Size inch(") mesh(#)	Weight %	Cumul. Weight % coarser	Bi			Cu		
			Assay	Units	Dist.	Assay	Units	Dist.
$-\frac{1}{4}'' + \frac{1}{8}''$	39.67	39.67	0.48	19.04	30.34	2.10	83.31	28.57
$-\frac{1}{8}'' + 7\#$	9.38	49.05	0.37	3.47	5.53	1.35	12.66	4.34
-7 #	50.95	100.00	0.79	40.76	64.13	3.84	195.65	67.09
Calc'd head	100.00		0.63	62.76	100.00	2.92	291.62	100.00

Table 4 (cont.)

Separating density (S.G.)	% Weight				Assay %		Distribution %							
	in fraction		of total				in fraction				of total			
	Direct	Cumul	Direct	Cumul			Direct		Cumul		Direct		Cumul	
					Bi	Cu	Bi	Cu	Bi	Cu	Bi	Cu		
< 2.7	58.98	58.98	23.40	23.40	0.092	0.22	11.23	6.17	11.23	6.17	3.41	1.76	3.41	1.76
2.7 -2.83	17.95	76.93	7.12	30.52	0.52	2.19	19.29	18.69	30.52	24.86	5.85	5.34	9.26	7.10
2.83-3.20	19.66	96.59	7.80	38.32	1.31	6.60	53.27	61.69	83.79	86.55	16.16	17.63	25.42	24.73
> 3.20	3.41	100.00	1.35	39.67	2.30	8.30	16.21	13.45	100.00	100.00	4.92	3.84	30.34	28.57
sub total	100.00		39.67		0.48	2.10	100.00	100.00			30.34	28.57		
< 2.7	66.01	66.01	6.19	6.19	0.059	0.12	10.50	5.88	10.50	5.88	0.58	0.26	0.58	0.26
2.7 -2.83	11.74	77.75	1.10	7.29	0.37	1.99	11.68	17.34	22.18	23.22	0.65	0.75	1.23	1.01
2.83-3.2	20.11	97.86	1.89	9.18	1.24	4.42	67.11	65.99	89.29	89.21	3.71	0.86	4.94	3.87
> 3.20	2.14	100.00	0.20	9.38	1.86	6.79	10.71	10.79	100.00	100.00	0.59	0.47	5.53	4.34
sub total	100.00		9.38		0.37	1.35	100.00	100.00			5.53	4.34		
	100.00		50.95		0.79	3.84					64.13	67.09		
			100.00								100.00	100.00		

at 2.7 S.G. removes 29.59% ($23.40\% + 6.19\%$) of the feed with a loss of 3.99% ($3.41\% + 0.58\%$) bismuth and 2.02% ($1.76\% + 0.26\%$) of copper. At $S.G. > 2.7 < 2.83$ these figures were 8.22% ($7.12\% + 1.10\%$) and 6.50% ($5.85\% + 0.65\%$) of bismuth and 6.09% ($5.34\% + 0.75\%$) of copper.

The total products which were lighter than 2.83 S.G. contained about 37.81% ($30.52\% + 7.29\%$) of the feed which could be removed with a loss of about 10.49% ($9.26\% + 1.23\%$) of bismuth and 8.11% ($7.10\% + 1.01\%$) of copper. These figures showed that in the coarse fractions there was too great a loss of bismuth and copper. Therefore, it was decided to crush the sample to pass 7 mesh. The procedure used is shown in Fig.2.

A 500 g. sample, crushed to pass 7 mesh, was wet-screened down to 200 mesh. The plus 200 mesh fraction was dry-screened. The minus 200 mesh fraction was sized by beaker decantation.

The results of size analysis are shown in Table 5 and plotted in Fig.4 and 5.

Table 5 shows that copper and bismuth increase with finer size reaching values well above 5% copper whereas bismuth increases slightly with finer sizes reaching a value of more than 0.7% bismuth in the minus 100 mesh fractions.

Fig.5 indicates that about 32% of the copper and 22% of the bismuth present in the crushed material is contained in the minus 72 mesh fraction which constitutes about 20% (Fig.4) of the feed by weight percent.

Table 5. Size Analysis and Distribution of Bi and Cu
of the Minus 7 Mesh Material

Size fraction	weight		Bi %			Cu %		
	%	Cumul. finer	Assay	Dist.	Cumul. Dist.	Assay	Dist.	Cumul. Dist.
-7+ 10	19.91	80.09	0.63	19.72	80.28	2.60	15.47	84.53
-10+ 14	16.15	63.94	0.58	14.73	65.55	2.75	13.27	71.26
-14+ 18	11.00	52.94	0.67	11.59	53.96	2.85	9.37	61.89
-18+ 25	10.72	42.22	0.63	10.61	43.35	2.94	9.42	52.47
-25+ 36	7.19	35.03	0.75	8.47	34.88	3.46	7.44	45.03
-36+ 52	5.47	29.56	0.74	6.37	28.51	3.85	6.29	38.74
-52+ 72	4.65	24.91	0.79	5.77	22.74	4.70	6.53	32.21
-72+100	3.97	20.94	0.82	5.13	17.61	5.20	6.17	26.04
-100+150	3.08	17.86	0.73	3.54	14.07	5.18	4.77	21.27
-150+200	2.05	15.81	0.74	2.39	11.68	5.70	3.49	17.78
-200 [#] + 60 ^u	5.47	10.34	0.67	5.75	5.93	6.20	10.13	7.65
-60+ 40	1.20	9.14	0.32	0.60	5.33	3.16	1.13	6.52
-40+ 20	1.88	7.26	0.35	1.04	4.29	3.08	1.73	4.79
-20+ 10	2.52	4.74	0.35	1.38	2.91	2.60	1.96	2.83
-10	4.74		0.39	2.91		2.00	2.83	
Calc'd head	100.00		0.64	100.00		3.35	100.00	

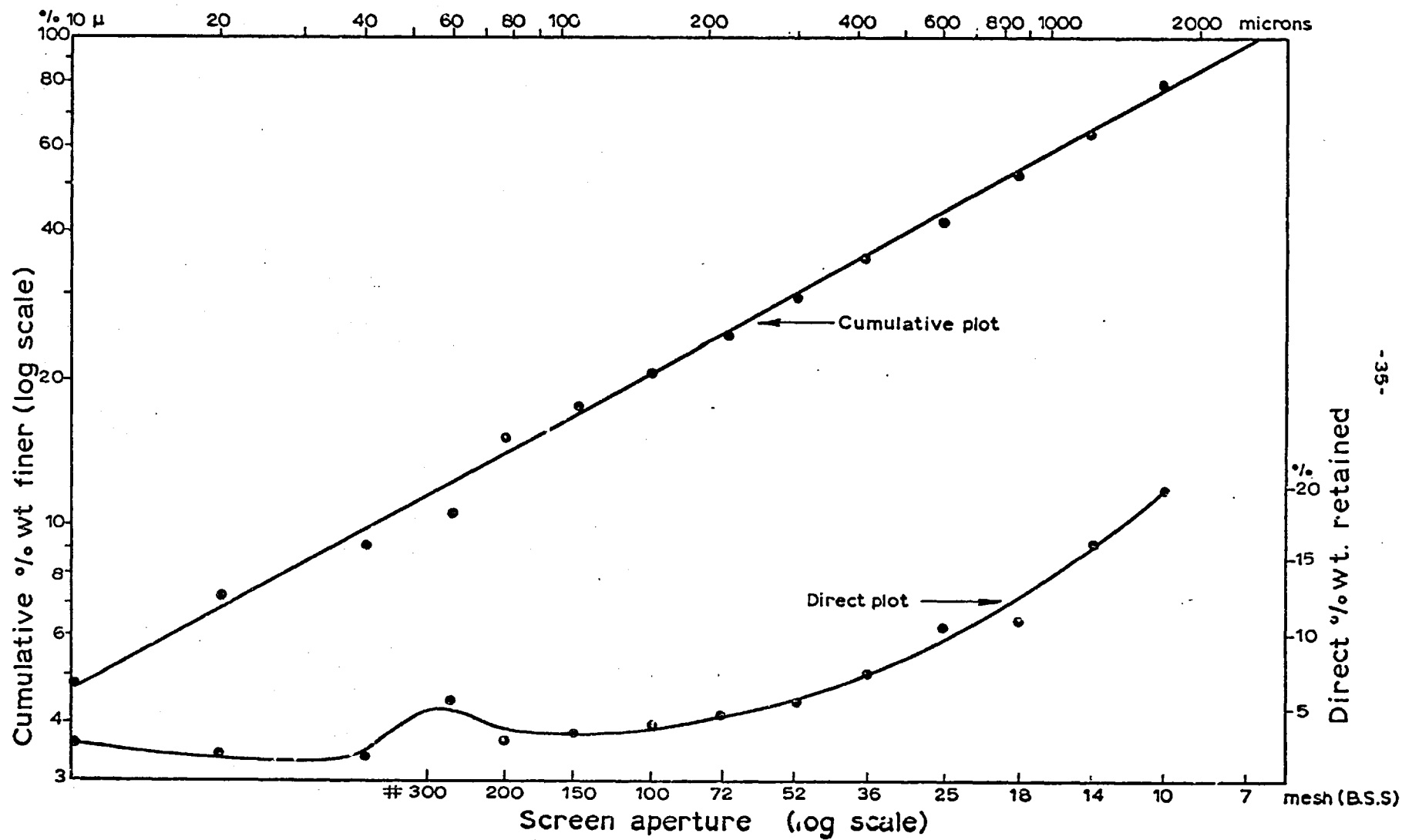


Fig. 4 Graphs of Screen Analysis in Table 5

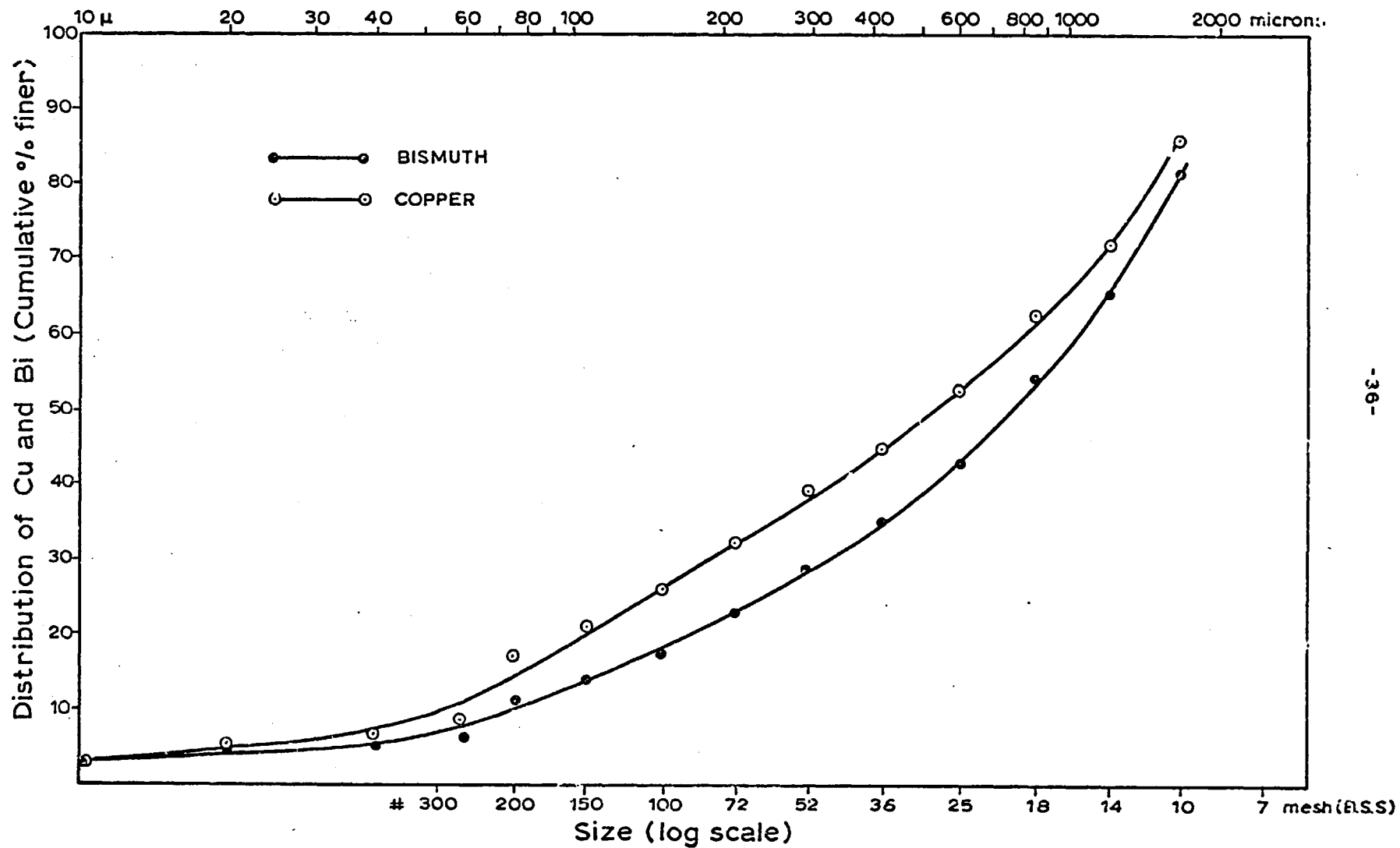


Fig. 5 Distribution of Bi and Cu on various sizes.

Heavy liquid separations of those size fractions which were finer than 7 mesh and coarser than 200 mesh were carried out using the previously described procedure. The separation was only extended down to 150 mesh and plus 200 mesh since about 72-200 mesh is usually considered as the lower limit of practical preconcentration methods, i.e. jig, cyclone, table and spiral concentrator (77).

The separated fractions were assayed by atomic absorption spectroscopy and results are shown in Table 6 and are plotted in Fig.6.

Table 6 shows the combined results of the sink-float separations in heavy liquids of density 2.7, 2.83 and 3.20. The sink and float products of the sized fractions are expressed in terms of the weight % of the fraction and the original minus 7 mesh feed.

Although the assays are not very consistent they show that percent of bismuth and copper in density fractions lighter than 2.7, and between 2.7 and 2.83 cluster around a value of 0.04 and 0.25 Bi, and 0.17 and 1.62 Cu respectively (Table 6).

Fig.6 shows the distribution of Bi and Cu in the various size ranges at a constant separating density, and indicates that increased fineness of the size fractions does not alter the assays (see Table 6) and distribution (Fig.6). This may be due to the fine dissemination of bismuth and copper in the gangue.

Table 6 and Fig.6 also show that a heavy liquid separation at 2.7 S.G. removes about 40.51% of feed with a loss of 2.6% of bismuth and 2.04% of copper and at S.G. 2.83 these figures are 19.51% and

Table 6. Results of Heavy Liquid Separation of Minus 7 Mesh Material

Feed						Float at S.G. 2.7 (T.B.E.)										
Size fraction (mesh)	Weight %	Assay %		Distribution %		% Weight			Assay %		Distribution %					
		Bi	Cu	Bi	Cu	in fraction	of total	Cumul of total	Bi	Cu	in fraction		of total		Cumul. of total	
											Bi	Cu	Bi	Cu	Bi	Cu
- 7+ 10	19.91	0.63	2.60	19.72	15.47	41.30	8.22	8.22	0.030	0.092	1.97	1.46	0.39	0.23	0.39	0.23
- 10+ 14	16.15	0.58	2.75	14.73	13.27	48.45	7.82	16.04	0.035	0.160	2.94	2.81	0.43	0.37	0.82	0.60
- 14+ 18	11.00	0.67	2.85	11.59	9.37	57.05	6.28	22.32	0.050	0.284	4.23	5.69	0.49	0.53	1.31	1.13
- 18+ 25	10.72	0.63	2.94	10.61	9.42	61.03	6.54	28.86	0.039	0.292	3.81	6.06	0.40	0.57	1.71	1.70
- 25+ 36	7.19	0.75	3.46	8.47	7.44	40.60	2.92	31.78	0.011	0.094	6.00	1.10	0.51	0.08	2.22	1.78
- 36+ 52	5.49	0.74	3.85	6.37	6.29	43.78	2.39	34.17	0.030	0.110	1.77	1.25	0.11	0.08	2.33	1.86
- 52+ 72	4.65	0.79	4.70	5.77	6.53	45.65	2.12	36.29	0.028	0.120	1.63	1.17	0.09	0.08	2.42	1.94
- 72+100	3.97	0.82	5.20	5.13	6.17	44.55	1.77	38.06	0.020	0.096	1.09	0.80	0.06	0.05	2.48	1.99
-100+150	3.08	0.73	5.18	3.54	4.77	42.92	1.32	39.38	0.030	0.071	1.78	0.59	0.06	0.03	2.54	2.02
-150+200	2.05	0.74	5.70	2.39	3.49	54.91	1.13	40.51	0.035	0.071	2.59	0.68	0.06	0.02	2.60	2.04
Calc'd head	84.19	0.56	2.75	88.32	82.22		40.51		0.041	0.169			2.60	2.04		

Table 6 (cont.)

Sink at S.G. 2.7 Float at S.G. 2.83											
% Weight			Assay %		Distribution %						
in fraction	of total	Cumul. of total	Bi	Cu	in fraction		of total		Cumul. of total		
					Bi	Cu	Bi	Cu	Bi	Cu	
27.12	5.40	5.40	0.32	1.85	13.81	19.28	2.72	2.98	2.72	2.98	
20.11	3.25	8.65	0.32	2.50	11.14	18.26	1.64	2.43	4.36	5.41	
13.21	1.45	10.10	0.32	2.88	6.27	13.36	0.73	1.25	5.09	6.66	
12.44	1.34	11.44	0.28	2.15	5.56	9.10	0.59	0.86	5.68	7.52	
33.60	2.42	13.86	0.15	0.83	6.76	8.06	0.57	0.60	6.25	8.12	
31.80	1.74	15.60	0.12	0.66	5.16	5.45	0.33	0.34	6.58	8.46	
28.64	1.33	16.93	0.11	0.40	4.01	2.44	0.23	0.16	6.81	8.62	
28.82	1.14	18.07	0.09	0.31	3.18	1.72	0.16	0.11	6.97	8.73	
34.19	1.05	19.12	0.35	2.15	16.48	14.18	0.58	0.67	7.55	9.40	
19.13	0.39	19.51	0.12	0.40	3.10	1.34	0.08	0.05	7.63	9.45	
	19.51		0.249	1.62			7.63	9.45			

Table 6 (cont.)

Sink at S.G. 2.83 Float at S.G. 3.20 (M.I.)											
% Weight			Assay %		Distribution %						
in fraction	of total	Cumul. of total	Bi	Cu	in fraction		of total		Cumul. of total		
					Bi	Cu	Bi	Cu	Bi	Cu	
24.75	4.93	4.93	0.98	6.48	38.59	61.62	7.61	9.53	7.61	9.53	
23.84	3.85	8.78	1.00	6.48	41.23	56.08	6.08	7.44	13.69	16.97	
21.09	2.32	11.10	0.81	6.60	25.34	48.88	2.94	4.58	16.63	21.55	
15.96	1.71	12.81	0.77	6.72	19.65	36.50	2.09	3.44	18.72	24.99	
11.90	0.85	13.66	0.79	6.80	12.62	23.38	1.07	1.74	19.79	26.73	
7.23	0.40	14.06	0.74	6.92	7.22	12.99	0.46	0.82	20.25	27.55	
5.87	0.28	14.34	0.81	7.00	6.04	8.74	0.35	0.57	20.60	28.12	
4.71	0.19	14.53	0.75	5.43	4.33	4.92	0.22	0.30	20.82	28.42	
5.72	0.18	14.71	0.78	7.00	6.14	7.72	0.22	0.37	21.04	28.79	
3.60	0.07	14.78	0.79	7.55	3.83	4.77	0.09	0.16	21.13	28.95	
	14.78		0.909	6.555			21.13	28.15			

Table 6 (cont.)

Sink at S.G. 3.20 (M.I.)											
% Weight			Assay %		Distribution %						
in fraction	of total	Cumul. of total	Bi	Cu	in fraction		of total		Cumul. of total		
					Bi	Cu	Bi	Cu	Bi	Cu	
6.83	1.36	1.36	4.20	6.72	45.63	17.64	9.00	2.73	9.00	2.73	
7.60	1.23	2.59	3.40	8.28	44.69	22.85	6.58	3.03	15.58	5.76	
8.65	0.95	3.54	5.00	10.56	64.16	32.07	7.43	3.01	23.01	8.77	
10.57	1.13	4.67	4.20	13.44	70.98	48.34	7.53	4.55	30.54	13.32	
13.90	1.00	5.67	4.00	16.80	74.62	67.46	6.32	5.02	36.86	18.34	
17.19	0.94	6.61	3.70	18.00	85.85	80.31	5.47	5.05	42.33	23.39	
19.84	0.92	7.53	3.50	20.76	88.32	87.65	5.10	5.72	47.43	29.11	
21.92	0.87	8.40	3.40	21.96	91.40	92.54	4.69	5.71	52.12	34.82	
17.17	0.53	8.93	3.20	23.40	75.61	77.51	2.68	3.70	54.80	38.52	
22.36	0.46	9.39	3.00	23.76	90.48	93.51	2.16	3.26	56.96	41.78	
	9.39		3.858	14.89			56.96	41.78			

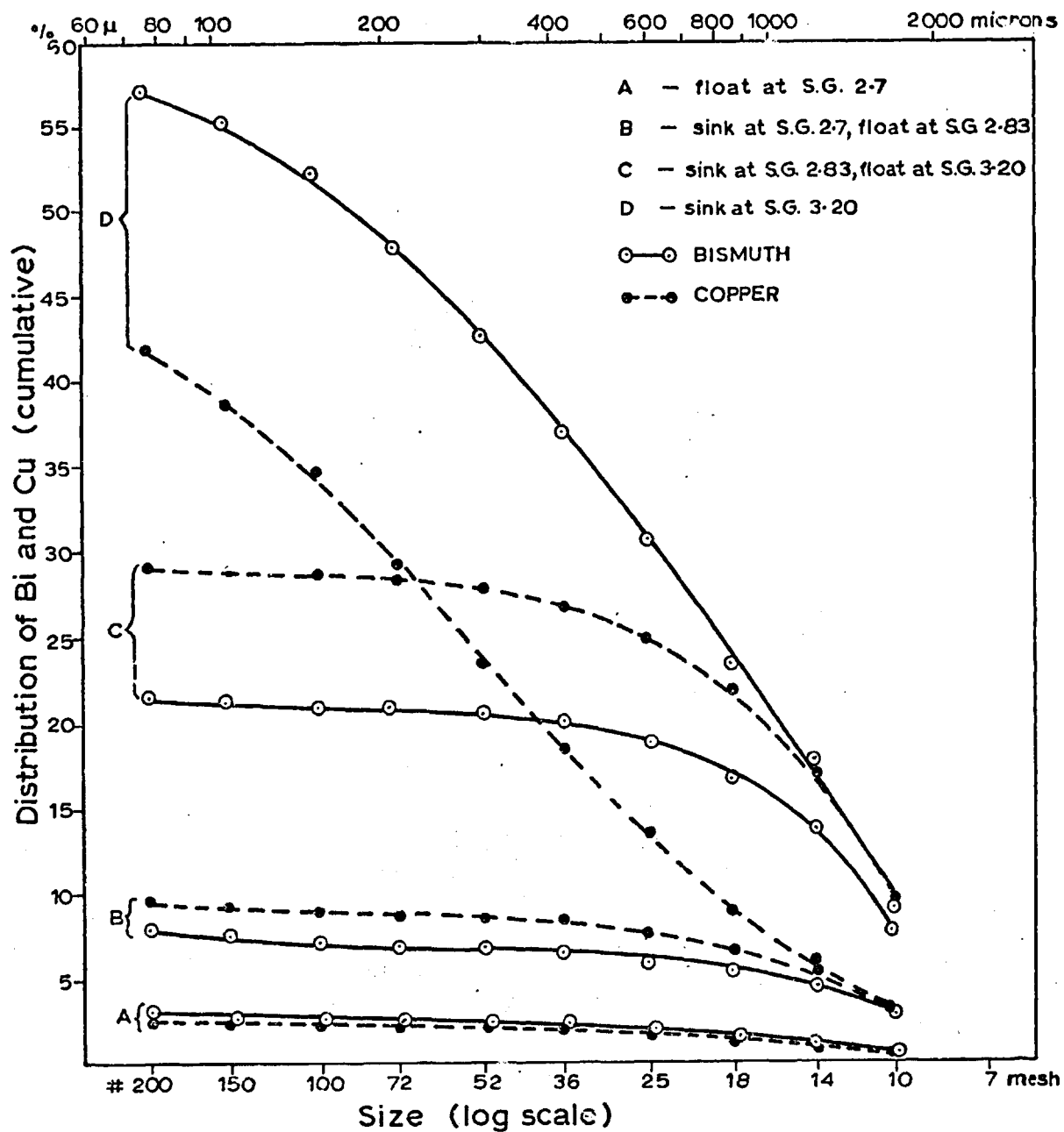


Fig. 6 Distribution of Bi and Cu in the various sizes at the constant separating density.

7.63% of bismuth and 9.45% of copper. The combined float products of specific gravity which is lighter than S.G. 2.83 contains almost 60% (40.51% + 19.51%) of the feed which could be removed with a loss of about 10.23% (2.60% + 7.63%) of bismuth and 11.49% (2.04% + 9.45%) of copper.

The average grades of each specific gravity product were calculated from Table 6 and results were as follows:

Products	wt.		Bi				Cu			
	%	Cumul.	Grade	Units	Dist.	Cumul. Dist.	Grade	Units	Dist.	Cumul. Dist.
S.G. < 2.7	40.51	40.51	0.041	1.65	2.60	2.60	0.169	6.83	2.04	2.04
S.G. > 2.7 < 2.83	19.51	60.02	0.249	4.85	7.63	10.23	1.621	31.62	9.45	11.49
S.G. > 2.83 < 3.20	14.78	74.80	0.909	13.44	21.13	31.36	6.555	96.88	28.95	40.44
S.G. > 3.20	9.39	84.19	3.858	36.23	56.96	88.32	14.890	139.82	41.78	82.22
-200 mesh	15.81	100.00	0.470	7.43	11.68	100.00	3.763	59.50	17.78	100.00
Calc'd. head	100.00		0.640	63.60	100.00		3.350	334.65	100.00	

These results, which show the relationship between separating density, weight percent and distribution of bismuth and copper, are plotted in Fig.7. The sink product at 3.20 specific gravity contained 56.96% of total bismuth and 41.78% of the total copper in the feed and amounted to 9.39% by weight with a calculated grade of 3.858% Bi, (a very low grade), and 14.89% Cu.

Fig.7 shows that with increasing separating density the distributions of bismuth and copper are not increased very much. This may be due to the very fine dissemination of bismuth and copper

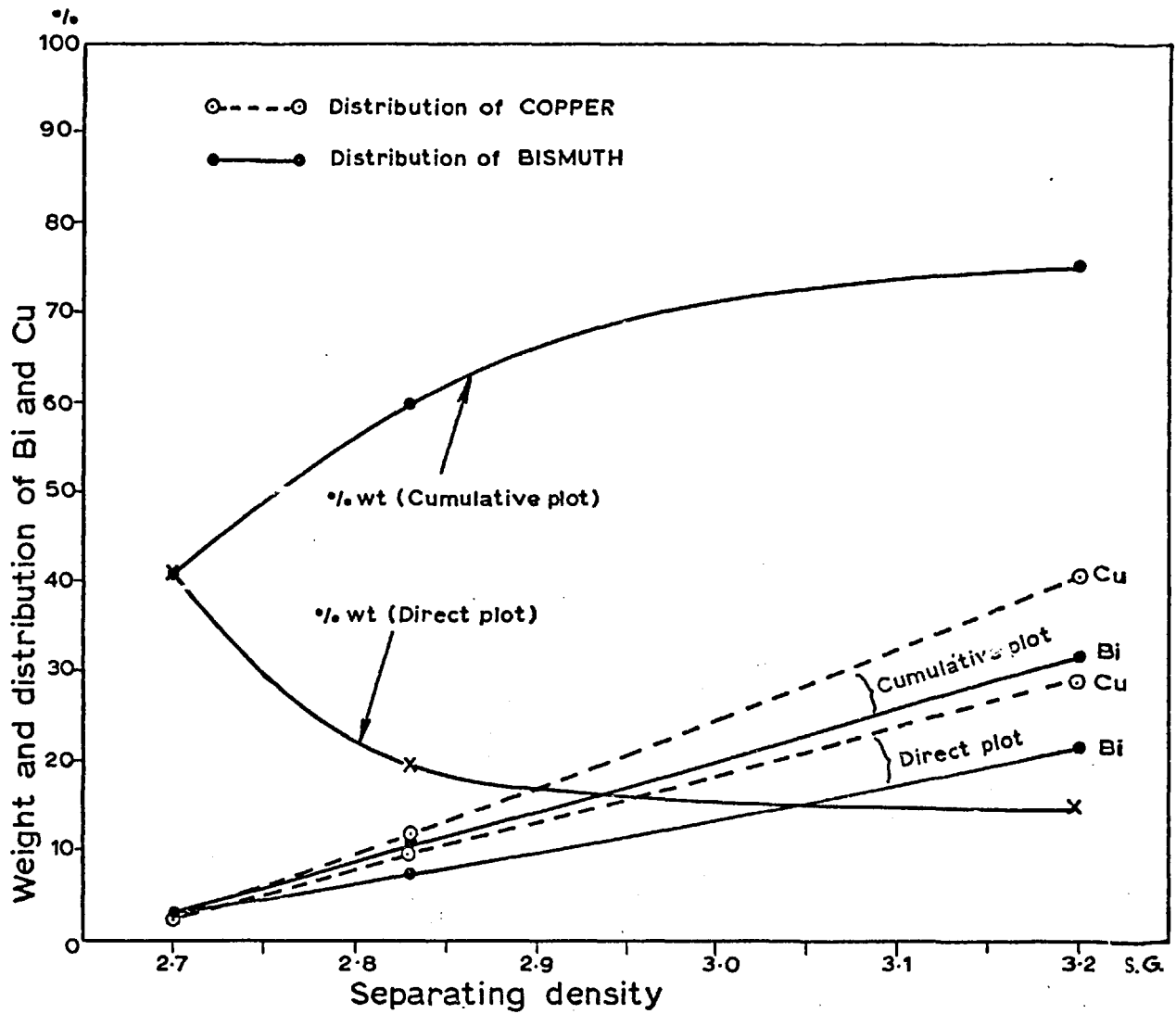


Fig. 7 Relationship between separating density, weight percentage and distribution of bismuth and copper.

in the gangue mineral.

The relationship between separating density, grade and distribution of Bi and Cu in the various size ranges, calculated from Table 6, are shown in Table 7. The results of Table 4 and 7 are plotted in Fig.8 and 9.

Fig.8 shows the relationship between separating density, grade percent of bismuth and copper, and cumulative percent weight of the various size fractions. In these figures it is seen that the light density grade of all fractions did not vary significantly different. However, the percent weight of the two coarse fractions, minus $\frac{1}{4}$ inch plus $\frac{1}{8}$ inch and minus $\frac{1}{8}$ inch plus 7 mesh, were much higher than the minus 7 mesh fractions. This figure also shows that with increasing separating density, the grade percent of copper is increased whereas grade percent of bismuth is only increased slightly. This indicates that bismuth is disseminated more finely than copper within the gangue mineral.

Fig.9 A and B show the relationship between separating density and cumulative distribution of bismuth and copper on the various size fractions. This figure shows that the Cu and Bi content of the coarser fraction is higher than fine fractions. In particular, the distributions of bismuth in $\frac{1}{4}$ inch plus 7 mesh fractions show larger differences and higher values than the other, minus 7 mesh, fractions.

Therefore in these coarse fractions there is too great a loss of bismuth and copper. All these results suggested that the optimum

Table 7. Distribution of Bi and Cu at the Various S.G. in a Certain Size Fraction

Size mesh B.S.S.	Separating density S.G.	% Weight				Assay %		Distribution %							
		in fraction		of total				in fraction				of total			
		Direct	Cumul	Direct	Cumul	Bi	Cu	Direct		Cumul		Direct		Cumul	
								Bi	Cu	Bi	Cu	Bi	Cu	Bi	Cu
-7 +10	< 2.7	41.30	41.30	8.22	8.22	0.03	0.092	1.97	1.46	1.97	1.46	0.39	0.23	0.39	0.23
	2.7 -2.83	27.12	68.42	5.40	13.62	0.32	1.85	13.81	19.28	15.78	20.74	2.72	2.98	3.11	3.21
	2.83-3.27	24.75	93.17	4.93	18.55	0.98	6.48	38.59	61.62	54.37	82.36	7.61	9.53	10.72	12.74
	3.27	6.83	100.00	1.36	19.91	4.20	6.72	45.63	17.64	100.00	100.00	9.00	2.73	19.72	15.47
		100.00		19.91		0.63	2.62	100.00	100.00			19.72	15.47		
-10 +14	< 2.7	48.45	48.45	7.82	7.82	0.035	0.16	2.94	2.81	2.94	2.81	0.43	0.37	0.43	0.37
	> 2.7 < 2.83	20.11	68.56	3.25	11.07	0.32	2.50	11.14	18.26	14.08	21.07	1.64	2.43	2.07	2.80
	> 2.83 < 3.20	23.84	92.40	3.85	14.92	1.00	6.48	41.23	56.08	55.31	77.15	6.08	7.44	8.15	10.24
	> 3.20	7.60	100.00	1.23	16.15	3.40	8.28	44.69	22.85	100.00	100.00	6.58	3.03	14.73	13.27
		100.00		16.15		0.58	2.75	100.00	100.00			14.73	13.27		
-14 +18	< 2.7	57.05	57.05	6.28	6.28	0.05	0.284	4.23	5.69	4.23	5.69	0.49	0.53	0.49	0.53
	> 2.7 < 2.83	13.21	70.26	1.45	7.73	0.32	2.88	6.27	13.36	10.50	19.05	0.73	1.25	1.22	1.78
	> 2.83 < 3.20	21.09	91.35	2.32	10.05	0.81	6.60	25.34	48.88	35.84	67.93	2.94	4.58	4.16	6.36
	> 3.20	8.65	100.00	0.95	11.00	5.00	10.56	64.16	32.07	100.00	100.00	7.43	3.01	11.59	9.37
		100.00		11.00		0.67	2.85	100.00	100.00			11.59	9.37		

Table 7 (cont.)

-18 +25	<2.7	61.03	61.03	6.54	6.54	0.039	0.29	3.81	6.06	3.81	6.06	0.40	0.57	0.40	0.57
	>2.7 <2.83	12.44	73.47	1.34	7.88	0.28	2.15	5.56	9.10	9.37	15.16	0.59	0.86	0.99	1.43
	>2.83 <3.20	15.96	89.43	1.71	9.59	0.77	6.72	19.65	36.50	29.02	51.66	2.09	3.44	3.08	4.87
	>3.20	10.57	100.00	1.13	10.72	4.20	13.44	70.98	48.34	100.00	100.00	7.53	4.55	10.61	9.42
		100.00		10.72		0.63	2.94	100.00	100.00			10.61	9.42		
-25 +36	<2.7	40.60	40.60	2.92	2.92	0.011	0.094	6.00	1.10	6.00	1.10	0.51	0.08	0.51	0.08
	>2.7 <2.83	33.60	74.20	2.42	5.34	0.15	0.83	6.76	8.06	12.76	9.16	0.57	0.60	1.08	0.68
	>2.83 <3.20	11.96	86.10	0.85	6.19	0.79	6.80	12.62	23.38	25.38	32.44	1.07	1.74	2.15	2.42
	>3.20	13.90	100.00	1.00	7.19	4.00	16.80	74.62	67.46	100.00	100.00	6.32	5.02	8.47	7.44
		100.00		7.19		0.75	3.46	100.00	100.00			8.47	7.44		
-36 +52	<2.7	43.78	43.78	2.39	2.39	0.03	0.11	1.77	1.25	1.77	1.25	0.11	0.08	0.11	0.08
	>2.7 <2.83	31.80	75.58	1.74	4.13	0.12	0.66	5.16	5.45	6.93	6.70	0.33	0.34	0.44	0.42
	>2.83 <3.20	7.23	82.81	0.40	4.53	0.74	6.92	7.22	12.99	14.15	19.69	0.46	0.82	0.90	1.24
	>3.20	17.19	100.00	0.94	5.47	3.70	18.00	85.85	80.31	100.00	100.00	5.47	5.05	6.37	6.29
		100.00		5.47		0.74	3.85	100.00	100.00			6.37	6.29		

Table 7 (cont.)

-52 +72	<2.7	45.65	45.65	2.12	2.12	0.028	0.12	1.63	1.17	1.63	1.17	0.09	0.08	0.09	0.08
	>2.7 <2.38	28.64	74.29	1.33	3.45	0.11	0.40	4.01	2.44	5.64	3.61	0.23	0.16	0.32	0.24
	>2.38 <3.20	5.87	80.16	0.28	3.73	0.81	7.00	6.04	8.74	11.68	12.35	0.35	0.57	0.67	0.81
	>3.20	19.84	100.00	0.92	4.65	3.50	20.76	88.32	87.65	100.00	100.00	5.10	5.72	5.77	6.53
		100.00		4.65		0.79	4.70	100.00	100.00			5.77	6.53		
-72 +100	<2.7	44.55	44.55	1.77	1.77	0.02	0.096	1.09	0.82	1.09	0.82	0.06	0.05	0.06	0.05
	>2.7 <2.38	28.82	73.37	1.14	2.91	0.09	0.31	3.18	1.72	4.27	2.54	0.16	0.11	0.22	0.16
	>2.38 <3.20	4.71	78.08	0.19	3.10	0.75	5.43	4.33	4.92	8.60	7.46	0.22	0.30	0.44	0.46
	>3.20	21.92	100.00	0.87	3.97	3.40	21.96	91.40	92.54	100.00	100.00	4.69	5.71	5.13	6.17
		100.00		3.97		0.82	5.20	100.00	100.00			5.13	6.17		
-100 +150	<2.7	42.92	42.92	1.32	1.32	0.03	0.071	1.78	0.59	1.78	0.59	0.06	0.03	0.06	0.03
	>2.7 <2.38	34.19	77.11	1.05	2.37	0.35	2.15	16.47	14.18	18.25	14.77	0.58	0.67	0.64	0.70
	>2.38 <3.20	5.72	82.83	0.18	2.55	0.78	7.00	6.14	7.72	24.39	22.49	0.22	0.37	0.86	1.07
	>3.20	17.17	100.00	0.53	3.08	3.20	23.40	75.61	77.51	100.00	100.00	2.68	3.70	3.54	4.77
		100.00		3.08		0.73	5.18	100.00	100.00			3.54	4.77		

Table 7 (cont.)

-150	< 2.7	54.91	54.91	1.13	1.13	0.035	0.071	2.59	0.68	2.59	0.68	0.06	0.02	0.06	0.02
+200	> 2.7	19.13	74.04	0.39	1.52	0.12	0.40	3.10	1.34	5.69	2.02	0.08	0.05	0.14	0.07
	< 2.38														
	> 2.38	3.60	77.64	0.07	1.59	0.79	7.55	3.83	4.77	9.52	6.79	0.09	0.16	0.23	0.23
	< 3.20														
	> 3.20	22.36	100.00	0.46	2.05	3.00	23.76	90.48	93.21	100.00	100.00	2.16	3.26	2.39	3.49
		100.00		2.05		0.74	5.70	100.00	100.00			2.39	3.49		
-200 +60 ^μ		100.00		5.47		0.67	6.20					5.75	10.13		
-60+40 ^μ		100.00		1.20		0.32	3.16					0.60	1.13		
-40+20 ^μ		100.00		1.88		0.35	3.08					1.04	1.73		
-20+10 ^μ		100.00		2.52		0.35	2.60					1.38	1.96		
-10 ^μ		100.00		4.74		0.39	2.00					2.91	2.83		
Calc'd head				100.00		0.64	3.35					100.00	100.00		

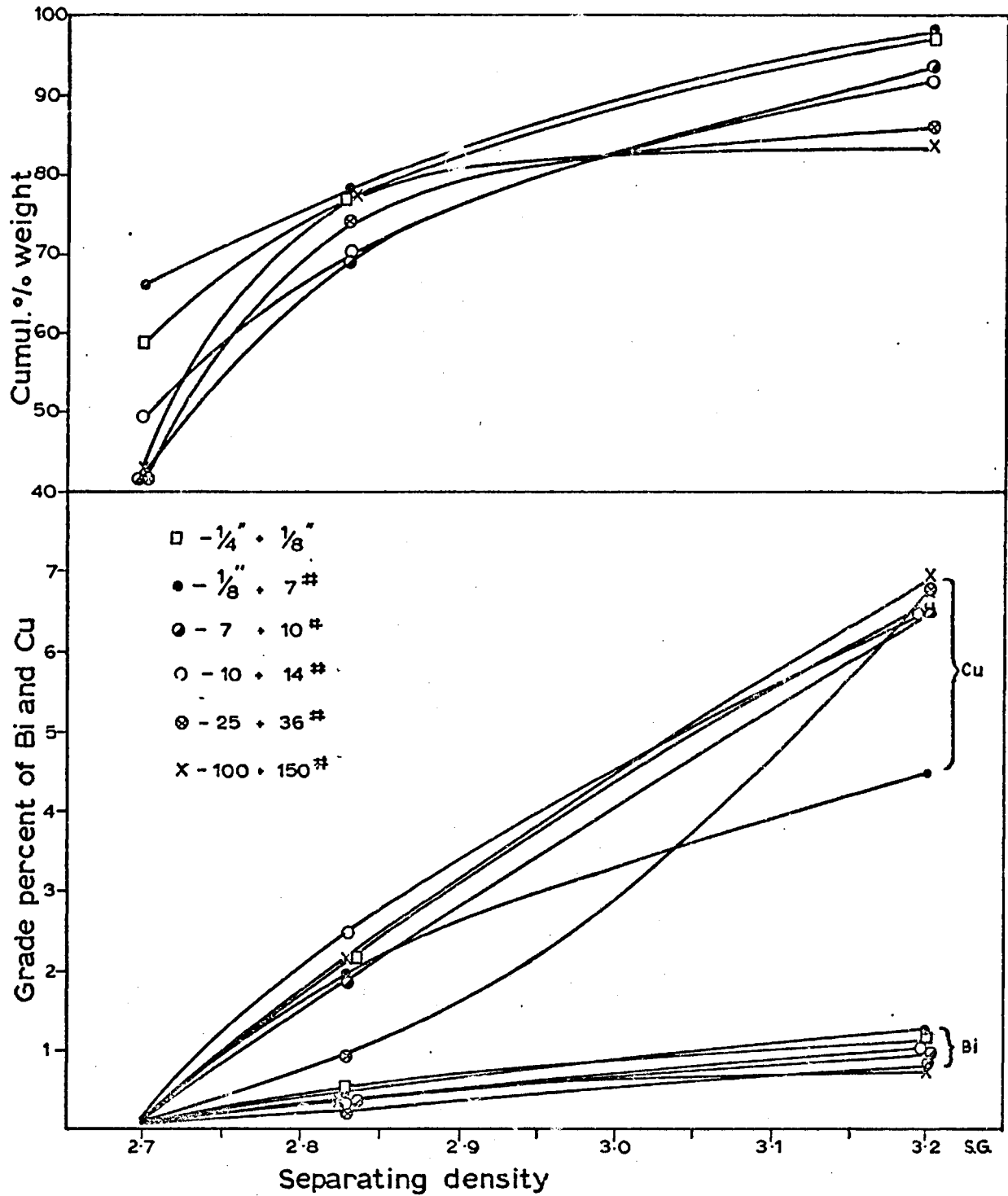


Fig. 8 Relationship between separating density, grade of Bi and Cu and weight in the various size fractions.

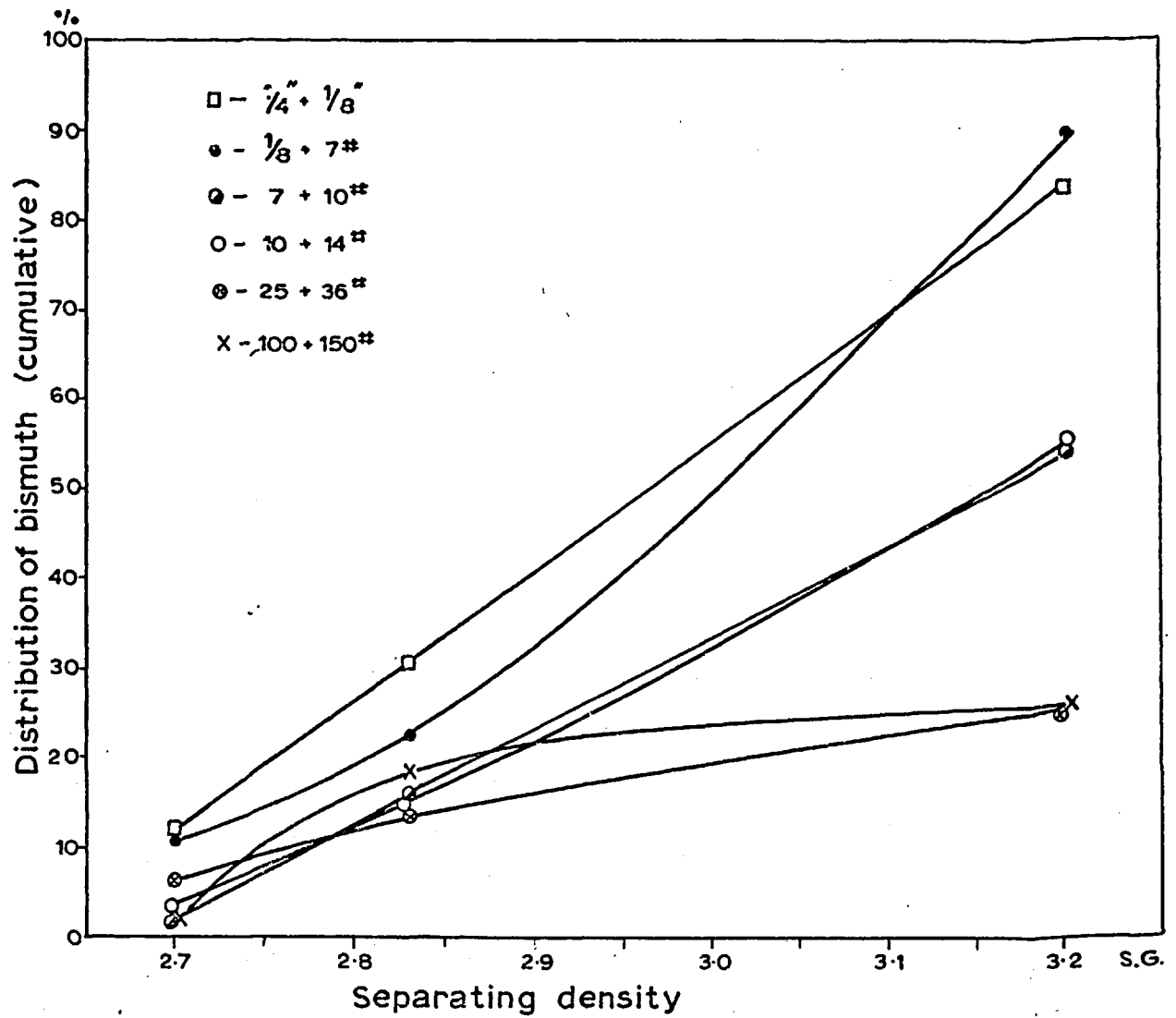


Fig.9(a) Relationship between separating density and distribution of bismuth in the various size fractions.

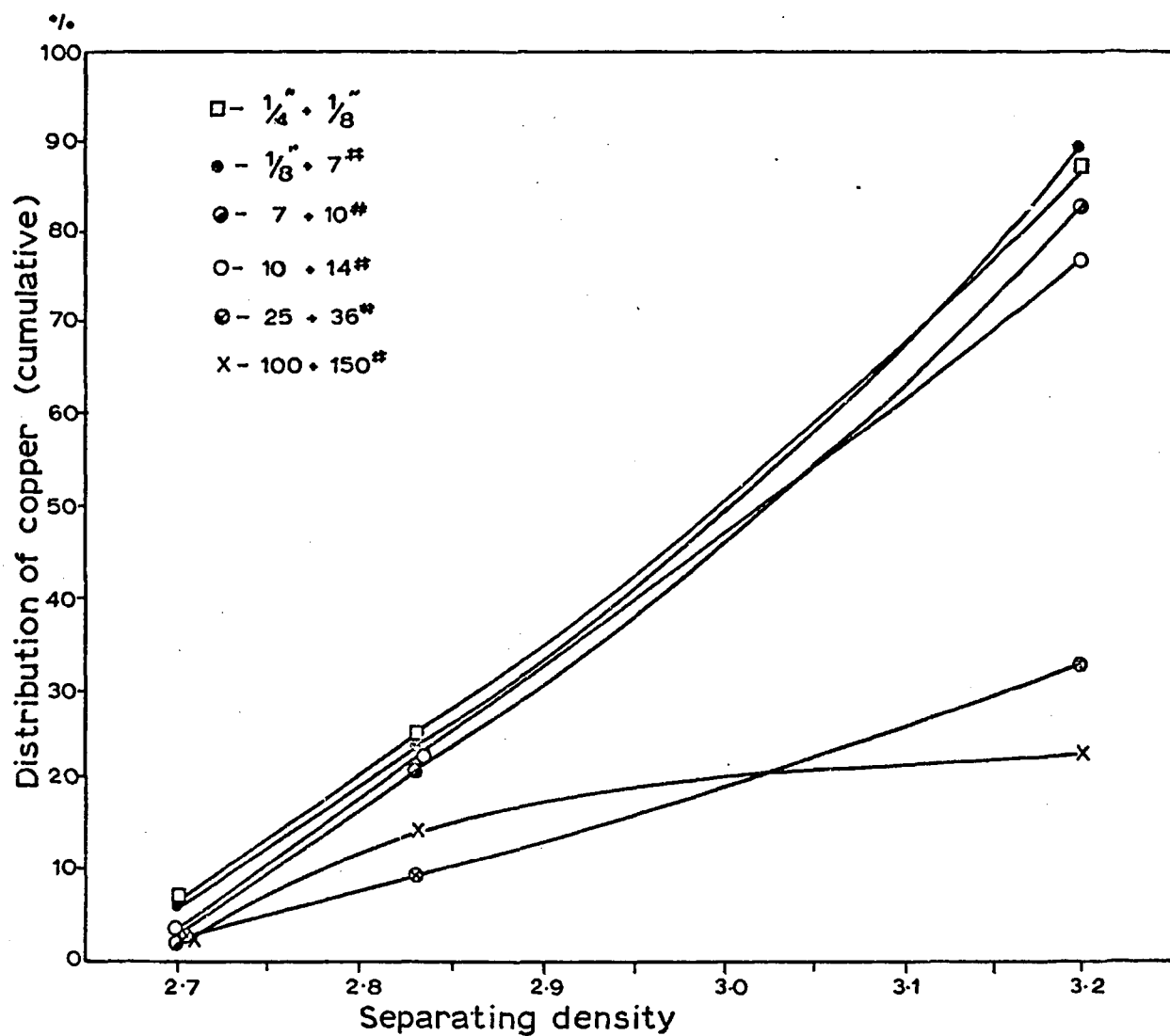


Fig.9(b) Relationship between separating density and distribution of copper in the various size fractions.

crushing size is minus 7 mesh and there is no possibility of preconcentration of the coarser size fractions.

In order to find out the nature of the liberation in heavier than 3.2 density fractions, samples of different size fractions were briquetted, sectioned and then polished. Examination of the polished sections under the microscope showed that in the plus 100 and 200 mesh fractions a number of chalcopyrite - bismuth - gangue middlings were present.

Plates 9-12 present photomicrographs of four different samples of heavy liquid separation products to illustrate the difference in grain size that is encountered in the ore. The particles are mainly chalcopyrite or Bi-Pb mineral with quartz inclusion. No fully liberated particles are visible.

These photographs indicate that it is not practical to break all of these attachments.

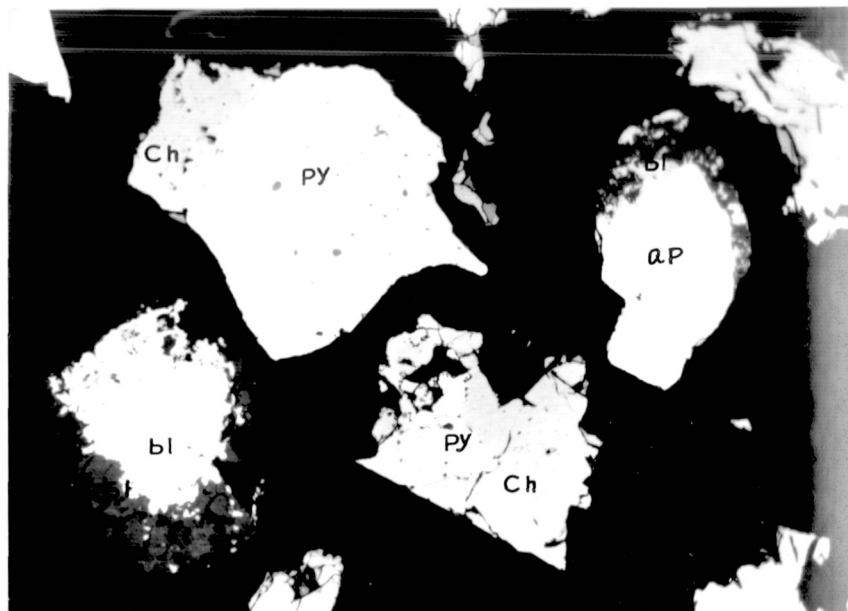


Plate 9 - (176X) The briquette of heavier fraction than S.G. 3.20 in a 72/100 mesh size. bl = Bi-Pb mineral, Py = pyrite, Ch = chalcopyrite, ap = arsenopyrite.

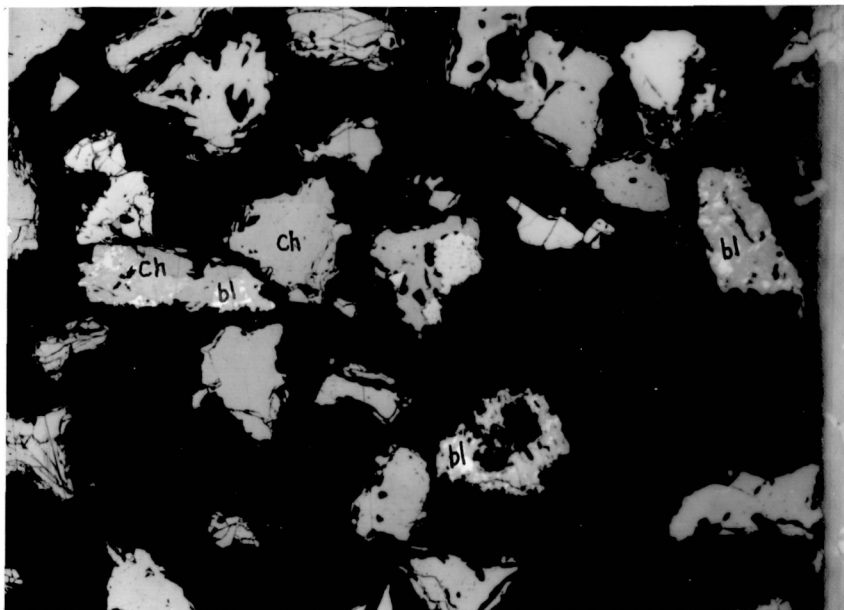


Plate 10 - (160X) The briquette of heavier fraction than S.G. 3.20 in 100/150 mesh size. bl = Bi-Pb mineral, Ch = chalcopyrite.

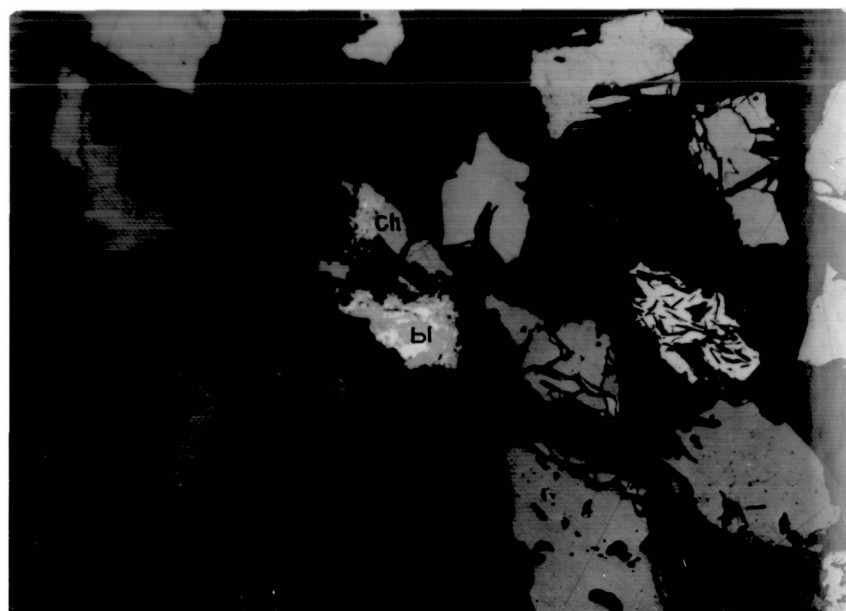


Plate 11 - (160X) The briquette of heavier fraction than S.G. 3.20 in a 150/200 mesh size. Ch = chalcopyrite, bl = Bi-Pb mineral.

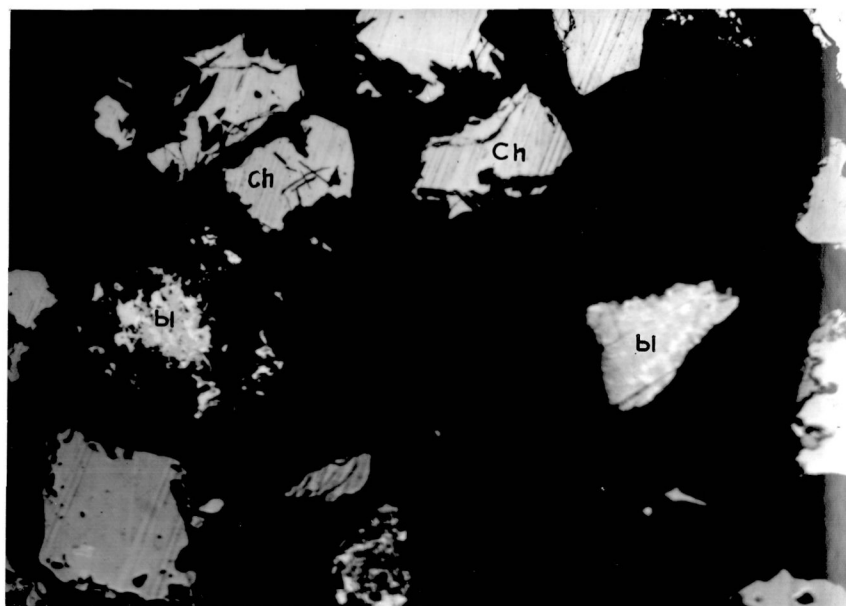


Plate 12 - (160X) The briquette of heavier fraction than S.G. 3.20 in a 150/200 mesh size. Ch = chalcopyrite, bl = Bi-Pb mineral, qu = quartz.

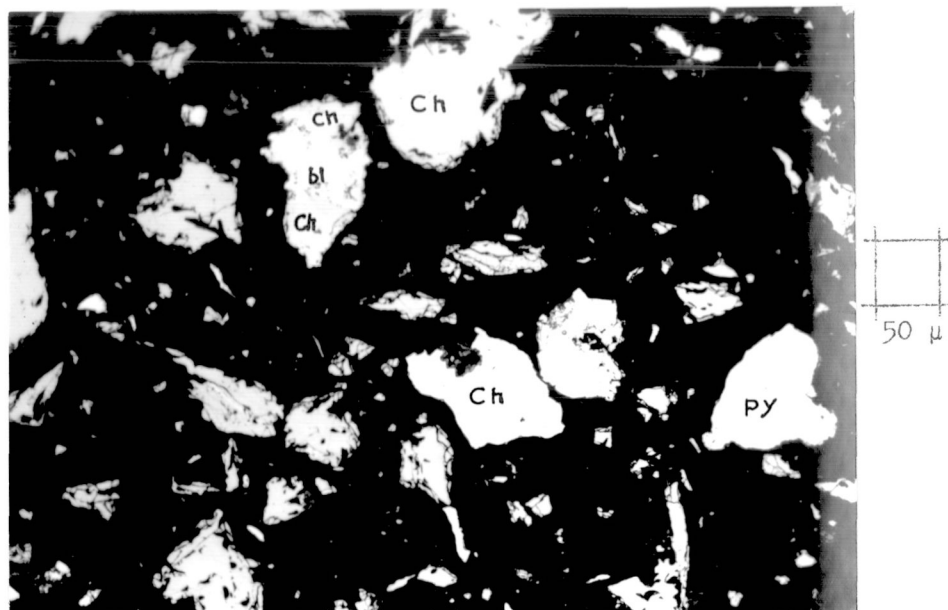


Plate 13 - (160X) The briquette of flotation concentrate (T.37)*

Ch = chalcopyrite, py = pyrite, bl = Bi-Pb mineral.

(* Flotation test No.)

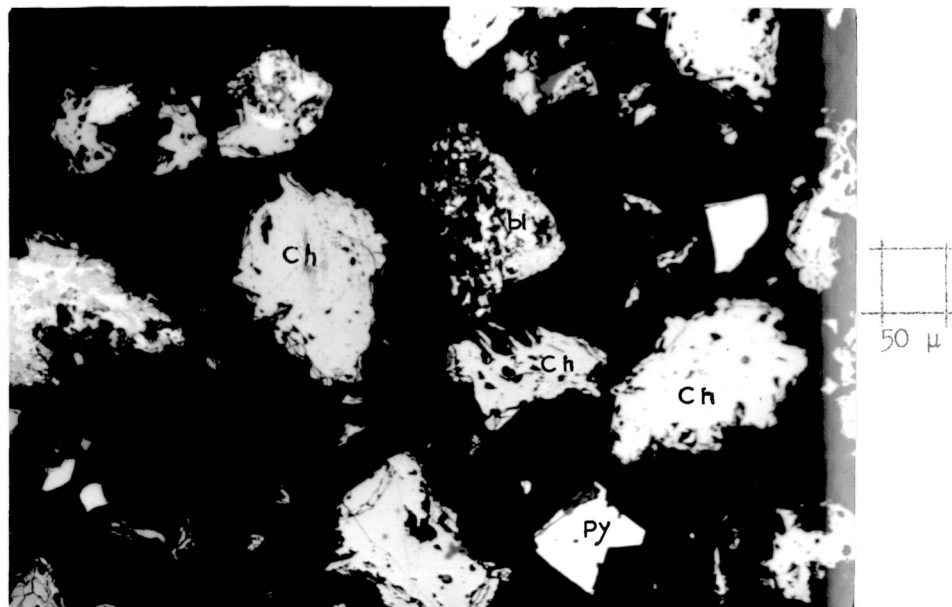


Plate 14 - (160X) The briquette of flotation concentrate (T.37)

Ch = chalcopyrite, py = pyrite, bl = Bi-Pb mineral.

4. PROCESS SELECTION

The mineralogical and liberation studies reveal that the principal copper mineral, chalcopyrite, exhibits very different textural properties in its association with gangue and other sulphide minerals, namely, Bi-Pb mineral and pyrite. The evidence of this was found in the polished sections examined, wherein chalcopyrite and Bi-Pb minerals were observed. The minuteness of the inclusions and the lack of structural discontinuity at the boundary are not clearly visible. It was also indicated that there are no redeeming structural features which allow rejection of a substantial portion of waste at a relatively coarse size.

Liberation studies also showed that there is too great a loss of bismuth (10.20% of total Bi) and copper (11.49% of total Cu) in the fraction of +200 mesh and lighter than S.G. 2.83. This result indicates that there is no possibility of preconcentration of these coarse size fractions.

In the microscopic examination of the polished briquette, which was prepared from the product of S.G. > 3.2, it was found that chalcopyrite and Bi-Pb minerals were still finely locked with quartz and there were no fully liberated particles. But they would appear to be better liberated at below 200 mesh. These results indicate that it is not practical to break all of these attachments of quartz and suggested that in order to produce concentrates with better grades and recoveries, most of the locked chalcopyrite and Bi-Pb

mineral may be recovered into the copper concentrate. However, the mineralogical composition and the liberation characteristics immediately suggest flotation as the separating process.

5. COMMUNUTION STUDIES

The results (Table 5) of chemical analysis of the different size fractions of the ground mineral sample showed that there were no large differences with respect to bismuth and copper contents. However, it was found that bismuth and copper contents were slightly higher in the size fractions between -200 mesh and 60 microns (Table 5).

Before any flotation testing was carried out, the grinding characteristics of the ore were investigated in order to prepare a suitable feed for flotation.

The mass frequency concept (28) was used to characterise the size distribution of the sample crushed to -7 mesh and the sample ground for 10, 15 and 20 minutes. The term mass frequency is defined as $\Delta C_K / \Delta \log K$, where ΔC_K states the percent distribution of either Bi or Cu in the fraction and $\Delta \log K$ is the logarithmic difference between the upper and lower limits of the size fraction. The results in Table 5 are plotted in Fig.10.

Fig.10 shows that with increasing fineness of the size fraction, distributions of Cu and Bi are decreased but from the 52 mesh size fraction the distribution of copper becomes higher than that of bismuth. In the size fraction -200 mesh + 40 microns, copper distribution showed a mass frequency peak which coincided exactly with the bismuth peak but it was higher than that of bismuth. The results of the experiment could be obscured by the beaker

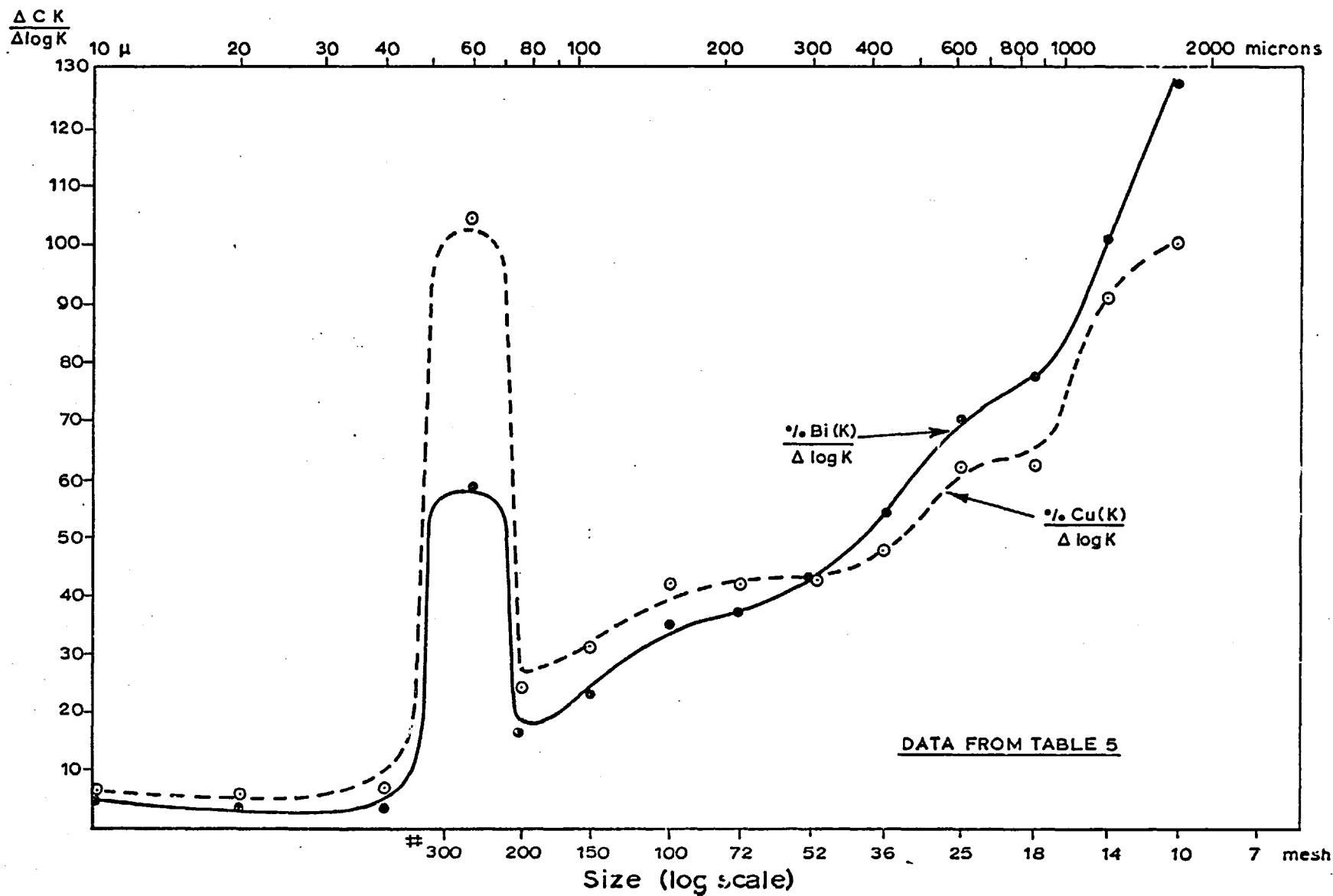


Fig.10 Distribution of Bi and Cu of the minus 7 mesh material (Coaser)

decantation technique used for sizing the minus 200 mesh fractions.

Grinding tests were carried out in a laboratory rod mill to determine the grinding time required. 500 g samples of -7 mesh were ground for 10, 15 and 20 minute periods in a laboratory rod mill with a rod charge of 4.555 Kg and 500 ml. of distilled water. The ground products were sized using B.S.S. sieves to 300 mesh. Each fraction was then analysed for bismuth and copper. Results are given in Table 8 and plotted in Figs.11 and 12 as mass frequency curves, as before.

Fig.11 shows that 50.38%, 63.48% and 77.84% minus 200 mesh were obtained in 10, 15 and 20 minutes grinding periods respectively. Fig.12 shows the mass frequency curves of bismuth and copper on the various grinding products. The mass frequency peaks of copper nearly coincided with the bismuth peaks. By increasing the grinding period the mass frequency peak was transferred to finer size fractions. After 15 minutes grinding characteristic Bi and Cu mass frequencies were found in the fraction -150 + 300 mesh. In coarser than 300 mesh fractions copper distribution was higher than bismuth distribution whereas bismuth distribution is higher than that of copper in finer than 300 mesh fractions.

Table 8. Composition of Product Obtained from a
Laboratory Rod Mill Batch Grind

Grinding time	Size (B.S.S.)	weight %		Bi		Cu	
		Direct	Cumul. (finer)	Grade	Dist.	Grade	Dist.
10 min.	+ 25	0.45	99.55	0.84	0.56	3.80	0.46
	- 25+ 36	0.35	99.20	0.87	0.44	4.99	0.48
	- 36+ 52	0.66	98.54	1.30	1.26	5.74	1.03
	- 52+ 72	2.75	95.79	0.72	2.89	3.02	2.26
	- 72+100	20.10	75.69	0.62	18.21	3.42	18.66
	-100+150	15.66	60.03	0.73	16.70	4.47	19.00
	-150+200	9.65	50.38	0.82	11.56	5.12	13.41
	-200+300	7.26	43.12	0.70	7.42	4.56	8.99
	-300	43.12		0.65	40.96	3.05	35.71
	Total	100.00		0.68	100.00	3.68	100.00
15 min.	+ 25	0.20	99.80	0.66	0.18	2.75	0.15
	- 25+ 36	0.09	99.71	0.97	0.13	3.58	0.08
	- 36+ 52	0.09	99.62	1.06	0.14	3.53	0.09
	- 52+ 72	0.23	99.39	0.84	0.27	1.70	0.10
	- 72+100	2.07	97.32	0.46	1.33	1.15	0.63
	-100+150	17.13	80.19	0.60	14.38	3.35	15.12
	-150+200	16.71	63.48	0.73	17.06	4.70	20.69
	-200+300	10.30	53.18	0.59	8.50	4.57	12.14
	-300	53.18		0.78	58.01	3.64	51.00
	Total	100.00		0.72	100.00	3.80	100.00
20 min.	+ 25	0.24	99.76	0.54	0.20	3.17	0.21
	- 25+ 36	0.08	99.68	0.57	0.08	3.16	0.07
	- 36+ 52	0.08	99.60	1.00	0.12	3.86	0.08
	- 52+ 72	0.09	99.51	0.91	0.12	2.88	0.07
	- 72+100	0.57	98.94	0.62	0.54	1.42	0.22
	-100+150	4.16	94.78	0.41	2.63	2.70	3.08
	-150+200	16.94	77.84	0.66	17.21	4.17	19.36
	-200+300	14.70	63.14	0.66	14.94	4.70	18.94
	-300	63.14		0.66	64.16	3.35	57.97
	Total	100.00		0.66	100.00	3.65	100.00

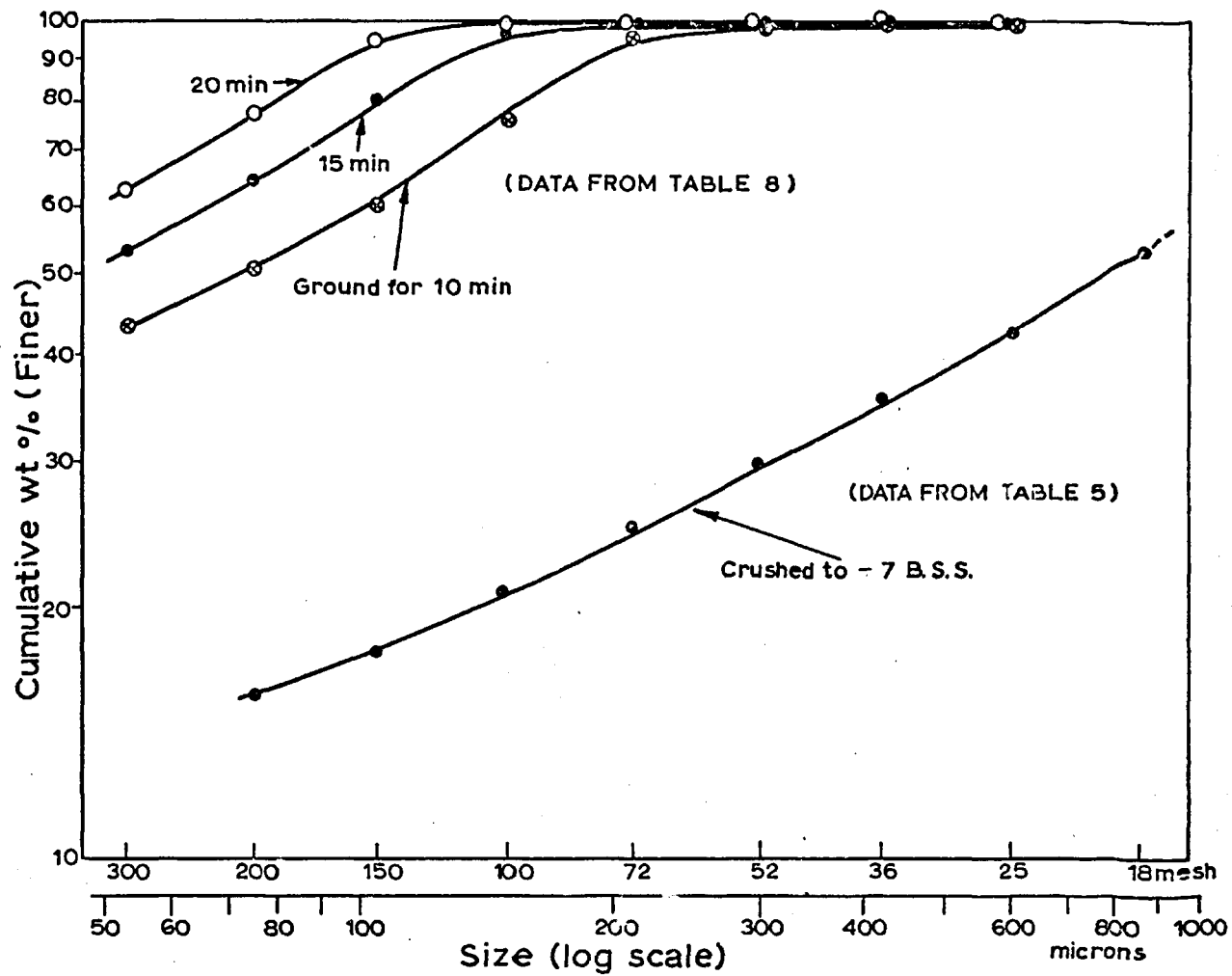


Fig.11 Relationship between the grinding time and cumulative weight percent of finer products. (Data from Tables 5 and 8)

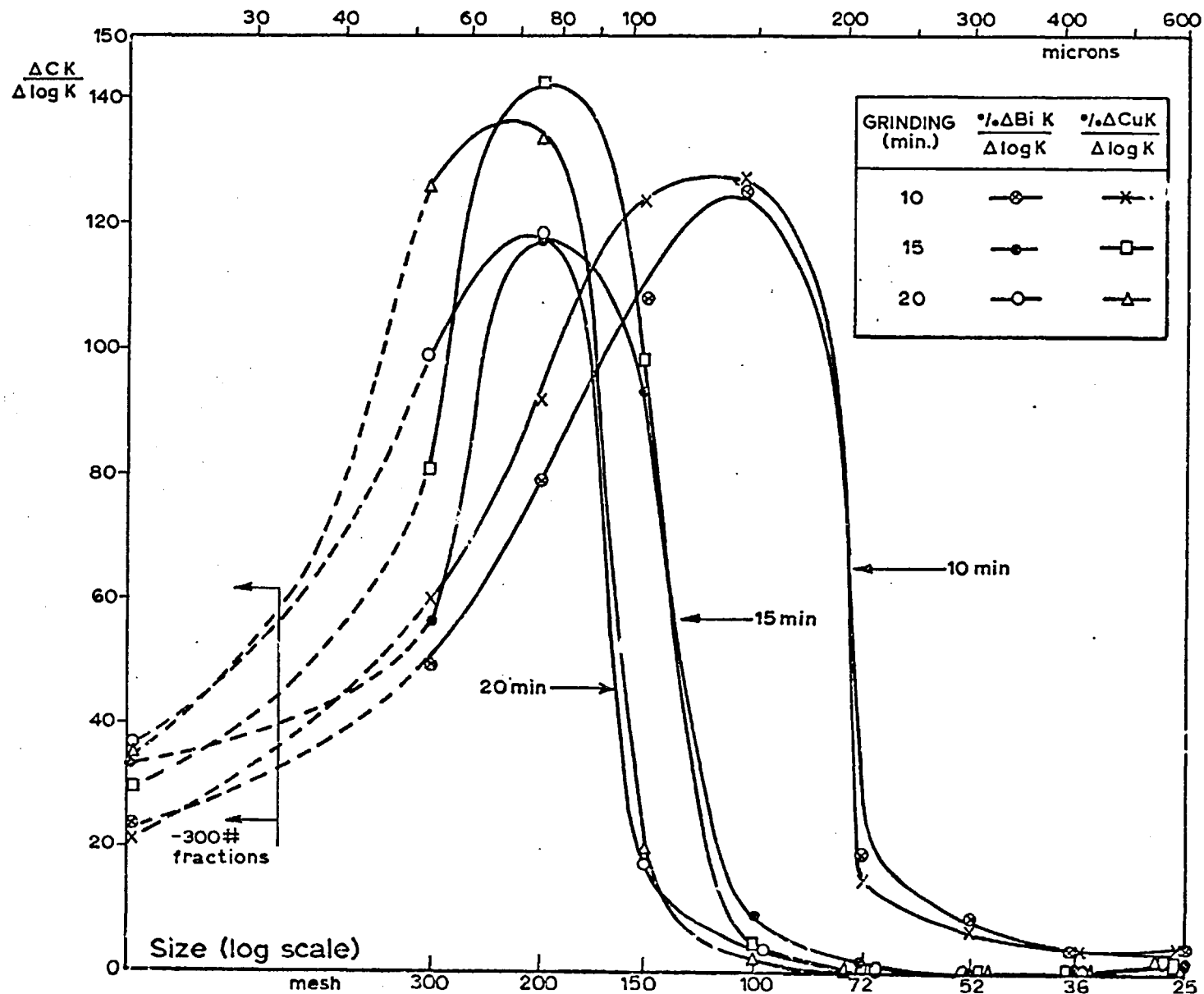


Fig.12 Distribution of Bi and Cu in the various grinding products. (Data from Table 8)

6. FLOTATION

6.1 Flotation Tests

Process selection showed that flotation was the most reasonable alternative for producing a copper concentrate as well as Bi-Pb mineral. Therefore, testwork was planned to assess the amenability of the ore to bulk flotation.

Initially a literature survey was carried out to establish the types and dosages of reagents currently used in flotation plants treating similar ores elsewhere in the world (see test section).

The flotation tests were carried out in a 500 g cell at a pulp density of 20 percent solids. Distilled water was used in all tests and the flotation machine was operated at 1000 r.p.m. with 4.4 litre per minute of air introduced. The flotation products were dried, weighed, passed through a 25 mesh screen, to break up any agglomerates formed during the drying, and then sampled for analysis

Consumption of Lime

In order to find out the required amount of lime (CaO) to obtain different pH values of the pulp during flotation tests, the following tests were carried out using distilled water and 500 g -7 mesh sample ground for 20 minutes, i.e. to 77.84% minus 200 mesh. The sample with a pulp density of 40% solid by weight was conditioned in a laboratory flotation cell. After the addition of a known quantity of lime it was conditioned for another 25 minutes and then the pH was measured. Results are shown in Fig.13 in which it can be

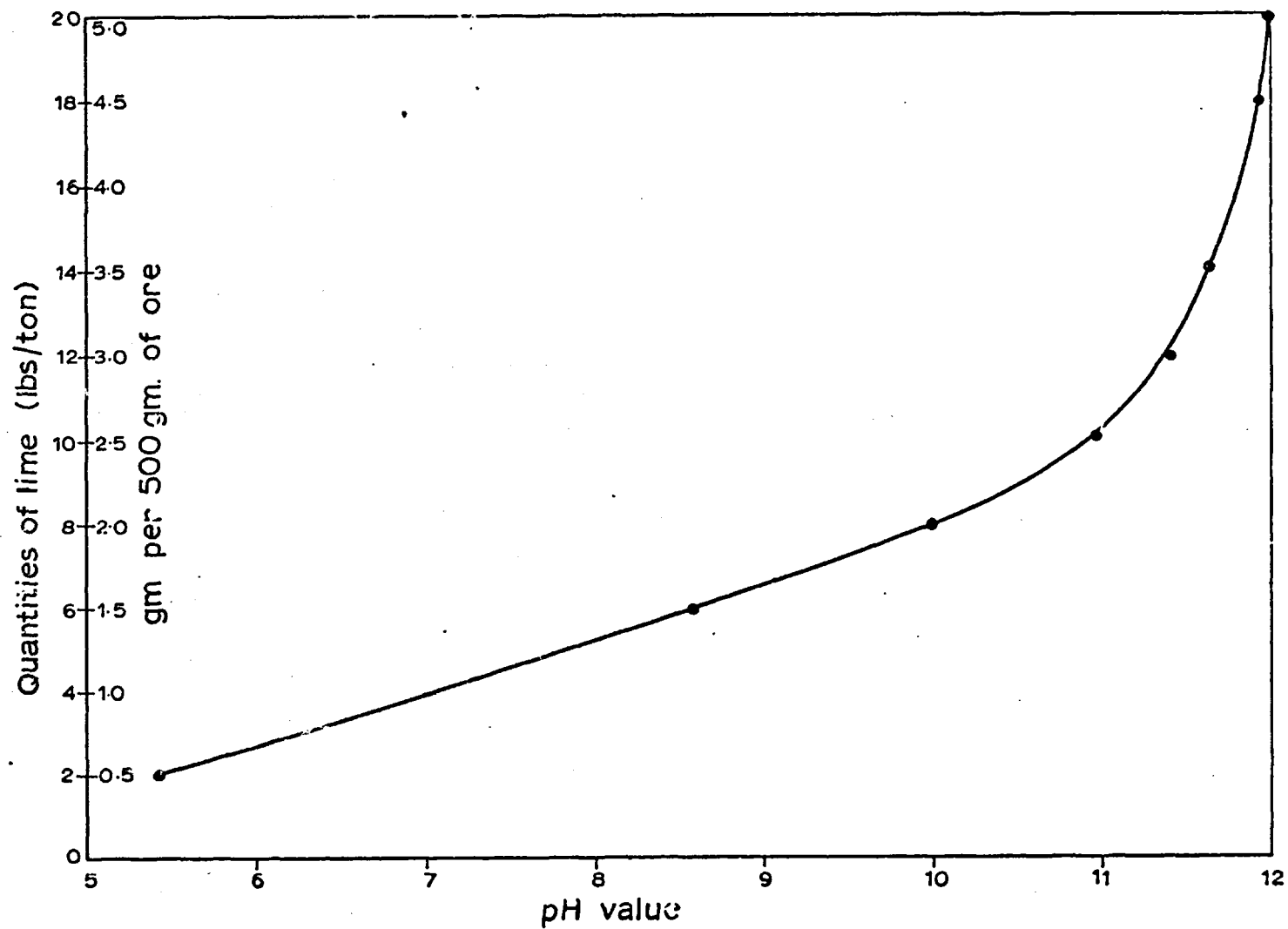


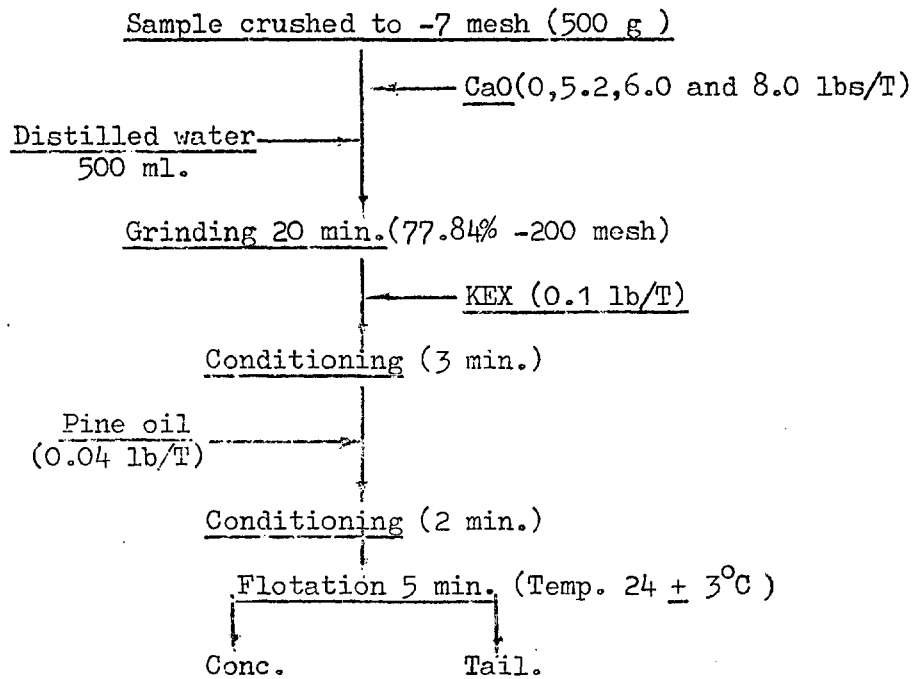
Fig.13 Relationship between quantities of lime and pH value.

seen that over pH 11 the amount of lime required to increase the pH value was extremely high.

6.2 Flotation 1 - Effect of pH with KEX

Preliminary tests were carried out to investigate the effect of pH on the recovery of bismuth and copper in bulk flotation using pine oil as frother and potassium ethylxanthate (abbreviated as KEX) as collector. pH control was provided by addition of CaO into the mill and later addition of H_2SO_4 prior to conditioning. The procedure followed is given below (Procedure of Flotation 1).

Procedure of Flotation 1



The results obtained are shown in Table 9 (Appendix) and plotted in Fig.14.

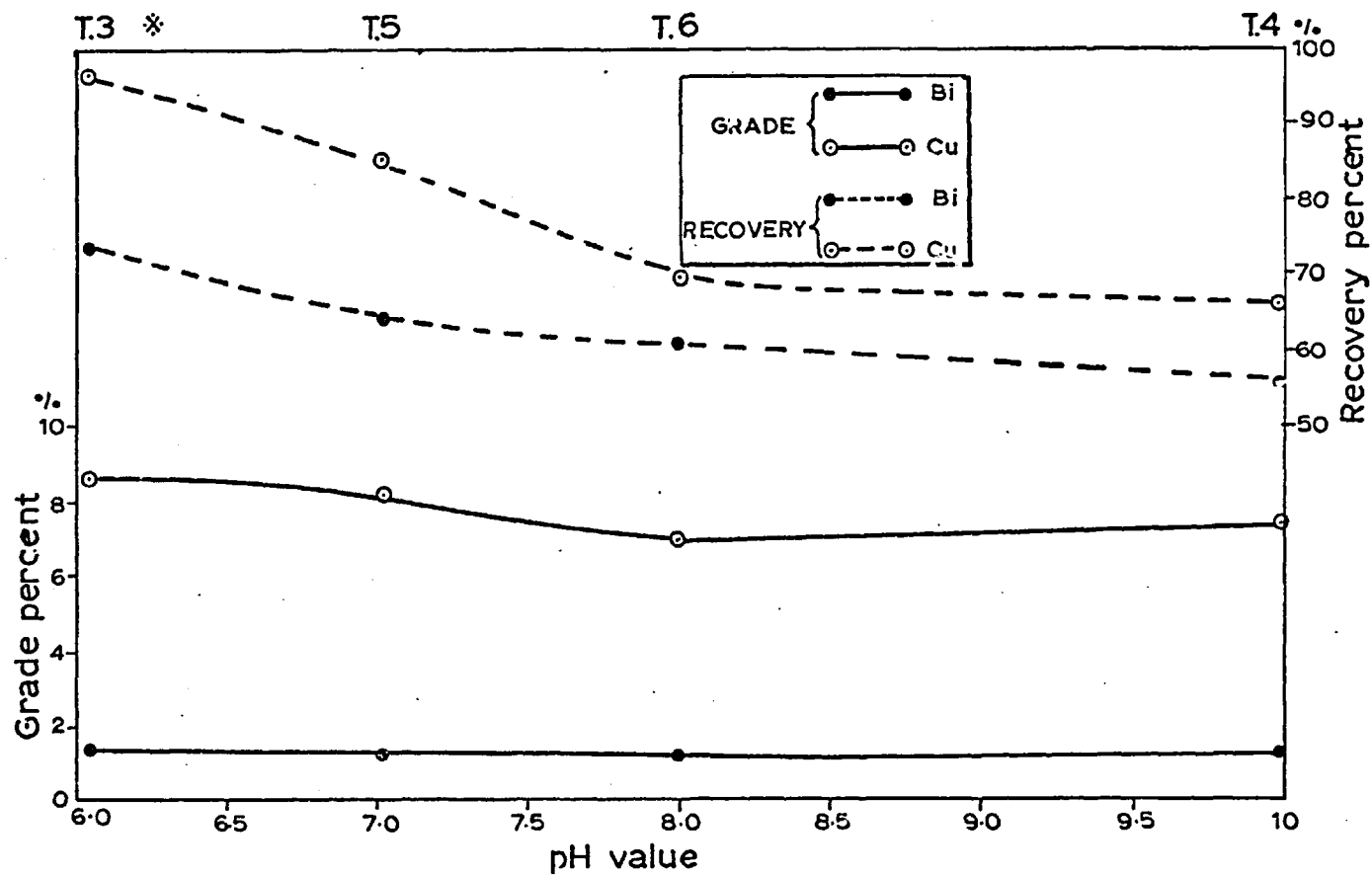


Fig.14 Results of flotation with KEX and pine oil on the various pH ranges. (Data from Table 9)

* Abbreviation of Test Number

Fig.14 shows that although there was no variation in the bismuth grade in these four flotation tests, the copper grade and recoveries of bismuth and copper are slightly increased with decreasing pH.

Microscopical examination of the products revealed that a considerable amount of quartz and mica particles were flocculated with the sulphide minerals. It was also found that the sulphide minerals which are locked with pyrite remained in the tailings.

6.3 Flotation 2 - Effect of Calgon and Sodium Silicate

The results of Flotation 1 suggested that the use of calgon as a dispersant and sodium silicate as a depressant for gangue slimes and silicious gangue minerals. Sodium carbonate was used instead of lime since sulphide minerals which were locked with pyrite seemed to be depressed.

This test was carried out in order to find out the effect of calgon and sodium silicate on the grade of bismuth and copper in bulk flotation. The procedure used in this test was similar to the preliminary tests (Flotation 1) except that calgon, sodium carbonate and sodium silicate were added in the mill and incremental floats were obtained, each of one minutes duration (total flotation time was 5 or 6 minutes). The products were called concentrate 1, 2, 3, 4, 5 and 6 respectively. Detailed results are given in Table 10 (Appendix) and plotted in Fig.15 which represents percent recovery versus percent grade, which are expressed as cumulative results

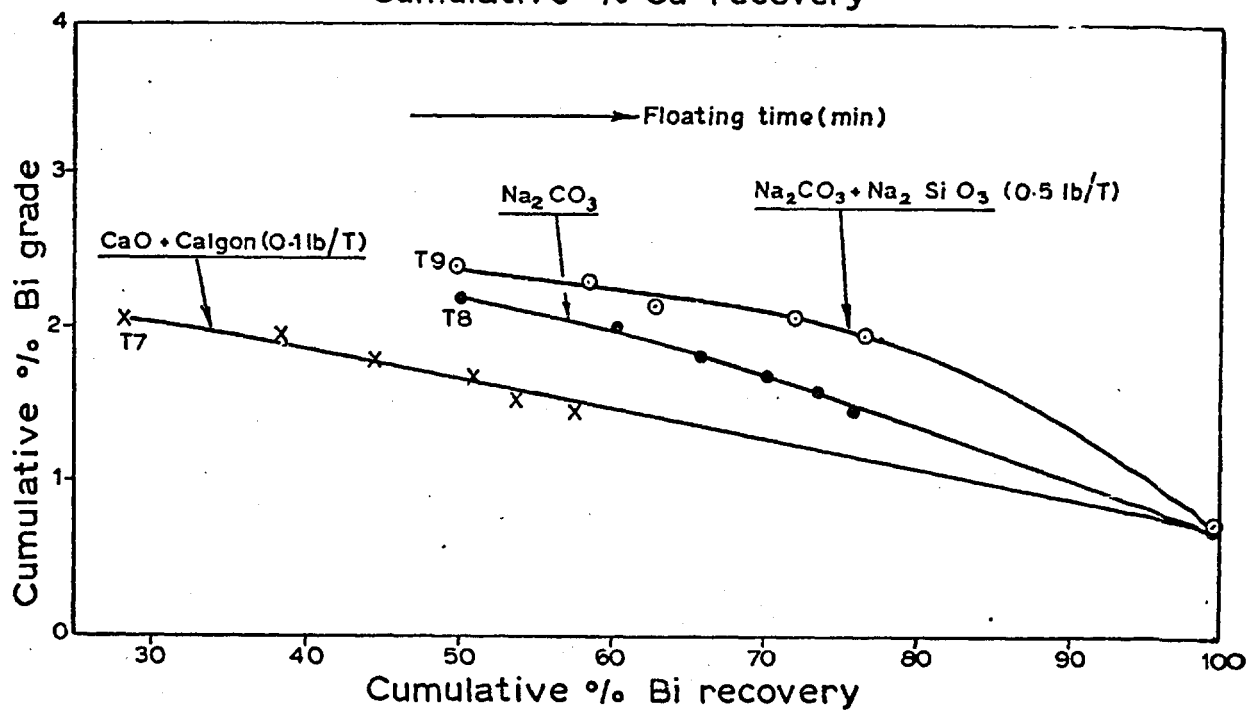
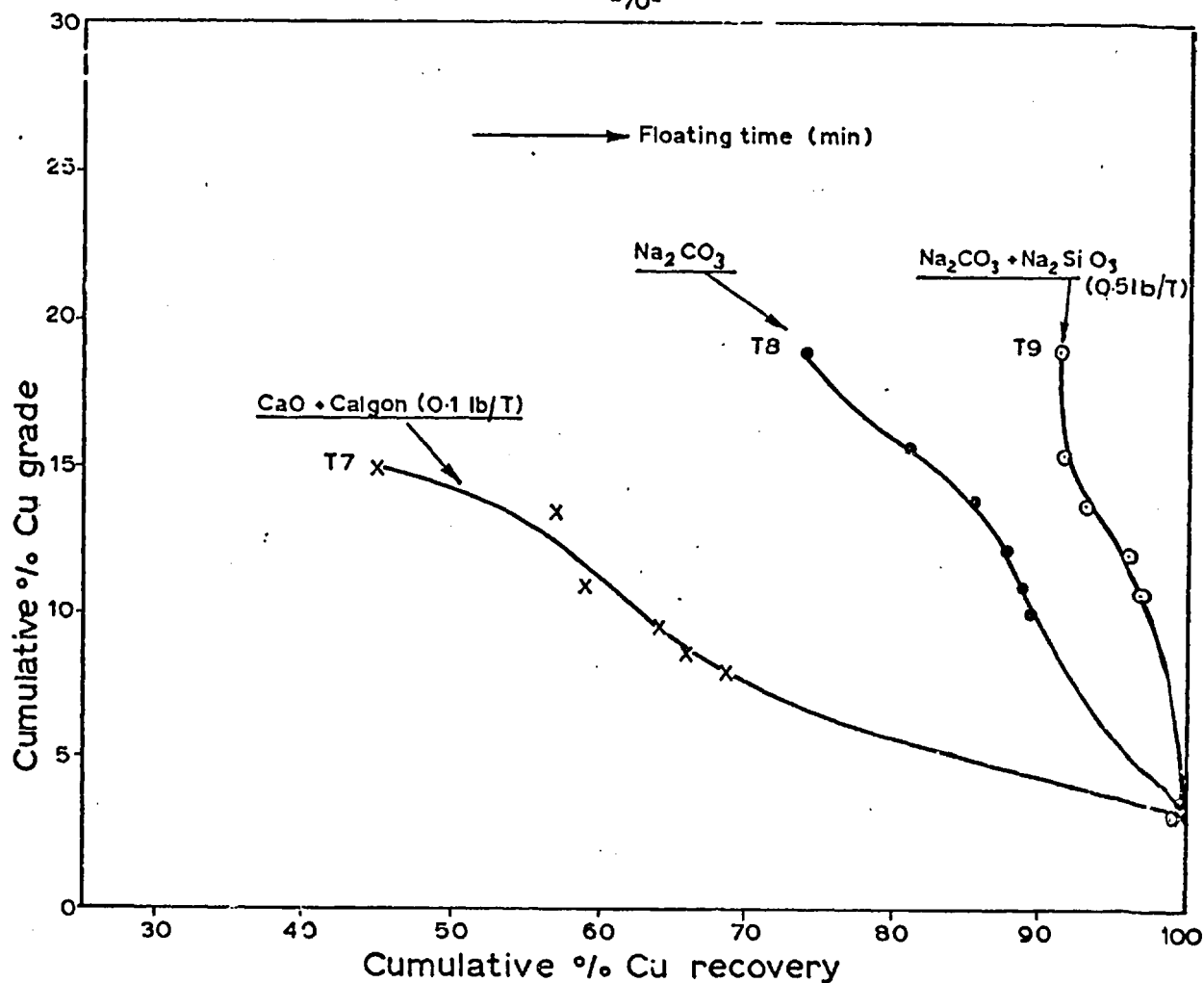


Fig. 15 Results of flotation with Calgon, Na_2SiO_3 and KEX at pH 8.0 ± 0.3 (Data from Table 10)

at different floating times (each one minute).

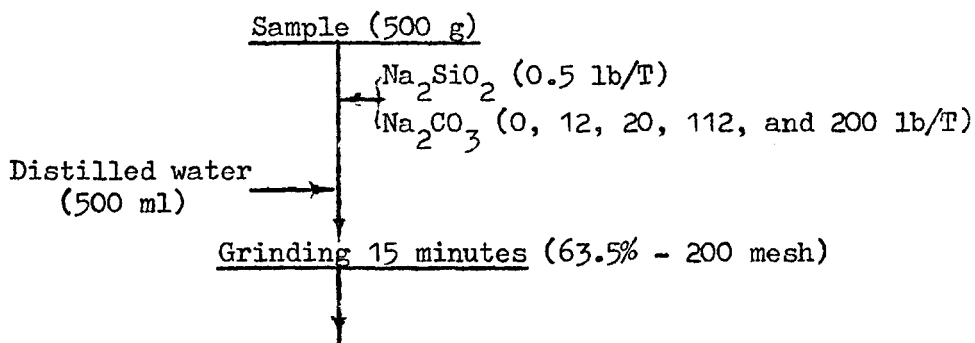
Comparison between the results of tests 6 and 8 (the effect of CaO and Na_2CO_3), test 4 and 7 (the effect of calgon), and test 8 and 9 (the effect of Na_2SiO_3) showed that under the conditions of test 9 it was possible to obtain the best recovery and grade. Therefore Na_2CO_3 and 0.5 lb Na_2SiO_3 /ton of ore were selected to be used for rougher flotation.

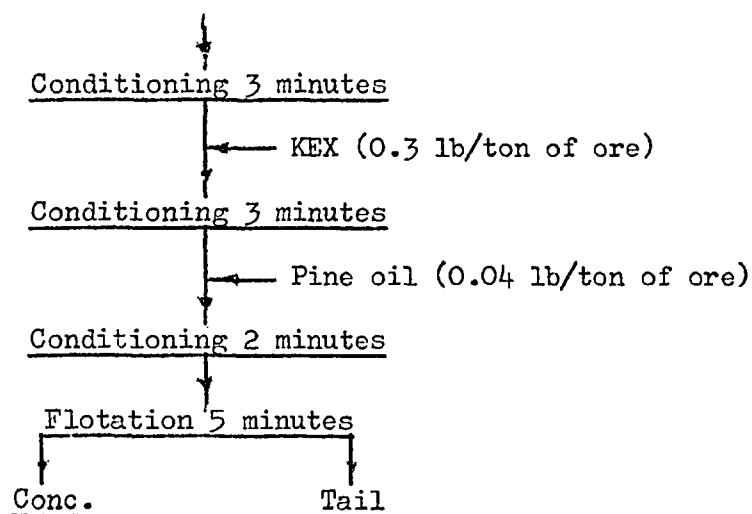
Microscopic examination of these products showed that a considerable amount of the sulphide minerals was not floated and still remained in the tailing. These results suggested a small increase in xanthate addition and that the sample should be ground for 15 minutes which is less than previous grinding time (20 minutes).

6.4 Flotation 3 - Effect of Na_2CO_3 with KEX

The purpose of this flotation test was to investigate the effect of pH, with sodium carbonate and 0.3 lb KEX/ton of ore on the grade and recovery of bismuth and copper in bulk flotation. The procedure used is given below (Procedure of Flotation 3).

Procedure of Flotation 3





The results obtained are given in Table 11 (Appendix) and plotted in Fig.16.

Fig.16 shows that the grades and recoveries did not vary very much but slightly higher Cu grade and lower Bi recovery were obtained at pH 8.0. In tests 9 and 12 the flotation conditions were the same except that 0.1 lb KEX per ton of ore was used in test 9 and 0.3 lb KEX per ton of ore was used in test 12. But it was found that there is no great difference between the results of tests 9 and 12 in grades and recoveries (Figs.15 and 16). These results indicate that potassium ethyl xanthate is not a suitable collector for this sample, and suggest the use of a stronger collector.

6.5 Flotation 4 - Effect of KAX

In the previous flotation tests, KEX was used as collector. However, it showed a low floatability of sulphide minerals and suggested the use of a stronger collector. Flotation tests with similar conditions, as used in Flotation 3 (T.11-T.15) were carried

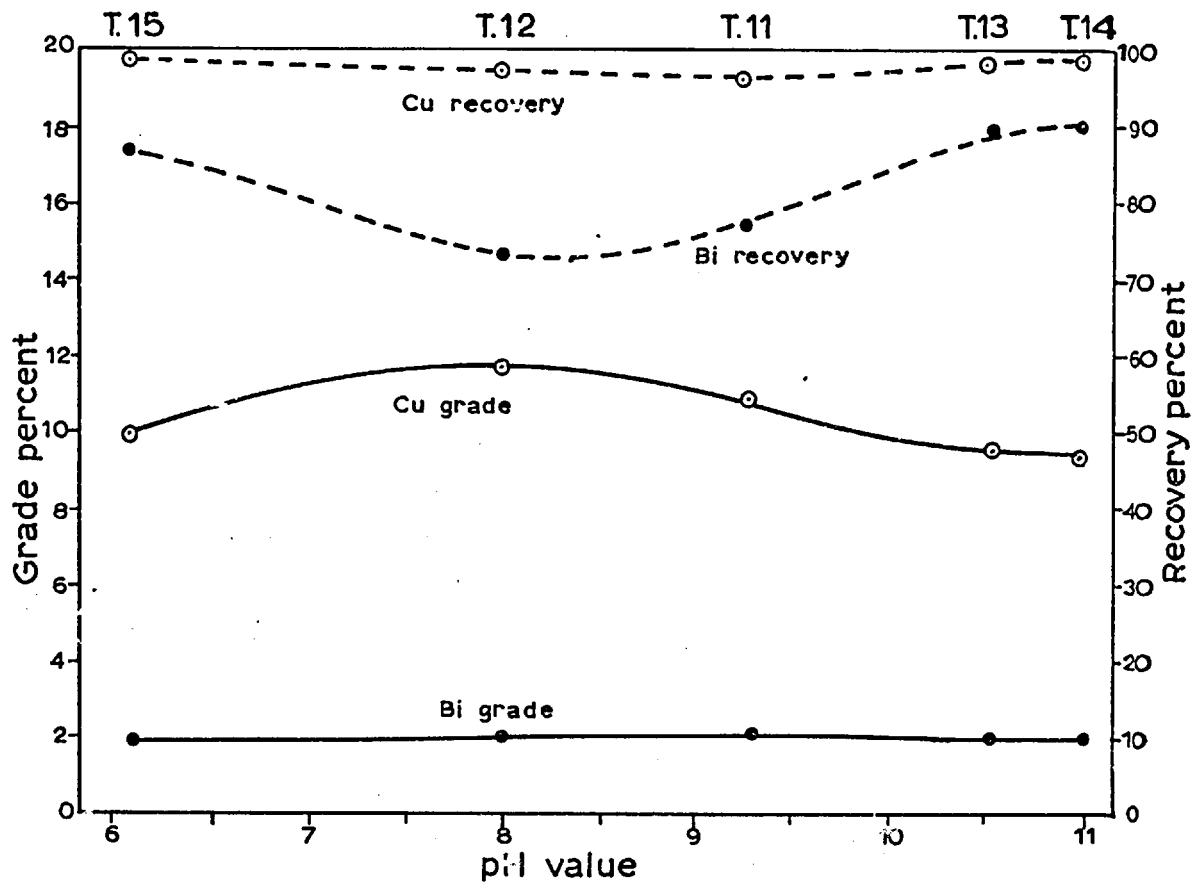


Fig.16 Results of flotation with Na_2CO_3 , Na_2SiO_2 and KEX at various values of pH (Data from Table 11)

out replacing Na_2CO_3 and KEX by CaO and 0.3 lb potassium amyl xanthate (KAX) per ton of ore respectively to investigate the effect of KAX and pH on the grade and recovery. The results obtained are given in Table 12 (Appendix) - ~~v~~ and plotted in Fig.17.

Comparison of Fig.16 and Fig.17 showed that at about pH7 it was possible to obtain about 86% Bi and 98% Cu recovery, and 2% Bi and 12.6% Cu grade using KAX without adding CaO. As a result, bulk flotation in neutral pH was chosen and used throughout the subsequent flotation tests.

6.6 Flotation 5 - Effect of Closed Circuit Grinding in Flotation

In order to determine the most suitable grinding method two flotation tests using closed circuit grinding were carried out, with and without Na_2SiO_3 . The grinding was carried out for 10 minutes with wet screening at 150 mesh, the oversize fraction being returned to the mill. These tests were carried out at a pH of about 7.5 and bulk rougher concentrates were cleaned by a second cleaning stage. The procedure used is given below (see Procedure of flotation 5) and results obtained are shown in Table 13. Each grade and recovery of concentrates calculated from Table 13 (Appendix) are shown graphically in Fig.18.

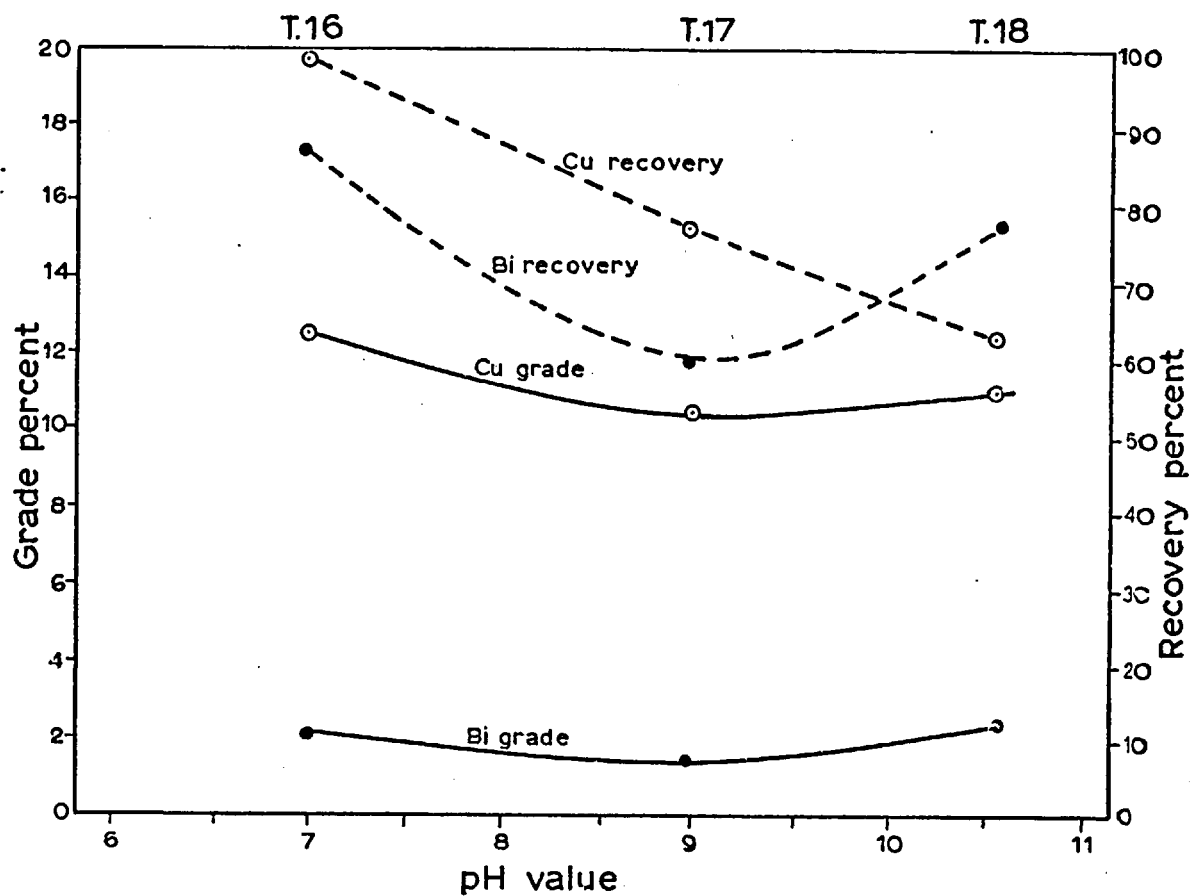
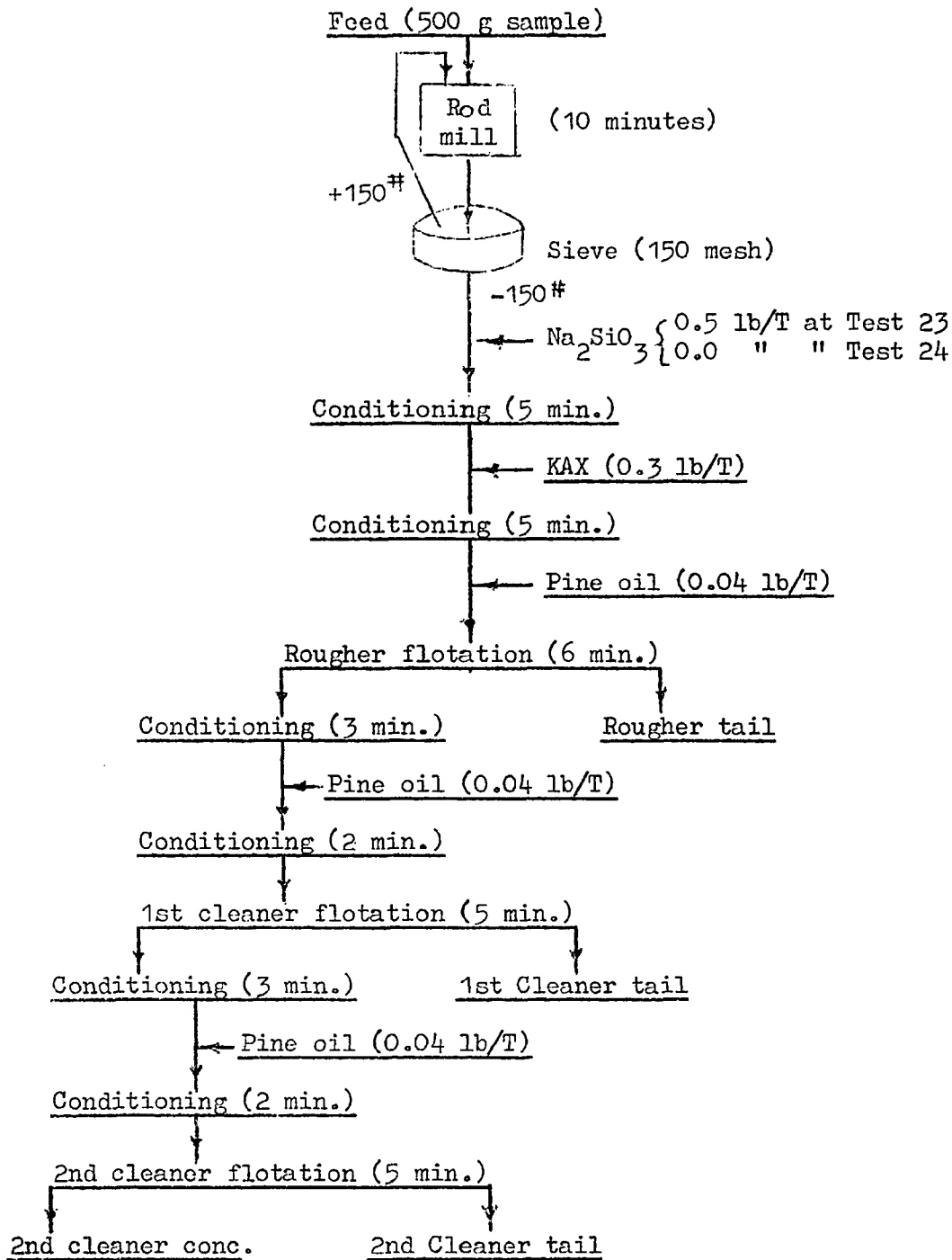


Fig.17 Results of flotation with CaO and KAX at the various pH values. (Data from Table 12)

Procedure of Flotation 5



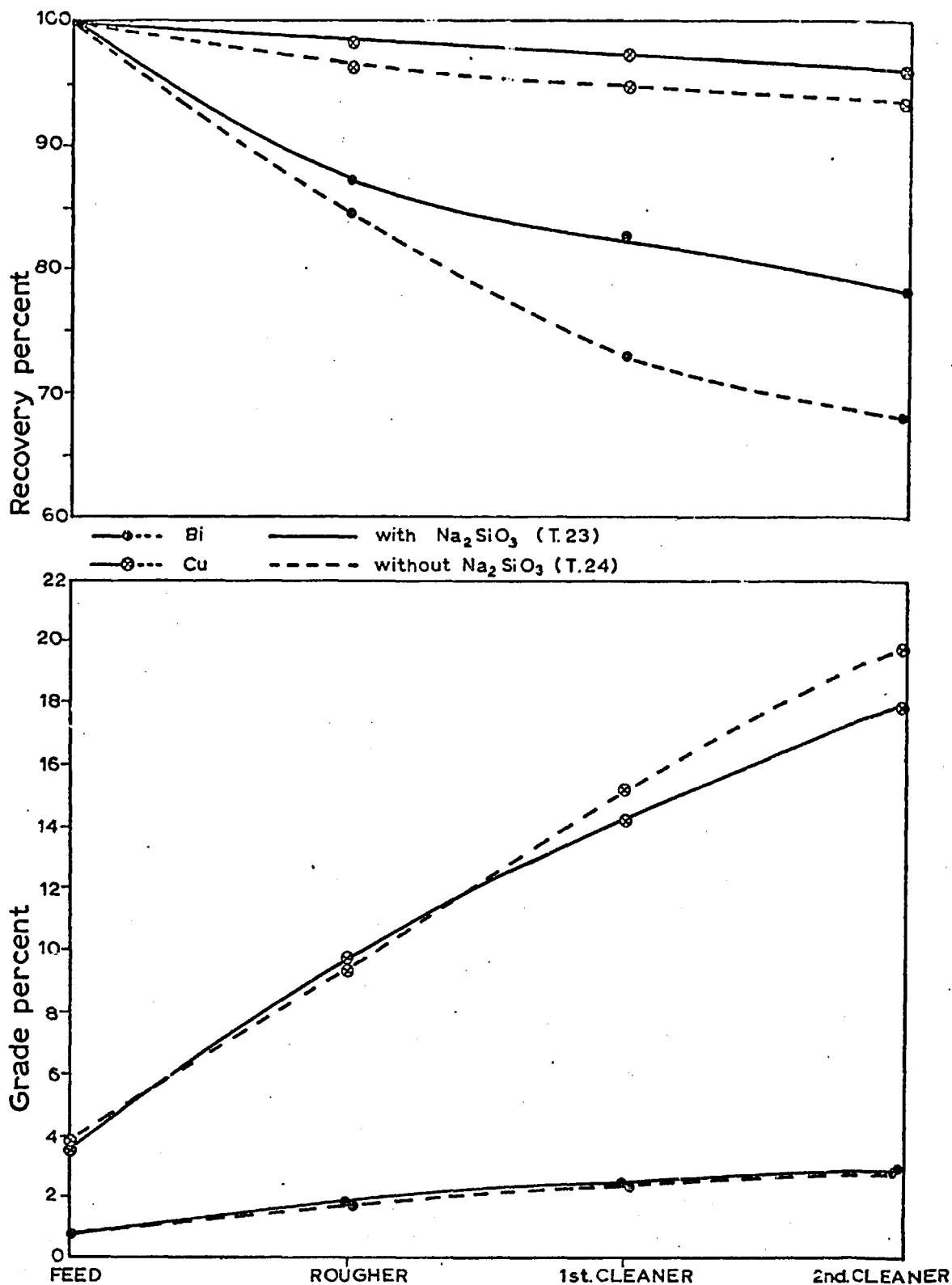


Fig.18 Comparison between results obtained with and without Na_2SiO_3 after closed circuit grinding and using KAX and pine oil (Data from Table 13)

Table 13 shows that the grades of Cu and Bi in the concentrate and the Bi grade in the tailing were higher when Na_2SiO_7 was not used, except in the case of the grades of the Bi concentrates which were the same with or without Na_2SiO_3 .

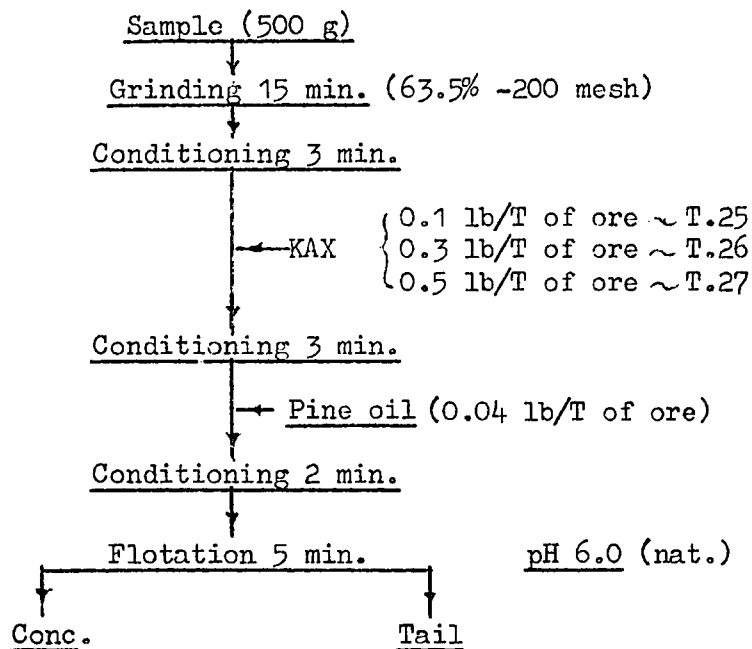
In Fig.18 the recovery and grade in the concentrate for both bismuth and copper are shown on the ordinate, the rougher and cleaner steps are the abscissa. The graph (Fig.18) shows that a concentrate grade of 3 per cent bismuth was produced from both with and without Na_2SiO_3 , but grade of copper was about 2 per cent higher with the latter.

Comparison between test 16 (Table 12 and Fig.17) and test 23 (Table 13 and Fig.18) shows that there were no differences in the grades of tailings, which illustrates that closed circuit grinding does not affect the production of higher grades and recoveries.

6.7 Flotation 6 - Effect of Dosage of KAX

The previous flotation test results showed that KAX is more effective, leading to higher grade and recovery of both bismuth and copper. Three tests were carried out to determine the minimum level of required KAX to achieve reasonable grades and recoveries. The procedure used is given below (procedure of flotation 6).

Procedure of Flotation 6



Incremental floats were obtained after each one minute interval and results obtained are shown in Table 14 (Appendix) and plotted in Figs.19 and 20.

In Fig.19 the grades of bismuth and copper in the cumulative concentrates of incremental floats are shown on the ordinate, recoveries on the abscissa. This figure shows that with increasing concentration of KAX there are no big differences in grades and recoveries for either bismuth or copper except that bismuth is slightly lower with 0.1 lb KAX per ton of ore.

In Table 14, it was found that with increasing concentration of KAX (0.1, 0.3 and 0.5 lb/ton of ore) the grades of copper in concentrate 1 (one minute floated product at the beginning of flotation process) and grades of both bismuth and copper in tailings

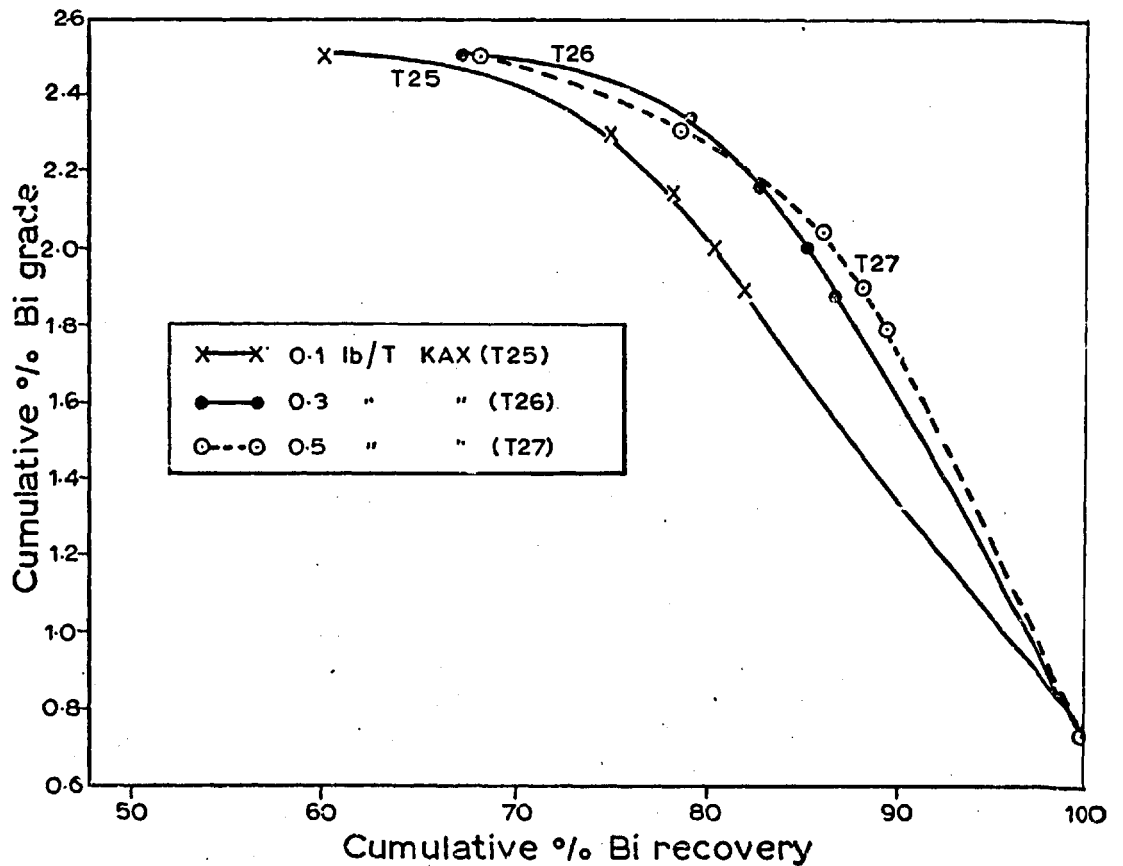
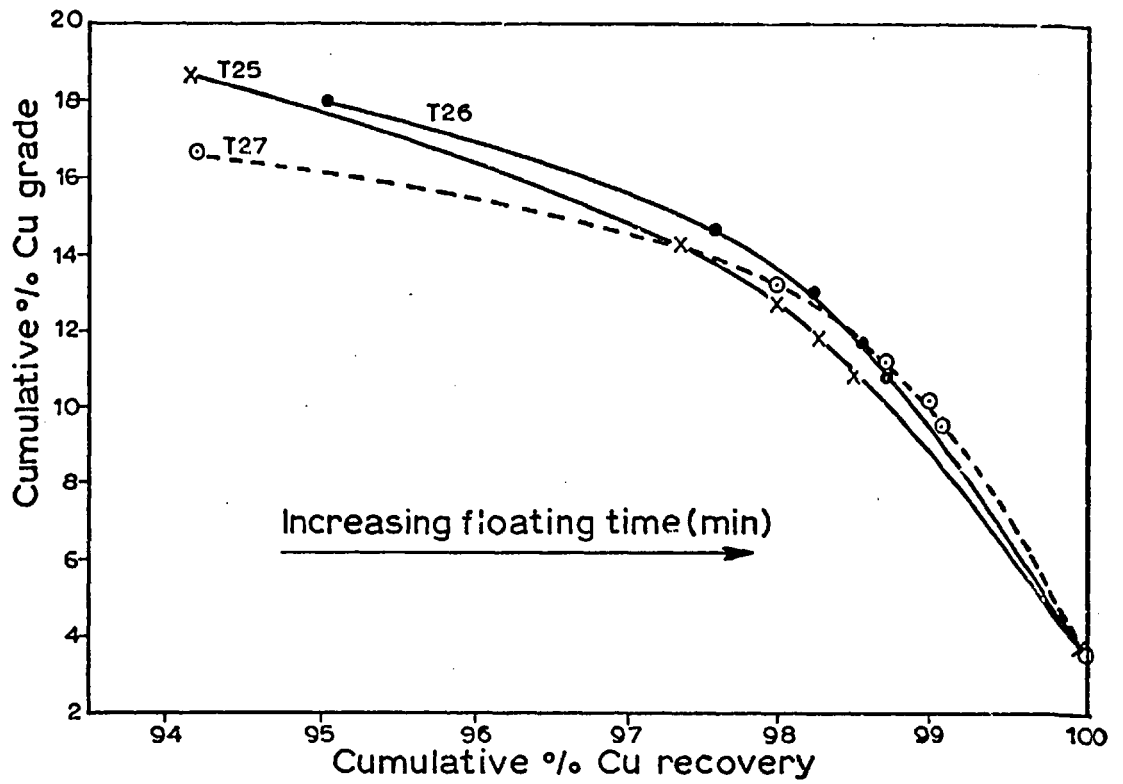


Fig. 19 Comparisons between results obtained using various concentrations of KAX (at pH 8). (Data from Table 14)

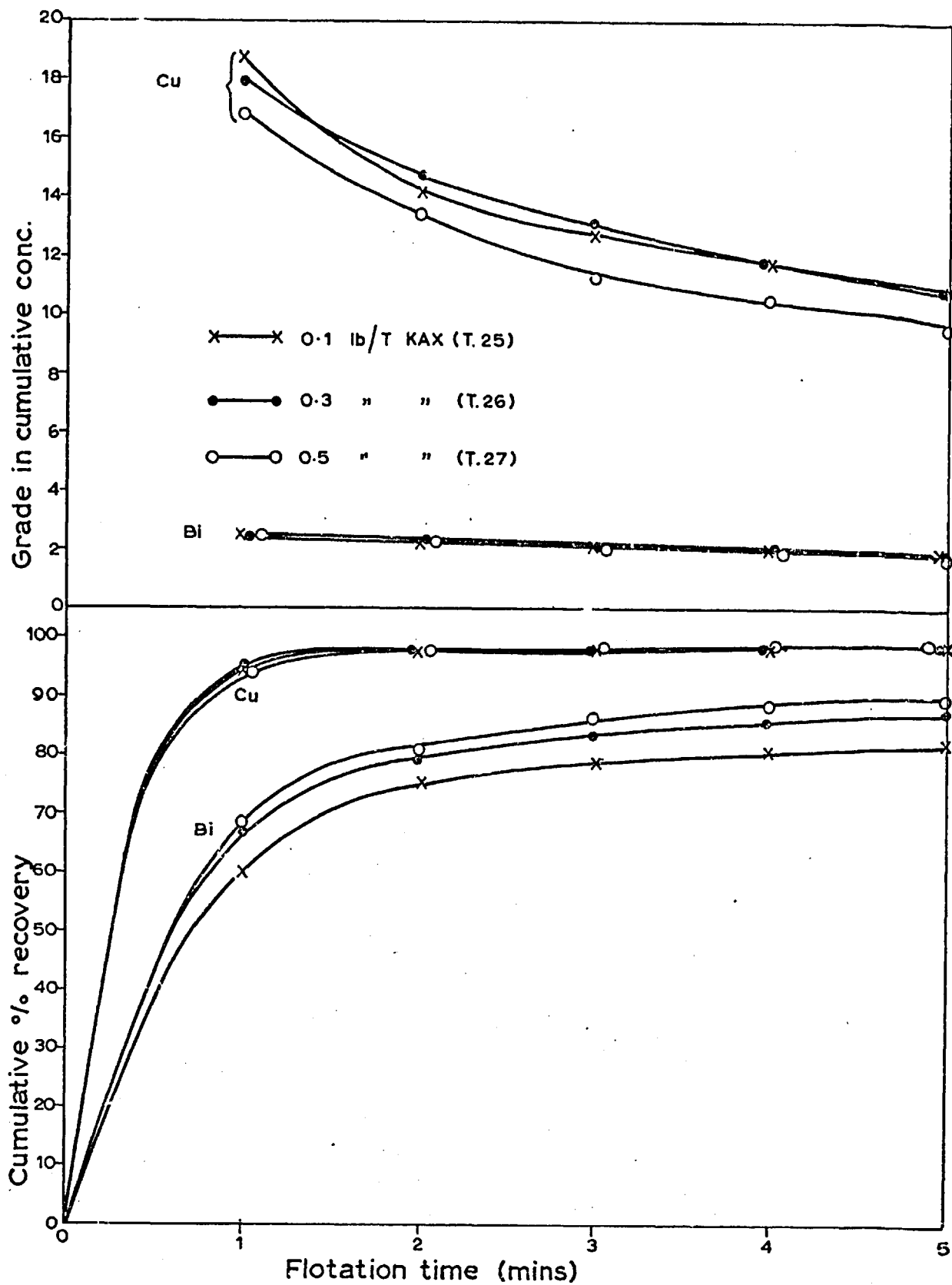


Fig. 20 Grade and recovery of the cumulative conc. versus flotation time. (Data from Table 14)

are decreased, whereas the grade of bismuth (2.5%) is the same as in concentrate 1.

Fig.20 shows a plot of cumulative per cent recovery and per cent grade in cumulative concentrate versus flotation time. In this figure almost 95% of the total copper was recovered in the first minute of the flotation, after 2 minutes the copper recovery did not increase and there were no changes in the recoveries for the different concentrations of KAX. The recovery of bismuth increased with increase in the concentration of KAX and flotation time. The grade of copper in the cumulative concentrate decreased with increasing flotation time and concentration of KAX. The grade of bismuth decreased very slowly with increasing flotation time but it did not change with concentration of KAX.

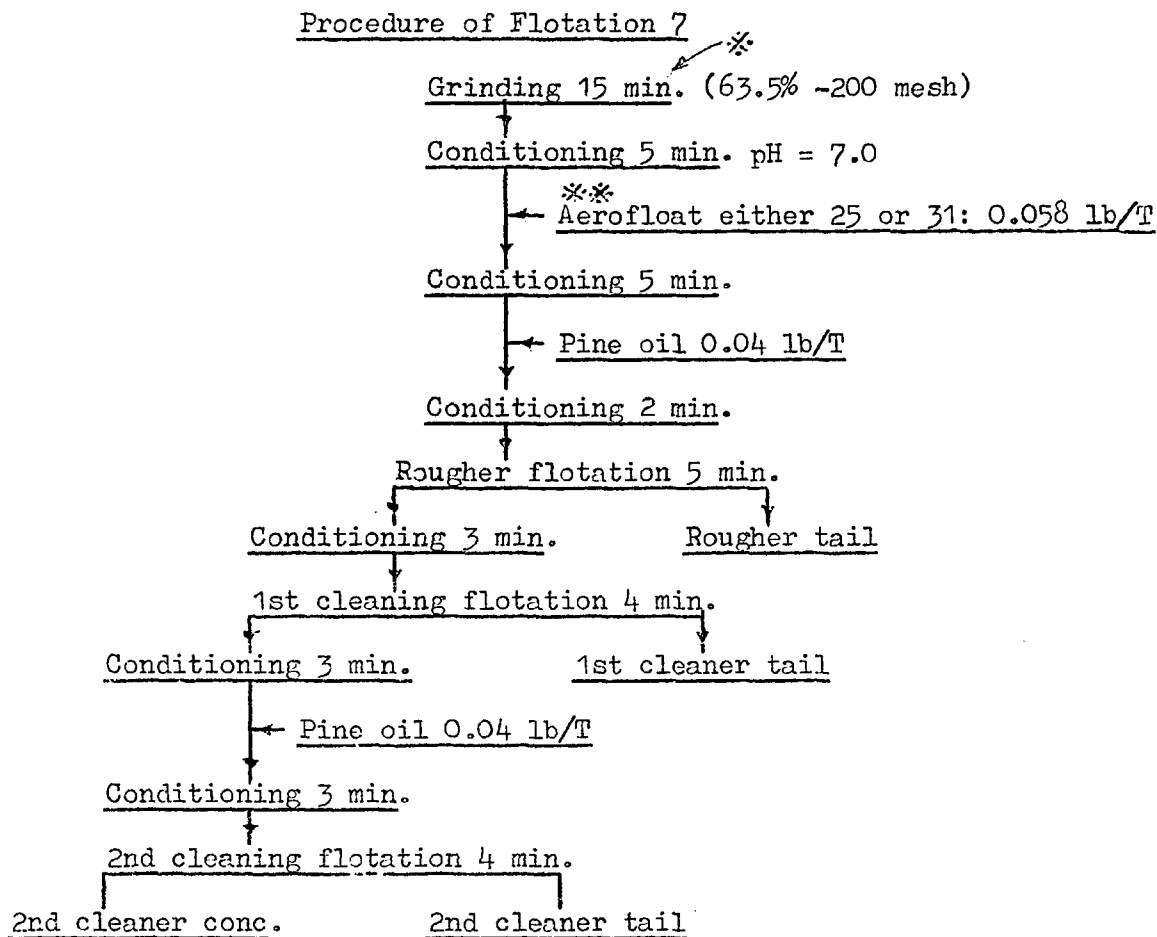
The tailing obtained from Test 26 (Flotation 6) was screened and separated by heavy liquid for examination under the microscope.

Microscopic examination of the products revealed that the tailing appeared to be reasonably free of any unfloated tarnished sulphide grains and gangue-sulphide middlings. The examination of floated products revealed that a considerable number of gangue particles with tiny sulphide inclusions began to show up in the concentrates after 2 minutes of flotation.

6.8 Flotation 7 - Effects of Aerofloats

This test was carried out in order to find the effect of aerofloats 25 and 31 with pine oil on the recovery of bismuth and

copper in flotation. In tests 28 and 30, aerofloat 31 (0.058 lb/T) were used and aerofloat 25 (0.058 lb/T) in test 29. These collectors were added to the flotation cell except, in test 30, where it was added to the mill. Rougher flotation product was cleaned to the second cleaning stage. The procedure used is given below (procedure of flotation 7). The results obtained are shown in Table 15 (Appendix) and plotted in Figs. 21A and B.



* In test 30, Aerofloat 31 (0.058 lb/T) was added in the mill instead of in the flotation cell.

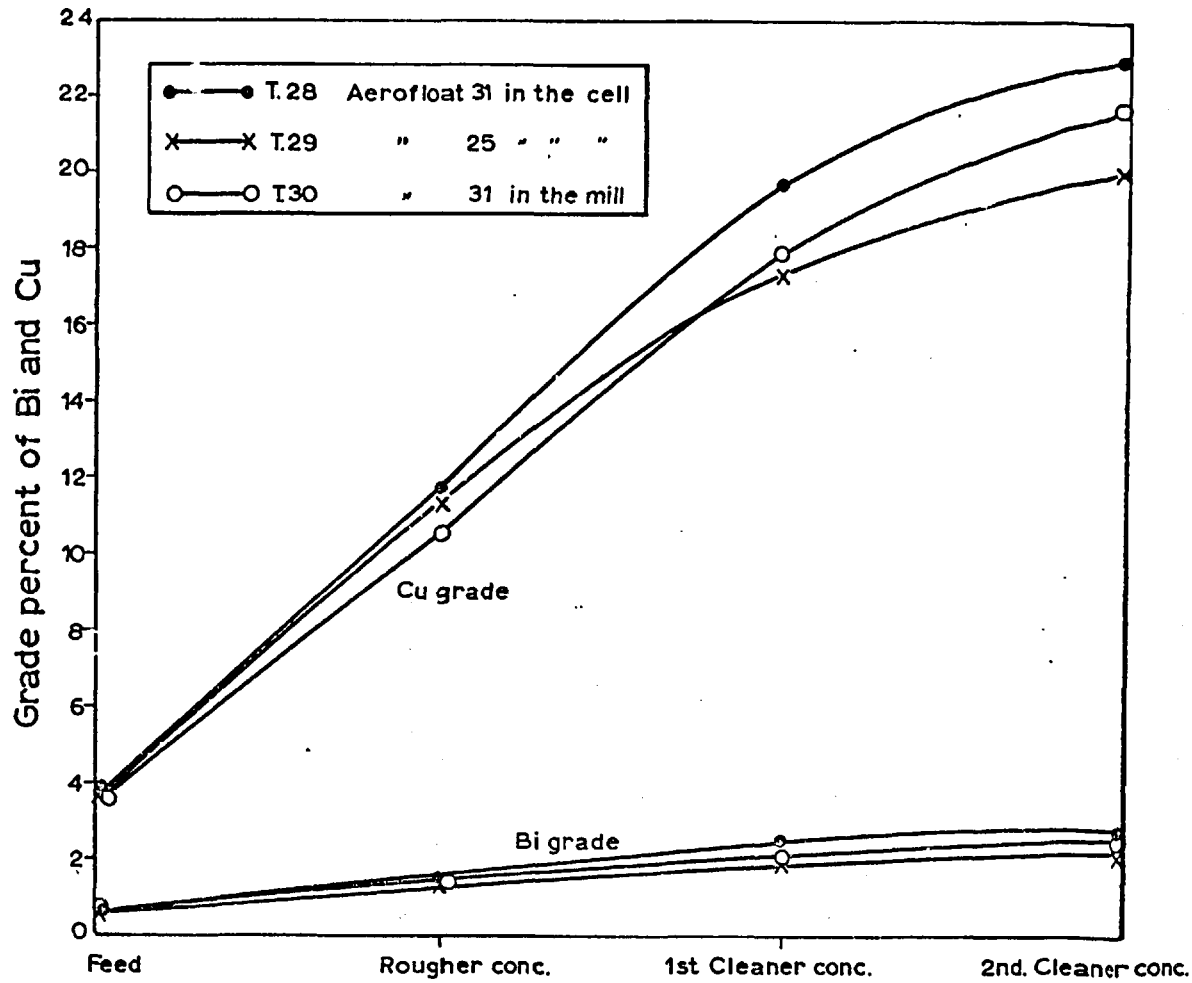


Fig. 21 (a) Comparison between grades obtained with Aerofloat 31 and 25 using pine oil. (Data from Table 15)

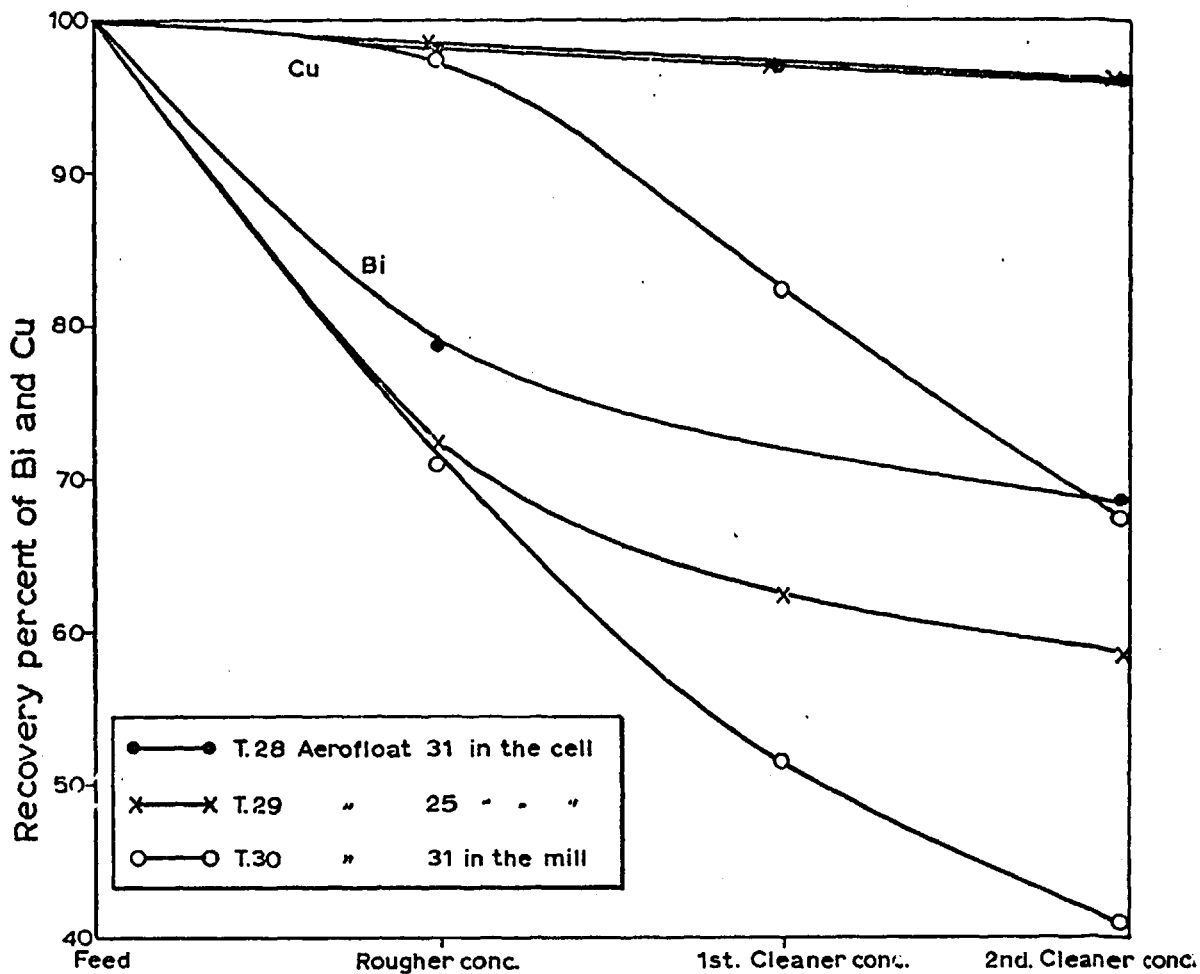


Fig.21 (b) Comparison between recoveries obtained with Aerofloat 31 and 25 using pine oil. (Data from Table 15)

✱✱ In test 28, aerofloat 31 (0.058 lb/T) was added in the flotation cell. In test 29, aerofloat 25 (0.058 lb/T) was added in the flotation cell.

In Fig.21A, the comparison between the results of tests 28 and 29 showed that grades of both bismuth and copper are higher with aerofloat 31 than with aerofloat 25. The comparison between the results of tests 28 and 30 also showed that grade of test 28 is higher than that of test 30 illustrating that aerofloat 31 should be added in the flotation cell instead of in the mill. It can be said that although there was very little variation in the bismuth grade from these three flotation tests, this figure shows the same pattern for all three % bismuth grade curves and suggests that they are not very different. In Figs.21A and B, the results of tests 29 and 30 showed that the higher values of grades in test 30 as compared with test 29 are associated with corresponding low values of recoveries.

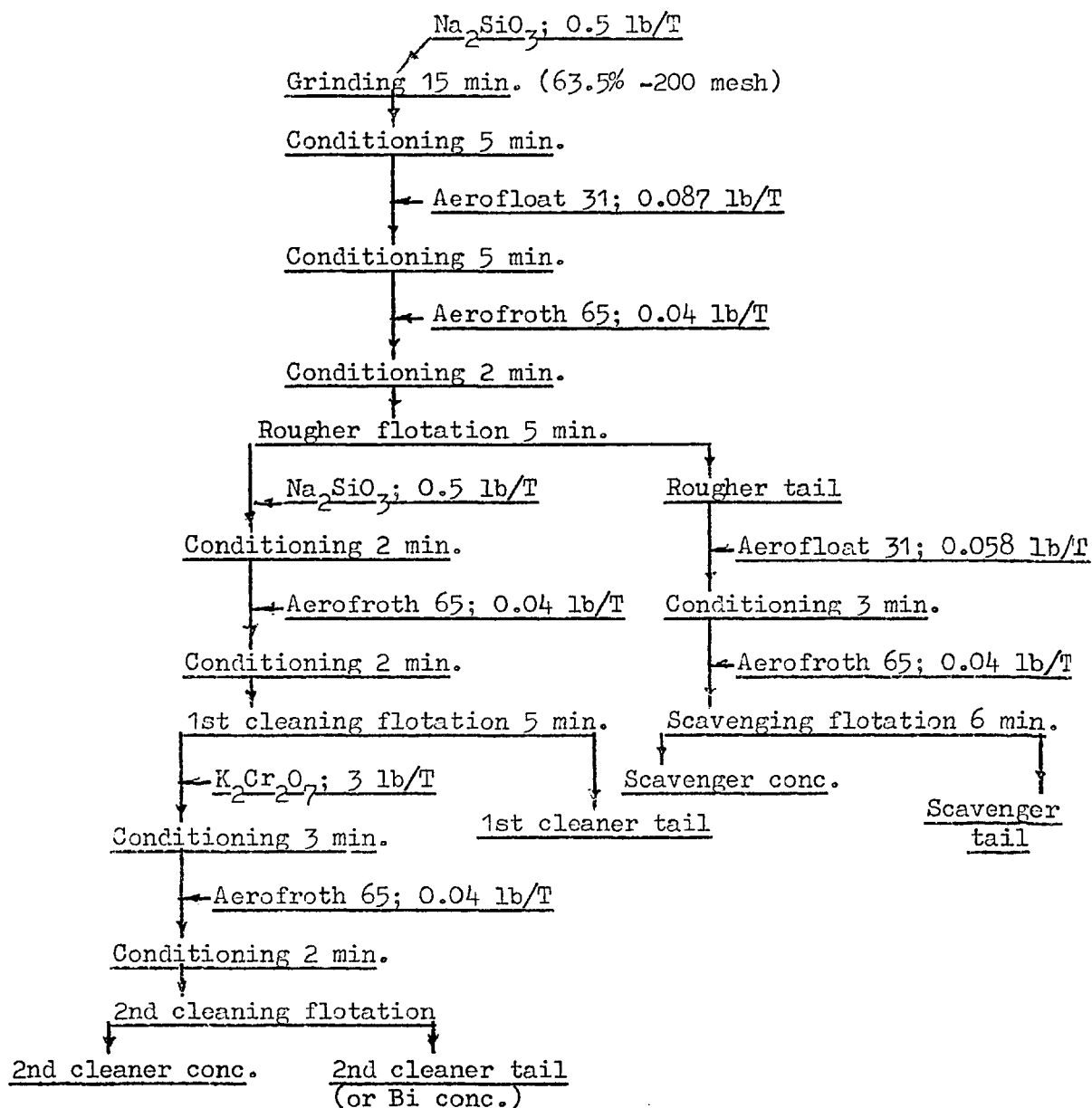
Comparison between the results of test 23 (in Fig.18) and test 28 (in Fig.21) shows that higher copper grade (23% Cu) was obtained with aerofloat 31 (T.28) than with KAX (T.23) where it was 18% Cu.

6.9 Flotation 8 - Effect of $K_2Cr_2O_7$ with Aerofloat 31 (2nd cleaning)

This test was carried out in order to find the effect of $K_2Cr_2O_7$ with aerofloat 31 and replacing pine oil with aerofroth 65 on the recovery of bismuth and copper. Na_2SiO_3 was added to the

mill, and to the first cleaner flotation cell, and 3 lb $K_2Cr_2O_7$ per ton of ore was added in the 2nd cleaner flotation cell. This test was carried out with aerofroth 65 as a frother and aerofloat 31 at pH values of 5 and 8, pH being adjusted by addition of H_2SO_4 or Na_2CO_3 . Procedure used is shown as follows (procedure of flotation 8) and results obtained are given in Table 16 and plotted in Fig.22.

Procedure of Flotation 8



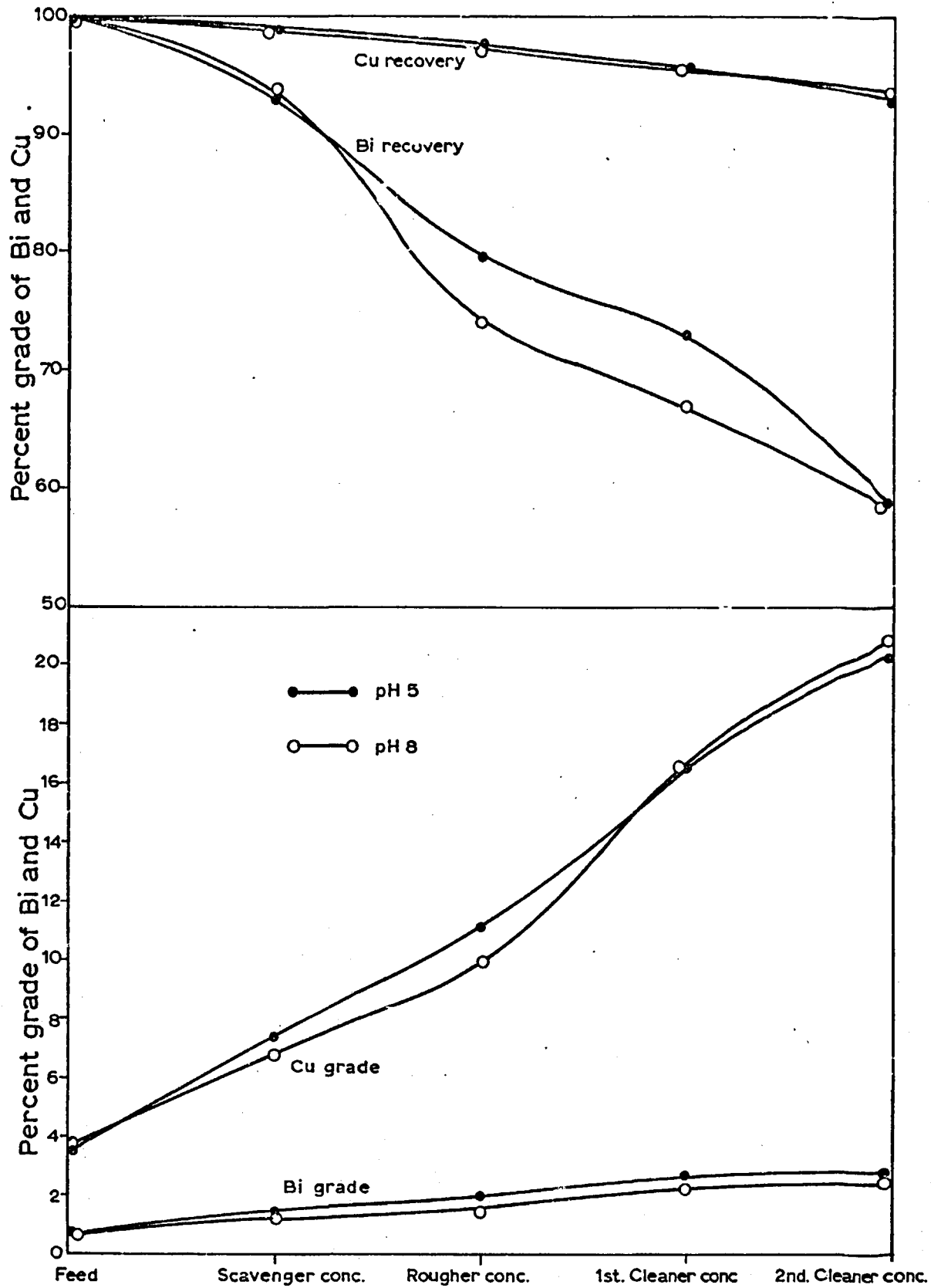


Fig.22 Flotation with Aerofloat 31 and 65 and $K_2Cr_2O_7$ on the pH 5 and 8 (Data from Table 16)

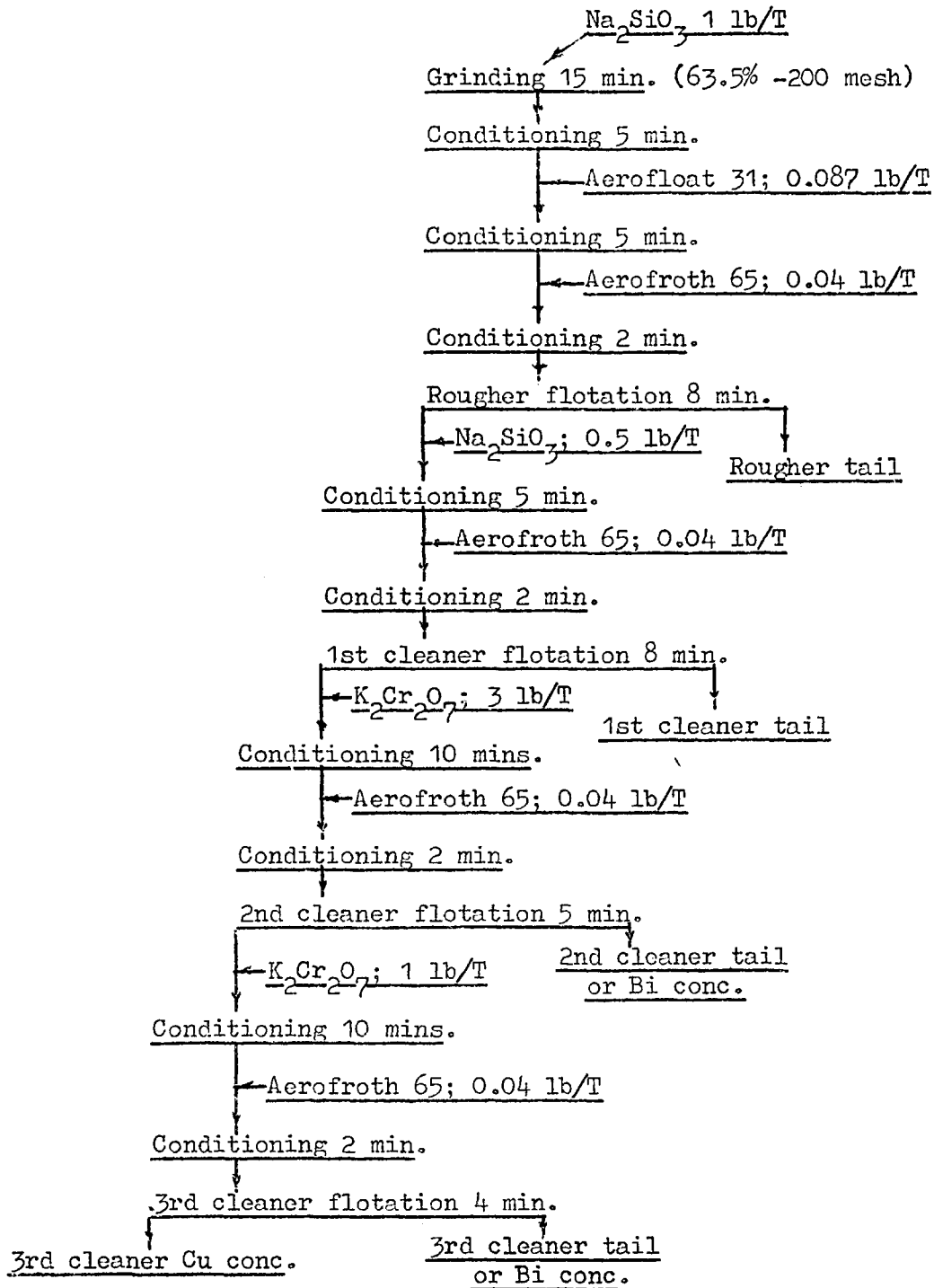
The result of test 31 (Table 16) shows that there were some variations in the bismuth grades of both the final concentrate and the 2nd cleaner tailing suggesting that $K_2Cr_2O_7$ effected very little the depression of bismuth. Fig.22 shows that slightly higher Bi grade was obtained with the flotation at pH5 than at pH8. In Fig.22, on increasing the number of cleaning stages the copper grade increased very rapidly, whereas the bismuth grade increased only slightly. This result suggested that further cleaner flotation seems to be required.

6.10 Flotation 9 - Effect of $K_2Cr_2O_7$ (3rd cleaning)

The concentrate grade obtained after two cleaning stages was not sufficiently high and a further stage of cleaning was required. Four tests were carried out at various pH values using a similar procedure to Flotation 8 but carrying out one more cleaning stage. pH was controlled with H_2SO_4 and Na_2CO_3 and Na_2SiO_3 was added to the mill and at the first cleaning stage. Aerofloat 31 was added once in the rougher stage. Aerofroth was also added in the rougher stage and in each cleaner stage. Procedure used is shown below (procedure of flotation 9) and the result obtained is given in Table 17 (Appendix) and plotted in Figs.23 and 24.

Procedure of Flotation 9

Flotation with $K_2Cr_2O_7$
on the various pH range 5.3, 7, 9.0, 10.8



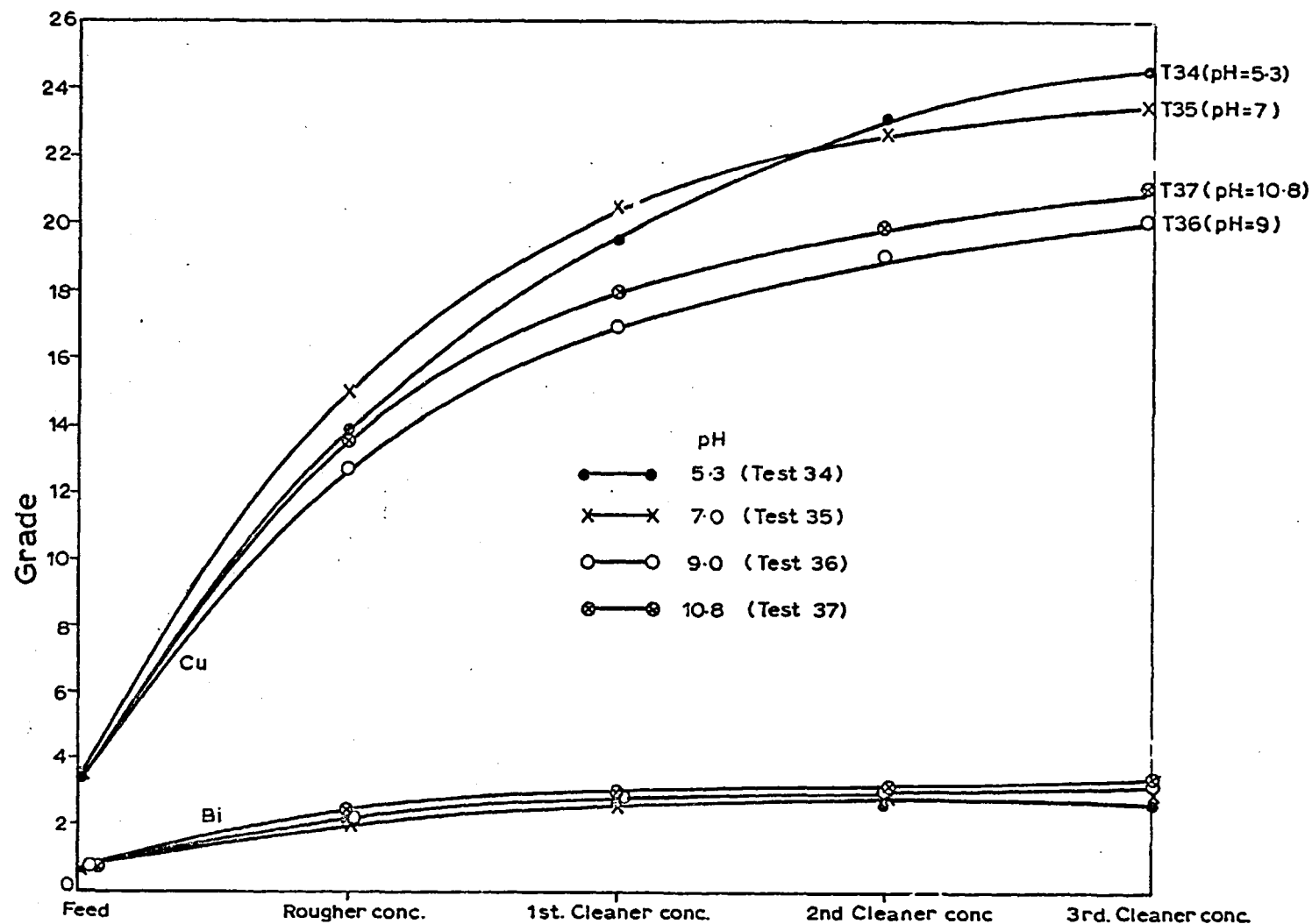


Fig. 23 Comparison between grades obtained with Aerofloat 31 and 65 and $K_2Cr_2O_7$ at various values of pH (Data from Table 17)

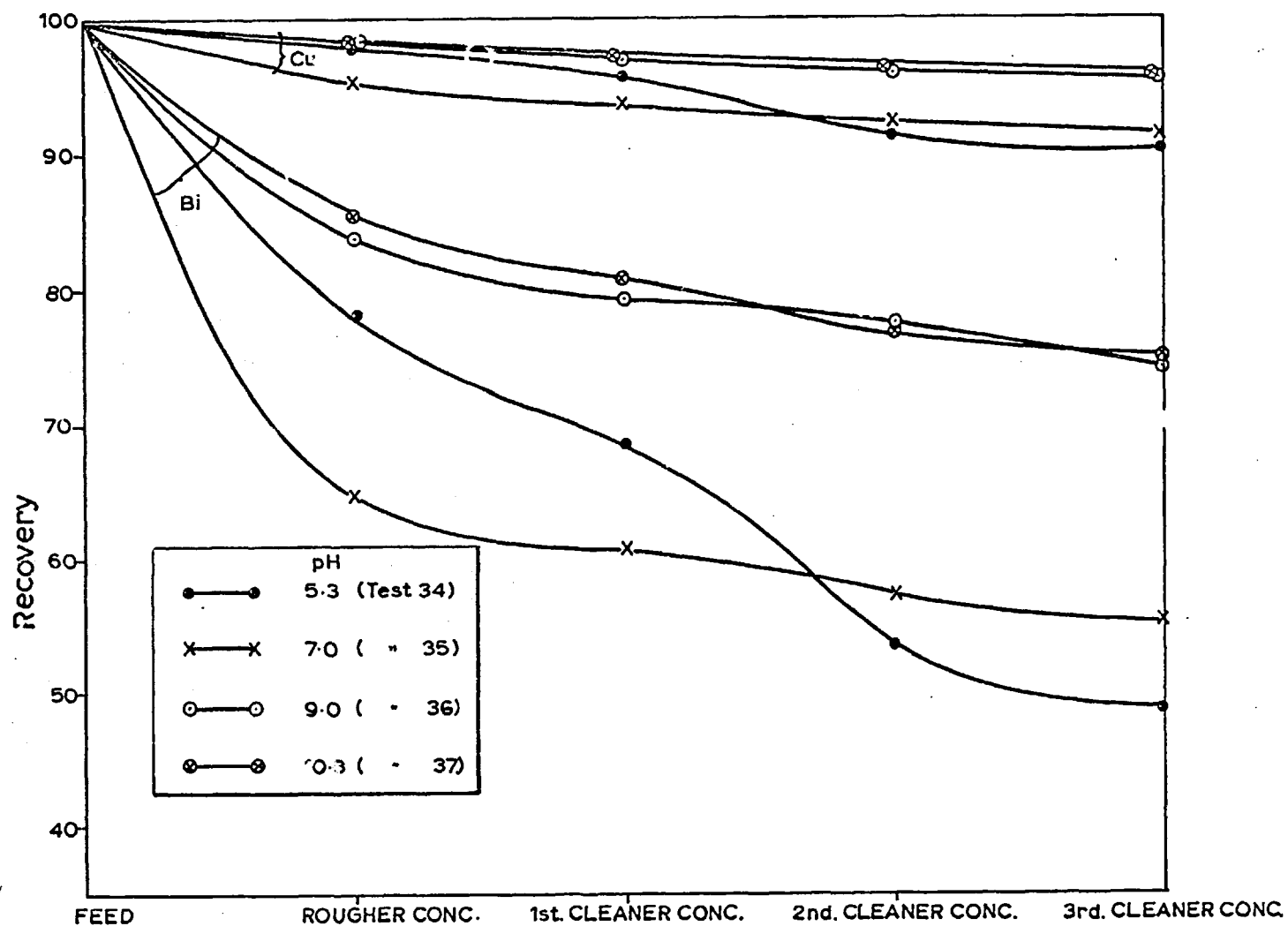


Fig. 24 Comparison between recoveries obtained with Aerofloat 31, Aerofloat 65 and K_2CO_3 at various values of pH. (Data from Table 17)

In Table 17 it is shown that the bismuth grades of the 3rd and 2nd cleaner tailings are lower than those of the 3rd cleaner concentrates, except in test 34 where it is higher than that of the 3rd cleaner concentrate illustrating that $K_2Cr_2O_7$ is more effective at pH5.3 than in alkaline pulp. Fig.23 shows that more higher copper grades were obtained at pH5.3 and 7.0 than at pH9 and 10.8. Comparison between Fig.23 and 24 shows that higher values of copper recoveries were associated with lower grades of copper concentrate grades, whereas higher values of bismuth recoveries were associated with higher values of bismuth concentrate grades. The copper concentrate grade obtained in these tests reached the grade required for efficient and economic treatment in the smelter, and although bismuth was not floated sufficiently, the highest bismuth grade was obtained in these tests.

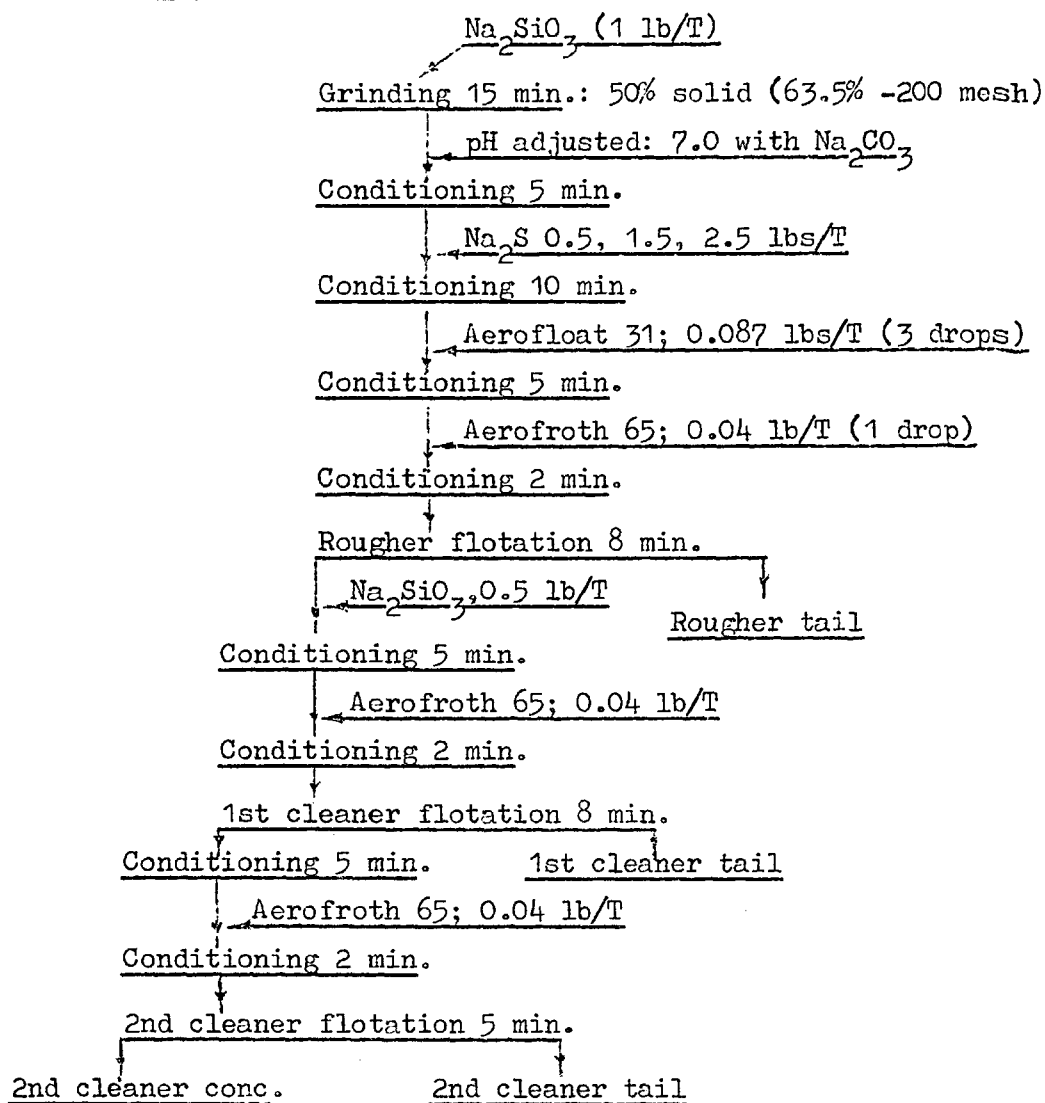
6.11 Flotation 10 - Effect of Na_2S

In the previous tests sufficient grade of copper concentrate could be produced but bismuth-lead mineral was not floated sufficiently. This result suggested investigation of the effect of sodium sulphide on the recovery and grade of bismuth in the flotation.

Na_2S is used as a regulating agent with xanthates in flotation of non-sulphide minerals of lead and copper, and also with oxidized sulphide minerals (5). Three flotation tests were carried out using various amounts of sodium sulphide (0.5, 1.5, and 2.5 lb per ton of ore) with "Aerofloat 31" and "Aerofroth 65" at a pH of 7.0. The

procedure used is shown below (procedure of flotation 10) and results obtained are given in Table 18 (Appendix) and plotted in Figs.25 and 26.

Procedure of flotation 10



In Figs.25 and 26, it can be seen that although there was some variation in the bismuth recovery from these three flotation tests, the same pattern was obtained for all three concentrate grade curves.

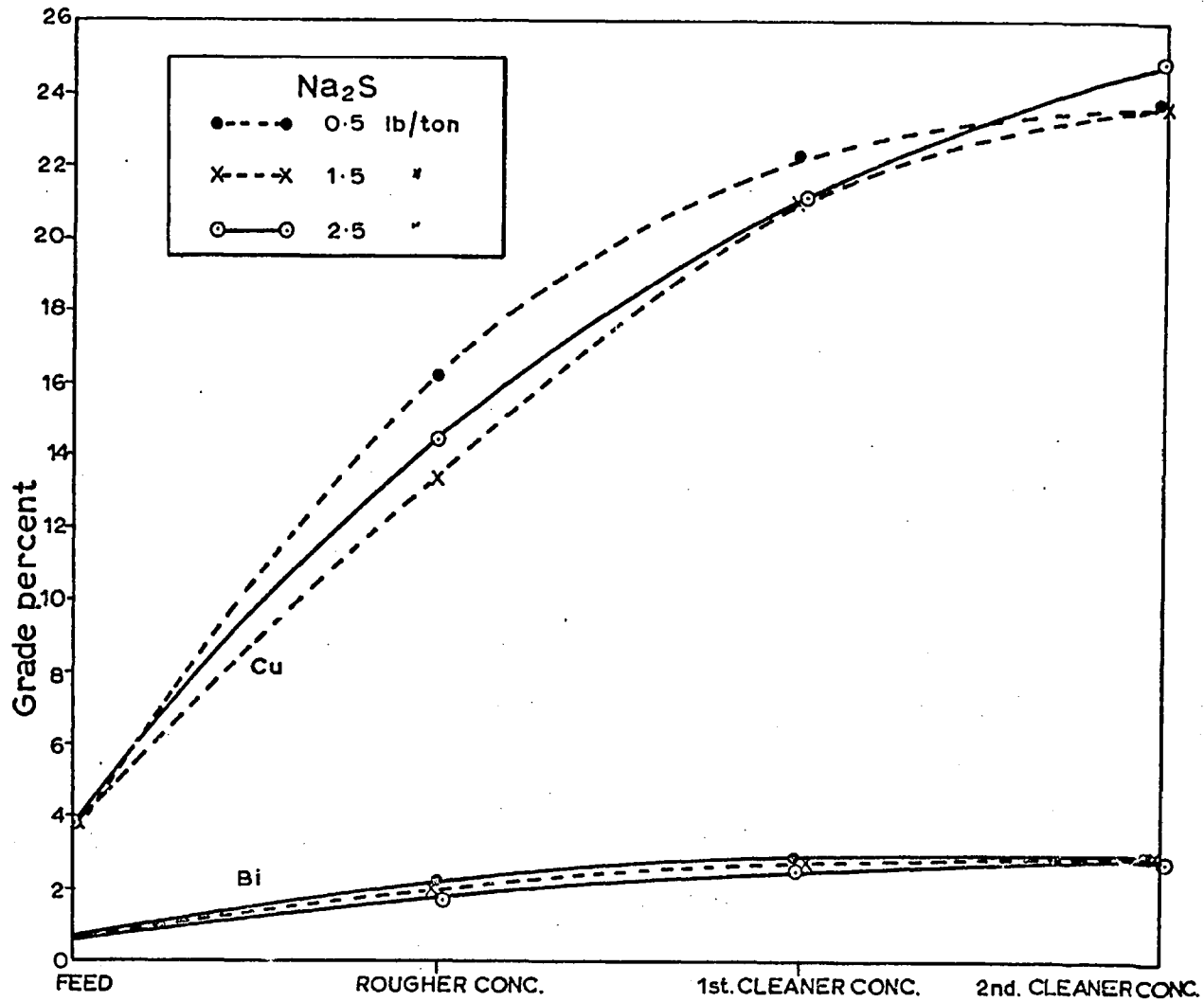


Fig. 25 Comparison between grades obtained with Na_2S , Aerofloat 31 and Aerofloat 65 (Data from Table 18)

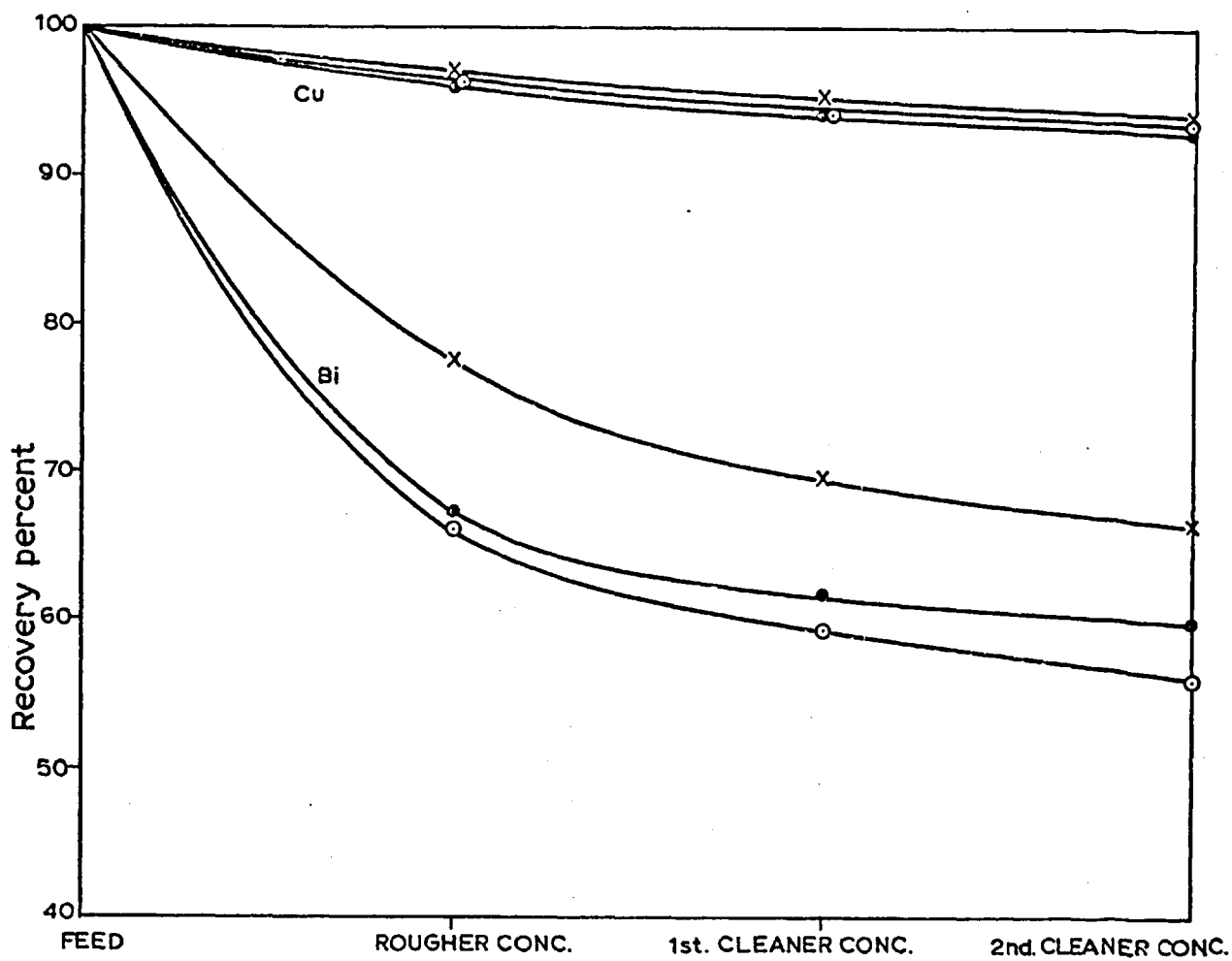


Fig. 26 Comparison between recoveries obtained with Na₂S, Aerofloat 31 and Aerofloat 65 (Data from Table 18)

Copper concentrate grade was sufficiently high but bismuth grade was still only about 3.0 per cent.

7. EXAMINATION OF FLOTATION PRODUCTS

In order to find out how bismuth and copper are distributed in flotation products, products obtained from test 37 which contained the highest value of bismuth grade were examined. In this test the final products obtained were rougher tailing, 1st, 2nd and 3rd cleaner tailings and final concentrate. 1st, 2nd and 3rd cleaner tailings were mixed to produce a composite, which was called a middling. Each of these three products was sized using B.S.S. sieves to 300 mesh. Each fraction was then analysed for bismuth and copper. Results are given in Table 19 (Appendix). From the results of Table 19, grades and distributions of both bismuth and copper in each size fraction of the flotation feed and distribution of total were calculated and given in Tables 20 and 21 (Appendix). The results from Table 21 are plotted in Figs.27-30.

Fig.27 shows that the copper concentrate curve approached the feed curve, which illustrates that copper was sufficiently recovered in finer than 72 mesh fractions, but all copper presented in coarser than 72 mesh fractions was not recovered but lost in the tailing. The highest copper content was found in the finest fraction (-300 mesh). This fraction showed a loss of 3.11% of copper in the tailing, i.e. a loss of 1.38% of the total copper.

Fig.28 shows that the bismuth concentrate curve approached the feed curve in only finer size fractions, which illustrates that bismuth was recovered in finer than 150 mesh fractions. In Table 20, it was found that sufficient bismuth recovery (95.34%) was

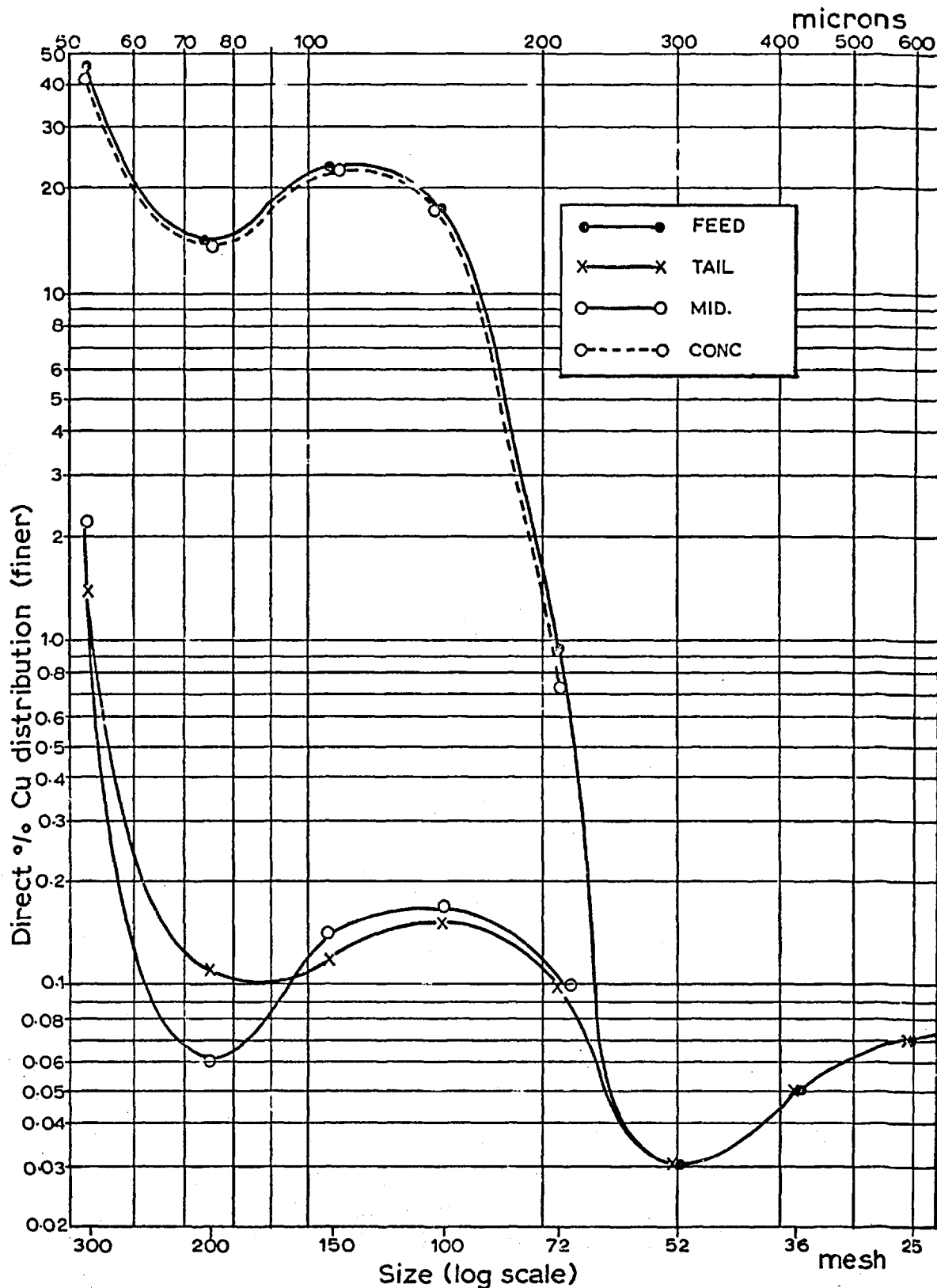


Fig. 27 Comparison between copper distributions obtained from flotation products. (Data from Table 21)

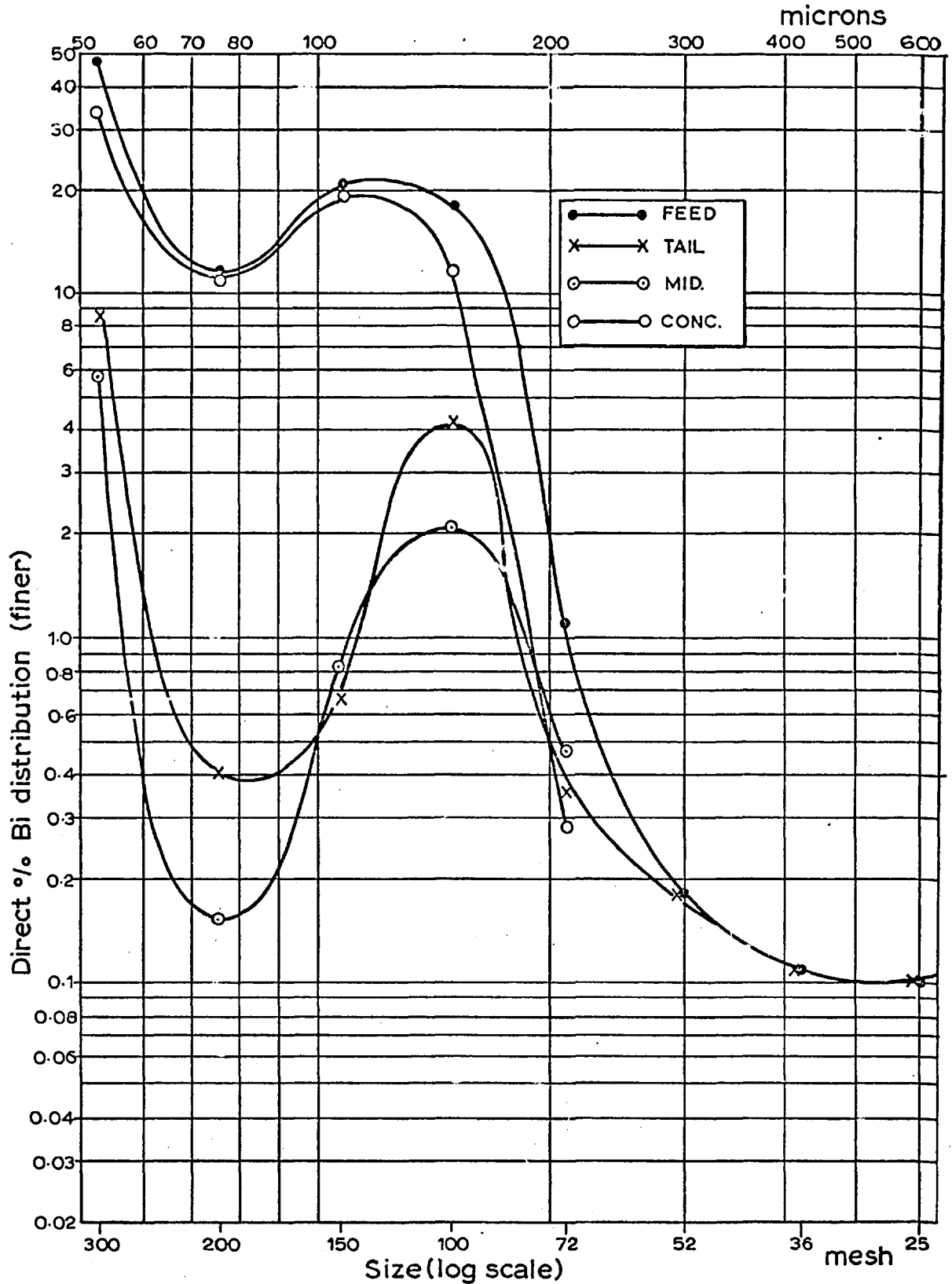


Fig. 28 Comparison between bismuth distribution obtained from flotation products (Data from Table 21)

obtained in the fraction -200 +300 mesh. In fractions coarser than 100 mesh bismuth recovery decreased, and in fractions coarser than 72 mesh it was not recovered but lost in the tailing as well as copper (see Fig.28). The finest fraction (-300 mesh) showed a higher bismuth content and 8.7% of total bismuth was lost in tailing (see Table 21).

Figs.29 and 30 show the cumulative copper and bismuth distribution in flotation products. In fractions coarser than 100 mesh 0.34% copper (see Fig.29) was lost, together 0.93% bismuth (see Fig.30), in tailing. Table 21 also shows that 2.10% of total Cu and 14.93% of total Bi were lost in tailing.

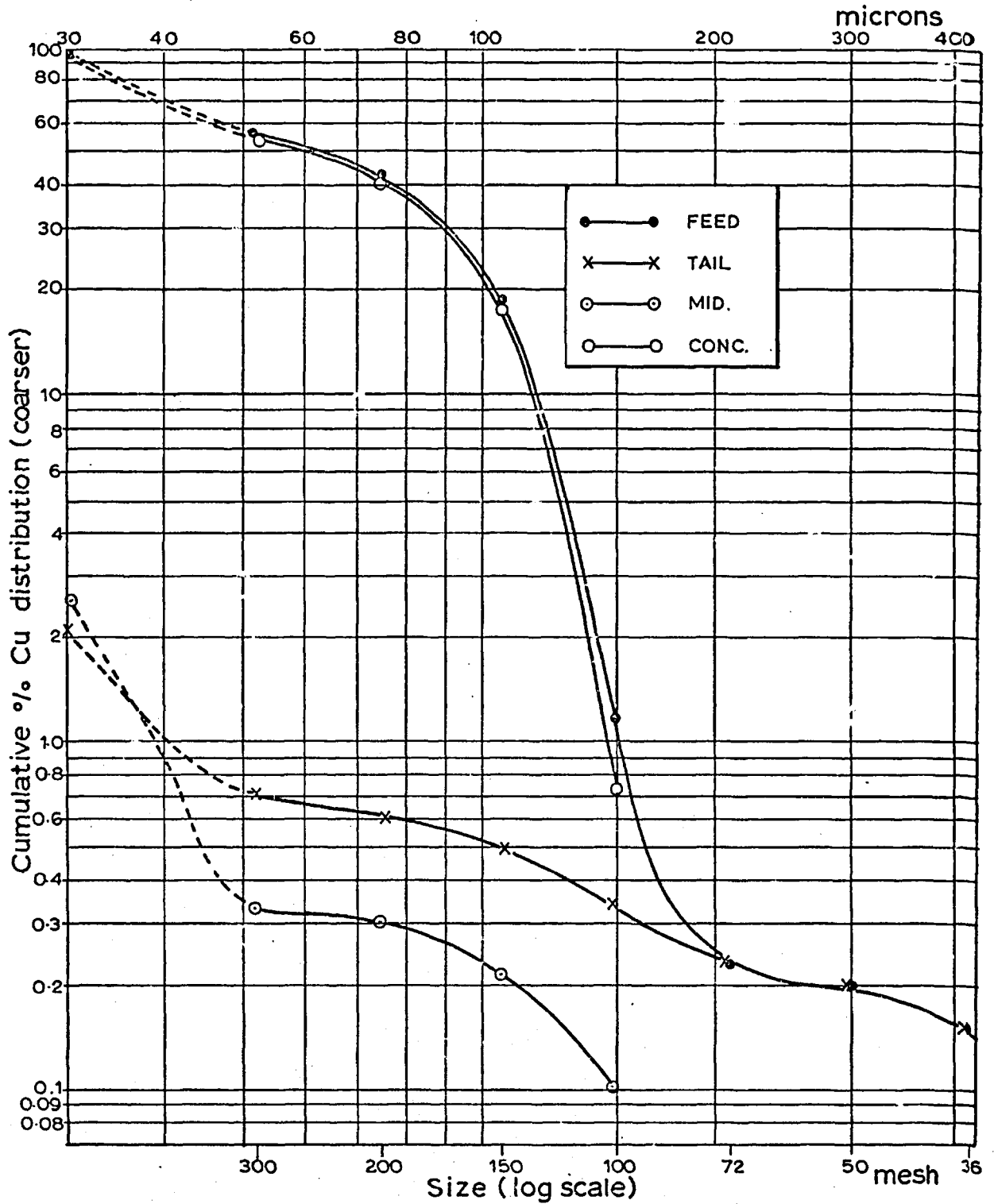


Fig. 29 Comparison between cumulative copper distributions obtained from flotation products. (Data from Table 21)

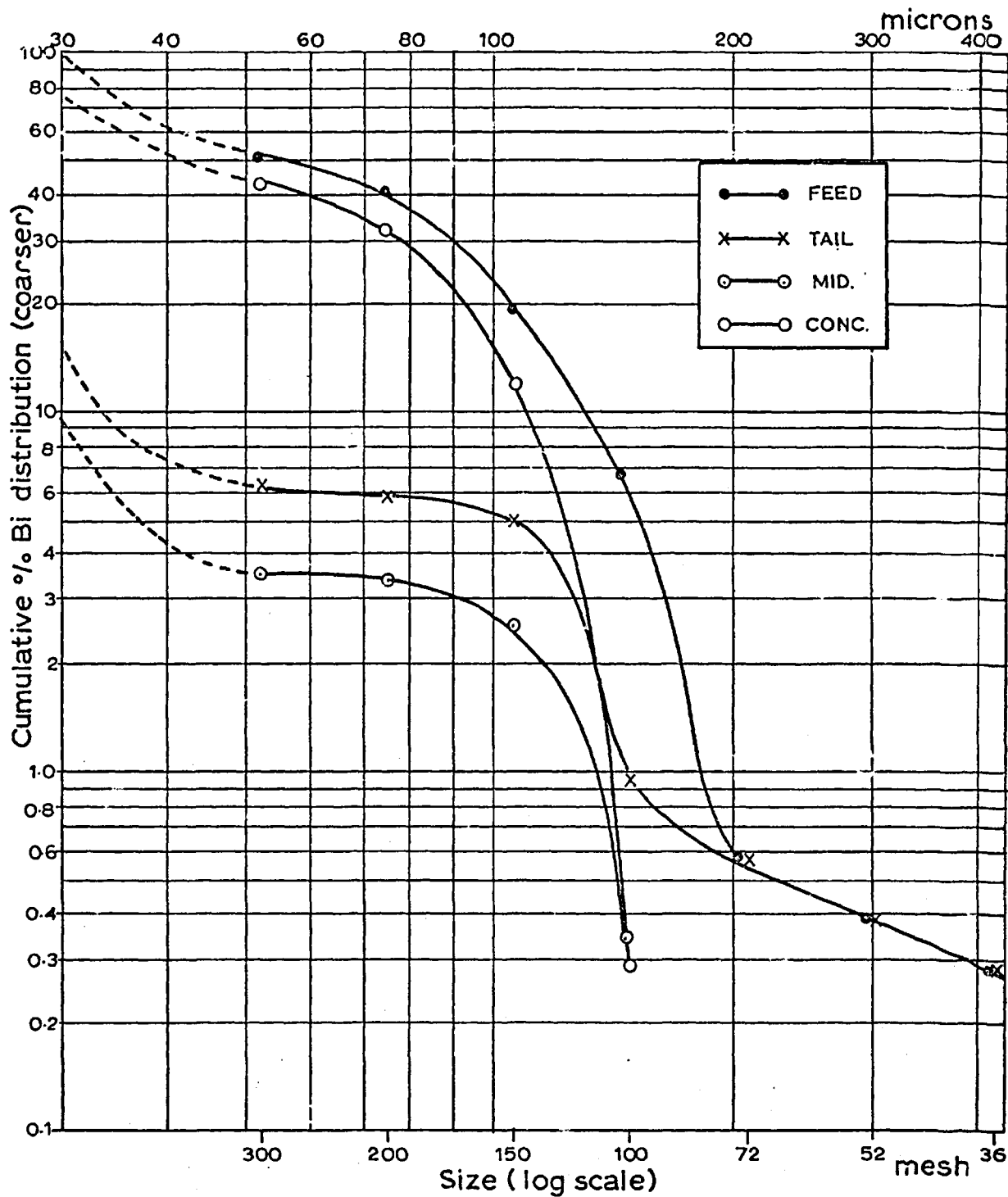


Fig. 30 Comparison between cumulative bismuth distributions obtained from flotation products. (Data from Table 21)

8. CONCLUSIONS

The study of the treatment of a copper-bearing bismuth ore from Shinhoong Mine, Korea, was carried out for the purpose of obtaining from it an economically attractive copper and bismuth concentrate. The following conclusions can be drawn from the previous results.

The mineralization is mainly a fine dissemination of sulphides in silicates. The copper minerals are mainly chalcopyrite with minor amounts of chalcocite. Other sulphide minerals identified were pyrite, arsenopyrite and sphalerite, which are present in very small quantities. Bismuth, as identified by electron microprobe analysis, is lead-bismuth mineral which is known to be a less important bismuth mineral (8). This lead-bismuth mineral is finely intergrown with other sulphide minerals and silicates. The principal gangue minerals are quartz and mica. The ore contains 3.45% Cu, 0.73% Bi, 0.54% Pb, 0.13% Zn, 5.90% Fe, 3.0% K, 11.0% Al and 38% Si. 0.90% of the total copper is present in water soluble form. 1.98% of the total copper is soluble in acid and 2.97% is soluble in ferric sulphate solution. Bismuth was not soluble in water but 55% and 67.69% of total bismuth is present in acid and ferric sulphate soluble form respectively.

Suspension in heavy liquid separates the mineral into density fractions such that the per cent distribution of Cu and Bi gradually decreases in the finer fractions. Cu sulphides show a coarser

liberation size than those of bismuth microscopic examination shows that at -150 mesh Cu sulphides are free of silicates.

The copper sulphides and bismuth mineral show no large differences in their breakage characteristics, but copper tends to be concentrated at coarser sizes than bismuth, due to the original differences in grain size. After grinding the -7 mesh sample to 63.5% -200 mesh the copper and bismuth were concentrated in the fraction -150 + 200 mesh. The copper distribution peak coincided with that of bismuth.

An initial stage of flotation with potassium ethyl xanthate and pine oil is of doubtful application because of the poor collection of Bi-Pb mineral obtained. The flotation using KAX collector and pine oil as a frother is better for the recovery of bismuth, but flotation using "Aerofloat 31" collector with "Aerofroth 65" as a frother is more promising. The optimum recoveries of copper and bismuth would be obtained at pH range of 6.0 - 9.0. Good results were obtained on grinding to 63.5% -200 mesh with Na_2SiO_3 (1.5 lb/ton of ore) and Na_2S (2.5 lb/ton of ore). "Aerofloat 31", 0.087 lb/ton and "Aerofroth 65", 0.04 lb/ton of ore were required. A final concentrate containing 23.7% Cu with a recovery of 94.2% and a bismuth content of 3% Bi with a recovery of 66.4% Bi were obtained.

Analysis of the flotation products revealed that the copper losses occurred principally in the size fractions coarser than 100 mesh and finer than 300 mesh. Bismuth losses occurred principally

in the size fractions coarser than 150 mesh and finer than 300 mesh.

After studying the more fundamental flotation characteristics of the bismuth mineral, it will be possible to make a further practical flotation study with closed circuit grinding.

A P P E N D I X

APPENDIX
CHEMICAL ANALYSIS of
BISMUTH by ATOMIC ABSORPTION

Procedure

The procedure for the sample preparation for the determination of Bismuth is almost the same as that for the determination of copper or zinc, so that the same solution, after the necessary dilution can be used for the determination of copper, zinc, iron and cadmium.

Weigh accurately an appropriate amount of finely ground sample (-200 mesh) depending upon the amount of bismuth likely to be present (0.2000-0.5000)g. into a 150 ml beaker. Moisten the sample in the beaker with 1 ml of water, add 5 ml of concentrated HCl and cover the beaker with a watchglass. Place the covered beaker on a hot plate, heat it to boiling and boil gently for 5 to 10 minutes to destroy the possibly present sulphides. Swirl the beaker occasionally to cool, and add carefully 5 ml of concentrated Nitric Acid. Allow the reaction to proceed without heating. When the reaction has subsided heat again gently the covered beaker for about 10 minutes. Evaporate the solution to near dryness. Redissolve the moist residue in a few ml of nitric acid by warming on a hot plate until the soluble salts have dissolved.

If the sample is not well decomposed add 6 drops of hydrofluoric acid, then add 1 ml of nitric acid and evaporate almost to dryness to displace the excess of hydrofluoric acid, repeating this procedure

if necessary.

Transfer the content of the beaker quantitatively, to a convenient volumetric flask and dilute to the mark with N/10 nitric acid.

Use bismuth hollow-cathode lamp

Operating current 30 ma.

Wavelength: 2230.61 Å.

Expected Bi %	sample weigh
.05	.5000 g
.05 — .5	.5000
.5 — 5.0	.2000
5.0 — 25.	.2000
25.0 — 50.	.2000
50	.2000

Table 9

Test No.	Product	weight %	Grade %		Recovery %		pH
			Bi	Cu	Bi	Cu	
3	Conc.	35.32	1.42	8.57	73.92	95.90	6.2
	Tail.	64.68	0.27	0.20	26.08	4.10	
	Total	100.00	0.68	3.16	100.00	100.00	
5	Conc.	34.32	1.32	8.17	64.47	84.72	7.1
	Tail.	65.68	0.38	0.77	35.53	15.28	
	Total	100.00	0.70	3.31	100.00	100.00	
6	Conc.	33.40	1.26	6.85	60.64	69.33	8.0
	Tail.	66.60	0.41	1.52	39.36	30.67	
	Total	100.00	0.69	3.30	100.00	100.00	
4	Conc.	29.96	1.30	7.39	55.83	66.39	10.0
	Tail.	70.04	0.44	1.60	44.17	33.61	
	Total	100.00	0.70	3.35	100.00	100.00	

Table 10. Metallurgical Results

Test No.	Product (Flotation) time	Direct						Cumulative			
		Weight %	Bi		Cu		Weight %	Bi		Cu	
			Grade	Recovery	Grade	Recovery		Grade	Recovery	Grade	Recovery
7	Conc. 1	9.74	2.06	28.72	14.91	45.04	9.74	2.060	28.72	14.91	45.04
	2	3.88	1.76	9.78	10.02	12.06	13.62	1.974	38.50	13.52	57.10
	3	3.65	1.16	6.05	1.49	1.69	17.27	1.802	44.55	10.98	58.79
	4	4.04	1.10	6.36	3.96	4.96	21.31	1.669	50.91	9.65	63.75
	5	2.94	0.64	2.69	2.11	1.92	24.25	1.544	53.60	8.73	65.67
	6	3.31	0.82	3.88	2.81	2.88	27.56	1.457	57.48	8.02	68.55
	Tail	72.44	0.41	42.52	1.40	31.45	100.00	0.699	100.00	3.23	100.00
	Total	100.00	0.70	100.00	3.23	100.00					
8	Conc. 1	15.18	2.18	50.12	18.53	73.73	15.18	2.18	50.12	18.53	3.73
	2	4.71	1.44	10.27	6.06	7.48	19.89	2.00	60.39	15.58	81.21
	3	3.91	0.90	5.33	4.48	4.59	23.80	1.82	65.72	13.75	85.80
	4	3.56	0.82	4.42	2.11	1.97	27.36	1.69	70.17	12.24	87.77
	5	3.30	0.67	3.35	1.12	0.89	30.66	1.58	73.49	11.03	88.66
	6	3.08	0.52	2.43	0.70	0.57	33.74	1.49	75.92	10.09	89.23
	Tail	66.26	0.24	24.08	0.62	10.77	100.00	0.66	100.00	3.81	100.00
	Total	100.00	0.66	100.00	3.82	100.00					

Table 10 (cont.)

Test No.	Product (Flotation) time	Direct					Cumulative				
		Weight %	Bi		Cu		Weight %	Bi		Cu	
			Grade	Recovery	Grade	Recovery		Grade	Recovery	Grade	Recovery
9	Conc. 1	15.08	2.40	49.63	18.98	91.40	15.08	2.40	49.63	18.98	91.40
	2	3.55	1.80	8.76	0.17	0.19	18.63	2.29	58.39	15.40	91.59
	3	2.69	1.14	4.21	2.11	1.81	21.32	2.14	62.60	13.72	93.40
	4	3.59	1.98	9.75	2.24	2.57	24.91	2.12	72.35	12.07	95.97
	5	3.34	0.88	4.03	0.77	0.82	28.25	1.97	76.38	10.73	96.79
	Tail	71.75	0.24	23.62	0.14	3.21	100.00	0.73	100.00	3.13	100.00
	Total	100.00	0.73	100.00	3.13	100.00					

Flotation Conditions

Test No.	Reagents lbs/ton of ore						pH
	CaO	Calgon	Na ₂ CO ₃	Na ₂ SiO ₃	KEX	Pine oil	
7	6.0	0.1			0.1	0.04	8.0
8			12		0.1	0.04	8.0
9			12	0.5	0.1	0.04	8.3

Table 11. Result of Flotation 3

Test No.	Product	Weight %	Bi		Cu		lb/ton	pH	Temp °C
			Grade	Recovery	Grade	Recovery			
15	Conc	33.00	1.90	86.13	9.89	98.58	Na ₂ CO ₃ 0	6.10	27.0
	Tail	67.00	0.15	13.87	0.07	1.42			
	Total	100.00	0.73	100.00	3.31	100.00			
12	Conc	27.29	1.90	73.26	11.74	96.71	Na ₂ CO ₃ 12	8.0	25.7
	Tail	72.73	0.26	26.74	0.15	3.29			
	Total	100.00	0.71	100.00	3.31	100.00			
11	Conc	30.07	2.08	77.48	10.81	95.87	Na ₂ CO ₃ 20	9.3	26.3
	Tail	69.93	0.26	22.52	0.20	4.13			
	Total	100.00	0.81	100.00	3.39	100.00			
13	Conc	34.10	1.86	89.76	9.49	98.79	Na ₂ CO ₃ 112	10.6	26.0
	Tail	65.90	0.11	10.24	0.06	1.21			
	Total	100.00	0.71	100.00	3.28	100.00			
14	Conc	34.29	1.88	89.10	9.37	98.59	Na ₂ CO ₃ 200	11.0	28.0
	Tail	65.71	0.12	10.90	0.07	1.41			
	Total	100.00	0.72	100.00	3.26	100.00			

Table 12. Result of Flotation 4

16	Conc	30.99	2.10	86.28	12.63	98.44	CaO 0	7.20	19.0
	Tail	69.01	0.15	13.72	0.09	1.56			
	Total	100.00	0.75	100.00	3.97	100.00			

Table 12 (cont.)

Test No.	Product	Weight %	Bi		Cu		lb/ton	pH	Temp °C
			Grade	Recovery	Grade	Recovery			
17	Conc	24.89	1.50	59.38	10.50	77.85	CaO 8	9.0	19.0
	Tail	75.11	0.34	40.62	0.99	22.15			
	Total	100.00	0.62	100.00	3.36	100.00			
18	Conc	21.23	2.78	78.11	11.25	63.01	CaO 20	10.6	20.0
	Tail	78.77	0.21	21.89	1.78	36.99			
	Total	100.00	0.75	100.00	3.79	100.00			

Table 13. Results of Flotation 5

Test No.	Products	Weight %	Bi		Cu		Remark
			Grade	Recovery	Grade	Recovery	
23	2nd cleaner conc	18.65	3.00	78.21	18.00	96.39	with Na ₂ SiO ₃ (0.5 lb/T)
	2nd cleaner tail	5.24	0.60	4.39	0.75	1.13	
	1st cleaner tail	11.23	0.30	4.71	0.25	0.81	
	Rougher tail	64.88	0.14	12.69	0.09	1.67	
	Total	100.00	0.72	100.00	3.48	100.00	
24	2nd cleaner conc	17.74	3.00	67.83	19.99	93.59	without Na ₂ SiO ₃
	2nd cleaner tail	5.84	0.70	5.21	0.90	1.39	
	1st cleaner tail	15.77	0.35	11.50	0.36	1.50	
	Rougher tail	60.65	0.20	15.46	0.22	3.52	
	Total	100.00	0.78	100.00	3.79	100.00	

Table 14. Results of Flotation 6

Test No.	Product	Time (mins)	Weight %	Bi				Cu				Remark
				Direct		Cumul.		Direct		Cumul.		
				Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	
25	Conc. 1	1	18.14	2.50	60.23	2.50	60.23	18.74	94.16	18.74	94.16	0.1 lb/T KAX . 0.04 lb/T pine oil pH 6.0
	2	2	6.64	1.70	15.00	2.29	75.23	1.75	3.22	14.19	97.38	
	3	3	2.92	0.90	3.49	2.14	78.72	0.80	0.65	12.78	98.03	
	4	4	2.45	0.56	1.82	2.01	80.54	0.40	0.27	11.77	98.30	
	5	5	2.74	0.45	1.63	1.88	82.17	0.28	0.21	10.81	98.51	
	Tail		67.11	0.20	17.83	0.75	100.00	0.08	1.49	3.61	100.00	
	Total		100.00	0.75	100.00			3.61	100.00			
26	Conc. 1	1	19.39	2.50	67.32	2.50	67.32	17.99	95.05	17.99	95.05	0.3 lb/T KAX . 0.04 lb/T pine oil pH 6.0
	2	2	4.95	1.75	12.03	2.35	79.35	1.87	2.52	14.71	97.57	
	3	3	3.38	0.80	3.75	2.16	83.10	0.72	0.66	13.01	98.23	
	4	4	2.96	0.60	2.47	2.01	85.57	0.40	0.32	11.79	98.55	
	5	5	2.87	0.38	1.51	1.87	87.08	0.23	0.18	10.80	98.73	
	Tail		66.45	0.14	12.92	0.72	100.00	0.07	1.27	3.67	100.00	
	Total		100.00	0.72	100.00			3.67	100.00			
27	Conc. 1	1	20.00	2.50	68.14	2.50	68.14	16.74	94.23	16.74	94.23	0.5 lb/T KAX . 0.04 lb/T pine oil pH 6.0
	2	2	5.89	1.60	12.84	2.30	80.98	2.25	3.93	13.44	97.96	
	3	3	5.20	0.76	5.38	2.04	86.36	0.54	0.79	11.29	98.75	
	4	4	3.27	0.45	2.00	1.89	88.36	0.25	0.23	10.24	98.98	
	5	5	2.56	0.38	1.32	1.78	89.68	0.18	0.13	9.54	99.11	
	Tail		63.08	0.12	10.32	0.73	100.00	0.05	0.89	3.55	100.00	
	Total		100.00	0.75	100.00			3.55	100.00			

Table 15. Results of Flotation 7

Test No.	Products	Weight %	Bi		Cu		Remark
			Grade	Recovery	Grade	Recovery	
28	2nd cleaner conc	16.20	2.74	68.64	22.93	96.07	Aerofloat 31 (0.058 lb/T) in the cell. Pine oil 0.04 lb/T pH 6.8
	2nd cleaner tail	2.86	0.78	3.45	1.13	0.83	
	1st cleaner tail	13.25	0.34	6.97	0.34	1.17	
	Rougher tail	67.69	0.20	20.94	0.11	1.93	
	Total	100.00	0.65	100.00	3.87	100.00	
29	2nd cleaner conc	17.35	2.00	58.57	19.98	96.32	Aerofloat 25 (0.058 lb/T) in the cell. Pine oil 0.04 lb/T pH 6.8
	2nd cleaner tail	2.88	0.78	3.80	0.94	0.75	
	1st cleaner tail	11.23	0.52	9.86	0.45	1.41	
	Rougher tail	68.54	0.24	27.77	0.08	1.52	
	Total	100.00	0.59	100.00	3.60	100.00	
30	2nd cleaner conc	11.30	2.49	40.95	21.68	67.38	Aerofloat 31 (0.058 lb/T) in the mill Pine oil 0.04 lb/T pH 6.8
	2nd cleaner tail	5.50	1.30	10.40	9.99	15.11	
	1st cleaner tail	19.94	0.80	19.72	3.25	15.14	
	Rougher tail	66.26	0.30	28.93	0.13	2.37	
	Total	100.00	0.69	100.00	3.64	100.00	

Table 16. Result of Flotation 8

Test No.	Products	Weight %	Grade	Bi Recovery	Grade	Cu Recovery	Remarks
31	Final conc	16.23	2.74	58.87	20.23	92.91	pH 5.0
	2nd cleaner tail	4.21	2.54	14.15	2.22	2.65	
	1st cleaner tail	10.59	0.46	6.45	0.63	1.89	
	Scavenger conc	15.95	0.64	13.51	0.30	1.35	
	Scavenger tail	53.02	0.10	7.02	0.08	1.20	
	Total	100.00	0.76	100.00	3.53	100.00	
32	Final Conc	16.77	2.48	58.55	20.99	93.91	pH 8.0
	2nd cleaner tail	4.86	1.22	8.35	1.30	1.69	
	1st cleaner tail	15.22	0.34	7.28	0.39	1.59	
	Scavenger conc	17.68	0.78	19.41	0.34	1.60	
	Scavenger tail	45.47	0.10	6.41	0.10	1.21	
	Total	100.00	0.71	100.00	3.75	100.00	

Table 17. Result of Flotation 9

Test No.	Products	Weight %	Bi		Cu		Remark
			Grade	Recovery	Grade	Recovery	
34	3rd cleaner conc	13.22	2.54	48.92	24.46	90.02	pH 5.3
	3rd cleaner tail	0.99	3.10	4.47	4.50	1.24	
	2nd cleaner tail	3.38	3.09	15.21	4.74	4.46	
	1st cleaner tail	7.67	0.86	9.62	1.03	2.20	
	Rougher tail	74.74	0.20	21.78	0.10	2.08	
	Total	100.00	0.69	100.00	3.59	100.00	
35	3rd cleaner conc	13.83	2.82	55.33	23.47	91.45	pH 7.0
	3rd cleaner tail	0.60	2.08	1.77	5.12	0.86	
	2nd cleaner tail	1.78	1.42	3.59	2.50	1.25	
	1st cleaner tail	6.39	0.46	4.17	1.03	1.86	
	Rougher tail	77.40	0.32	35.14	0.21	4.58	
	Total	100.00	0.71	100.00	3.55	100.00	
36	3rd Cleaner conc	16.93	3.14	74.42	19.98	95.52	pH 9.0
	3rd cleaner tail	1.01	2.08	2.94	2.22	0.63	
	2nd cleaner tail	2.33	0.60	1.96	1.25	0.82	
	1st cleaner tail	7.18	0.44	4.43	0.48	0.98	
	Rougher tail	72.55	0.16	16.25	0.10	2.05	
	Total	100.00	0.71	100.00	3.54	100.00	
37	3rd cleaner conc	16.52	3.26	74.84	20.98	95.62	pH 10.8
	3rd cleaner tail	1.06	1.38	2.03	2.22	0.65	
	2nd cleaner tail	2.02	1.42	3.99	1.50	0.83	
	1st cleaner tail	6.29	0.54	4.72	0.61	1.06	
	Rougher tail	74.11	0.14	14.42	0.09	1.84	
	Total	100.00	0.72	100.00	3.63	100.00	

Table 18. Result of Flotation 10

Test No.	Products	Weight %	Grade	Bi Recovery	Grade	Cu Recovery	Remark
38	2nd cleaner conc	15.06	3.00	59.74	23.73	92.75	Na ₂ S. 0.5 lb/T
	2nd cleaner tail	1.14	1.30	1.96	4.32	1.28	
	1st cleaner tail	6.50	0.65	5.59	1.16	1.96	
	Rougher tail	77.30	0.32	32.71	0.20	4.01	
	Total	100.00	0.76	100.00	3.85	100.00	
39	2nd cleaner conc	15.47	3.00	66.39	23.72	94.22	Na ₂ S. 1.5 lb/T
	2nd cleaner tail	2.16	1.08	3.33	1.97	1.09	
	1st cleaner tail	10.87	0.50	7.78	0.76	2.12	
	Rougher tail	71.50	0.22	22.50	0.14	2.57	
	Total	100.00	0.70	100.00	3.89	100.00	
40	2nd cleaner conc	14.59	2.85	55.98	25.03	92.87	Na ₂ S 2.5 lb/T
	2nd cleaner tail	2.23	1.06	3.18	2.05	1.16	
	1st cleaner tail	9.33	0.56	7.03	0.93	2.21	
	Rougher tail	73.85	0.34	33.81	0.20	3.76	
	Total	100.00	0.74	100.00	3.93	100.00	

Table 19. Analysis of Flotation Product
(from test 37 product)

Products	Weight %	Size fraction B.S.S.	Weight %	Bi		Cu	
				Grade	Dist.	Grade	Dist.
Tailing	74.11	+ 25	0.20	0.87	1.18	2.26	3.99
		- 25+ 36	0.10	0.90	0.62	3.48	3.10
		- 36+ 52	0.14	0.80	0.76	1.96	2.40
		- 52+ 72	0.44	0.40	1.25	0.32	1.24
		- 72+100	3.50	0.10	2.43	0.17	5.32
		-100+150	20.47	0.20	28.32	0.04	7.27
		-150+200	15.90	0.04	4.43	0.04	5.67
		-200+300	9.73	0.04	2.70	0.06	5.14
		-300	49.52	0.17	58.31	0.15	65.87
		Total	100.00	0.14	100.00	0.11	100.00
Middling	9.37	+100	1.09	3.31	5.12	4.12	3.97
		-100+150	4.35	3.65	22.54	1.63	6.27
		-150+200	4.71	1.34	8.96	1.25	5.21
		-200+300	2.80	0.40	1.59	0.87	2.16
		-300	87.05	0.50	61.79	1.07	82.39
		Total	100.00	0.70	100.00	1.13	100.00
Concentrate	16.52	+100	0.79	1.55	0.37	22.25	0.76
		-100+150	17.17	2.95	15.42	24.21	18.04
		-150+200	22.83	3.65	25.38	24.23	24.00
		-200+300	13.35	3.65	14.84	24.98	14.47
		-300	45.86	3.15	43.99	21.47	42.73
		Total	100.00	3.28	100.00	23.05	100.00

Table 20. Bi and Cu distribution in flotation product

Size mesh B.S.S.	Product	Weight %		Cu			Bi		
		of total	each size fraction	Grade	Unit	Dist.	Grade	Unit	Dist.
+ 25	Tail	0.15	100.00	2.26	226	100.00	0.87	870	100.00
- 25+ 36	Tail	0.08	100.00	3.48	348	100.00	0.90	90.0	100.00
- 36+ 52	Tail	0.10	100.00	1.96	196	100.00	0.80	80.0	100.00
- 52+ 72	Tail	0.33	100.00	0.32	32	100.00	0.40	40.0	100.00
- 72+100	Tail	2.59	91.84	0.17	15.61	11.75	0.10	9.18	32.69
	Mid	0.10	3.55	4.12	14.63	11.02	3.31	11.75	41.85
	Conc	0.13	4.61	22.25	102.57	77.23	1.55	7.15	25.46
	Total	2.82	100.00	(1.33)	132.81	100.00	(0.28)	28.08	100.00
-100+150	Tail	15.17	82.35	0.04	3.29	0.86	0.20	16.47	23.50
	Mid	0.41	2.23	1.63	3.64	0.96	3.65	8.14	11.61
	Conc	2.84	15.42	24.21	373.32	98.18	2.95	45.49	64.89
	Total	18.42	100.00	(3.80)	380.25	100.00	(0.70)	70.10	100.00
-150+200	Tail	11.78	73.67	0.04	2.95	0.51	0.04	2.95	3.18
	Mid	0.44	2.75	1.25	3.44	0.60	1.34	3.69	3.98
	Conc	3.77	23.58	24.23	571.34	78.89	3.65	86.07	92.84
	Total	15.99	100.00	(5.78)	577.73	100.00	(0.93)	92.71	100.00
-200+300	Tail	7.21	74.56	0.06	4.47	0.78	0.04	2.98	3.42
	Mid	0.26	2.69	0.87	2.34	0.41	0.40	1.08	1.24
	Conc	2.20	22.75	24.98	568.30	98.81	3.65	83.04	95.34
	Total	9.67	100.00	(5.75)	575.11	100.00	(0.87)	87.10	100.00
-300	Tail	36.70	69.98	0.15	10.50	3.11	0.17	11.90	18.24
	Mid	8.16	15.56	1.07	16.65	4.93	0.50	7.78	11.93
	Conc	7.58	14.46	21.47	310.46	91.96	3.15	45.55	69.83
	Total	52.44	100.00	(3.38)	337.61	100.00	(0.65)	65.23	100.00

Table 21. Bi and Cu Distribution in Flotation Product (from test 37)

Size mesh B.S.S.	Feed					Tailing										
	Weight %	Grade %		Distribution %		Weight %			Grade		Distribution					
		Cu	Bi	Cu	Bi	each fraction	of total	Cumul. of total	Cu	Bi	of each fraction		of total		Cumul. of total	
											Cu	Bi	Cu	Bi	Cu	Bi
+ 25	0.15	2.26	0.87	0.08	0.18	100.00	0.15	0.15	2.26	0.87	100.00	100.00	0.08	0.18	0.08	0.18
- 25+ 36	0.08	3.48	0.90	0.07	0.10	100.00	0.08	0.23	3.48	0.90	100.00	100.00	0.07	0.10	0.15	0.28
- 36+ 52	0.10	1.96	0.80	0.05	0.11	100.00	0.10	0.33	1.96	0.80	100.00	100.00	0.05	0.11	0.20	0.39
- 52+ 72	0.33	0.32	0.40	0.03	0.18	100.00	0.33	0.66	0.32	0.40	100.00	100.00	0.03	0.18	0.23	0.57
- 72+100	2.82	1.33	0.28	0.94	1.11	91.84	2.59	3.25	0.17	0.10	11.75	32.69	0.11	0.36	0.34	0.93
-100+150	18.42	3.80	0.70	17.50	18.04	82.35	15.17	18.42	0.04	0.20	0.86	23.50	0.15	4.24	0.49	5.17
-150+200	15.99	5.78	0.93	23.11	20.81	73.67	11.78	30.20	0.04	0.04	0.51	3.18	0.12	0.66	0.61	5.83
-200+300	9.67	5.75	0.87	13.90	11.77	74.56	7.21	37.41	0.06	0.04	0.78	3.42	0.11	0.40	0.72	6.23
-300	52.44	3.38	0.65	44.32	47.70	69.98	36.70	74.11	0.15	0.17	3.11	18.24	1.38	8.70	2.10	14.93
Total	100.00			100.00	100.00		74.11		(0.11)	(0.14)			2.10	14.93		

Table 21 (cont.)

Middling										
Weight %			Grade		Distribution					
each size fraction	of total	Cumul. of total	Cu	Bi	each size fraction	of total	Cumul. of total	Cu	Bi	Cumul. of total
0.-					0.-	0.-	-	-		
0.-					0.-	0.-	-	-		
0.-					0.-	0.-	-	-		
0.-					0.-	0.-	-	-		
3.55	0.10	0.10	4.12	3.31	11.02	41.85	0.10	0.47	0.10	0.47
2.23	0.41	0.51	1.63	3.65	0.96	11.61	0.17	2.09	0.27	2.56
2.75	0.44	0.95	1.25	1.34	0.60	3.98	0.14	0.83	0.41	3.39
2.69	0.26	1.21	0.87	0.40	0.41	1.24	0.06	0.15	0.47	3.54
15.56	8.16	9.37	1.97	0.50	4.93	11.93	2.18	5.69	2.65	9.23
	9.37		(1.13)	(0.70)			2.65	9.23		

Table 21. (cont.)

Concentrate										
Weight %			Grade		Distribution					
each size fraction	of total	Cumul. of total	Cu	Bi	each size fraction		of total		Cumul. of total	
					Cu	Bi	Cu	Bi	Cu	Bi
0.-					-	-	-	-		
0.-					-	-	-	-		
0.-					-	-	-	-		
0.-					-	-	-	-		
4.61	0.13	0.13	22.25	1.55	77.23	25.46	0.73	0.28	0.73	0.28
15.42	2.84	2.97	24.21	2.95	98.18	64.89	17.18	11.71	17.91	11.99
23.58	3.77	6.74	24.23	3.65	98.89	92.84	22.85	19.32	40.76	31.31
22.75	2.20	8.94	24.98	3.65	98.81	95.34	13.73	11.22	54.49	42.53
14.46	7.58	16.52	21.47	3.15	91.96	69.83	40.76	33.31	95.25	75.84
	16.52		(23.05)	(3.28)			95.25	75.84		

PART II

AN EXPERIMENTAL STUDY OF THE EFFECTS OF COLLECTORS
AND INFLUENCE OF DICHROMATE ON THE CONTACT ANGLE
AT BISMUTHINITE SURFACES

INTRODUCTION

Whereas bismuth was produced probably as early as the thirteenth century, it was neglected by metallurgists because the metal was so impure that early workers confused it with lead, zinc, or antimony, with which it has many properties in common (7). The principal bismuth ores are bismite, bismuthinite, bismutite, and bismutospharite. Bismite, or bismuth ochre, is bismuth trioxide, Bi_2O_3 ; it is hydrated and usually impure. Bismuthinite is the trisculphide, Bi_2S_3 , often containing a little copper and iron. Bismutite, possibly $\text{Bi}_2\text{S}_3\text{CO}_3\text{H}_2\text{O}$, is a basic carbonate, and bismutospharite, of secondary origin, is also a carbonate, $\text{Bi}_2(\text{CO}_3)_3 \cdot 2\text{Bi}_2\text{O}_3$. Ores of lesser importance are bismutoplagionite, $5\text{PbS}4\text{Bi}_2\text{S}_3$, bismutosmaltite, $\text{Co}(\text{As},\text{Bi})_3$, and bismutotantalite, a bismuth tantalate and niobate, probably $(\text{BiO})_2(\text{Ta},\text{Nb})_2\text{O}_6$ (8).

Generally, bismuth is a by-product of the smelting operations by which tin, lead, copper, and silver are produced. Although bismuth minerals have been found in various places, no ore is mined for the bismuth content alone. The chief world producers of bismuth are Peru, U.S.A., Mexico, Korea, Bolivia, Japan and Canada (8). Generally, from a mineral-processing point of view, we can classify the bismuth ores into (1) main product ore, where the bismuth content is so high that bismuth alone can be produced economically (Peru, Bolivia, Germany and Spain etc.), and (2) by-product ore which is of so low grade that it cannot be treated for its bismuth content alone.

If the grade of bismuth is high and it occurs in large lumps, it can be separated by hand-picking. But often bismuth is disseminated very finely with other sulphide minerals; such bismuth mineral is not treated by differential flotation but by bulk flotation, or even concentrated from the tailings (9). The prospect of obtaining higher grade and greater recovery of bismuth in a concentrate is promised by the use of a delicate flotation technique. To evaluate the effectiveness of flotation as a mineral separation technique, a knowledge of the surface properties and the flotation characteristics of each mineral in the concentrate is essential.

The flotation of sulphide minerals, such as chalcopyrite (CuFeS_2), pyrite (FeS_2), galena (PbS) and sphalerite (ZnS), has been successfully practiced for 45 years, particularly with the introduction of xanthates in 1925 and dithiophosphates in 1926 as sulphide collectors (17). Flotation has now almost reached the stage where improvements in the process can only come about through a better understanding of the mechanisms involved. Although many investigations on sulphide minerals, mainly mono or disulphide minerals, have been carried out there are very few references dealing with trisulphide mineral flotation, particularly bismuth flotation. Recently (1968), Glembolskii, Sokolov and Solozhenkin (10) have published a study of the electrochemical potential of bismuth minerals but no exact mechanism has been established to explain the collector adsorption phenomena and depression of bismuthinite. Many

fundamental details are still lacking and further work is required for the understanding of the characteristics of bismuth flotation.

The depression of bismuthinite is also of great importance as bismuthinite flotation is usually a part of a series of differential mineral concentrations. An increased understanding of bismuthinite-collector attachment and of the mechanism of bismuthinite depression may lead to improved control of bismuth separation from other minerals.

After an extensive search of the literature, it was decided to determine whether the effect of xanthates, dithiocarbamate and dithiophosphoric acid, and the influence of potassium dichromate as a depressor could be evaluated quantitatively by the "contact angle" method.

Significance of Contact Angle in Flotation

The concept of contact angle is of great importance, not only to the theory of flotation but, generally, in all fields of surface chemistry which deal with the coexistence of solid, liquid and vapour phases (39). A solid and one fluid phase in contact meet at an "interface". A solid and two fluid phases meet at a line of contact. The angle of inclination of the fluid-fluid interface against the solid-fluid interfaces is termed contact angle (θ). By convention the contact angle is measured across the water phase if water is one of the phases involved.

When a drop of liquid is placed on a flat solid surface or,

more likely, it may remain as a drop having a definite angle of contact with the solid surface (Figure 1).

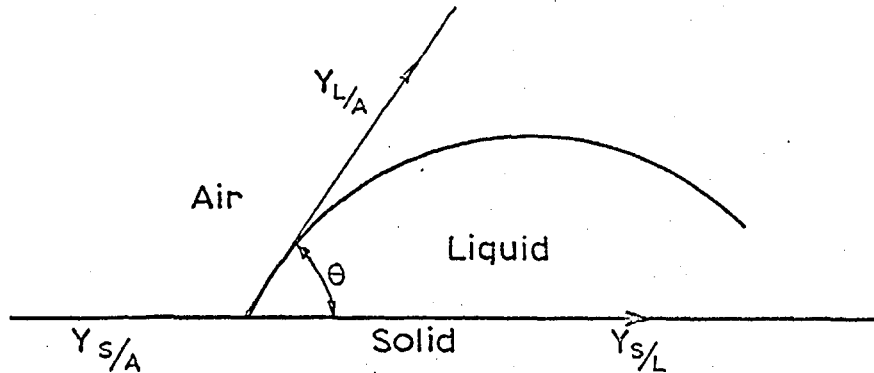


Fig.1 Solid-liquid system in equilibrium

Assuming that the various surface forces can be represented by surface tensions acting in the direction of the surfaces, and then equating the horizontal components of these tensions gives (40)

$$\gamma_{S/A} = \gamma_{S/L} + \gamma_{L/A} \cos \theta \quad (1)$$

The same condition of equilibrium may also be described in terms of the work of adhesion which is given by the Dupré equation (40) (37).

$$W_{S/L} = \gamma_{L/A} + \gamma_{S/A} - \gamma_{S/L} \quad (2)$$

In this equation $W_{S/L}$ is the work required to separate reversibly a unit area of contact of the liquid phase from the solid phase which is submerged in the air phase (37) (40). The work of adhesion may also be regarded as a measure of the resistance of liquid phase against being displaced by air phase from the solid phase.

Expression (2), as can be seen, involves the two solid interfacial tensions which cannot be measured. A combination of equations (1) and (2), however, eliminates these two unknowns and leads to the expression

$$W_{S/L} = \gamma_{L/A} (1 + \cos \theta) \quad (3)$$

which is known as Young's equation (40)(37). Therefore, zero contact angle results when the forces of attraction between liquid and solid are equal to, or greater than those between liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself. The solid is completely wetted by the liquid if the contact angle is zero and only partially wetted if the contact angle is finite. Complete non-wetting implies a contact angle of 180° .

Equation 3 shows how the tendency of the mineral to become attached to an air bubble, and therefore to float, is dependent upon the contact angle (41). When the contact angle, θ , is zero the tenacity of adhesion between mineral and air becomes zero and $W_{S/L}$ becomes a maximum of $2\gamma_{L/A}$ in which case there is no tendency to stick to the air bubble, and this surface is said to be hydrophilic. When θ is greater than zero, the surface is said to have attained a degree of hydrophobicity. A completely hydrophobic surface is obtained when contact angle is 180° and $W_{S/L}$ becomes zero in which case the tenacity of adhesion between mineral and air becomes a maximum and the greatest tendency to stick to the air bubble is found (41)(40)(13).

These three cases are shown in Fig. 2 (42).

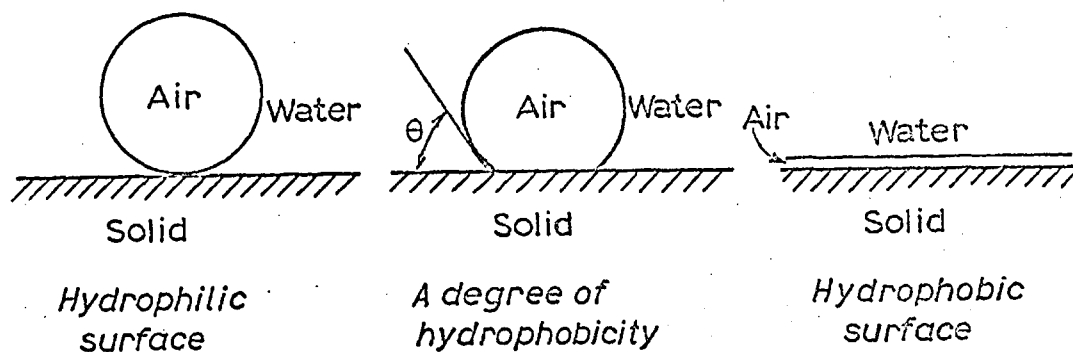


Fig. 2

It is important to note that both $\gamma_{L/A}$ and θ can be measured experimentally, and that the measurement of contact angles has been so valuable in the development of the theory of flotation. It is obvious that the primary requisite for flotation is adhesion between air and mineral, or, more strictly, a sufficient attraction between mineral and air for air to be able, partly at least, to replace water at the mineral surface. If replacement of water by air is possible, flotation will be possible (23). Any factor that influences contact angle may influence flotation, but, not every factor that influences flotation also influences contact angle. Thus many frothers have no significant influence on contact angle: they may lower the surface tension of water only slightly and not influence the surface of the solid (41)(23).

Measurement of Contact Angle

Difficulties of two kinds have arisen in measuring the contact

angles at mineral surfaces. Firstly, accidental contamination, which is in fact due to adsorption, changes the values of $\gamma_{S/A}$ and $\gamma_{S/L}$: it therefore influences the value of the contact angle (41).

Secondly, at most surfaces the angle of contact is not the same when air is advancing as when it is receding and the early experimentalists, not knowing what the difference was due to, found it difficult to decide which angle should be measured (23)(6).

As depicted in Figure 3, if a drop of liquid 1 is held stationary on the surface under liquid 2, the angles measured on either side of the drop should be equal. If the solid is caused to move from under the drop, a condition similar to that depicted in Figure 4 is obtained where the angles on either side of the drop are not equal. The difference between the maximum and minimum values of the contact angle, obtained when the drop is actually moving over the surface, is called the "hysteresis" (43).

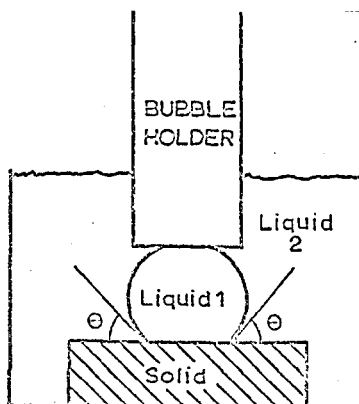


Fig. 3 Contact angles in a typical liquid-liquid solid system

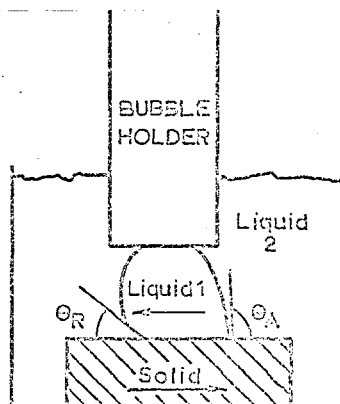


Fig. 4 Hysteresis of contact angles in same system

(These figures are from Reference 43)

If water is one of the liquids, the contact angle is measured across the aqueous phase. When there is hysteresis, the angle formed by the water phase advancing over the surface is called the "advancing angle" (θ_A), the other is the "receding angle" (θ_R), and the difference between these two angles is the hysteresis ($\Delta\theta = \theta_A - \theta_R$) (6)(37)(43).

The importance of contact angle hysteresis in actual flotation systems has been a matter of controversy for many years. It has been claimed that hysteresis is a necessary prerequisite for successful flotation (43-46). Many theories have been proposed to explain hysteresis. While it is generally accepted that hysteresis of contact angles cannot be explained by one phenomenon only, controversy still persists as to its interpretation for particular systems (37).

Current theories to explain hysteresis are primarily based on the concepts of surface roughness, surface heterogeneity, friction, hysteresis of adsorption and orientation of adsorbates (43)(37). Unintentional adsorption or contamination is one of the most frequently encountered explanations. This contamination, the result of inadequate experimental technique, is at the root of much of the difficulty encountered in this area of science; it was for some time accepted as the sole reason for hysteresis (37). Hysteresis is greatly reduced by using polished mineral surfaces and Wark and Cox (41) found it possible to measure equilibrium angles.

1. EXPERIMENTAL APPARATUS, MATERIALS AND TECHNIQUES

1.1 Apparatus for Measuring Contact Angles

An air-mineral-water contact was effected at a horizontal mineral surface by bringing a small bubble of air downward into contact with the surface of a small submerged specimen of the mineral. The bubble was suspended at the bottom end of a vertical glass capillary tube of small diameter. A magnified image of the contact angle was projected on to a photographic ground-glass screen on which the angle of contact was easily measured.

The contact-angle measurement was closely followed by the method described by Shergold and Mellgren (3)(4). The apparatus used in this work has been constructed on an optical bench as shown in Figs. 5 and 6. The glass cell (30 mm x 30 mm x 35 mm) containing the polished specimen and the collector solution was mounted on a mechanical stage which permits movements in the upward and downward directions. The bubble holder is attached to a vertical rack and pinion arrangement which enables it to be raised or lowered. The bubble may thereby be conveniently brought into contact with the surface of the mineral.

It has been found desirable to place the lamp in a plane slightly higher than that of the surface of the mineral (23). Light was then reflected from the mineral surface and the image of the bubble on the screen was seen in juxtaposition with an inverted image which arises by reflection at the surface of the mineral. A copper sulphate

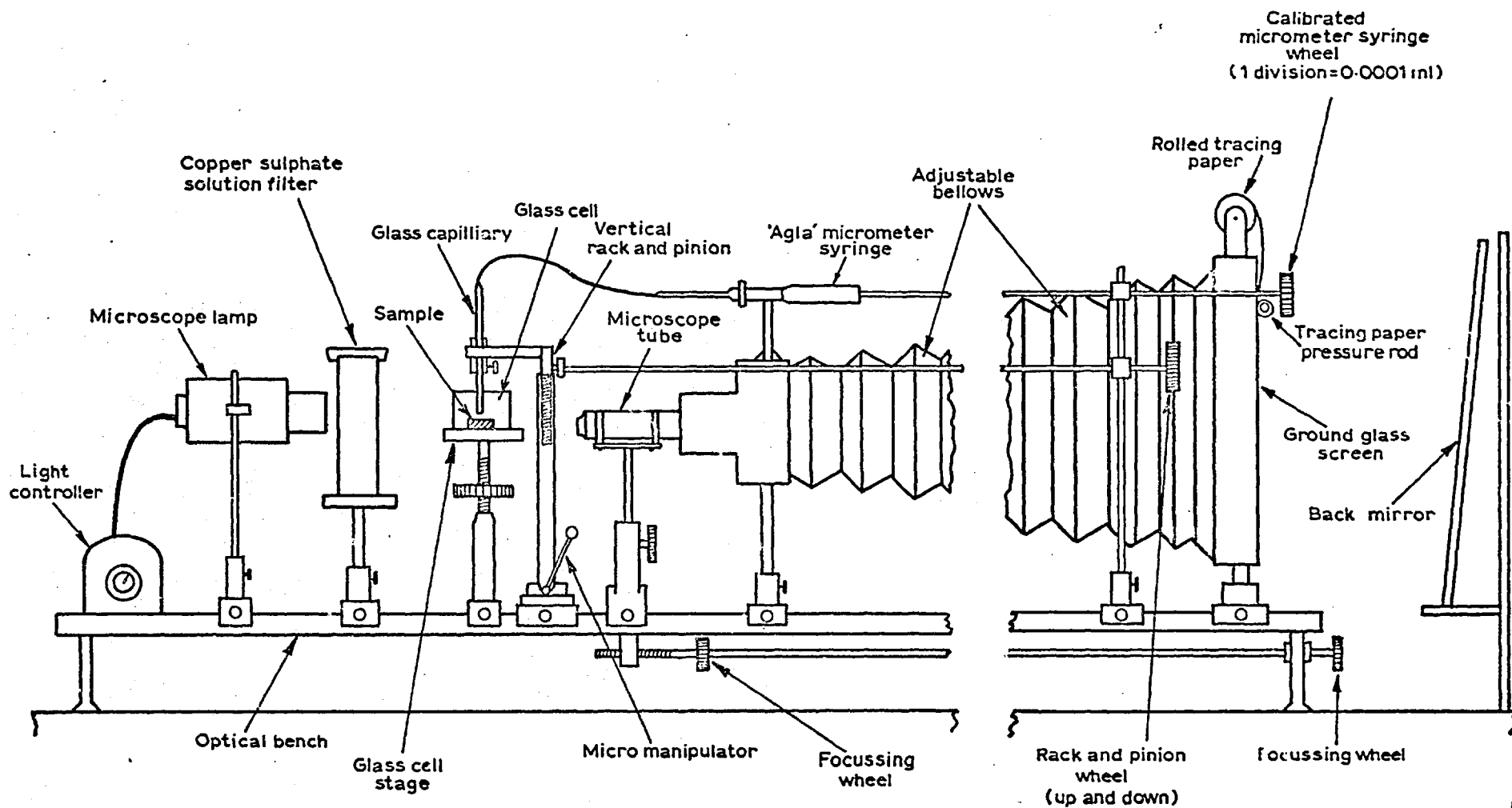


Fig.5 *Contact angle measurement apparatus*

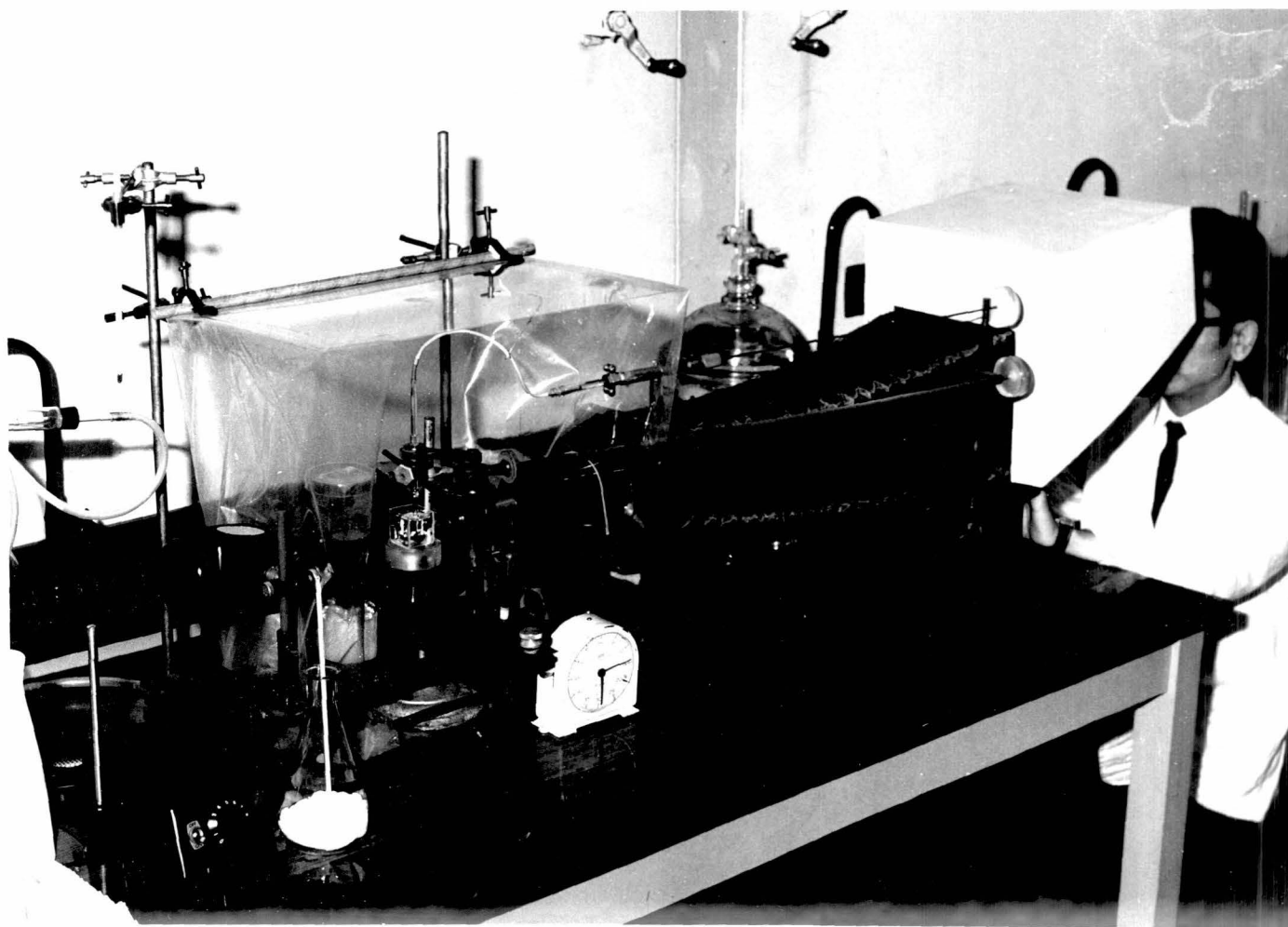


Fig.6 Contact Angle Measurement Apparatus

solution filter was placed in front of the lamp to keep the heat from the light source to a minimum (4).

1.2 Experimental Materials

1.2.1 Bimuthinite sample:

A small piece of bismuthinite, which was obtained from the Geology Department, Royal School of Mines, was used for the contact angle studies. This piece was divided into two fractions, one fraction being for chemical analysis and the other for contact angle determination. A microscopic examination of this sample revealed no impurity. One fraction was ground very finely for analytical purposes and sent to Analytical Services of the Royal School of Mines for 9 qualitative elemental analyses (Bi, S, Pb, Zn, Cu, Fe, Mo, Sn, As) by the X-Ray fluorescence method. The sample contained larger than 3% of Bi and S, larger than 0.05% of Sb and traces of Ca and K were detected. From the results of these analyses three elements were assayed, quantitatively by X-Ray fluorescence method, 87 pct bismuth, 11.2 pct sulphur and 0.77 pct antimony (therotical, for Bi_2S_3 : Bi 81.2, S 18.8 pct) (29). The other small piece of bismuthinite sample was ground on a fine diamond wheel. After the surface had been examined under the microscope, it was embedded (25 mm diameter) in "Araldite" so that the purest and most homogeneous surface was exposed. The sample was then polished on successively finer grades of silicon carbide 'paper'. The finest polishing was conducted on a well worn 600 grade paper followed by a

light polish with the various grades of alumina on a selvyt cloth (6). Final polishing was carried out with levigated "Microid" gamma polishing alumina.

1.2.2 Chemicals:

All reagents and solvents used in this work were of the analytical reagent grade. Double distilled water was used in the preparation of any solutions. The pH values were adjusted by the use of sodium hydroxide and hydrochloric acid.

All glasswares used were cleaned by soaking it in 5 per cent alcoholic sodium hydroxide (22) followed by treatment with 50 per cent nitric acid, and by rinsing with distilled water and dried in an oven.

1.3 Preparation and Purification of Collectors

1.3.1 Potassium Ethyl Xanthate

Recrystallized commercial potassium ethyl xanthate (abbreviated as KEX), which was produced by Hopkin & Williams Ltd., was purified in the standard manner (1)(47). KEX was dissolved in acetone and filtered to remove insoluble material. The xanthate was then precipitated from acetone solution with ether and filtered and then washed with ether three times. This process was repeated and the xanthate was transferred to a stock bottle. Sufficient ether was left in the bottle to cover the xanthate and prevent exposure to air. The bottle was kept in the refrigerator (approx. 5°C) for later use.

The small quantity of this sample was dissolved in acetone and reprecipitated in ether. The xanthate was centrifuged and washed

three times with fresh ether. The ether-xanthate slurry was transferred to a weighing bottle and covered with a filter paper which was held in position by a rubber band. The bottle was placed in a desiccator, and the ether was carefully evaporated at low vacuum. After most of the ether had been removed, the desiccator was evacuated with a high vacuum pump, to remove the last traces of ether. The xanthate was kept in the desiccator under high vacuum except during the short time interval taken for weighing out the necessary quantities. The xanthate was prepared fresh every week and hence the reagent used in the experiments was never more than seven days old.

A xanthate solution of 20 grams per litre was prepared, as xanthate seems to be more stable in high concentration.

1.3.2 Potassium amyl and hexyl xanthate:

The amyl and hexyl xanthates (abbreviated as KAX and KHX) were prepared (23) by slowly adding excess carbon disulphide to a mixture of the respective alcohol (amyl and hexyl alcohol) with a slight excess over the theoretical amount of a saturated solution of potassium hydroxide in water. The mixture was kept below 20°C until all the carbon disulphide was added. Stirring was continued for about 15 minutes. Finally, excess carbon disulphide was removed by decantation. The yellow crystalline mass was then dissolved in a small quantity of acetone, decanting from the small residual aqueous solution of red polysulphides. The addition of ether precipitated

the xanthates as pale yellow crystals. These xanthates were used in this work after three times of purifications with acetone and ether as previously mentioned (1)(48).

1.3.3 Purification of diethyldithiophosphoric acid

Diethyldithiophosphoric acid was purified by the method described by Maycock (36). 100 ml of diethyldithiophosphoric acid (abbreviated as DETA) produced by Albright and Wilson was diluted to 250 ml with double distilled water in a volumetric flask. The flask was shaken by 'Microid flask shaker' (for 12 hours) until only a tarry layer remained in the bottom. The clear solution was removed and centrifuged to remove any small tarry globules. Concentrated hydrochloric acid was added to the clear solution until diethyldithiophosphoric acid appeared as yellow oily drops. Diethyl ether was then added and the mixture shaken, centrifuged and the aqueous layer discarded. A 0.5 M sodium hydroxide solution was added to the ether layer and after shaking, the two phases were again separated, this time discarding the ether layer. Concentrated hydrochloric acid was added to the aqueous phase until the yellow drops appeared once more. These drops were allowed to collect on the bottom of a separating funnel and then removed. Calcium chloride lumps were added to the purified aerofloat to remove moisture. The flask was put under vacuum to remove traces of ether and then the final product was filtered. Specific gravity of this acid was 1158.4 mg per ml. 20 g per litre of stock solution was made with double distilled water.

2. STANDARDIZING OF EXPERIMENTAL WORK

2.1 Experimental Method

A solution containing a particular amount of collector and having a particular pH was made. 20 ml of this solution was taken in a cell into which the polished specimen of the bismuthinite was transferred from under double distilled water.

The specimen was left in the first cell for 10 minutes. This was then transferred to another cell containing the same volume of the same solution. This operation was done in order to prevent the solution from being diluted by distilled water adhering to the surface of the specimen and by the adsorption of xanthate on Araldite surface (4). In all cases where the sample was transferred from one solution to another, it was transferred by using glass chopsticks under the nitrogen gas and the surface was not allowed to become dry.

The sample was equilibrated in the fresh solution for ten minutes 1.35 ml volume of air was introduced to form a bubble. A period of 20 minutes has been found by preliminary tests to be sufficient to permit development of maximum contact angle, and all measurements are made after at least this much time has elapsed. The magnified image on the ground screen was 60 mm in diameter on the horizontal. This bubble was brought just into contact with the sample surface. After the bubble had advanced over the surface and reached an equilibrium position (about 1 minute), the contact angle

which was termed the advancing contact angle was measured through the aqueous phase by drawing the angle on the tracing paper and using a transparent protractor.

The volume of the bubble in contact with the mineral was then increased by passing another 0.01 ml of air and the system left to equilibrate (about 30 seconds). After this equilibration period the bubble was decreased (0.01 ml) to its original volume and then after a further equilibration period the contact angle, which was termed the receding contact angle (4), was measured by the same method as before.

In all cases at least six positions on the mineral surface were examined and the contact angle on both the left and right sides of the projected image were measured. An average of the two values was taken, any recorded angle is therefore the mean of at least twelve measurements. An example is given below (Table 1).

Table 1

Conditioning time (min.)	Advancing			Receding			Remark
	left	right	average	left	right	average	
20	59	59	59.0	80	78	79.0	Test No. 218 KAX 100mg/litre pH 6.05 Temp. 22°C
23	61	57	59.0	75	74	74.5	
26	61	56	58.5	78	73	75.5	
29	62	61	61.5	80	79	79.5	
32	65	61	63.0	79	79	79.0	
36	58	52	55.0	74	69	71.5	
40	58	58	58.0	76	78	77.0	
Over-all average	$\frac{4140}{7} = 59.142$			$\frac{5360}{7} = 76.6$			

No attempt was made to control the temperature during the contact angle measurements. In these tests the temperature varied between 20° and 25°C.

2.2 Preparation of Clean Mineral Surfaces

The method of polishing was adopted from that described by Wark (23). After the measurement of each contact angle the bismuthinite sample was cleaned by soaking it in 0.1 M sodium hydroxide solution followed by treatment with 0.1 M hydrochloric acid solution (33) for 5 min. Washing was repeated with distilled water and double distilled water. The specimen was then polished with levigated "Microid" gamma polishing alumina on a "Selvyt" cloth (6) covered glass polishing wheel. Handling of the specimen during polishing was done with latex rubber gloves, cleaned in 50% nitric acid solution and 5% alcoholic sodium hydroxide solution and then thoroughly washed with distilled water. The "Selvyt" polishing pads were first washed in a solution of sodium hydroxide (5%) and then ether to free them from grease (33). During polishing, the specimen was held against the rotating cloth wheel with gloves; it was thoroughly flushed with distilled water so that the polished surface was scrubbed with the bare, wet "Selvyt" cloth. The polished specimen was thoroughly washed again by pouring double-distilled water over it. (Polishing method 1).

After polishing the specimen was rubbed (70 times) on "Selvyt" cloth, which had also been washed carefully with sodium hydroxide

and ether and then stretched over a photographic glass plate under distilled water. During rubbing the specimen was held by glass chopsticks. Special care was exercised to prevent exposure of the clean surface to air or any other source of contamination. This specimen was finally washed and stored under double-distilled water and then used for contact angle measurements (polishing method 2).

2.3 Test of Cleanliness

2.3.1 General Concept

Past work by many workers on the wettability of clean surfaces by water has established the fact that the presence of hydrophobic organic contaminations on the surface results in an increase in the contact angle on the surface. These organic contaminations are most often small amounts of oil or grease that are present in normal laboratory ambients and are adsorbed on to the surface, changing its wetting characteristics. In order to eliminate this effect, many workers have taken great care to purify the ambient in which the contact angle measurements have been made. Even when this has been done, however, there still arise some discrepancies in wettability results.

Weining and Palmer state (23) that fresh cleavage faces of calcite, sphalerite, galena, pyrite and magnetite are wetted by water. Ince (34) says "The bubble showed the very slight adhesion and distortion common to slightly contaminated sulphide surfaces". Taggart (35) and his collaborators commenced tests with galena

crystals already showing contact angles up to 34° in distilled water and state that it is difficult to get mineral particles so clean that they show no tendency at all to attach to air bubbles. Wark and Cox (23) state that several tests prove that there is no tendency for a bubble of air to replace water at the surface of any of the common zinc, lead, iron or copper minerals or at surfaces of the associated gangue minerals.

In the absence of collector, a contact angle of 56° on chalcocite was obtained by Paterson and Salman (17). Bewing and Zisman (64) measured zero contact angle of water of a polished gold sample in a variety of gases which were purified by passing them through cooled charcoal.

It is possible that the nature of the ambient (hydrogen in one case and air in the other) affects the wettability of the surface but another factor that should be considered is the presence of residual contaminants from the operations used to prepare the specimen surface. There is some evidence in the literature that mechanical polishing with alumina slurry results in retention of alumina particles on the surface. White and Drobek (32) detected some alumina in electron diffraction examinations on mechanically polished gold surface. In this work when gold surfaces were prepared by polishing with alumina abrasives, the contact angles of water were found to be $34-56^{\circ}$, even after some of the surface had been removed by etching with aqua regia. Reflection electron diffraction patterns

on the surfaces show evidence of residual abrasive material on the surface which was not removed by etching. When gold surfaces were prepared by vacuum evaporation of high-purity metal on silica substrates or by polishing of gold with diamond abrasive followed by firing in oxygen at 1000°C, the contact angles of water on these surfaces are 55-65°. The authors stated "These results show that the presence of hydrophilic inorganic contaminations on surfaces can affect wettabilities as seriously (but in the opposite direction) as the more commonly discussed contamination by hydrophobic organic material."

2.3.2 Experimental and Result

In this work two methods were considered to prepare clean surfaces of bismuthinite and standardize the polishing technique for contact angle measurements.

Polishing method 1:

The specimen was polished by the method mentioned previously and was thoroughly washed again by pouring double distilled water over it.

Polishing method 2:

It was the same as polishing method 1 except the rubbing of the specimen was carried out (70 times) on "Selvyt" cloth.

By these two polishing methods, contact angles of water on bismuthinite surface were measured at various pH values (without any collector).

RESULTS

Advancing contact angles on bismuthinite as a function of pH in double distilled water are shown in Fig. 7.

It is seen that, using the polishing method 1, zero contact angles were obtained in double-distilled water (in the absence of collector) at all pH values. Using the polishing method 1, no contact angle was formed at any pH even with potassium ethyl xanthate. More than 170 tests (in each test more than 12 angles were measured) were carried out with potassium amyl xanthate by the polishing method 1 but it was found that either no contact angle was formed or results of contact angle measurements were completely scattered which cannot be reproduced in any case.

From these results it was concluded that the presence of residual hydrophilic alumina abrasive, which could not be removed by thoroughly flushing with water, resulted in either increasing the wettability or preventing the contact angle formation on the bismuthinite surface. When the bismuthinite surface was prepared by polishing method 2, the contact angles on this surface were found to be about 25° (which was doubtful sign of clinging) below pH 9. (see Fig. 7). When the specimen was polished by method 2 and used for contact angle measurements, it was found in all tests with collectors that the bubbles advanced towards the right and left very evenly and smoothly. It was also found that the results could be reproduced. The procedure of polishing method 2 had perforce to

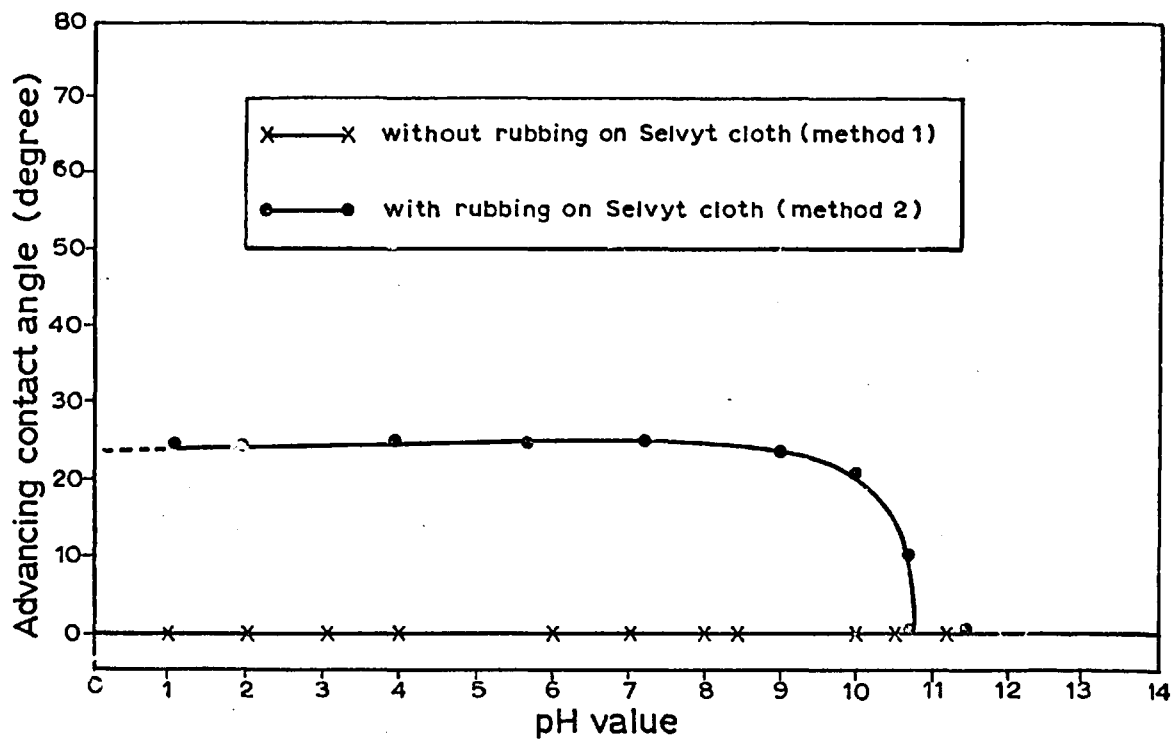


Fig. 7 Advancing contact angle on bismuthinite as a function of pH in the double-distilled water. (Without any collector)

be adopted in order to obtain reproducible results. By comparing the two methods it was decided that method 2 of polishing gave the more reliable results.

There is a comparable evidence in the surface properties of hydrophobic solids. Arbiter, Fujii, Hansen and Raja (72) measured the contact angle with stibnite (Sb_2S_3) to confirm whether it is a hydrophobic mineral. They obtained 35° in distilled water (pH 6.2) and a maximum contact angle of 42° at pH 3, and they have reported that stibnite is a hydrophobic mineral. This hydrophobic character of stibnite could support the idea that bismuthinite may be a weakly hydrophobic mineral because the bismuthinite (Bi_2S_3) has the same crystal structure (70)(74)(75) and mineralogical properties (29) as stibnite, namely,

Crystal structure : Isomorphous.

Crystal bond : Weaker and longer secondary (Sb-S, Bi-S) bond.

Cleavage : Perfect (010). The crystals are very elongated in the c direction.

Hardness : 2. Lusture:metallic.

Composition : Trisulphide, Sb_2S_3 , Bi_2S_3 .

Fusibility : Very easily fusible at 1 (in the candle flame).

2.4 Comparison between Advancing and Receding Contact Angle

Contact angle measurements of potassium amyl xanthate on the bismuthinite surface were carried out to compare the advancing and receding contact angle as a function of pH and concentration of

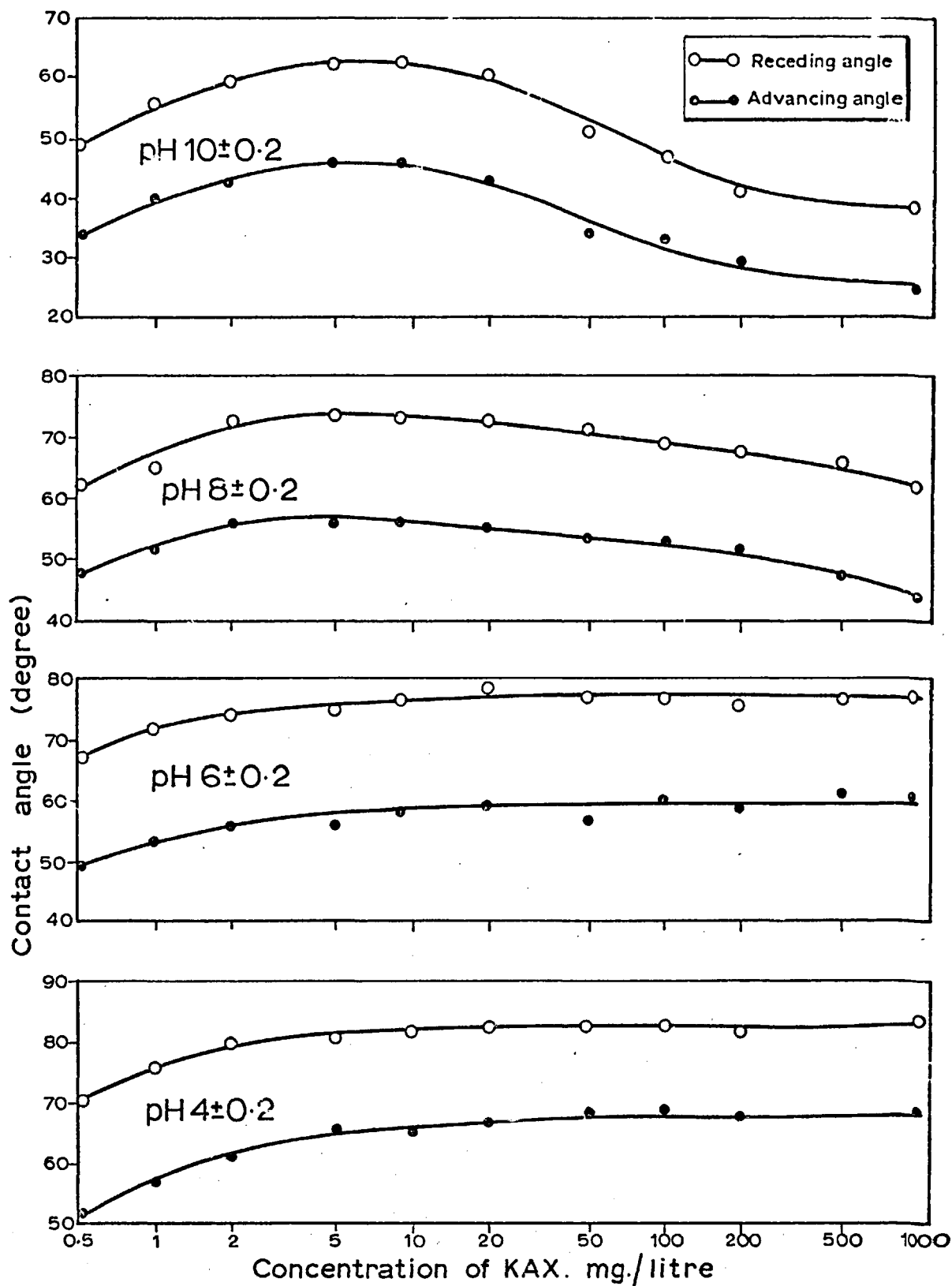


Fig. 8 Comparison between advancing and receding contact angle on bismuthinite.

potassium amyl xanthate. Results obtained are shown in Fig. 8. In this figure, 12° - 20° differences are found between advancing and receding contact angles but it is found that there is very little variation in the shape of the curve over the concentration range tested. A comparison of the advancing and receding contact angle measurement shows that it is advantageous to measure the advancing contact angle only as it can be done quickly.

3. THE EFFECTS OF XANTHATES

3.1 General Concept

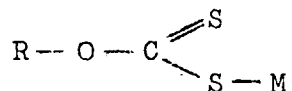
The historical development of the flotation theory has been reviewed by a number of authors (5)(6)(25)(31) and the present day understanding of the flotation theory has been given concisely by Fleming and Kitchener (49). The discovery of xanthates led to a rapid development of the flotation process. Xanthates are used in the flotation of nearly all sulphide ores. They are also utilized in the flotation of oxidized ores of heavy metals after sulphidization of the surface by soluble sulphide salts (31)(5).

Briefly stated, the known facts concerning the effect of these reagents on the flotability of minerals are as follows (48):

1. Xanthates are without effect on silicates, silica, and generally on mineral currently regarded as "gangues".
2. Xanthates in very small amounts increase enormously the floatability of sulphides of copper, lead, silver, iron and mercury.
3. If zinc sulphides are first activated, as by treatment with a copper salt, they are readily floated by xanthates; otherwise not.
4. Elemental copper, silver and gold have their floatabilities increased by xanthates.
5. Sulphides of elements that are not typically metallic - e.g. stibnite $4(\text{Sb}_2\text{S}_3)$, realgar $16(\text{As}_2\text{S}_3)$, molybdenite $2(\text{MoS}_2)$, are not made to float markedly better by treatment with xanthates.
6. Oxidized minerals of lead and copper are floated if treated with large amounts of xanthates, but not so if treated

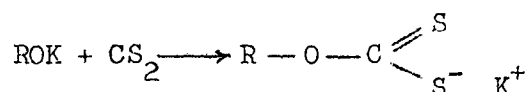
with amounts of the same order of magnitude as required for sulphide flotation. Oxidized zinc minerals are not floated unless xanthates having unusually long hydrocarbon chains (e.g. eight carbon atoms or more) are used. Iron oxides and carbonate are not floated by xanthates.

Xanthates are salts of acid ethers of dithiocarbonates. Their general chemical formula is:



R = hydrocarbon radical M = metal

In flotation practice, potassium and sodium xanthates are generally used (5). The basic materials for the preparation of technical xanthates are alcohols, hydroxides and carbon disulphide. The simplest method of preparation consists of dissolution of hydroxide in alcohol. In this way, alcoholate is obtained ($\text{KOH} + \text{ROH} = \text{ROK} + \text{H}_2\text{O}$), which reacts with carbon disulphide according to the equation:



3.2 The Result using Potassium Ethyl Xanthate

Contact angle measurements with potassium ethyl xanthate were carried out. The relationship between pH and contact angle at bismuthinite surfaces in the presence of 2.20 and 200 mg per litre of potassium ethyl xanthate is shown in Fig. 9. The pH of the potassium ethyl xanthate solution had very little effect on the contact angle, decreasing very slowly over the range pH 3.0 to 12.0.

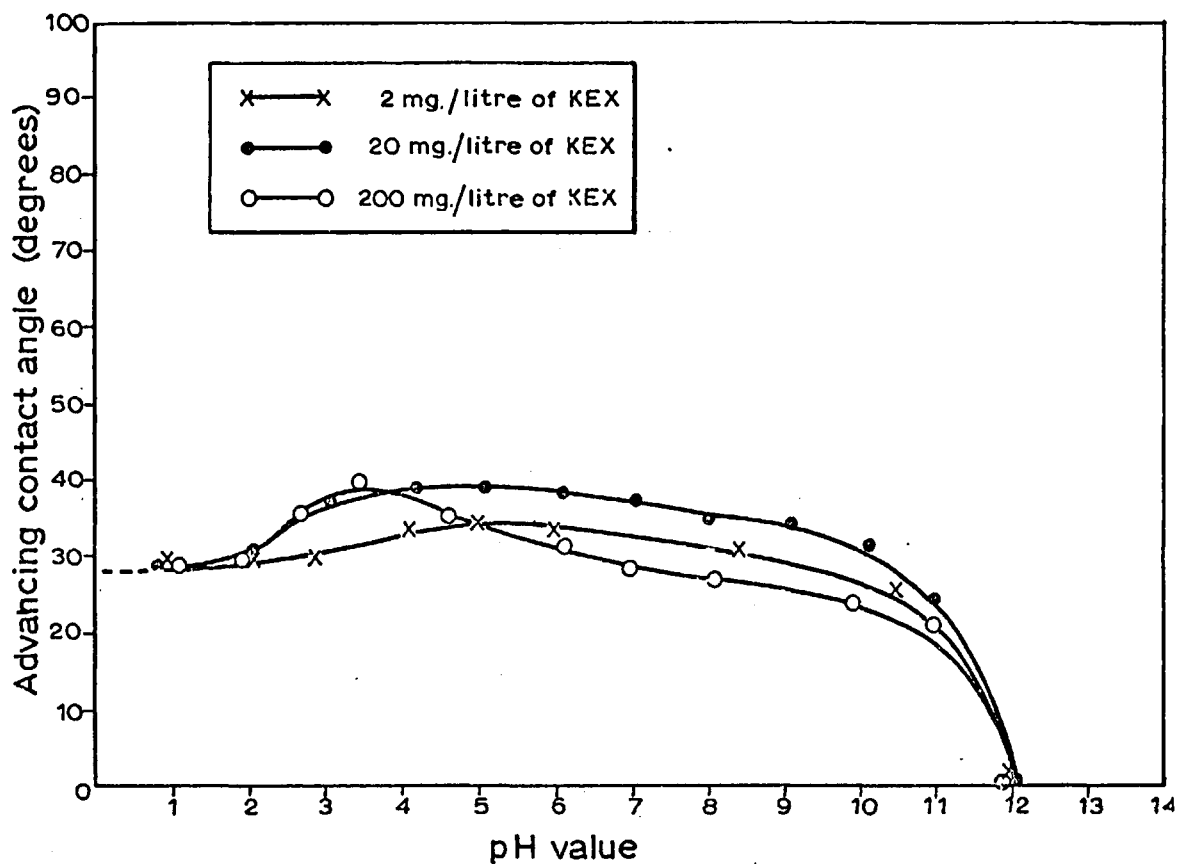


Fig.9 Advancing contact angle on bismuthinite as a function of pH in the presence of various concentrations of potassium ethyl xanthate.

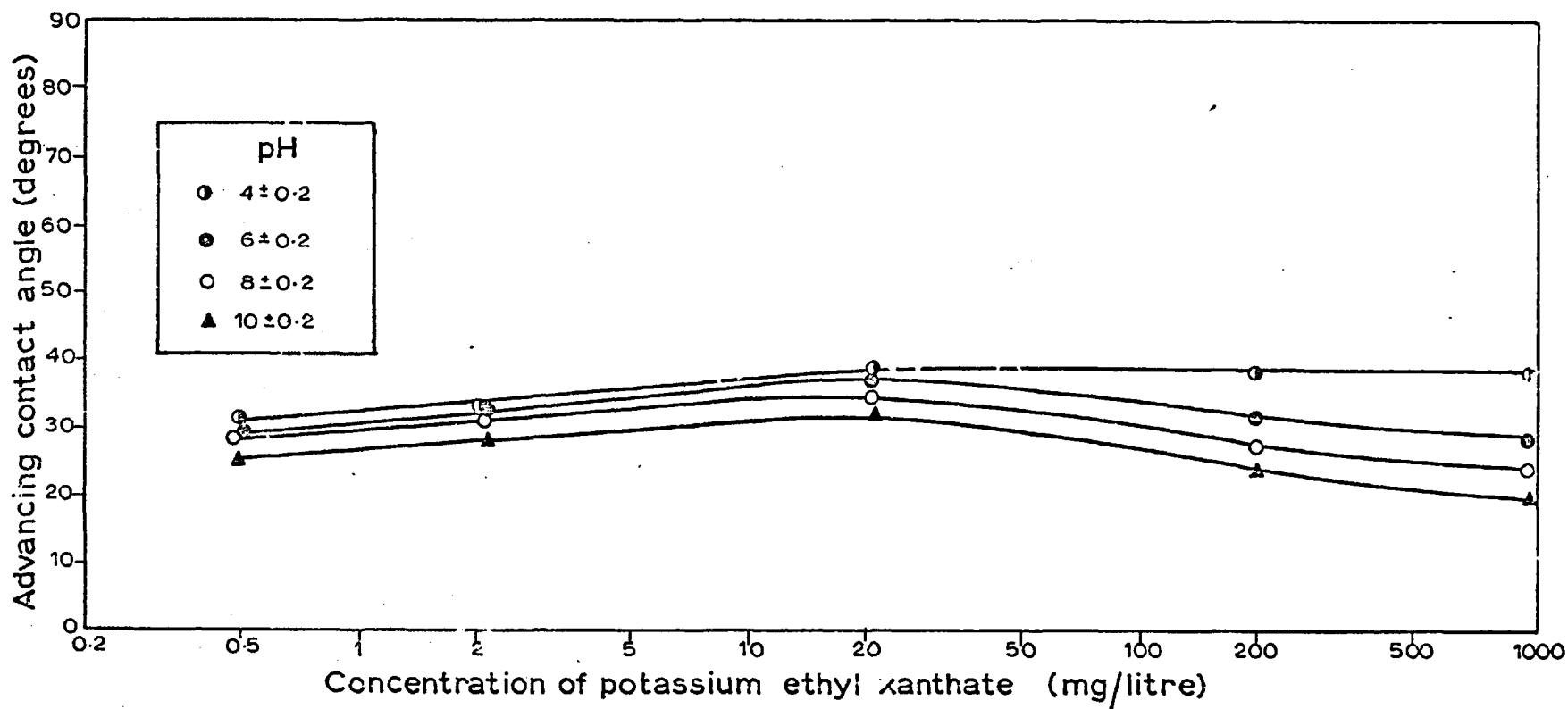


Fig.10 Advancing contact angle on bismuthinite as a function of potassium ethyl xanthate concentration on the various pH ranges.

There was little variation in the shape of the curve over a concentration range 2 to 200 mg/l. At xanthate concentration of 20 and 200 mg per litre, the contact angle slowly dropped from 39° to zero degree with an increase in pH from 3.5 to 12.0.

The correlation between the advancing contact angle and the potassium ethyl xanthate concentration on the various pH ranges is shown in Fig. 10. In this figure, the contact angle was found to increase linearly to a maximum of 32° to 39° at a concentration of 20 mg per litre but decrease very slowly above a concentration of 20 mg per litre with increasing concentration of potassium ethyl xanthate.

The results show that, within the system investigated, low contact angles are obtained which indicates that flotation of bismuthinite with potassium ethyl xanthate would be inefficient (if not actually impracticable).

3.3 The Result using Potassium Amyl Xanthate

With potassium amyl xanthate on the bismuthinite surface contact angle was observed. The relationship between pH and advancing contact angle at bismuthinite surfaces in the presence of 2, 20 and 200 mg per litre of potassium amyl xanthate is shown in Fig. 11. The contact angle varied with pH, decreasing slowly over the range pH 4.0 to 12.0 but rapidly between pH 4.0 and 3.0. There is a transition range across the curve from higher contact to lower contact in acid solution. This transition zone is extremely narrow

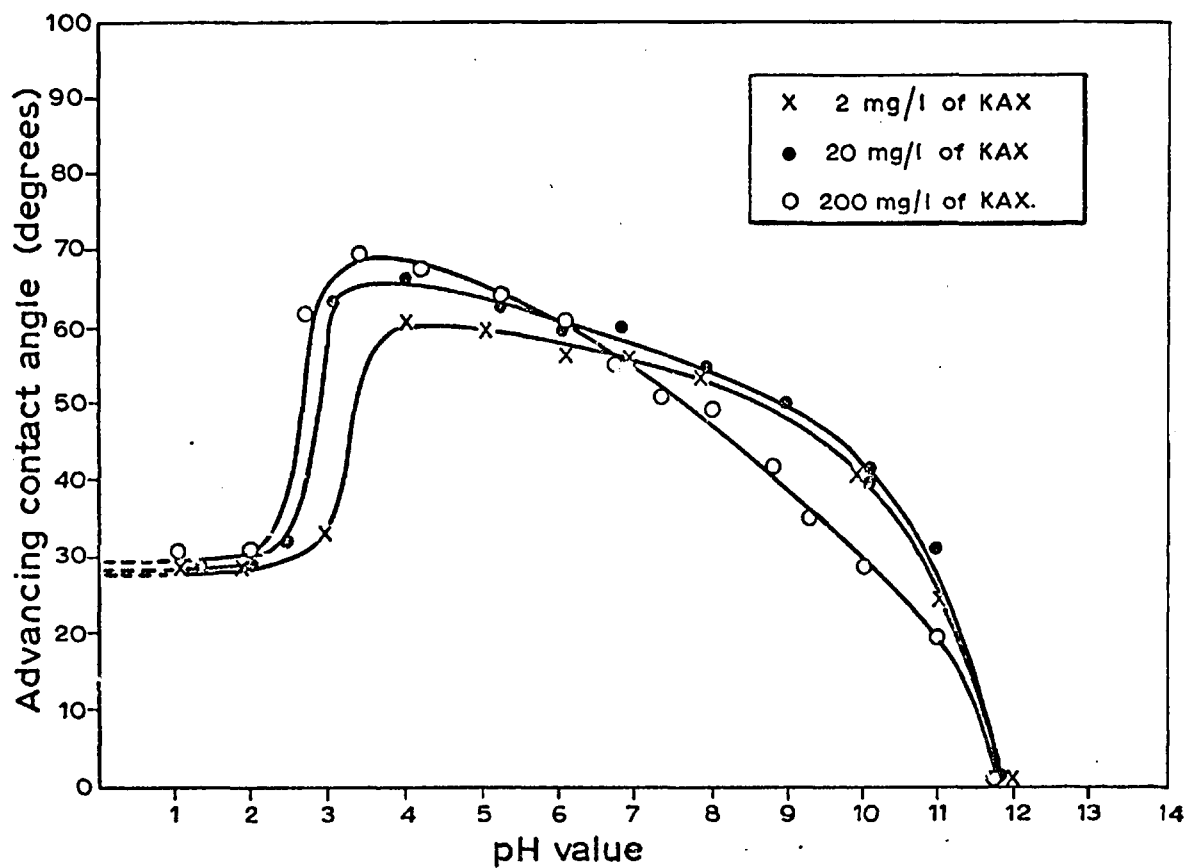


Fig:11 Advancing contact angle on bismuthinite as a function of pH in the presence of various concentrations of potassium amyl xanthate.

which is less than one pH unit over the range pH 2.5 to 4.0.

There was little variation in the shape of the curve over a concentration range 2 to 200 mg per litre. At xanthate concentration of 2, 20 and 200 mg per litre the contact angle rapidly dropped from about 60° - 70° to 30° with a decrease in pH from 4.0 to 2.5.

The correlation between the advancing contact angles and the potassium amyl xanthate concentration on the various pH ranges is shown in Fig. 12. The contact angles increased over the pH range 4.0 to 6.0 but decreased very slowly above pH 8.0 and 10.0 with increasing concentration of potassium amyl xanthate. Over the pH range 4.0 to 6.0 maximum contact angles were obtained at a concentration of 20 mg per litre but it was obtained at a concentration of 10 mg per litre when pH was 8.0 to 10.0.

Comparison between Fig. 9 (with KEX) and Fig. 11 (with KAX) shows that potassium amyl xanthate is more effective than potassium ethyl xanthate to induce contact at bismuthinite surface.

The relationship between pH and the concentration of potassium amyl xanthate necessary to induce contact at bismuthinite surfaces is shown in Fig. 13. Contact angle measurements were carried out at progressively higher potassium amyl xanthate concentrations until the concentration was high enough to prevent contact. These tests were repeated for various pH values and the critical curve was drawn to represent the transitional region between 0° — 30° , 31° — 50° and larger than 51° . This illustrated figure shows that

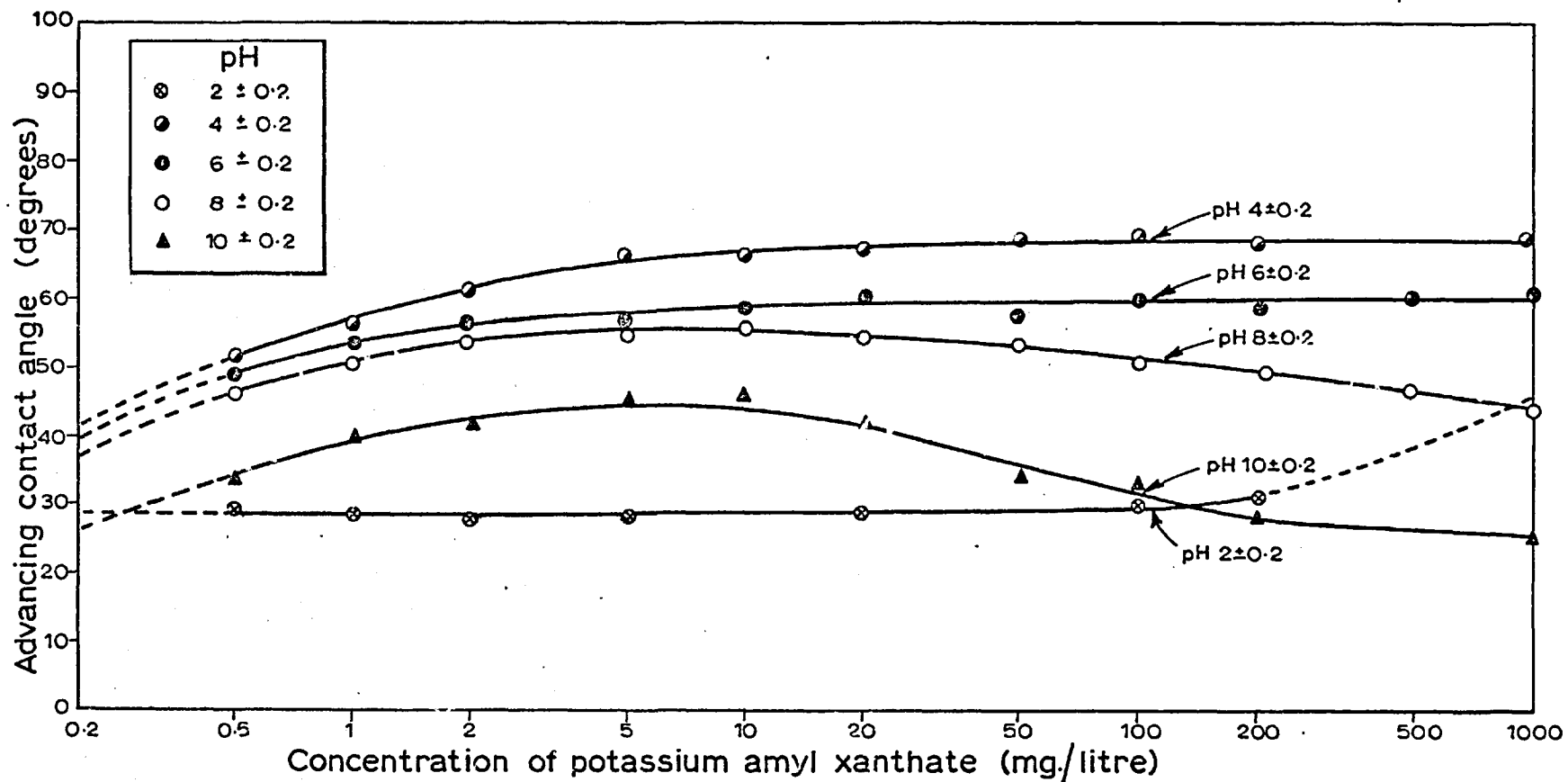


Fig. 12 Advancing angle on bismuthinite as a function of potassium amyl xanthate concentration on the various pH ranges.

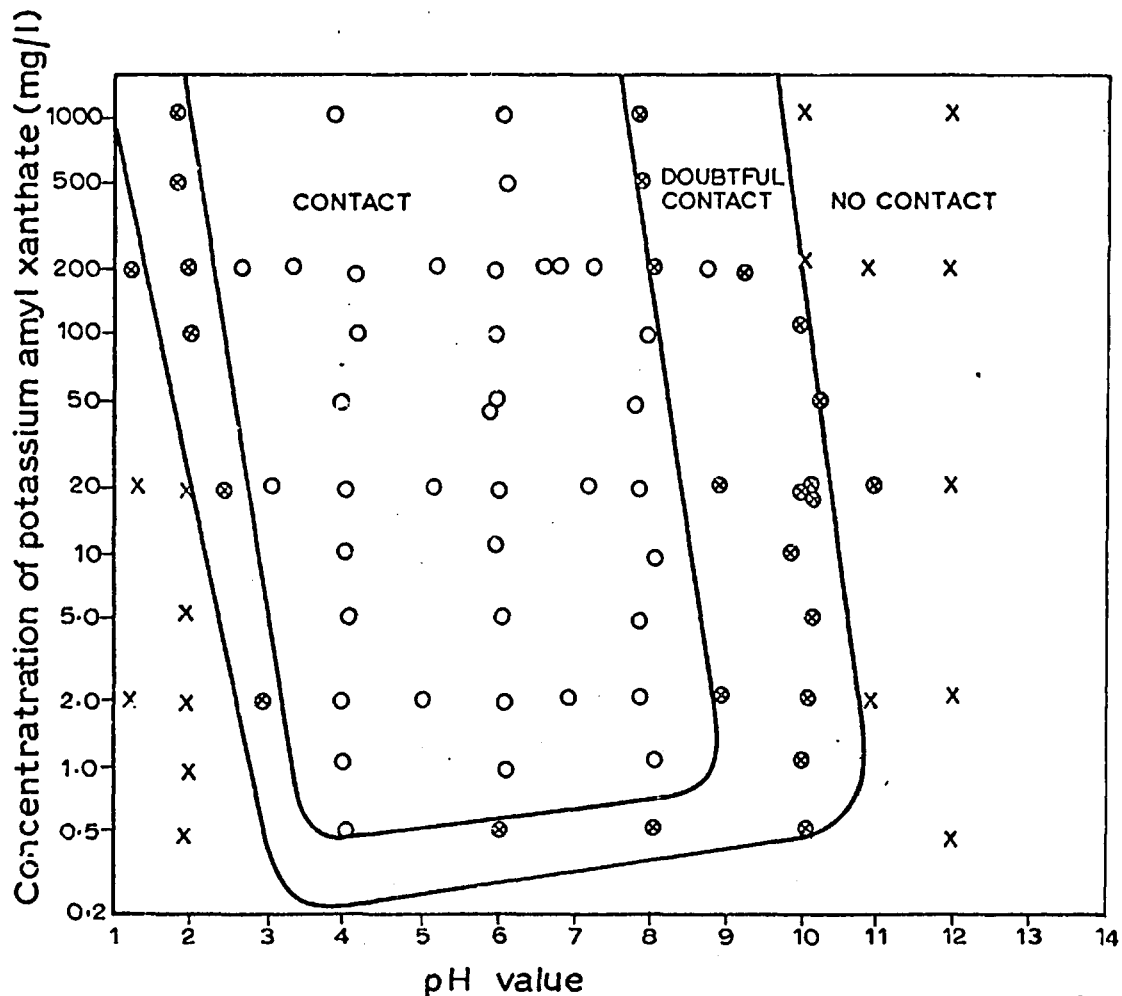


Fig. 13 Relationship between pH and the concentration of potassium amyl xanthate necessary to induce contact at bismuthinite surface.

- X - Solution in which contact is not possible (less than 30°)
- ⊗ - Solution in which contact is doubtful (31° - 50°)
- O - Solution in which contact is possible (more than 51°)

critical pH is about 8.0 and 3.0. However, it proved to be difficult to determine the possibility of flotation by the curve and the curve can only be considered as approximation.

3.3 The Result Using Potassium Hexyl Xanthate

Contact angle was also measured on the bismuthinite surface with potassium hexyl xanthate. The relationship between pH and advancing contact angle on bismuthinite surfaces in the presence of 2, 20 and 200 mg per litre of potassium hexyl xanthate is shown in Fig. 14. This figure shows that the contact angle varied greatly with pH, decreasing slowly from 74° to zero degree over the range of pH 4.0 to 12.0 but rapidly between pH 4.0 and 2.0. Very little variation was found in the shape of the curve over a concentration range 2 to 200 mg per litre.

Comparison between Fig. 9 (with KEX), Fig. 11 (with KAX) and Fig. 14 (with KHX) shows that the shape of the curves are similar. Maximum contact angle was obtained at pH 4.0 with a concentration of 20 mg per litre.

The correlation between the potassium hexyl xanthate concentration and the advancing contact angles on the various pH ranges is shown in Fig. 15. With increasing concentration of potassium hexyl xanthate, the contact angle increased over the pH range 4.0 to 6.0 but decreased very slowly above the pH range 8.0 and 10.0. Maximum contact angle was obtained at a concentration of 20 mg per litre over all the pH ranges except pH range 6.0 where it was found at 200 mg per litre.

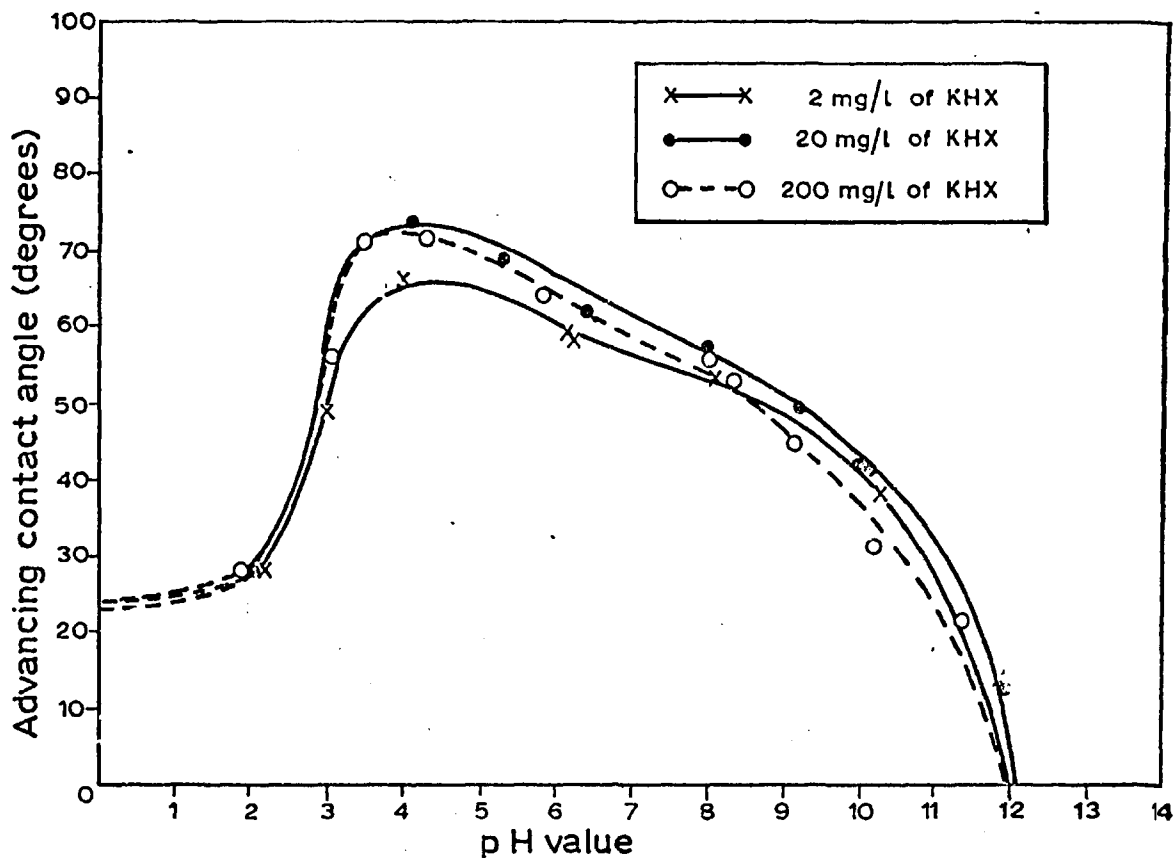


Fig.14 Advancing contact angle on bismuthinite as a function of pH in the presence of various concentrations of potassium hexyl xanthate

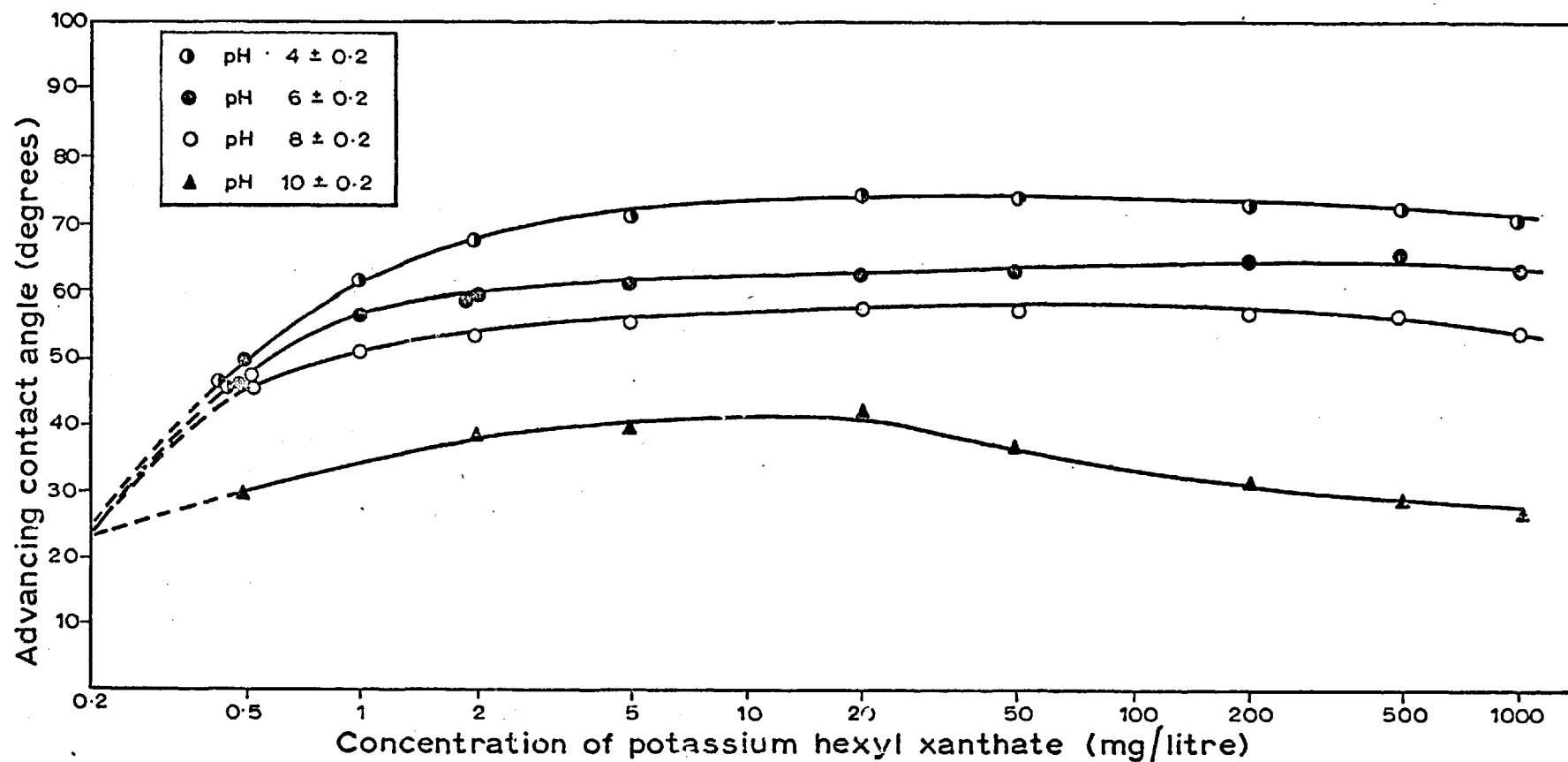
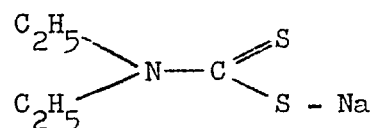


Fig. 15 Advancing contact angle on bismuthinite as a function of potassium hexyl xanthate concentration on the various pH ranges.

4. THE EFFECT OF DIETHYLDITHIOCARBAMATE

4.1 General Concept

Di-substituted dithiocarbamates possess the same polar group as xanthates and have been used experimentally as collectors for the flotation of sulphide minerals (55)(6)(51)(56)(53)(50). The structural formula of the sodium diethyldithiocarbamate, which has been used in this work, can be represented as



Their high cost precludes their use in industry (56). Consequently information relevant to the use of these substances in mineral processing is less abundant than that related to their use in medicine and rubber technology (56)(31)(50). Most recently (1968), Mellgren and Rao (55) have published a "Heat of adsorption and surface reactions of potassium diethyldithiocarbamate on galena" and reported that diethyldithiocarbamate reacts chemically with the oxidation products on galena.

Electrochemistry of the galena-diethyldithiocarbamate-oxygen flotation system was investigated by Yarar, Haydon and Kitchener (53). Their laboratory experiments have established that galena is not floated with sodium diethyldithiocarbamate until air is introduced to the pulp. They also determined the oxidation potential of diethyldithiocarbamate to be -68 mV relative to the hydrogen electrode. This (-68 mV) compares with -81 mV (54) for ethyl xanthate. Thus the

dithiocarbamate is more electropositive and, consequently, less readily oxidized than ethyl xanthate. Gaudin (31) has reported that the heavy-metal alkyl dithiocarbamates are rather more stable than the corresponding xanthates.

4.2 Results

Contact angles on the bismuthinite surface were measured with 'Analar' sodium diethyldithiocarbamate (abbreviated as DEDTC) produced by Hopkin and William Ltd. Fig. 16 shows the relationship between pH and advancing contact angle at bismuthinite surfaces in the presence of 2, 20 and 200 mg per litre of sodium diethyldithiocarbamate. The contact angle varied little with pH. With increasing pH contact angles increased very slowly over the range of pH 2.0 to 10.0 but decreased rapidly between pH 10.0 to 12.0. The concentration of diethyldithiocarbamate had no effect on the contact angle and there was no variation in the shape of the curve over a concentration range 2, 20 and 200 mg per litre (see Fig. 16).

The correlation between the advancing contact angles and the sodium diethyldithiocarbamate concentration on the various pH ranges is shown in Fig. 17. This result shows that there are three variations in the shape of the curve over the pH ranges 2.0 to 4.0, 6.0 to 10.0 and 12.0 respectively. With increasing concentration of sodium diethyldithiocarbamate contact angles did not vary except that contact angle increased very slowly at the pH 12.0. Within the system investigated, the low contact angles were obtained and

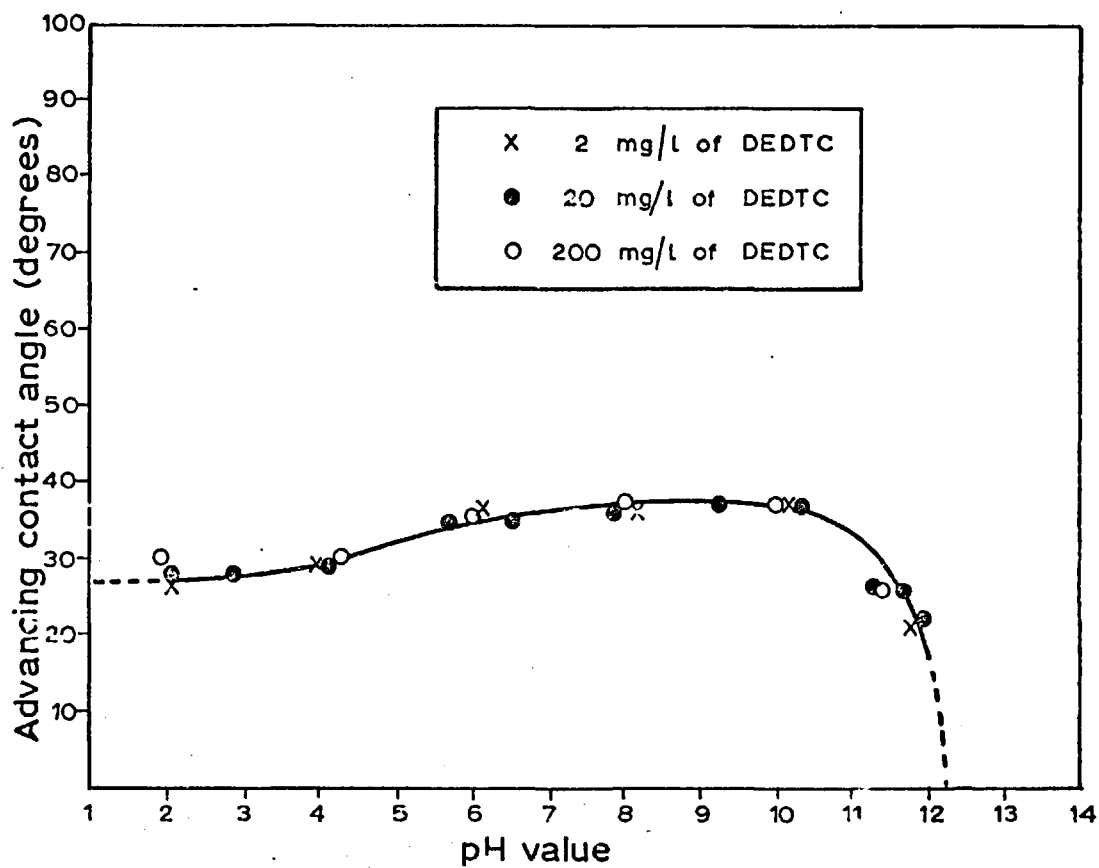


Fig. 16 Advancing contact angle on bismuthinite as a function of pH in the presence of various concentrations of sodium diethyldithiocarbamate. (DEDTC)

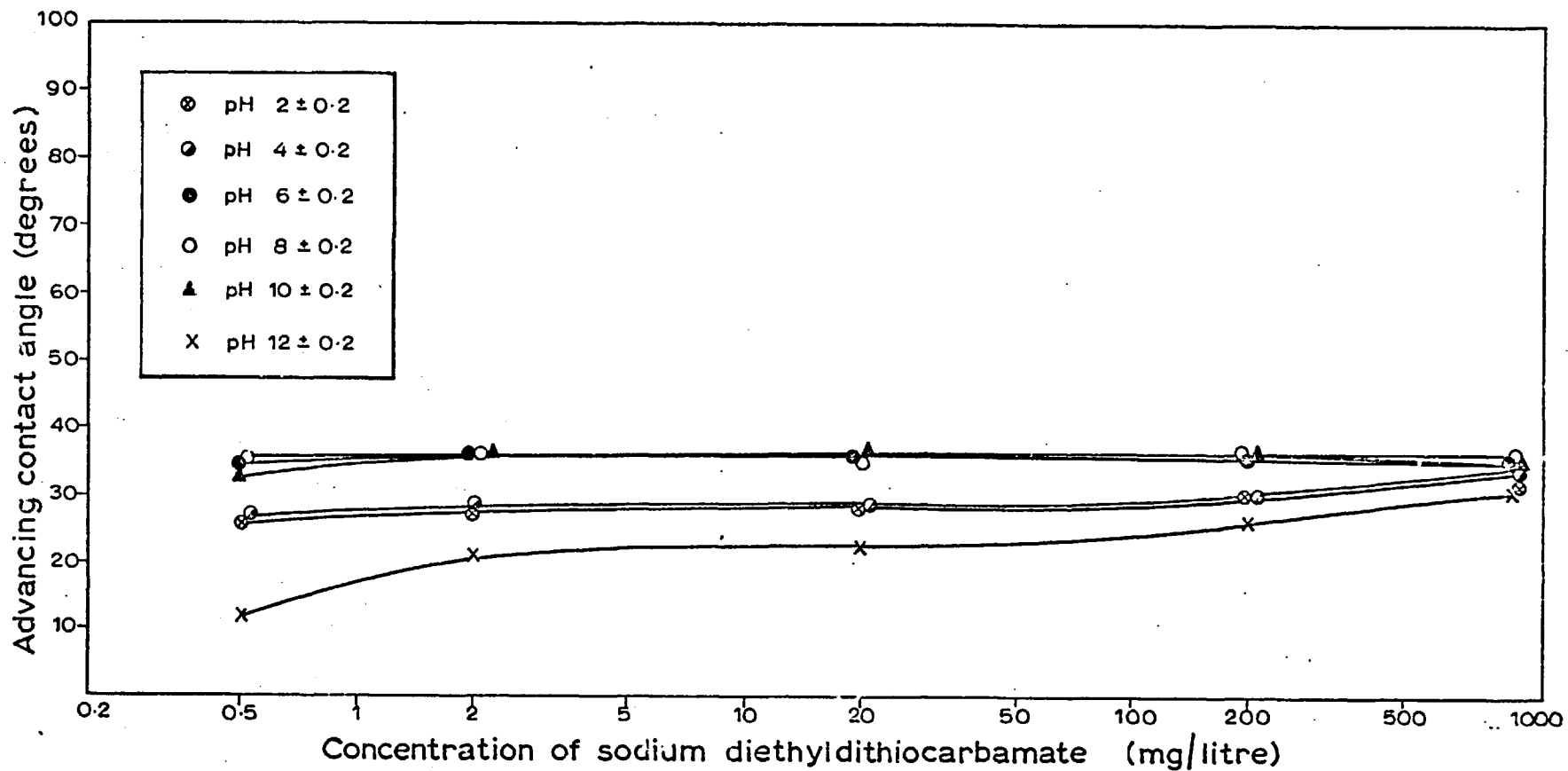


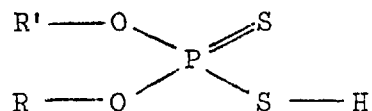
Fig.17 Advancing contact angle on bismuthinite as a function of sodium diethyldithiocarbamate concentration on the various pH ranges.

evidently diethyldithiocarbamate is not useful collector for
bismuthinite.

5. THE EFFECT OF DIETHYLDITHIOPHOSPHORIC ACID

5.1 General Concept

Alkyl and aryl dithiophosphoric acids and their salts are widely used as sulphide collectors under the proprietary name of Aerofloats (31). They are members of the group of flotation reagents collectively known as sulphydryl anionic collectors. The xanthate polar group can be changed by introducing a substituent into the centre of the group. The carbon atom can be replaced by other multivalent atoms. If it is replaced by pentavalent phosphorous, then a polar group of an aerofloat or dithiophosphate is obtained. The structural formula (31)(5)(6) of the dithiophosphates can be represented as:



where R and R' are either alkyl chains or aryl rings. In this work diethyldithiophosphoric acid has been used so that both the R and R' are ethyl chains.

In spite of the apparent wide use of these compounds very little indeed is known about their exact structure and chemical properties (33). Kakovsky (52) determined the oxidation potential of the diethyldithiophosphate ion to be +450 mV relative to the hydrogen electrode. This compares with -68 mV (53) for diethyldithiocarbamate and -81 mV (54) for ethyl xanthate. Thus the dithiophosphate ion is more electropositive and consequently less readily oxidized than

ions of the other two compounds.

5.2 Results

With diethyldithiophosphoric acid on the bismuthinite surface contact angle was similarly observed. The results for the effect of pH in the presence of 2, 20 and 200 mg per litre of diethyldithiophosphoric acid is given in Fig. 18. The pH of the diethyldithiophosphoric acid solution had very little effect on the contact angle, particularly for the range of pH 4.0 to 10.0. This figure shows that very doubtful and low contact angles were formed at any pH but there was a slight tendency for angle to increase with decreasing pH. Very little variation was also found in the shape of the curve over a concentration range 2 to 200 mg per litre.

Fig. 19 shows the correlation between the advancing contact angles and the diethyldithiophosphoric acid concentration on the various pH ranges. With increasing concentration of diethyldithiophosphoric acid contact angle decreased at any pH except pH 2.0 where it is found to increase slightly. Evidently diethyldithiophosphate is not a useful collector for bismuthinite.

5.3 Comparison of the Effects of Different Collectors

According to the system investigated, all the results revealed that the optimum concentration of collectors which produced the maximum contact angle is about 20 mg per litre except for diethyldithiophosphoric acid where it is found at the 1000 mg per litre of

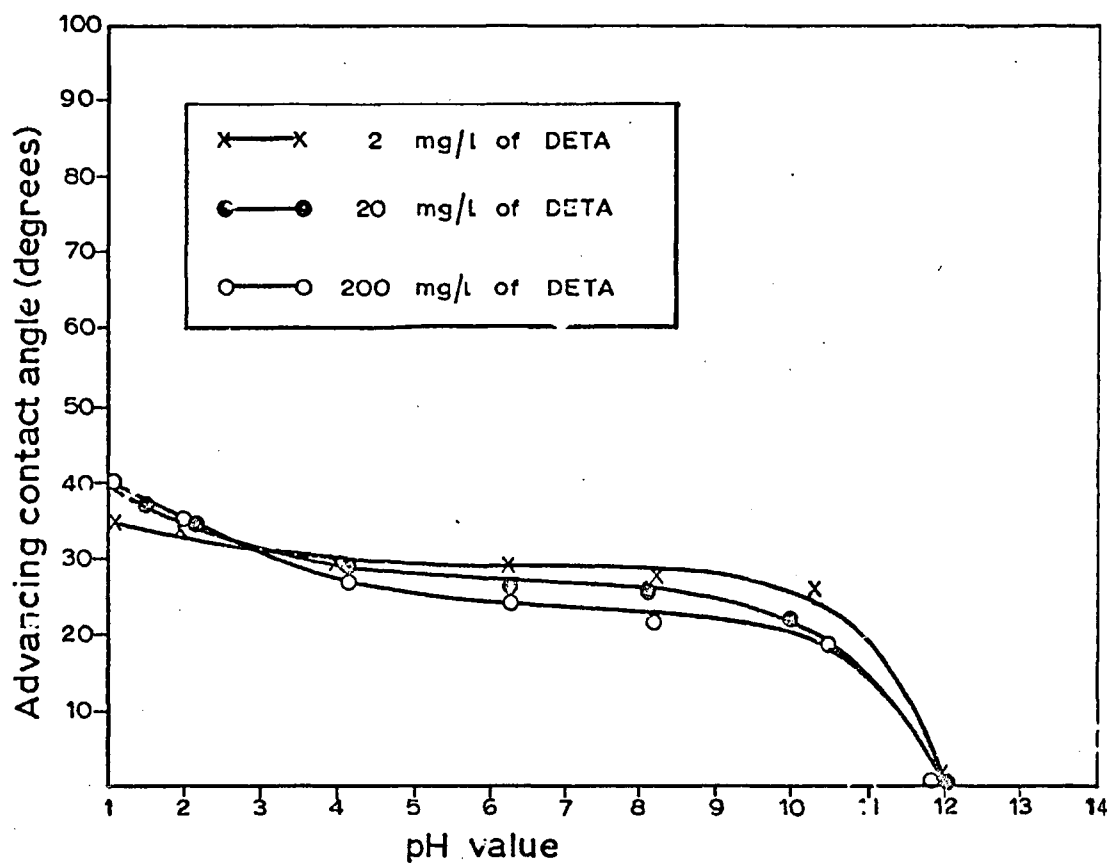


Fig.18 Advancing contact angle on bismuthinite as a function of pH in the presence of various concentrations of diethyldithiophosphoric acid. (DETA)

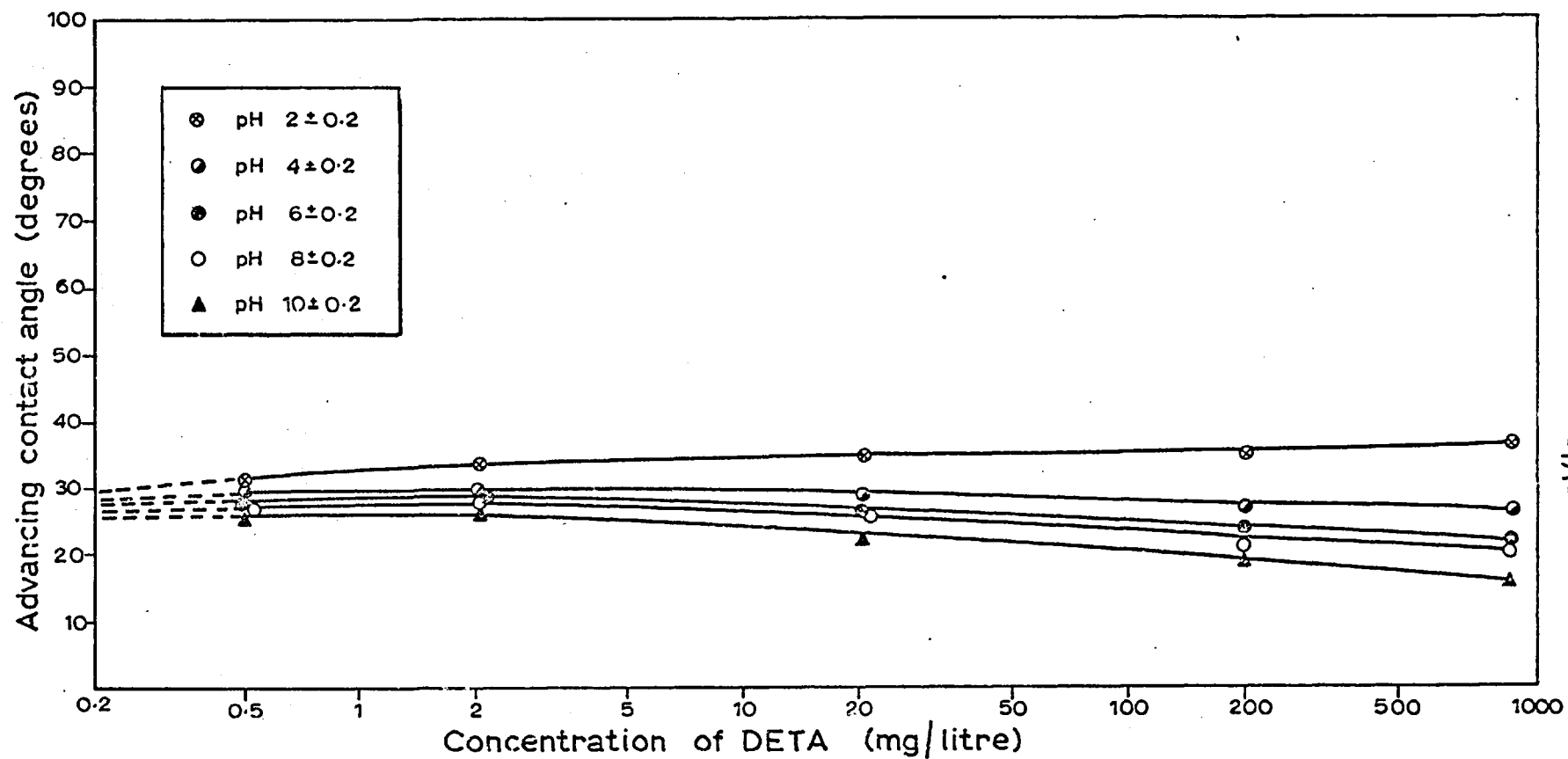


Fig. 19 Advancing contact angle on bismuthinite as a function of diethyldithiophosphoric acid concentration on the various pH ranges.

concentration and with very low pH (lower than 2.0).

In order to compare the effect of different collectors, the results for the effect of pH and advancing contact angle in the presence of 20 mg per litre of various collectors are plotted in Fig. 20. This figure shows that with the xanthates (KEX, KAX and KHX) the biggest contact angles were obtained at pH about 4.0 but at pH 10.0 and sufficiently low pH (about lower than 2.0) with diethyldithiocarbamate and diethyldithiophosphoric acid respectively.

The contact angle varied very much with the different collectors and pH. With increasing pH the contact angle decreased over the range pH 4.0 to 12.0 by any collectors except diethyldithiocarbamate where it is found to increase slightly over the range pH 2.0 to 10.0. Over the range pH 10.0 to 12.0 the contact angle by any collector decreases very rapidly and eventually becomes zero at the sufficiently high pH which is about 12.0. Below the pH 3.0 the contact angle never becomes zero by any collector.

The correlation between the advancing contact angles and the various collectors concentration on the pH 4.0 is shown in Fig. 21. In this figure the contact angle increased slowly with increasing concentration of collectors and 20 mg per litre of collector has been found as critical collector concentration.

It can be seen that ethyl xanthate, diethyldithiocarbamate and diethyldithiophosphoric acid cannot be applicable to bismuthinite flotation. Amyl and hexyl xanthate have been found suitable collectors.

but hexyl xanthate has not been widely used in practical flotation.
It's improvement over amyl xanthate is, indeed, small.

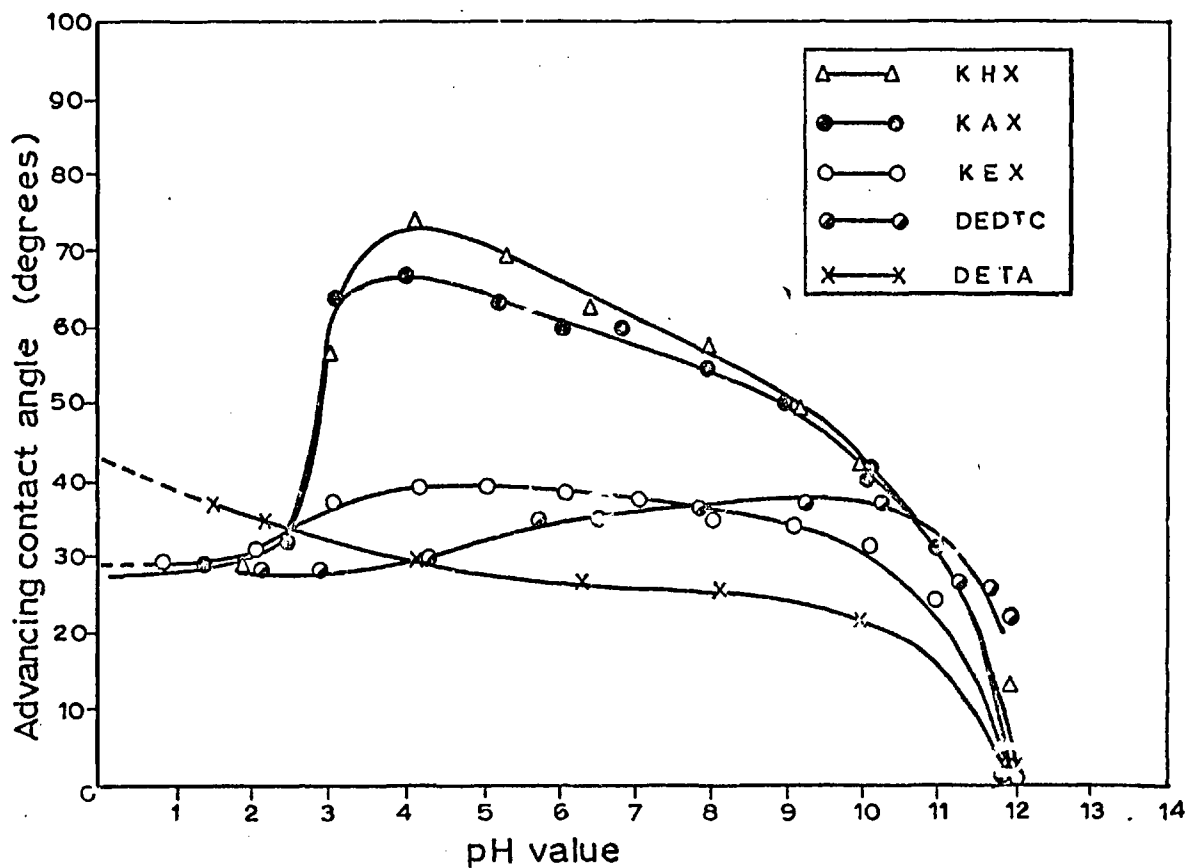


Fig. 20 Advancing contact angle on bismuthinite as a function of pH in the presence of 20 mg per litre of various collectors:-

KHX - Potassium hexyl xanthate

KAX - Potassium amyl xanthate

KEX - Potassium ethyl xanthate

DEDTC - Sodium diethyldithiocarbamate

DETA - Sodium diethyldithiophosphoric acid

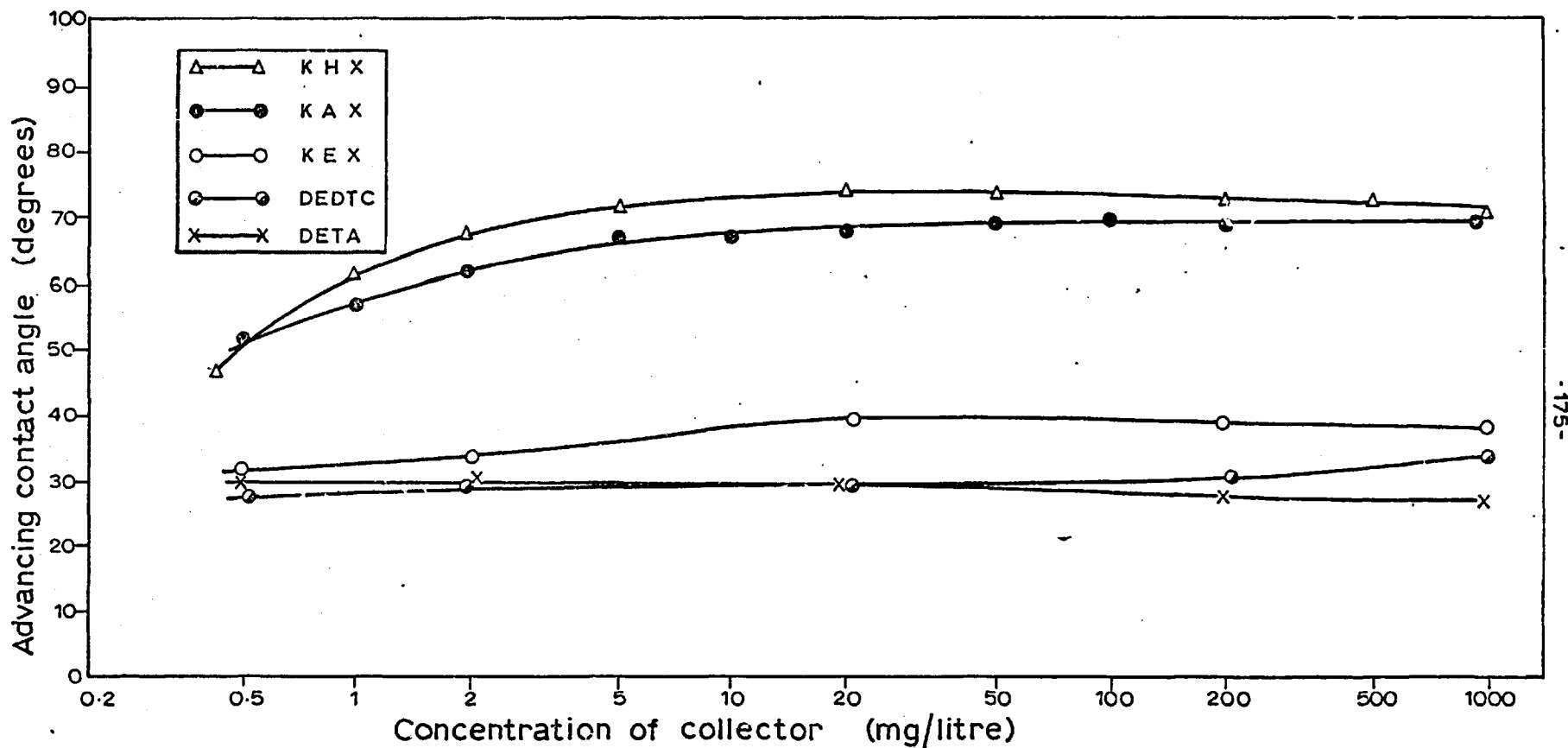


Fig. 21 Advancing contact angle on bismuthinite as a function of various collector concentrations on the pH 4 ± 0.2

6. THE EFFECT OF POTASSIUM DICHROMATE

6.1 General Concept

Depressants are reagents which adsorb on the surfaces of minerals and suppress adsorption of collectors and thus lower the flotation activity of minerals. The action of depressants is very complex and varied, and it is impossible to classify all cases of mineral depression in any one plan and system of depressant mineral reaction. The same reagents can act as a depressant for one mineral, an activator for another, or a pH regulator. For example, sodium sulphide is a depressant for galena, an activator for cerussite, $4(\text{PbCO}_3)$ and anglesite, $4(\text{PbSO}_4)$, but in all cases it is a pH regulator (5). The same flotation regulators can act either as an activator or a depressant, depending on the amount added to the pulp. Thus sodium silicate, which is a depressant for most minerals (including fluorite) becomes an activator for fluorite and apatite when used in very small amounts.

It has been known that the depressing action of regulating reagent is due mainly to the hydration of the surface of minerals by films of highly hydrated compounds (5). Such mechanism of depression is obtained with starch, tannin and often with sodium silicate. In a more complex system, the regulating reagents remove the adsorbed collector from the mineral surface. Sodium sulphide acts in this way, desorbing xanthates from the surface of sulphides. In the same way oleate ions are desorbed from the surface of calcium minerals by

sodium silicate, sodium carbonate and other reagents.

Gaudin (31) and Wark (6) showed in an exploratory way that many anions are depressants for the sulphide minerals. Since Lowry and Greenway (59) introduced that sodium dichromate was a depressant for lead mineral, chromate and dichromate have been used for surface closure of galena in lead-zinc differential flotation, in particular xanthate flotation (57)(38)(6)(23)(58)(5). But there is little detailed information about the ways in which these depressants function. However, the following experiments and discussion are limited to the action of potassium dichromate, which may be used as a depressant for galena in sulphide flotation.

6.2 Results

Potassium dichromate was selected as a depressant to ascertain its effect on bismuthinite in potassium amyl xanthate flotation.

'Analar' potassium dichromate was used in this work.

The test solutions were prepared (33)(63) by adding reagents in the following order: (1) 90 to 95 ml of double distilled water, (2) potassium dichromate (20 g per litre of soln.), (3) pH regulators (hydrochloric acid or sodium hydroxide solution) to adjust the solution approximately to the required pH value, (4) potassium amyl xanthate, (5) a small fraction of 1 ml of double distilled water, hydrochloric acid or sodium hydroxide for the final adjustment of pH value to standard volume (100 ml).

The effect of potassium dichromate on the bismuthinite surface

contact angle was observed. The relationship between pH and advancing contact angle at bismuthinite surface in the presence of 20 and 200 mg per litre of potassium dichromate with 20 mg per litre of potassium amyl xanthate is shown in Fig. 22. Curve 1 shows the contact angles which were obtained in the only presence of 20 mg per litre of potassium amyl xanthate (without $K_2Cr_2O_7$). Over the range pH 8 to 12, the potassium dichromate had very little effect on the contact angle which shows very narrow transition zone (7° to 15°). Below pH of 8, the effect of potassium dichromate very rapidly increased with decreasing pH. The contact angle in 20 mg per litre amyl xanthate solution, particularly at pH 3, was reduced from 64° to zero by 200 mg per litre of $K_2Cr_2O_7$.

The effect of concentration of potassium dichromate on the contact angle is shown in Fig. 23. It can be seen that the contact angle was unaffected when the pH was above 8.0 (curves of pH 8 and 10) with increasing potassium dichromate concentration. Below pH of 6.0, with increasing potassium dichromate concentration, the contact angle slowly decreased and eventually became zero at potassium dichromate concentration in excess of 200 mg per litre and pH 3.0. Within the system investigated, the results showed that potassium dichromate rapidly destroyed the contact angle with decreasing pH.

A critical pH curve showing the potassium dichromate concentration and pH necessary to induce contact at bismuthinite surface is illustrated in Fig. 24. Contact angle measurements were made at

progressively higher potassium dichromate concentrations until the concentration was high to prevent contact. Tests were repeated for various pH values and a critical curve was drawn to represent the transitional region between 0° — 30° , 31 — 50° and larger than 51° . This figure (Fig. 24) shows that the critical pH values to be about 4 and 8.

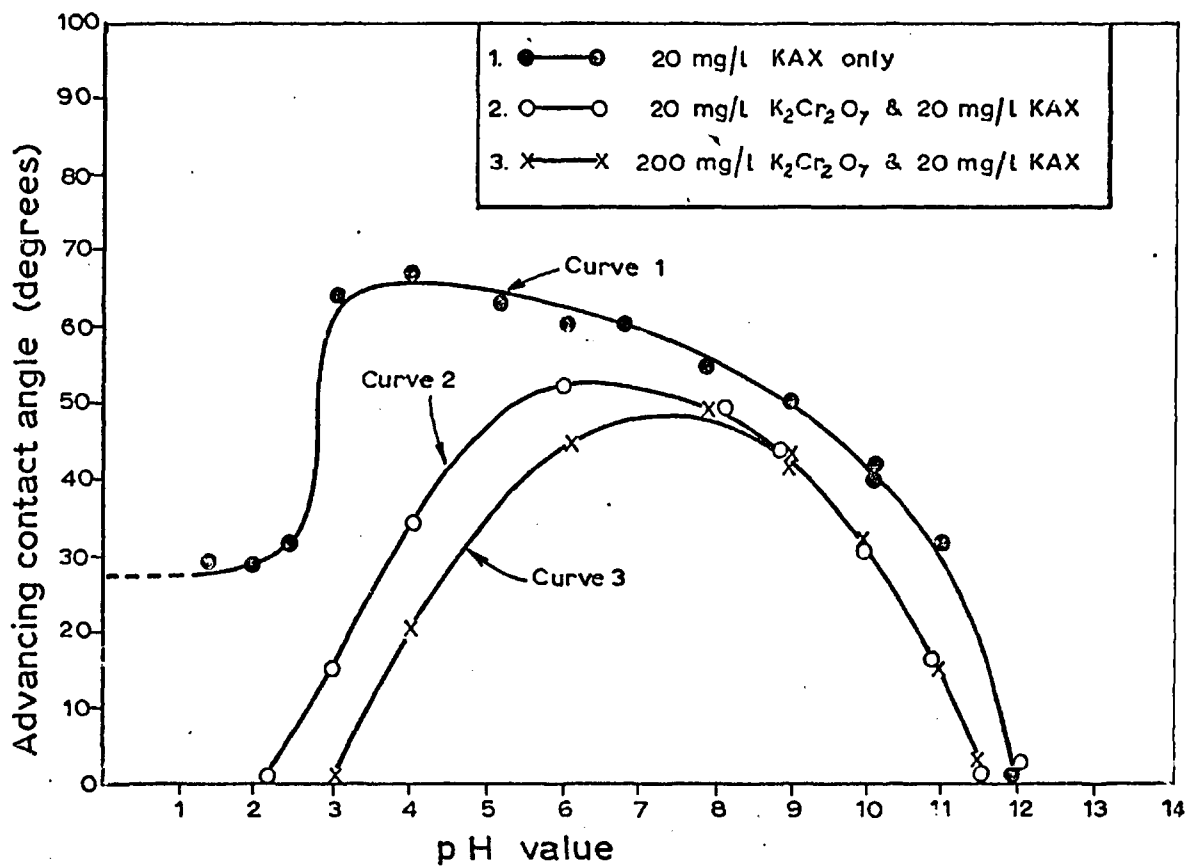


Fig.22 Advancing contact angle on bismuthinite as a function of pH in the presence of 20 mg per litre of KAX, and with 20 and 200 mg per litre of potassium dichromate concentration.

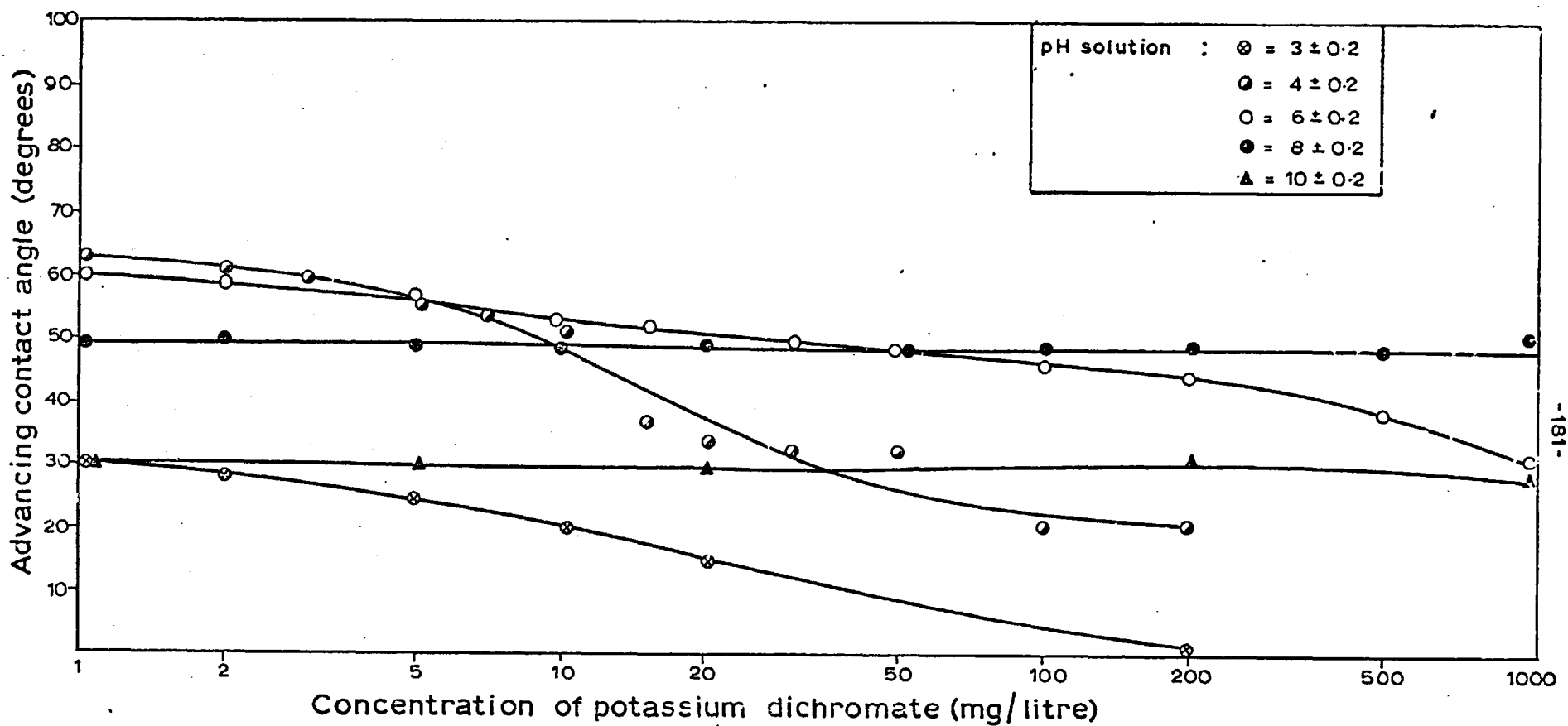


Fig. 23 The effect of potassium dichromate concentration on the contact angle with 20 mg per litre of potassium amyl xanthate.

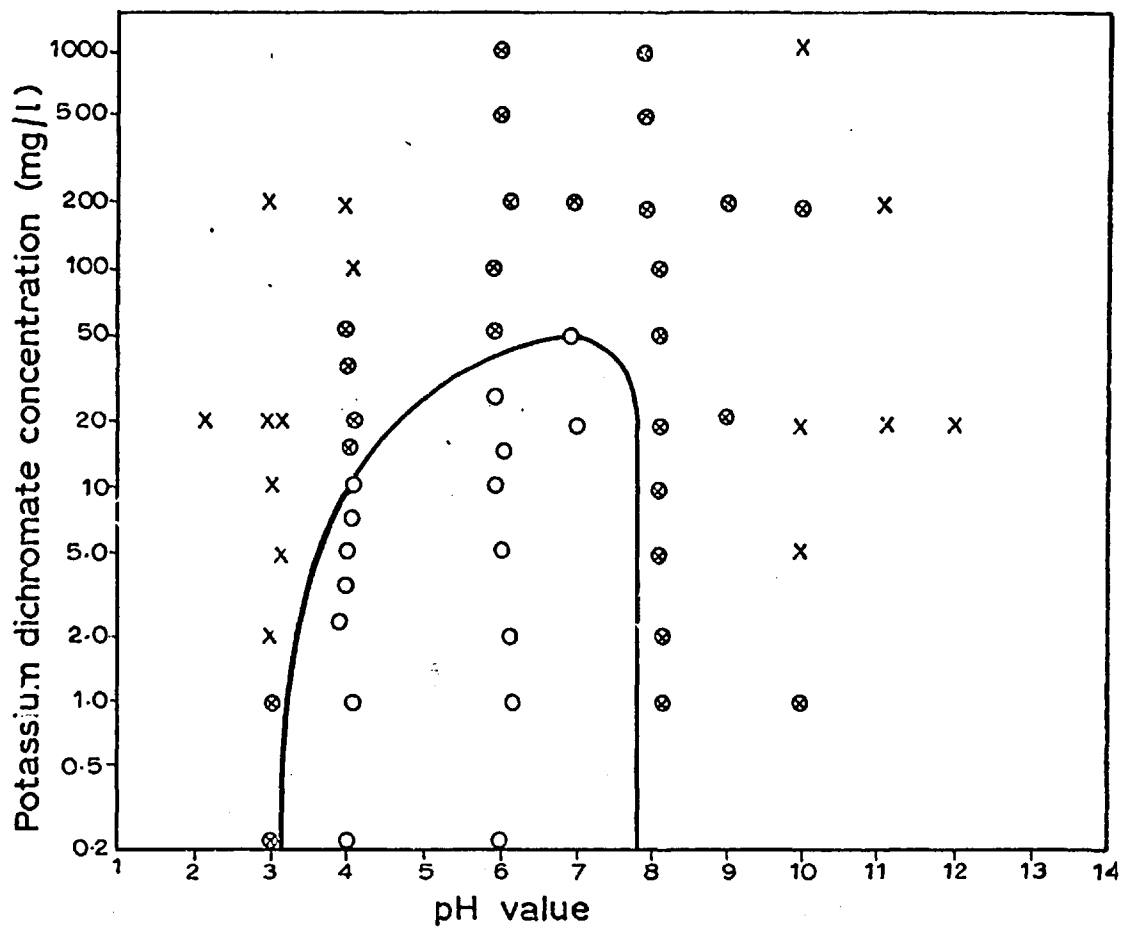


Fig. 24 Critical pH curve for bismuthinite in the presence of potassium dichromate.

- X = Solution in which contact is not possible (less than 30°)
- ⊗ = Solution in which contact is doubtful (31° - 50°)
- O = Solution in which contact is possible (larger than 51°)

7. DISCUSSION

7.1 Hydrophobicity and Crystal Structure of Bismuthinite

It has been known that flotation owes much to crystal chemistry and native flotability of minerals is related to crystal structure and surface properties. Gaudin (24) has put more emphasis on the types of bonds broken to form the surface, i.e., "Native floatability results when at least some fracture or cleavage surfaces form without rupture of interatomic bonds other than residual bonds. Natural lack of flotability results when all natural fracture or cleavage surfaces offer ionic bonds to the surrounding liquor in greater density than some threshold value."

Wrobel (73) classified all minerals into six groups depending upon the degree of surface polarity. The response to flotation is correlated to the non-polarity or polarity of surfaces. As a result of contact of solid particles with water, a physical or chemical interaction between the mineral surface and water-dipoles inevitably takes place. Also at the same time, a series of reactions may occur between air dissolved in water and the surfaces of mineral. All these reactions have a profound influence upon the subsequent flotability of minerals. The nature and extent of these reactions depend to a large measure upon the strength of free unsaturated bonds prevailing at the crystal surfaces.

The non-polar minerals (graphite, sulphur, molybdenite etc.) are composed of covalent molecules held by van der Waal's forces (73).

The surfaces of these minerals are characterised by intermolecular bonds which are rather weak. Therefore, the non-polar surfaces of minerals make less favourable conditions for attachment of the water dipoles and in consequence such faces are "water-repellent".

The minerals with polar surfaces are characteristic of the ionic or covalent and/or universal polar bonds. These types of bonds are strong and consequently they give rise to high free energy values at the polar mineral surfaces. As a result of the strong bonds, the polar surfaces react with water molecules which latter become strongly attached, particularly as water itself is a polar liquid.

The polar groups of minerals are further subdivided into various classes which differ in the magnitude of polarity (preference for water) i.e. weakly polar surface, medium-weakly polar, medium polar, strongly polar, very strongly polar surface (73). It is found, in the classification of polarities of minerals, that the degree of polarity increases from sulphide minerals through sulphates, to carbonates, halides, phosphates, etc., then oxides-hydroxides and finally silicates and quartz.

The structure of the bismuthinite is the same as stibnite as shown in Fig. 25, projected along the short c axis. All the atoms lie upon two reflection planes, at heights $c/4$ (plain) and $3c/4$ (shaded). Bismuthinite occurs in long striated prisms parallel to the c axis. The structure is composed of chains or rather bands of closely-linked

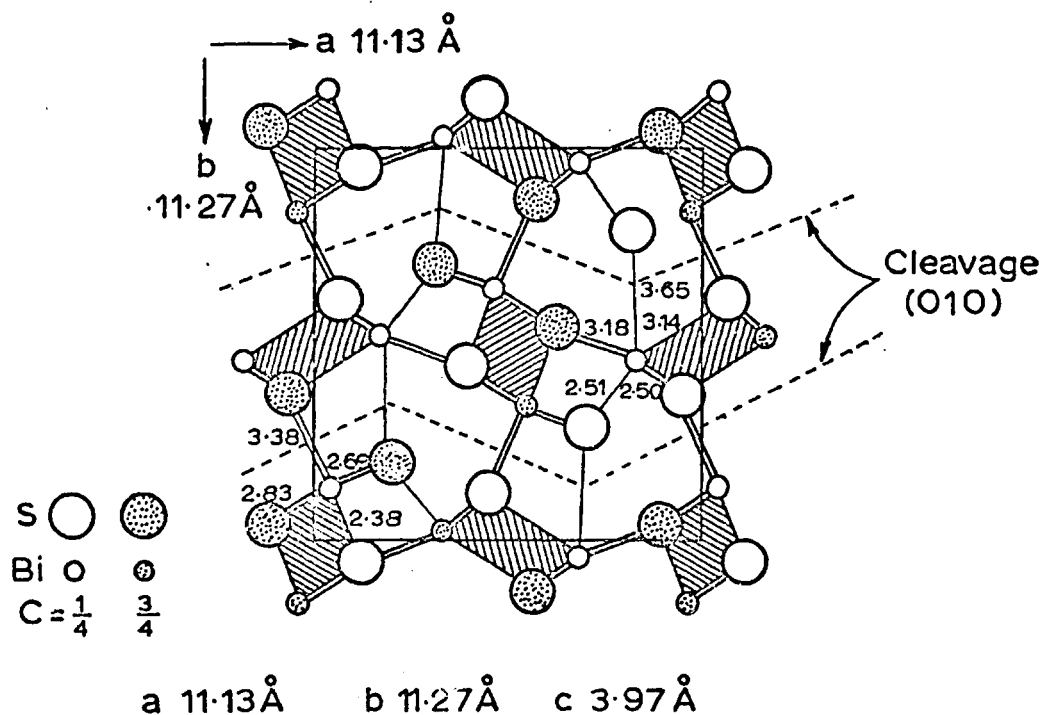


Fig. 25 The structure of bismuthinite (Bi_2S_3) projected on (001). All atoms lie in reflection planes at height 75 (shaded) or 25 (unshaded)

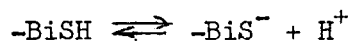
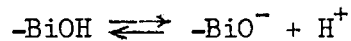
(From BRAGG, L. and CLARINGBULL, G.F., 1965)

Bi and S atoms which are parallel to c and are therefore seen end on in the projection. The distances Bi-S in the chains are about $2.5\text{\AA}$ and these are close covalent links. Any two atoms belonging to separate chains are at least $3.2\text{\AA}$ apart and these are weaker links. The structure is thus composed of clearly defined bands held to each other laterally by much weaker forces. The perfect cleavage of bismuthinite (010) is indicated as a zigzag line (Fig. 25) (74). Unlike the case of molybdenite, in which the exposed sulphur atoms, as well as internal molybdenum atoms are fully saturated with respect to any but van der Waal's type bonding, - cleavage of bismuthinite breaks bismuth-sulphur bonds. Although the potential adsorption sites made available are not strong - Wells describing them as "weak secondary Bi-S bonds" - they are not of van der Waal's type. However, as a result of these weak secondary Bi-S bonds, bismuthinite can be readily split along cleavage planes between the layers (weak secondary Bi-S bonds) and it becomes weakly polar surfaces and then an air bubble can attach itself weakly to the water-repellent cleavage plane surface.

The lower contact angle for this mineral may thus be related to the formation of a surface containing bismuth atoms in exposed positions, originally joined to sulphur atoms, which can co-ordinate with water molecules. The overall hydrophobicity would then depend upon the relative proportion of such hydrophilic sites as compared to exposed and covalently saturated sulphur atoms which by analogy

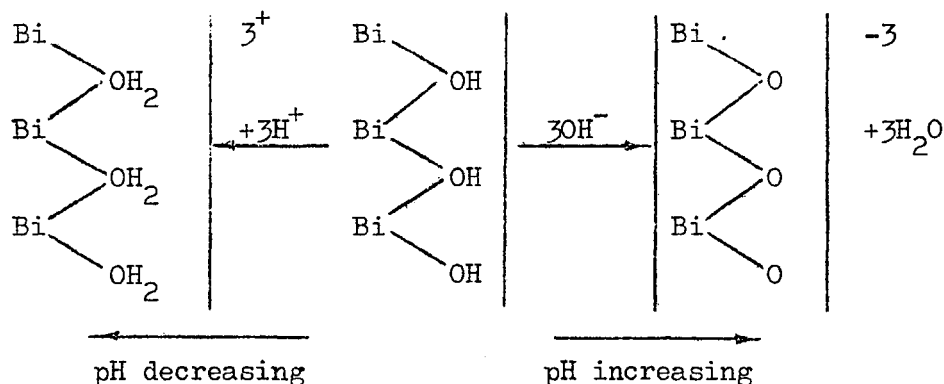
with molybdenite and native sulphur are hydrophobic sites.

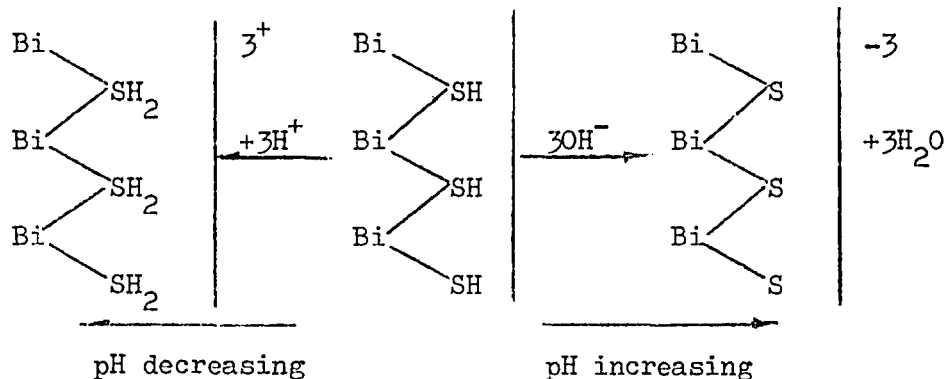
The loss of hydrophobic properties in alkaline solutions follows from the existence of weak Bi-S bonds in the mineral (see Fig. 7). The contact angle lost at $\text{pH} > 10.7$ is restored by immersion in a $\text{pH} < 8.5$ solution. This reversible hydrolytic scission of the Bi-S bond is postulated to take place in contact with alkaline solutions, resulting in formation of BiOH and BiSH sites in equilibrium with BiO^- and S^- sites as determined by the pH.



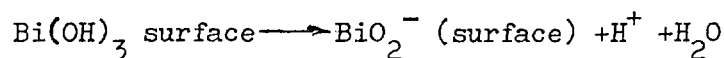
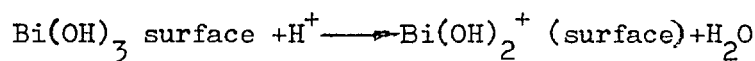
The proportion of these ionic sites determines the extent of contact angle lowering; their elimination by pH lowering restores the original hydrophobicity.

Alternatively the mechanism can be explained in the following way. The process by which the bismuthinite surface charge is established may be viewed either as an adsorption of H^+ or OH^- ions, or as a dissociation of surface sites. A schematic representation (4) of the reactions taking place would be





Alternatively the dissociation of the hydroxide surface to yield a positively or a negatively charged surface may be represented by the following reactions

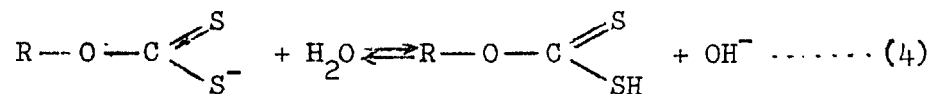


These reactions suggest that a positive surface is produced by the binding of a proton (H^+) to the hydroxide surface; this is of course equivalent to the removal, by dissociation, of one OH^- group from the surface. A negative surface is produced by the removal of a proton by dissociation (or the addition of an OH^- ion).

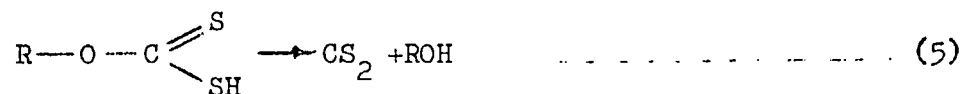
7.2 The Effects of Xanthate

Sodium and potassium xanthates are readily soluble in water. On dissolution xanthates dissociate, forming cations of alkali metals and xanthate anions. The latter are sufficiently stable in water but under some conditions as discussed below, they can hydrolyse (5).

Hydrolysis leads to the formation of xanthic acid:



Xanthic acids are very unstable compounds and rapidly decompose into carbon disulphide and alcohol (23)(5):



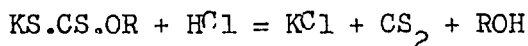
Decomposition of xanthic acid occurs much faster than formation due to the hydrolysis (5).

Experiments (5) on the effects of concentration and temperature on the decomposition of xanthate in an acid medium, have shown that the higher the concentration and temperature of the solution the more intense the decomposition of xanthate. An increase in temperature leads to an increase in the rate of decomposition of xanthate. However, it should not be thought that xanthate will float minerals best at temperatures approaching that of frozen water.

The data of Figs. 9, 11 and 14 summarise the contact angle tests on bismuthinite in the presence of various concentrations of xanthates as a function of pH. The outstanding fact shown by these results is the important effect of pH upon the contact angle. These results indicate that the contact angle varies with pH, decreasing slowly over the range pH 4.0 to 12.0 but rapidly between pH 4.0 and 3.0. Acid rapidly destroys the contact in xanthate solutions, provided that the pH value is approaching unity. Rapid decomposition of the xanthates in acid solutions explains the difficulty of xanthate flotation (5). As can be expected from the hydrolysis equation (equations 4 and 5), the stability of aqueous solution of xanthate is

strongly affected by the pH of the medium. Lowering of pH, i.e. decreasing the concentration of OH^- ions, favours the reaction from left to right, that is, rapid formation of xanthic acid or decomposition of xanthates in aqueous solutions.

It is also known that acids decompose the xanthates, the reaction for the xanthate being



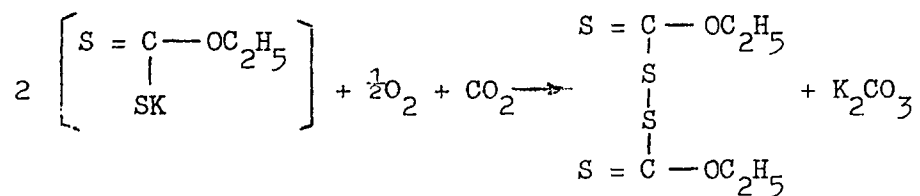
in solution. No xanthate can be detected by the copper sulphate tests, and subsequent addition of alkali is unable to regenerate the xanthate (23).

In this work, a xanthate solution of pH about 11.0 was made as it has been known that the decomposition of xanthates in an alkaline medium is very slow and the xanthates are sufficiently stable in an alkaline medium (5). Alkalis are not so effective in preventing contact with air in xanthates solutions. But Figs. 9, 11 and 14 indicate that bismuthinite has zero contact angle in any concentration of xanthates when pH is 11.7 to 12.0. Wark and Cox (23) found a similar critical pH value of 11.8 using a concentration of 25 mg potassium amyl xanthate per litre on a galena surface.

It has been shown that the xanthates are most active in weakly alkaline pulp of pH 7 to 12 (5). Examples are known where an increase in alkalinity leads to a decrease in the flotability, and even to complete suppression of minerals like pyrite and galena (5) (1)(25)(6)(51)(23). However, decomposition of collector is not

responsible for this behaviour. Active adsorption of OH^- ions on bismuthinite may prevent adsorption of xanthate anions on its surface, in other words this is ascribed to the competition of hydroxyl ions with the collector anions for a suitable site on the bismuthinite surface.

It is probable that the decomposition is due to the combined action of oxygen and carbon dioxide, dioxanthogen being formed according to the equation (5)(6):



During decomposition of xanthate, potassium thiosulphates and potassium sulphides can be formed; these may act as depressants in flotation (5)(6).

The effects of concentration of xanthate are shown in Figs. 10, 12 and 15. These results show that with increasing concentration of xanthates, the contact angles were found to increase to a maximum at a concentration of 20 mg per litre, but the curves either nearly straighten out or decrease slowly above a concentration of 20 mg per litre, particularly in high alkali solutions. In other words, these results indicate that an excessively high addition of xanthate lowers the recovery of bismuthinite in the bismuthinite flotation.

This is very often attributed to the reverse orientation of the second layer of adsorbed molecules, but such an explanation is

not feasible (5). The orientation of heteropolar molecules on adsorption at the solid/liquid interface depends on the concentration and length of the non-polar radical and particularly on the nature of its polar group. The term 'hydrophobic' (that is, antagonistic towards water) describes the non-polar radical in a purely relative way. The non-polar radical does not repulse the molecules of water but only attracts them weakly. In fact they hardly interact with water. Non-polar radicals attract one another more strongly the longer they are, and the closer they are together (5). With very low concentration of molecules in the adsorbed layer, the non-polar radicals can be oriented in different manners. Two-dimensional mono-molecular films which have no inter-molecular interactions are termed 'gaseous films' (Fig. 26-a). With an increased concentration of molecules the non-polar radicals begin to attract each other more and more, and the increased density of packing leads to molecular orientation at a definite angle to the solid surface, forming on it a 'liquid two-dimensional film' (Fig. 26-b).



Fig. 26 'Two-dimensional' films : (a) gaseous; (b) liquid

There is much data confirming that collectors form multi-layer coatings on minerals. The main indicator for the presence of multi-layer coatings of adsorbed collectors is a calculation of the quantity adsorbed on the unit area of the surface of the mineral. Such calculations are not exact because of the non-uniform distribution of reagents on the mineral surface. However, the error involved can only give the lower limit of the resulting multi-layer adsorption. Generally, it is considered that the collector is uniformly distributed over the surface. Even in this case, calculations have shown that the quantity of collector adsorbed on the mineral sometimes exceeds many times the amount necessary for the formation of a mono-layer. If we accept that the actual area covered by the collector is considerably less than that calculated, then the thickness of the multi-layer film will be even greater (5).

The structure of these multi-layers is important for all reagents. The first suggestion was that an ideal mono-layer was formed with a second layer of inverted molecules adsorbing on the first. After formation of the mono-layer an increased concentration of the reagent causes 'the formation of a second adsorbed layer with a reverse orientation of the hydrophobic film' (5). Gaudin (31) gives a schematic representation of the formation of the second layer with an inverse orientation of the molecules.

In the formation of the second molecular layer, the molecules should be oriented with polar groups towards the water. Since these

groups are strongly hydrated, the formation of the second adsorbed layer should hydrate the surface and depress flotation, even with small additions of collector. However, this is not observed in flotation (5). Kakovsky et al (76) have concluded that depression of flotation with large additions of collector (observed very rarely), is not the result of the formation of a second layer of adsorbed molecules. Consequently, molecular collector aggregates must be formed in the surface layer without reversal of their molecular orientations.

The results of comparisons between the effects of different xanthates (Figs. 9-15 and 20-21) indicates that the length of the hydrocarbon chain has a great influence on the collecting properties of the potassium ethyl, amyl and hexyl xanthates in the bismuthinite flotation. It is known that with the xanthates having different hydrocarbon chain lengths, the contact angle and the collecting ability of the reagent increases with the length of the carbon chain (5)(23)(6)(57). Methyl xanthate, for instance, is a very weak collector and is not used in practical flotation; ethyl xanthate is more active and butyl and amyl xanthates are considerably more active than ethyl.

7.3 The Effect of Diethyldithiocarbamate

It has been reported that diethyldithiocarbamate is used extensively in analytical chemistry and has chemical properties similar to those of xanthate (55).

It was found (in Fig. 16) that very low contact angle was formed with diethyldithiocarbamate as with ethyl xanthate but maximum contact angle was obtained in weak alkali solutions, at pH 9-10, while it was obtained in acid solutions (pH 4.0) with ethyl xanthate. Also, no effect of concentration of diethyldithiocarbamate on the contact angle was found (Fig. 17). It may be postulated that contact angle lowering in acid solution is due to the decomposition of the diethyldithiocarbamate in acid solutions.

Experiments by Yarar (66), on the stability of diethyldithiocarbamate in the presence of air at pH 9.2, indicated that no change in the optical density was observed, which suggests that the solution is stable for at least 7 days under these conditions. The forming of the maximum contact angle at pH 9-10, in Fig. 16, is in agreement with the result of stable diethyldithiocarbamate at pH 9.2 as Yarar states. It is reported (66) that a polished galena crystal does not give a visible contact angle in a solution of diethyldithiocarbamate. It would mean that diethyldithiocarbamate cannot be used as a flotation agent for galena, but Sutherland and Wark (6) determined that the contact angle of various minerals with diethyldithiocarbamate is about 59° ; galena 59° , pyrite 58° , chalcopyrite 59° and bonite 62° .

An experiment by Wark and Cox (51) has shown the relationship between the concentration of diethyldithiocarbamate and the critical pH value for sphalerite, which responds only to a high concentration

of the collector. Owing to the rapid decomposition of the dithiocarbamate in acid solutions, the determination of the curve had to be discontinued at pH 6.5 (51).

Sutherland and Wark (6) reported bubble pick-up up to a pH of 10.5 on unactivated sphalerite, and up to a pH of 12.8 on pyrite and chalcopyrite with 42.3 mg per litre of potassium di-n-amyl dithiocarbamate. But Steininger (65) has shown that practically no sphalerite flotation was obtained at any pH in the Hallimond tube with ethylxanthate, amylxanthate, diethyldithiocarbamate and diethyldithiophosphate. However, low contact angles on the bismuthinite would suggest that diethyldithiocarbamate is not a collector for bismuthinite.

7.4 The Effect of Diethyldithiophosphoric Acid

Although aerofloats are widely used as collectors of sulphide minerals, relatively little is known in detail of the collection mechanism of dithiophosphates on sulphide minerals. It is generally assumed that the mechanism is similar to that involving xanthates (31).

The comparison of the results shown in Fig. 18 (with DETA) and Fig. 9 (with KEX) shows similar contact angles with both, but it indicates a lower collecting property for dithiophosphoric acid than for ethyl xanthate. This contact angle measurement confirms the lower collecting properties of diethyldithiophosphoric acid in comparison with that of ethyl xanthate, and it is in agreement with the statement by Kakovsky (5) which says that sodium aerofloat has a

lower collecting property than that of ethyl xanthate.

The effects of dithiophosphoric acid represented in Figs. 18 and 19 indicate a slight tendency for the contact angle to increase with decreasing pH, forming very low contact angles. This slight tendency for the contact angle to increase in acid solution corresponds to the stable solution of dithiophosphoric acid in the acid solution. It is reported (36) that aerofloat solutions were found to be stable for more than three weeks at pH values between 2.5 and 3.8, but solutions outside this pH range were found to be stable for only five to seven days.

Wark and Cox (51) have found that the heavy metal dithiophosphates are more soluble than the corresponding xanthates or dithiocarbamates and that, as collectors, they of the three, are the most easily affected by depressants. Aerofloats are not good collectors for pyrite and are often used where depression of the latter is desirable (57). Since the iron sulphides are the most easily depressed, the aerofloats are useful for differential work involving iron depression. On the other hand, in pulp of low alkalinity or slightly acid, they are effective to float iron sulphides (57).

It has also been shown (51) that galena and pyrite do not respond to 25 mg per litre of the collector in neutral or slightly acid solutions. By the captive bubble tests of Wark and Cox (6), it has been confirmed that the sodium diethyldithiophosphate is not a collector for galena except in solutions of pH value less than 3, but

that the use of copper sulphate in conjunction with the collector results in excellent recovery in neutral or alkaline circuits. However, it is found that diethyldithiophosphate is not a useful collector for bismuthinite.

7.5 The Effect of Potassium Dichromate

Generally it has been assumed that depressants change the surface of the mineral in such a way that the collector cannot be adsorbed or the depressant allows the mineral to desorb the collector from the surface. In the first case, the change has frequently been attributed to the formation, by double decomposition, of an insoluble surface coating (6). Thus Gaudin and his co-workers (60) considered that chromate depresses galena because it forms an insoluble coating of lead chromate, which will not react with ethyl xanthate.

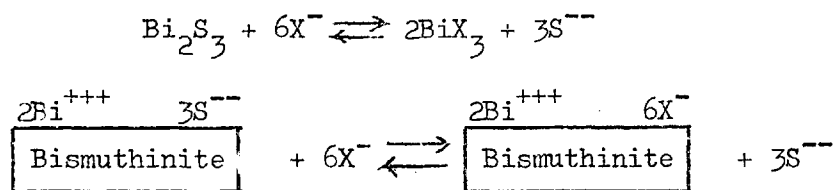
To explain the effect of dichromate depressant in the bismuthinite-xanthate system, one must consider how bismuth chromate compound will be formed. Although normal bismuth chromate, $\text{Bi}_2(\text{CrO}_4)_3$, has not been prepared, Preis and Rayman (69) obtained what they regarded as potassium bismuth chromate, $4\text{K}_2\text{CrO}_4 \cdot \text{Bi}_2(\text{CrO}_4)_3$. It has been known that there is a marked tendency to form basic bismuth salts, usually formulated as containing the univalent bismuthyl radical $-\text{Bi} = \text{O}$ (68).

Bismuth chromate, $(\text{BiO})_2\text{CrO}_4$, was formed by treating a solution of bismuth nitrate with an excess of potassium chromate or dichromate (69). The product has been reported to consist of

$\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ that is, bismuthyl dichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$ or bismuth hydroxy-chromate, $\text{Bi}(\text{OH})\text{CrO}_4$ (67)(68).

The results of the advancing contact angle measurements on the bismuthinite, presented in Fig. 22, indicate that dichromate is an effective depressant for the bismuthinite-xanthate system in acid solutions. The mechanism of bismuthinite depression by dichromate is suggested to be due to the easy oxidizability of bismuthinite and the formation of a hydrophilic film of $(\text{BiO})_2\text{Cr}_2\text{O}_7$ on its surface. Recently (1969) Sologub and Mitrofanov (58) reported that the selective depression of galena by $\text{K}_2\text{Cr}_2\text{O}_7$ is attributable to the easy oxidizability of galena and formation of hydrophilic film of PbCrO_4 on its surface.

The mechanism of bismuthinite flotation suggests that the bismuthinite (Bi_2S_3) system in xanthate solution enters into an ion exchange with aqueous solution of xanthate acquiring a monolayer of xanthate anions. The evidence (31) available in case of galena surface suggests that the ion exchange on the bismuthinite surface should take place according to the following equations:

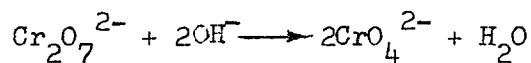
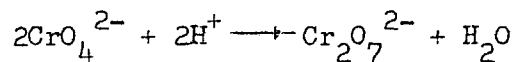


But when $\text{K}_2\text{Cr}_2\text{O}_7$ is added with acid to the bismuthinite-xanthate system, the depression of bismuthinite observed may be due to the following reasons.

The bismuth xanthate (2BiX_3) formed on the surface of the bismuthinite might have reacted with the $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of acid forming bismuthyldichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$, which forms a thin film over the bismuthinite surface. The xanthate ion is displaced from the surface of the bismuthinite and hence, the contact angle decreases and may become zero.

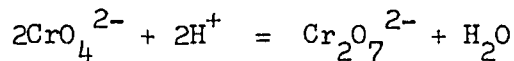
Secondly, the bismuthinite surface, when it comes in contact with $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of acid, might undergo oxidation by the strong oxidizing agent $\text{K}_2\text{Cr}_2\text{O}_7$ forming a film (coating) of Bi_2O_3 . This bismuth oxide thus may further undergo change to form hydrophilic film of bismuthyl dichromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$, which will not react with xanthates and will definitely have some depressing effect.

In Figs. 22-24 it is found that bismuthinite was depressed by $\text{K}_2\text{Cr}_2\text{O}_7$ more effectively in acid solution than alkaline solution. This increase in depressing action is in agreement with the result of more powerful oxidizing action of dichromate in acid solution than alkaline solution. In acid solution chromates become dichromates and in alkaline solution the reverse change takes place and dichromates become chromates (70)(71).

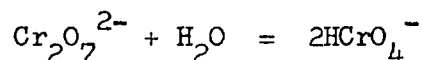


In basic solution it exists as the yellow tetrahedral chromate ion, CrO_4^{2-} . As the pH is lowered, solutions of chromate ions turn orange

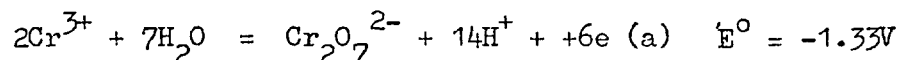
because of the formation of dichromate ions according to the equilibrium:



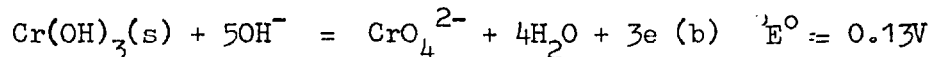
This equilibrium is quite labile and, on adding cations which form insoluble chromates in moderately acid solutions, the chromates can be immediately precipitated. There is an additional equilibrium:



Acid solutions of dichromate are powerful oxidizing agents.



The chromate ion in basic solution is much less oxidizing however (70)



Some additional information is available on the action of soluble chromate or dichromate on the flotation properties of minerals though little experimental detail is given and no explanations are suggested for the effects observed. Wark and Cox (23) reported that bubble tests show that potassium dichromate is an effective depressant both for galena and activated sphalerite. The depression of galena is generally attributed to the formation of an insoluble chromate film on its surface but this explanation is inadequate, for it has since been shown that no contact on the crocoite (PbCrO_4) was possible in 25 mg per litre KEX solution but at 2 g per litre KEX the angle of contact was 63° (23). They also

reported that prolonged treatment of sphalerite (30 mins.) with 100 mg per litre of dichromate, followed by 30 mins. in 10 mg per litre copper sulphate solution resulted in failure to collector-coat with ethyl xanthate. It is usually assumed that sphalerite will not be influenced because of the relatively high solubility of zinc chromate and zinc dichromate (23).

Gaudin and his collaborators (60) reported depression of pyrite with relatively low concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ (about 0.3 lb per ton), with potassium ethyl xanthate collector, while at the same time K_2CrO_4 had no effect at concentrations up to 2 lb per ton of solid. Since the dichromate of iron is soluble, this should not be a surface closure. But the dichromate is a strong oxidizer, while ferric xanthate is particularly susceptible to decomposition by oxidation; the chromate, on the other hand, is much less powerful in its oxidizing effect. The postulate that oxidation is responsible for the dichromate effect is confirmed by the fact that potassium permanganate has an almost equal depressing effect (60).

However, Rogers (67) states that dichromate and permanganate are strong oxidizing reagents changing xanthates to dixanthogen which, although also a collector, is apparently not so effective. Tolun and Kitchener (54) have shown by an electrochemical technique that a mixed lead xanthate-dixanthogen film is necessary as a flotation surface on galena.

In the experiment by Mitrofanov and Koushnikova (38), the

possibility of selectivity control with tridecylamine as a collector for heavy metal sulphide minerals (chalcopyrite, sphalerite, galena and pyrite), was demonstrated by adsorption studies. The flotation tests indicate that galena and chalcopyrite can be separated from sphalerite with this collector using of potassium dichromate and adjusting pH. A study by Podnek (61), on flotation of galena with potassium ethylxanthate using sodium sulphide and potassium dichromate as depressants, shows that the depressing action of sodium sulphide is due to a decreased sorption of xanthate (sorption was determined by radiometric methods). In the case of increased addition of potassium chromate, flotation was depressed despite the fact that the adsorption of xanthate on galena remained unchanged. The hypothesis of Eigeles (62) is obviously confirmed; depression takes place on adsorption of regulators on those portions of surface not covered by collector. In this case the overall hydration of the surface can increase.

SUMMARY OF CONCLUSIONS

The effects of potassium ethyl, amyl and hexyl xanthate, diethyldithiocarbamate and diethyldithiophosphoric acid, and the influence of potassium dichromate with amyl xanthate on the contact angle at a bismuthinite surface have been investigated.

The following information was obtained as a result of this investigation:

- (1) Two polishing methods were considered to prepare clean surfaces of bismuthinite and to standardize the polishing technique. One (method 1) was wet alumina polishing, and another one (method 2) was rubbing of the specimen on "Selvyt" cloth after wet alumina polishing. Using polishing method 1, no contact angle was formed at any pH, even with potassium ethyl xanthate. When the bismuthinite surface was prepared by polishing method 2, the contact angles on this surface were found to be about 25° below pH 9. The procedure of polishing method 2 had to be adopted in order to obtain reproducible results and it was decided that polishing method 2 gave the more reliable results.
- (2) With bismuthinite, alkalis at pH values about 9-10.7 introduce considerable difficulty in effecting contact.
- (3) The behaviour of bismuthinite in water is related to its crystal structure, which permits reversible development of ionic sites in alkaline solutions (pH 10.7) with complete loss of contact angle.
- (4) About 12° - 20° differences are found between advancing and

receding contact angles, but it was found that there is very little variation in the shape of the curve over the concentration range tested.

(5) Potassium ethyl xanthate has a very low affinity for bismuthinite, forming a low contact angle which slowly drops from 39° to zero degrees, with an increase in pH from 3.5 to 12.0. The contact angle was found to increase linearly to a maximum of 32° to 39° at a concentration of 20 mg per litre, but to decrease very slowly above a concentration of 20 mg per litre with increasing concentration of potassium ethyl xanthate.

(6) Potassium amyl xanthate has a very high affinity for bismuthinite. The contact angle varied with pH, decreasing slowly over the range pH 4.0 to 12.0 but rapidly between pH 4.0 and 3.0. Over the pH range 4.0 to 6.0, maximum contact angles of 60° - 69° were obtained. 20 mg per litre of potassium amyl xanthate was found as a critical concentration which produces the maximum contact angle over the pH range 3.0 to 6.0.

(7) It was found that potassium hexyl xanthate is the most effective collector. The contact angle varied greatly with pH, decreasing slowly from 74° to zero degrees over the range of pH 4.0 to 12.0 but rapidly between pH 4.0 and 2.0. Maximum contact angle was obtained at pH 4.0 with a concentration of 20 mg per litre.

(8) Diethyldithiocarbamate has very low affinity for bismuthinite but a maximum contact angle of 37° was obtained at pH 9-10. It was

found that diethyldithiocarbamate is not a useful collector for bismuthinite.

(9) The pH of the diethyldithiophosphoric acid solution had very little effect on the contact angle, particularly for the range of pH 4.0 to 10.0, in which a maximum contact angle 30° was obtained. But it was found that there is a slight tendency for angle to increase with decreasing pH.

(10) In comparison between the effects of different collectors, it can be seen that ethyl xanthate, diethyldithiocarbamate, and diethyldithiophosphoric acid cannot be applicable to bismuthinite flotation. Amyl and hexyl xanthate have been found to be suitable collectors, but hexyl xanthate has not been widely used in practical flotation. Its improvement over amyl xanthate is, indeed, small.

(11) It was found that potassium dichromate is an effective depressing agent in the bismuthinite-xanthate system in acid solution. Over the range pH 8 to 12, the potassium dichromate had very little effect on the contact angle, which shows a very narrow transition zone (7° to 15°). Below a pH of 8, the potassium dichromate is affected very rapidly by decreasing pH. The contact angle in 20 mg per litre amyl xanthate solution, particularly at pH 3, was reduced from 64° to zero by 200 mg per litre of $K_2Cr_2O_7$.

(12) The mechanism of bismuthinite depression by dichromate is suggested to be due to the easy oxidizability of bismuthinite and the formation of a hydrophilic film of $(BiO)_2Cr_2O_7$ on its surface.

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