STUDIES IN THE PROCESSING OF A CARBONACEOUS GOLD ORE

by

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ABSTRACT

Investigation of a "refractory" carbonaceous gold ore from Ghana has been carried out with a view to obtaining information relevant for improving the processes for treating the ore.

The thesis is divided into three parts. The first part is devoted to a detailed mineralogical study of Prestea carbonaceous gold ore. The results showed that the refractoriness of the ore is due to the presence of active carbon and sulphide minerals which comprise mainly pyrite, arsenopyrite, chalcopyrite, tetrahedrite, and sphalerite. The native gold is alloyed predominantly with silver and occurs in various forms and sizes ranging from visible to sub-microscopic, and is intimately associated with nearly all the minerals in the ore.

In the second part, the surface chemical properties of gold and graphite (chosen as a model for the carbon) have been studied to understand the basic factors which influence the separation of gold from carbon by flotation. The study involved measuring the adsorption of xanthate and starch on gold and graphite, and their effects on the wettability on these materials. The results suggested that gold could be separated from graphite by flotation in a xanthate-starch-O_2 system.

In the third part, some of the processes for treating the ore have been studied. These include the flotation of gold and graphite, and the carbonaceous gold ore with xanthate, starch and quebracho. The results are in agreement with earlier predictions.

Flocculation and filtration tests on the ore and synthetic graphite have shown results which are contrary to the theory of La Mer and Smellie concerning the permeability of flocculated materials. The possible reasons for the contradiction have been discussed.

Possible processes for treating the ore have been considered and the methods for processing the ore based on mineralogical and economic considerations have been suggested. The most promising appears to be by gravity concentration, flotation, roasting, grinding of the calcine, cyanidation and precipitation of the gold.

CONTENTS

		Page
ACKNOWLEDGEMENT		1
ABSTRACT		2
TABLES		9
FIGURES AND PLATES		11
SYMBOLS		16
INTRODUCTION		18
PART I:		
CHAPTER 1	MINERALOGICAL INVESTIGATION OF PRESTEA CARBONACEOUS GOLD ORE.	31
1.1	Introduction	32
1.2	Experimental	37
1.2.1	Materials and techniques used	37
1.2.2	Methods of analysis	37
1.2.3	Mineralogical examination	46
1.3	Results	49
1.3.1	Gangue minerals	49
1.3.2	Ore minerals	59
1.4	Discussion of results	75
1.4.1	The gold-bearing reef	75
1.4.2	Possible origin of the carbonaceous matter	76
1.4.3	The refractoriness of the ore in processing	76
1.4.4	Liberation of gold and the processing of the ore	80
1.5	Summary of conclusions	82

		Page
PART II:	STUDIES OF THE SURFACE CHEMICAL PROPERTIES OF GOLD AND GRAPHITE	
	General Introduction	84
CHAPTER 2	THE WETTABILITY OF GOLD	88
2.1	Introduction	88
2.1.1	Theoretical consideration	88
2.1.2	Zeta-potential determination method	94
2.1.3	Previous work on the wettability of gold	95
2.2	Experimental	100
2.2.1	Materials	100
2.2.2	Methods	100
2.2.2.1	Vapour condensation method	100
2.2.2.2	Electrochemical method	103
2.2.2.3	Captive bubble method	106
2.2.2.4	Contact angle on gold in xanthate and starch solutions	110
2.3	Results	111
2.4	Discussion	125
2.5	Conclusions	134
CHAPTER 3	THE WETTABILITY OF GRAPHITE	136
3.1	General	136
3.2	Introduction	140
3.2.1	Previous work on the hydrophobicity of graphite	140
3.3	Experimental	143
3.4	Results	144
3.5	Discussion	148
3.6	Conclusions	151

		Page
CHAPTER 4	ADSORPTION OF XANTHATE AND STARCH ON GOLD	152
4.1	Introduction	152
4.1.1	Surface properties of gold	152
4.1.2	Xanthate in water under atmospheric conditions	157
4.1.3	Interaction of xanthate with gold in aqueous solution	159
4.2	Experimental	162
4.2.1	Material	162
	Purification of xanthate used.	162
	Preparation of starch solution.	162
	Gold powder used in the investigation.	163
4.2.2	Experimental method	164
4.3	Results	167
4.3.1	Adsorption of KEX as related to time	167
4.3.2	Adsorption of xanthate at various concentrations	171
4.3.3	Adsorption of xanthate at different pH values	171
4.3.4	Nature of adsorbed xanthate on gold	171
4.4	Discussion	174
4.5	Conclusions	181
CHAPTER 5	ADSORPTION OF XANTHATE, STARCH AND DEXTRIN ON SYNTHETIC GRAPHITE	182
5.1	Introduction	182
5.1.1	Oxidation of graphite and carbon by oxygen at moderate temperatures	182
5.1.2	Adsorption of some surface-active reagents on carbon and graphite	185
5.2	Experimental	187
5.2.1	Materials	187

		Page
5.2.2	Method for xanthate adsorption tests.	188
	Adsorption of xanthate on the synthetic graphite and Prestea carbonaceous matter.	189
	Determination of the adsorbed xanthate.	189
	Zeta-potential determination of synthetic graphite in aqueous solution.	190
5.3	Results	194
5.3.1	Adsorption of KEX on synthetic graphite.	194
5.3.2	Adsorption of starch and dextrin on graphite	198
5.3.3	Co-adsorption of xanthate and starch from xanthate + starch solutions	201
5.4	Discussion	205
5.5	Conclusions	217
PART III:	THE IMPLICATIONS OF PROCESSING PRESTEA CARBONACEOUS GOLD ORE.	
	General Introduction	219
CHAPTER 6	FLOTATION OF GOLD AND GRAPHITE AND PRESTEA CARBONACEOUS GOLD ORE	220
6.1	Introduction	220
6.2	Experimental	225
6.2.1	Materials	225
6.2.2	Flotation of gold and synthetic graphite	225
6.2.3	Flotation of Prestea carbonaceous matter	228
6.2.4	Preliminary flotation of Prestea carbonaceous gold ore	228
6.3	Results and Discussion	230
6.4	Conclusions	249
CHAPTER 7	FLOCCULATION AND FILTRATION OF PRESTEA ORE AND FLOTATION CONCENTRATE	251
7.1	Introduction	251
7.1.1	Some basic concepts about flocculation	251
7.1.2	Factors affecting flocculation	253

		Page
7.1.3	Coagulation	255
7.1.4	Filtration	255
7.1.5	Aim of this work	256
7.2	Experimental	257
7.2.1	Materials	257
7.2.2	Methods of flocculation and filtration	258
7.3	Results and Discussion	261
7.4	Conclusion	270
CHAPTER 8	THE IMPLICATIONS OF PROCESSING PRESTEA CARBONACEOUS GOLD ORE	271
8.1	Introduction	271
8.2	Possible processes	272
8.3	Summary	303
9	SUMMARY OF CONCLUSIONS	305
REFERENCES		313
APPENDICES		331

LIST OF TABLES

Tables		Page
1.1	Sampling errors as related to particle size and weight, calculated from Gy's formula.	39
1.2	Grade of ore (a) leached direct with aqua regia (b) after roasting the residue prior to further leach with aqua regia.	42
1.3	The head grade of Prestea carbonaceous gold ore.	42
1.4	Results of the analysis of Prestea ore.	44
1.5	X-ray diffraction data for the crystalline carbon of Prestea carbonaceous matter.	52
1.6	The constituents of Prestea carbonaceous matter.	53
1.7	X-ray diffraction pattern for sericite in the ore.	56
1.8	X-ray powder diffraction data for plagioclase in the Prestea ore.	56
1.9	X-ray powder diffraction data for chlorite in the Prestea ore.	58
1.10	X-ray diffraction pattern for ankerite in the ore.	58
1.11	Relative abundance of minerals in the Prestea ore.	60
1.12	The nature of the Prestea gold.	70
1.13	Screen analysis of the -1.2 mm fraction of the Prestea ore.	70
1.14	Dense medium separation of -1.2 mm ore.	71
1.15	Distribution of gold in the size fractions to the float and sink.	72
1.16	Results of analysis for Au,Cu,Fe,Pb,Zn,As, Sb, and Mn in the float and sink.	74
2.1	The effect of treating gold with some common reagents and high temperature treatment on the wettability of the surface.	113
2.2	Contact angle of an air bubble on gold treated in various ways, in conductivity water at 22°C.	119
2.3	Contact angles on hydrophilic gold exposed to the atmosphere.	130

Tables		Page
4.1	Amount of xanthate adsorbed on gold at different pH values in the presence of air at constant xanthate concentration.	172
5.1	Analysis of synthetic graphite.	187
5.2	Analysis of Prestea carbonaceous matter.	188
5.3	Zeta-potentials of graphite at different pH values with and without xanthate.	197
5.4	Co-adsorption of maize starch and KEX on graphite (5.4a: Graphite was conditioned with starch for .5 h prior to the addition of xanthate. 5.4b: Both xanthate and starch were initially in solution.)	203
5.5	Co-adsorption of xanthate and starch on graphite (5.5a: Graphite was conditioned with xanthate prior to the addition of starch. 5.5b: Both xanthate and starch were initially in solution.)	204
6.1	Flotation of Prestea carbonaceous gold ore with KAX at different pH values.	245
6.2	Flotation of Prestea carbonaceous gold ore at different sizes at pH 9.5.	246
6.3	Flotation of Prestea carbonaceous gold ore with KAX in the presence of various starch concentrations.	247
8.1	Critical hydroxyl ion concentrations at room temperature in 25 mg/l KEX for sulphide minerals.	277
8.2	The operation cost of Prestea gold extracting plant and the estimated costs of the proposed methods for processing Prestea ore.	301

LIST OF FIGURES

Figure		Page
1.1	Geological map showing principal goldfields in Ghana.	33
1.2	Flow-sheet of the Prestea gold extracting plant.	35
1.3	Sketch of sample preparation stages.	40
1.4	Infra-red spectra of (a) benzene (b) benzene/methanol azeotrope extracts of the Prestea carbonaceous matter in CCl_4.	54
1.5	Distribution of gold to the sink and float fractions.	73
2.1	Liquid under equilibrium in contact with solid.	89
2.2	Apparatus for studying the wettability of gold.	101
2.3	Electrochemical apparatus for studying the wettability of gold.	104
2.4	Sketch of apparatus for preparing clean gold free of organic contamination.	109
2.5	Polarograph for gold in 0.2 M $KHPO_4$ + 0.2 M NaOH suffer solution at pH 7.	115
2.6	Polarographs for gold in 1 M HCl and 0.1 M H_2SO_4.	116
2.7	Contact angle of an air bubble on gold in KEX solution as a function of time.	121
2.8	Contact angle of an air bubble on gold in O_2-saturated KEX solutions at pH 6.5 - 7.0.	121
2.9a	Contact angle of an air bubble on gold as a function of pH.	123
2.9b	Histograms showing the effect of high pH (11.8) on gold made hydrophobic by conditioning it in 20 mg/l KEX solution at pH 8.6.	123
2.10	The effect of starch on the contact angle on gold at pH 7 in xanthate solution.	124
3.1	Possible graphite orbital structure.	137
3.2	Structure of starch polymers.	139
3.3	Contact angle of an air bubble on graphite in water and KEX solution as related to pH.	145

		Page
3.4	Contact angle on graphite as a function of xanthate concentration.	145
3.5	Contact angle of an air bubble on graphite in 1 g/l KAX solution as related to time.	146
3.6	Advancing contact angle on graphite as related to time at various starch concentrations.	146
4.1	Adsorption of KEX on gold as a function of time.	168
4.2	Adsorption of KEX on gold at different xanthate concentrations.	169
4.3	Adsorption of KEX on gold at different pH values.	170
4.4	The u.v. spectra of (a) 10 mg/l KEX (b) dixanthogen (c) alkaline decomposition product of dixanthogen.	178
5.1	Adsorption of KEX on synthetic graphite and the carbonaceous matter at different concentrations in air- and N_2-saturated solutions at pH 6.7 - 7.2 as related to time.	195
5.2	Adsorption of KEX on synthetic graphite in air-saturated solution at various pH values.	196
5.3	Zeta-potentials of synthetic graphite in water and 20 mg/l KEX solution at different pH values.	197
5.4	Adsorption of maize starch and dextrin on graphite as related to time and pH.	199
5.5	Adsorption of starch and dextrin as related to pH.	200
5.6	Adsorption isotherm of starch at pHs 6.5& 8.8.	200
5.7	Co-adsorption of xanthate and starch from xanthate + starch solutions at pH 6.5.	202
5.8	Elovich adsorption plots of q versus log t for the adsorption of KEX on synthetic graphite and carbonaceous matter.	207
5.9	Kawecka adsorption plot of $\frac{t}{m}$ versus time for the adsorption of starch and dextrin on synthetic graphite at pH 6.5.	210

		Page
5.10	Langmuir plot of $\frac{(S)}{m}$ versus (S) for the adsorption of maize starch on synthetic graphite.	213
6.1	Modified Hallimond tube for flotation.	226
6.2a	Influence of pH on the flotation of gold with KEX.	231
6.2b	Comparison of flotation recovery of gold with contact angle and adsorption density of xanthate at various pH values.	232
6.3	Flotation recovery of gold in the presence of KEX + starch, and KEX + quebracho S at various pH values.	234
6.4	Flotation of gold as related to starch concentration at pH 7.	235
6.5a	Flotation recovery of synthetic graphite in absence and presence of 40 mg/l starch and quebracho S at various pH values.	238
6.5b	Comparison of flotation recovery of graphite with contact angle at different pH values.	238
6.6	Depressing of synthetic graphite at different concentrations of starch and quebracho S at pH 9.	239
6.7	Flotation recovery of synthetic graphite at various KEX concentrations in the presence of 40 mg/l starch or quebracho S at pH 9.	240
6.8	Flotation of synthetic graphite at various KAX concentrations in the presence of 40 mg/l starch or quebracho S at pH 9.	240
6.9	Flotation of Prestea carbonaceous matter with and without xanthate at various pH values.	242
6.10	Flotation of Prestea carbonaceous matter at various concentrations of starch and quebracho S at pH 9.	242
7.1	Apparatus for filtration.	259
7.2	Flocculation of Prestea carbonaceous material as related to polymer dosage.	262
7.3	Height of the settled bed of the flocculated carbonaceous matter as a function of polymer dosage.	262

		Page
7.4	Theoretical form of the refiltration rate against dosage curve, according to the theory of La Mer and Smellie.	265
7.5	Effect of flocculation on refiltration rate of Prestea carbonaceous material.	266
7.6	Effect of flocculation on refiltration rate of synthetic graphite.	266
8.1	Proposed flow-sheet for processing Prestea carbonaceous gold ore.	298
8.2	Proposed flow-sheet for processing Prestea carbonaceous gold ore.	299

LIST OF PLATES

Plate		Page
1.1	Arsenopyrite (white) aligned almost parallel in quartz (grey) matrix.	50
1.2	Corroded pyrite (white) in quartz.	50
1.3	Gold (yellow) disseminated in pyrite (pale yellow) and quartz (Q) with sericite (SE) cutting across the pyrite.	61
1.4	Chalcopyrite (dirty yellow) associated with tetrahedrite (T) and sphalerite (S).	61
1.5	Gold (yellow) in tetrahedrite (T), sphalerite (S) and pyrite (P); all in quartz matrix.	63
1.6	Association of sphalerite (S) with tetrahedrite (T), pyrite (P), chalcopyrite (yellow) and iron carbonate (IC).	63
1.7	Gold (white), sphalerite (S) and tetrahedrite in the cracks of quartz.	67
1.8	Finely divided gold (white) in quartz.	67
1.9	Gold (white) in arsenopyrite (grey) and quartz (dark).	68
1.10	Gold (white) not fully liberated from arsenopyrite.	68

LIST OF SYMBOLS

Symbol

σ_e^2	=	variance of the assay distribution, expressed as a fraction of the mean of the grade.
a^1	=	fineness of the gold in the ore.
a	=	the grade of the ore.
ρ_m	=	the density of the ore.
ρ_M	=	density of gold.
d	=	size of the largest piece in the lot.
W_A	=	work of adhesion between a liquid and a solid.
W_A^d	=	dispersion force contribution to the work of adhesion between solid and liquid.
W_A^h	=	the contribution of the interfacial hydrogen-bonding to the work of adhesion.
W_A^π	=	the contribution of the interfacial pi-bonds to the work of adhesion.
W_A^p	=	the contribution of other polar interfacial interactions to the work of adhesion.
W_A^e	=	the contribution of electrical double layers to the work of adhesion.
π_ε	=	spreading pressure or the decrease in surface free energy of substrate resulting from adsorption of another substance.
γ_W^d	=	dispersion force contribution to the surface free energy of water.
γ_{WV}	=	surface tension or surface free energy of the water/vapour interface.
γ_{SL}	=	surface tension or surface free energy of solid in contact with liquid.
γ_S^d	=	dispersion force contribution to the surface free energy of the solid.
γ_L^d	=	dispersion force contribution to the surface free energy of the liquid.
γ_{LV}	=	surface tension or surface free energy of Liquid/Vapour interface.
γ_{SV}	=	surface tension or surface free energy of Solid / Vapour interface.

Symbol

ΔF_{ads}	=	free energy change of solid surface upon adsorbing vapour (in equilibrium with liquid) onto bare solid surface.
ΔH_{ads}	=	enthalpy change of the heat of adsorption.
ΔF_i	=	free energy change of bare solid surface when immersed in liquid.
ΔH_i	=	enthalpy change of heat of immersion.
A_{131}	=	Hamaker constant for two materials of material 1 immersed in medium 3.
A_{11}, A_{33}	=	Hamaker interaction constants of the individual materials 2 and the medium 3.
A_{13}	=	Hamaker interaction constant between material 1 and the medium 3.
K_3	=	the dielectric constant of water.
κ	=	specific conductance of solution.
ζ	=	zeta-potential.
q_m	=	amount of reagent adsorbed.
m_0, a_∞	=	amount of surfactant adsorbed at saturation of the adsorbent.

INTRODUCTION:

The Problems of Processing "Refractory" Gold Ores.

Gold has been used since antiquity as an ornament, as a concentrated form of wealth and as money. So much attention has been directed to the monetary use that its increasing application in the arts and sciences has not been generally appreciated even though more than half of the gold available in recent years has gone into these important non-monetary fields. Its freedom from tarnish and its distinctive colour and high specific gravity made it conspicuous among the rocks and easy to concentrate by man before the advent of modern methods of extraction.

In recent years there has been a renewal of interest in gold for scientific and industrial purposes, though incidentally this has coincided with the high price of gold. Thus , though for economic reasons, its use in the scientific and industrial fields may decline, this high price will lead to a renewed interest in the processing of the low grade ores and ores which are difficult to treat. Such interest has led to the present research into one particular "refractory" gold ore - the term "refractory" meaning that it presents technical difficulties for the mineral processor.

Gold in ore deposits.

Unlike many other minerals, native gold scarcely combines with oxygen or sulphur, but does react with tellurium to form tellurites (calaverite and sylvanite) of commercial importance. The most common form is the native gold which usually alloys with silver. The amount of silver in the gold is often 10 - 20%.

"Placer" gold in any district usually has a higher gold content than the native metal in the veins from which the nuggets were derived. Native gold may also contain small amounts of Cu, Pb, Zn, but silver is often the only metal of quantitative significance occurring with the gold as a natural alloy. Maldonite, a gold-bismuth metal and gold amalgam, a solid solution of gold in mercury are also known but are not of economic importance.

Work on the geochemistry of gold has been published by Goldschmidt[1], Rankana and Sahama[2] and Mason[3]. The description of gold deposits and the discussion of their genesis are contained in the work of Lindgren[4], Bateman[5] and Emmons[6].

Kinds of gold deposit and origin.

Classification of gold deposits can be made on the basis of origin, or geological structure, of properties that influence mining, of extraction processes or on other properties that are of concern to the investigator. Such a detailed classification has been made by Emmons[6]. It is intended here simply to enumerate some of the types of gold deposit which are frequently encountered in nature. Gold occurs chiefly in the following situations:-

1) Deposits along, or in, fractures and fracture systems as in the Ashanti Goldfields, West Africa and El Oro in Mexico.
2) Massive deposits, which are predominantly siliceous or sulphide replacements.
3) Disseminated deposits, for example, gold in "porphyry coppers" e.g. Kennecott Copper Corporation at Bingham, Utah, U.S.A.
4) Residual and mechanical concentration (placers).

Although many gold deposits might have been primarily of igneous origin, the present leading gold mines are of placer deposits for instance the banket deposits of South Africa and the placers of U.S.S.R.

Distribution of gold in the world.

Gold deposits occur in the pre-Cambrian to late Tertiary period and are found throughout the world, mostly where igneous activity had occurred.

In North America the greatest gold belt lies in the Canadian shield of the pre-Cambrian system. The gold deposits of the Pacific coast region, that from California to Alaska, the numerous gold-bearing lodes association of smaller intrusives of the Black Hill, the Appalachians and the Tertiary volcanic belt have been described in detail by Lindgren[4] and Emmons[6].

In South America, much of the gold occurs as small scattered gold veins and replacement throughout the Andean chains in association with Tertiary and older intrusives. Some of the deposits are found in Brazil and Guiana Highlands.

Africa is the largest producer of gold with South Africa as the leading country. Other producers include West Africa, Rhodesia and Zaire. The gold in these countries occurred generally in the pre-Cambrian system.

The gold deposits of Australasia occur as lodes and placers in Australia, New Guinea and New Zealand.

Europe's gold deposits are found in Scandinavia, in the mountainous parts of central and southern Europe and the Urals in Russia.

In Asia, the Siberian placer and the lode deposits, the deposits of the Philippines, Japan, Indo-China, Burma and the Kola district of India are among the most important.

Gold production[5-7]

By 1905 South Africa had become the leading producer of gold in the world, with the U.S.A. as the second largest producer until 1931 when Canada took the second position briefly. In 1934 U.S.S.R. gained the second position which it has maintained ever since.

World production of gold in recent years has been reported by Fells[8] and is shown in Table 1. As shown, South Africa produces more than half of the world's output, U.S.S.R. produces about 29%, followed by Canada (3.6%), U.S.A.(2.34%) and Ghana in decreasing order.

Mining and processing of gold[7]

Gold mining started with the placer deposits. The methods ranged from panning to highly mechanical dredging. But in some cases, where the gold content permits (e.g. in the Tertiary channel of the Sierra Nevada, California), gravels in old river channels are mined by underground methods. In both cases the particles of gold are concentrated by gravity after washing mechanically by putting huge tonnages of gravel through trommels, with jigs or over classifying tables.

Much of the gold is being mined at present by conventional methods of deep underground mining. The ore produced, if easy to treat by amalgamation and cyanidation to extract the gold is said to be "free milling" but if the gold occurs in minerals which are difficult to treat, it is said to be "refractory". The common associate of gold, namely pyrite, generally does not offer much trouble in treatment, except that the ore needs fine grinding and, in some cases, roasting. The presence of copper sulphide minerals, arsenopyrite,

TABLE 1. GOLD PRODUCTION 1970-1974

Metric Tons

	1970	1971	1972	1973	1974
SOUTH AFRICA	1000	976.6	908.7	852.3	758.5
CANADA	74.9	68.7	64.7	60.0	52.2
U.S.A.	54.2	46.4	45.1	36.2	34.9
OTHER AFRICA					
Ghana	21.9	21.7	22.5	25.0	21.4
Rhodesia	15.0	15.0	15.6	15.6	18.6
Zaire	5.5	5.4	2.5	2.5	4.4
Other	2.0	2.5	1.7	1.7	1.0
TOTAL OTHER AFRICA	44.4	44.6	42.3	44.8	45.4
LATIN AMERICA					
Brazil	9.0	9.0	9.5	11.0	13.8
Colombia	6.8	5.9	6.3	6.7	8.2
Mexico	6.2	4.7	4.7	5.0	3.9
Nicaragua	3.6	3.3	2.8	2.8	2.4
Peru	3.2	3.0	2.6	2.6	2.2
Other	6.6	8.2	9.0	7.9	5.9
TOTAL LATIN AMERICA	35.4	34.1	34.9	36.0	36.4
ASIA					
Phillippines	18.7	19.7	18.9	18.1	18.9
Japan	8.4	7.7	9.6	10.4	5.5
India	3.2	3.7	3.3	3.3	3.2
Other	2.8	2.1	1.7	2.7	2.7
TOTAL ASIA	33.1	33.2	33.5	34.5	30.3
EUROPE	7.4	7.6	13.2	14.3	16.0
OCEANIA					
Papua/New Guinea	0.7	0.7	12.7	20.3	20.5
Australia	19.5	20.9	23.5	17.2	16.2
Other	3.6	3.1	3.2	3.2	3.2
TOTAL OCEANIA	23.8	24.7	39.4	40.7	39.9
FREE WORLD TOTAL	1273.2	1235.9	1168.6	1118.8	1013.6
U.S.S.R.	335.5	344.8	360.2	370.6	420.0
OTHER COMMUNIST COUNTRIES	18.4	18.4	18.4	19.4	20.4
TOTAL WORLD PRODUCTION	1627.1	1599.1	1547.2	1508.8	1454.0

sphalerite, stibnite, tellurite and carbon, which adsorbs dissolved gold, makes the ore "refractory" and could make the extraction of gold uneconomic.

The present conventional methods of processing gold ores.

The first step in processing a consolidated gold ore is comminution, the purpose of which is to crush and grind the ore sufficiently to liberate the gold. Stamp mills were employed for this purpose for many years, but they have largely been replaced by conventional crushers, namely jaw, gyratory and cone crushers, followed by rod-mills or ball-mills.

Gravity concentration

The free gold from placers or liberated by comminution is separated from the gangue by gravity concentration. Mercury can then be used to amalgamate the gold.

Although the position which gravity concentration occupied in gold recovery before the advent of the cyanidation process has diminished, nevertheless it still plays an important role in the recovery of gold, particularly where the ore is refractory and the gold is liberated at coarse sizes. Thus, in many modern plants, gravity concentration is still in use. The concentrators usually used include

(1) the corduroy blanket strakes, followed by

(2) Johnson concentrator[9]

(3) plane tables which consist of riffled rubber covering a series of inclined smooth surfaces with steps between them,

(4) endless-belt concentrator developed to replace the corduroy blankets and

(5) jigs.

Cyanidation

The invention of the cyanidation process by MacArthur and Forrests[10] in 1887 and its introduction in 1890[7] into gold processing is one of the main achievements in the field. Since then many theoretical and practical developments have taken place to make the process economical for many ores. The process is now used not only to supplement amalgamation but as a single procedure to recover gold.The process is most successful in extracting gold from non-refractory ores. Direct cyanidation may be uneconomic for some refractory ores. In such circumstance some pre-cyanidation processes such as flotation and roasting are employed.

The dissolution of gold in cyanide solution has been extensively studied and it has been realized that the presence of oxygen is essential for the dissolution. For example, Barsky, Swainson and Hedley[11] determined the effect of oxygen on the rate of gold dissolution with a 0.10% NaCN at 25^{o}C and found that in the absence of oxygen the rate of dissolution was 0.04 $mgcm^{-2}h^{-1}$, in the presence of 20.9% oxygen it was 2.36 $mgcm^{-2}h^{-1}$, and with 99.5% oxygen it was 12.62 $mgcm^{-2}h^{-1}$. The pH for maximum dissolution is generally above 10 and it is regulated with lime.

The rate of dissolution of gold at normal atmospheric conditions is slow so that it is necessary that the gold particles should be very finely divided. According to Barsky et al[12] the rate of dissolution of pure gold is about 2.99 $mgcm^{-2}h^{-1}$ in 0.10% NaCN and that of silver under the same conditions is 1.54 $mgcm^{-2}h^{-1}$ indicating that gold dissolves twice as fast as silver. Thus the rate of

dissolution of native gold containing silver may therefore be between the values for gold and silver.

In nature some of the gold particles may be tarnished with iron oxide coating and thus rendered difficult to dissolve. Besides this, the presence of many sulphide minerals, for instance of copper, zinc etc, in gold ores will increase cyanide consumption substantially if these minerals are not rendered less harmful to cyanide by roasting. In practice, therefore many cyanidation processes use more cyanide than the theoretical value of 0.0098% NaCN for gold dissolution.

Flotation

The froth flotation process is widely used in treating base metal ores and in the separation of various sulphide components of ores, as well as for removing the barren gangue. It is often used in the gold processing industry if the ore is "refractory". The gold is floated with the sulphide minerals with which it is usually associated, by use of xanthates, dithiophosphates, frothers and $CuSO_4$. The pH of the flotation pulp is controlled with lime instead of caustic soda or soda ash because of its lower cost. The flotation concentrate can be directly cyanided. If the gold in the concentrate is a by-product, the concentrate can be smelted and the gold finally removed by electro-winning. But if the flotation concentrate is primarily a gold concentrate where the sulphides are worthless, roasting is normally employed.

Roasting

Gold ores or flotation concentrates which contain sulphide minerals such as pyrite, arsenopyrite, stibnite, Pb-Cu bearing sulphides which are of no economic importance are roasted to liberate the gold. The oxidation products are by far less harmful to cyanidation.

The optimum conditions of roasting will depend on the particular type of minerals associated with the gold in that ore. However, a comprehensive description of roasting practices is contained in a series of articles by von Bernewitz[13], later by Archbald[14] and Djingeluzian[15].

In practice, four general types of roasting furnaces are in use. These are:-

1) a horizontal, multi-spindle type, of which the Edwards furnace is typical,
2) the rotary kiln,
3) the vertical, multiple-hearth furnaces with rabble arms attached to a central shaft, of which the Wedge furnaces are typical,
4) the fluosolids reactor.

Of these four furnaces the Edwards horizontal, multi-spindle furnace and the fluosolids roasters have been most commonly used for roasting gold ores.

Extraction of gold with chlorine[16].

Chlorine was used in the past for the extraction of gold from its ores until the advent of cyanidation, when the process was discontinued. Although the chlorination process has some advantages over cyanidation, as outlined by Putman[17], it has some serious disadvantages. For instance, because of its highly corrosive action it is difficult to obtain suitable materials for plant construction. Chlorine also reacts with sulphide minerals in the ore in aqueous medium, thus leading to a high consumption of chlorine. It is also many times the cost of cyanide. As a result, the process is now used only by one plant, the Kalgurli Ore Treatment Co.[17], for the treatment of gold slimes.

Recovery of gold from solutions[18].

The most widely used method for precipitating gold from cyanide solution is by zinc precipitation, patented by Sulman and Pichard in 1894[18]. Zinc is used in the form of zinc dust or shavings. Other methods of gold precipitation involve the use of aluminium, charcoal and electrodeposition. Besides the precipitation methods, ion-exchange and solvent-extraction (liquid-liquid extraction) methods have been used in extracting gold from solution, though these last two methods are still in the experimental stages.

Treatment of the solution before precipitation[19-21].

For efficient precipitation of the gold, the solution should be clear and entirely free from colloidal particles. A clear solution will ensure low tailing value, decreased consumption of the precipitant and satisfactory smelting and refining operation[19].

Another factor in efficient and thorough recovery of gold from cyanide solution is the removal of dissolved oxygen. The efficiency of the zinc-dust precipitation is largely dependent on the removal of dissolved oxygen and the prevention of its re-absorption into solution[20]. The most efficient and widely used method of de-aeration is the Crowe vacuum process[21] which was introduced in 1916. This process was one of the major innovations in zinc precipitation since that of Merrill[22] in 1897.

Merrill-Crowe zinc precipitation process.

The Merrill-Crowe simultaneous clarification-precipitation process[18,23] developed in 1932 is most universally applied.

The process consists of clarification and de-aeration of the pregnant solution units. The solution is clarified with

vacuum-clarifying leaf filters, and later de-aerated in a tank under a vacuum to reduce the oxygen to acceptable amount (0.5 mg/l). Zinc dust is added by means of a mixing cone and avoiding introduction of air with it. The gold and silver and the excess zinc are separated from the barren solution by pressure filters.

Aluminium and charcoal as precipitants of gold and electrodeposition methods.

Aluminium as a precipitant for precious metals was patented by Moldenhauer[18] in 1893 and has been used as a substitute for zinc. It is used mainly for the precipitation of silver but a minimum amount of silver in gold solution is necessary before it can precipitate both silver and gold[23]. Its mechanism of reaction with gold is different from that of zinc with gold.

Johnstone[18] obtained a patent in 1894 for the use of charcoal as a precipitant of gold from cyanide solution. This method was later tried in New Zealand with indifferent results. But further investigations into its adsorption properties has led to the use of charcoal at present in practical gold extraction[24].

The electrodeposition process was patented for gold by Pfleger[19] in 1895. It employed zinc anodes and iron cathodes; the anodes being placed in an alkali or cyanide solution and the cathodes in the gold-bearing solution, and the two electrolytes were separated by a porous membrane. This process was used in South Africa for a short time, but at present this process is uncommon because of the use of the improved zinc-lead precipitation process.

The processes mentioned are those which are often employed in the extraction of gold. The selection or development of processes for treating an ore may vary from ore to ore because each ore may present special problems, the solutions of which may not be found in any record of experience.

Aim of this work.

The Prestea carbonaceous gold ore (mined in Ghana) is one of the few gold ores in the world which contains both active carbon and sulphide minerals. In spite of many years of gold extraction, the information available about the ore is inadequate for understanding the causes of the relatively poor recovery of gold, namely between 85-89%. It has been observed that gold losses are greatest at the flotation stage, followed by losses at the cyanidation process.

The primary aim of this research, therefore, was to carry out a systematic investigation into the causes of gold losses and with the ultimate aim of improving the existing processes or developing processes which could increase the overall recovery of gold. To achieve these objectives detailed knowledge about the ore is required.

This work is divided into three parts.The first part deals with the mineralogical investigation of the ore, to define the causes of its refractoriness, the occurrence, the nature and the association of gold with other minerals.

The second part deals with the surface chemical properties of gold and graphite (model for carbon in the ore) in collector and depressant solutions. These involve the study of the wettability of these minerals in water, aqueous solutions of xanthate and starch and the adsorption of xanthate and starch on gold and graphite. These properties were studied

in order to understand the factors controlling the separation of carbon from gold by flotation.

The third part is concerned with the processes and the implications of processing the ore. The flotation of gold and "carbon" was investigated. Preparation of the flotation concentrate and the carbonaceous matter by means of flocculants and the study of the filtrability of these materials were carried out . The implications of processing the ore have been discussed.

P A R T I

CHAPTER 1

MINERALOGICAL INVESTIGATION OF PRESTEA CARBONACEOUS GOLD ORE.

1.1 INTRODUCTION

The Prestea carbonaceous gold ore studied in this thesis comes from Ghana, West Africa. It belongs to the same group of carbonaceous gold ores of which the Ashanti and the Konongo goldfields form the northern section[25]. The Prestea mines form the southern section of this group of mines which occur generally at the contact of the lower and the upper Birimian formations (Fig.1.1). These formations, which are of pre-Cambrian origin, consist of phyllites, schists, tuffs and greywackes, exhibit north - north-east trend with a general dip of 70° to the east. Periods of tectonic activity caused extensive shearing, faulting and brecciation along the contact of the lower and upper Birimian. The complexity of the geological history is reflected in the mineralisation in the fissure zone. Cooper[26] and Junner[25] published detailed account of the geology of the Prestea mines.

The gold-bearing lode is a quartz reef. Between the quartz reef and the country rock is often "sandwiched" a carbonaceous material, the origin and nature of which have not been satisfactorily explained. The only published work on this carbonaceous material is that of Feldtmann[27] which dealt with the adsorption of aurocyanide by the carbonaceous material. Since then there has not been any specific study of the Prestea carbonaceous material. The country rock, which is a phyllitic schist, contains feldspar, quartz, sericite, and chlorite interbedded with carbonaceous material, pyrite and arsenopyrite. The ore body is primarily

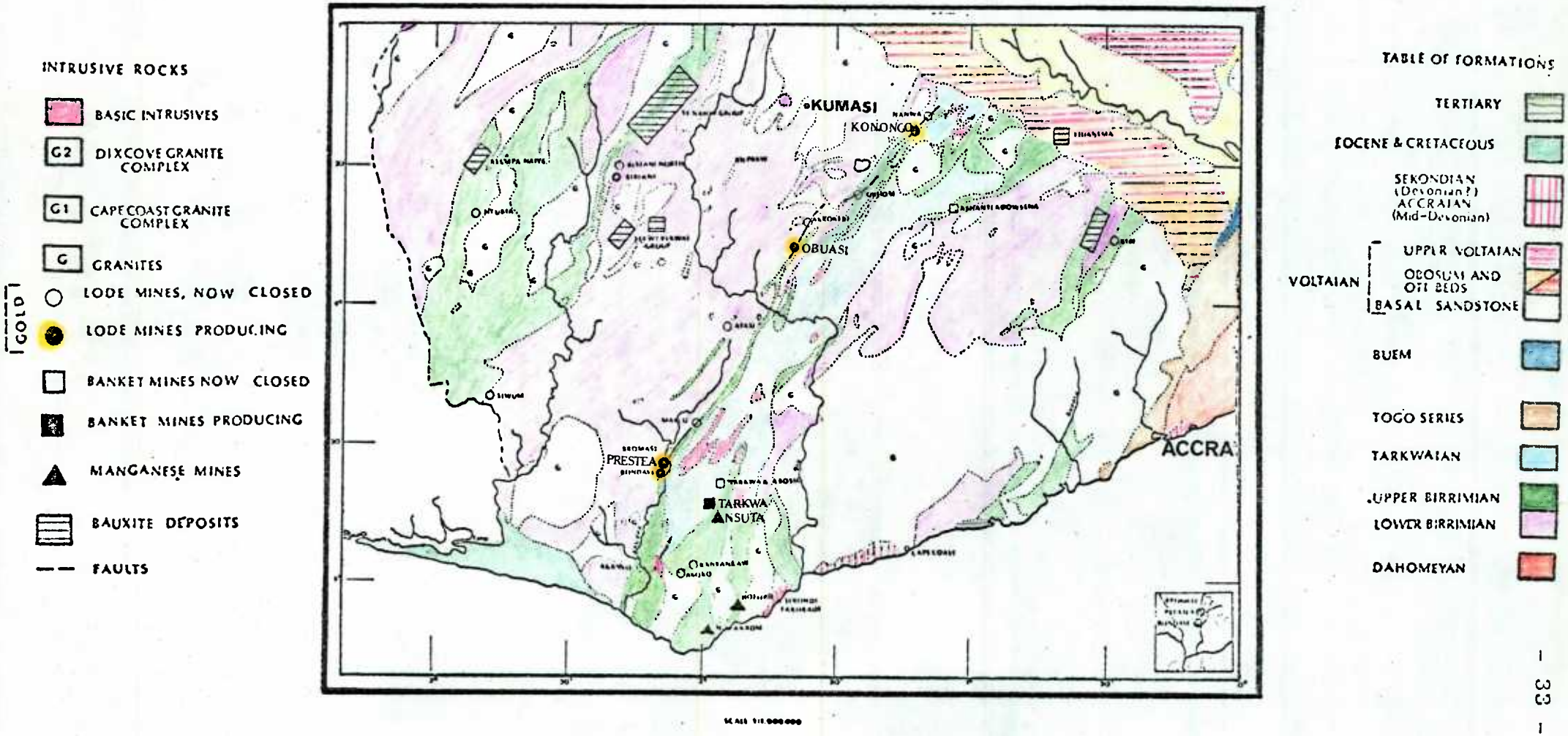


Fig.1.1 GEOLOGICAL MAP SHOWING PRINCIPAL GOLDFIELDS IN GHANA.

a quartz vein with native gold, and sulphide minerals namely, pyrite, arsenopyrite, chalcopyrite, bournonite, tetrahedrite, pyrrhotite. Other minerals include limonite and disseminated carbonaceous material. Until recently[28] little was known about the association of gold with other sulphide minerals except pyrite and arsenopyrite.

1.1.1 Metallurgical treatment of the ore.

Before 1940 gold in this carbonaceous ore was extracted, after fine grinding, by gravity concentration, flotation and direct cyanidation of the flotation concentrate. The total gold recovered as reported by Howat[29] was 91.1% in spite of the high cyanidation residue grade of 30 g Au/t. At the same time the gravity concentration recovery accounted for 83.7% of the total gold, while the flotation tailing grade was 0.45 g Au/t. Since then a roasting process has been included in the plant circuit to treat the flotation concentrate prior to cyanidation. This led to the reduction in the grade of the cyanidation residue to about 7.5 g Au/t. This means that the recovery of gold due to incorporating a roasting process in the circuit had exceeded 91% at that time. However, at the present conditions of lower ore grade, the gravity concentration accounts for 60-65% of the total gold and the flotation tailing grade has doubled. The total gold extracted under the present conditions is between 85% and 89%. (A sketch of the flow-sheet for processing the ore is shown in Fig.1.2.This steady decline in the gold extraction appears to have coincided with the increase in the depth of the mines. It is apparent, therefore, that more knowledge

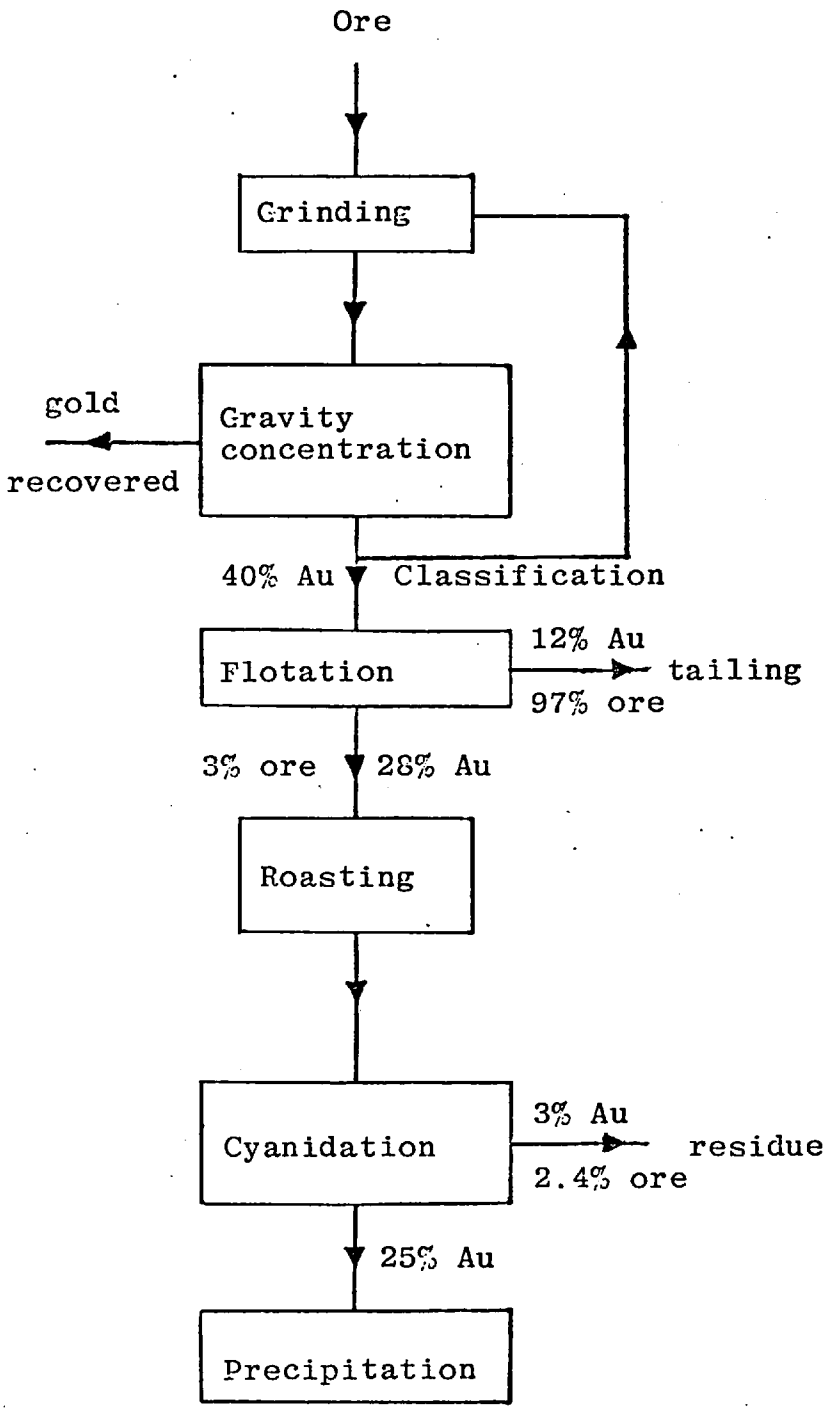


Fig. 1.2 Flow-sheet of the Prestea gold extraction plant.

about the ore is needed if improvement in the extraction of the gold is to be made.

From the work of Howat[29] some deductions can be made about the ore and the nature of the gold, as follows:-

1. The nature of the ore has gradually changed, making it more refractory to processing.
2. More gold occurs in sub-microscopic forms.
3. More gold has been locked up in the refractory minerals which comprise the sulphides and the carbon.
4. Fine gold could be found in other sulphide minerals which are difficult to float, besides pyrite and arsenopyrite.

1.1.2 The aim of this work.

The aim of this work is, therefore, to investigate the nature of the ore, define the causes of its refractoriness; the nature, occurrence and distribution of gold in the ore.

Detailed study of the mineralogy of the ore, the nature, occurrence and distribution of the gold was not carried out when the mines were shallow. For that reason, the data obtained in this investigation would, therefore, reflect generally the nature of the ore at the deeper levels. The view held by some geologists[25,26.28] and metallurgists that the carbon and the arsenopyrite are the cause of the refractoriness of the ore may not be entirely correct. Why the ore appears to be more refractory as the depths of the mines increase has not been examined, neither has the mode of occurrence of silver in the ore been studied. Cooper[26] in his report stated that though silver was known to be present in the ore, its mode of occurrence was not known. The occurrence of silver and other minerals associated with gold have been dealt with in this investigation.

1.2. Experimental

1.2.1. Materials and techniques used.

(a) Materials. The three types of sample provided for the mineralogical investigation of the ore were as follows:-

1. 28 kg of -0.635 cm size sample of Prestea carbonaceous gold ore, "representative" of the ore being processed. This sample has been previously crushed with cone crushers.

2. Hand-picked rock samples containing visible gold in quartz and sulphide matrix.

3. 1 kg of hand-picked clean carbonaceous material, friable and interbedded with sericite, chlorite, quartz and some amount of carbonates.

(b) Techniques used. Chemical analysis, atomic absorption spectrophotometry, infra-red spectrometry, microscopic examination, electron probe micro-analysis and X-ray diffraction techniques were employed in the mineralogical investigation.

1.2.2. Methods of analysis

1.2.2.1 Theoretical consideration of sampling a vein type of gold ore.

A major problem in assaying for gold is in defining a representative sample weight to be taken since gold, like other minerals, for example diamond, is never uniformly distributed and neither does it easily break down into dispersed fine sizes on grinding[30]. The standard method adopted in this work in defining the weight of a sample for the head assay of the ore is that formulated by Gy[31].

This formula, which is applicable to a vein type of gold ore of which the present ore is one, is based on statistical (random) occurrence of gold in a size fraction. The weight of the sample required can be calculated from the equation,

$$\sigma_e^2 = cd^3 \left(\frac{1}{p} - \frac{1}{q}\right) \qquad (1)$$

$$\text{where } c = \frac{1}{8}\left(\frac{a^1}{a} - 1\right)\left(\frac{\rho_m \rho_M}{(1-a^1)\rho_M + a^1\rho_m}\right) \qquad (2)$$

where a^1 is the fineness of the gold in the ore; a is the grade of the ore; ρ_m, the density of the ore; ρ_M, the density of gold; p, the weight of the sample required; q, the weight of the initial sample of ore; d, the size of the largest piece in the lot; and σ_e^2, the variance of the assay distribution, expressed as a fraction of the mean of the grade.

By knowing the values of c, d, σ_e and q, the sample weight, p can be calculated. By substituting a = 10 g Au/t, $a^1 = 9 \times 10^5$ g Au/t, $\rho_m = 3.0$, $\rho_M = 19.3$ g cm^{-3}, d = 0.635 cm and $p = 28 \times 10^3$ g into equation (1), assuming $q = \infty$ (i.e. very large), the value of σ_e is 0.0928. By taking 95% confidence limit it can be shown that the standard error of the mean assay value is ± 1.85 g Au/t. This means that without reducing the size of the particles before taking samples, would result in substantially large sampling errors. Consideration of the sampling errors and the use of the ore for other purposes made it necessary to grind and sample the 28 kg sample in stages.

1.2.2.2 Sampling procedure

The 28 kg sample was ground dry with a steel disc grinder to -1200 μm and riffled into two portions of 14.8 kg and 13.2 kg. The 14.8 kg fraction was ground down to -500 μm making certain that more than 95% of it was -500 μm. This size material was also riffled into two and a portion of it weighing 7.3 kg was further ground down to -300 μm and the material riffled. Further stage grinding and riffling were carried out as shown in Fig.1.3. 1.8 kg of the -100 μm material was pulverised in a stainless steel pot to -40 μm. The standard error of sampling introduced at each stage of grinding and riffling was calculated and tabulated in Table 1.1. The portions of the ore which were not pulverised were used in subsequent experiments.

Table 1.1 Sampling errors as related to particle size and weight, calculated from Gy's formula.

Dia. of largest piece (μm)	p(kg)	q(kg)	σ_e^2	$2\sigma_e$	% Error
1200	14.8	28.0	77.05×10^{-4}	0.1755	17.55
500	7.3	14.8	12.14×10^{-4}	0.0697	6.97
300	3.7	7.3	5.04×10^{-4}	0.0447	4.47
100	1.8	3.7	0.04×10^{-4}	0.0063	0.63
40	0.92	1.8	0.54×10^{-6}	0.0014	0.147
40	0.03	0.89	2.82×10^{-4}	0.0336	3.36
Total Error			97.47×10^{-4}	0.1976	19.76
For 10 g Au/t grade					± 1.976 g Au/t

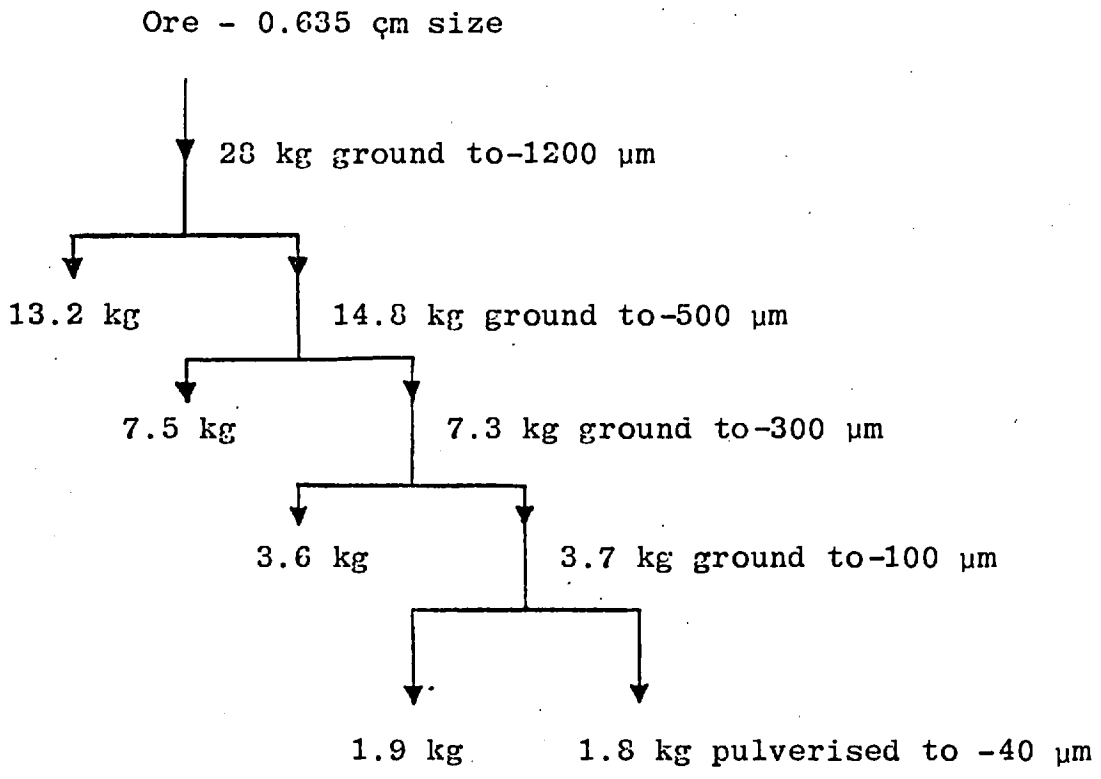


Fig.1.3 Sketch of sample preparation stages.

1.2.2.3 Assaying for gold.

Samples weighing 30 g each were taken from the pulverised ore and leached direct with boiling aqua regia in 250 ml"Pyrex" beakers for 6 hours. Concentrated HCl was added to the sample during leaching to remove all excess HNO_3, taking care not to evaporate the solution to dryness. The leached sample was filtered through a Whatman filter paper into a 100 ml flat-bottom flask and the residue washed thoroughly with 1 M HCl and the solution made to the mark.

An aliquot portion of the filtrate was pipetted into a 250 ml spherical separating flask and the gold chloride was extracted with a known volume of methyl iso-butyl ketone (MIBK) [32,33] to which 1 ml HBr acid was added. Hilger and Watts atomic absorption spectrophotometer model 705 was used for the gold analysis at wavelength of 242.8 nm, slit width of 30 cm and lamp current of 10 mA. The absorption values for gold in the solution was compared with the absorption values of standard gold chloride solutions.

The preliminary analysis of the head sample of the ore leached direct with aqua regia showed retention of gold from solution. Results of these analyses are shown in Table 1.2. For this reason for all further analyses for gold, the ore was roasted to 800°C to burn off the carbon prior to aqua regia leach. The results of the head assay values for gold and the fire assay result obtained for the -40 µm size sample by Robertson research laboratory are tabulated in Table 1.3.

Table 1.2 Grade of ore (a) leached direct with aqua regia (b) after roasting the residue prior to further leach with aqua regia.

No. of samples	(a) direct leach (g Au/t)	(b) leached after roasting (g Au/t)	Total gold (Au/t)
1	0.74	9.70	10.40
2	0.80	9.62	10.42
3	1.60	7.70	9.30
4	1.64	8.50	10.14
5	0	9.70	9.30
6	0	10.50	10.53
7	0	10.30	10.33
Mean grade			10.11

Table 1.3 The head grade of Prestea carbonaceous gold ore. (Every sample was roasted prior to aqua regia leach).

No. of samples	Grade of ore (g Au/t), x	$(x - \bar{x})^2$	Fire assay by Robertson research
1	10.50	--	
2	11.50	--	
3	11.80	1.69	
4	10.60	0.01	
5	11.20	0.49	
6	9.30	1.44	
7	10.10	0.16	
8	10.40	0.01	
9	10.50	--	
10	10.20	0.09	9.34
Mean ($\bar{x}$)	10.50	3.89	
For 95% confident limit	10.50 ± 0.33		

1.2.2.4 Analysis for other elements in the ore.

(a) Preliminary determination of the elemental constituents of the ore was carried out on the -40 μm size sample with an X-ray fluorescence by the Analytical Services of the Metallurgy Department. The carbon content was determined by a fusion method.

(b) Atomic absorption spectrophotometric analysis of the elements.

For the atomic absorption analysis for Cu, Pb, Zn, Mn, As and Sb, about 1 to 2 g of the pulverised sample was fused with Na_2O_2/Na_2CO_3 in the ratio 1:6 as described by Vogel[34] in a nickel crucible. The fused sample was dissolved in concentrated HCl and the solution transferred into a 250 ml volumetric flask and the volume made to the mark with 5 M HCl. An aliquot portion of the solution was used for the determination of the elements. The operating conditions for analysing these elements were obtained from the Hilger and Watts atomic absorption operation manual. When fusing the ore for the determination of As and Sb, special precautions were taken to avoid loss of these elements. By 'carpeting' the mixture of the flux and the sample with Na_2O_2 and heating the sample gently to red heat, it was possible to reduce the loss of the As and Sb. The results of the X-ray fluorescence and atomic absorption analysis are tabulated in Table 1.4.

Table 1.4

Results of the analysis of the Prestea Ore.

Elements	by Analytical Services	A.A. Spec.
Au	--	10.50 g/t
As	0.422%	0.40%
S	0.95%	--
Fe	4.48%	3.05%
(Quartz)	67.0%	--
C	2.63%	--
Sb	50 p.p.m.	0.013%
Al	4 - 8%	--
Pb	--	0.014%
Cu	--	0.019%
Ca + K	1 - 5%	--
Ni	--	0.01%
Mn	--	0.03%
Ag	trace	
Zn	--	0.023%

1.2.2.5 Analysis of the carbonaceous material.

(a) Leaching of the carbonaceous material.

As the carbonaceous matter is intimately associated with sericite, chlorite and quartz it was essential to remove these impurities before the nature of the carbon could be studied. Quartz and the silicates were removed by leaching the carbonaceous material (ground in a silica mortar to -100 μm) with 60% HF in a plastic container. When the sample had been leached for 2 days, it was filtered and the residue was treated with concentrated H_2SO_4 to dissolve the insoluble aluminium fluoride compound formed. Fresh HF was added to the sample after H_2SO_4 treatment and the leaching resumed. Leaching proceeded until no silicates were observed. The sample was finally leached with concentrated

HNO_3 to remove any sulphide impurities. The sample was thoroughly washed, dried and analysed with X-ray diffractometer, using Co-K_α radiation. The diffraction data are summarised in Table 1.5 (see page 52)

(b) Analysis of the organic carbon and organic compounds associated with the carbonaceous matter.

A sample of the carbonaceous material was pulverised in a stainless steel pot and divided into two. One portion was treated with dilute HCl to remove any inorganic carbonate and the sample was analysed on a Perkin-Elmer elemental analyser, model 240 for organic carbon and nitrogen.

The remaining portion of the sample was treated with benzene and benzene/methanol azeotrope in succession to extract any organic compounds associated with the carbon. The extraction was carried out by the Oil Technology Department of the Royal School of Mines on a weighed amount of sample placed in a porous container and put into an extraction apparatus made of "Pyrex". The extractant was placed in a compartment below the sample container. When the extractant was heated to its boiling point, the vapour condensed above the sample, percolated through it and extracted any soluble organic compounds into the boiling extractant below. This recycling process went on for several days until the extraction was assumed to be complete and the extract was removed and the volume of the extract was reduced by heating in another apparatus. The extract was finally transferred into a test tube and the remaining extractant evaporated on a water-bath.

The two organic extracts obtained with benzene and benzene/methanol azeotrope were hard, pale brown materials. Each extract was dissolved in CCl_4 and examined with a Perkin-Elmer infra-red spectrometer, model 157 using the NaCl disc technique.

The results of the elemental analysis and the infra-red spectra of the extracts are shown in Table 1.6 and Fig.1.4 respectively (see pages 53 and 54).

1.2.3. Mineralogical examination.

1.2.3.1 X-ray diffraction analysis.

The X-ray scan on hand-picked pulverised carbonaceous material was carried out by the Analytical Services of the Metallurgy Department. Quartz, sericite, albite, chlorite and ankerite (Fe-dolomite) were identified. The identification of the minerals was done by comparing the d-spacing values and the corresponding relative intensities of the unknown minerals with the d-spacing values and the relative intensities of known minerals in the standard X-ray diffraction data book. The X-ray diffraction patterns for the minerals in the carbonaceous material compared with minerals of similar X-ray data are tabulated in Tables 1.7 - 1.10 (pages 56 & 58).

1.2.3.2 Chemical analysis.

The type of ankerite was determined by analysing liberated grains of carbonate, by dissolving a known weight of the carbonate grains in 1 M HCl and the amounts of Fe, Ca and Mg present were determined with the atomic absorption spectrophotometer. The ratio of Ca:Mg:Fe was 1:2:1. This ratio is similar to that for ordinary ankerite.

1.2.3.3 Microscopic examination.

Microscopic examinations of the screen fractions, dense medium fractions (described in 1.2.3.5) and hand-picked polished specimens were carried out. From the liberation study, it was observed that the minerals were sufficiently liberated at -100 µm + 75 µm size. For this reason, 500 g of -100 µm + 75 µm size of the ore was separated with tetrabromethane (TBE) of specific gravity (s.g.) 2.7 into float and sink and the minerals in the two fractions were identified and counted. The float consisted mainly of quartz, carbonaceous material associated with sericite, feldspar, chlorite and some carbonates. The quartz and the carbonates appeared well liberated but the sericite, chlorite, feldspar and the carbonaceous material phases were not clearly distinguishable and were thus considered a phase in point counting.

The sink fraction consisting of the sulphide minerals, was similarly examined and the pyrite, pyrrhotite, arseno-pyrite, chalcopyrite and sphalerite grains counted. Because the amount of other sulphide minerals present was small, the identification of the phases of tetrahedrite, bournonite, boulangerite, galena was carried out with the electron probe micro-analyser. The amounts of the sulphide minerals in the ore were therefore calculated from the data of the chemical analysis and grain counting. The results showing the relative abundance of the minerals in the ore are summarised in Table 1.11 (page 60).

Microscopic examination of polished specimens containing visible gold associated with other minerals was also carried out.

1.2.3.4 Electron probe micro-analysis.

The electron probe micro-analyser was employed for the determination of the sulphide minerals and the composition of the native gold in the ore. Polished briquettes of the sulphide concentrates and polished hand-picked specimens with visible gold were carbon coated and the phases and the composition of the sulphides and the gold were determined by the X-ray signal scan for the elements constituting the mineral phases. Sulphide minerals, especially bournonite, boulangerite, galena, sphalerite, tetrahedrite and the minor and trace elements e.g. Ag, Cu, Pb, Zn, Hg and Te in the gold were determined. Table 1.12 (page 70) shows the elements which alloyed with the native gold.

1.2.3.5 Heavy medium separation.

1470 g of -1200 μm size sample of the ore was wet-screened with B.S.S. of sizes ranging from 14 mesh to 200 mesh. Each size fraction was weighed and separated with TBE of s.g. adjusted to 2.7, into float and sink. The float and sink of each size fraction were analysed with the atomic absorption spectrophotometer for gold, copper, lead, zinc, arsenic, iron, antimony and manganese , as described earlier. The grades and distribution of gold and the other elements are shown in Tables 1.13-1.16 & Fig.1.5.

1.2.3.6 X-ray micrographic techniques for the detection of gold.

It was thought that X-ray micrographic technique could be suitable for the detection of gold, a high atomic number mineral, in a matrix of carbon, a low atomic number mineral. By choice of a suitable type of X-ray and other factors, gold in the carbonaceous matter would absorb the X-ray whereas the carbon would be almost transparent to the X-ray. This technique was used in an attempt to determine the presence

of gold in the carbonaceous matter.

The general procedure for the tests was similar to that outlined by Cohen and Schloegl [35]. A series of X-ray micrographs of the carbonaceous matter was taken using tungsten and cobalt targets, and examined under the microscope for the presence of gold particles. But because of poor resolution and the low gold content, no satisfactory information was obtained about the nature of the gold in the carbonaceous matter.

1.3. Results

The minerals identified with the various techniques are tabulated in Table 1.11. These minerals have been divided into two groups, namely, the gangue and the ore minerals.

1.3.1. Gangue minerals

1.3.1.1 Quartz, the most abundant mineral in the ore, forms the matrix of all the other minerals. As shown in Table 1.11, it constitutes about 67% of the ore. Under the microscope at least two generations of quartz were observed. In some polished specimens the "primary" quartz showed signs of deformation and cracks.Some of the cracks were filled with recrystallised quartz which carried sulphide minerals that showed unidirectional orientation. The "secondary" quartz was granular or crypto-crystalline. These two types of quartz may probably have differences in their rate of fracture under conditions of comminution. In some polished sections quartz, carbonaceous matter, sericite and chlorite had been schistosed. The tendency for the minerals, especially the sulphides which occurred in the bands, was to align parallel to the schistocity (Plate 1.1). It was observed that the two



Plate 1.1 Arsenopyrite (white) aligned almost parallel in quartz (grey) matrix. The dark spots are carbonaceous matter.

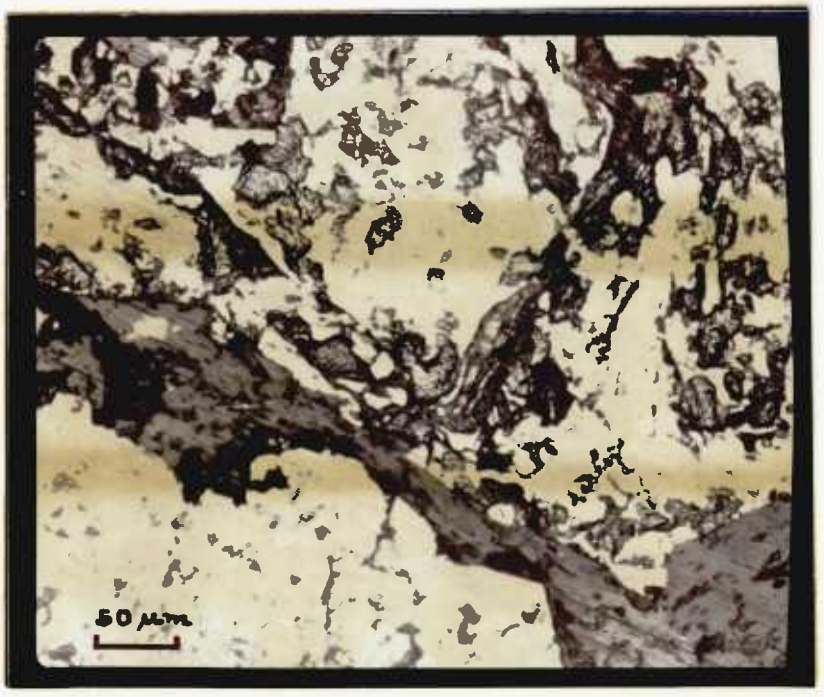


Plate 1.2 Corroded pyrite (white) in quartz.

generations of quartz carried gold, as pointed out by Cooper[26] and Barko[28].

1.3.1.2 Carbonaceous matter.

(a) The carbonaceous matter forms about 4% of the ore. From the microscopic examination and X-ray analysis, it was observed that it was intimately associated with sericite, chlorite, quartz and to a less extent with the carbonates and pyrite and arsenopyrite. Gold associated with the carbonaceous matter was about 0.63 g Au/t and accounted for 0.03% of the total gold. Gold in the carbonaceous matter is said to be rounded or elongated and coated with carbon[28]. In the present investigation it was observed that gold in the carbonaceous matter was coated with carbon.

Recent work in South Africa[36] on the carbon in the gold reefs of the Witwatersrand which is almost similar to this carbon, has shown that at least some of the gold in that carbonaceous matter might have been redeposited by plants.

Although data so far gathered about the nature of gold in Prestea carbonaceous matter is inadequate, it is reasonable to suppose that dissolved gold in the ore can be absorbed by the carbon and redeposited presumably as finely divided particles which may be impossible to extract by a physical means.

That the carbon shows X-ray diffraction patterns (Table 1.5) indicates that, at least part of the carbon is crystalline (graphitic). The characteristic diffraction patterns exhibited are mainly of the basal planes corresponding to (002), (004) and (006) with the d-spacings similar to those of the basal planes of graphite. The diffraction due to other planes are less common.

Table 1.5 X-ray diffraction data for the crystalline carbon of the Prestea carbonaceous matter.

I/I_0	Co-K_α radiation d(Å)	(hkl)
100	3.36	002
4	2.13	100
12	2.03	101
42	1.678	004
4	1.120	006

Preliminary adsorption tests have shown that the carbon in the native state has adsorbent properties and that it adsorbed dissolved gold from auric chloride solution to an amount of 0.18 g Au/g at 22°C. The adsorption properties were lost when the carbon was heated above 600°C in air.

b) Chemical and infra-red analysis of the carbonaceous matter

The results of the elemental analysis and the amount of the organic extracts are summarised in Table 1.6. The results show that the organic carbon constituted about 2.47%, nitrogen about 0.16% and the organic compounds about 0.067% of the carbonaceous material. The organic extracts were pale brown liquids which became hard when dry. Figure 1.4 shows the infra-red spectral frequencies of the benzene and benzene/methanol azeotrope extracts respectively. The benzene extract showed absorption peaks at 2950, 2850, 1465 cm^{-1}

and 1380 cm^{-1} while the benzene/methanol azeotrope showed absorption peaks at 2950 cm^{-1}, 2850 cm^{-1}, 1745 cm^{-1}, 1450 cm^{-1} and 1410 cm^{-1}. The absorption peaks at 2950 cm^{-1}, 2850 cm^{-1} are characteristic of CH_3 stretching frequencies while 1465 cm^{-1} and 1380 cm^{-1} are characteristic of CH_3 scissor vibration frequencies. These spectral frequency peaks are characteristic of alkanes. The characteristic frequencies for the benzene/methanol azeotrope extract included 1745 cm^{-1} , 1450 cm^{-1} and 1410 cm^{-1} which are characteristic of carbonyl groups. From these spectral data, the most probable compounds in the extract are long-chain alkanes and carboxylic acids. It is to be noted that there was absence of N-H characteristic frequency in spite of the presence of nitrogen in the carbonaceous matter.

Table 1.6 The constituents of Prestea carbonaceous matter.

Constituents of the carbonaceous matter.	% Weight
organic carbon	2.47
nitrogen	0.16
sulphur	--
organic compounds	0.067

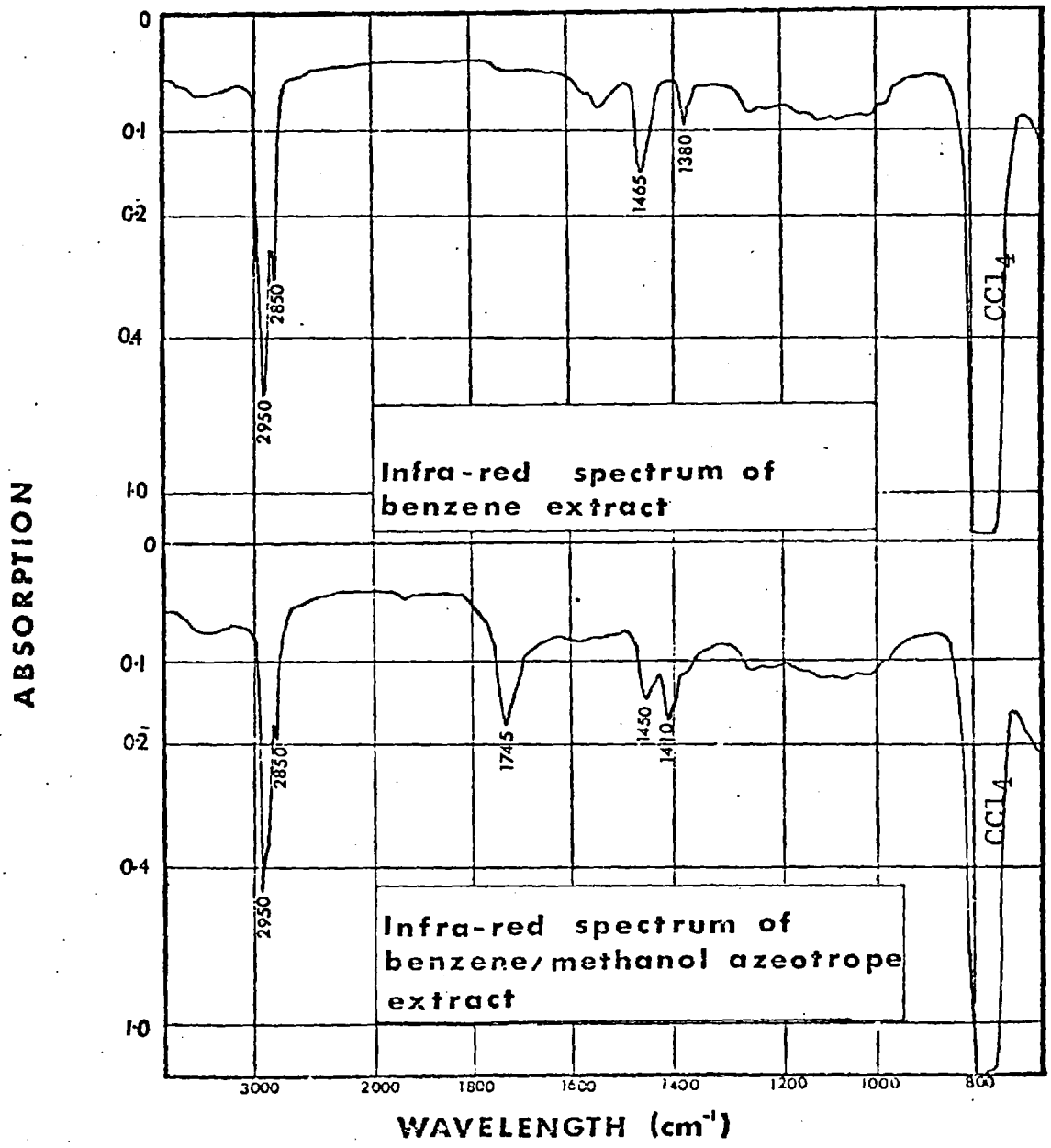


Fig. 1.4 Infra-red spectra of (a) benzene (b) benzene/ methanol azeotrope extracts of the Prestea carbonaceous matter in CCl_4

1.3.1.3 Sericite, $\{KAl_2(Si_3Al)O_{10}(OH,F)_2\}$ In polished sections sericite occurred as a single mineral in quartz, or cut across both "primary and secondary" quartz and pyrite, or as fine micaceous mineral intimately associated with the carbonaceous matter and chlorite. It was easily identified with X-ray diffraction by its characteristic basal diffraction peaks at d(001) = 9.976 Å as shown in Table 1.7. Barko[28] stated that sericite occurred generally with quartz crystals and in the phyllites but did not seem to infiltrate quartz. In the present microscopic examination, however, it was observed that sericite cut across quartz crystals and pyrite. Although Cooper and Barko indicated that gold was associated with sericite, in the present work no gold was observed in a sericite flake. Instead, dark fine minerals (about a few micrometers in size), probably carbon or limonite were often attached to or included in the sericite flakes.

Green sericite in the Prestea ore was reported to carry gold and had been used by geologists as gold indicator. The importance of the green sericite was first observed by Skeats[37] in 1903. Recently Barko[28] pointed out that the distribution and association of the green sericite with gold was so irregular that it could not be used successfully as gold indicator.

1.3.1.4 Plagioclase and chlorite.

The presence of plagioclase was easily detected with X-ray diffraction by the characteristic diffraction peaks at d=6.37 Å and d = 3.19 Å. These X-ray diffraction data are similar to those of albite, as shown in Table 1.8. In some polished sections the plagioclase showed intergrowths with quartz or was imbedded in the carbonaceous material.

Table 1.7 X-ray diffraction pattern for sericite in the ore as compared with that for muscovite (7-42) 3T type.

"Sericite" in Prestea ore		Muscovite (7-42) 3T type	
d(Å)	I/I_1	d(Å)	I/I_1
9.976	100	9.97	100
4.988	50	4.99	53
		4.49	19
4.462	21	4.46	10
3.864	9	3.873	10
3.478	10	3.59	8
3.342	100 + qtz	3.31	100
2.991	21	2.884	16
2.559	16	2.589	15
1.996	20	1.992	17

Table 1.8 X-ray powder diffraction data for plagioclase in the Prestea ore as compared with that for albite (9-466)

Plagioclase in Prestea Ore		Albite 9-466	
d(Å)	I/I_1	d(Å)	I/I_1
6.371	21	6.39	20
4.022	17	4.030	15
3.767	20	3.780	25
		3.684	20
3.652	19	3.663	15
		3.509	10
		3.375	7
3.190	100	3.196	100
2.929	17	2.933	15

The plagioclase was reported to have some micaceous inclusions[28] and was believed by Cooper and many other geologists that it was the plagioclase that was altered by metamorphism to form sericite. Association of gold with it was not observed.

Chlorite (Mg,Al silicate) was identified under the microscope by its green colour and with X-ray diffraction by its characteristic diffraction peaks at d(001)=14.029 Å and d(002)= 7.053 Å as shown in Table 1.9. It was common to find it in quartz, in carbonaceous material, and with the plagioclase. Unlike many other chlorites, the chlorite in this ore appeared to be deficient in magnesium. Association of gold with the chlorite was not observed nor had it ever been reported.

1.3.1.5 Carbonates.

In polished sections the carbonates were found associated with the carbonaceous matter, sericite and quartz. X-ray diffraction and chemical analysis indicated that the carbonate present is similar to ankerite. The X-ray diffraction data for the carbonate are shown in Table 1.10. Some pyrite and arsenopyrite grains occurred in the carbonate and were cemented together by it. Barko and Cooper reported the presence of calcite and a mixture of iron and magnesium carbonates in addition. Association of the carbonate with gold was not observed.

The carbonate, sericite, chlorite and plagioclase made up about 26% of the ore, and, being relatively soft, may not present serious comminution problems.

Table 1.9

X-ray powder diffraction data for chlorite in the Prestea ore as compared with that for Bavalite chlorite (12-88).

Chlorite in Prestea ore		Bavalite Chlorite 7 - 166	
d(Å)	I/I_1	d(Å)	I/I_1
14.029	40	14.0	60
7.053	100	7.08	100
4.695	45	4.681	30
3.525	58	3.523	50
		2.821	10
2.385	14	2.405	20

Table 1.10

X-ray diffraction pattern for ankerite in the ore as compared with that for ankerite (12-88).

Carbonate in Prestea ore		Ankerite (12 - 88) $Ca(Mg,Fe)(CO_3)_2$	
d(Å)	I/I_1	d(Å)	I/I_1
2.891	100	2.89	100
		2.685	3
		2.552	1
		2.441	3
2.189	15	2.199	6
1.783	20		
1.430			

1.3.2. Ore minerals.

Sulphide minerals, though constituting not more than 3% of the ore, are very important as gold carriers. Table 1.11 summarises the sulphide minerals identified and their relative abundance. Pyrite and arsenopyrite make up about 95% of the sulphide minerals. Of the rest, the copper-bearing minerals are predominant. The sulphide minerals identified are as follows:-

1.3.2.1 Pyrite (FeS_2)

Pyrite forms about 57% of the sulphide minerals and about 1.3% of the ore. It was the most corroded sulphide mineral (Plate 1.2). Where the corrosion was complete a void remained or was filled with other sulphide minerals. Pyrite is widely dispersed in the ore and occurs in the cracks of quartz, in the carbonaceous and sericitic bands with carbonates. Intergrowths of boulangerite, chalcopyrite and arsenopyrite are common in pyrite. Gold of various sizes ranging from 500 μm to sub-microscopic was observed as crack-fillings or as locked-up grains in it (Plate 1.3). The presence of Cu, Pb, Zn detected in pyrite might probably be due to substitution or impurities.

1.3.2.2 Arsenopyrite (FeAsS)

Arsenopyrite is the second most abundant sulphide mineral and constitutes about 38% of the sulphides and about 0.9% of the ore. In polished sections it appeared white to dull cream. It commonly showed rhombic, elongated, rectangular and triangular forms. Though an anisotropic crystal, some of the rectangular forms exhibited isotropism. Some of the large crystals contained chalcopyrite intergrowths. Arsenopyrite also occurred in carbonaceous and sericitic

Table 1.11

Relative abundance of minerals in the Prestea ore.

Mineral	% Wt. of ore	% sulphide
quartz	67.0	
sericite, chlorite } feldspar, carbonate etc }	26.0	
carbonaceous material	4	
Pyrite, pyrrhotite, limonite (calc)	1.43	57.23
arsenopyrite, FeAsS "	0.96	38.27
chalcopyrite, $CuFeS_2$ "	0.018	0.72
bournonite, $PbCuSb_3S$ "	0.018	0.72
boulangerite, $Pb_5Sb_4S_{11}$ "	0.016	0.64
sphalerite, ZnS "	0.030	1.20
galena, PbS "	0.006	0.22
tetrahedrite-tennantite "	0.025	1.00

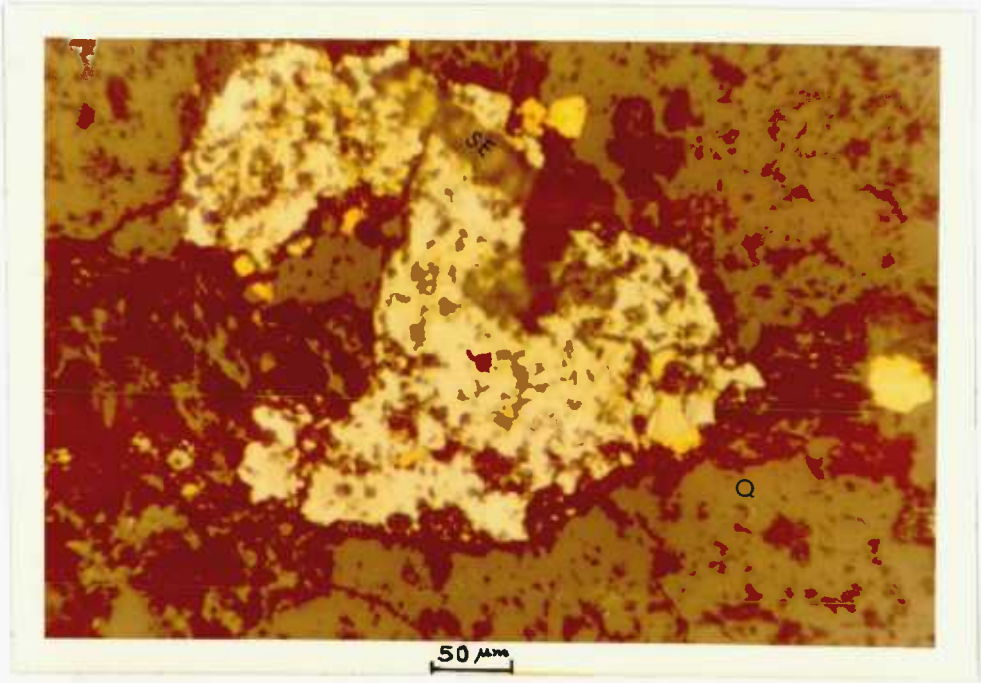


Plate 1.3 Gold (yellow) disseminated in pyrite (pale yellow) and quartz (Q) with sericite (SE) cutting across the pyrite; dark spots are carbonaceous matter.

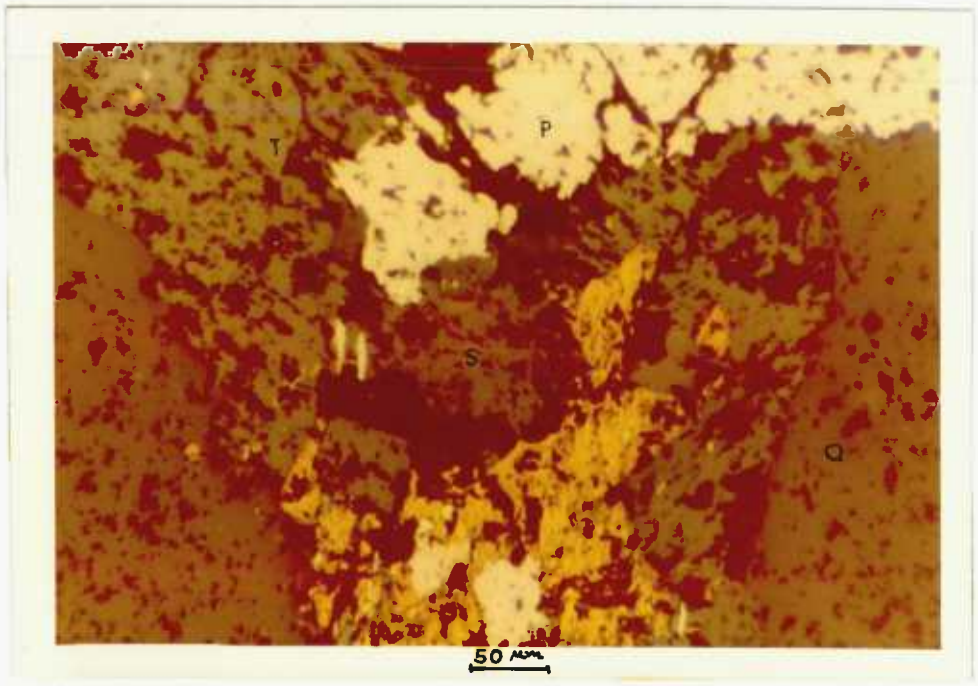


Plate 1.4 Chalcopyrite (dirty yellow) associated with tetrahedrite (T) and sphalerite (S).

bands and orientated parallel to the schistosity. Gold of various sizes, particularly the fine sizes, formed inclusions in arsenopyrite. Below 75 μm, gold was often observed attached to arsenopyrite or included in it.

1.3.2.3 Limonite, ($Fe_2O_3nH_2O$) and Pyrrhotite, ($Fe_{1-x}S$)

Limonite was identified by its yellowish-brown colour and magnetic nature. In polished sections it was found with corroded pyrite, carbonaceous matter, sericite and as fine (less than -10 μm) particles in the carbonates. Where gold occurred in corroded pyrite, the gold was rimmed with limonite.

Pyrrhotite was associated with pyrite, but unlike pyrite it is magnetic and dirty-brown. In the polished sections examined only a few grains were observed.

1.3.2.4 Chalcopyrite (CuFeS)

Chalcopyrite forms about 0.7% of the sulphide minerals. Although it is orthorhombic or tetragonal, it did not show well-defined crystal forms in the polished sections examined. It has a yellowish-brown colour and high reflectivity. But in contact with gold it appeared as a dirty brown mineral. It was found often associated with pyrite, arsenopyrite and sphalerite (Plate 1.4).

Gold was observed locked up in chalcopyrite. The presence of traces of gold in chalcopyrite was reported by Barko though he did not observe any microscopic size gold in it. These observations confirmed that chalcopyrite contained gold in microscopic to sub-microscopic sizes.

1.3.2.5 Copper-bearing sulphide minerals.

Minerals identified in this group include the tetrahedrite-tennantite series, $(Cu, Fe, Zn)_{12}Sb_4S_{13}$-$(Cu, Fe, Zn)As_4S_{13}$ and bournonite, $PbCuSbS_3$.(The formula for tetrahedrite-

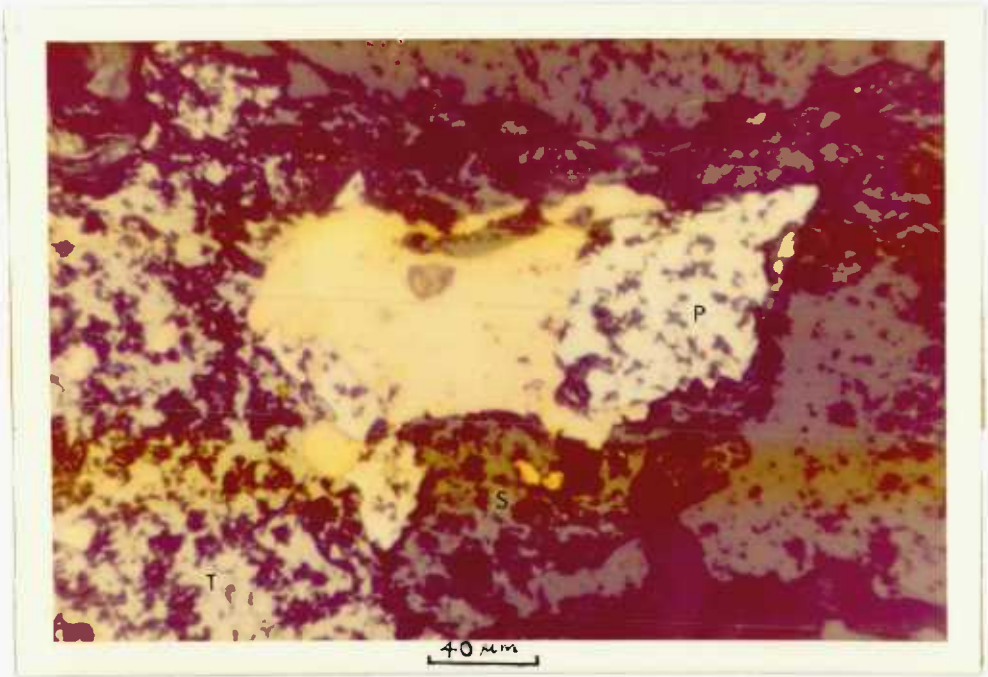


Plate 1.5 Gold (yellow) in tetrahedrite (T), sphalerite (S) and pyrite (P) ; all in quartz matrix.

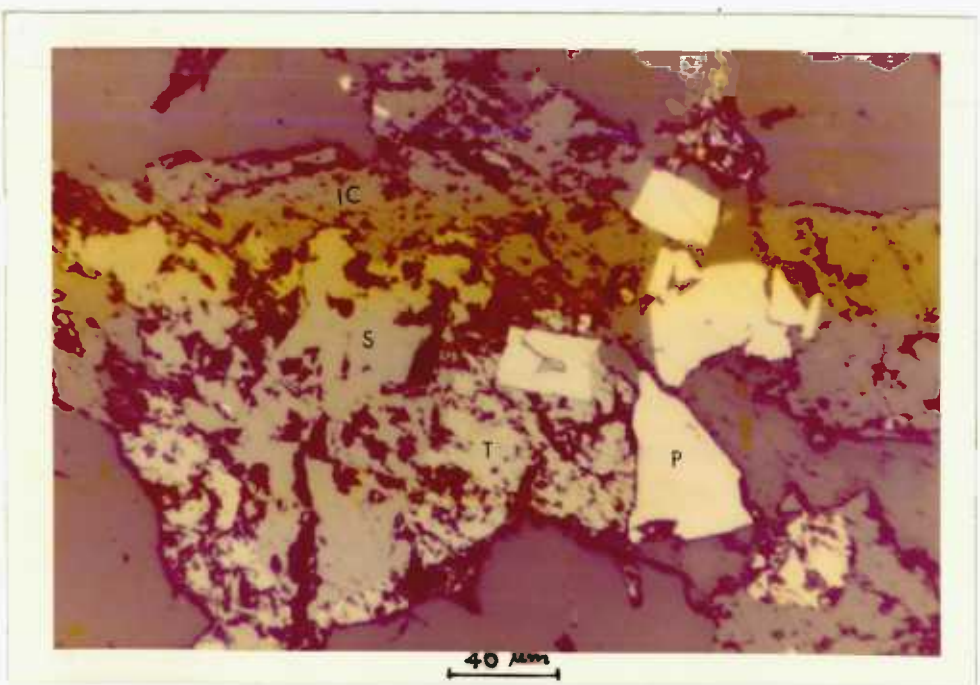


Plate 1.6 Association of sphalerite (S) with tetrahedrite (T), pyrite (P), chalcopyrite (yellow) and iron carbonate (IC).

tennantite series is in accordance with that suggested by Uytenbogaardt and Burke[38]). The end members of this series do not seem to appear in nature. It is not surprising that the minerals of this series identified were intermediate of the end-members. The mineral referred to as tetrahedrite in this work is intermediate of the end members. Tetrahedrites with possible compositions of $(Cu,Fe,Zn)_{12}\cdot Sb_xAs_yS_{13}$ and $(Cu,Fe)Sb_xAs_yS_{13}$ were detected. In Plate 1.5 the gold is in corroded tetrahedrite with the possible composition of $(Cu,Fe,Zn)_{12}Sb_xAs_yS_{13}$. Traces of Hg, Pb and Te were common in this group of solid solutions. Tetrahedrite is cubic and has various colours depending on the elemental substitution. Those identified were grey to dull grey.

Bournonite constituted about 0.7% of the sulphide minerals. It appeared to be associated with tetrahedrite and sphalerite. Although gold could occur in it, its direct association with gold was not observed.

1.3.2.6 Boulangerite ($Pb_5Sb_4S_{11}$).

The amount of boulangerite in the ore was about 0.02% and about 0.6% of the sulphides; thus it was not commonly distributed in the ore. In some specimens it was associated with pyrite, arsenopyrite and sphalerite. It was dull cream and under the crossed Nicols it was anisotropic grey to brown.

1.3.2.7 Sphalerite,(ZnS) and galena (PbS).

Sphalerite is the most abundant zinc bearing mineral in the ore and about 1.2% of the sulphide minerals. In the -100 μm + 75 μm size fraction of the sink of the heavy medium, a few grains were identified by their greenish grey streaks. In some polished sections it occurred with pyrite,

arsenopyrite, and chalcopyrite. Plate 1.5 also shows gold associated with sphalerite and in Plates 1.4 and 1.6 sphalerite is associated with the other sulphides minerals.

The amount of galena in the ore was very small and in the dense medium concentrate only a few grains were observed. In polished sections it showed perfect cubic crystals with its characteristic pits. Its association with gold was not observed, possibly because it was uncommon.

1.3.2.8 The occurrence and distribution of gold.

(a) Gold was studied in polished sections with a Zeiss Ultraphot microscope. Although gold is cubic and isotropic, the gold in this ore is strongly anisotropic with greenish yellow stripes and tints. Its microhardness ranges from 48-50 in comparison with the standard hardness of 51 from Vickers hardness table. The mineralogical examination showed that gold was associated with nearly all the minerals in the ore in various forms and sizes. About 52% or more of the gold occurs in the gangue and the rest occurs in the sulphide minerals (Table 1.15). Quartz probably carried over 99% of the gold in the gangue. Most of the gold in the sulphides was associated with pyrite and arsenopyrite which form about 95% of the sulphides minerals. Pyrite and arsenopyrite may carry over 90% of the gold in the sulphides. The rest of the gold is associated with tetrahedrite, chalcopyrite, bournonite, boulangerite and sphalerite.

(b) Association of gold with the gangue minerals.

Gold occurs in sizes ranging from over 1 cm to sub-microscopic in quartz. Although it has a cubic crystal structure, it was never found in such a form; instead it occurs as dendritic, lenticular, euhedral and anhedral.

Gold tends to be elongated and orientated parallel to the lamination in the elaminated zones of the quartz. The orientation may indicate the effect of directional force in the rock. Gold did not appear to be confined to any particular generation of quartz. It was stated by Cooper[26] that the smoky quartz is barren in gold. Barko[28], however, observed that some of the smoky quartz contain free gold when fractured. Euhedral gold occurred in a matrix of carbonaceous matter and sericite. In the carbonaceous matter the gold was heavily coated. Although the association of gold with green sericite has been reported, the actual occurrence of gold in the sericite flake was not observed. This is also true of the carbonates, chlorite and albite. Plates 1.7 & 1.8 show the occurrence of gold in quartz.

(c) Association of gold with the sulphide minerals.

Gold was found associated with nearly all the sulphide minerals ranging from microscopic to sub-microscopic sizes . In pyrite, gold occurs in sizes greater than 100 μm to 1 μm. Some of the pyrite grains have traces of gold which may probably be sub-microscopic. Where the pyrite was oxidized around the gold, a thin coating of limonite remained around it.

Finely divided gold was often seen locked up in arsenopyrite and even after grinding to -50 μm, gold was still attached to arsenopyrite (Plates 1.9 & 1.10). From the examination of many polished sections and ground ore size fractions it appeared that more fine gold was locked up in arsenopyrite than any other sulphide, except perhaps pyrite. The presence of gold in chalcopyrite and tetrahedrite, as well as its association with boulangerite, and sphalerite was observed.

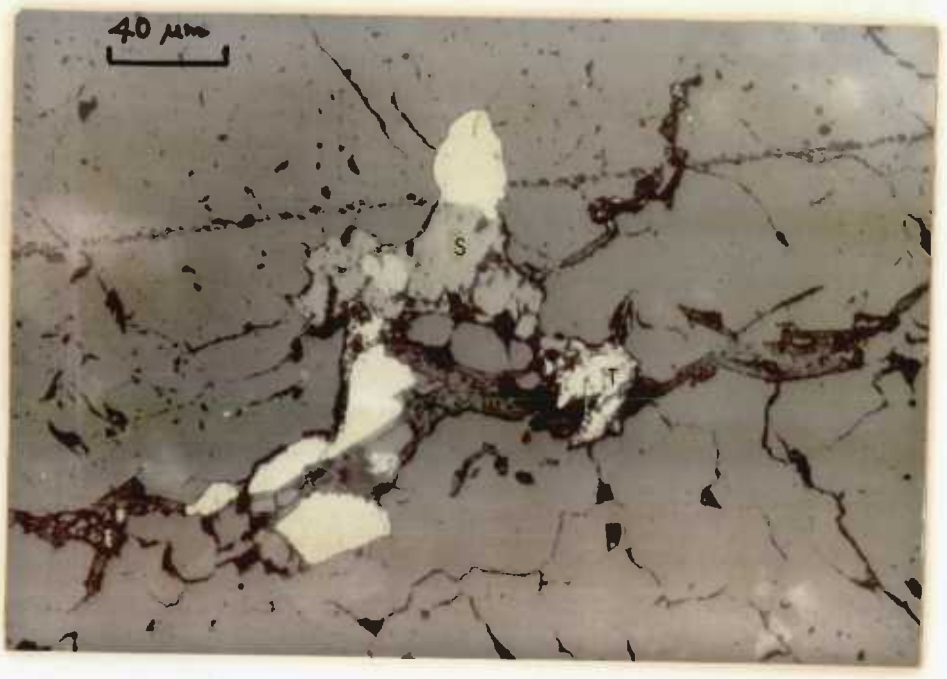


Plate 1.7 Gold (white), sphalerite (S) and tetrahedrite in the cracks of quartz.

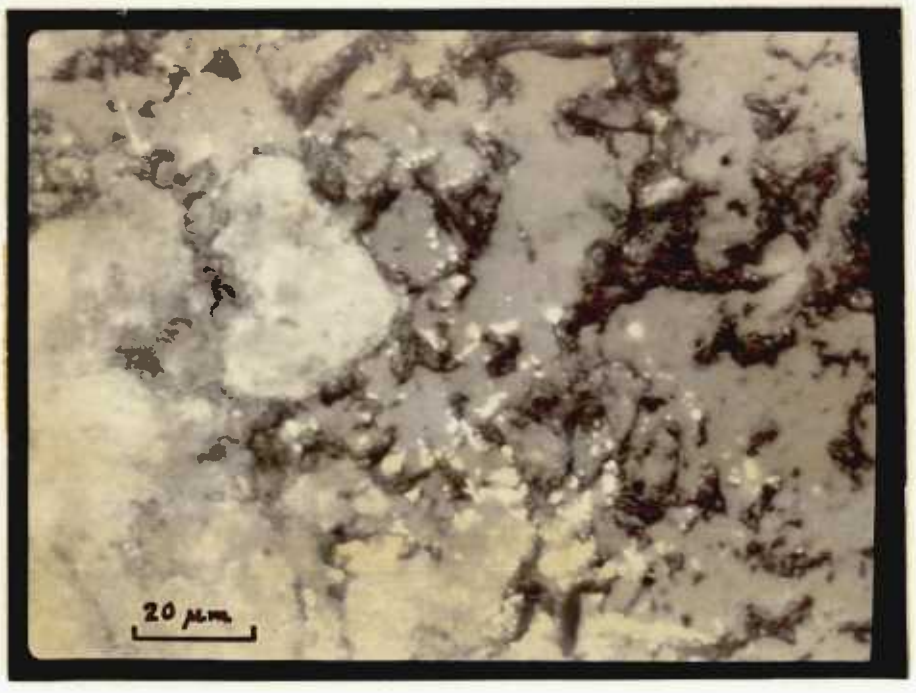


Plate 1.8 Finely divided gold (white) in quartz.



Plate 1.9 Gold (white) in arsenopyrite (grey) and quartz (dark).



Plate 1.10 Gold (white) not fully liberated from arsenopyrite (grey).

(d) Nature of the gold in the ore.

Chemical analysis and electron probe micro-analysis of the native gold indicated the presence of silver as a minor element in all specimens, and Cu, Pb as common trace elements while Zn, Hg and Te as occasional trace elements (Table 1.12). The analyses show that the native gold was made up of about 90% or more gold and about 1-10% of silver with the trace elements making up the remaining amount. Thus native gold in the ore is alloyed with Ag, Cu, Pb, Zn Hg, and Te. It can be anticipated that the presence of these less noble metals would almost certainly influence the surface chemical properties of the gold in flotation and cyanide leaching.

1.3.2.9 Liberation study of gold.

The results of the distribution of gold in the size fractions are summarised in Table 1.15 and Fig.1.5. They show that the size fractions with specific gravity greater than 2.7 formed about 19% of the total ore and contained 52% of the gold. At -104 μm + 75 μm size about 94% of the gold reported in the sink fraction. It appears that at sizes less than 104 μm, the greater part of the gold in the quartz would have been liberated and that about 94% of it would be partly free or locked up in the sulphide minerals. The low recovery of gold in the -75 μm size may certainly be due to poor separation of the heavy minerals by the heavy medium.

Attempts were made to improve the separation in the -75 μm size by dispersing the ore in methanol and introducing it into the column of the TBE (s.g. = 2.7) and shaking it ultrasonically; but the result was similar to subsizing rather than by separation according to differences in densities.

Table 1.12 The nature of the Prestea gold.

Mineral	Major element ≮ 90%	Minor element 1-10%	Trace element
gold	Au	Ag	Cu, Pb, Hg
"	Au	Ag	Cu,Pb,Te,Zn
"	Au	Ag,Zn	Pb
"	Au	--	Cu
"	Au	--	Ag,Pb,Cu,Zn
"	Au	Ag	Cu,Pb,Zn

Table 1.13 Screen analysis of the -1.2 mm fraction of the Prestea ore showing the distribution gold to the size fraction.

Size B.S.M.	% wt.	Grade (g Au/t)	% Au Distribution
+ 14	30.50	5.0	18.58
- 14 + 18	13.70	7.4	12.35
- 18 + 25	9.80	6.2	7.40
- 25 + 36	8.40	8.5	8.70
- 36 + 52	5.90	15.0	10.79
- 52 + 72	5.00	9.0	5.48
- 72 + 100	4.70	16.4	9.39
- 100 + 150	4.50	10.4	5.70
- 150 + 200	3.30	14.4	5.79
- 200	14.20	9.0	15.82
		Av. 8.2	100.00

Table 1.14 Dense medium separation of -1.2 mm ore into float and sink. (s.g. of medium = 2.7)

Size B.S.M.	% Wt.		% Wt. of percentage wt. size fraction.		
	Float	Sink	Float	Sink	Total
+14	85.70	14.30	26.14	4.36	30.50
-14 + 18	65.95	34.05	9.04	4.66	13.70
-18 + 25	70.30	29.70	6.87	2.93	9.80
-25 + 36	75.28	24.72	6.32	2.08	8.40
-36 + 52	76.69	23.31	4.52	1.38	5.90
-52 + 72	77.37	22.63	3.87	1.13	5.00
-72 +100	77.52	22.48	3.64	1.06	4.70
-100 +150	87.76	12.24	3.95	0.55	4.50
-150 +200	88.33	11.67	2.91	0.39	3.30
-200	97.00	3.00	13.77	0.43	14.20
	81.03	18.97	81.03	18.97	100.00

Table 1.15 Distribution of gold in the size fractions to the float and sink. (s.g. of medium = 2.7)

B.S.M. Size	Grade (g Au/t)				% Au Dist. in size fraction	
	Size fract.	Float	Sink	Calc.	Float	Sink
+14	5.0	8.00	10.00	8.28	82.74	17.26
-14 + 18	7.4	6.00	10.00	7.36	53.75	46.25
-18 + 25	6.2	5.00	17.10	8.59	40.90	59.10
-25 + 36	8.5	1.70	17.50	5.61	22.83	77.17
-36 + 52	15.0	2.00	27.50	7.94	19.31	80.69
-52 + 72	9.0	1.40	25.00	6.74	16.07	83.93
-72 +100	16.4	1.40	55.00	13.32	6.45	93.55
-100 +150	10.4	1.20	70.50	9.78	10.88	89.12
-150 +200	14.4	1.00	113.73	14.16	6.24	93.76
-200	9.0	6.66	32.96	7.46	86.73	13.27
Mean Grade	8.20	5.26	21.02	8.24	51.67	48.33

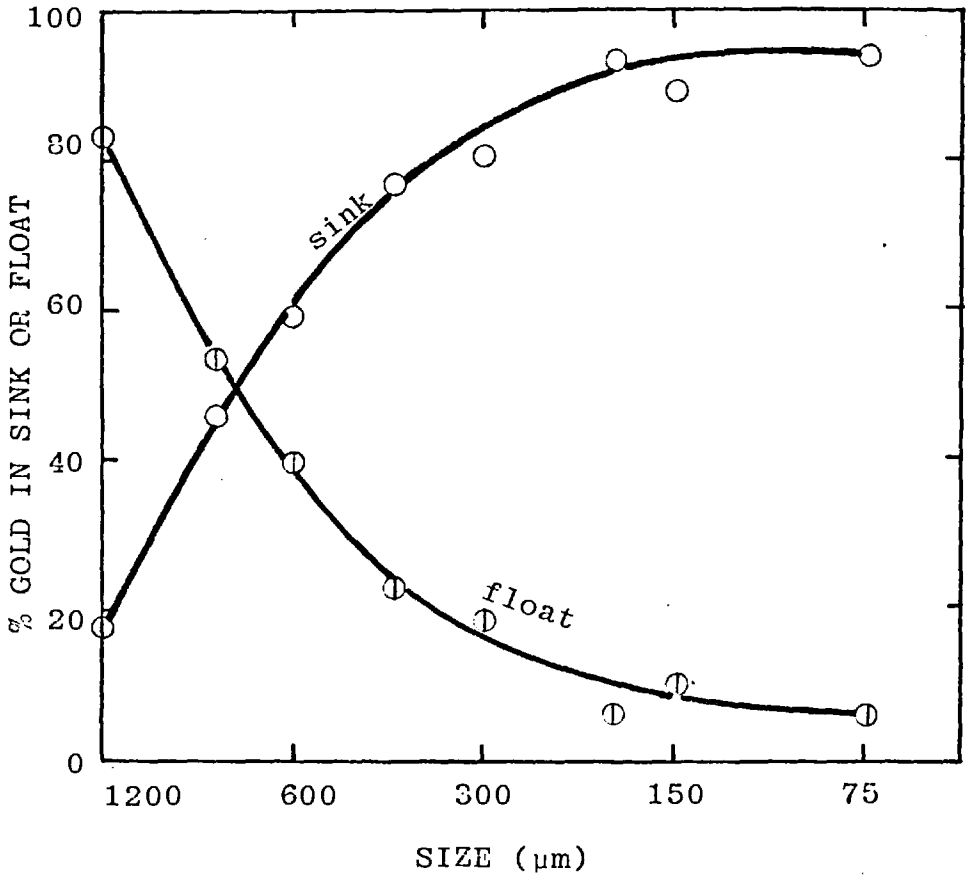


Fig.1.5 Distribution of gold to the sink and float fractions.

Table 1.16 Results of analysis for Au, Cu, Fe, Pb, Zn, As, Sb and Mn in the float and sink.(s.g.2.7)

B.S.M.	Float		% wt. sink							
Size	g.Au/t	% Fe	g.Au/t	Fe	Cu	Pb	Zn	As	Sb	Mn
+14	8.00	1.98	10.0	10.52	0.0532	0.0788	0.2033	3.30	0.075	0.175
-14 + 18	6.00	0.93	10.0	9.50	0.0470	0.0300	0.0176	1.10	0.050	0.051
-18 + 25	5.00	0.99	17.10	8.00	0.0400	0.0462	0.0974	0.95	0.050	0.135
-25 + 36	1.70	1.20	17.50	9.50	0.0540	0.0570	0.0974	1.77	0.060	0.149
-36 + 52	2.00	1.27	27.50	10.12	0.0575	0.0712	0.0712	1.77	0.060	0.164
-52 + 72	1.40	1.35	25.00	10.00	0.0740	0.0912	0.4284	2.12	0.070	0.206
-72 +100	1.10	1.10	55.00	10.62	0.1000	0.0570	0.1550	2.25	0.095	0.172
-100 +150	1.20	1.98	70.50	5.28	0.0450	0.0496	0.1048	0.95	0.050	0.130
-150 +200	1.00	1.20	113.00	9.09	0.1743	0.1137	0.3691	5.03	0.078	0.147
-200	6.66	3.20	32.96	9.88	0.0536	0.0840	0.2629	4.04	0.044	0.270
Mean	5.26	1.788	24.63	9.51	80.0561	0.0583	0.1845	1.97	0.0617	0.136
Calc.head assay	4.263	1.449	3.987	1.806	0.0110	0.0110	0.0185	0.374	0.0117	0.025
Head assay					0.0190	0.0140	0.0228	0.422	0.0130	0.030

1.4 Discussion of Results

1.4.1 The gold-bearing reef.

Evidence so far gathered [25,26] gives a strong indication that the gold-bearing reef, called the quartz reef, might be of a hydrothermal origin.That being the case, the quartz reef could be formed from an intrusive "solution" made of silica, gold and sulphide mineral forming ions or components. This gold-bearing solution might have invaded the contact between the upper and lower Birimian rocks which had been metamorphosed, braciated and faulted before and after the intrusion. In such a case, there could be the formation of such a secondary mineral like sericite from feldspar due to metamorphism and the assimilation and inclusion of part of the country rocks in the quartz vein.

The inclusion of the carbonaceous matter in the quartz vein[28], even though the carbonaceous matter is not considered to belong to the gold-bearing vein proper, may indicate the intrusive nature of the vein. The association of green sericite with gold as observed by Skeat[38] may be explained by the new evidence of sericite cutting across both "primary and secondary" quartz and pyrite. As gold occurs in nearly all the minerals it could be suggested that gold was one of the last minerals to form, an opinion held by many geologists. It is, therefore, possible that at least some of the sericite could be formed at the same time of gold mineralisation or later as a result of metamorphism of post mineralisation, so that sericite could not necessarily be found everywhere gold is found. Recently Barko[28] observed that there was a tendency for the formation of green sericite at the contact of some quartz veins and the country rock but that its distribution was

irregular and did not necessarily occur where gold was found.

The complexity of the ore and the association of gold with many minerals are indications of the complex geological history of the rocks.

1.4.2 Possible origin of the carbonaceous matter

An aspect of the carbonaceous matter that is still speculative is its origin. Hitherto, there exist two main theories about the origin of the carbon, namely, the formation of the carbon from gaseous and liquid hydrocarbons and from plant remains.

The recent work of Hallbauer[36] and still more recently the review by Feather and Koen[39] about the origin of the carbon in the Witwatersrand gold reefs, have pointed to the biogenic origin of that carbon. As the geology of the carbon-bearing rock in West Africa (where this carbonaceous matter is mined) is considered to be similar to that of the Witwatersrand, it would appear that the Prestea carbonaceous matter could also be of biogenic origin. But the apparent intrusive nature of the Prestea ore and the fact that the carbonaceous matter is confined generally to the peripheries of the gold-bearing veins appear to favour the hydrothermal origin of the carbon. However, detailed investigation is needed to substantiate any of these theories.

1.4.3 The refractoriness of the ore in processing.

As had been stated, gold occurred in the quartz, the carbonaceous matter and in the sulphides. But the presence of the carbonaceous matter and the sulphide minerals are the greatest concern in the processing of the ore, since they are the main causes of the "refractoriness" of the ore.

1.4.3.1 Carbonaceous matter.

The carbon of the carbonaceous matter is an active adsorbent of dissolved gold. Although the amount of gold in the carbonaceous matter is small (about 0.03% of the total gold) its adsorption of dissolved gold (e.g. from leach liquors) demands that the carbonaceous matter be removed before leaching the gold. The occurrence of free gold in the carbonaceous matter was seldom noted but nevertheless occurs. It is possible that the bulk of the gold in the carbonaceous matter might be sub-microscopic due, presumably, to diffusion of the gold-bearing fluid and adsorption of the dissolved gold. Such adsorbed gold may not be observed under the microscope on account of its small size. Merwin[40], working on a similar type of carbonaceous matter, reported that 90% of the gold in his ore was of particle sizes between 0.2 μm and 0.005 μm. If, therefore, the present carbonaceous matter contained sub-microscopic gold the disposal of it in the early processing stage would mean the loss of some amount of gold. But the present data show that the amount of gold associated with the carbonaceous matter is not great.

Another problem created by the presence of the carbonaceous matter is that of coating the gold and minerals which carry locked-up gold. In such instances there would be a real danger of losing appreciable amount of gold should the carbonaceous matter be got rid of by depressing it during flotation.

The only report on the nature of the carbonaceous matter was that of Feldtmann[27] who suggested that the carbonaceous matter was amorphous graphite. In the present work, the X-ray diffraction data of the pure carbon

show that at least a portion of the carbon is crystalline. The characteristic diffraction peaks of the crystalline carbon are those of the basal planes of (002), (004), and (006) at the d-spacing of 3.36 Å, 1.678 Å and 1.20 Å respectively. But as the carbon is an active adsorbent of dissolved gold, appears amorphous and burns easily in air above 600°C, it could be assumed that a substantial proportion of the carbon is non-graphitic or sub-crystalline. Sheiner and his co-workers[41] also reported the occurrence of similar type of carbonaceous matter comprising of graphite-type and activate carbon in the Carline carbonaceous ore of Nevada.

The analysis of the organic compounds associated with the activate carbon showed the possible presence of alkanes and carboxylic acids. There was no indication of the presence of N-H and -OH groups. However, the nitrogen in the carbonaceous matter might come partly from the organic compounds extracted and could be present in the chains of the organic compounds or could have formed a chelating compound with the carbonyl group as -CO-N-S, similar to that postulated by Scheiner and his co-workers[41]. The possibility that heterocyclic compounds with N in the ring could be present could not be ruled out. The organic compounds associated with the carbon did not appear to adsorb dissolved gold.

1.4.3.2 Sulphide minerals.

Like the activate carbon, the presence of sulphide minerals adds to refractoriness of the ore because gold occurs in various forms and sizes in the sulphides from which it is generally difficult to extract it. The association of gold with pyrite and arsenopyrite is most

common. It would therefore be expected that the occurrence of these minerals could lead to the occurrence of gold. Indeed geologists used the arsenic as an indicator for gold. But from the work of Barko and the present studies it appears that even though arsenopyrite carries gold, the presence of arsenopyrite does not necessarily indicate the occurrence of gold. It is possible that the amount of gold in arsenopyrite could decrease while it could increase in pyrite and the other minerals and vice versa. This may partly explain why, according to Barko, the increase in the grade of gold did not necessarily coincide with increase in arsenic. Instead, the increase in the grade of gold corresponded with increase in Cu, Fe, Pb, Zn, the constituent elements of the sulphide minerals in which the gold occurred. This result is in agreement with the present observation that gold occurs in nearly all the sulphide minerals. Consequently, a bulk flotation of the sulphide minerals is essential.

As there had not been any previous detailed work on the association of gold with other minerals in the ore at the time when the mines were shallow, it is difficult to know with certainty why it appears that the ore has become more refractory with increase in depth of the mines. It is only possible to make a suggestion based on the published work of Howat[29] and the present work. It seems possible that at lower levels in the mine, more unoxidized sulphide minerals carry gold, while at the higher levels the minerals might have been oxidized and the gold easier to liberate and leach. Scheiner and his co-workers[41] working on a similar type of carbonaceous ore containing no sulphides reported that the carbonaceous matter exposed to

the atmosphere was not activate and that it was easy to extract the gold from the ore by direct cyanidation. However, the carbonaceous ore at lower level was activate and the gold could not be extracted by direct cyanidation. It is, therefore, possible that in addition to the presence of more unoxidised sulphide minerals, carbon is also more activate at lower levels.

1.4.4 Liberation of gold and the processing of the ore.

Liberation of gold in the ore is a foremost consideration in processing the ore. As clear from the microscopic examination and liberation study, gold occurs as coarse to sub-microscopic in size. Coarse gold is liberated at about 75 μm size. The fine locked-up and sub-microscopic gold would then present the major problems in further treatment of the ore. While some locked-up fine gold would be liberated on finer grinding, the sub-microscopic gold might be hardly liberated and might remain insufficiently extracted even after roasting and extraction e.g. by cyanide leach. However, finer grinding as a way of liberating the locked-up gold should be considered but preferrably after the removal of the carbonaceous matter.

Because of the complexity of the ore and the difficulty in extracting the gold in the ore, the removal of the coarse gold immediately after grinding ahead of the subsequent processes would remain a necessity. In addition to the existing processes, namely, gravity concentration, flotation, roasting and cyanidation, finer grinding of the ore could be incorporated in the circuit after roasting prior to cyanidation.

Two ways of floating the ore could be considered;
(1) the flotation of gold and the sulphide minerals while depressing the carbon,
(2) bulk flotation of the gold, the sulphide minerals and the carbonaceous matter.

A preliminary flotation study of the ore in accordance with the above ways has been dealt with in Part III Chapter6 and the possible effect on the nature of the ore on processing the ore has been discussed in Chapter 8.

As a result of the present mineralogical work and other data available on the ore, the following statements could be made:-

1. That the ore may in future become more refractory or at best not easier to treat than it is at present.

2. That the occurrence of gold with other sulphides besides pyrite and arsenopyrite might be more common at lower levels in the mines.

3. That if the amount of gold in the pyrite and quartz decreased the ore would become more fractory.

4. That if the gold-to-silver ratio in the native gold decreased the rate of the cyanidation of the native gold would decrease as silver dissolves at a slower rate than gold.

1.5 Summary of Conclusions

1. The minerals identified in the Prestea carbonaceous gold ore comprise quartz, sericite, chlorite, albite, ankerite, activate carbon, pyrite, arsenopyrite, chalcopyrite, sphalerite, boulangerite, bournonite, tetrahedrite, pyrrhotite, limonite, galena and gold.
2. Gold is associated with nearly all the minerals and occurs in various forms and sizes ranging from over 1 mm in quartz to sub-microscopic sizes.
3. The presence of activate carbon and the sulphide minerals are responsible for the refractoriness of the ore. The refractoriness of the ore appears to increase with the depth of the mine.
4. The gold in the ore is alloyed with silver, copper, Pb, zinc, tellurium and mercury in various proportions. Silver formed the minor constituent while the other metals occur in trace amounts.
5. Major difficulties in extracting the gold would be encountered in the extraction of the fine locked-up and sub-microscopic gold in the refractory minerals.
6. It can be suggested that the essential processes for treating the ore should include gravity concentration, flotation, oxidation (i.e. roasting, chemical oxidation in solution), leaching and precipitation of the gold.

P A R T II

STUDIES OF THE SURFACE CHEMICAL PROPERTIES OF GOLD AND GRAPHITE.

General Introduction.

The occurrence of graphite or carbon in many ores is common. In certain gold ores where graphite or carbonaceous matter occurs, direct cyanidation of the gold has been employed successfully, as the carbon has no significant adsorption effect on the aurocyanide complex.

However, it had been shown in Part I of this thesis that the Prestea gold ore is complex, refractory and that its refractoriness is due to the presence of sulphide minerals and carbon which adsorbs dissolved gold. Possible processes for treating the ore, which include gravity concentration, flotation, oxidation, leaching and extraction of the gold from solution, were suggested. The successful extraction of the gold will depend on the pre-leaching processes. But as the associated carbon readily adsorbs dissolved gold, its removal from the ore prior to leaching is vital. Possible processes of removing the carbon could be by flotation, followed by roasting. For the purpose of the present work, flotation as a means of removing the carbon in the ore has been chosen. This demands that such properties of carbon that can be used to separate it from the gold and the gold-bearing minerals in the ore be studied.

Choice of materials and reagents.

Gold and carbon were chosen for detailed study because gold is the most important economic mineral in the ore, and the carbon, being an active adsorbent of dissolved gold, is undesirable. But because of the complexity of the carbonaceous matter, synthetic graphite from Hopkin and Williams Ltd. has been used in this part of the present study. There exist ,

nevertheless some similarities between the carbonaceous matter and the synthetic graphite. In the first place the carbonaceous matter has some graphitic nature (Part I) and secondly its adsorption of xanthate is similar to that of the synthetic graphite (Chapter 5). Although it is known that graphite does not adsorb dissolved gold, the mechanisms of its adsorption of xanthate and starch might be similar to the adsorption by the carbonaceous matter. There would be differences about the extent of their adsorption of these surfactants.

Among the thio-compounds, xanthates are generally employed as collectors in the flotation of sulphides because of their selectivity. Although some other thio-compounds, e.g. dithiocarbamate and dithiophosphate are also used as collectors for sulphides and metals, they are more expensive than the xanthates. For this reason and for the fact that xanthates are generally used for the flotation of gold ores, potassium xanthates were chosen as collectors for study. (The reactions of xanthates in aqueous solutions will be outlined in Chapter 4 in this part).

Starch and its derivatives have been used for depressing and flocculating many minerals, particularly the oxides and the silicates. However, little information exists about the extent of its effects on gold. The general view appears to be that starch adsorbs on minerals primarily through a hydrogen-bonding mechanism. But since it is generally held that the surface of gold is oxide free, it would be expected that starch and perhaps its derivates would not adsorb strongly on it, but their effect on graphite, which is known to have oxygen complexes on the surface, would be stronger. In the gold-graphite-xanthate-starch system,

therefore, it is expected that gold could be hydrophobic while graphite is rendered hydrophilic and could be separated from gold. This expectation was confirmed in the work that followed.

Scope of investigation

The work in Part II can be divided into two sections.

The first section comprises chapters 2 and 3, which deal with the wettability of gold and graphite in water and in aqueous solutions containing xanthate and starch. The work involved the investigation of the hydrophobicity or hydrophilicity of gold and graphite. In the case of graphite it has been established that it is naturally hydrophobic. In this work, therefore, the effects of xanthate and starch on the contact angles on graphite were most important. No consensus of opinion has so far emerged about the wettability of gold. In the present work, therefore, the wettability of gold was investigated using various techniques prior to the study of the effects of the surfactants on it.

The second section, which comprises chapters 4 and 5, is concerned with the study of the adsorption of xanthate, starch and dextrin on gold and graphite. The effects of time, pH and concentrations of the adsorbates on the extent of adsorption were investigated. Such factors as the nature of the adsorbed species, especially that of adsorbed xanthate on gold and graphite, were examined. In addition the following aspects were also considered in some cases.
1. the shape of the adsorption curves and fitting the curves to equations, 2. the significance of the adsorption limits or the plateau, 3. the extent to which the adsorbate was

adsorbed, 4. whether the adsorption was confined to single or double layer, 5. the orientation of the adsorbed molecule, 6. the existence of physical, chemical and electrochemical adsorption.

Water and reagents used.

Water used in all experiments was double distilled and referred to also as "conductivity" water. All acids and NaOH employed were of "Analar" grades.

CHAPTER 2

2. THE WETTABILITY OF GOLD

2.1 INTRODUCTION

2.1.1 Theoretical consideration

The hydrophobicity of gold is essential in its flotation. The results of the work carried out in this field have been contradictory and the controversy as to whether pure gold free from any impurities is hydrophobic or hydrophilic still remains. This is so because of the difficulty of preparing high purity gold free of inorganic and organic contaminations. Thus in the determination of contact angles on gold the question of the cleanliness of the surface remains the most difficult problem, as solids which are hydrophobic can be rendered hydrophilic by surface impurities and vice versa.

If a solid surface is hydrophobic, it simply means that water does not spread on it but stands on it to form drops; a contact angle can be measured at the three-phase boundary line. The resolution of forces at the three-phase boundary is expressed by Young's equation as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \qquad (1)$$

where γ_{SV}, γ_{SL}, γ_{LV} are the surface tensions at the solid-vapour, solid-liquid and liquid-vapour phases. However, if a drop of pure water is placed on a hydrophilic surface, it spreads spontaneously and exhibits a zero contact angle with the surface.

The wettability of a solid depends on the forces exerted on the liquid in contact with it. It is considered, therefore, that the basic factor in wettability is the free energy of

interaction between the liquid and the solid phases across the interfaces[42]. This energy is equal to the reversible work of adhesion, W_A. This work of adhesion between a liquid and a solid is represented by a sum of terms for different kinds of interactions, as follows,

$$W_A = W_A^d + W_A^h + W_A^\pi + W_A^p + W_A^e \qquad (2)$$

where W_A^d is the interfacial contribution provided by London dispersion forces, W_A^h is the contribution of the interfacial hydrogen-bonding, W_A^π is the contribution of interfacial pi-bonds, W_A^p is the contribution of other polar interfacial interactions and W_A^e is the contribution of electrical double layers. The liquid in contact with the solid will spread or form round drops depending on the relative magnitude of these energies.

In the case of water in contact with oxide-free gold surface, if it is assumed that the W_A^h, W_A^π and W_A^p contributions are insignificant, equation (2) can be simplified to,

$$W_A = W_A^d + W_A^e \qquad (3)$$

This equation may be valid if the electrical double layer effect is not negligible.

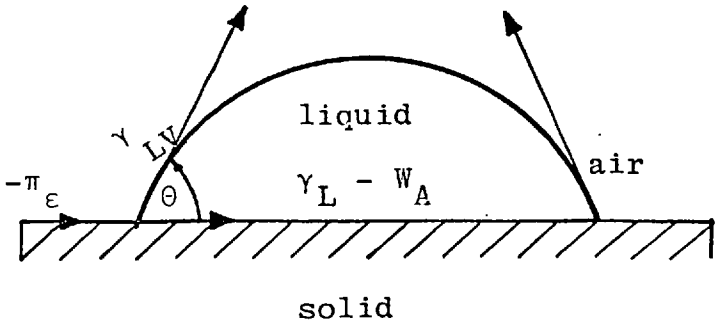


Fig.2.1 Liquid under equilibrium in contact with solid.

Consider Fig. 2.1, where the three forces operating on the periphery of the liquid determine the contact angle. The superficial tension of the liquid in contact with the solid, $(\gamma_L - W_A)$ plus $\gamma_{LV}\cos\Theta$ plus the film pressure, π_ε of the adsorbed film on the solid, tend to keep the drop from spreading. At equilibrium the sum of these forces is zero and hence,

$$\gamma_{LV}\cos\Theta = -\gamma_L + W_A - \pi_\varepsilon \qquad (4)$$

where $-W_A$ and $-\pi_\varepsilon$ are free energies of interaction of solid with the fluid and vapour respectively. To determine the value of the contact angle, the values of $-W_A$ and $-\pi_\varepsilon$ must be obtained. Fowkes'[43] model for liquid-solid pairs can be used to evaluate $-W_A$ and $-\pi_\varepsilon$. By choice of a saturated hydrocarbon as one member of the pair, the interaction other than the London dispersion forces can be eliminated so that W_A is equal to W_A^d. These London dispersion forces are presumed to exist in all types of matter and always give an attractive force between adjacent atoms, or molecules no matter how dissimilar their chemical natures might be. The work of adhesion, W_A is expressed as,

$$W_A = \gamma_{LV} + (\gamma_{SV} - \gamma_{SL}) \qquad (5)$$

$$= \gamma_{LV}\,(1 + \cos\Theta) \qquad (6)$$

and $W_A^d = 2\sqrt{\gamma_L^d \gamma_S^d}$

where γ_S^d and γ_L^d are the dispersion force contributions to the surface free energies of the solid and the liquid respectively.

since $W_A = W_A^d$, (7)

$$\gamma_{LV}(1 + \cos\Theta) = 2\sqrt{\gamma_L^d \gamma_S^d} \qquad (8)$$

But for polar liquid, e.g. water, if $\gamma_L = \gamma_{LV}$,

$$\gamma_{LV}\cos\theta = -\gamma_{LV} + 2\sqrt{\gamma_L^d\gamma_S^d} + W_A - W_A^d - \pi_\varepsilon \qquad (9)$$

In predicting the contact angle of a polar liquid on an oxide-free metal surface, Fowkes assumed that W_A is equal to W_A^d, so that

$$\gamma_{LV}\cos\theta = -\gamma_{LV} + 2\sqrt{\gamma_L^d\gamma_S^d} - \pi_\varepsilon \qquad (10)$$

π_ε is the free energy of adsorption and is called spreading pressure. When the adsorbed film on the solid reached the liquid state at p_o, the saturated vapour pressure (s.v.p.)

$$\pi_\varepsilon = 2\sqrt{\gamma_S^d\gamma_L^d} - 2\gamma_{LV} \qquad (11)$$

But under conditions of low supersaturation ratio ($p/p_o < 1.13$) for water,

$$\gamma_{WV}(1 + \cos\theta) = 2\sqrt{\gamma_S^d\gamma_W^d} \qquad (12)$$

By knowing the value of γ_S^d, the contact angle can be calculated.

The magnitude of γ_S^d can be determined experimentally from (a) the heat of adsorption (b) the heat of immersion (c) the long range attractive forces.

(a) <u>From heats of adsorption</u>.

The integral heat of adsorption H_{ads}^o of a vapour, L on a solid, S at $p/p_o = 1$, can be derived from the eqn (11) according to Fowkes,

where $\pi_\varepsilon = -F_{ads}^o$

$$\therefore \Delta F_{ads} = 2\gamma_{LV} - 2\sqrt{\gamma_S^d\gamma_L^d} \qquad (13)$$

$$\text{and } \Delta H = \Delta F_{ads} - T\left(\frac{d\Delta F_{ads}}{dT}\right)$$

$$= 2\gamma_{LV} - 2\sqrt{\gamma_S^d \gamma_L^d} - 2T\left(\frac{d\gamma_L}{dT} - \sqrt{\gamma_L^d}\cdot\frac{d\sqrt{\gamma_S^d}}{dT}\right.$$

$$\left. - \sqrt{\gamma_S^d}\cdot\frac{d\sqrt{\gamma_L^d}}{dT}\right) \qquad (14)$$

From the measured values of ΔH^o_{ads} with reference adsorbate having only dispersion force interactions, the γ_S^d for gold for instance can be calculated when the temperature coefficients and γ_L^d are known. This value will then be used to calculate the contact angle.

(b) Heats of immersion method.

The heat of immersion of the powdered solid in aqueous liquid can be calorimetrically determined for the solid-liquid interactions. These values are calculated from the free energy of immersion, ΔF_i in the same manner as for the heat of adsorption.

$$\Delta F_i = \gamma_{SL} - \gamma_{SV} = \gamma_{LV} - 2\sqrt{\gamma_S^d \gamma_L^d} \qquad (15)$$

$$\Delta H_i = \Delta F_i - T\left(\frac{d\Delta F_i}{dT}\right)\cdot$$

$$= \gamma_{LV} - 2\sqrt{\gamma_S^d \gamma_L^d} - T\left(\frac{d\gamma_L}{dT} - 2\sqrt{\gamma_L^d}\cdot\frac{d\sqrt{\gamma_S^d}}{dT} - 2\sqrt{\gamma_S^d}\cdot\frac{d\sqrt{\gamma_L^d}}{dT}\right)$$

(16)

The value of γ_S^d for gold can be calculated from the above equation if ΔF_i and the temperature coefficients are known and the contact angle determined from equation (12).

(c) Calculation from long range attractive forces.

The concept that dispersion forces operate over longer distances than other intermolecular forces held by London[44] and Hamaker[45] was used to establish a relation between the Hamaker constant and γ_S^d.

The Hamaker constant for two similar materials immersed in a medium can be expressed as

$$A_{131} = A_{11} + A_{33} - 2A_{13} \qquad (17)$$

where A_{131} is the Hamaker constant for two materials of material 1 embedded in a medium 3, and A_{13}, the interaction constant between material 1 and the medium 3, and A_{11}, A_{33} are the Hamaker constants for the individual materials and the medium. From the above equation the Hamaker constant for gold, for example, in water can be calculated if the other constants are known.

The inaccuracy of the Hamaker constant A_{131} as expressed above has been pointed out by Visser[46] and Kitchener[47]. Many other methods for calculating the Hamaker constant in aqueous medium have been outlined in the review of Visser[46]. By the use of some of the methods, various Hamaker constant values for gold immersed in water were obtained. Fowkes[42] related the Hamaker constant to the dispersion contribution of the surface energies of the solid ($\gamma_S^d = \gamma_1^d$) and water ($\gamma_W^d = \gamma_3^d$) as follows:

$$A_{131} = 12.2 \frac{(d_1\sqrt{\gamma_1^d} - d_3\sqrt{\gamma_3^d})^2}{K_3\lambda_{13}} \qquad (18)$$

where d is the interfacial separation of the atomic centres at contact, $\lambda_{13} = 0.9$ and K_3, the dielectric constant of water.

Data available on Hamaker constant for gold in water vary widely. For example, the Hamaker constant calculated from the flocculation experiments of Reerink and Overbeek[48] ranged from 0.5 to 1.4 x 10^{-20} J. But the Hamaker constant calculated by the method considered to be most accurate[49]

gave a value of 33.4×10^{-20} J. These values substituted in equation (18) gave γ_1^d values of $50 - 144 \times 10^{-7}$ J cm^{-2} for Hamaker constants calculated from Reerink and Overbeek's experiments while the Hamaker constant (33.4×10^{-20} J) calculated by Krupp, Schnabel and Walter[49] gave 510×10^{-7} J cm^{-2} for γ_1^d.

Since it is expected that no appreciable interaction other than dispersion forces should exist between water and oxide-free gold, the γ_1^d values can be substituted in equation (12), giving contact angle values of $95^o - 57^o$ for $50 - 144 \times 10^{-7}$ J cm^{-2} and zero for 510×10^{-7} J cm^{-2}. Thus Reerink and Overbeek's Hamaker constants indicate that gold should be hydrophobic while the more accurate Hamaker constant predicts that gold should be hydrophilic. Such is the nature of Hamaker constant for gold in water so far obtained that its use in predicting the wettability of a surface is questionable. Fowkes[43], however, used the Hamaker constant based on Reerink and Overbeek's work to calculate the contact angle on gold to support his theoretical model for the hydrophobicity of oxide-free gold surface. At that time the Hamaker constant calculated by Krupp, Schnabel and Walter[49] from Lifshitz's equation was not available.

2.1.2 Zeta-potential determination method.

In the electrophoretic study of gold by Harrison and Elton[50] an attempt was made to deduce the surface nature of gold. Their results led to the conclusion that the surface of gold is non-ionogenic since the charge density tended to zero as the bulk ionic concentration approached infinite dilution. Such a deduction is open to criticism since it is questionable whether zeta-potentials can be

used to determine the true nature of a solid surface[51]. In the work of Hurd and Hackerman[52] in which the zeta-potential of gold was determined, from streaming current measurements, it was observed that on prolonged contact of the gold capillary with dilute nitric acid, the zeta-potential increased markedly. However, when the capillary was kept in distilled water for many days, the zeta-potential decreased until it attained an equilibrium state at -60.8 mV. The high zeta-potential was attributed to the oxidised state of the surface. Benton and Sparks[53] on the other hand reported a zeta-potential of -50 ± 3 mV by an electrophoretic method; they used commercial gold power. Some investigators, for example de Boer and Verwey[54], attributed such a negative zeta-potential to a layer of chemi-sorbed oxygen on the surface. Such adsorbed oxygen was thought to have a profound effect on the wettability of gold.

2.1.3 Previous work on the wettability of gold.

Surface contaminations of solids may be organic or inorganic or both in nature. It is therefore necessary that in the preparation of a surface for contact angle determination both organic and inorganic contaminations be removed. Often a fresh surface is made by polishing the solid with an abrasive to remove the previous contaminated surface. But the problem of surface contamination is not completely solved since some residual abrasives remain on the polished surface. In the preparation of gold surface for contact angle determination the major difficulty lies in the removal of inorganic and organic contaminations. Many investigators tried to eliminate one type of contamination only to introduce the other.

Adam[55] in summarising the knowledge of the spreading of ordinary liquids on inorganic solids, stated that most organic liquids and water formed zero contact angle with clean glass, silica and metallic surfaces. The reviews of Wark and Sutherland[56] and Gaudin[57] pointed out that clean surfaces of almost all minerals including oxides and most sulphides, have zero or small contact angles. Later, the investigation of the wettability of high-energy surfaces by Fox, Hare and Zisman[58] led to the conclusion that all pure liquids spread spontaneously on high-energy surfaces unless they belong to the special class of organic liquids which are either "autophobic" or are hydrolysed on contact with the solid surface. From their work it was also concluded that pure water will spread on a high-energy surface if it is free from organic contamination. Organic contamination is therefore considered the cause of the hydrophobic nature of many "pure" metallic surfaces. This view was supported by the establishment of contact angles with non-polar organic vapours e.g. of pure benzene and hexane on gold[59].

However, the view that a clean high-energy surface is naturally wettable was alleged by some investigators to be not generally true. In the experimental technique used by Bartell and Smith[60] it was possible to prepare a surface in a vacuum and to measure the contact angle assumed by any desired combination of fluid phases on the surface without admission of air. Using this technique, it was found that the contact angle of water on gold had an advancing angle of $7^{o} \pm 1^{o}$ and zero receding contact angle. Fowkes[61] later developed a theoretical model for the non-wettability of oxide-free metal surfaces, based on the London dispersion force contributions of the solid and the liquid in contact.

According to this theory all oxide-free metal surfaces are hydrophobic. In the following year White[62] investigated the wettability of gold in a"Pyrex"and metal system using condensed pure water vapour and concluded that non-oxidised gold surface is hydrophobic, and only when there was a surface oxide present was there a zero angle of contact. They also reported that gold could be made hydrophilic by anodic polarisation. Further support for White's finding was given by Fowkes' [43] theoretical calculation which showed that water should not spread on oxide-free metal surfaces because of the large relative contributions of the metallic bond forces and London dispersion forces to the total surface energy, these forces not contributing significantly to any interaction with water. The whole accepted view about the hydrophilic nature of gold was soon to be questioned. By a continuous condensation method, Erb[63] determined the contact angles on gold in the range of 55^{o} - 85^{o} and claimed that under his experimental conditions both physically adsorbed and chemisorbed contaminants were removed. He also concluded that gold needed surface oxidation to exhibit a zero contact angle.

As a result of the findings of White and Erb, Bewig and Zisman[64] carried out further work on the wettability of gold to verify their results. One significant aspect of their work was the polishing of their gold with alumina under distilled water on a clean "Selvyt" cloth until it exhibited a zero contact angle. The gold was then placed in a special heating cell and heated by high-frequency induction in a purified hydrogen stream, in room air or in high purity inert gases. When the gold had cooled to room tempurature, a sessile drop of clean water was touched to the gold surface.

In general the water wetted the gold surface, but in some cases small contact angles between 4^{o} to 10^{o} were observed. Because of the results of Bewig and Zisman, White and Drobek[65] investigated the effect of residual abrasive on the wettability of polished gold surfaces. They observed that when gold was polished with alumina abrasive the contact angles on these surfaces were found to be 34^{o} - 56^{o}, even after some of the surface had been etched with aqua regia prior to high temperature treatment. On preparing the gold surface by polishing with diamond followed by heating to $1000^{o}C$, the contact angles of water on the surface were 55^{o} to 65^{o}. They concluded that hydrophilic inorganic contaminants of surface could affect wettability as seriously (but in opposite direction) as the more commonly hydrophobic organic material. Plaksin and Bessonov[66] also reported contact angles of 58^{o} - 78^{o} on gold.

Besides polishing gold with abrasives or cleaning by heating to high temperatures, gold has been cleaned electrochemically or with oxidizing reagents. Particularly in the investigation of flotation of gold many investigators [67-69] found that gold could not be floated with frothers only and so concluded that gold is hydrophilic in spite of the treatment of their gold with oxidising acids which would oxidise the surface.

2.1.4 Aim and scope of work.

This investigation is concerned with the study of the wettability of gold with a view to getting some insight into its floatability. The work involved the study of contact angles on gold in (i) clean water (ii) alkylxanthate solutions (iii) alkylxanthate-maize starch solutions.

The techniques employed in this study were:

(a) Vapour condensation method

(b) Electrochemical method

(c) Captive bubble method using Taggarts modified type of equipment[70].

(a) In the vapour condensation method, the gold sheet used was polished with stainless steel rollers by the manufacturers. Cleaning of the gold during the investigation was with chemical reagents and heat.

(b) For the electrochemical method, gold was made the electrodes and polarised in chosen electrolytes. Test for wettability was conducted by making nitrogen gas bubble contact with the test electrode.

(c) Gold samples used in the captive bubble method, were (a) mechanically polished with abrasives (b) etched with acids (c) heated to high temperatures, as means of cleaning the gold. High temperature treatment as a means of cleaning gold is based on data so far gathered from thermodynamic analysis and experimental evidence that gold does not form an oxide on heating to high temperatures in air. Indeed, any pre-existing oxide (e.g. formed by oxidising reagents) is decomposed.

2.2 Experimental

2.2.1 Materials

The gold specimens and chemicals used in the investigation were,

(a) A polished sheet of "Specpure" gold 0.25 mm thick, 1.6 cm wide and 6 cm long of 99.99% purity supplied by Johnson Matthey Chemical Ltd. This was used in the vapour condensation and electrochemical study of the wettability of gold.

(b) Two gold plates of 0.4 cm diameter by 0.2 cm and 1 cm^2 by 1 mm made from precipitated gold of 99.99% purity supplied by Hopkin and Williams. They were made by cupelling the gold powder with borax put in lead foil in a muffle furnace heated to 1000°C. The two pieces of gold were flattened between 600 mesh smoothened steel block surfaces lined with a clean sheet of paper, with a hydraulic press. They were then etched with hot concentrated nitric acid and annealed at 1000°C in air.

(c) Purified potassium ethyl xanthate (KEX) and potassium amyl xanthate (KAX), maize starch No. 8204.00 EM supplied by Hopkin and Williams Ltd. (The purification of the xanthate and the preparation of starch solution are described in Chapter 4).

2.2.2 Methods

2.2.2.1 Vapour condensation method

(a) Apparatus. The apparatus is shown in Fig. 2.2 and consists of a specimen chamber (3 cm dia. by 21 cm), a specimen tube (1 cm dia. by 15 cm), an inner glass tube for evacuating the specimen chamber and a distilled water

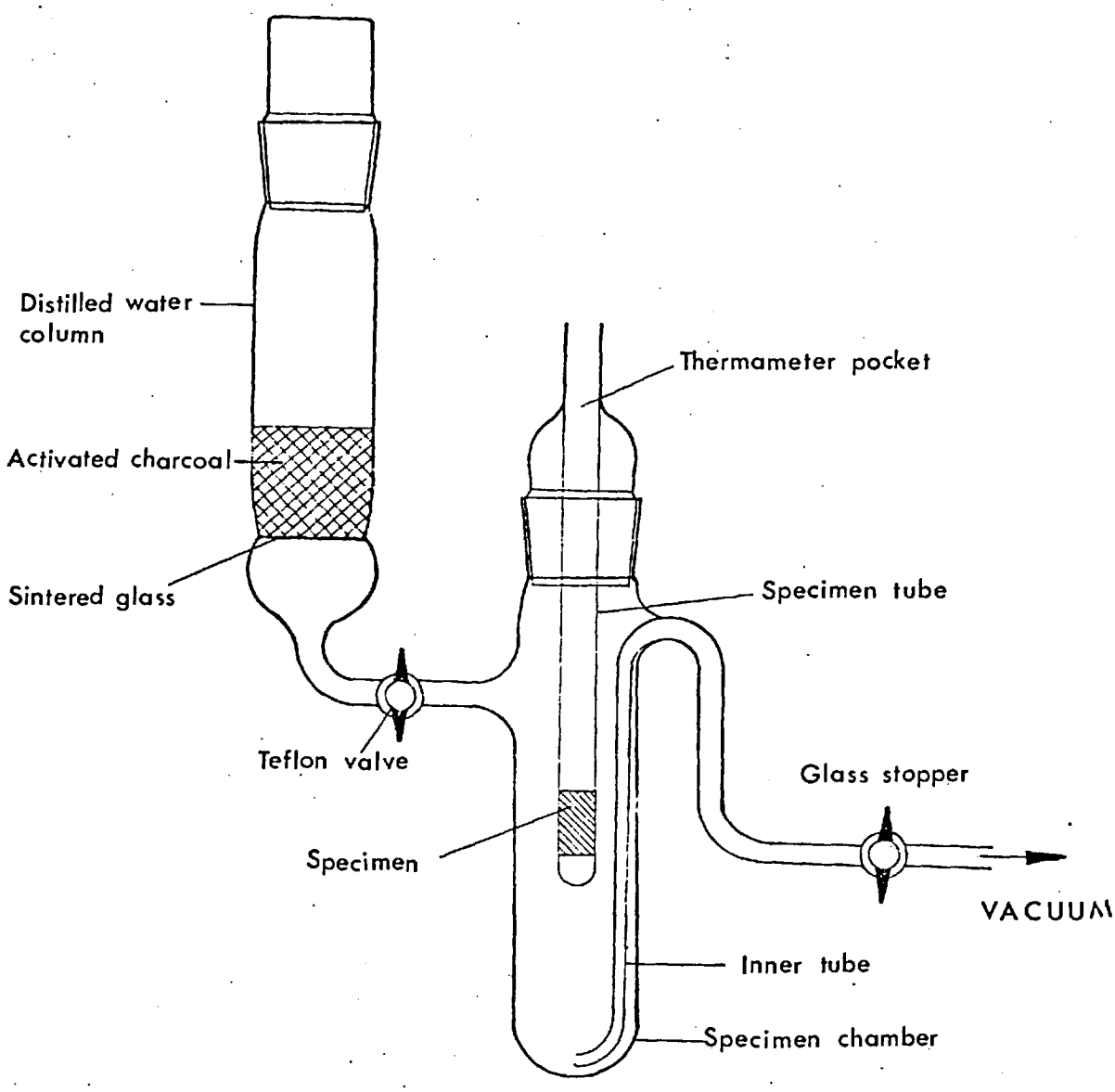


Fig. 2.2 Apparatus for studying the wettability of gold.

column (3 cm dia. by 15 cm). The apparatus was all Pyrex except the specimen tube which was made of silica.

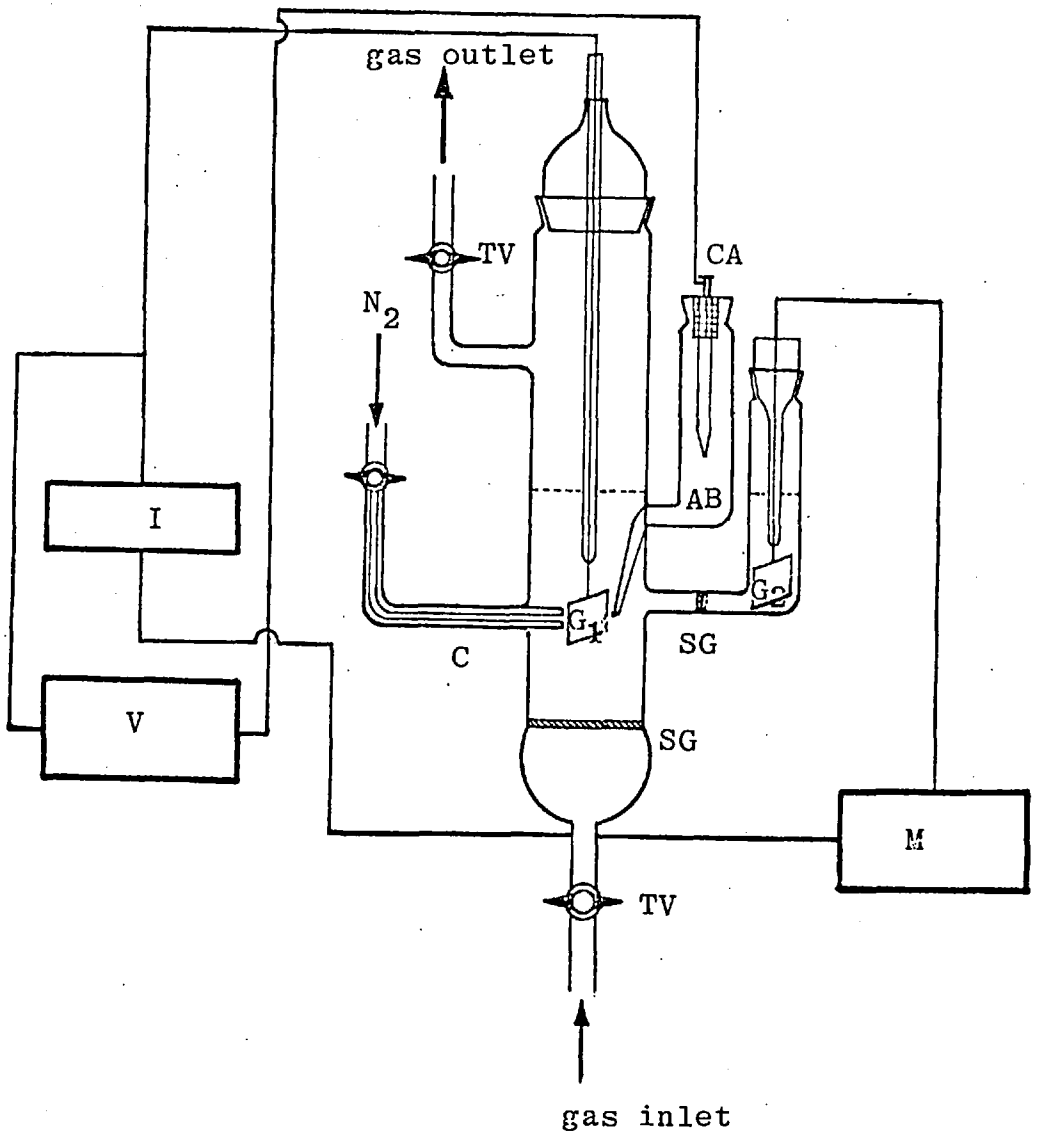
(b) Method of operation. The apparatus was cleaned with chromic acid and washed thoroughly with distilled water before used. The Specpure sheet of gold, 0.25 mm thick, 1.6 cm wide and 4 cm long was rolled securely around the specimen tube and the tube fitted to the specimen chamber as shown. The reagent for cleaning the gold was poured direct into the specimen chamber and the specimen tube was fitted; or the reagent introduced into the specimen chamber through the distilled water column. When the latter method was used, the reagent was let into the specimen chamber by a partial vacuum created in the chamber with a water-pump. The vacuum was high enough to allow sufficient reagent into the chamber to cover the specimen. A heating coil was fixed around the specimen chamber to heat the reagent when desired. The temperature of the reagent was determined with a thermometer placed in the thermometer pocket. The reagent was heated for some time and then extracted under vacuum. Conductivity water, stored in the distilled water column containing activated charcoal of about 2 mm in size, was used to flush the specimen chamber and wash off the reagent from the specimen. When the specimen was thoroughly cleaned, a small amount of fresh distilled water was introduced into the chamber when the specimen was dry. The two valves were closed and the water warmed up. To condense the water vapour on the gold, acetone was poured into the thermometer pocket and air bubbled through it. This cooled the gold and caused the formation of water droplets on its surface. For a hydrophobic surface, discrete droplets of water were formed uniformly and coalesced as they grew bigger and ran down the

surface, only to have new small droplets formed in their places. When the surface was hydrophilic, the droplets were unstable and coalesced to wet the surface. The gold surface was examined with a "travelling" microscope while a beam of light was focused on its surface.

Tests for the wettability of gold were carried out by treating it with diethyl ether, 30% hydrogen peroxide, dilute and concentrated sulphuric acid, sodium hypochlorite, chromic acid and heating in air at 900^{o}C. The results are summarised in Table 2.1.(see page 113)

2.2.2.2 Electrochemical method.

(a) Apparatus. Fig.2.3 shows the sketch of the apparatus used. The electrochemical cell consists of a three-electrode system composed of two 1 cm^2 gold plate electrodes, one as the test electrode and the other as the counter-electrode, and a calomel reference electrode. The calomel reference electrode made a contact with the electrolyte through an Agar-KCl bridge. The cell has also a gas inlet and outlet, and a capillary tubing connection through which "white spot" N_2 bubbles were introduced to make contact with the test electrode. A sintered glass No.2 separated the counter electrode column from that of the test electrode and a similar sintered glass separated the test electrode column from the gas inlet. The input voltage was controlled with a Multireg 731 and the electrode potential test electrode was recorded with D.V. Meter 500 Mk III, while the current was recorded with a digital multimeter D.MM2.



AB - Agar-KCl bridge
C - Capillary
CA - Calomel reference electrode
G_1 - Test gold electrode
G_2 - Counter gold electrode
I - Digital multimeter DMM2
M - Multireg 731
SG - Sintered glass
TV - Teflon valve
V - D.V. Meter 500 MkII

Fig. 2.3 Electrochemical apparatus for studying the wettability of gold.

(b) Method. Before introducing an electrolyte into the electrochemical cell, the cell was cleaned with chromic acid and washed thoroughly with distilled water. The gold electrodes were heat-fused to a platinum wire. Care was taken not to immerse the platinum wire in the electrolyte solution in the test. The cathodic and the anodic parts of the polarographs were constructed by polarising the test electrode cathodically and anodically and the potentials and the currents were recorded every 20 minutes. After a complete run the test electrode was heated to 600°C before being re-fused. "White spot" nitrogen gas was allowed into the cell to make contact with the test electrode through the capillary (C). The electrolytes used for studying bubble contact with the gold were,

(1) nitrogen-saturated 0.2 M KH_2PO_4 + 0.2 M NaOH buffer solution at pH 7,

(2) oxygen-saturated 0.2 M KH_2PO_4 + 0.2 M NaOH buffer solution at pH 7,

(3) nitrogen-saturated 0.1 M H_2SO_4 solution,

(4) nitrogen-saturated 1 M HCl solution.

The possible organic contamination on the working electrode was not removed before all tests were conducted except when the polarisation was carried out in 1 M HCl solution. The test electrode was cleaned then with chromic acid and washed in distilled water before being used.

The results are shown in Figs. 2.5 and 2.6 (pages 115, 116). All potential values are relative to a saturated calomel electrode (SCE).

2.2.2.3 Captive bubble method.

(a) Apparatus. The apparatus consists of a glass cell fixed to the stage of a microscope which had been rotated through ninety degrees . Polished specimens were placed in the cell with conductivity water or a reagent solution, and light passed through the cell to the polished surfaces. The reflected light and some of the incident light was directed through the microscope and brought to focus on a ground glass screen. The microscope was fitted with a long distance objective and there was no eye-piece . Copper sulphate solution was used to reduce the heat from the light source when necessary.

Air or nitrogen bubble (about 3 mm in diameter) was formed at the tip of the glass capillary by the use of an 'Agla' micrometer syringe. The micrometer was fixed to the platform and was capable of being moved horizontally and vertically. A bubble was brought into contact with the polished specimen at any desired site of the surface. Contact angles were measured at the water/air/solid line of contact on the ground screen. The result of each contact angle recorded is an average of at least six measurements.

Before the apparatus was used, the glass cell, the glass capillary and the 'Agla' micrometer syringe were cleaned with chromic acid and washed thoroughly with conductivity water.

(b) Sample preparation and contact angle measurement. (i) Specimen 1. The gold plate (0.4 cm dia. by 0.2 cm) was mounted with Araldite on a quartz cube (1 cm^3) and polished with 3 - 8 μm size diamond abrasives under distilled water. The specimen was washed with distilled water and examined

under a Zeiss "Ultraphot" microscope. Some residual particles of diamond abrasive were found embedded in the gold. At this stage, the gold was hydrophobic (possibly due to organic contaminations). The specimen was then polished with γ-alumina on a clean degreased "Selvyt" cloth under conductivity water until it became hydrophilic. It was finally polished on the clean "Selvyt" cloth under conductivity water and transferred into the glass cell containing conductivity water. The contact angles of air bubbles on the gold were measured.

(ii) Specimen 2. Specimen 2 (1 cm^2 by 0.1 cm thick) was polished with 3 μm diamond abrasive and finally with "Silvo" metal polish. The specimen was later washed thoroughly in conductivity water, acetone and kept for 12 h in ether and transferred into 30% hydrogen peroxide (H_2O_2) and heated to boiling for 1 h. Fresh solution of H_2O_2 was added at intervals to maintain a constant volume. The specimen was washed in conductivity water and transferred into the glass cell containing conductivity water and the contact angles measured.

Before polishing the gold degreased plastic gloves were put on. The sample polishing was done on a "Selvyt" cloth placed on a glass plate which had been cleaned with chromic acid.

(iii) Specimen 2 was later treated as follows:-

(1) with aqua regia (2) with hot concentrated nitric acid. Each treatment was followed by heating in hot concentrated HCl to etch away any oxide on the surface.(3) heating in air to 900°C.

(1) With aqua regia followed by concentrated HCl.

The specimen was immersed in aqua regia for 1 minute, removed with tweezers and washed with conductivity water to remove any residual acid. A brown coating was observed on the surface of the gold. This surface was definitely hydrophilic. When the gold was treated with hot concentrated HCl for a long period, the brown surface was removed, leaving clean hexagonal patches on the surface. The surface so produced was hydrophobic and the contact angles in conductivity water were measured.

(2) With concentrated HNO_3 followed by concentrated HCl.

Specimen 2 was also heated in hot concentrated nitric acid and removed after every ten minutes, washed in conductivity water and the contact angles determined as before. After boiling for about 20 minutes the surface appeared yellowish brown even after repeated boiling in water. The surface was then hydrophilic. On treating it in hot boiling concentrated HCl the surface became clean and hydrophobic. The contact angles in distilled water were measured.

(3) By heating specimen 2 to $900^{o}C$.

The specimen was placed in a silica crucible and heated to $900^{o}C$ in a horizontal tube furnace lined with alumina after which the crucible was removed and covered with a red hot lid. When cooled to room temperature the sample was tipped (within a second) into a clean glass cell with clean water and the contact angle measured using N_2 gas bubble.

All the results of these experiments are summarised Table 2.2.(see page 119).

(iv) Techniques of sealing gold in a silica tube under conditions of no organic contamination.

(a) Apparatus. The apparatus (Fig. 2.4) consists of a long tube, 1.5 cm in diameter by 60 cm, with a constriction dividing the tube into two compartments.

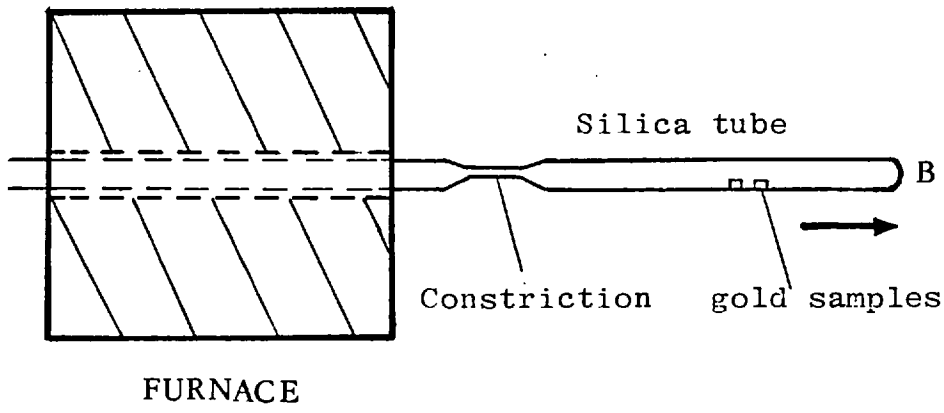


Fig. 2.4 Sketch of apparatus for preparing clean gold surface free of organic contamination.

(b) Method. Before the gold samples were put into the sample compartment both ends of the tube were open. The tube was cleaned with chromic acid and annealed. All the pieces of gold used in the previous experiments (five in all) were cleaned by treating with HCl and heating to 1000°C, and put into the sample compartment and that end (B) was sealed. The silica tube was put into a horizontal tube furnace set at 800°C. The tube was kept in the furnace for about 1 hour and then drawn slowly out from the furnace with the sample end coming out first. (Arrow in Fig.2.4 shows direction of tube withdrawal). The tube withdrawal from the furnace was carried out a little at a time to ensure that no organic contamination was retained in the sample compartment. Any air entering the chamber had to pass through a red-hot

silica tube, so that organic vapours would be destroyed. When the constriction was out of the furnace, the open end was still in the furnace, before the tube was sealed at the constriction.

The sample tube was then cleaned with chromic acid and distilled water just before it was broken under clean conductivity water contained in a wide neck, thick glass bottle. The tube was broken by tapping the end against the bottom of the bottle. "White spot" nitrogen gas which had passed through a silica tube heated to 900^{o} was used for the bubble contact test. The open end of the silica tube was fitted with a capillary tubing with a glass valve to control the N_2 gas bubble. The result is also shown in Table 2.2.

2.2.2.4 Contact angles on gold in xanthate and starch solutions.

(a) Sample preparation and contact angle determination.

Specimen 1 gold was used in this experiment and was polished with γ-alumina on "Selvyt" cloth under conductivity water until the surface became hydrophilic and washed thoroughly in distilled water before being used. The gold was conditioned in the xanthate solution contained in the glass cell and the contact angles of air bubbles on the gold measured. The contact angles were determined in xanthate solutions containing dissolved air, saturated with oxygen or nitrogen as follows,

(1) at various conditioning times,

(2) at various xanthate concentrations,

(3) at different pH values,

(4) in starch-xanthate solutions.

The results are shown in Figs.2.7 - 2.10 (pages 121- 123).

2.3 Results

2.3.1 Vapour condensation technique.

2.3.1.1 Treatment with diethyl ether. Ether was poured direct into the specimen chamber while the Teflon valve was closed. The specimen tube with the gold fixed around it was fitted to the specimen chamber with the gold immersed in the ether and kept under it for 12 h with occasional shaking of the ether. The ether was drained off and the specimen heated to 200°C for 13 h, under vacuum. When cooled, distilled water stored in the distilled water column was introduced into the specimen chamber to clean it. The washing was repeated until no steady air bubbles were formed on shaking the water, indicating the probable absence of organic contamination. When the condensation test for wettability of gold was conducted, the surface was found to be hydrophobic.

2.3.1.2 With hydrogen peroxide (H_2O_2). 30% H_2O_2 was filtered through the activated charcoal bed to remove any organic impurities in it. Sufficient H_2O_2 was let into the specimen chamber to cover the gold and the H_2O_2 was heated to 100°C for 2 h and drained off. On washing the specimen many times with distilled water, the surface was tested for its wettability and found to be hydrophobic.

2.3.1.3 With 3 M sulphuric acid(H_2SO_4). The dilute H_2SO_4 was run down the specimen chamber under vacuum through the activated charcoal bed and heated to boiling for one hour. When the acid was drained off and the specimen cleaned with distilled water it was observed that the surface was still hydrophobic but less strongly so than in previous cases.

2.3.1.4 With concentrated hydrochloric acid. The acid was filtered through the activated charcoal bed and heated to boiling for 1 hour, and the system cleaned with distilled water as before. The surface was found to be hydrophobic. This observed hydrophobicity is significant since the HCl treatment followed directly the dilute H_2SO_4 treatment of the gold when the gold was weakly hydrophobic. The HCl possibly removed the slightly oxidised surface caused by H_2SO_4 acid treatment.

2.3.1.5 With concentrated sulphuric acid. Concentrated H_2SO_4 was used for cleaning the surface of the gold at 240^{o}C for 1 hour. When the gold surface was washed with distilled water and tested, droplets of water were hardly formed, showing that the surface was hydrophilic.

2.3.1.6 With sodium hypochlorite (NaOCl). Because NaOCl reacts readily with charcoal it was poured direct into the specimen chamber and heated to 80^{o}C for 1 hour. After cleaning the specimen with distilled water and testing, it was observed that the surface was totally wet with water draining continuously down the surface indicating that the surface was definitely hydrophilic.

2.3.1.7 With chromic acid. Chromic acid cleaning of the gold surface was carried out at room temperature for 1 hour followed by washing.The surface was found to be hydrophilic.

2.3.1.8 High temperature treatment.After the preceding treatments, the specimen was heated in a furnace to 900^{o}C for 2 hours and removed while hot and fitted to the specimen chamber which had been heated to 200^{o}C; the vacuum was applied immediately. This procedure was designed to minimise

Table 2.1 The effect of treating gold with some common reagents and high temperature treatment on the wettability of the surface.

reagent	cleaning time (h)	cleaning temp.(^{o}C)	drying time (h)	drying temp.(^{o}C)	whether hydrophobic	remarks
diethyl ether	4	* r.t.	13	200	yes	surface less hydrophobic
H_2O_2(30%)	0.5	100	4	200	yes	
3 M H_2SO_4	1.0	boiling	--	r.t	yes	
conc. H_2SO_4	1.0	240	--	r.t	no	
conc. HCl	1.0	boiling	--	r.t	yes	
sodium hypochlorite	1.0	80	--	r.t	no	
chromic acid	1.0	r.t.	--	r.t	no	
heated	2.0	900	--	r.t	yes	

*r.t = room temp.

contamination of the specimen by impurities from the air. When the system cooled to room temperature, the gold surface was tested as previously and found to be hydrophobic.

In summary, the results (Table 2.1) show that gold was hydrophilic when treated with concentrated H_2SO_4 at elevated temperature, with chromic acid and with sodium hypochlorite, but hydrophobic when treated with ether, hydrogen peroxide, hydrochloric acid and after heating to 900° C in air.

2.3.2 Electrochemical method.

Fig. 2.5 shows the polarographs of gold in N_2- and O_2 - saturated 0.2 M $KHPO_4$ + 0.2 M NaOH buffer solution at pH 7.

(i) N_2- saturated buffer solution. The steady-state potential of gold in the N_2-saturated buffer solution was about 0.181 ± 0.020 V (SCE). Strong contact of N_2 gas bubble with the gold was established at the rest potential and remained so on cathodic polarisation until the potential of -1.0 V was attained when the bubble contact became feeble. The bubble contact did not completely terminate on the evolution of hydrogen. When the gold was anodically polarised the bubble contact was maintained, but less strongly; when a potential of 1.0 V was reached when it became feeble. At potentials greater than 1.0 V the bubble contact was virtually zero.

(ii) O_2- saturated buffer solution. The steady-state potential of gold in the buffer solution was 0.292 ± 0.020 V (SCE). At this potential there was strong bubble contact

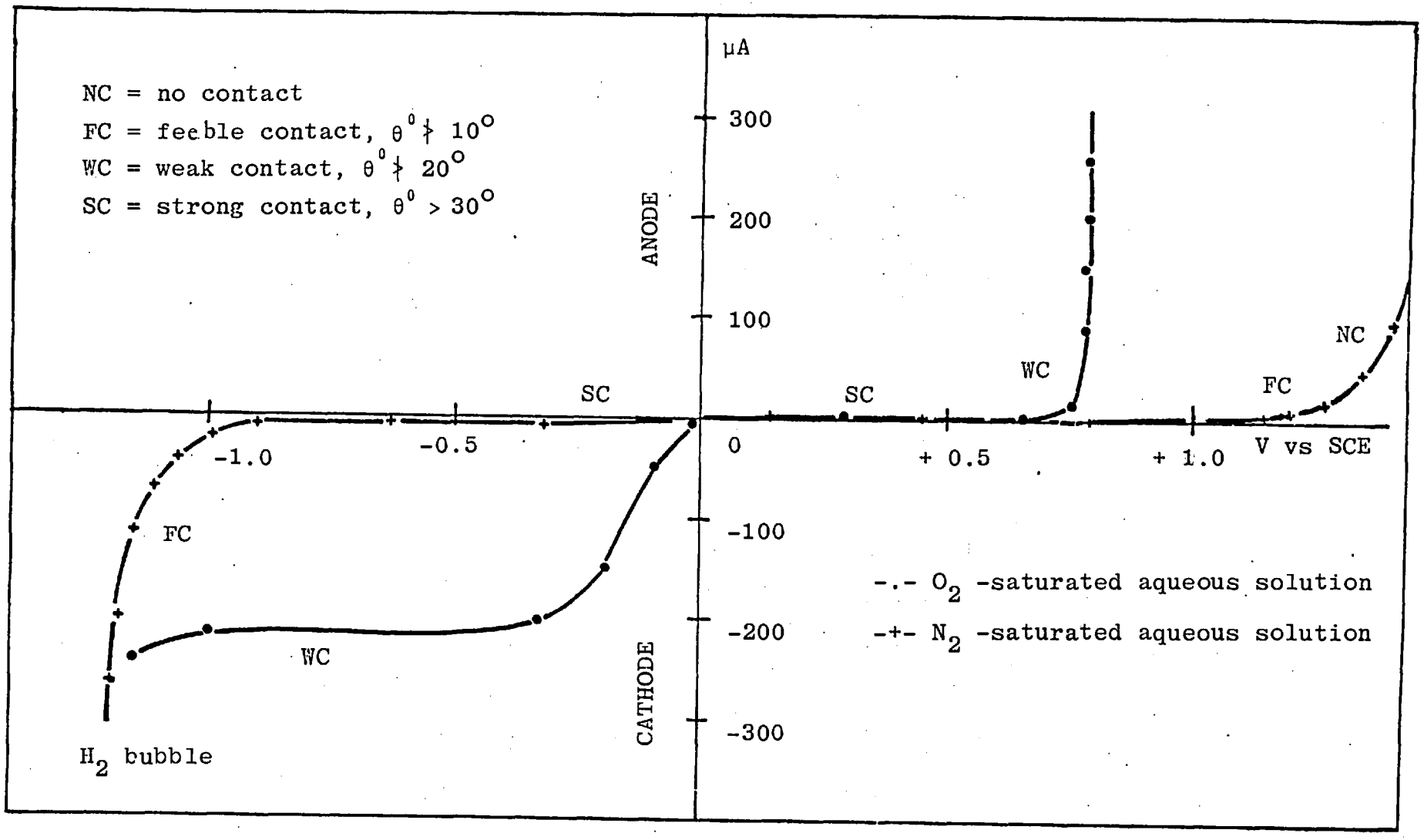


Fig.2.5 Polarograph for gold in 0.2 M $KHPO_4$ + 0.2 M NaOH buffer solution at pH 7.

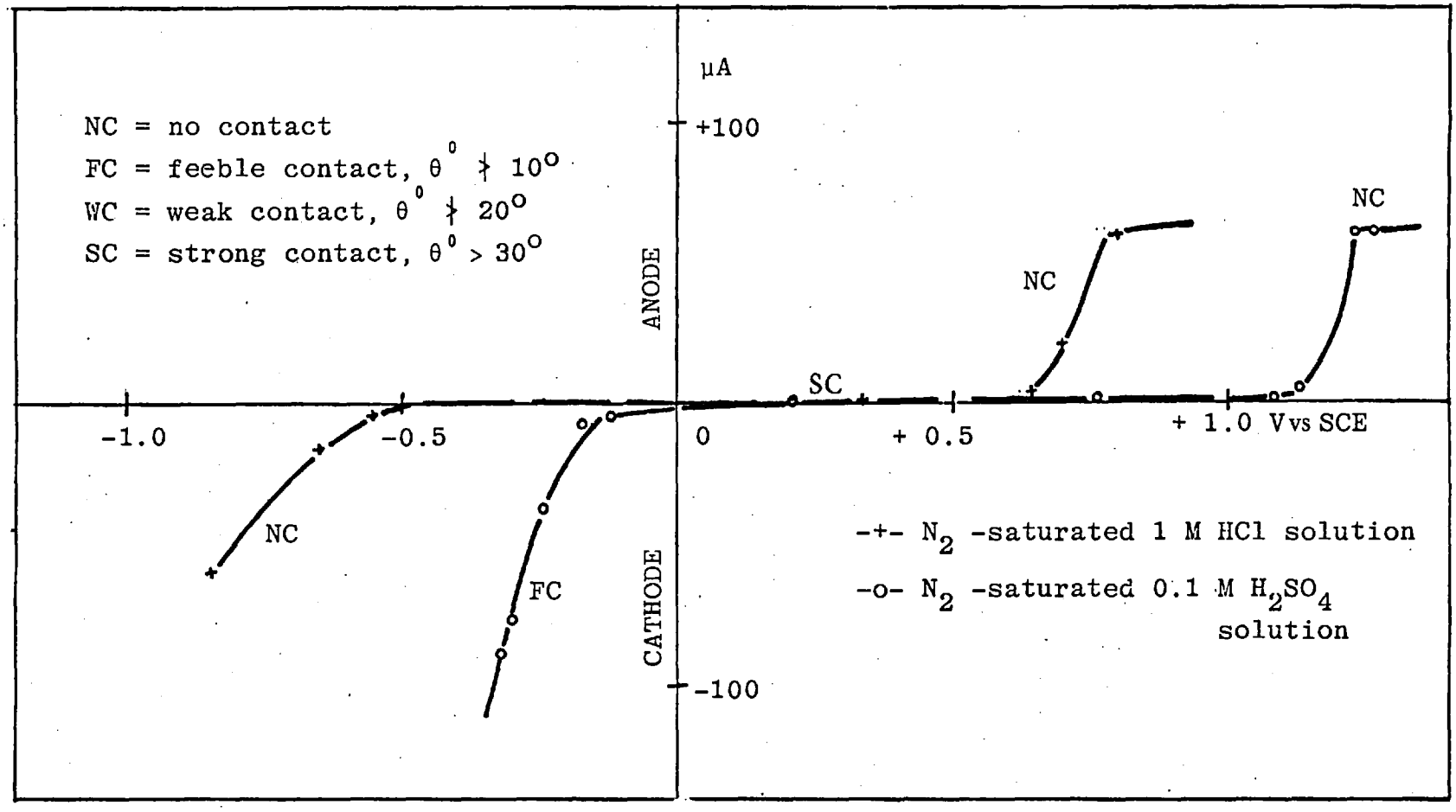


Fig. 2. 6 Polarographs for gold in 1 M HCl and 0.1 M H_2SO_4 solutions.

and remained so on anodic polarisation until a potential greater than 0.75 V was reached when it became weak.This potential is considered to correspond to the formation of Au-O[71]. When the polarity was reversed i.e. made cathodic, the current increased sharply as the potential exceeded -0.05 V and continued until a potential of about -0.4 V was attained when the current became steady. The increase of the current may correspond to the reduction of Au-O. The bubble contact was weak at this potential for possible oxygen reduction.

The strong bubble contact with gold at the potentials lower than those for hydrogen and oxygen evolution was expected since organic contamination picked up by the gold electrode was not removed before it was polarised in these experiments.

(iii) Au electrode in N_2- saturated 0.1 M H_2SO_4

In Fig.2.6 the initial bubble contact at low anodic potentials was strong until a potential of 1.0 V was attained. Above this potential the surface of the gold was rendered hydrophilic. Potentials above 1.0 V in H_2SO_4 medium are known to correspond to the potentials for gold oxide formation and naturally the surface would become hydrophilic. On cathodic polarisation the current increased markedly at potentials more negative than -0.2 V. This may correspond to reduction of the gold oxide. At these potentials the bubble contact was feeble.

(iv) Au in N_2 -saturated 1 M HCl solution.

In this test the electrode was cleaned with chromic acid and washed with distilled water just before use.The polarograph (Fig.2.6) shows rapid increase in current above

potential of 0.5 V on both anodic and cathodic polarisation. The anodic current increase corresponds to the dissolution of gold while the increase of the cathodic current corresponds to the deposition of gold[72]. The bubble contacts at potentials just before visible gold dissolution and deposition were very feeble and estimated to be less than 10^{o}. At potentials of dissolution and deposition there were hardly any bubble contacts with the gold.

2.3.3 Captive bubble method.

Table 2.2 shows the summary of the results of contact angles on gold surface prepared in various ways, in conductivity water and indicate the following:-

1. Gold polished with alumina and finally on clean, degreased "Selvyt" cloth under conductivity water or polished with "Silvo" and boiled in 30% H_2O_2 is hydrophobic with large contact angles between 56^{o} and 70^{o}. (The equivalent equilibrium contact angles were evaluated by using the method of averaging the receding and advancing contact angles suggested by Adam[73]).

2. Gold treated with aqua regia and hot concentrated HNO_3 (oxidising acids), was hydrophilic. A coating of gold oxide was formed. However, on further treatment with hot concentrated HCl to remove the oxide, the surface became hydrophobic with contact angles values of 48^{o} to 55^{o}.

3. When gold was heated to $900^{o}C$ in a silica crucible and allowed to cool to room temperature while covered with the lid, the contact angle was 60^{o}.

4. When gold was heated in a silica tube to $800^{o}C$ and sealed up under conditions of no possible organic contamination, the contact angle was zero, indicating that the surface was hydrophilic.

Table 2.2 Contact angle of an air bubble on gold treated in various ways, in conductivity water at 22°C.

Treatment processes	Time	Receding contact angle, degree	Advancing contact angle, degree
1. Gold polished with γ-alumina and finally on "Selvyt" cloth.	--	55±2	85±2
2. Gold polished with "Silvo" and boiled in 30% H_2O_2.	30 min.	41±2	70±2
3a Gold treated with aqua regia.	1 min.	zero	zero, brown yellow coating
3b Gold (3a) treated with hot concentrated HCl.	several hours	40±2	69±2
4a Gold treated with hot concentrated HNO_3.	10 min. 20 min.	0;15;13;5,5. zero	0;48,45;30, 30. zero
4b Gold (4a) treated with hot concentrated HCl.	several hours	30±4	65±5
5. Gold heated in silica crucible to 900°C and covered with the lid to cool.	30 min	47±2	73±1
6. Gold sealed in silica tube under conditions of no organic contamination.	1 hour	zero	zero

These results are significant because they have shown how very difficult it was to keep the surface of gold clean, in spite of the general view that gold is inert. The discussion and conclusions of the above observations will be presented later.

2.3.4 Contact angles on gold in xanthate, and starch solutions.

Figs.2.7-2.10 show the effect of potassium ethyl xanthate (KEX) and KEX-starch on the hydrophobicity of gold.

2.3.4.1 Contact angles related to time.

Fig.2.7 shows the effect of time on the contact angles on gold in 20 mg/l KEX air- and O_2-saturated solutions at pH 7.0. The contact angles did not increase after conditioning time of 30 minutes. Plaksin and Bessonov[66] however, reported a maximum contact angle for the same conditioning time for gold in 100 mg/l butyl xanthate solution. The contact angles in air-, and O_2-saturated solutions did not differ greatly. However, there was an indication of slight increase (of 3^o - 5^o) in contact angle values when the xanthate solution was saturated with air and then with oxygen. The induction time for bubble adhesion in O_2-saturated solution might be expected to be less than that for air-saturated solution; but this was not observed, possibly because of the small difference.

2.3.4.2 Effect of KEX concentration on contact angle.

In Fig. 2.8, the contact angles on gold in various solutions of KEX concentrations in the presence of oxygen at pH 6.5-7.0 for a conditioning time of 0.5 h are shown. The contact angles ranged from 51^o to 62^o in KEX solutions of 20-10^3 mg/l.This is similar to contact angle values obtained by the adsorption of KEX on sulphide minerals[56,57]. There was apparently no further increase in contact angles above

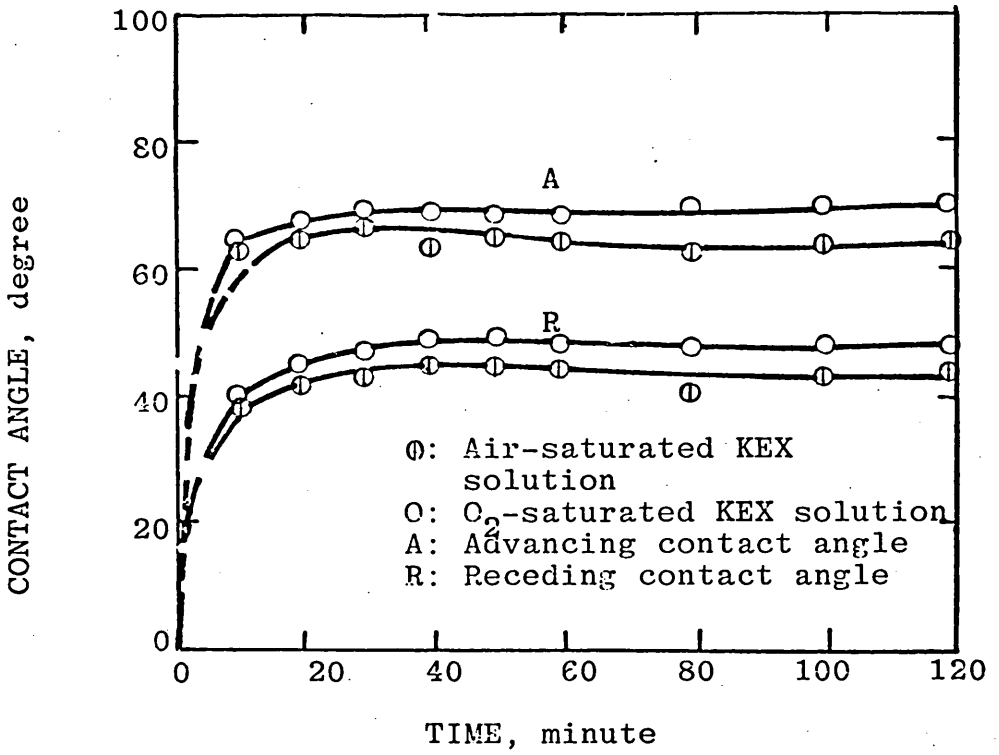


Fig.2.7 Contact angle of an air bubble on gold in potassium ethyl xanthate solution as a function of time.(KEX concentration = 20 mg/l at pH 7.0)

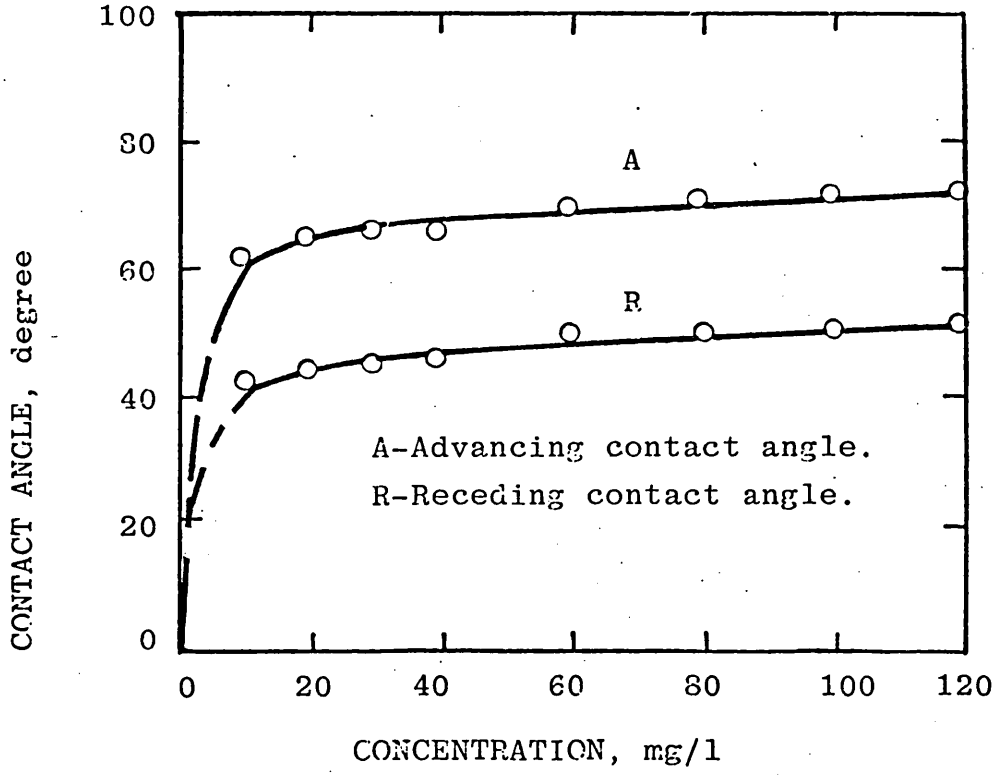


Fig.2.8 Contact angle of air bubble on gold in O_2-saturated KEX Solutions at pH 6.5-7.0 (time = 30 minutes temp = 22°C.

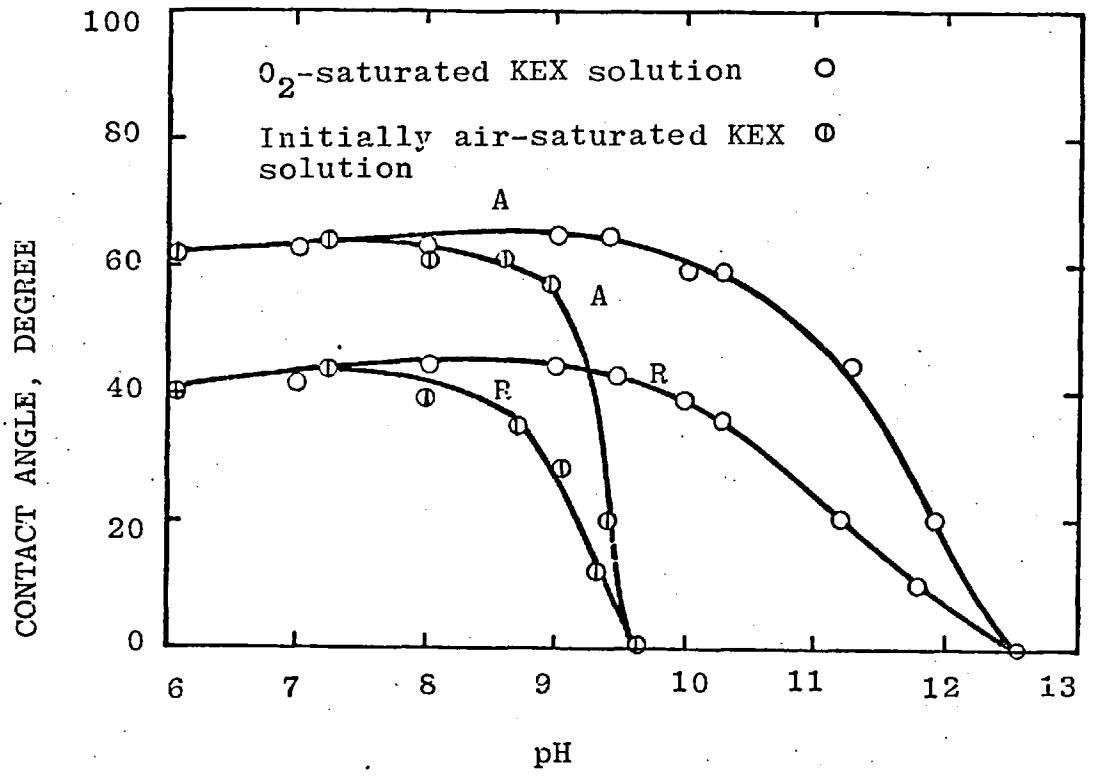


Fig.2.9a Contact angle of air bubble on gold as a function of pH.(KEX concentration = 20 mg/l; Conditioning time = 30 minutes).

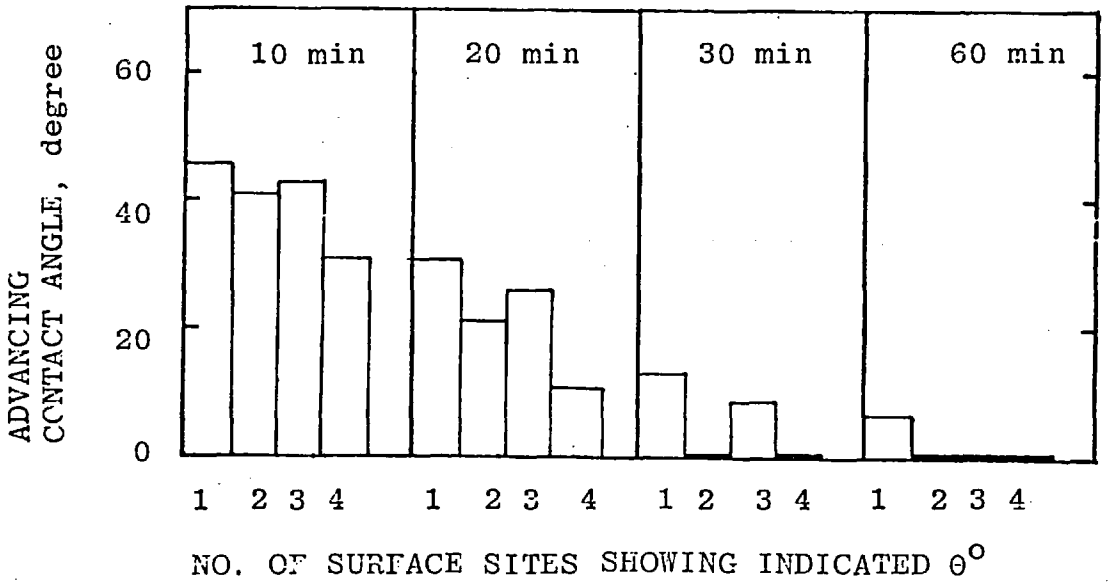


Fig.2.9b Histograms showing the effect of high pH (11.8) on gold made hydrophobic by conditioning it in 20 mg/l KEX solution at pH 8.6.

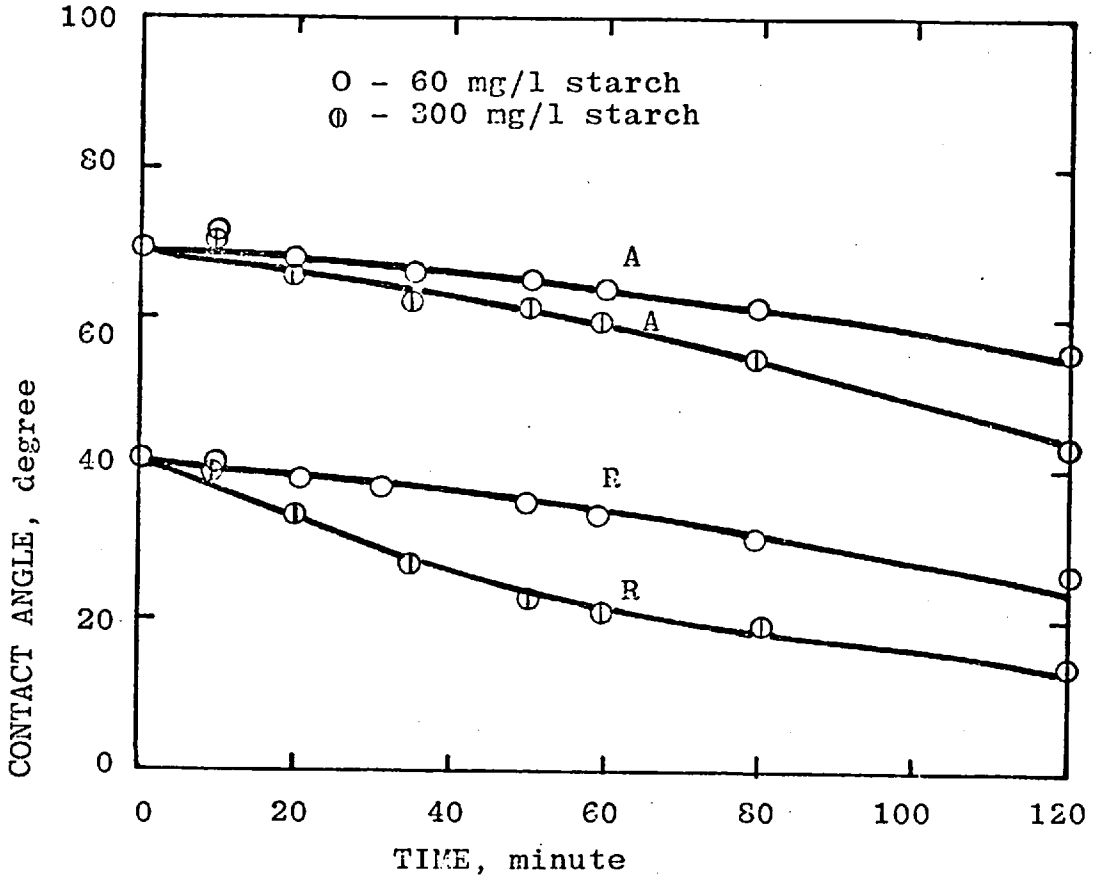


Fig.2.10 The effect of starch on the contact angle on gold at pH 7. (Gold made hydrophobic by conditioning initially in 20 mg/l KEX for 30 minutes.)

KEX concentration of 60 mg/l.

2.3.4.3. Effect of pH on contact angle

Fig.2.9a shows the contact angles on gold in 20 mg/l solutions of KEX as related to pH. In solutions prepared with air-saturated conductivity water, the contact angle (62^{o} advancing) remained almost constant up to pH~ 9. But at pH >9 it decreased sharply to zero at about pH 9.5, while in oxygen-saturated solutions the contact angle (62^{o} advancing) began to decrease at about pH 9.5 and gradually became zero around pH 12.5. Although the contact angle values are relative, they nevertheless show their dependence on pH and concentration of oxygen. The effect of pH and oxygen concentration is also shown by Fig.2.9b obtained by transferring a gold specimen previously conditioned in 20 mg/l solution of pH 8.6 and exhibited advancing contact angle of 60^{o}, into a 20 mg/l KEX solution at pH 12. The contact angle decreased gradually to zero after 1 hour.

2.3.4.4 Contact angle on gold in KEX–starch solution.

Fig.2.10 shows the contact angles of an air bubble on gold in 20 mg/l KEX + 60 mg/l, or 300 mg/l maize starch solutions at pH 7.0. The gold was conditioned in 20 mg/l xanthate solution for 30 minutes before the starch was added. The contact angles values were not greatly affected by starch. In the flotation of gold in xanthate-starch solution, therefore, the depressing effect of starch would be expected to be negligible.

The results of contact angles on gold (not shown) determined in air– and O_2– saturated KAX solutions, gave contact angle values of 65^{o}–75^{o}.

2.4 Discussion

2.4.1 Wettability of gold.

That gold is hydrophobic or hydrophilic has been controversial on account of the conflicting experimental results. Consequently there exist two schools of thought on the matter. The 'hydrophilic school' argued that the hydrophobic nature of gold as reported by many investigators (62,63,65,66) was due to organic contamination while the 'hydrophobic school' stated that the hydrophilic nature of gold was due to inorganic contamination introduced during the sample preparation. It is known that gold oxide formed on anodic polarisation of gold is hydrophilic. In favour of the hydrophobic view is the theory that all oxide-free metal surfaces ought to be hydrophobic because the metal/water interaction would be weaker (if only London dispersion forces operated) than the water/water interaction (which includes hydrogen-bonding also). In addition it has been generally accepted that gold does not form oxides when heated to high temperature in air, and that gold can be cleaned by high temperature treatment, because organic matter is oxidized, while gold oxide is decomposed.

The results of the present work showed some similar contradictions for which possible reasons for the discrepancies were given in the discussion that followed.

2.4.1.1 Vapour condensation method. The results obtained by vapour condensation method are summarised in Table 2.1 and show that gold was hydrophilic when treated with concentrated H_2SO_4 at elevated temperatures, chromic acid, or sodium hypochlorite; but was hydrophobic when treated with ether, hydrogen peroxide, hydrochloric acid and when heated to

900°C in air.

That gold becomes hydrophilic when treated with the above oxidising reagents means that organic contamination on the surface has been removed does not seem to take into account that these reagents also react with gold (Appendix 1). At elevated temperatures, in particular, they etch the surface of gold. Concentrated sulphuric acid above 200°C is very oxidising and reacts with gold. It was also observed that gold etched with aqua regia and hot concentrated HNO_3 left reaction patches which tarnished the surface brown. These patches were slowly removed with hot concentrated HCl. The patches also disappeared on heating gold to 900°C. Thus the chemical state of a freshly etched solid depends on the etchant used and the way in which the attack was stopped. These reagents may attack gold through an intermediate reacting layer of definite thickness which may remain when the etching is stopped. Both these, and those etchants which contain components or impurities which can deposit on the surface are to be avoided, as a chemically pure surface is the prime requirement. The amounts of deposit left by an etchant on the surface are dependent on the way in which the etching is concluded and the reagents are washed away. Radioactive tracer experiment by Holmes and others[74] have shown that removing germanium from an etchant and plunging it into de-ionized water can leave a considerable but widely variable amount of residue. Once formed, this can subsequently be removed only by chemical dissolution or prolonged water washing. There is hardly any information about the etching effects of the reagents used for cleaning gold in this work, on its intrinsic hydrophobicity. To eliminate any impurities introduced during such chemical

treatments further cleaning, for example, high temperature treatment would be required.

It cannot also be accepted that gold was clean because it was hydrophobic after treatment with ether, hydrogen peroxide, or hydrochloric acid since the question of total absence of organic contamination would remain. The organic contamination may even come from these reagents. To overcome the problem of organic contaminations, treatment of gold at elevated temperature, as carried out, by heating it to 900°C appears to be a reliable method of destroying any oxide layers or organic impurities. The result of heating gold to 900°C shows that such gold is hydrophobic (see Table 2.1) under those conditions. This observation has been disproved, however, by later experiment in which there was no possibility of organic contamination (see Table 2.2). But as the mist condensation method is capable of revealing feeble hydrophobicity[75,76], it may be possible that the gold prepared under such conditions could be rather weakly hydrophobic with contact angle <5°.

2.4.1.2 Electrochemical method.

On anodic and cathodic polarisation of gold in oxygen-, and nitrogen-saturated 0.2 M KH_2PO_4 + 0.2 M NaOH buffer solutions and in nitrogen-saturated 0.2 M H_2SO_4 solution, the bubble contact with the electrode was expected to be strong as the possible adsorbed organic contamination was not removed before the tests were conducted. This could be removed by cold chromic acid treatment of the electrode[77] and washing with distilled water just before the electrode was put into the electrolyte. As this precaution was not taken in these cases, strong bubble contacts were established with the gold at potentials below those of hydrogen evolution

and oxide formation (Figs.2.5 and 2.6). The bubble contacts became generally less strong, however, as the cathodic potentials increased. This can be ascribed to increase in the intensity of the electrical double layer repulsion. During anodic polarisation bubble contact was strong until oxygen adsorption became significant at potential above 0.75 V (i.e. in oxygen-saturated solution) or at potentials above 1.0 V when oxide formation[77-83] was apparent.

The reduction of the oxide film on cathodic polarisation did not re-establish strong bubble contact with the gold even after prolonged polarisation or when polarisation terminated. Under such conditions it might be possible that the oxide was not completely removed[81,82]. Dickinson and his co-workers[83] found that a gold electrode treated with aqua regia and H_2SO_4 when polarised cathodically at potential of 0 - 0.6 V and analysed with X-ray photoelectron spectroscope still retained some oxygen. The amount of oxygen retained by gold under such conditions might be small and might not have great effect on the contact angle.

When the gold electrode was treated with chromic acid, washed with distilled water and polarised in HCl, the bubble contact was below 10^{o} at all potential studied. This observation is consistent with the recent work of Gardner and Woods[77].

If the point of zero charge is taken as 0.18 V vs SHE[84,85] i.e. about-.06 V vs SCE, and the rest potentials of gold in the N_2- and oxygen-saturated buffer soln. are 0·18V&0.292 V vs SCE (see 2.3.2) respectively, the contact angle on gold in ordinary distilled water containing dissolved oxygen used for contact angle work, would not be greatly affected by the electrical double layer repulsion since the potential

of gold in such water would not be far from the p.z.c. Hence the contact angle of an air bubble on gold would be similar to its value at the p.z.c.[86]. This could also mean that the adsorption of oxygen on gold in ordinary distilled water would not significantly reduce its contact angle, particularly if the contact angle were greater than, 10^{o}, for instance, as reported by many investigators. It appears therefore that the electrochemical results point to the conclusion that clean gold, free of organic contamination should be hydrophilic. As there can be some uncertainity about the purity of the electrolytes used it would be more appropriate to clean such gold finally by high temperature treatment as carried out by Kostelitz and Oudar[87].

2.4.1.3 Captive bubble method.

The results obtained (Table 2.2) show that (1) gold polished with "Silvo" and heated in boiling 30% H_2O_2, (2) gold polished with alumina and finally cleaned on "Selvyt" cloth, (3) gold etched with aqua regia, nitric acid followed by concentrated HCl treatment (4) gold heated to 900^{o} in a silica crucible, covered with a lid and allowed to cool to room temperature gave mean contact angle value of $57^{o} \pm 2^{o}$. Although this value is in agreement with those of other investigators, the techniques employed possibly may not exclude completely all organic contamination. This is evident by comparison with the result of gold in the "sealed tube" technique.

The regaining of hydrophobicity of gold etched with aqua regia or concentrated HNO_3 followed by concentrated HCl treatment may indicate the removal of oxidised surface of gold.

The removal of such surface might enhance the ability of the surface to adsorb organic contamination possibly from the HCl or the atmosphere. The effect of these oxidising acids could not be that of the removal of organic impurity only, since under the experimental conditions the gold so treated with them was never found hydrophobic. Further support for this idea is possibly shown by the fact that gold treated with these acids readily became hydrophobic when heated to 900^{o}C in silica crucible and covered with a lid before cooling to room temperature. Under such conditions it was observed that the gold became hydrophobic before it cooled to room temperature.

The adsorption of organic impurity by gold made hydrophilic by etching with aqua regia, and made hydrophilic by sealing in a silica tube as described earlier, kept under distilled water and drained off the water with a filter paper and exposed to the atmosphere at the same time are shown in Table 2.3. As shown, the adsorption of organic impurity occurred in a matter of seconds on gold previously heated to an elevated temperature while the formation of hydrophobic sites on gold etched with aqua regia was slow.

Table 2.3 Contact angles on hydrophilic gold exposed to the atmosphere.

Sample	Exposure Time	Contact angles, degree
Gold etched with aqua regia.	1 minute	zero
	10 minutes	0, 13, 5.
	60 minutes	32,20,0,33,8.
Gold heated to 900^{0}C and sealed in silica tube.	0	0
	20 seconds	33, 43, 50.

The technique of sealing gold in a silica tube where organic impurities are destroyed appears to be a reliable method. This method can be used to determine the temperature at which the adsorption of organic contamination can be detected.

Although the result of the most reliable technique indicates that gold is hydrophilic, the theoretical expectation is that clean metal surfaces ought to be hydrophobic as the only significant metal/water interaction is that due to London dispersion forces, these being weaker than water/water interaction (including hydrogen-bonding). Assuming that the theoretical expectation is correct, it can only be supposed that gold chemisorbs oxygen on cooling in air, although not forming a bulk oxide under these conditions. It is not known for certain whether such cleaned gold carries a monolayer of oxygen. (Ultra-pure metal surfaces can only be studied by the special techniques employed in ultra-vacuum research).

The possibility that the contact angles of water on oxide-free gold could be just close to zero should not be ruled out as indicated by the work of Bartell and Smith[60] since at such low values gas bubbles cannot adhere to a solid surface, but as stated earlier, the mist condensation test can reveal feeble hydrophilicity.

The result of gold sealed in silica tube technique is in agreement with that of Bewig and Zisman[64] who used alumina abrasive for polishing prior to heating their gold to 1000°C. It is impossible to know to what degree the residual alumina could have contributed to the observed

hydrophilicity of the surface. By removing residual alumina on gold surface White and Drobek observed that the contact angle increased; but this may also indicate that cleaner gold surface has greater capacity for adsorbing organic impurity.

It must also be borne in mind that high purity gold is not absolutely free from metallic and the inorganic elements and such impurities can accummulate on the exposed surface during etching or annealing of the specimen.

2.4.1.4 Contact angles of air bubble on gold in xanthate and xanthate-starch solutions.

If the magnitude of contact angle is an indication of the degree of hydrophobicity then, the hydrophobicity acquired by gold in air-saturated KEX solution at pH 6.5 in 20 minutes is close to the maximum that may be attained in KEX solution. For flotation, it would still be satisfactory to have a conditioning period of ten minutes because the contact angle of 50^{o} obtained in such a time is sufficient for good flotation. In terms of contact angles it appears that there is no advantage in using oxygen-saturated instead of air-saturated xanthate solution for flotation even though the amount of adsorbed xanthate in the former would be greater (See Fig.2.7). This may imply that some amount of xanthate would have been adsorbed before contact can be established. As oxygen is needed for the formation of a strong contact angle in the xanthate-gold system, the induction time for establishing bubble contact would be shorter in oxygen-saturated solution than in air-saturated xanthate solution[88]. For many sulphide minerals the time for attainment of maximum contact angle is shorter[89].

As shown in Fig. 2.8 the contact angles did not change markedly above a concentration of 10 mg/l. The contact angle values as plotted against KEX concentration have a logarithmic form with the maximum angle being approached asymptotically. Similar curves for gold and platinum were reported recently by Gardner and Woods[77].

In Figs.2.9a and 2.9b the effects of oxygen and pH on the hydrophobicity of gold in KEX have been clearly shown. The differences in the two sets of contact angles (Fig.2.9a) were possibly due to (a) the amount of dissolved oxygen in solution affecting the rate of xanthate adsorption and (b) the effect of pH in reducing the rate of adsorption of KEX on gold. For KEX solution prepared with air-saturated distilled water through which no air was bubbled during the conditioning time, it would be expected that with increased pH the amount of adsorbed xanthate should decrease faster than that through which oxygen was passed continuously. The present results are consistent with this expectation.

The decrease in contact angle from 62^{o} to zero (Fig.2.9b) in a period of 1 hour at pH 11.8 could be due in part at least to the decomposition of the adsorbed xanthate, i.e. dixanthogen, on the surface of gold since dixanthogen decomposes rapidly in aqueous solution of pH> 11 (Chapter 4).

In the anodic polarisation of gold in xanthate solution[69,77] it has been shown that dixanthogen is the species responsible for the hydrophobicity of the surface. The present finding can also be compared with the results of Majima and Takeda[90] and Tolun and Kitchener[91] and Golikov[92], which showed that dixanthogen enhanced bubble adhesion to some sulphides in sulphide-xanthate-oxygen system.

2.5 Conclusions

1. Truly "clean" gold is hydrophilic but only weakly so. Although it exhibits zero contact angle with pure air or nitrogen gas in clean water, it is, however, possible that condensed water vapour could form very small contact angles just greater than zero on its surface which could not make gas bubbles adhere to it. Consequently it is rendered hydrophobic by brief contact with ordinarily "clean" water or with London air. Evidently it has a strong affinity for organic impurities. Thus large contact angles often observed on gold surfaces can only be due to organic contamination.

2. The stability of the hydrophilic condition of gold which has been treated with sodium hypochlorite, aqua regia, chromic acid, hot sulphuric or nitric acid is probably due to the oxidised state of the surface.

3. Residual alumina abrasive on polished gold surface could stabilise its hydrophilicity; but it may not necessarily be the cause of the hydrophilic nature of the surface as suggested by some investigators.

4. Contact angles of air-bubbles on gold in air- or 0_2-saturated KEX solutions were found to range from 52^{o} to 62^{o}.

5. Concentrations of potassium ethyl xanthate solutions greater than 20 mg/l do not significantly affect the contact angles. In solutions of a long-chain xanthate, potassium amyl xanthate, the contact angle values are about 10^{o} greater.

6. The hydrophobicity of gold in air- or oxygen-saturated xanthate solution may be due to the formation of dixanthogen; the presence of oxygen being essential for the formation of the adsorbed xanthate.

7. Starch at low concentrations (below 300 mg/l) does not markedly affect the hydrophobicity of gold in oxygen-saturated xanthate solutions.

CHAPTER 3

3. THE WETTABILITY OF GRAPHITE

3.1 General

The structures of graphite and of starch molecules are first briefly reviewed.

(a) Nature of graphite[93-95]

It is accepted that graphite is a semi-metal in which the valence and the conduction bands overlap slightly, so that always, regardless of the temperature, a few holes and electrons are available to carry current. In pure graphite the electron and the hole densities are small and equal, and the carrier-effective masses are low. These features dominate the electron transport properties.

The possible orbital structures for a plane of atoms in a crystalline graphite and the interplanar interactions are represented in Fig.3.1. The carbons are arranged in layer planes with in-plane bond distance, a_o (the a-axis spacing) of 1.42 Å. Each plane can be regarded as an extended aromatic system. The valence electrons of carbon are $2s^2 2p^2$. As in the aromatic molecules, the three of the four valence electrons in graphite occupy trigonal sp^2 hybrid orbitals directed at 120^o to each other and lie in the basal plane. These sp^2 hybrids overlap with those on adjacent carbon atoms to form tight, localised sp^2 σ-bonds. The remaining occupied orbital is the $2p_z$ state directed at right angles to the nodal carbon plane. Linear π-type molecular orbitals extend over either side of the lattice plane. As a result, the interplanar spacing is about 3.40 Å. Such a large distance is assumed to arise from weak van der Waals type, interlayer bonding. The estimated interaction

is about one hundred times smaller than the tight binding interaction between in-plane neighbours. For instance the bond strength of the planar bonds in graphite is about 113 kcal per mol as compared with that of benzene, 121 kcal per mol, and diamond about 83 kcal per mol.

It is observed that the electrical properties are consistent with this model. For example, graphite is a good conductor of electricity and heat parallel to the atomic planes, but a poor conductor normal to the planes. The π-electrons are delocalised and extend throughout each plane, and so the electrons can move quite freely in the plane to conduct electricity and heat while conduction perpendicular to the planes requires the transfer of electrons from one set of π-orbitals into another set.

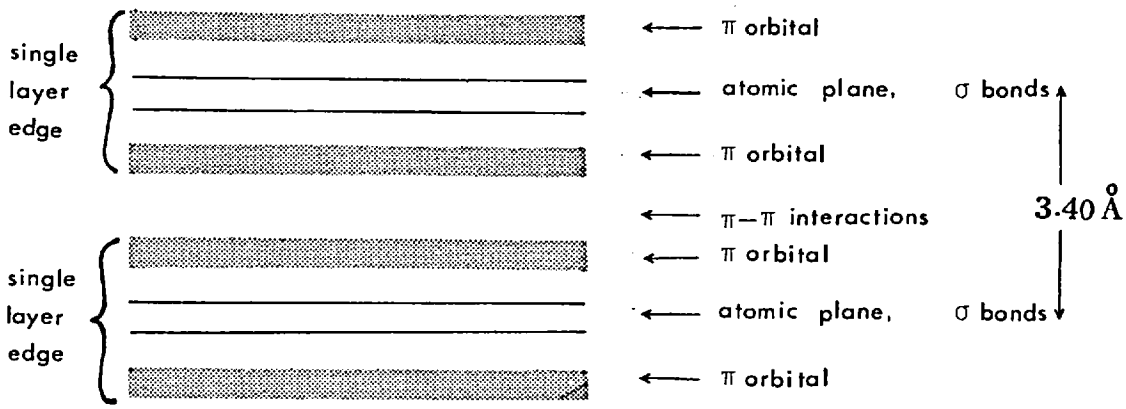


Fig.3.1 Possible graphite orbital structure.

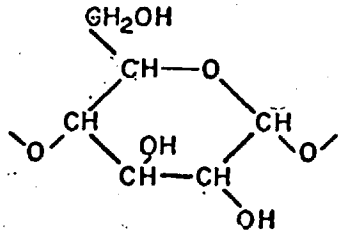
The wettability of graphite is considered to depend on these characteristics[96,97]. When graphite is crushed under water, the plane cleavage surfaces are weakly hydrated because of the weak van der Waals interacting forces between

graphite and water. On the other hand, the edge ends of the planes are presumably reactive, and probably undergo oxidation leading to increase hydration.

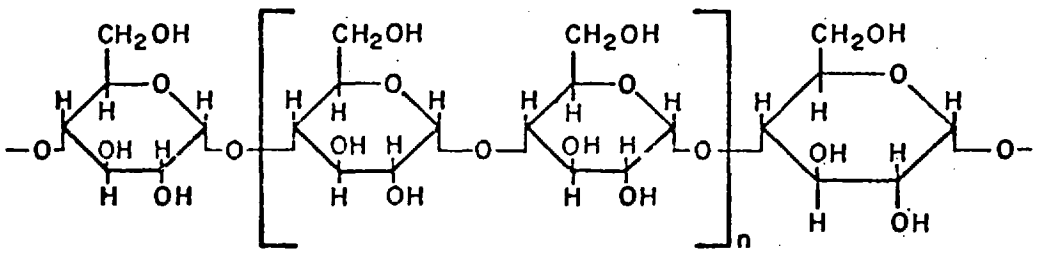
(b) Nature of starch.[98,99]

Starch is a high polymeric carbohydrate built up of D-(+)-glucose units, with a molecular weight ranging from 500,000 up to several millions. Maize starch[98] consists of about 25% linear glucosidic chain amylose and 75% branched amylopectin molecules. Amylose has relatively a lower molecular weight. (The molecule contains a few hundred glucose residues with only one non-reducing end group per molecule). Amylopectin, however,has a higher molecular weight. (The molecule contains over 1000 glucose residues with one non-reducing end-group for every 20 to 30 glucose residue (Fig.3.2)). The composition of starch is variable and depends on the initial raw material and the conditions of preparation.

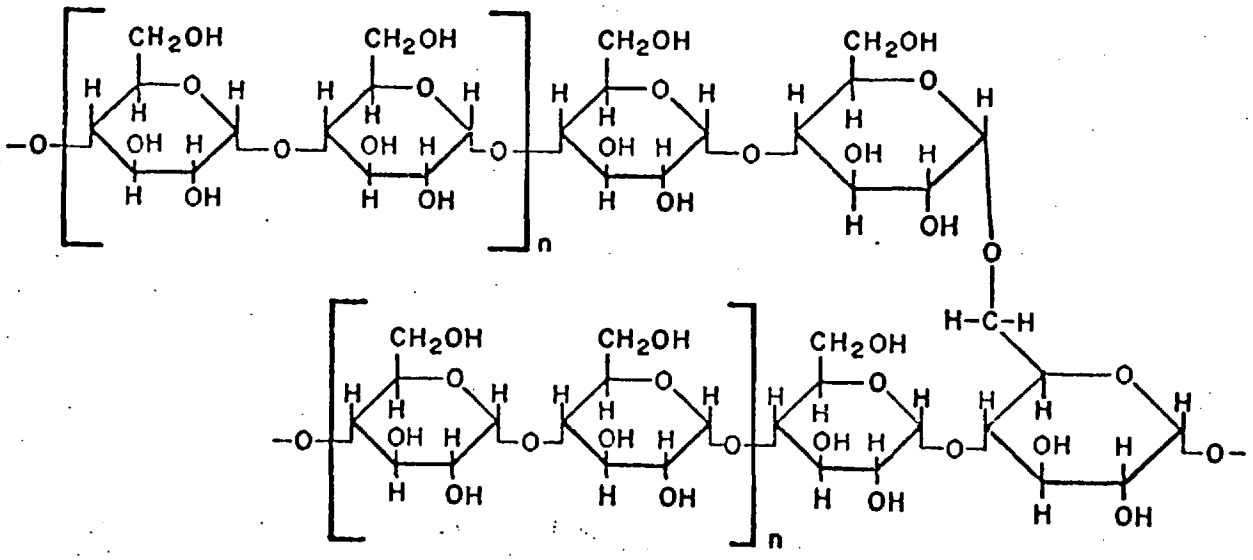
Aqueous solution of starch represent complex systems in which one portion of the reagent exists in the molecularly dispersed condition and the other in the form of associated molecules. The properties of aqueous solutions of starch also depend on the pH of the medium. Starch reacts with alkali to form compounds, the natures of which have not been well-defined . It is easily changed into dextrins in the presence of acids. (The name dextrin has been loosely applied to a large variety of starch degradation products intermediate in molecular weight between that average for starch and the oligosaccharides. The degration may be produced by acid, heat, enzymes or other reagents or by a combination of these agencies. If a substantial amount of



D-Glucose unit.



Segment of Amylose Polymer



Segment of Amylopectin Polymer

Fig.3.2 Structure of Starch Polymers.

acid is added to the starch for dextrination, the product so formed is called the "white dextrin").

3.2 Introduction

3.2.1 Previous work on the hydrophobicity of graphite.

It is well known that graphite is hydrophobic and naturally floatable. The degree of hydrophobicity in terms of contact angles has been determined by many investigators[100-102]. Rebinder[100] in 1933 found the contact angle of water on graphite to be 60°. Majumdar[101], however, obtained contact angles of 17°-25°, while Sun[102] obtained 38° on Ceylon graphite. Sun also advanced a hypothesis to explain the floatabilities of various coals, carbons and hydrocarbon minerals. He stated that these materials consist of both floatable and non-floatable chemical constituents and that their floatabilities are governed by the balance between these two groups of components. The material with surface predominated by the floatable component which is oil-avid and water repellent is more readily floatable than that material with surface predominated by non-floatable component which is water-avid and oil-repellent. This simply means that the floatability of these materials including graphite depends on the balance of the hydrophobic and the hydrophilic sites on the surface. Other workers[103,104] hold a similar view. Further investigations in this field included those of Arbiter, Fujii, Hansen and Raja[105] and Fowkes and Harkins[106] who obtained contact angles ranging from 69° to 85.7°.

The theoretical evaluation of contact angle of water on graphite can be made from Fowkes' formula;

$$\cos\theta = -1 + 2\sqrt{\gamma_S^d \gamma_L^d} - \pi_\varepsilon/\gamma_{LV} \qquad (1)$$

This formula demands that the values, γ_S^d and π_ε be determined experimentally. But the experimental values of these factors depend on the solid. For this reason the values of the contact angles obtained by different methods, for instance, by heat of adsorption, integral heat of immersion and from Hamaker constant, will depend on the type of graphite employed.

Much of the work done to determine the value of γ_S^d for graphite has been on "Graphon" (i.e. graphitized carbon black). Isirikya and Kiselev[107] and Fedorov et al[108] determined γ_S^d for Graphon by means of heat of adsorption and obtained 108 x 10^{-7} J cm^{-2} and 107 x 10^{-7} J cm^{-2} respectively, which are in line with the values of 108 x 10^{-7} J cm^{-2} calculated by substituting the contact angle of 85.7° obtained for graphite by Fowkes and Harkins[106] into equation 1, and 109 x 10^{-7} J cm^{-2} calculated from the value of π_ε, the decrease in free energy due to adsorption, determined by Harkins[109].

Large contact angles close to that on Graphon can only be obtained on surfaces with negligible polar sites[110]. It can therefore be expected that natural graphite with more polar sites and synthetic graphite which is also more polar than Graphon[104] should be less strongly hydrophobic with lower contact angle values.

3.2.2 Aim of work.

In the separation of carbonaceous matter (modelled by graphite) from gold by flotation it is useful to know the effect of the reagents to be used on the hydrophobicity of the carbon. Thus the aim of this part of the work is to study the influence of pH, xanthate and starch on the wettability of graphite in aqueous medium.

3.3 Experimental

3.3.1 Materials

The materials employed here were:

(a) synthetic graphite in the form of a block was kindly provided by the British Acheson Electrodes Ltd., Sheffield, with the composition shown in Tables 5.1, Chapter 5.

(b) maize starch No.8204.00 EM, used in earlier experiments (see Chapter 2). (The preparation of the starch solution is described in Chapter 4).

(c) purified potassium ethyl and potassium amyl xanthates (KEX and KAX).

3.3.2 Methods

Sample preparation and contact angle measurement.

A piece of the graphite was mounted on a glass cube with Araldite and polished on a 600 mesh emery paper under distilled water. The specimen was later put into distilled water contained in a glass cell, of a captive bubble apparatus, which had been cleaned with chromic acid . The contact angle of an air bubble on the graphite was determined as described in Chapter 2, page 106 . (Polishing of the graphite on dry Whatman No.542 filter paper gave reproducible contact angle values which were not different from the values obtained by polishing graphite on the emery paper).

The contact angles were determined under the following conditions: (a) at pH values from 5 to 11 in conductivity water using NaOH solution to adjust the pH of the water. (b) at the same pH values and in 20 mg/l KEX solution after a conditioning time of 30 minutes. (c) in various concentrations of KEX and KAX solutions at pH 7 after 30 minutes of

conditioning. (d) in 1 g/l KAX at various times at pH 7.0 and (e) in different concentrations of starch solutions and different conditioning times at pH 7.

Oxygen was bubbled through each solution continuously, since xanthate does not adsorb on graphite in absence of O_2, and stopped only when measuring the contact angles. The results of the tests are shown in Figs.3.3 to 3.6.

3.4 Results

3.4.1 The effect of pH on contact angle on graphite.

The advancing and receding contact angles of air bubbles on synthetic graphite in distilled water were $80^{o}\pm 2^{o}$ and $50^{o}\pm 3^{o}$ respectively. The mean might correspond to an equilibrium contact angle of about $65^{o}\pm 2^{o}$ and falls between the contact angle values of 61^{o} and 69^{o} obtained by Rebinder[101] and Arbiter and his co-workers[105] on Ceylon graphite.

The effect of pH on the contact angles on the graphite is shown in Fig.3.3. These results show that the effect of pH is not great. Decrease in the contact angles became apparent only at pH >9. At pH 11 the contact angle was about half of its value in distilled water. The general trend of contact angle in relation to pH is in line with the results of Arbiter and co-workers.

3.4.2 Effect of xanthate concentration on contact angles.

Fig.3.3 also shows the effect of 20 mg/l KEX on the contact angles at different pH values. The results show that the contact angles were slightly lower than in distilled water. The advancing contact angle in 20 mg/l KEX solution decreased from 72^{o} at pH 5 to about 63^{o} at pH 10.8, whereas

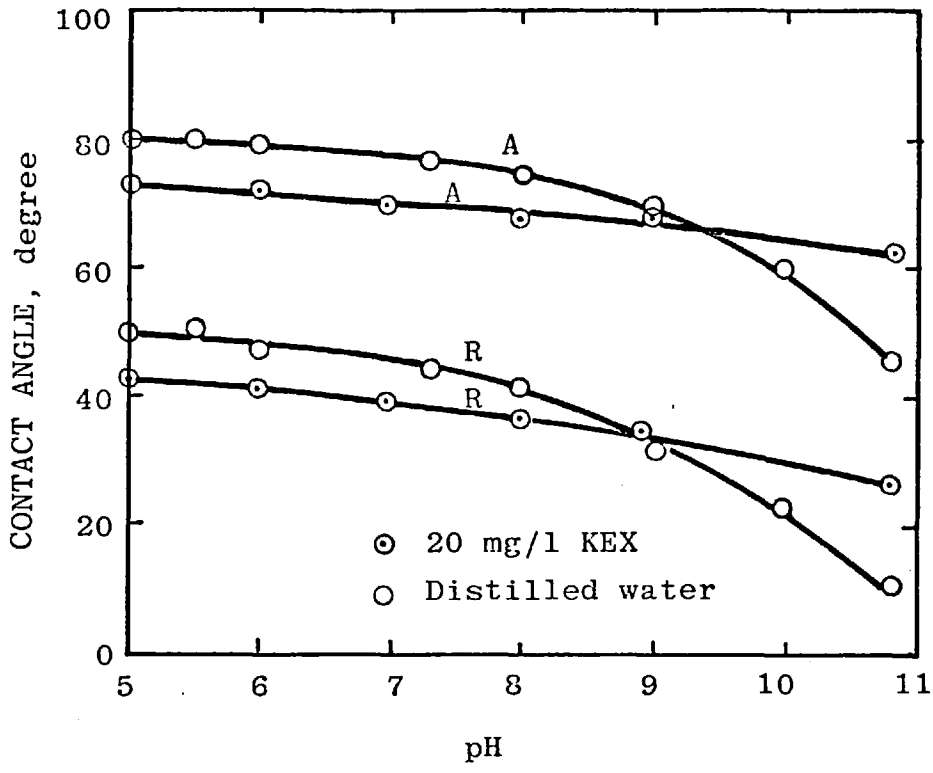


Fig.3.3 Contact angle of an air buble on graphite in Water and KEX solution as related to pH.
(Conditioning time = 30 min. Temperature = 22°C
A & R, advancing and receding contact angles)

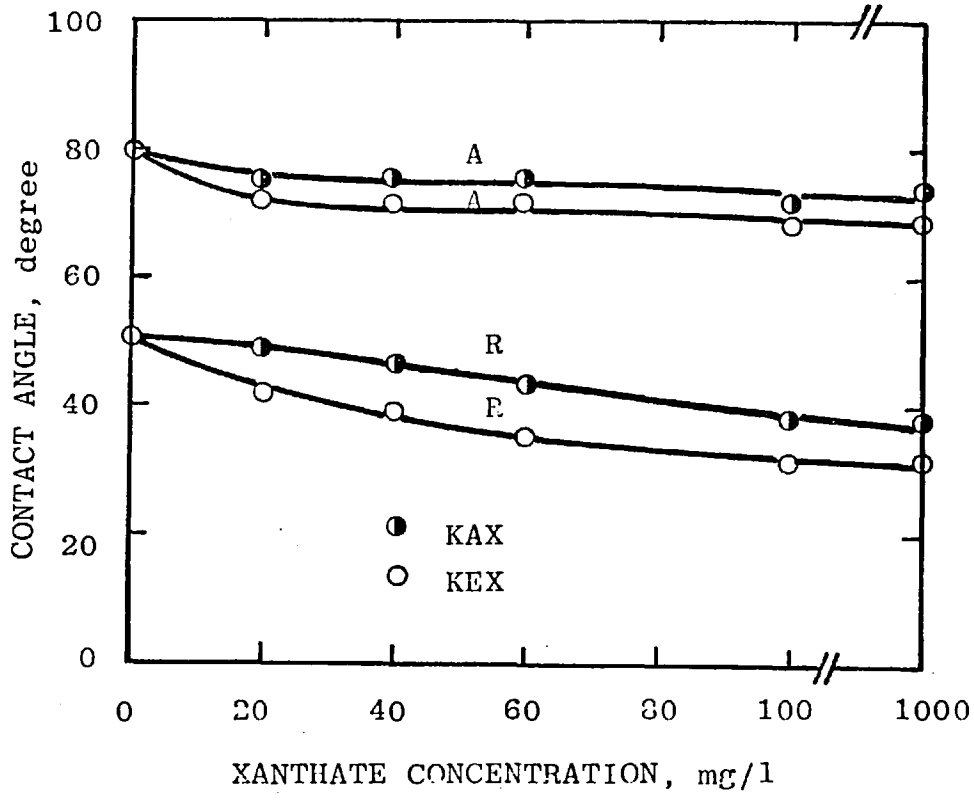


Fig.3.4 Contact angle on graphite as a function of xanthate concentration. (pH of solution = 7.0, temp.= 22)

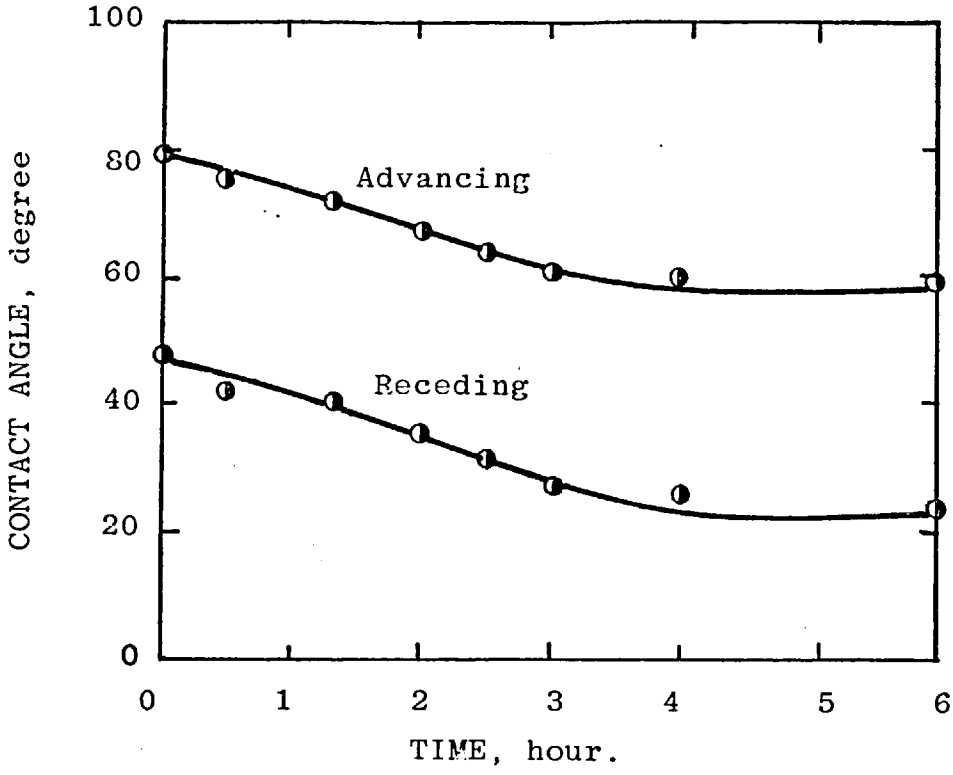


Fig.3.5 Contact angle of an air bubble on graphite in 1 g/l KAX solution as related to time.
(pH of solution = 7.0, temperature = 22°)

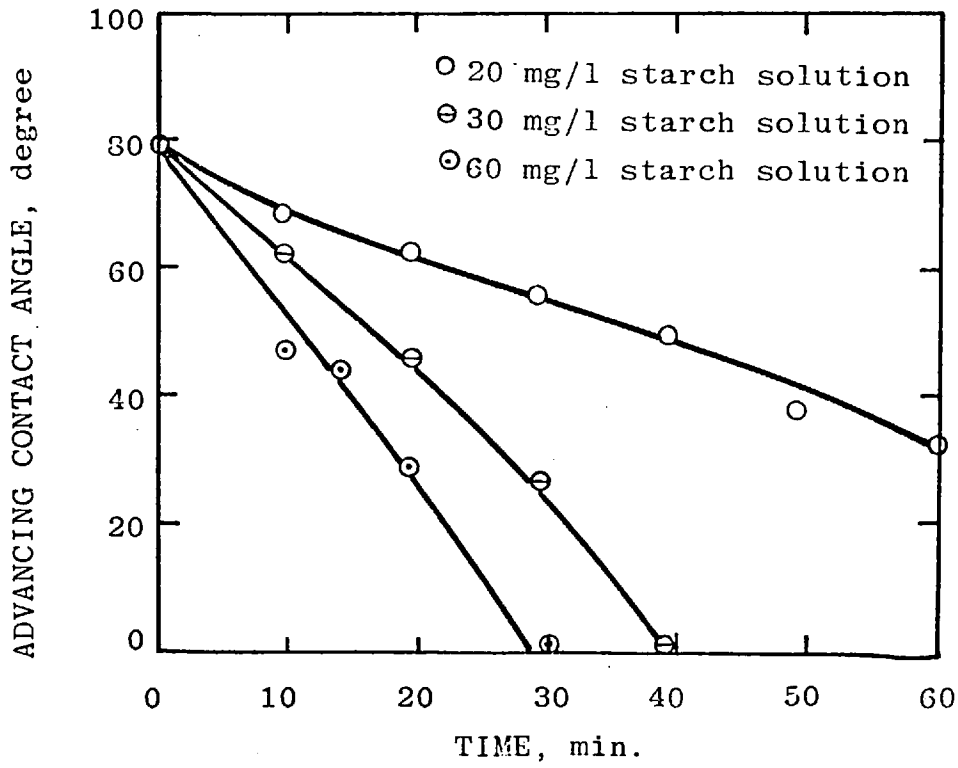


Fig.3.6 Advancing contact angle on graphite as related to time at various starch concentrations.
(pH of solution = 7.0 temperature = 22°C.)

in distilled water it decreased from 80° to 45° for the same range of pH values. It appears therefore that the presence of xanthate decreased the hydrophobicity of the surface at pH <9.

In Fig.3.4 the contact angles determined in KEX and KAX solutions were also lower than the value in distilled water. Increase in concentration of KEX and KAX did not seem to increase the contact angles above the values for 20 mg/l. But surprisingly when graphite was kept in 1 g/l KAX solution for a prolonged period the contact angles decreased with time (Fig.3.5).

3.4.3 Effect of starch on contact angles.

The effects of starch concentrations and time on the contact angles on graphite are shown in Fig.3.6. As expected, the contact angles decreased with time and with increase in starch concentration. For example in 60 mg/l of starch solution the surface became totally hydrophilic with zero contact angle in 30 minutes. The results suggest that starch is only very slowly adsorbed on graphite. This, however, is not the case as has been shown by the data on starch adsorption (Chapter 5) and by the flotation results (Chapter 6). It is puzzling that starch appeared to be adsorbed rather slowly on graphite. The reason, however, is not clear. But it could be suggested that the slow adsorption of starch onto the polished surface could be due to the slow rearrangement of the "hydrophobic" side towards graphite.

3.5 Discussion

3.5.1 Hydrophobicity of graphite in water.

Many investigators[100-102,105,106] determined the contact angles on graphite in water and reported various values from 17° to 85.7°. The wide differences in the contact angles can be attributed to the heterogeneity of the surfaces of different graphites. Some of the major causes include the structural defects of the basal plane and the chemisorbed oxygen on these defect sites or on the edge sites. The ease of chemisorption of oxygen is ascribed to the free valences at the edge of the graphite layer planes. These free valences are very reactive and form compounds with any suitable foreign atoms present. Consequently, polar groups or surface compounds can be expected at the layer edges and foreign atoms or molecules are weakly adsorbed on the basal planes by means of the graphitic π-electrons system except where they are bound at lattice defects.

In aqueous medium, therefore, graphite would adsorb water molecules onto the chemisorbed oxygen sites primarily at the layer edges in a similar way to oxide minerals as suggested by Campbell and Sun[111]. In a strongly acidic or basic medium the edge sites should be positively or negatively charged and be strongly hydrophilic. The adsorption of hydronium ions or hydroxyl ions on to the basal face under the same conditions would also increase leading to increase in surface charge and decrease in contact angle. This expectation was confirmed by Arbiter and his co-workers who observed that at pH <2 and pH >9,

the contact angles on graphite decreased. Between pH 2 and 9, however, the contact angle remained constant. The present results (Fig.3.3) are reasonably consistent with this observation. That the hydrophobicity should be maximum at the p.z.c.[112] (for graphite the p.z.c. is said to be between pH 2 and 5[104,113]) is not apparent from the contact angle results of Arbiter and others. It can be assumed that the relatively lower contact angles obtained for graphite in water in this work were due primarily to the presence of hydrophilic sites on the polished surface.

3.5.2 The effect of xanthate on the contact angles on graphite.

The effects of xanthate on the contact angles on graphite under various conditions shown in Figs.3.3-3.5 indicate a slight general decrease of contact angles in O_2-saturated xanthate solutions as compared with that in distilled water. The explanation of these observations can be made by considering the type of graphite surface exposed during polishing and the nature of the adsorbed xanthate species. Although the synthetic graphite is more polar on the basal plane than Graphon, it may be less polar than natural mineral graphite. On polishing graphite, the basal plane is the plane which is easily exposed. This may possibly make the catalytic oxidation of xanthate to dixanthogen occur less readily by the polished surface. As is demonstrated later (Chapter 5) by zeta-potential measurements of graphite in KEX solution, xanthate ion is probably adsorbed initially on graphite through hydrophobic association of the hydrocarbon group on to the non-polar sites of the surface with the polar group directed into solution. This might therefore increase the electrical double layer repulsion effect. In addition, oxidation of xanthate ion may be slow. The result

may therefore be a decrease in contact angle. Horsley, El-Sinbawy and Smith[114] measured the contact angles on coal in KAX solution and found that there was no change in the contact angles (except when $CuSO_4$ was added to the solution or when amyl dixanthogen emulsion solution was used did the contact angles increase).

Under the present conditions, dixanthogen might have been formed but possibly not in such amount as to offset the effect of the physically adsorbed xanthate ions. This effect can be compared with that of gold in xanthate solution where the hydrophilic surface became hydrophobic in a period of a few minutes. The collector effect of xanthate on graphite is evident, however, as is shown by the flotation results (see Chapter 6).

3.5.3 The effect of starch on the contact angles.

In oxygen-saturated solutions the adsorption of starch on graphite should be rapid because oxygen is readily adsorbed by graphite. This would enhance the adsorption of starch on graphite. Increase in the concentration of starch or time of conditioning would result in more starch being adsorbed , resulting in the decrease of contact angles. The results of the contact angles (Fig.3.6) are in agreement with this expectation. As starch is not strongly negatively charged in aqueous solution in the whole pH range of 3 to 11[115], the adsorption and consequently the contact angles should not be significantly different from that at pH 7 for which the contact angles were determined. In xanthate + starch solutions the contact angles might be more influenced by starch because of its macromolecules and possibly faster rate of adsorption than xanthate as has been shown in Chapter 5.

3.6 Conclusions

1. The contact angle of an air bubble on the synthetic graphite in distilled water is found to be $65^{o} \pm 2^{o}$. The contact angle on graphite is not strongly affected by pH, except in highly alkaline media.

2. Pure xanthate does not increase the contact angle on graphite. In fact it slightly decreases it. The effect of any catalytic oxidation of oxygen-saturated xanthate solution on the contact angles is not apparent.

3. The contact angle of an air bubble on graphite in starch solution is readily decreased and the surface ultimately rendered hydrophilic. Prolonged conditioning time and increase starch concentration enhance hydrophilic surface formation.

CHAPTER 4

4. ADSORPTION OF XANTHATE AND STARCH ON GOLD

4.1 Introduction

4.1.1 The surface properties of gold.

Literature on gold has much on the inertness of the metal and the ability of its salts or compounds to revert to the metal at high temperatures, unlike compounds of many other metals. Its inertness at normal atmospheric conditions has long been realised and Pourbaix's Eh - pH diagrams[116] for the stability of gold at normal atmospheric conditions in water summarised the facts. The application of Pourbaix's equilibrium diagram to the chemistry of gold was recently reviewed by Finkelstein and Hancock[117] and a new approach to the stability of gold complexes formed with liquids advanced. Johnson[118] in a review also pointed out the need for the presence of complexing reagents for the oxidation of gold.

In order that gold should react in its common environment at ambient temperature in more or less wet air, it must oxidise, for example, to its monovalent or trivalent state. The tendency of gold to oxidise to Au^+, i.e.

$$Au \longrightarrow Au^+ + e \qquad (1a)$$

is given by Nernst equation as follows,

$$Eh = E^0 - 2.3 \frac{RT}{F} \log \frac{\{Au\}}{\{Au^+\}} \qquad (1b)$$

where E^0 is the standard reduction potential for the reaction, R is the gas constant, F is the Faraday, and T, the absolute temperature. By taking the activity of the metal, {Au} as unity and the activity of the dissolved species $\{Au^+\}$ to be equal to its molar concentration {Au} , then at 25°C the

reduction potential can be expressed as[116],

$$Eh = 1.67 + 0.0591 \log\{Au^{+}\} \quad (1c)$$

Similarly the reduction potential for the alternative oxidation i.e.

$$Au \longrightarrow Au^{3+} + e \quad (2a)$$

can be expressed as,

$$Eh = 1.498 + 0.0197 \log\{Au^{3+}\} \quad (2b)$$

During oxidation, the metal may interact with its environment, water as follows:

$$Au + 3H_2O \rightleftharpoons Au(OH)_3 + 3H^{+} + 3e \quad (3a)$$

and the reduction potential can be expresses as,

$$Eh = 1.457 - 0.0591\ pH \quad (3b)$$

and $$Au(OH)_3 \rightleftharpoons AuO_2 + H_2O + H^{+} + e \quad (4a)$$

giving $$Eh = 2.630 - 0.0591\ pH \quad (4b)$$

As the reduction potential for reactions 1a, 2a, 3a are high, these reactions can only take place if powerful oxidants are present in the water. If oxygen dissolves in the water to form an O_2-water equilibrium system then the redox couple can be expressed as

$$2H_2O \rightleftharpoons O_2 + 4H^{+} + 4e \quad (5a)$$

and the reduction potential can be given as

$$Eh = 1.228 - 0.0591\ pH + 0.0147\ Po_2 \quad (5b)$$

But evidence available so far indicates that under atmospheric conditions oxygen does not exist in electrochemical equilibrium with water[119]. The relatively high potential of oxygen reduction means that oxygen should be a better oxidising reagent than most oxidising agents, e.g. ClO_4^{-} ion, with less favourable potentials. In reality, however, the reaction of oxygen at room temperature

is much slower. According to Latimer[120], oxygen in the presence of hydrogen ion is generally reduced to hydrogen peroxide. This product and peroxyl ion (HO_2^-) form intermediate products of oxygen reduction. But it was observed that hydrogen peroxide is the most stable intermediate of oxygen reduction. The work of Sato[119] and Allgeir, Hafford and Judy[121] showed that the oxidation of minerals occurred in the Eh - pH stability zone for H_2O_2 - O_2 couple. Thus the oxidation potential of an aqueous system in contact with free oxygen is controlled by the potential of the H_2O_2 - O_2 couple. At equilibrium the reaction of the couple can be expressed as

$$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^- \qquad (6a)$$

with the potential

$$Eh = 0.682 - 0.0591\ pH + 0.0295 \log \frac{P_{O_2}}{\{H_2O_2\}} \qquad (6b)$$

where $\{H_2O_2\}$ is expressed in activity. By choosing the ratio $\frac{P_{O_2}}{\{H_2O_2\}}$ equal to 10^6[119], to correspond to the upper limit of the oxidising zone of minerals at P_{O_2} = 0.2 atm, the equilibrium redox potential becomes

$$Eh = 0.859 - 0.0591\ pH \qquad (6c)$$

A species having a lower potential than that of H_2O_2 - O_2 in equation 6c in aqueous system will tend to be oxidised by oxygen while that having potentials greater will decompose hydrogen peroxide. By comparing the reduction potentials of Au^+ and Au^{3+} as expressed in equations 1c and 2b respectively and assuming a unity molar concentration each for $\{Au^+\}$ and $\{Au^{3+}\}$ it is apparent that at no pH will the Eh values equal to that of H_2O_2 - O_2 couple.

In fact the electropotentials of Au - Au^{+} and Au - Au^{3+} couples are greater than that of H_2O_2 - O_2 at all pH values. These indicate that the oxidation of gold is unfavourable in aqueous system containing dissolved oxygen. The work of Bockris and Oldfield[122] showed that the rest potential of gold in H_2O_2 at 25°C can be given as

$$Eh = 0.842 - 0.059\ pH \qquad (7)$$

In O_2-saturated solution the potential increased by about 14 mV and fell back to its initial value when N_2 gas was bubbled through the solution. Their work though does not show that gold can be oxidised by H_2O_2 at the rest potentials; it seems that dissolved oxygen in water will be adsorbed on gold under normal atmospheric conditions, as has been proved by many investigators.

The affinity of oxygen for gold in aqueous solutions making possible,for instance, the dissolution of gold with alkali cyanide, is well known. Many workers[71,123-128] agreed that oxygen adsorbs on gold in solutions and Bockris and his co-workers[129] reported a value of about 0.03 for oxygen coverage of gold under open circuit conditions. The nature of the adsorbed oxygen was not established. Hoare[71], however, proposed that oxygen might form an Au–O bond with gold. The rest potential for the formation of an Au - O bond could be represented as Eh =0.98 - 0.0591 pH in oxygen-saturated solution. Such bond formation will precede the interaction of certain reagents with gold. The adsorption of oxygen may produce variable potential sites on the surface of gold which may be similar to the types on sulphide mineral surfaces described by Plaksin[130].

There have been disagreements, however, about the adsorption of oxygen on gold in the dry state. For instance, Hoare's[78] experimental evidence indicated that gold did not adsorb oxygen in the dry state. This view was supported by many other workers[131-133], who also stated that oxygen is physically adsorbed at -183°C. Some other investigators [134-138], on the other hand, held the view that oxygen is chemisorbed on gold[135,136]. Kul'Kova and Levchenko[136] stated that chemisorption occurred in the range of 50° - 400°C with an activation energy of 3.2 kcal/mol. They found the rate of uptake to be very slow at 50°C, indicating that at 0°C adsorption would be observed only after a long time. MacDonald and Hayes[123] obtained two adsorption maxima for the uptake of oxygen at -50°C and 250°C, whilst at room temperature and temperatures greater than 300°C the adsorption was slow. Ford and Pritchard[139] found that atomic oxygen was adsorbed at -196°C, but stated that molecular oxygen did not adsorb on gold at ordinary temperature.

From the foregoing the following conclusions can be drawn. (a) That molecular oxygen adsorbs on gold in the dry state at ordinary temperature is still unknown and that if any adsorption occurs, it is not in such quantity to be easily detected. (b) That oxygen is adsorbed in aqueous solutions at normal atmospheric conditions to facilitate the interaction of some reagents with gold. The nature of the adsorbed oxygen is still not fully understood. (c) That the oxidation of gold to valence states of 1^+ and 3^+ by oxygen in distilled water is thermodynamically unfavourable.

4.1.2 Xanthate in water under atmospheric conditions.

The salts and S-esters of the mono-O-esters, ROCSSH, of dithiocarbonic acid are known as xanthates. The word xanthate in the present work refers mainly to the alkali metal xanthates and potassium xanthate in particular, which are coloured.

There is considerable amount of information about structure and the chemistry of xanthates[140].

The reactions of potassium xanthates in aqueous solution at different pH values have been studied by many investigators[141-145], and it has been recognised that xanthates are unstable in aqueous solution and they decompose by a number of mechanisms. Below pH values of 7, the predominant mechanism is hydrolysis of the xanthate ion to the acid which in turn decomposes to the corresponding alcohol and carbon disulphide, as represented by

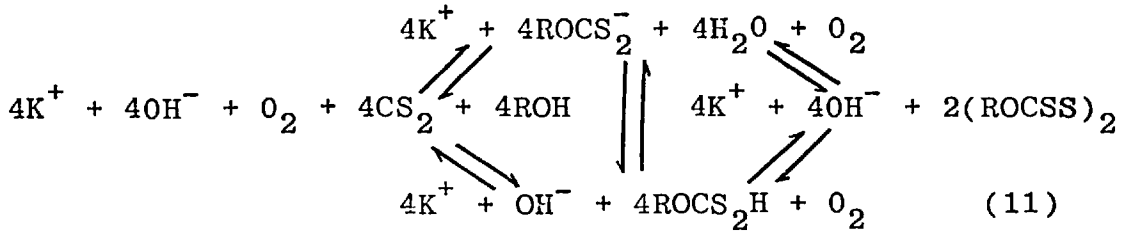
$$ROCS_2^- + H_2O \rightleftharpoons ROCS_2H + OH^- \qquad (8)$$

$$ROCS_2H \rightleftharpoons ROH + CS_2 \qquad (9)$$

where R represents an alkyl group. In solutions having pH values between 7 and 12, it is supposed that xanthate ion is more stable. Theoretically it is assumed to be oxidised to the corresponding dixanthogen

$$4ROCSS_2^- + O_2 + 2H_2O \longrightarrow 2(ROCS_4COR) + 4OH^- \qquad (10)$$

This reaction was considered irreversible, but Pomianowski's work[141] indicated that dixanthogen formation is reversible, and suggested that the following reactions (11)



(11)

should be considered in describing an aqueous xanthate solution at a given pH.

Finkelstein[145], however, showed that the decomposition of aqueous xanthate in the pH range of 7 to 11 is not influenced by the presence of oxygen and that the oxidation of xanthate ion to dixanthogen does not take place in a homogeneous system. He also stated that potassium ethyl monothiocarbonate is one of the species formed. His work also showed that the rate of the formation of monothiocarbonate at high pH values was slow at room temperature but increased as the temperature was raised. Tipman and Leja[146] also confirmed that dissolved oxygen in xanthate solution does not lead to the formation of dixanthogen. But they found that the decomposition of dixanthogen in alkaline solutions proceeds not according to the reversible reaction suggested by Pomianowski[141] but by a two-step process giving EtX^- and a presumed EtX-OH intermediate which decomposes to give CS_2 product. They proposed these reactions:

$$(EtX)_2 + OH^- \longrightarrow EtX^- + EtXOH \qquad (12)$$

and $$EtXOH \longrightarrow EtOH + CS_2 \qquad (13)$$

Recently Harris and Finkelstein[147] reported the formation of monothiocarbonates during the reaction between xanthates and pyrite and galena in the presence of excess oxygen at high pH values. Their work showed that the formation of monothiocarbonate at high pH depends also on the type of mineral.

Information so far available thus shows that xanthates in aqueous solutions of pH below 6 decompose to form alcohol and carbon disulphide; but the decomposition products in the alkaline medium are complex and may include monothiocarbonate.

The types of the adsorbed xanthate species identified include metal xanthate and dixanthogen, both of which may contribute to the hydrophobicity of the mineral.

4.1.3 Interaction of xanthate with gold in aqueous solution.

It has been established that many sulphide minerals and some metals react with potassium or sodium xanthates in the presence of oxygen to form metal xanthates and dixanthogen[140] and some other species[146]. Xanthate reacts with metals which are oxidisable by oxygen. Thus, for example, copper and silver which are in the same periodic group as gold can react with xanthate to form the corresponding metal xanthates and dixanthogen, whereas the products of the interaction between gold and xanthate in the presence of oxygen are difficult to predict because the chemistry of gold is not entirely similar to those of copper and silver. For example, although gold probably adsorbs oxygen from aqueous solution, the nature of the adsorbed species is still not fully understood and the idea of chemisorbed oxygen on gold is still speculative.

For instance, Kakovskii[148] postulated that gold would react with xanthate in the presence of oxygen to form gold xanthate and hydroxyl ion, according to the reaction,

$$2Au + 2ROCSS^- + H_2O + \tfrac{1}{2}O_2 \longrightarrow 2ROCSSAu + 2OH^- \qquad (14)$$

Using the thermodynamic data compiled by Leonov and Matiskin[149] (Appendix 2) it can be shown that the free energy change of the reaction is about -21.9 kcal mol^{-1}, meaning that the reaction is thermodynamically favourable. This reaction however, has not been experimentally substantiated. The work of Plaksin and Tyurnikova[150] using a radiographic technique did not confirm the presence of gold xanthate on gold.

Mitrofanov[151] on the other hand, stated that gold could react with xanthate in the presence of oxygen to form gold xanthate and dixanthogen as follows:

$$3Au + 3O + 3H_2O + 6ROCSS^- \longrightarrow 2(ROCSS)_3Au + 6OH^- \quad (15)$$

$$(ROCSS)_3Au \longrightarrow ROCSAu + (ROCSS)_2 \quad (16)$$

The free energy change of the overall reactions is about -19.5 kcal mol^{-1}, indicating the spontaneity of the total reaction. Zelenov and Yavorskaya[152] by analysing the adsorbed species of KEX on gold in CCl_4 with u.v. spectrophotometry did not detect the presence of dixanthogen and therefore concluded that the reaction of xanthate with gold was probably by reaction 14. Other investigators like Plaksin and Zaitseva[153] observed increased adsorption of xanthate on gold in the presence of O_2, while N_2 and H_2 seemed to have no effect. On the nature of adsorbed xanthate on gold, Lopatin and Plaksin[154] found that xanthate was most adsorbed at pH around 7 and that there was a mosaic pattern of xanthate distribution on the surface of gold (showing that its surface properties were not absolutely uniform) and by increasing the concentration of xanthate the thickness and the width of the xanthate film coverage increased. At still higher xanthate concentration (i,e.>0.1 g/l) the adsorption of xanthate continued without the formation of gold

xanthate.

It appears possible that the adsorbed xanthate referred to in Lopatin and Plaksin's work was dixanthogen. If so, their result is in agreement with that of Woods[155]. Other workers, for instance, Nikulin, Shafeev and Chanturiya[156] studied the adsorption of sulphydryl and oxyhydryl collectors on gold powder electrochemically and observed that the electropotential of gold was rendered more electronegative as the concentration of the xanthate solution was increased; the potential was most negative between pH 6 and 8, indicative of maximum adsorption of xanthate in aqueous solution around the neutral pH.

4.1.4 Adsorption of starch on gold.

There is hardly any information about the interaction between gold and starch. In view of the nature of gold it might be expected that the adsorption of starch by gold would be negligible as starch is usually considered to adsorb on materials primarily through a hydrogen-bonding mechanism.

4.1.5 Aim of this work.

The aim of the present work is to study the adsorption of xanthate and starch on gold to obtain insight into their effect on the floatability of gold, and determine the nature of the adsorbed xanthate products which are responsible for rendering gold hydrophobic and the possible limits of the effects of the adsorbed species on the hydrophobicity.

Consequently, the following factors were studied:

1) The rate of the adsorption of xanthate,

2) The effect of pH and concentration of xanthate, and

3) The nature of the adsorbed xanthate species on gold.

4.2 Experimental

4.2.1 Material

(a) Purification of xanthate used[157].

Commercial potassium ethyl xanthate (KEX), supplied by Cyanamid of G.Britain was purified by dissolving a sufficient quantity in acetone and filtering the solution through a Whatman filter paper No.541. The KEX was precipitated in a beaker by adding diethyl ether to the filtrate. The precipitate was filtered and dissolved again with acetone and reprecipitated as before. This operation was carried out four times and the final KEX precipitate was transferred into a clean bottle and the ether extracted under water-pump vacuum until the KEX was dry. The bottle was "sealed" off under vacuum and kept in a desiccator. This stock of solid xanthate was used when required.

(b) Preparation of starch solution[158].

The maize starch used in this experiment was the same as the one used earlier (Chapters 2 and 3). Starch solution can be prepared in the following ways:

1. By heating with stirring a known quantity of starch dispersed in distilled water to a temperature where the starch is solubilised.

2. Starch dispersed in distilled water can be caustised by mixing it with an equal volume of caustic soda solution of such concentration that the final mixture can be of the required molarity of NaOH. The mixture can then be agitated with stirring for a specified time at a moderate temperature (e.g. 55^{o}C) or at a high temperature.

In the present work the starch solution was prepared by using the first method. 0.11 g of the maize starch (containing 10% moisture) was dispersed in 75 ml warm conductivity water contained in 250 ml three-neck round bottom flask and heated to 100°C with stirring for 20 minutes. The solution was transferred into 100 ml flask and made to the mark when cooled to room temperature. This was the stock of maize starch solution used. Freshly prepared solution was used in all tests.

(c) Gold powder used in the investigations.

Two types of gold powder were used. They were:

1. Gold powder precipitated from Specpure gold sponge
2. Specpure gold sponge of grade 99.99%. All Specpure gold sponge was supplied by Johnson Matthey.

1. Preparation of gold powder.

The need to prepare gold powder with greater surface area arose as some of the gold sponge supplied was coarse and had very low specific surface area.

Method. The method of preparing gold powder outlined by Block[159] was used with slight modifications. 10 g of coarse gold was dissolved in a 200 ml beaker with 75 ml aqua regia and the resulting solution evaporated to 20 ml and 30 ml concentrated HCl added, and the evaporation repeated to remove all the HNO_3. The final volume of 20 ml was diluted with water and filtered through a medium sintered-glass funnel. The beaker and the funnel were washed thoroughly with distilled water and added to the filtrate to give 400 ml (i.e. about 20 times the recommended volume). The filtrate was heated to 90°C and the gold was precipitated by adding hydroquinone solution dropwise to the solution.

The gold was precipitated in small quantities at a time to avoid agglomeration of the particles. The precipitate was filtered and washed many times with methanol until it was clean. The gold was later treated with concentrated HCl, water, acetone and dried in an oven. The dissolution and the precipitation reactions can be represented as,

$$Au + HNO_3 + 4HCl \longrightarrow HAuCl_4 + NO + 2H_2O \qquad (17)$$

$$3C_6H_4(OH)_2 + 2AuCl_4^- \longrightarrow 2Au + 3C_6H_4O_2 + 6H^+ + 8Cl^- \qquad (18)$$

The surface area of the gold powder produced was 0.215 m^2g^{-1} as determined by the B.E.T. krypton adsorption method.

2. Specpure gold sponge treatment.

This gold was wet screened with the B.S.S. and the -75 μm size fraction was treated with hot concentrated HNO_3 for 20 minutes and thoroughly washed with distilled water to remove the acid, and dried. The surface area was 0.0825 $m^2\ g^{-1}$.

4.2.2 Experimental Method.

The test for the adsorption of xanthate on gold was conducted by taking 1 - 5 g of the gold powder and shaking it in 20 ml solution of a known concentration of KEX in 50 ml conical flask with a flask shaker at temperature of 21 - 22°C. Nitrogen, air or oxygen was bubble through the solution continuously. Every xanthate solution was prepared with N_2-, air- or O_2-saturated distilled water. After shaking the flask for some time, the solution was filtered and the residual xanthate in the filtrate was determined with a Perkin-Elmer spectrophotometer Model 124 at the wavelength of 301 nm. The amount of xanthate adsorbed was taken as the difference between the initial and the final xanthate concentrations in solution.

The experimental procedure in the tests for starch adsorption was similar to that for xanthate adsorption. The amount of starch adsorbed was also determined by the difference between the initial and final starch concentrations. The starch solution after adsorption was pipetted out of the flask and analysed. The methods of determining the xanthate and the starch concentrations in solutions are as follows:-

(a) Determination of the amount of xanthate in solution.

The procedure for the determination of the amount of xanthate in solution was the same as that developed by Bushell and Malnarich[160]. It was based on the linear relation between u.v. absorbance and xanthate concentrations.

For this work series of xanthate solutions of 1 - 20 mg l^{-1} were prepared with conductivity water whose pH was adjusted to 7 with NaOH. The corresponding absorbance values for each solution was recorded with a Perkin-Elmer Double Beam Spectrophotometer Model 124 using 10 mm quartz cells at a wavelength of 301 nm. A straight line plot of absorbance against the corresponding xanthate concentration was obtained. To determine the concentration of xanthate in a solution, the absorbance of the solution was recorded and the corresponding concentration read on the graph. For xanthate concentrations greater than that for which Beer's Law is obeyed, the solution was diluted to the concentration which fell within the range where a straight line was obtained.

(b) Determination of the amount of starch in solution.

The technique used in determining the amount of starch in solution was the same as that developed by Dubois and his co-workers[161]. This method is based on the permanent

yellow-orange colour formed when starch reacts with concentrated H_2SO_4 in the presence of phenol.

Preliminary work to determine the wavelength for maximum absorbance in the visible spectrum was carried out by adding 5 ml of concentrated H_2SO_4 to 2 ml of 10 mg l^{-1} starch solution in the presence of 1 ml of 5% phenol and the resulting solution which was of yellow-orange colour was scanned through the wavelengths of the visible spectrum using 10 mm quartz cell and the Perkin-Elmer double beam spectrometer model 124. The wavelength of maximum absorbance was at 485 nm. This wavelength was used in the construction of the calibration curves. A straight line graph of absorbance against starch concentration from 1 to 20 mg l^{-1} was plotted. The concentration of starch in a solution was determined from the graph when the corresponding absorbance of starch solution was known.

(c) Specpure gold and precipitated gold were employed in studying the adsorption of xanthate at (1) pH of 6.7 to 7.0 at various periods of time at temperature 21 - 22°C. Precipitated gold was used to investigate the adsorption of xanthate at (2) different concentrations for 2 hours at 21 - 22°C and (3) at different pH values for 0.5 hours at the same temperature.

The adsorption of xanthate on specpure gold at different pH values and xanthate concentrations were also carried out but the trends of the adsorption densities as related to pH or concentration were similar to those for the precipitated gold. The results of the adsorption densities are shown in Figs.4.1-4.3.

Preliminary tests for the adsorption of starch on gold (using 10 g of sample for each test) showed no detectable adsorption. It could not have amounted to more than 0.005 mg/g Au (For comparison of adsorption on graphite (Chapter 5) was about 1 mg/g.) On account of this result further work on starch adsorption was not pursued.

4.3 Results

4.3.1 Adsorption of KEX as related to time.

Fig.4.1 shows that the adsorption of KEX in the absence of oxygen was negligible while there was considerable adsorption of xanthate in the presence of air or oxygen. In the case of specpure gold, the adsorption in oxygen-saturated solution was twice that in air-saturated solution. The rate of uptake of xanthate in air-saturated solution was rapid in first 10 minutes when more than half of the total xanthate adsorbed in 2 hours was abstracted. By the end of 1 hour the uptake of xanthate was apparently complete. For precipitated gold the adsorption was slightly faster than that of specpure gold and completed in 30 minutes. Comparison of the rates of adsorption of xanthate by specpure gold with that for precipitated gold indicated that the type of gold had some effect on the rate of adsorption. For example, the rate of uptake of xanthate was about $6\ mol/cm^2 \times 10^{10}$ for specpure gold as compared with $9\ mol/cm^2 \times 10^{10}$ for the precipitated gold in 10 minutes.

In oxygen-saturated solution (Fig.4.1) the adsorption of xanthate on specpure gold continued to increase steadily after 1 hour, though at a reduced rate. After 2 hours it appeared to have come to a halt.

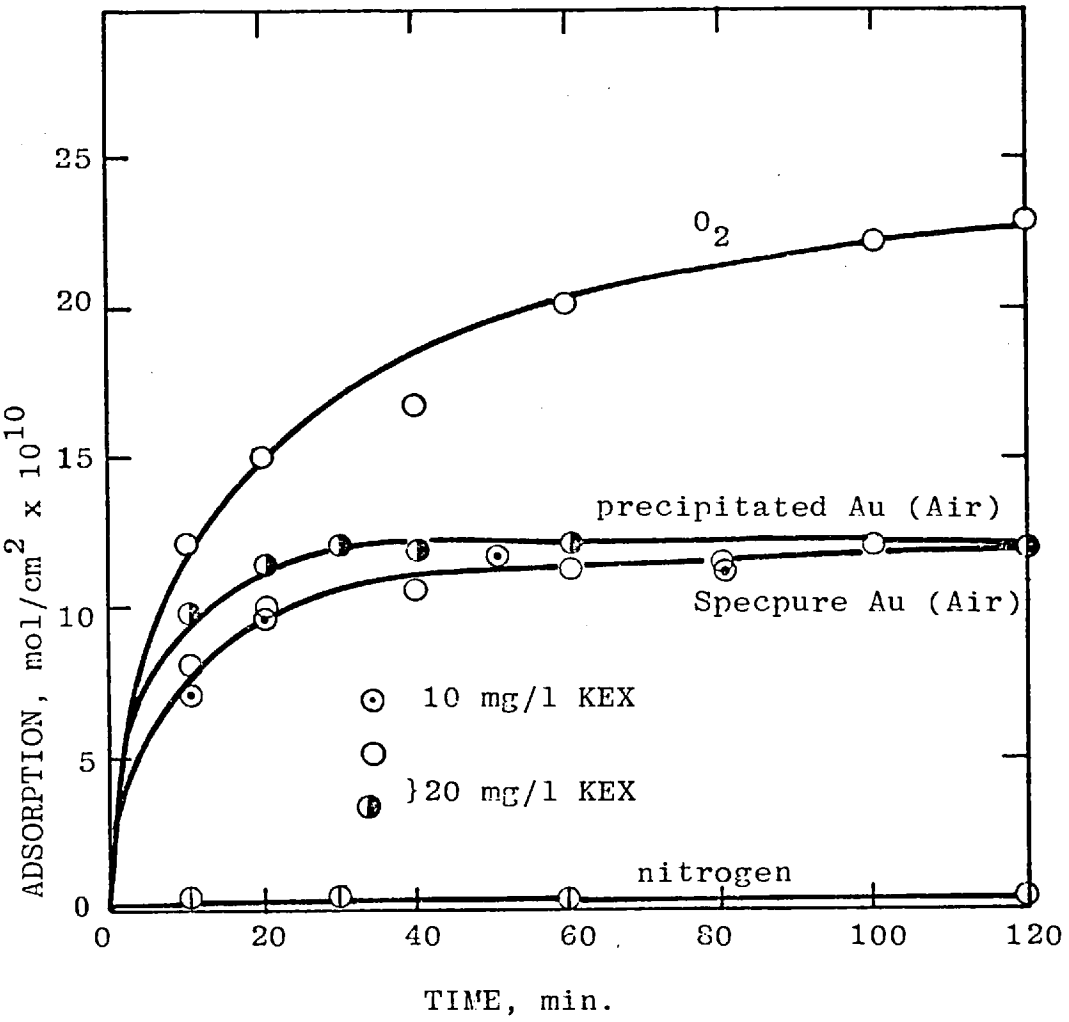


Fig.4.1 Adsorption of potassium ethyl xanthate on gold as a function of time. (pH of solution = 6.7 - 7.0, temperature 21-22°C)

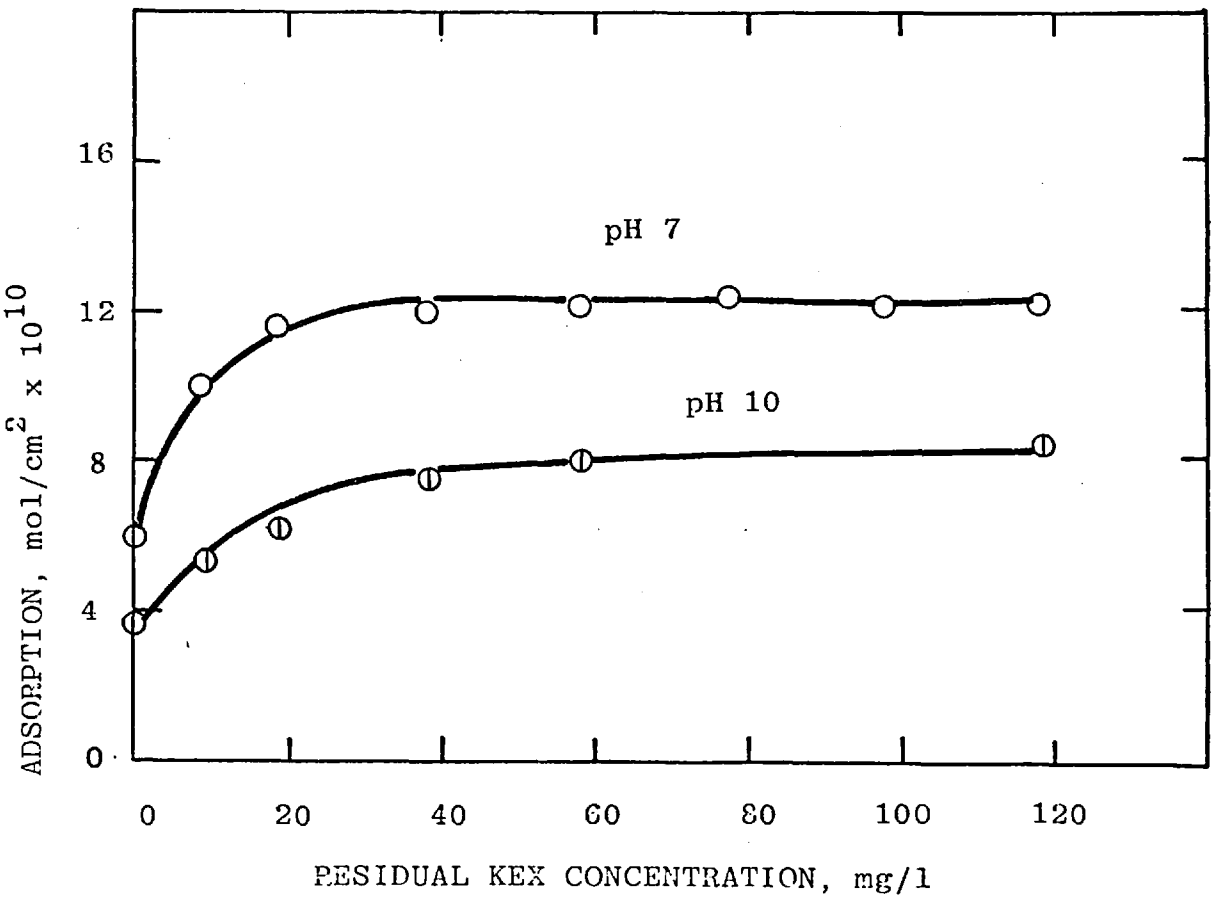


Fig.4.2 Adsorption of potassium ethyl xanthate on gold at different xanthate concentrations.
(Time of adsorption = 2 h, Temperature = 22°C).

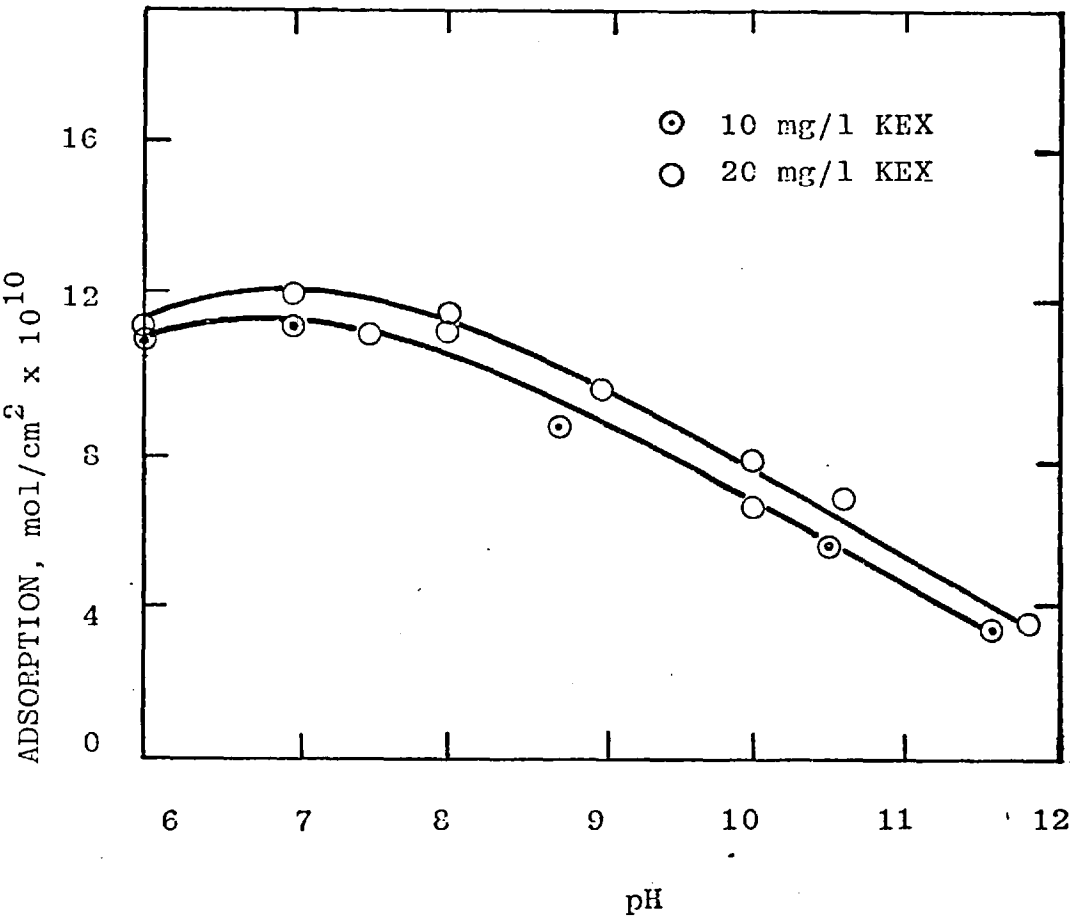


Fig.4.3 Adsorption of potassium ethyl xanthate at different pH values (temperature = 21-22°C)

4.3.2 Adsorption of xanthate at various concentrations.

Fig.4.2 shows the adsorption isotherm of KEX at pH 7 and 10. The results show that adsorption attained a steady state of about 12 mol/cm^2 x 10^{10} for pH of 7 while for a solution of pH 10 the steady state was reached at about 8 mol/cm^2 x 10^{10}. A similar isotherm was obtained by Nikulin, Shafeev and Chanturiya[156] for native gold containing copper. The isotherm, however, differs slightly from the adsorption of xanthate on pure gold obtained in an electrochemical system by these authors, where adsorption of xanthate increased slightly with increase in xanthate concentration.

4.3.3 Adsorption of xanthate at different pH values.

Fig.4.3 shows the adsorption of KEX at pH of 6 to 12. (In these tests just as in those of adsorption isotherm , precipitated gold was used). The results show that pH has a significant influence on the adsorption of xanthate on gold. The maximum adsorption was obtained in the region of pH 7 and decreased linearly as the pH increased. The uptake also decreased slightly at pH 6. This result is in line with that of Plaksin and Tyurnikova[150] and some other investigators[156].

4.3.4 Nature of adsorbed xanthate on gold.

The nature of adsorbed xanthate was determined by extracting the adsorbed species with diethyl ether and analysing the extract with the u.v. spectrophotometer. Because of the small area of the specpure gold used, more than 5 g of it was used in each adsorption test at pH 7. The ether extracts were scanned through the wavelengths of the u.v. spectrum and two absorption peaks at 240 nm

and 280 nm were obtained. The absorption peak at 280 nm is rather broad. These peaks are similar to those for dixanthogen in ether reported by Pomianowski and Leja[141]. When the ether was evaporated and the residue treated with M/20 Na_2S, and analysed with the u.v. spectrometer one maximum absorbance peak at 301 nm was obtained. The xanthate peak at 226 nm was suppressed. This was in line with the analysis of a mixture of xanthate with M/20 Na_2S. The average of six results gave about 80% adsorbed xanthate recovered. The amount of xanthate abstracted from the surface of gold when xanthate interacted with specpure gold powder in the presence of air are summarised in Table 4.1. The results show reasonable agreement between xanthate abstracted from the surface of gold powder and that unaccounted for by the residual solution.

Table 4.1 The amount of xanthate adsorbed on gold at different pH values in the presence of air at constant xanthate concentration.
(Initial concentration of xanthate = 20 mg/l)

pH	Volume of solution (ml)	Concentration of solution		%
		As abstracted from solution (mg/l)	As extracted from the surface (mg/l)	
7	50	16.8	16.1	96
9	50	13.5	12.8	95
10.6	50	9.8	8.9	93

4.3.5 Attempt to determine the presence of gold xanthate on gold surface.

In this method (unlike the radio-isotope technique[154]) an attempt was made to grow visible gold xanthate on the surface of a large piece of gold and examined it under the microscope.

As the characteristic properties of gold xanthate are not available in the literature, preliminary work on its preparation and characterisation with infra-red spectrometer, X-ray diffractometer and optical method with the Zeiss Ultraphot microscope were carried out, as reported in Appendix 3. It was observed that gold xanthate is anisotropic and has monoclinic crystals which exhibit twinning. Gold xanthate of few micrometer size should be easily observed under a powerful microscope if discrete crystallites are formed.

Accordingly a large piece of gold was polished with alumina and half of it was blanked with Araldite and placed in 1 g l^{-1} KEX solution at pH 9, and air was bubbled continuously through the solution for two weeks. The xanthate solution was replaced with a fresh solution after every 24 hours. At the end of the period the gold was put in chloroform and the Araldite was removed. The gold surface was examined with the microscope. The surface which interacted with xanthate was slightly darker than the area covered with Araldite, and showed mosaic patches. However, no gold xanthate crystallites were observed, in spite of the fact that the sites which reacted with xanthate underwent some colour changes; and the sites did not exhibit

anisotropism as would have been expected if gold xanthate had been formed in sufficient quantity. Some amount of dixanthogen was observed but evidence for the presence of gold xanthate is inconclusive.

4.4 Discussion

4.4.1 Effect of time on xanthate adsorption.

As shown in Fig.4.1, the adsorption of KEX in the presence of nitrogen was negligible whilst the adsorption of xanthate in air- and oxygen-saturated solutions was fast and in significant amount. The rate of KEX adsorption in oxygen-saturated solution was twice that in air-saturated solution. These results show clearly that oxygen is essential for the adsorption of xanthate on gold. This observation is in agreement with the result of Plaksin and Zaitseva[153]. The results also showed that the xanthate adsorption was apparently complete in 1 hour for adsorption from air-saturated xanthate solution. This observation is also in line with the result of Finkelstein and Ashurts[162] who worked with native gold containing silver. In the case of oxygen-saturated solution the adsorption appeared to proceed after 1 hour though at a reduced rate. This demonstrates the importance of oxygen in the gold-xanthate system. The main consumption of xanthate appears to be by catalytic oxidation.

That the rate of uptake of xanthate by the precipitated gold is faster than that of specpure gold is an indication that the surface chemical properties of the two type of gold samples were slightly different. The

Johnson Matthey gold was more catalytic than the precipitated gold. For the two types of gold the adsorption curves for xanthate in air-saturated xanthate solution showed rapid loss of catalytic effect. This could be attributed partly to the surface poisoning of the gold by the adsorbed xanthate, so preventing the transfer of electrons from the gold to oxygen on gold, a mechanism by which xanthate could be oxidised[155]. Such a situation could be more pronounced if the gold surface were covered by a monolayer of dixanthogen, which appears to be the case when a constant adsorption density was obtained. But this alone cannot explain the rapid loss of catalytic effect, since graphite, which is a semi-metal, retains its catalytic property even after equivalent monolayer of dixanthogen formation (Chapter 5). The poor catalytic property of gold, which has been observed by many investigators, has been ascribed to the nature of the valence electrons ($5d^{10}6s^{1}$).

4.4.2 Adsorption isotherm.

The adsorption isotherms at pH 7 and 10 are shown in Fig.4.2. The isotherm at pH 7 plateaus off at about 12×10^{-10} mol/cm^2. By taking a surface area covered by ethyl xanthate radical to be 29 Å[163], it can be shown that the adsorption density of 12×10^{-10} mol/cm^2 corresponds to two xanthate radical layer coverage. But since the adsorbed xanthate is probably in the form of dixanthogen, it can be assumed that the plateau corresponded to a monolayer of dixanthogen coverage. However, the adsorption isotherm at pH 10 flattened off at a lower adsorption density corresponding to 67% coverage of dixanthogen. This

implies that a monolayer coverage may not occur in solutions of high pH air-saturated xanthate solutions. At pH around 7 a monolayer or double layer of dixanthogen can be formed on gold surfaces in air- or oxygen-saturated solutions.

4.4.3 Effect of pH on the adsorption of xanthate.

The influence of pH on the adsorption of KEX is shown in Fig.4.3. The amount of xanthate adsorbed on gold decreased almost linearly from pH 7 to pH 12. Similar results were obtained by Plaksin and Tyurnikova[150] and Nikulin and his co-workers[156]. The decrease of the adsorption of xanthate with increase in pH fits into the general theory of competition of OH^- ion with X^- ion for surface sites on gold. The slight decrease of adsorption at pH 6 may be due to the decomposition of xanthate. The formation of dixanthogen on gold needs the presence of oxygen. But since oxygen does not affect oxidation of xanthate in a homogeneous solution, the rate of adsorption of xanthate in the acid media may appear to depend on the rate of xanthate decomposition and the rate of catalytic oxidation of xanthate. In the lower pH range the rate of xanthate decomposition might exceed that of catalytic oxidation of xanthate to dixanthogen and this would result in lower xanthate retention but greater total comsumption. In an alkaline medium, however, the xanthate ion is more stable but its adsorption on gold can be influenced by its decomposition at high pH values e.g. above pH 9 and by the competition of OH^- ions with the xanthate ions for surface sites on gold. The maximum xanthate adsorption would be expected therefore to be in the region of pH 7 as indicated in Fig.4.3. With other minerals which easily oxidise the

maximum adsorption pH region may be entirely different.

4.4.4 Adsorbed xanthate on gold.

As stated earlier the adsorbed xanthate species detected on the surface of gold is dixanthogen. This result is in agreement with the findings of Wood[155] and Plaksin and Zaitseva[153]. In recent times Finkelstein[145] pointed out that monothiocarbonate was one of the species formed as a decomposition product of xanthate in the pH range of 9 to 11 in the presence of nitrogen or oxygen; under such conditions the half-life of KEX is 560-570 h. In the present work the analysis of the residual xanthate solution with the u.v. spectrophotometer did not detect the presence of monothiocarbonate which shows a characteristic absorption peak at 221 nm. Since the half life of xanthate in the alkaline medium is large as compared with 2-4 hours used in the present tests, it could be assumed that under the conditions of the present tests, decomposition of xanthate to monothiocarbonate was negligible. This is supported by the results of recovering adsorbed xanthate on gold with sodium sulphide (Table 4.1). These results showed little loss of xanthate extracted from gold surface as compared with xanthate abstracted from solution. Supposing that monothiocarbonate could be formed significantly, the recent work of Harris and Finkelstein[147] showed that this species eventually came out into solution. It can be concluded, therefore, that the formation of monothiocarbonate may account for some of the xanthate lost in some systems[164], although not for the hydrophobicity of gold. The detected adsorbed xanthate responsible for the increased hydrophobicity of gold is dixanthogen.

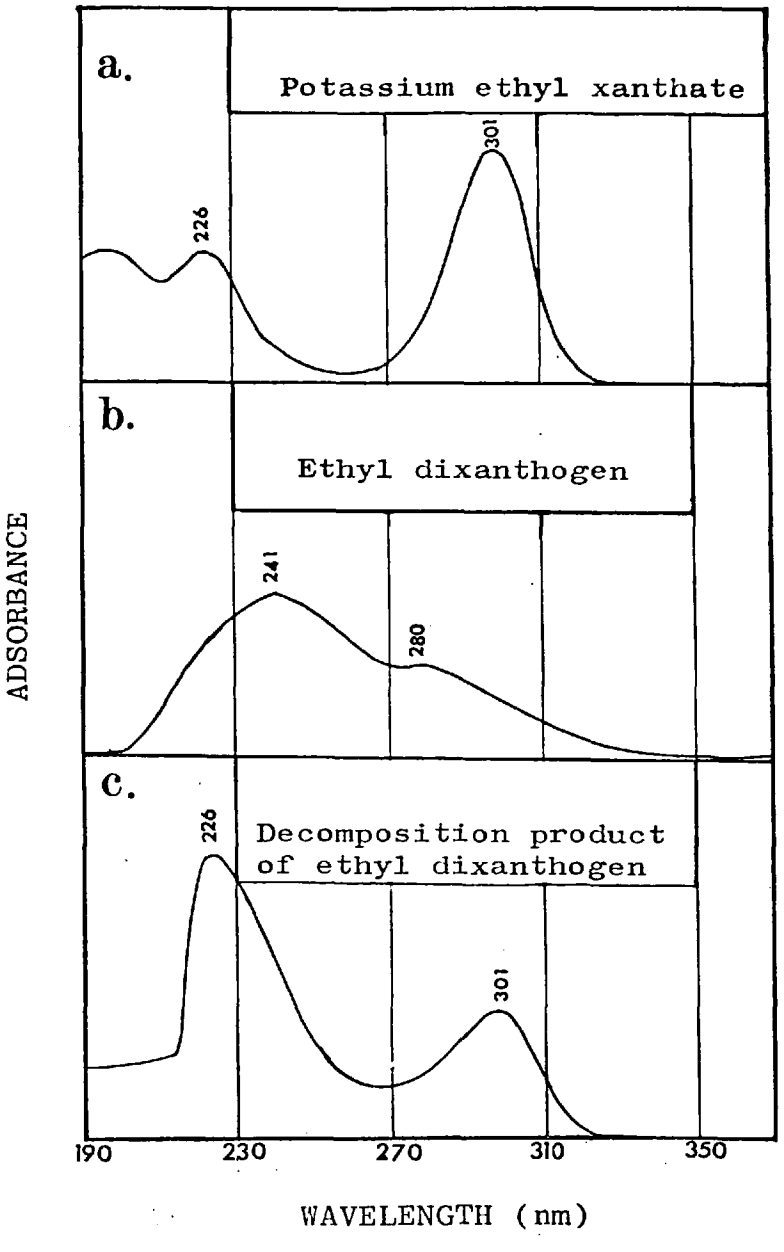


Fig.4.4 The u.v. spectra of

(a) 10 mg/1 KEX

(b) adsorbed dixanthogen on gold

(c) abstracted dixanthogen (b)

treated with solution of NaOH at pH 12.

It was, however, observed that when dixanthogen was treated with NaOH solution at pH 12 it immediately decomposed. Fig.4.4c shows the u.v. spectrum of decomposed dixanthogen as compared with those of KEX and dixanthogen. The u.v. spectrum indicated that the decomposition products of dixanthogen was xanthate ion, and possibly another unidentified species which increased the absorption peak height at 226 nm as compared with that at 301 nm. Under normal conditions the absorption peaks of xanthate at 226 nm and 301 nm show higher peak height at 301 nm than at 226 nm (Fig.4.4a). This result may explain why gold which was hydrophobic in KEX solution at pH 8.6 became hydrophilic in KEX solution at pH 11.8 (Chapter 2). The instability of dixanthogen at high pH values was observed by Pomianowski and Leja[141]. Recently Tipman and Leja[146] investigated the decomposition of dixanthogen in the pH range of 10 to 12 and reported that xanthate ion was one of the products of its decomposition, the other product being C_2H_5OSSOH.

As stated earlier, the formation of gold xanthate in addition to dixanthogen in gold-xanthate-oxygen system is thermodynamically favourable. Because of this the possibility of the formation of gold xanthate cannot be ruled out. Woods[165] stated that about 1% of xanthate formed gold xanthate on anodically polarised gold in KEX solution. In the work of Zelenov and Yavorskaya[152] dixanthogen was not detected as the interaction product of xanthate with metallic gold. This led to the belief that gold xanthate was the product formed. Such a deduction is possible particularly as the amount of gold powder used was only

1 g with small surface area. It should be pointed out that the surface area of 1 g of gold powder of 1 μm particle diameter (assuming a spherical particle) is about 0.31 m^2 and that for most adsorption work with xanthate, the surface area might be much less.

The mechanism of adsorption of some other flotation reagents, for instance, the alkyl ammonium bromide and alkyl pyridinium bromide series (cationic) on gold has been attributed to physical association of the non-polar groups of the reagent to the surface of the gold[68]. However, the adsorption of hexyl mercaptan from the vapour phase was considered to be accomplished by chemisorption[166], Recently, Popova and her co-workers[167] showed by electron para-magnetic resonance (EPR) that the desorbed surface compound of the interaction of iminoxylxanthate with gold at pH 5.7 indicated a mixture of gold iminoxylxanthate complex and dixanthogen. Thus it could be possible that xanthate could chemisorb on gold. But in the present work, the evidence so far obtained suggests that if gold xanthate was formed in gold-xanthate-oxygen system it might be negligible and might not significantly contribute to the hydrophobicity of gold.

4.5 Conclusions

1. The presence of oxygen is a prerequisite for the adsorption of xanthate on gold.

2. The adsorbed species on gold when xanthate interacts with gold in the presence of oxygen is mainly dixanthogen. This species decomposes in high pH solution, giving xanthate ion and another product which could not be identified. The decomposition of dixanthogen in strongly alkaline solutions may be partly responsible for rendering gold that had been made hydrophobic by dixanthogen, again hydrophilic. The presence of gold xanthate as an additional species was looked for but not detected.

3. At equilibrium at pH 7, the adsorption of xanthate appears to correspond with a mono- or double layer of dixanthogen.

4. Gold loses its catalytic property quickly in a xanthate solution. Retention of its catalytic activity may depend on the nature of the gold.

5. The adsorption of xanthate on gold is greatest in the region of pH 7 but decreases almost linearly as the pH increases. There is indication that the adsorption would decrease also as the pH decreases below 6.

6. Starch is scarcely at all absorbed on pure gold.

CHAPTER 5

5. ADSORPTION OF XANTHATE, STARCH AND DEXTRIN ON SYNTHETIC GRAPHITE

5.1 Introduction

For better understanding of the interactions of xanthate, starch and dextrin with graphite in the presence of oxygen it may be useful to consider what is known about the reaction of graphite with oxygen at moderate temperatures.

5.1.1 Oxidation of graphite and carbon by oxygen at moderate temperatures.

The reaction of oxygen and carbon until recently was difficult to understand because of the impurities in carbon. Preparation of pure graphite and carbon has made their reactions with oxygen easier to study. But even so it has been realised that the kinetic process is complicated. The different crystallographic directions in the basal plane are attacked at different rates and the basal plane itself contains considerable crystal defects which become sites of localised attack[168]. Minute amounts of foreign atoms can have enormous effect on the rates of oxidation.

Many investigators[169-172] have found that the edges of the crystals, flakes and microcrystallites oxidised away more rapidly than the surface, which consists of basal planes. Examination of the latter shows that oxidation is due to the recession of surface steps and to the formation of hexagonal etch pits. The pits were shown to have arisen from lattice defects and often coupled with the presence of impurity atoms. The rate of oxidation of the atoms in the basal plane of crystallographically perfect lattices was observed to be negligible. In the review of the rate

of oxidation, Volkov[173] pointed out that the oxidation of the edges is usually 4 to 100 times faster than that perpendicular to the basal plane. Hennig[174] showed that the edge atoms are at least 10^{12} times as reactive as those in the basal plane. He also stated that about 10% of the basal plane consisted of edge atoms[175].

For ungraphitised carbon, it had been assumed that the rates of oxidation were inherently greater than that of well-graphitised material. But the recent work of Lang[176] on pure carbon before and after graphitisation showed that the specific reactivities were unchanged. Hennig[177] observed that impurities catalyse the oxidation of carbon and graphite.

Natural and synthetic graphite can therefore chemisorb oxygen on their surfaces and more so at the edge surfaces. Investigation into the nature of the chemisorbed layer on charcoal indicated that carboxylic, phenolic and quinoid groups may be present. The recent study of the nature of the surface groups has been reviewed by Boehm[178]. Other workers [179,180] also determined the presence of carboxylic and tertiary hydroxyl groups when the surface oxides of graphite were exposed to water vapour.

Most of the recent investigations into the role played by the surface oxide in controlling the carbon-oxygen reactions have been made by Walker and his colleagues[181]. Much of the work was carried out on Graphon, which presents essentially basal planes. By use of isotopic O^{18} it was possible to determine the active sites of Graphon. Walker et al then proposed a distinction between total BET area and active surface area (ASA), which took part in the

oxidation reaction. Their studies showed that the reaction was confined solely to the exposed edge-type atoms so that ASA is a measure of the amounts of these. It was assumed, therefore, that this same area was responsible for adsorption of oxygen. Above 300°C the increase in BET area was due mainly to increase in ASA. Vastola et al[182] and Walker et al[183] are in agreement that the first stage in the carbon-oxygen reaction is the formation of a transient complex of adsorbed oxygen $C(O_2)_t$ which then reacts with a second atom to form an intermediate complex $C(O)_i$. The complex may break down to form CO and CO_2, leaving a "free site" C_f on the surface, or change to the relatively stable complex, $C(O)_s$. It is thought that this latter complex is normally present on graphite and at temperatures below 500°C the stable complex blocks off part of the ASA. At temperatures above 500°C the reaction,

$$C(O)_i \longrightarrow C(O)_s$$

is reversible. The work of Walker et al[184] showed that no less than five different types of sites could be identified when the chemisorption of oxygen on Graphon was studied from pressure range of 0.7 torr to 1 atm. Lang and Noblet[185] also found that active sites were created by adsorption at 25°C followed by desorption at 900°C.

With many other types of carbon, e.g. charcoal and carbon black, it has been recognised that the surfaces are heterogeneous to an extent which has not been sufficiently taken into account. It is therefore proposed that these types of carbon should be considered not as elementary carbons but as polynuclear hydrocarbon[186]

interspersed with a variety of oxygen complexes[187,188] and in some cases containing other elements (e.g.N,S).

From the foregoing it is clear that chemisorbed oxygen on graphite and other carbons occurs mainly at the edge surface; that the causes of the heterogeneity of the surface include oxygen complexes, structural defects and impurities. The extent of the adsorption of surface-active agents would also depend on these factors and the nature of adsorbent.

5.1.2 Adsorption of some surface-active reagents on carbon and graphite.

The adsorption of many compounds on carbon and graphite has been extensively studied. In particular, the adsorption isotherms of gases and surface-active agents on graphite, Spheron, carbon black, Graphon and charcoal have been investigated. A variety of the adsorption isotherms obtained has been summarised by Kipling[189]. The adsorptions were often physical and therefore reversible. In general the adsorption was assumed to occur on polar or on hydrophobic sites which are confined to the basal plane. For example, the effect of complete removal of oxygen complexes from carbon surface showed preferential adsorption of benzene from alcohol-benzene mixtures by Graphon, while Spheron 6, which is known to have considerable concentration of oxygen on the surface[190], showed preferential adsorption of alcohols over a wide range of concentration[191]. This suggests that in the absence of polar sites, the π-electrons would ensure interaction with suitable groups of the adsorbate.

The literature on the adsorption of xanthate on graphite and other forms of carbon is very limited. The work of Horsley and his co-workers[114] on coal-xanthate system showed that any collector action attributed to xanthate was due to dixanthogen. In the flotation of copper-activated nickel from a segregation roast, Iwasaki, Takahasi and Kahata[192] attributed the high consumption of xanthate to the presence of coke in the sample and showed that a substantial amount of xanthate was adsorbed by the coke. Mellgren and Wallum[193] also showed that consumption of xanthate is catalysed by graphite in the presence of oxygen to dixanthogen but pointed out that the high adsorption of xanthate was due to the impurities in graphite.

Starch has been used as a depressant for graphite[102] and hematite and quartz[158,194]. In relation to the depression of graphite with starch in a flotation system in which xanthate is used as the collector, it will be useful to understand the adsorption action of xanthate and starch together on graphite.

5.1.3 Aim of this work.

It is the aim of the present work, therefore, to study the adsorption of xanthate, starch and dextrin on graphite with a view to knowing how they affect the flotation of graphite. Accordingly, the following systems were investigated: (a) graphite-xanthate-O_2,-N_2 systems.

(b) graphite-starch (dextrin)-O_2 systems.

(c) graphite-xanthate-starch-O_2 systems.

5.2 Experimental

5.2.1 Materials. (1) Synthetic graphite No.4451 of 99.5% purity supplied by Hopkin and Williams Ltd. was used in the investigation. Preliminary X-ray fluorescence analysis of it showed traces of Fe,Ni and Cu. Consequently the sample was leached with dilute HCl to remove the impurities, (at least from the surface) and washed thoroughly with distilled water and acetone, dried under vacuum and kept in a stoppered bottle. The specific surface area determined by the B.E.T. method with krypton was 4.32 $m^2\ g^{-1}$. The analysis of the graphite is shown in Table 5.1.

Table 5.1 Analysis of synthetic graphite No.4451.

	% Weight
Fixed carbon	99.5
Volatile matter	0.2
Ash	0.1
Moisture	0.1
Fe	< 0.05
Silica (SiO_2)	0.05
Size	- 53 μm

(2) Hand-picked Prestea carbonaceous matter was washed with distilled water and ground in a silica mortar to -75 μm size. The sample was leached with dilute HCl to remove the iron impurities and washed with water and dried as before and kept in a stoppered bottle. The specific surface area was 3.64 $m^2\ g^{-1}$. Its analysis is shown in Table 5.2.

Table 5.2 Analysis of Prestea carbonaceous matter.

	% Weight
Fixed carbon	32.1
Sericite } Chlorite } Quartz }	67.3
Fe	0.1
Cu, Ni, Pb	traces

(3) Reagents. Potassium ethyl xanthate and maize starch employed were parts of the stocks used in the previous work. The maize "white" dextrin No.380800 consisting of 30% amylose and 70% amylopectin was also supplied by Hopkin and Williams Ltd.

The preparation of the maize starch solution was reported in Chapter 4. The dextrin was prepared by dissolving a known quantity in distilled water since dextrin is water-soluble.

5.2.2 Method for xanthate adsorption tests.

The apparatus and the experimental procedure used in these adsorption tests were similar to those described in Chapter 4. For each adsorption test, 0.5 g samples of graphite were weighed into 250 ml conical flasks and 50 ml of known concentration of KEX solution prepared with air-saturated distilled water was added to each and shaken by a flask-shaker for a specified time while air was bubbled through the solution continuously. For the adsorption from oxygen-free xanthate solution, nitrogen gas was passed through the solution which had been prepared with nitrogen-

saturated distilled water. The contents of the flasks were filtered through Whatman No.541 filter-papers and the residual xanthate in solution analysed with u.v. spectrophotometry at wavelength 301 nm. The xanthate unaccounted for was assumed to have been adsorbed on the graphite.

(a) Adsorption of xanthate on the synthetic graphite and the Prestea carbonaceous matter.

Preliminary tests of adsorption of KEX from 60 mg/l solution at pH 6.7 - 7.0 on the synthetic graphite and the carbonaceous matter were carried out at 23°C for various times. The results shown in Fig.5.1. show reasonable similarity.

The adsorption of KEX under the following conditions has been investigated.

(1) The adsorption of KEX for various times at different KEX concentrations in air- and nitrogen-saturated solutions at pH 6.7 - 7.2.

(2) The adsorption of KEX at pH values of 6 - 12 for concentrations of 10 - 40 mg/l, using NaOH to regulate the pH.

Every test was repeated and the mean value was recorded. The results are shown in Figs.5.1 and 5.2.

(b) The determination of the adsorbed xanthate.

The adsorption of KEX on 0.5 g graphite was carried out as described earlier for xanthate concentrations of 30, 60, 80 mg/l in 50 ml solution for 2 hours at pH 7 in the presence of air. When the solution was filtered, the graphite was treated with diethyl ether and the extract was scanned with the u.v. spectrophotometer. The u.v. spectra showed absorption peaks at wavelengths of 241 nm

and 286 nm, with rather broad peak at the latter wavelength. These peaks correspond to those for dixanthogen in ether[141]. The abstraction of dixanthogen from the graphite surface with M/20 Na_2S gave wide variation from 37-60%. Prolonged contact of the sodium sulphide with the graphite did not improve xanthate recovery.

(c) Zeta-potential determination of synthetic graphite in aqueous solutions.

1. Experimental. The apparatus used for the determination of mobility of graphite was the Rank Bros. Particle Electrophoresis Apparatus (Mark II), (Cambridge, England), with a quartz cell 1 x 10 mm. The effective length of the cell, the interelectrode distance, L (cm) was determined by measuring the resistance (RΩ) of 0.1 M KCl solution of specific conductance κ of $1.289 \times 10^{-2}\ \Omega^{-1}cm^{-1}$ across the electrodes in the cell, with a Portland conductivity meter. The resistance across the electrodes being given as,

$$R = \frac{L}{\kappa A} \qquad (1)$$

where A is the cross-sectional area of the cell ($0.1 \times 1\ cm^{-2}$). From eqn 1, the effective length of the cell was obtained. The microscope eye-piece square graticule was measured to be 97.5 μm. The two stationary levels in the cell were taken at 19.4% and 80.6% of the observed distance between the two inside planes of the cell. If the micrometer reading on the inside planes of the cell were a and b (b being greater than a), the stationary levels were {a + 0.194(b-a)} and {a + 0.806(b-a)} . 100 V was applied across the electrodes at 25°C and the time (t seconds) taken by a particle to move one square in the graticule at the

stationary level was recorded. To calculate the zeta-potential it was assumed that the Smoluchowski equation was applicable. The zeta-potential was calculated from the equation,

$$\xi(mV) = 12.9\ u \qquad (2)$$

where u is the mobility,

$$\text{i.e. } \xi(mV) = 12.9\ \frac{(\text{Velocity, } \mu m/sec)}{(\text{potl. gradient, in Volt/cm})} \qquad (3)$$

$$= 12{,}9\ \frac{X/t}{V/L} \qquad (4)$$

Equation 4 was reduced to

$$\xi(mV) = \frac{98.97}{t(sec)} \qquad (5)$$

when the values for X, V, and L were fitted into the equation. By reading t the zeta-potential was calculated.

2. Procedure. 0.3 g of the sample of -53 µm size was dispersed in distilled water at pH 5.7 in a beaker and agitated ultrasonically and allowed to settle for 10 minutes. The suspension was decanted into another beaker and the pH was adjusted with NaOH solution and the suspension kept for 20 minutes before being introduced into the cell. When KEX solution was used the pH of the suspension was adjusted and the suspension transferred into 50 ml volumetric flask, KEX solution at the required pH was added and the solution made to the mark with distilled water at the same pH to give the required KEX concentration. When the suspension was introduced into the cell, 100 V was applied across the electrodes. The time taken for a particle to move one square in the graticule was recorded. Ten such readings were taken and the potential reversed and a similar number of measurements made. A set of two such readings were taken at each stationary level and the

mean value was used to calculate the zeta-potential from equation 5. The sample was kept in solution for a maximum of 1 hour. Tests were run at pH of 6 - 11 for synthetic graphite in distilled water, and in 20 mg/l KEX solution. The results are shown in Table 5.3 and Fig.5.3.

(d) The adsorption of maize starch and maize white dextrin on graphite.

The procedure for the adsorption tests for starch and dextrin was almost the same as that of KEX adsorption: but in this case the starch or dextrin solution after the adsorption test was centrifuged at 800 r.p.m. to obtain a clear solution. Given volumes of the solution were pipetted into each of three similar test-tubes, and the same amount of phenol was added to each solution followed by the addition of concentrated H_2SO_4. The solutions were analysed at the wavelength of 485 nm with the double beam spectrophotometer. The solutions were freshly prepared each time to avoid degradation. The adsorption of starch and dextrin on graphite was measured as a function of time, of pH over the range 6 – 12 and of starch concentration of 10 – 240 mg l^{-1} at pHs 6·5 & 8·8.

The results are shown in Figs.5.4.-5.6.

(e) Co-adsorption of xanthate and starch from xanthate + starch solution.

(i) A series of adsorption tests was conducted to study the effect of co-adsorption of xanthate and starch on graphite in the presence of air.(Dextrin was not used for further tests as its adsorption was similar to that of starch and it was less adsorbed than starch). The experiments were run with (1) solutions containing equal amounts of KEX and starch for concentrations of 30 - 100 mg/l.

(2) graphite conditioned for 0.5 hour with starch prior to the addition of KEX to solution and the experiment was run for a further 0.5 hour. The maximum volumetric error introduced by adding xanthate solution to the original starch solution was 1%.

(3) graphite conditioned for 0.5 hour with KEX before starch was added to the solution and the experiment run for a further 0.5 hour. The maximum volumetric error due to the addition of starch was 2%. This slightly higher volumetric error was inevitable as starch solution at the concentration used was viscous and might not easily disperse in the xanthate solution at the experimental temperature, 23°C. The added starch solution was therefore made more dilute before it was added. The results of all tests are shown in Fig.5.7 and Tables 5.4 and 5.5.

(ii) Analysis of xanthate and starch from xanthate + starch solution.

Preliminary u.v. spectrophotometric tests for the absorbance of starch solutions of concentrations from 10 to 100 mg/l at wavelength of 301 μm (wavelength used for xanthate determination) gave values from 0.005 to 0.058. Consequently, for starch concentrations greater than 20 mg/l the solution was diluted to render the absorbance for starch negligible at 301 nm. For the determination of xanthate and starch from the same solution, the concentration of xanthate was determined first. The amount of xanthate in solution was used to prepare the reference solution for the determination of starch.

5.3 Results

5.3.1 Adsorption of potassium ethyl xanthate on synthetic graphite.

Fig.5.1 shows the adsorption density of xanthate as related to time in air- and nitrogen-saturated solutions at pH 6.7 - 7.2. The results show that the adsorption of xanthate in air-saturated solution was fast in the first 1 hour but slowed down with prolonged time whereas in nitrogen-saturated (i.e.oxygen-free) solution, the xanthate uptake was negligible. For concentrations used for these tests, more than half of the total xanthate adsorbed in 5 hours was consumed in the first 1 hour. Increased xanthate solution concentration resulted in greater uptake and the attainment of equilibrium was beyond 8 hours. These general trends of adsorption are in agreement with those of Mellgren and Wallum[193] for the adsorption of xanthate on natural graphite. The rate of adsorption was rather slow compared with that for the adsorption of xanthate on gold (Chapter 4).

The adsorption of xanthate on graphite as a function of pH is shown in Fig.5.2. The results show that the xanthate adsorption was greatest around pH 6 - 7 but decreased almost linearly to zero at pH >11. As shown in Fig.5.3 the zeta-potential of graphite in aqueous solution was markedly negative and became more negative with increase of pH (ionization of weak acid). In xanthate solution the zeta-potential became still more negative around pH 7, but its negative value decreased with increase in pH until the effect of xanthate on the zeta-potential was negligible around pH 11. By comparing the pH

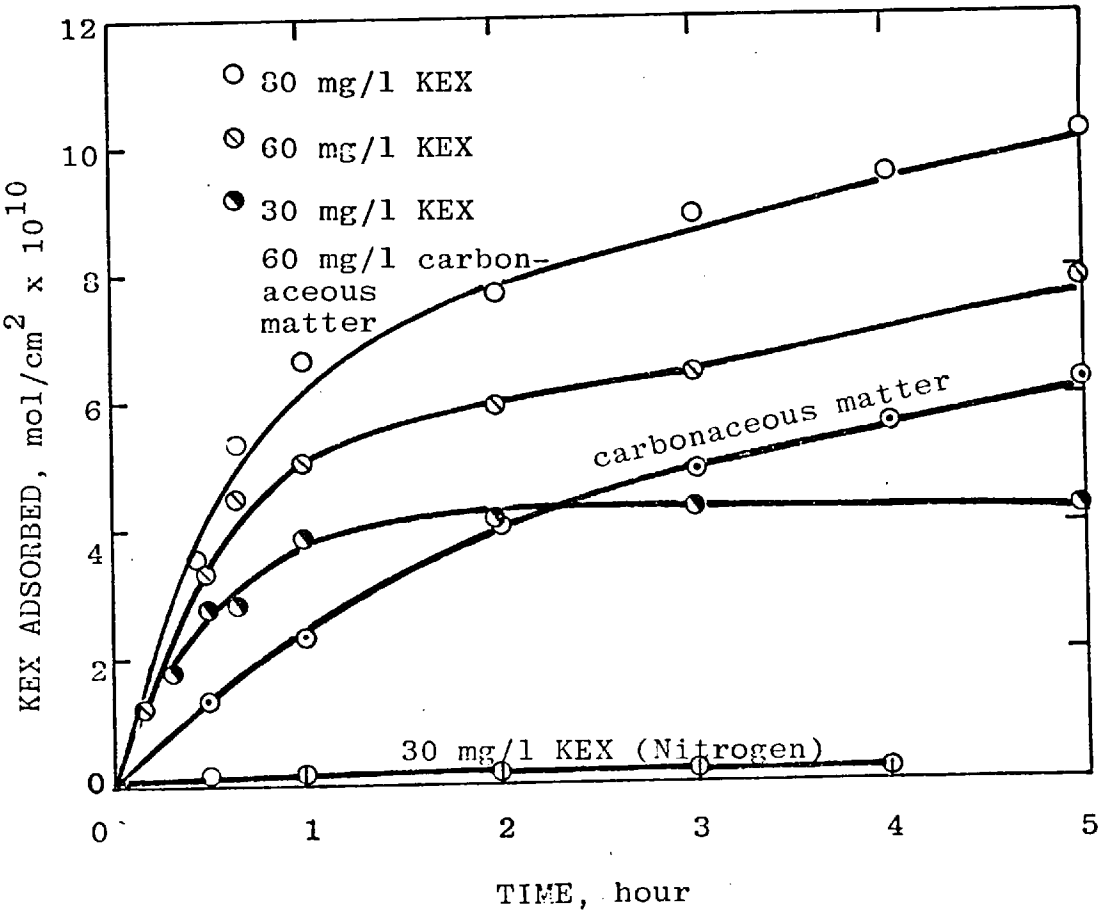


Fig.5.1 Adsorption of KEX on synthetic graphite and carbonaceous matter at different concentrations in air- and N_2-saturated solution at pH 6.7 - 7.2.

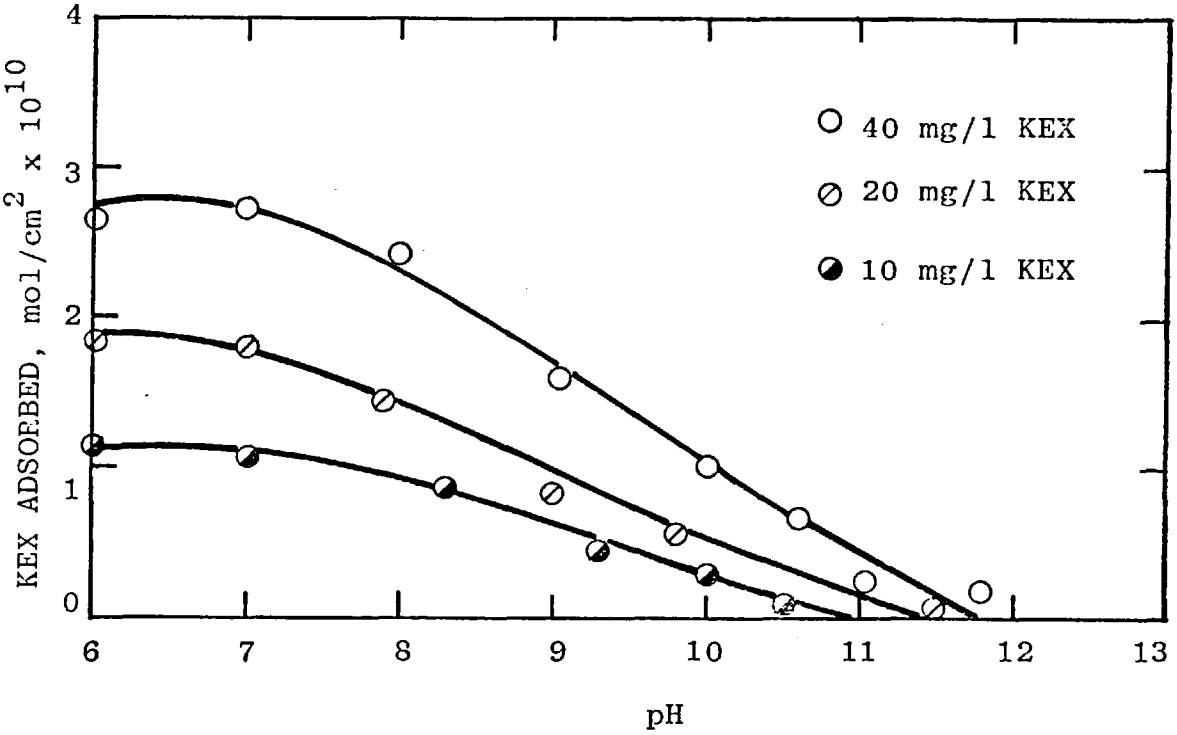


Fig.5.2 Adsorption of KEX on synthetic graphite in air-saturated solution at various pH values.

Table 5.3 Zeta-potentials of graphite at different pH values with and without xanthate. (KEX concentration = 20 mg/l, temperature = 25°C).

pH	Zeta-potential (mV)	
	No KEX	With KEX
6.0	-29	-42
6.7	-30	--
6.8	--	-42
8.0	-32	-41.5
9.5	-33	-41
10.5	-39	-38

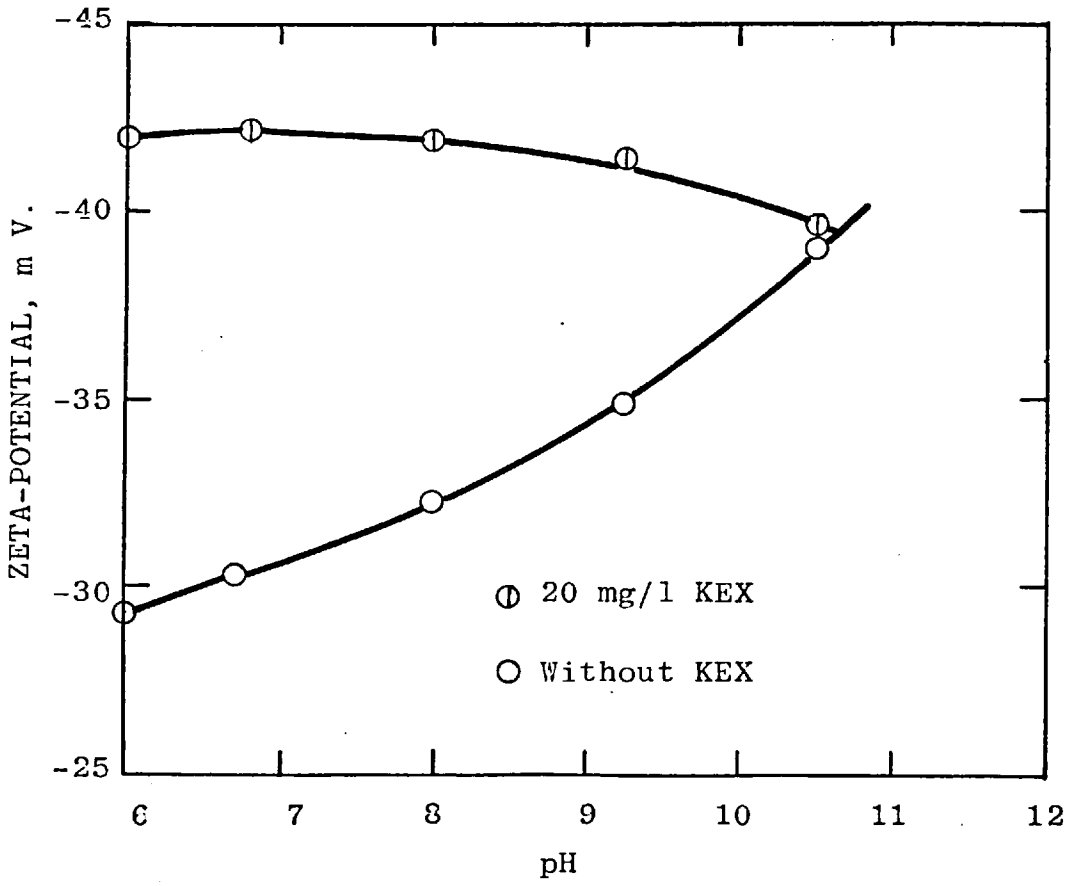


Fig.5.3 Zeta-potentials of synthetic graphite in water and 20 mg/l KEX solution at different pH values.(temp.= 25°C).

at which the zeta-potential curves for graphite in 20 mg/l KEX solution and that for graphite in water only intercepted with the pH at which the adsorption curve for 20 mg/l KEX is zero (i.e. pH 11 - 11.5), it can be seen that there is reasonable agreement between the pH values obtained by the two methods.

5.3.2 Adsorption of starch and dextrin on graphite.

The results in Fig.5.4 show that about 80% of the equilibrium value of the adsorbed starch and dextrin was consumed in the first 10 minutes and equilibrium was established in 1 hour. These results are consistent with the adsorption of some macromolecules on carbon[189]. The results also show that the adsorption density of dextrin was lower than that of starch for the same concentration, presumably because of the lower molecular weight of dextrin.

Fig.5.5 shows that the adsorption of starch and dextrin decreased only slightly as the pH of the solution increased from 6 to 12. Similar observations were made by Iwasaki and Lai[158] for the adsorption of starch on hematite and quartz. Wie and Fuerstenau[195], however, found that the adsorption of their dextrin on molybdenite was not affected by pH.

The adsorption isotherms for starch at pH 6.5 and 8.8 are summarised in Fig.5.6. As expected, the adsorption at pH 8.8 was slightly lower than that at pH 6.5. The general pattern of the isotherms is similar to those for adsorbed polymers and appears to be of Langmuir type adsorption and comparable to those of the adsorption from hematite-starch system reported by Schultz and Cooke[194] and Iwasaki and Lai.

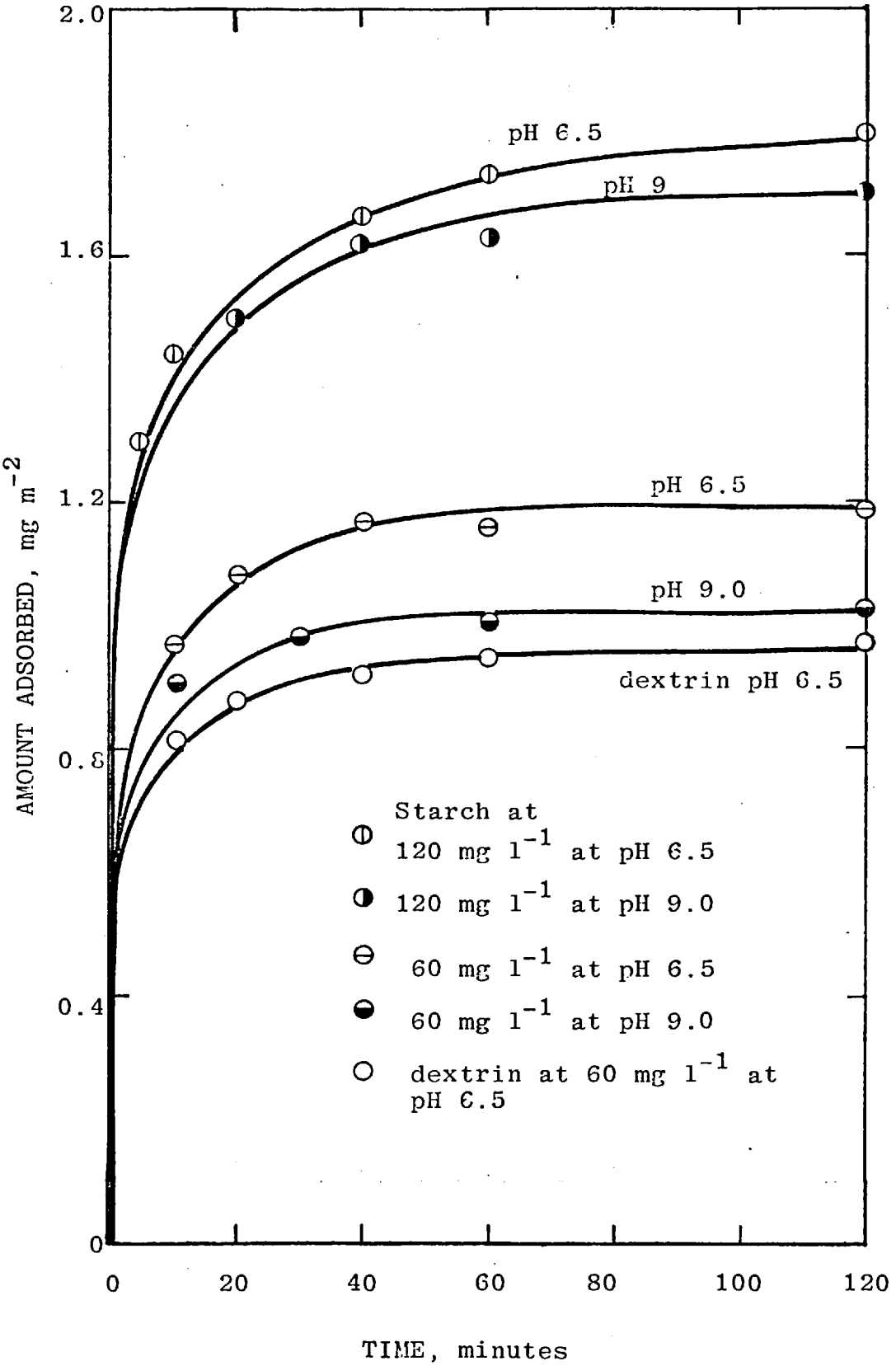


Fig.5.4 Adsorption of maize starch and dextrin on graphite as related to time and pH.

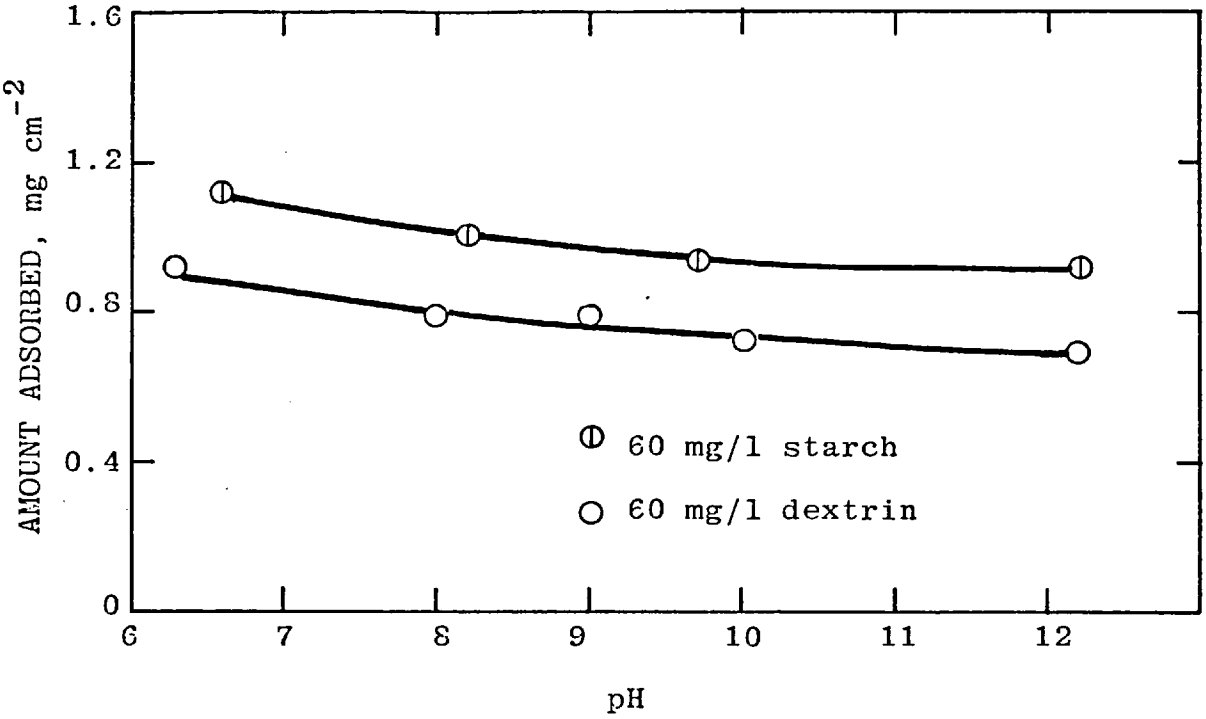


Fig.5.5 Adsorption of starch and dextrin as related to pH (Time = 0.5 hour, adsorbent = graphite.)

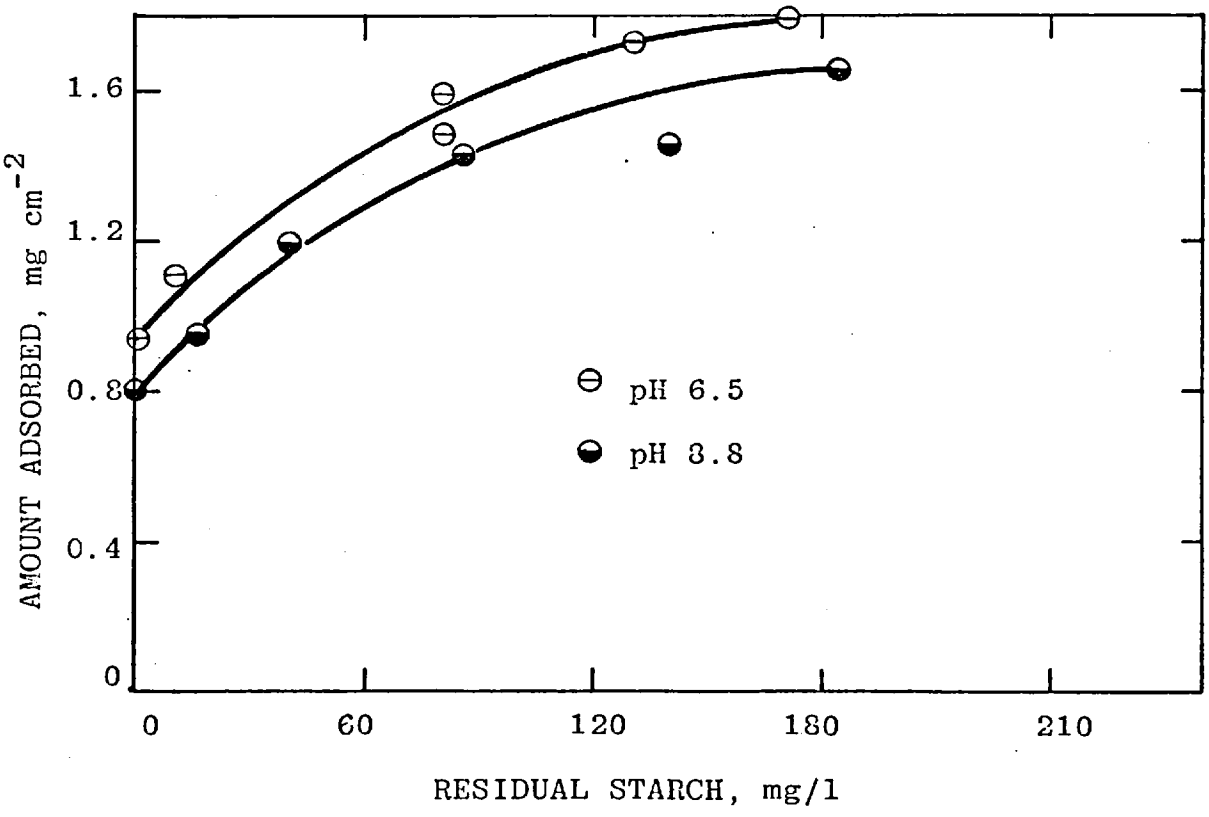


Fig.5.6 Adsorption isotherm of starch at pH 6.5 and 8.8. (Adsorption time = 0.5 hour, adsorbent=graphite.)

5.3.3 Co-adsorption of xanthate and starch from xanthate + starch solutions.

Fig.5.7 shows the results of the adsorption of xanthate and starch from xanthate + starch solutions containing equal amounts of each adsorbate in the presence of air. The results show a small decrease in the adsorption of xanthate, but the trend of increase of xanthate uptake with increase in initial xanthate concentration in solution was maintained. The adsorption of starch, however, was apparently not decreased by the presence of xanthate in solution. When various starch concentrations were used and the graphite was conditioned in starch solution for 0.5 hour prior to the addition of xanthate to give 60 mg/l solution and tests were run for further 0.5 hour , the xanthate uptake decreased by 66% when the starch concentration was increased from 30 - 400 mg/l (Table 5.4a). When xanthate and starch were co-adsorbed from xanthate + starch solution in which the adsorbates were initially in solution and the adsorption run for 0.5 hour (Table 5.4b), the amount of starch adsorbed was about the same as for the former tests (Table 5.4a) while the adsorption of xanthate was slightly greater than the former, especially at starch concentrations less than 200 mg/l.

When the xanthate concentration was increased from 30 - 400 mg/l while the starch concentration was kept constant at 60 mg/l and the graphite was conditioned for 0.5 hour with xanthate before the introduction of starch (Table 5.5a), the uptake of xanthate increased with increased xanthate concentration, but the uptake of starch decreased by about 26.4%. This value can be compared with 66% for the decrease of xanthate adsorption in similar

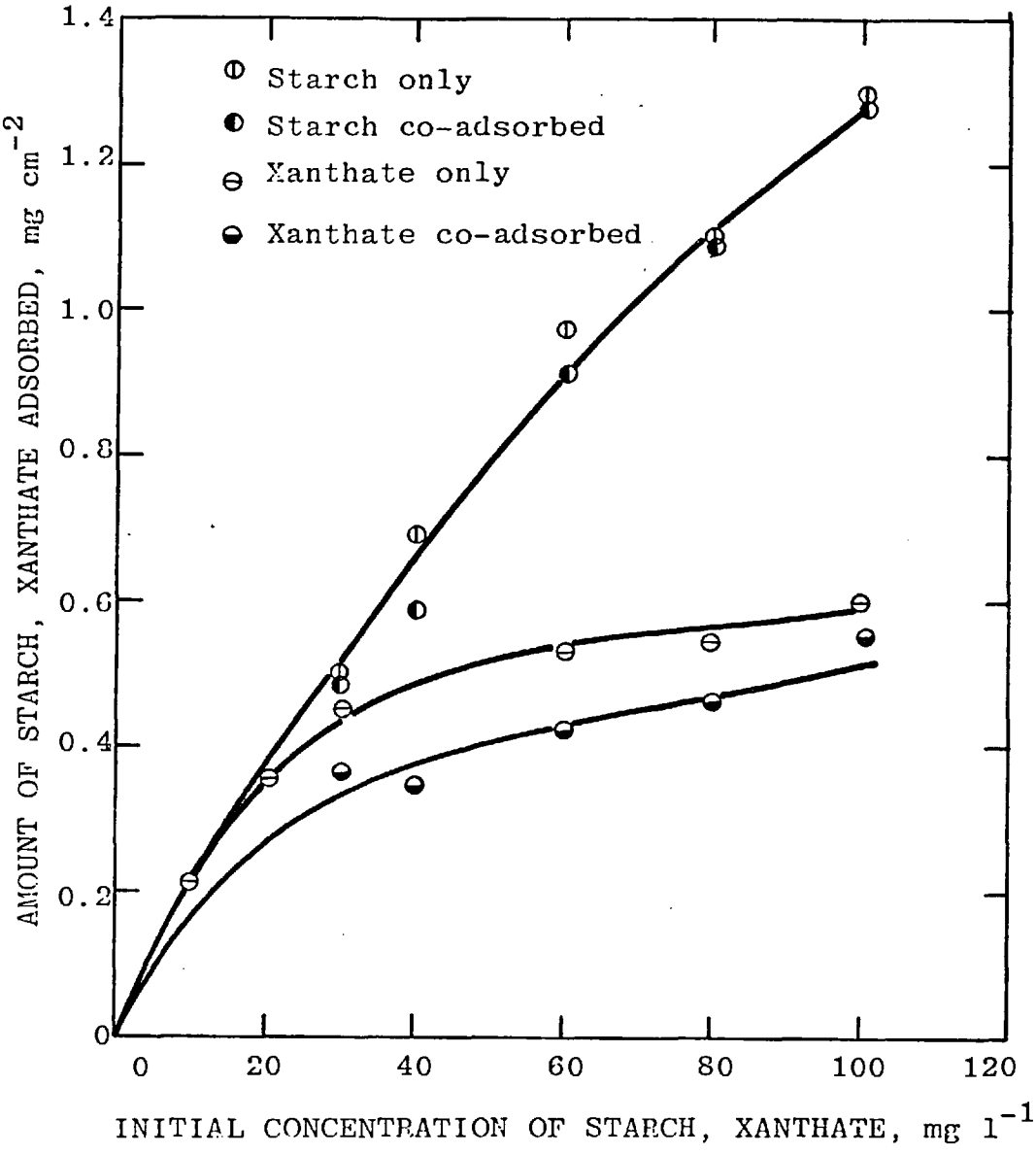


Fig.5.7 Co-adsorption of xanthate and starch from xanthate + starch solutions at pH 6.5. (adsorbent = graphite)

Table 5.4a Adsorption of maize starch and KEX on graphite. (Graphite was conditioned with starch for 30 min. and then xanthate was added. Total time = 1 hour. pH = 6.5 - 7.2 . Temperature = 22 - 23°C.)

Initial starch conc.(mg/l)	Initial xanthate conc.(mg/l)	Amount adsorbed		
		Starch only (mg/m^2)	xanthate in starch (mg/m^2)	xanthate only (mg/m^2)
30	60	0.502	0.444	0.532
60	60	0.978	0.374	
120	60	1.700	0.278	
200	60	2.06	0.138	
400	60	2.546	0.150	

Table 5.4b Adsorption of starch and xanthate on graphite from starch + xanthate solution. (Both starch and xanthate were initially in solution. Adsorption time = 30 min. pH = 6.5 - 7.2. Temperature = 22 - 23°C.)

Initial starch conc. (mg/l)	Initial xanthate conc. (mg/l)	Amount adsorbed	
		starch in xanthate (mg/m^2)	xanthate in starch (mg/m^2)
30	60	0.500	0.524
60	60	0.972	0.428
120	60	1.700	0.310
200	60	2.060	0.138
400	60	2.546	0.162

Table 5.5a Adsorption of xanthate and starch on graphite. (Graphite was conditioned with xanthate for 30 min. before starch was introduced into the system. Total time = 1 hour. pH = 6.7 - 7.4. Temperature = 22 - 23°C.)

Initial xanthate conc. (mg/l)	Initial starch conc. (mg/l)	Amount adsorbed		
		xanthate (mg/m^2)	starch (mg/m^2)	starch only
30	60	0.578	0.925	1.100
60	60	0.652	0.891	
120	60	1.157	0.856	
200	60	1.226	0.845	
400	60	1.273	0.810	

Table 5.5b Adsorption of xanthate and starch on graphite from xanthate + starch solution. (Both xanthate and starch were initially in solution. Adsorption time = 30 minutes. pH = 6.5 - 7.2. Temperature = 22 - 23°C.)

Initial xanthate conc. (mg/l)	Initial starch conc. (mg/l)	Amount adsorbed		
		xanthate in starch (mg/m^2)	starch in xanthate (mg/m^2)	xanthate only (mg/m^2)
30	60	0.300	0.937	0.449
60	60	0.428	0.914	0.532
120	60	0.509	0.879	0.602

circumstances (Table 5.4b).

When the adsorbates at various concentrations were initially in solution and the adsorption tests run for 0.5 hour , the xanthate uptake decreased by about 50%, while the uptake of starch decreased by about 8% for starch concentration of 30 - 120 mg/l (Table 5.5b).

It appears, therefore, that at low xanthate and starch concentrations (i.e. <120 mg/l), the adsorption of each adsorbate from the same solution was not strongly influenced by the other, whereas at high concentrations, the adsorption of xanthate from xanthate + starch solution in the presence of air was greatly reduced due to the presence of starch.

5.4 Discussion

It is known that graphite has a heterogeneous surface with polar and non-polar sites, the latter being confined to the basal plane. The degree of heterogeneity varies from one graphite to another. For example, the polar sites on Graphon were determined to be only 1/1500 of the surface sites by Young, Chessick, Healey and Zettlemoyer[110] and 3/1013 by Groszek[104] whereas the polar sites on synthetic graphite similar to the type used in the present tests were about 18.5% of the total surface sites. The adsorption of surfactants on carbon with predominantly inert basal planes attained monolayer whilst multilayer adsorptions were observed on highly polar graphites[103,104].

5.4.1 Adsorption of xanthate on graphite.

In the adsorption of xanthate on the present graphite in the presence of air, the xanthate uptake was generally less than a monolayer (if 12×10^{-10} mol cm^{-2} is taken to be a monolayer layer of dixanthogen). However, on prolonged adsorption at high concentration (e.g. 200 mg l^{-2}) "equivalent" multilayers of adsorbed xanthate were formed. The negligible adsorption in the absence of oxygen is an indication that oxygen is essential for xanthate "adsorption" on graphite. The rates of adsorption in air-saturated xanthate solution for concentrations of 60 mg/l and 80 mg/l (Fig.5.1) obeyed the Elovich equation, which can be expressed as

$$q = k \log t \qquad (6)$$

where q is the amount of xanthate adsorbed, k is a constant and t is the time of adsorption. A plot of q versus logt gave straight lines for the stated concentrations as shown in Fig.5.8. Equation 6 can be compared with the Elovich equation for an electrical charge,

$$q_m = \int_0^t i\,dt \qquad (7)$$

where i is the current density and t is the time. Woods[155] observed that the Elovich equation was obeyed for high concentration of xanthate for electrochemical oxidation of xanthate on galena. It can be realised from Fig.5.8 that the Elovich equation was obeyed where there was excess xanthate in solution as in the case when the xanthate concentration was 60 or 80 mg/l as compared with 30 mg/l solution where about 86.5% of the xanthate was adsorbed in the first 1 hour and there was apparently complete adsorption in two hours and therefore the Elovich equation

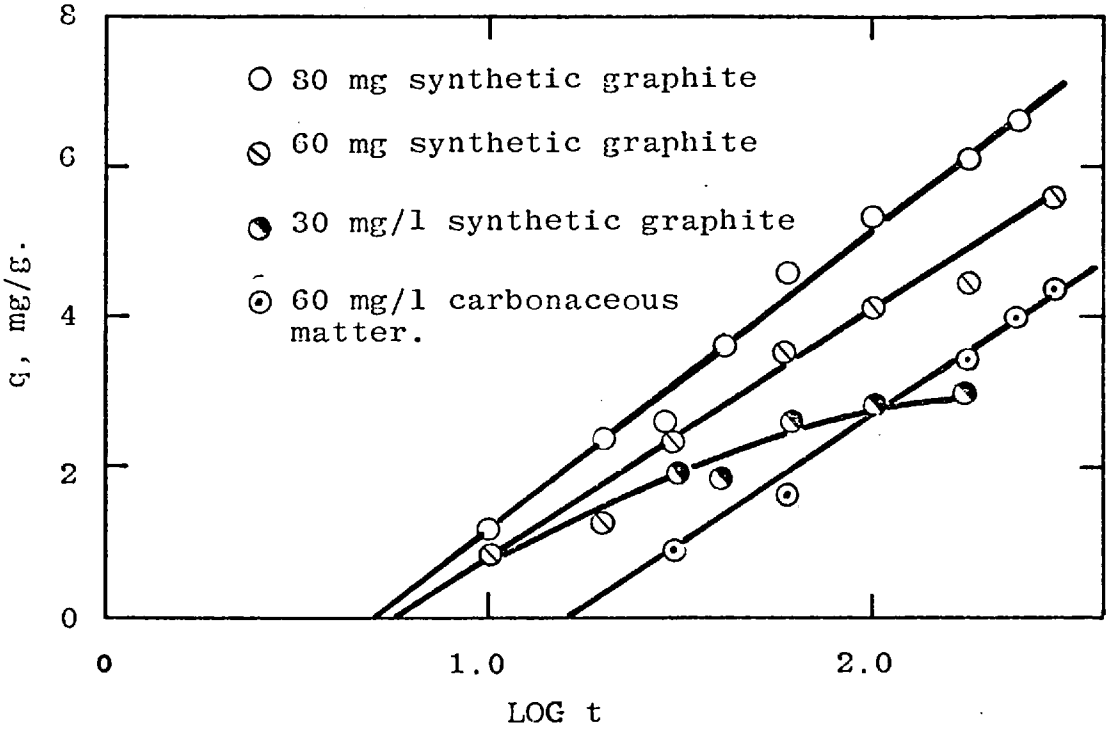


Fig.5.8 Elovich adsorption plot of q versus log t, for the adsorption of KEX on synthetic graphite and carbonaceous matter.(Graph drawn with the data from Fig.5.1).

was not obeyed. If the straight lines for 60 mg/l and 80 mg/l were extrapolated to zero, i.e. q = 0, it can be seen that the apparent "induction" times are 5.7 min and 4.2 min respectively, whereas the induction time for the adsorption of xanthate from 60 mg/l solution of Prestea carbonaceous matter is about 13 min. These induction times may not be entirely correct but they show that by increasing the xanthate concentration the induction time is lowered and also show that the induction time can differ with different samples.

As stated earlier, the adsorbed xanthate was found to be mainly in the form of dixanthogen. This means that xanthate was catalytically oxidised to dixanthogen in the presence of oxygen. It was, however, impossible to extract all the dixanthogen with ether. The maximum dixanthogen extracted was 62% as compared with 80% extracted from gold surface (Chapter 4). Golikov[196] also observed that dixanthogen could not completely be removed by organic solvent even though the postulated mechanism of dixanthogen attachment is molecular. Since sodium sulphide could not remove all the xanthate from the graphite surface, unlike the case of xanthate abstraction from the surface of gold, it can be assumed that the porosity of graphite was responsible, at least in part, to the incomplete abstraction of xanthate from the surface of graphite. The possibility that other products could be formed should also be considered.

The effect of pH on the adsorption of xanthate, as shown in Fig.5.2, was to reduce the adsorption as the pH was increased. This trend can be explained by the mechanism of competition of hydroxyl ions with xanthate ions for

surface sites on graphite as explained in Chapter 4.

That the zeta-potentials of graphite became more negative when xanthate was adsorbed may indicate that xanthate ion was physically adsorbed on graphite with the non-polar group associated with the hydrophobic sites on the graphite while the polar end was directed into solution. But since the adsorbed xanthate is mainly in the form of dixanthogen, it could be assumed that the formation of dixanthogen was preceded by the physical adsorption of the xanthate ion. In addition, as xanthate does not have a metathesis reaction with carbon, the possible mechanism of xanthate oxidation may be through electrochemical steps[155], where, due to the adsorption of O_2 on the graphite surface, separate anodic and cathodic sites are formed. At the anodic site, xanthate ion is oxidised to dixanthogen

i.e. $2C_2H_5OCS_2^- \longrightarrow (C_2H_5OCSS)_2 + 2e$ (8)

and at the cathodic site, oxygen is reduced to OH^- in the presence of water

$$\tfrac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^- \quad (9)$$

in a manner as proposed by some workers[197-199] for other systems.

5.4.2 Adsorption of starch and dextrin on graphite.

(a) Rate of adsorption.

The rapid rate of adsorption of starch and dextrin followed by almost zero rate of adsorption (Fig.5.4) is characteristic of the adsorption of many macromolecules e.g. polymers[200]. The rate of the adsorption obeys the adsorption rate equation of Kawecka et al[201] given by

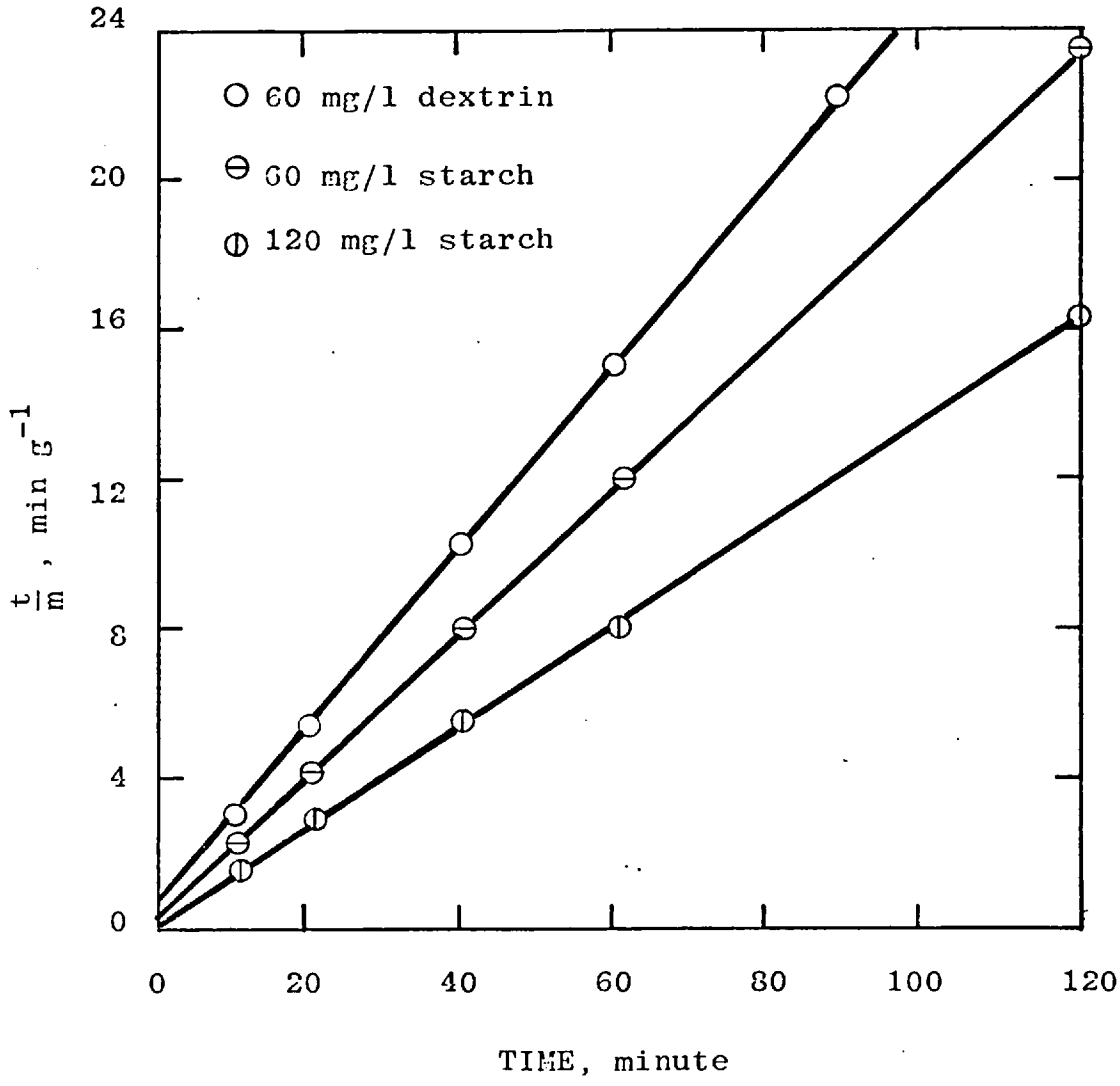


Fig.5.9 Kawecka adsorption plot of $\frac{t}{m}$ versus t, time for the adsorption of starch and dextrin on synthetic graphite at pH 6.5.(Graph drawn with the data from Fig.5.4).

$$a = \frac{a_\infty t}{t + k} \qquad (10)$$

where a is amount adsorbed in time t, a_∞ is the amount adsorbed at saturation of the adsorbent. By rearranging equation 10, equation 11 is obtained.

$$\frac{t}{a} = \frac{k}{a_\infty} + \frac{t}{a_\infty} \qquad (11)$$

A plot of $\frac{t}{a}$ versus t gave a straight line (Fig.5.9) for adsorption from starch solutions of 60 and 120 mg/l and dextrin solution of 60 mg/l at pH 6.5 with the corresponding time required for half-saturation of graphite of 1.5, 1 and 3 minutes respectively. The adsorption at the time of half-saturation, k, of graphite in 60 mg/l of starch solution (which is 1.5 minutes) is about 0.58 mg m^{-2}. The same weight of xanthate can be adsorbed from 60 mg/l KEX solution in the presence of air in 15 minutes and shows that the rate of adsorption of starch was greater than that of xanthate under similar conditions.(The Kawecka et al adsorption equation is known to fit the adsorption of p-cresol from aqueous solution by activated charcoal[201]).

(b) Effect of pH on starch and dextrin adsorption.

That the adsorption of starch and dextrin was not strongly dependent on pH may suggest that

(i) The mechanism of adsorption is non-ionic interaction and might be due presumably to the hydrogen-bonding of the OH group of starch molecule to the oxygen complex sites on graphite.

(ii) That the electrostatic repulsion force between starch and the polar surface sites is weak (starch carrying only small negative charge density due to carboxyl end-groups).

In the case of dextrin, in the recent work of Nie and Fuerstenau[195], it was reported that pH has no effect on the adsorption of their dextrin. It is not clear why in the present work pH appears to have slight effect on the dextrin adsorption.

(c) Adsorption isotherm of starch on graphite.

The adsorption isotherms of starch on graphite (Fig.5.7) are comparable to that obtained by Iwasaki and Lai[158] for corn starch adsorbed on hematite and quartz. Their isotherms were of Langmuir type. Thus by assuming Langmuir type-adsorption isotherm for the present isotherm, the adsorption can be represented by

$$G| + S \;\text{—}\; G{:}S \qquad (12)$$

where S represents starch in solution in equilibrium with graphite surface sites G| and G:S represents starch in the adsorbed state. If K is the equilibrium constant for the adsorption reaction, then the Langmuir equation can be represented as

$$\frac{m}{m_0 - m_0} \cdot \frac{1}{(S)} = K = \exp\left(\frac{-\Delta G^0}{RT}\right) \qquad (13)$$

where (S) is the equilibrium concentration of starch in solution, m is the equilibrium quantity of starch adsorbed, and m_0 is the amount adsorbed at saturation. By rearranging, equation 13 becomes

$$\frac{(S)}{m} = \frac{1}{m_0 K} + \frac{(S)}{m_0} \qquad (14)$$

A plot of $\frac{(S)}{m}$ versus (S) should give a straight line with a slope of $\frac{1}{m_0}$ and an intercept of $\frac{1}{m_0 K}$. By substituting

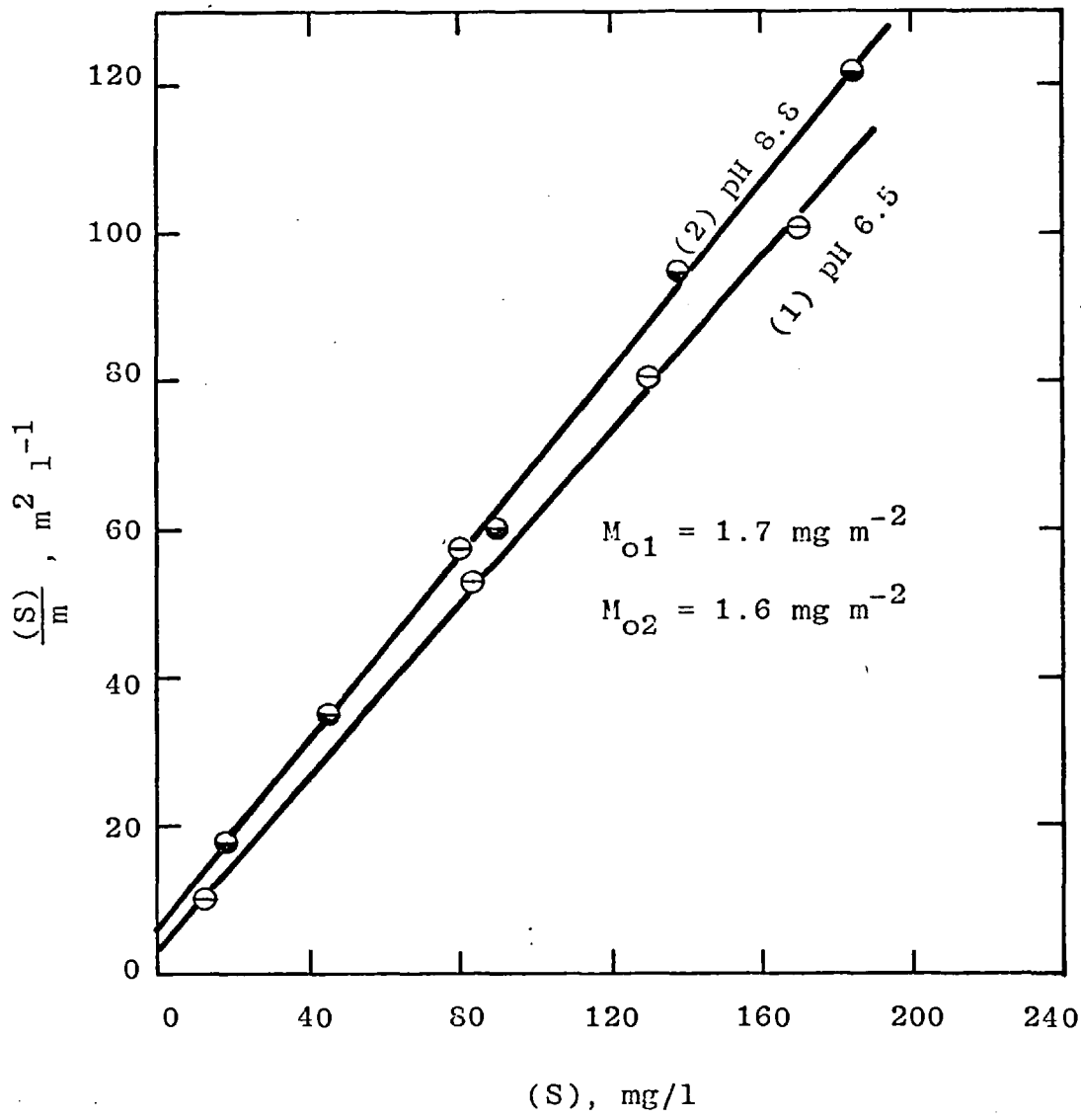


Fig.5.10 Langmuir plot of $\frac{(S)}{m}$ versus (S) for the adsorption of maize starch on synthetic graphite. (Graph drawn with the data from Fig.5 6)

the results of Fig.5.7 into $\frac{(S)}{m}$ and (S) straight lines for the isotherms at pH 6.5 and 8.8 were obtained with m, the saturation values of 1.7 and 1.6 mg m^{-2} respectively (Fig.5.10). A similar Langmuir adsorption isotherm was obtained for the adsorption of dextrin on molybdenite[195] and quebracho on graphite[202]. For the adsorption of quebracho on graphite, Iskra[202] obtained saturation values ranging from 0.7 to 1.2 mg m^{-2} which were consistent with a surface covered with a close-packed monolayer of polyphenolic molecules. But it is difficult to estimate the covering power of branched macromolecules such as starch.

(d) Possible mechanisms of adsorption of starch and dextrin on graphite.

A number of investigators[115,158,194] studied the depressing behaviours of starch and its derivatives in the flotation of hematite and quartz. Hydrogen-bonding and electrostatic interaction have been suggested by Balajee and Iwasaki[115] as the mechanisms for the adsorption of starch on hematite and quartz. In the work of the same authors on non-modified starch at pH 3 - 11,it was found that starch was negatively charged. Thus, below the p.z.c. the electrostatic interaction between starch and the adsorbents will predominate, whilst above the p.z.c. the interaction may be predominantly that of hydrogen-bonding as there will be electrostatic repulsion between the starch and the adsorbents. In the graphite-starch system where the pH of the solution is greater than 6, i.e. above the p.z.c. of graphite, the possible mechanisms of adsorption of starch on graphite will be that of hydrogen-bonding as the electrostatic interaction between starch and graphite will be that of

repulsion. In addition if any part of the starch molecule has hydrophobic character, it may be associated to the hydrophobic sites on graphite. In the case of dextrin the mechanism of hydrophobic association seems more likely since dextrin is said to be non-ionic in aqueous solution. In addition to possible hydrophobic association there will be a hydrogen-bonding between dextrin and the oxygen complex sites on graphite.

5.4.3 Co-adsorption of xanthate and starch from xanthate + starch solutions.

In the co-adsorption of xanthate and starch from xanthate + starch solutions containing equal amounts of each adsorbate (Fig.5.7) at initial concentrations not greater than 100 mg l^{-1}, the results show that xanthate adsorption was slightly lower while the adsorption of starch was not reduced. This can be ascribed partly to the faster rate of adsorption of starch. Assuming that each adsorbate was adsorbed primarily on different sites, with the xanthate ions on the hydrophobic sites and starch molecules on the polar sites, it is possible that as the starch adsorbed faster, it could tend to inhibit the adsorption of xanthate by its larger molecular size. Because starch carries only small negative charge, the electrostatic force of repulsion between the adsorbed starch molecule and xanthate might be negligible and might not account for the reduction in xanthate adsorption.

The possible combined effect of rate of adsorption and concentration of adsorbates are shown by the results in Tables 5.4a & 5.4b. In Table 5.4a, adsorption of xanthate was reduced by 66% in solutions containing initial

starch concentrations of 30 - 400 mg/l. At high starch concentrations (i.e. 100 mg/l), it appears therefore that starch adsorption was not confined only to the polar sites and makes the idea of adsorption on different surface sites less acceptable. This raises the question of whether part of the starch molecule did not adsorb on the hydrophobic sites on the graphite.Also at high starch adsorption densities intermolecular interactions between the adsorbed starch molecules, and the adsorbed and non-adsorbed molecules might occur and reduce the surface sites for xanthate adsorption.

As shown in Table 5.5a, the presence of high concentration of xanthate did not greatly decrease starch adsorption. The reduction in starch adsorption was 12.5% in xanthate concentrations of 30 - 400 mg/l. This result appears to support the idea that xanthate and starch were primarily adsorbed on different sites, and much more so when the concentrations of the adsorbates are low. The results in Table 5.5b seem to be consistent with the idea that the faster rate of the adsorption of starch and the size of molecule might account for low xanthate adsorption.

It can be concluded that xanthate and starch appear to be adsorbed at least in part on the same sites or on adjoining sites. These findings may be compared, on one hand, with those of Iskra, Gutierrez and Kitchener[203] for quebracho and oleate on calcite and fluorite, where the collector and the depressant were strongly competitive, and on the other hand with those of Somasundaran[204] for starch and oleate on calcite, where there was no competition for adsorption (indeed, a mutual enhancement).

5.5 Conclusions

1. The adsorption of xanthate on graphite proceeds mainly by catalytic oxidation of xanthate to dixanthogen in the presence of oxygen. The adsorption is negligible in absence of oxygen.

2. Xanthate ions are physically adsorbed by hydrophobic association of the non-polar groups of xanthate with the hydrophobic sites on graphite.

3. The adsorption of xanthate on graphite is significantly affected by pH variation. Adsorption is greatest at pH of 6 - 7 and negligible at pH>11.

4. The adsorptions of starch and dextrin on graphite is several times faster than that of xanthate and attains equilibrium within about 1 hour.

5. The adsorption of starch and dextrin is not strongly dependent on pH. The adsorption isotherm of starch (and possibly dextrin) obey a Langmuir-type isotherm. Starch is adsorbed on graphite as a thicker layer than dextrin.

6. Starch and xanthate appear to adsorb at least in part on the same sites or on to adjoining sites on graphite.

7. The order of addition of xanthate and starch has greater effect on xanthate uptake than on starch adsorption.

P A R T III

THE IMPLICATIONS OF PROCESSING PRESTEA CARBONACEOUS GOLD ORE.

GENERAL INTRODUCTION

In Parts I & II the basic nature of this ore and the surface chemical properties of gold and carbon (graphite) were studied with a view to understanding the factors that may influence the processing of the ore.

As a follow-up, Part III has been devoted to a short investigation of some of the processes for treating the ore and the implications of the work for processing it. It has been divided into three chapters. The first is concerned with the investigation of the flotation of gold and graphite with xanthate, starch and quebracho. The flotation tests were extended to Prestea carbonaceous matter and the ore in order to separate the carbonaceous matter from the gold and the sulphides which carry gold, by depressing the carbon and floating the gold and the sulphides.

The second chapter deals with the flocculation and filtration of the carbonaceous matter and the flotation concentrate. These processes are primarily aimed at preparing the flotation concentrate for roasting.

In the third chapter the implications of processing the ore have been discussed. It outlines the problems involved in and the possible processes for treating the ore.

CHAPTER 6

6. FLOTATION OF GOLD AND GRAPHITE AND PRESTEA CARBONACEOUS GOLD ORE.

6.1 Introduction

6.1.1 Some basic factors in flotation.

Flotation has been used for the concentration of minerals for many years. Naturally, many aspects of flotation have been studied with the result that it is well recognised that there are very many factors which influence flotation. These factors have been divided into three main groups[205] according to,

(1) ore and mineral properties,

(2) the total aspects of reagent treatment,

(3) the total effect of the flotation machine on the flotation system.

In the first group the mass, shape, size and the physico-chemical properties of the mineral predominate. In the second ground the concentration of collector on the mineral surface is probably the most important factor, whereas in the third group the bubble size, number and the hydro-dynamic nature of the bubble-particle-fluid are outstanding. Because of the many variables it is often useful to study a limited number of variables at a time.

In the present flotation investigation emphasis will be laid on the effect of physico-chemical properties of the minerals in question and the effects of adsorbates (i.e. collectors and depressants) on their floatibility. Consequently the general relationship between floatibility, contact angle and the collector adsorption on minerals will be briefly discussed.

Flotation is only feasible for a hydrophilic mineral if the surface is rendered hydrophobic with a collector. When the surface is hydrophobic, the condition can be expressed by Young's equation in the form,

$$\gamma_{SV} - \gamma_{SL} < \gamma_{LV}. \qquad (1)$$

This equation is considered to express the thermodynamic conditions for flotation[206,207]. As the value $(\gamma_{SV} - \gamma_{SL})$ decreases the contact angle increases when a collector is adsorbed on the surface.

The relationship between the interfacial tension and adsorption taking place at the interface is given by the Gibbs equation

$$d\gamma = -\sum_{2}^{r} \Gamma_i d\mu_i \ (\text{const.T}) \qquad (2)$$

where Γ_i is the adsorption density of the component i relative to that component 1 which is defined as zero and $d\mu_i$ is the increase in chemical potential of the adsorbate. For the adsorption of collector at the solid/gas and solid/liquid interfaces, de Bruyn and Agar[207] predicted that if $\Gamma_{H_2O}^{SL} = 0$,

$$\text{then} \quad \Gamma_R^{SV} > \Gamma_R^{SL} \qquad (3)$$

where Γ_R^{SV} is the adsorption of the collector at the solid/gas interface and Γ_R^{SL} represents the adsorption of the collector at the solid/liquid interface. They concluded that any increase in contact angle in collector solution must be due to the decrease in γ_{SV}. This was verified experimentally by Smolders[86] and Somasundaran[208].

Combination of Gibbs' free energy, ΔG with Young's equation gives the equation,

$$\Delta G = \gamma_{LV}(\cos\theta - 1) < 0 \qquad (4)$$

where ΔG is the decrease of the free energy of the system when a liquid and its vapour make contact with a solid. Eqn (4) is interpreted[89] to mean that the more negative the ΔG value, the greater is the probability of flotation. Such thermodynamic expressions of conditions for flotation are really of little assistance in current flotation resarch. They do not take into account the intermediate stages which are important in flotation. Scheludko[209], however, stated that the contact angle could directly characterise flotation if the kinetic resistances depended on the same parameters as the angle of contact. In the work of Laskowski and Iskra[210] it was shown that although the contact angle, induction time and flotation recovery are related, in some instances close correlations do not exist. Nevertheless in absence of hydrophobicity of a mineral surface, flotation will not be possible.

6.2.1 Previous work on the flotation of gold and graphite.

Flotation of gold-bearing sulphide minerals with xanthate is common[211]. During the flotation of such sulphide minerals, gold is also recovered. However, the flotation of native gold as such is limited presumably because of the ease of its concentration by gravity processes and by cyanidation which is by far the most wide-spread method yet for extracting gold.

Some of the early work on the flotation of gold were carried out by Leaver and Woolf[212] and Johns[67]. In the work of Leaver and Woolf it was observed that gold of size lessthan 60 mesh was readily floated with the normal flotation reagents used for sulphide ores but that gold

did not float as readily or as rapidly as most of the sulphides. Later Johns also working with native gold containing silver observed that practically no gold was floated by use of frothers only. Recently Benton and Sparks[68] using anionic and cationic compounds of pyridinium bromides and trimethyl ammonium bromides found that the maximum flotation recovery of gold was obtained around $\frac{1}{10}$th the critical micellar concentration (c.m.c.). Still more recently Zelenov[213] found that isoamyl ether of isonicotinic acid could be used as a collector for gold. In the electrochemical flotation of gold, Gardner and Woods[69] showed that flotation was only effected when the potential for dixanthogen formation was attained.

The foregoing suggests that gold could not be floated readily without the use of collectors. Although it has been shown that gold is hydrophilic, in a normal flotation system it tends to lose its hydrophilicity by adsorbing organic impurities. Nevertheless, its successful flotation may depend on the use of collectors.

Graphite, on the other hand, is naturally hydrophobic and floats readily. Although its hydrophobicity is normally reduced on oxidation or by the adsorption of oxygen, often frothers alone are sufficient for its flotation. The reagents often used for graphite flotation[214] are

(a) non-polar compounds e.g. paraffin or kerosene,

(b) hetero-polar reagents for example, alcohols, mono-carboxylic acids and xylenols,

(c) inorganic electrolytes, e.g. NaCl.

6.1.3 Aim of this work.

The aim of the present section of the investigation is (1) to study the effects of xanthate, starch and quebracho on the flotation of gold and graphite with the ultimate objective of possibly separating gold from graphite.
(2) to apply the flotation tests using the same reagents to Prestea carbonaceous matter.
(3) to float Prestea carbonaceous gold ore with xanthate in the presence of starch as depressant for carbon, and to find the effects of xanthate and starch on the gold recovery.

The effects of the adsorption of xanthate and starch on gold and graphite were described in Part II of this thesis. The effect of the adsorption of quebracho on graphite was reported by Iskra[202], but its effect on gold was not investigated by him.

6.2 Experimental

6.2.1 Materials. Gold used in these flotation tests was part of the "Specpure" spongy gold of grade 99.99% from Johnson Matthey employed in the adsorption tests in Chapter 4. The synthetic graphite and the maize starch used were also part of those employed in the earlier work.

Quebracho S was supplied by the Instituto Tecnico del Extracto de Quebracho. Quebracho has been introduced at this stage in order to study its effects on graphite, as it was thought that quebracho with its phenolic structure, which is analogous to that of graphite, could adsorb more strongly on graphite than starch would. (The present state of knowledge about the structure of quebracho is presented by the Instituto del Quebracho Ideq[215]). Quebracho "S" is a sulphited form of ordinary quebracho. It is water-soluble and has an average molecular weight of about 1000, which is about half the molecular weight of quebracho "O".

The frother used was "Aerofroth 65" which is a Cyanamid product. It is a water-soluble synthetic frother of poly-glycol type, capable of producing "closely-knit and less brittle type of froth". It was used as supplied.

6.2.2 Flotation of gold and synthetic graphite.

The synthetic graphite was dry-ground and wet-screened with the B.S.S. and the -300 + 150 μm size fraction was used for all flotation tests. The spongy gold was dry-screened and a similar size fraction to that for graphite was also used. Flotation was conducted in a modified Hallimond tube (Fig.6.1) with steady air velocity of 50 ml/min.

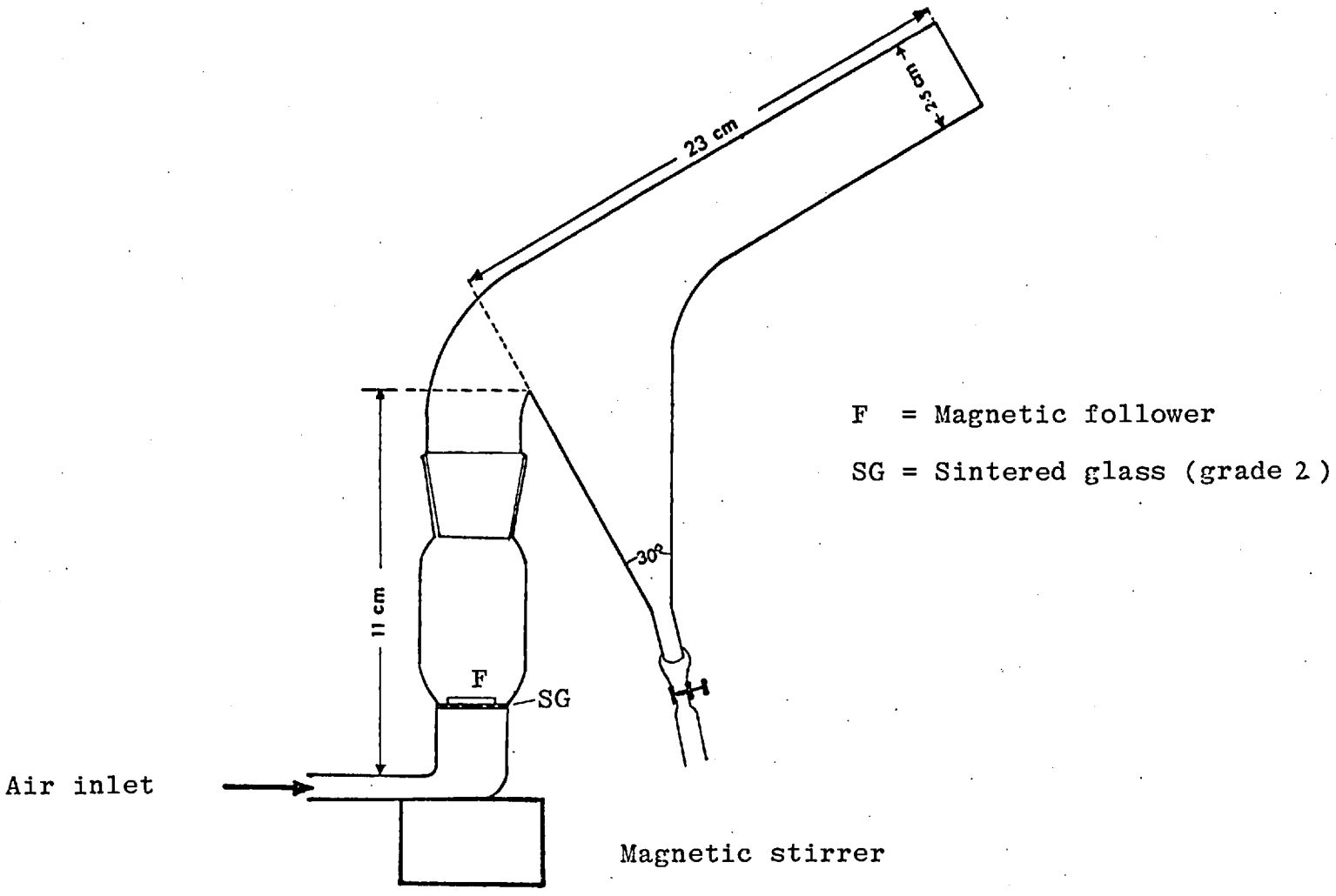


Fig.6.1 Modified Hallimond tube for flotation.

1 g of gold or graphite was used for each test. Because gold adsorbs organic contamination rapidly (which could lead to non-reproducibility of results), the weighed sample was first etched with hot concentrated nitric acid for about 20 minutes and the acid diluted with distilled water and decanted ensuring that the gold was kept under water all the time. The sample was then transferred into the flotation cell with the reagent solution and conditioned. No such precaution was taken in the case of graphite because preliminary flotation tests gave reproducibility of 3 - 6%. The pH of solutions were adjusted with NaOH solution. Distilled water was used to prepare the reagent solutions. Temperature of the flotation medium was about $22^{o} \pm 1^{o}C$. 3 drops of "Aerofroth 65" corresponding to about 0.12 g was added to the solution of 100 ml after conditioning for 5 minutes and the sample floated for 5 minutes.

(a) The flotation of gold was carried out under the following conditions:(1) with 40 mg/l KEX at various pH values. (2) in starch and quebracho S solutions with KEX at various pH values.(3) with KEX at different concentrations of starch. All flotation results are summarised in Figs.6.2 - 6.4.

The flotation of graphite was conducted (1) at different pH values in the presence of 40 mg/l of starch and quebracho S solutions. (2) with different concentrations of starch and quebracho S at pH 9. (3) with different concentrations of KEX and KAX in the presence of 40 mg/l starch and quebracho S. These flotation results are shown in Figs. 6.5 -6.8.

6.2.3 Flotation of Prestea carbonaceous matter.

-300 + 150 μm size fraction of the carbonaceous matter used for adsorption tests (Chapter 5) was employed in the present flotation tests. As in the case of synthetic graphite, 1 g of the carbonaceous matter was used in each test. The conditioning and the flotation times were the same as those used for graphite. Flotation tests were carried out at (1) different pH values with and without KAX (2) in the presence of various concentration of starch and quebracho S and the results are shown in Figs.6.9 & 6.10.

6.2.4 Preliminary flotation tests on Prestea carbonaceous gold ore.

This work was undertaken to find out the depressing effect of starch on the flotation of gold and the carbonaceous material in the ore. Quebracho S, although it is a good depressant for the carbonaceous matter, is also a strong depressant for gold (as has been reported later); for that reason it was not used in these tests.

(i) Flotation apparatus and flotation conditions.

The flotation cell was a small Denver type of cell. The flotation machine is sub-aerating and has an adjustable impeller speed system. After a series of trial tests the impeller speed for conditioning was fixed at 1800 r.p.m., and that for floatation at 1600 r.p.m. The conditioning and the flotation time was 5 min in each case. The concentration of "Aerofroth 65" was about 100 mg/l and the pulp density was 18% solid.

(ii) Method.

(a) 50 g of ore of grade 10.5 g Au/t that was wet ground in a steel rod-mill to -75 μm size (i.e. 35% -75+53 μm

and 65% -53 μm) was floated with 40 mg/l KAX at different pH values using London tap-water at temperature of 22°± 1°C. The pH at which maximum gold recovery was obtained was chosen for the pH of the pulp in the subsequent flotation tests.

(b) Further flotation tests were carried out at the pH for maximum gold recovery (i.e. pH 9.5) for various sizes below 100 μm. (The choice of -100 μm size was based on data obtained from gold liberation studies described in Part I). The size for maximum gold recovery which was about 80% -75 μm was used in subsequent experiments.

(c) A series of flotation tests on the ore was conducted with 40 mg/l KAX in the presence of starch concentrations of 20 to 80 mg/l at pH 9.5 and particle size of 80% -75 μm .

The flotation results of all tests are shown in Tables 6.1 - 6.3.

(iii) Sample preparation for flotation and assaying for gold and carbon.

As reported in Part I about 54% of the gold occurred as free or locked gold with the sulphide minerals at -100 μm size. This influenced the size to which the ore was ground. In addition, no attempt was made to deslime the ore so as to avoid loss of fine gold and minimise the problem of having samples for flotation with widely varied head grades.

Assaying for gold had been described in Part I of this thesis. As before, the essential part of the work was to roast the ore prior to aqua regia leach, and the subsequent processes are as stated earlier.

The organic carbon was analysed by the Analytical Services of the Metallurgical Department.

6.3 Results and Discussion

6.3.1 Flotation of gold.

Fig.6.2a shows the flotation recovery of metallic gold at different pH values when KEX was used as the collector. The results show a high recovery of about 97% at pH of 6 to 9. Between pH 9 and 11, however, the recovery fell from 97% to 70%, whilst the flotation recovery fell further sharply to about 5% at pH 11.8. The constant flotation recovery between pH 5 to 9 followed by relatively gradual decrease in recovery between pH 9 and 11, and with subsequent sharp decrease at pH values above 11, is compatible with the trend of contact angle values and the adsorption densities for KEX (Fig.6.2b). In Fig.6.2b, the flotation recoveries are more closely in line with the contact angles.

As pointed out earlier (Chapter 4), dixanthogen, which is possibly the species responsible for the hydrophobicity of gold, is unstable beyond pH 10 and more pronouncedly so beyond pH 11. This is clearly shown by the sharp decrease of the flotation recovery beyond pH 11. Tipman and Leja[146] observed a first order rate of decomposition of dixanthogen in this pH range, and this shows that the formation at such high pH is unfavourable. In addition, at high pH values the hydroxyl ions would also interact strongly with the gold and make its zeta-potential more negative and therefore less favourable for xanthate ions to adsorb on gold surface. As a result, flotation recovery of gold would decrease at high pH.

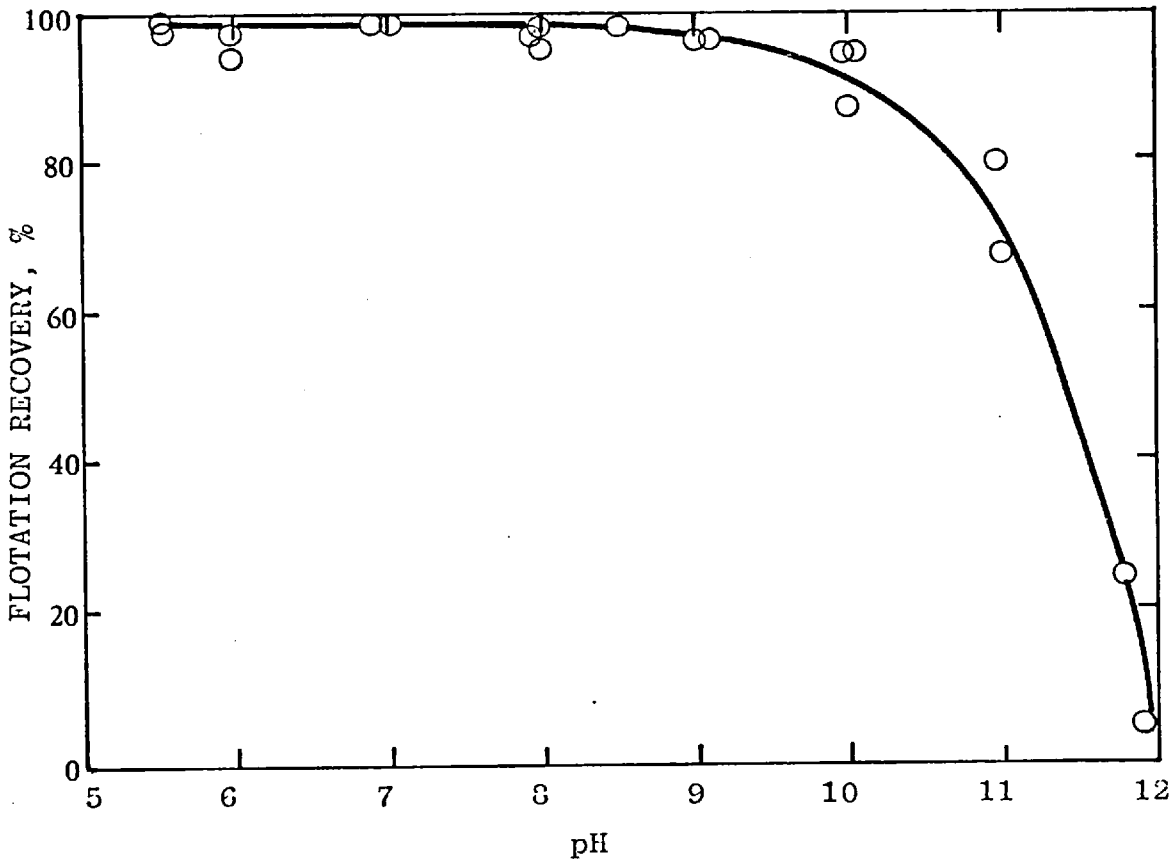


Fig.6.2a Influence of pH on the flotation of gold with KEX. (KEX conc.= 40 mg/l).

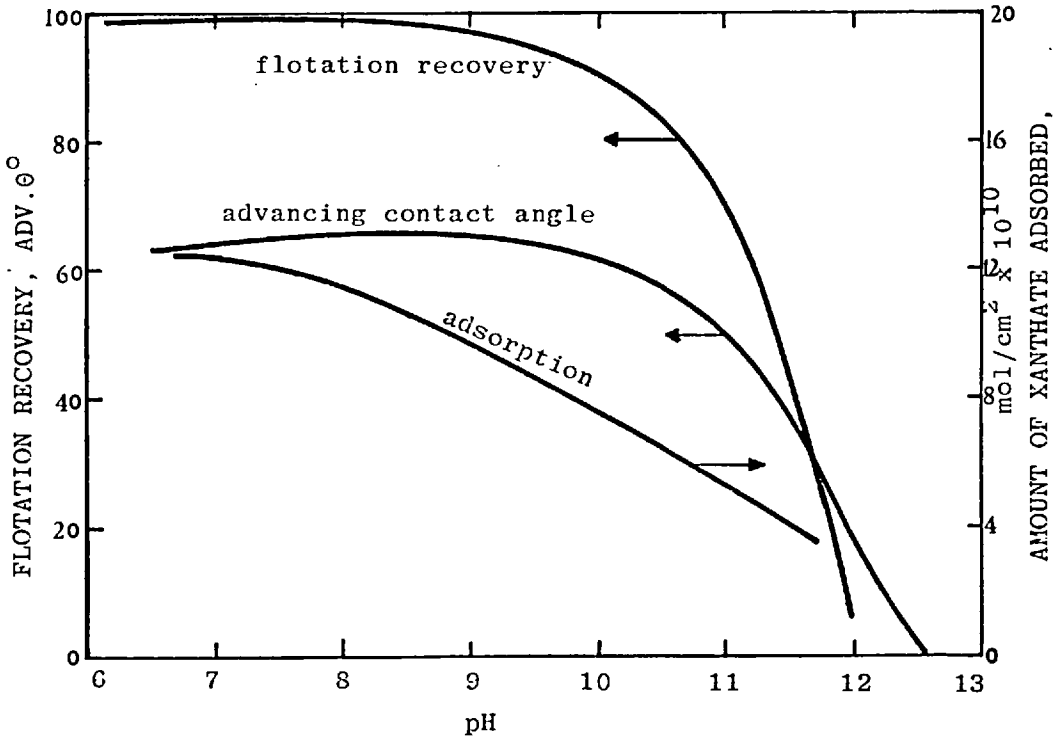


Fig.6.2b Comparison of flotation recovery of gold with contact angle and adsorption density of xanthate at various pH values.
(Graphs drawn with the data from contact angle values, xanthate adsorption densities and gold flotation recoveries).

As the gold was initially hydrophilic it is only natural that it could not be floated by the frother alone. Other investigators for instance, Leaver and Woolf[212], Johns[67] and Gardner and Woods[69] observed that the flotation of gold with frother alone is not feasible unless a collector is used. By use of KAX, Leaver and Woolf obtained about 99% flotation recovery of -60 mesh gold. Johns on the other hand obtained recoveries of 80-94% in the pH range of 8.8 to 10.4 under his experimental conditions. They did not state what species might be responsible for the gold flotation. Gardner and Woods, however, by use of a particulate bed electrode technique showed that gold was floated by dixanthogen. The observations so far made in this work support this idea. These flotation results also compare closely with those of the flotation of pyrite with KEX reported by Fuerstenau, Kuhn and Elgillani[216] where no further pyrite was floated at pH>12.

It was observed during the flotation, particularly at pH 5 - 9, that most of the gold floated in the first three minutes, and that the time was reduced slightly as the xanthate concentration increased from 10 to 100 mg/l. This slight rate of increase in flotation can be explained by considering the reversible potential E_r, of the xanthate-dixanthogen couple given by[69]

$$E_r = E^o_{pH} - 0.0591 \log\{x^-\}$$

where E^o_{pH} is the standard redox potential at a given pH and $\{X^-\}$ is the molar xanthate concentration. By increasing the xanthate concentration the reversible potential decreases and hence the oxidation of xanthate to dixanthogen is more favoured at a lower potential.

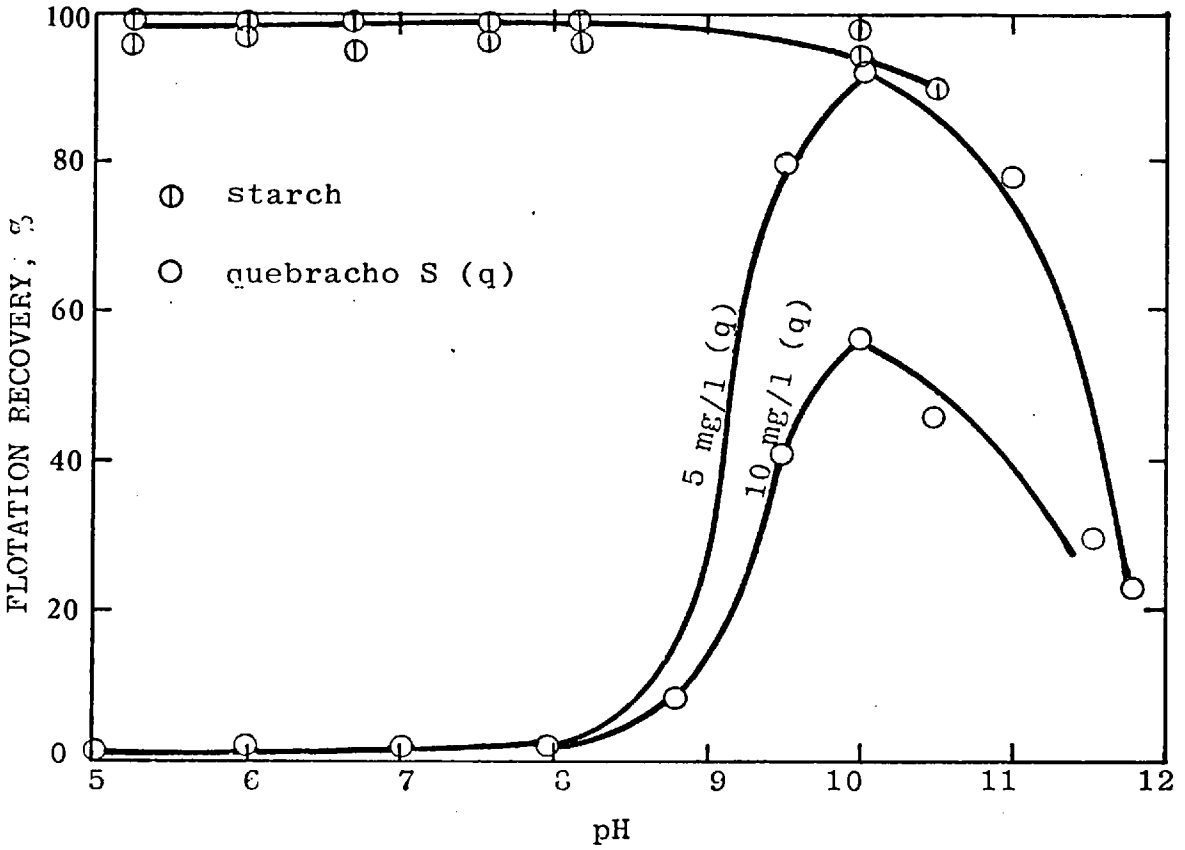


Fig.6.3 Flotation recovery of gold in the presence of 40 mg/l KEX + 10 mg/l starch; and 40 mg/l KEX + 5 mg/l and 10 mg/l quebracho S at various pH values.

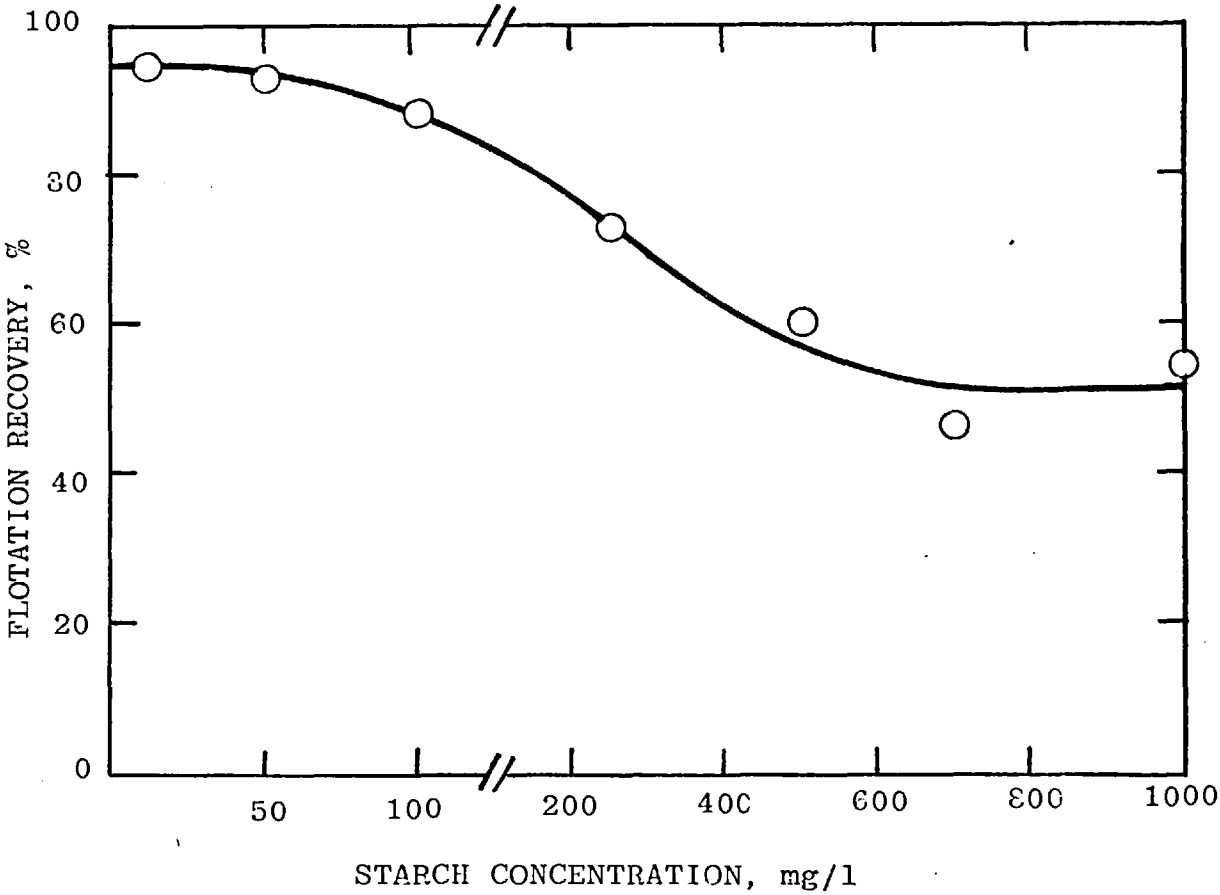


Fig.6.4 Flotation of gold as related to starch concentration at pH 7.
(Concentration of KEX = 40 mg/l).

The effects of quebracho S and starch on the flotation of gold with 40 mg/l KEX at different pH values are shown in Fig.6.3. The results show that the depression of gold by quebracho S is strongest between pH 5 and 9. In fact there was no flotation of gold at pH 5 - 9 even in the presence of as little as 2 mg/l quebracho S. Addition of quebracho S to a xanthate solution containing gold that had been floated with xanthate, instantaneously depressed the gold. At pH>9, however, some of the gold was floated, the maximum recovery being between pH 10 and 11. The loss of the depressing effect of quebracho S at such high pH values has been ascribed to its ionisation by hydroxyl ions[202]. The interaction between quebracho S and the OH^- ions at high pH was shown by the change in the colour of the quebracho S on standing. In spite of the ionisation of quebracho S at high pH, it still exhibited some depressing effects on gold. As expected, the depressing effect increased with increase quebracho S concentration. This depression effect of quebracho S is consistent with the finding of Iskra[202]. Above pH 11 the flotation recovery of gold with xanthate in the presence of quebracho S decreased again in accordance with the normal flotation recovery at high pH.

Under similar conditions when gold was floated with xanthate in the presence of 10 mg/l starch, the gold recovery was not affected at all pH values investigated. The recovery of gold with as little as 10 mg/l KEX was still not affected by starch concentrations up to 100 mg/l, (Fig.6.4). Above this concentration, however, the recovery

decreased gradually from 97% to 50% at starch concentration as high as 1 g/l. These results are in agreement with the earlier observation that starch is hardly adsorbed on gold.

6.3.2 Flotation of graphite

The flotation of graphite with "Aerofroth 65" alone and its depression with starch and quebracho S are shown in Fig.6.5a. The results show that the flotation recovery with the frother alone does not depend on pH. This is evident by the constant flotation recoveries of about 85% obtained at pH values between 6 and 10, followed by only a small decrease to 75% at pH 12. A similar trend of flotation recovery for natural graphite was reported by Iskra[202] and Arbiter, Fujii, Hansen and Raja[105]. These results show marked similarity with the contact angle values shown Fig.6.5b.

The depressing effects of starch and quebracho S on graphite are similar at all pH values except at pH>10 where quebracho S lost its effect slightly more than starch. Similar results were also obtained for natural graphite by Iskra and the reasons for loss of the depressing effect of quebracho S are the same as stated earlier. The depression effect of starch on graphite appears to be consistent with the adsorption densities on graphite at different pH values reported earlier and it is in support of the observation that the adsorption of starch is not strongly dependent on pH.

Fig.6.6 shows the recovery of graphite for various starch and quebracho S concentrations at pH 9. These results confirm the results in Fig.6.5a which show that the depressing effects of starch and quebracho S (at pH lower than that for significant ionisation of quebracho S)

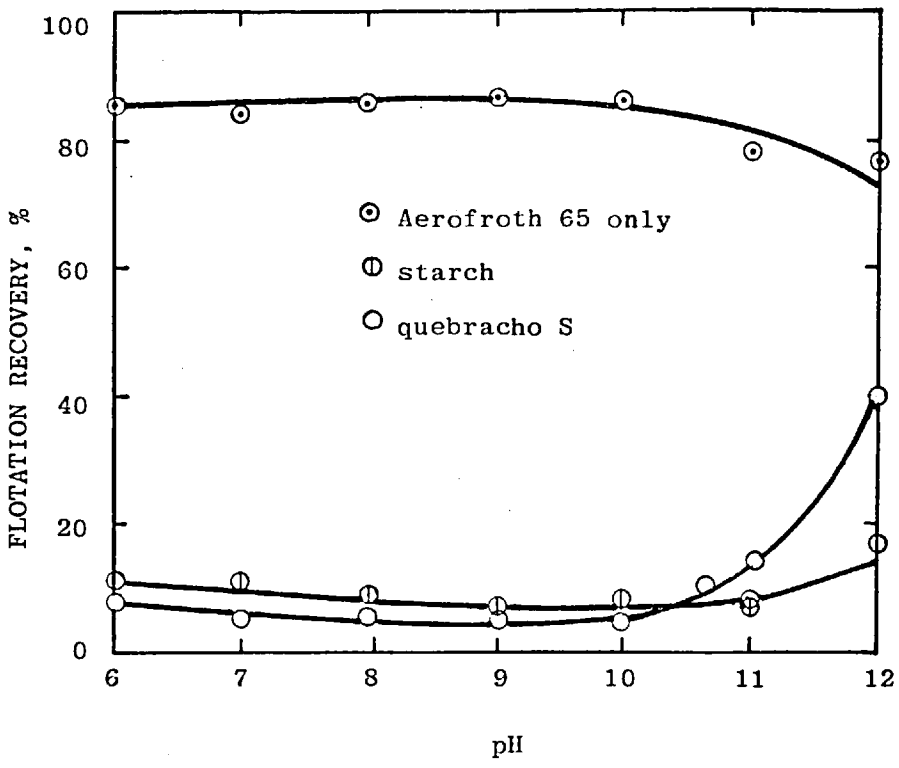


Fig.6.5a Flotation recovery of synthetic graphite in absence and presence of 40 mg/l starch and quebracho S at various pH values.

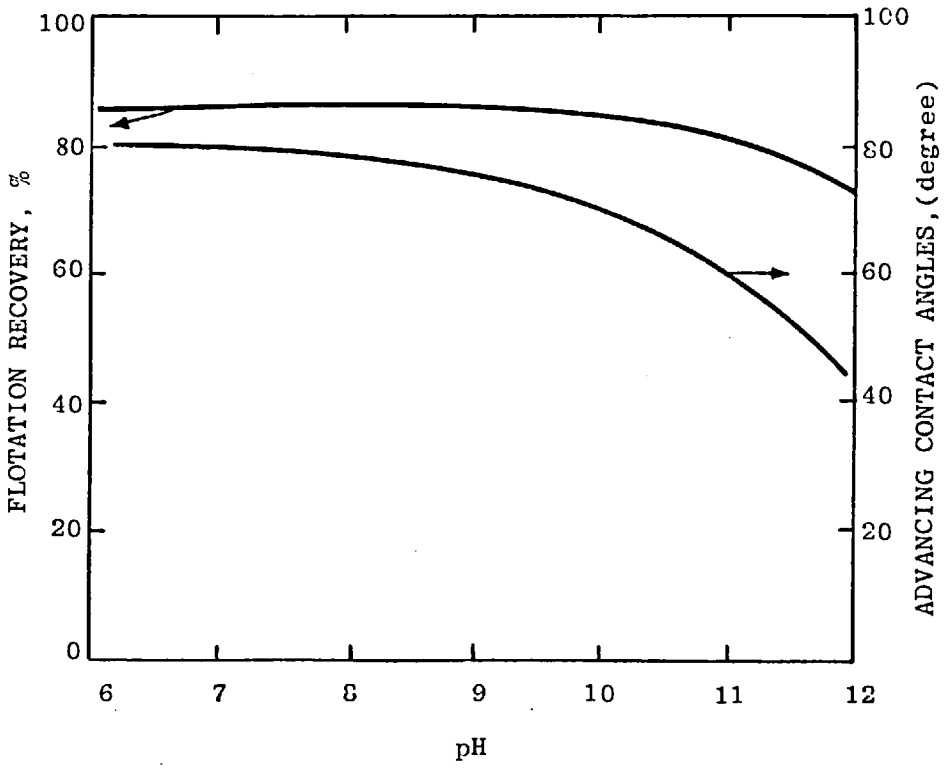


Fig.6.5b Comparison of flotation recovery of graphite with contact angle at different pH values.

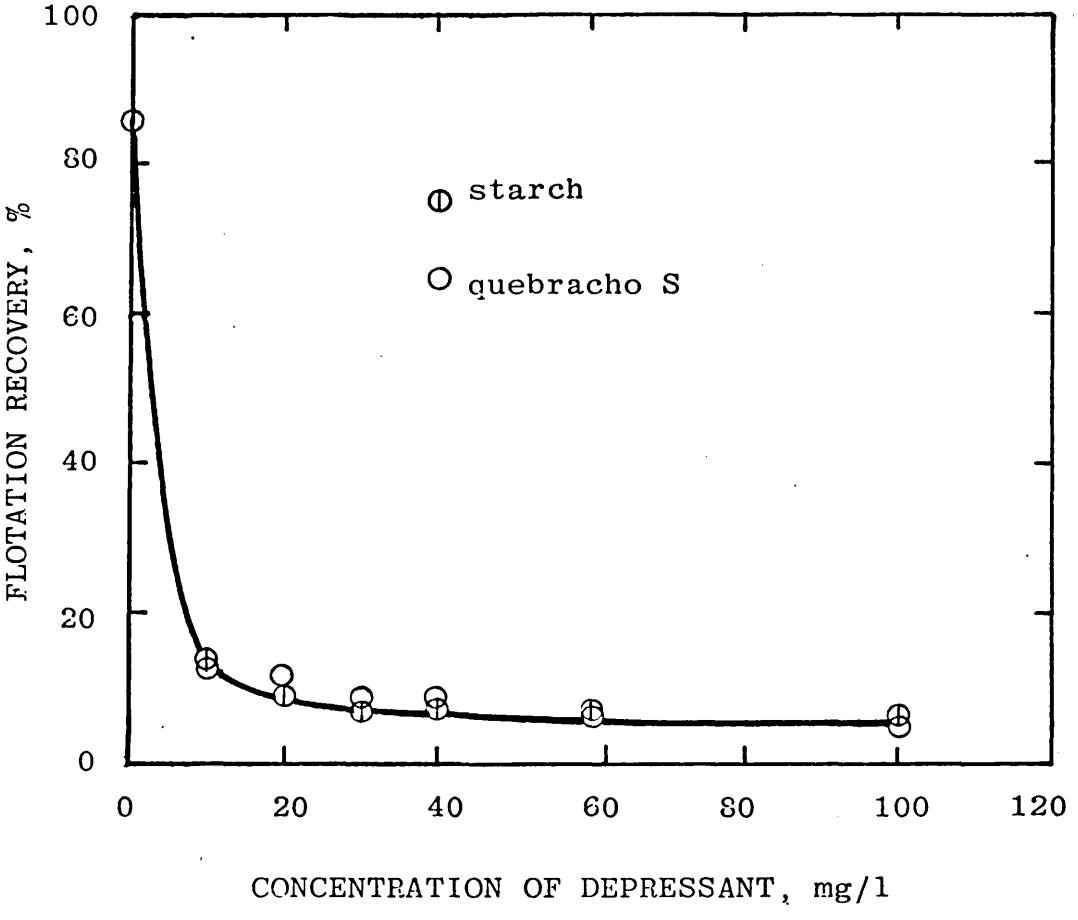


Fig.6.6 Depressing of synthetic graphite at different concentrations of starch and quebracho S at pH 9.

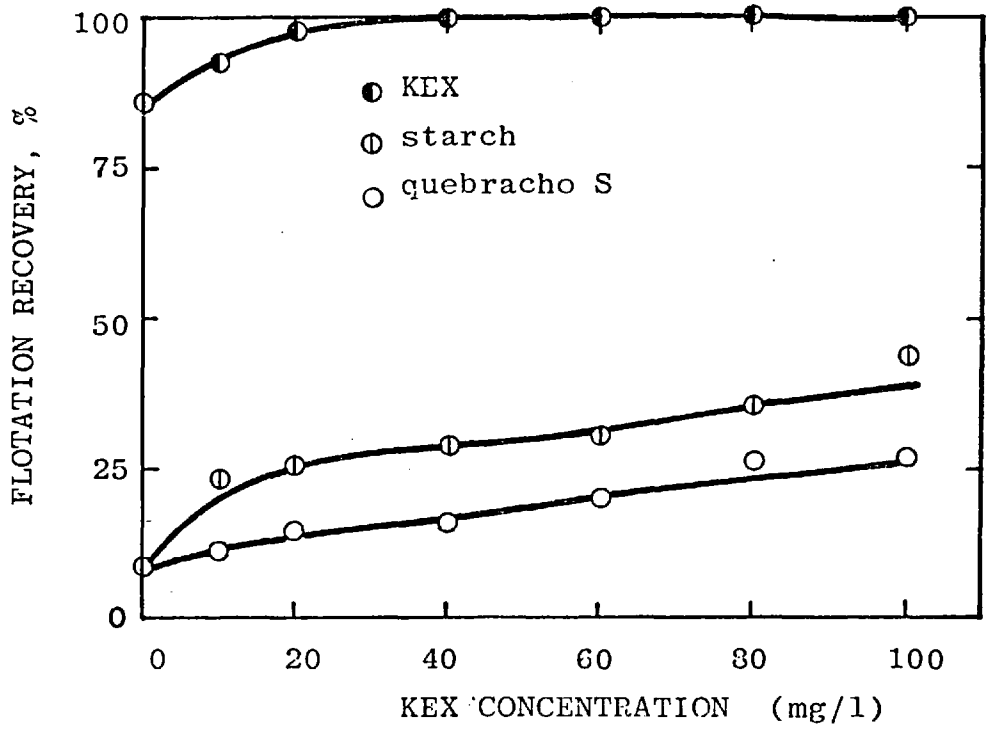


Fig.6.7 Flotation recovery of synthetic graphite at various KEX concentrations in the presence of 40 mg/l starch or quebracho S, at pH 9.

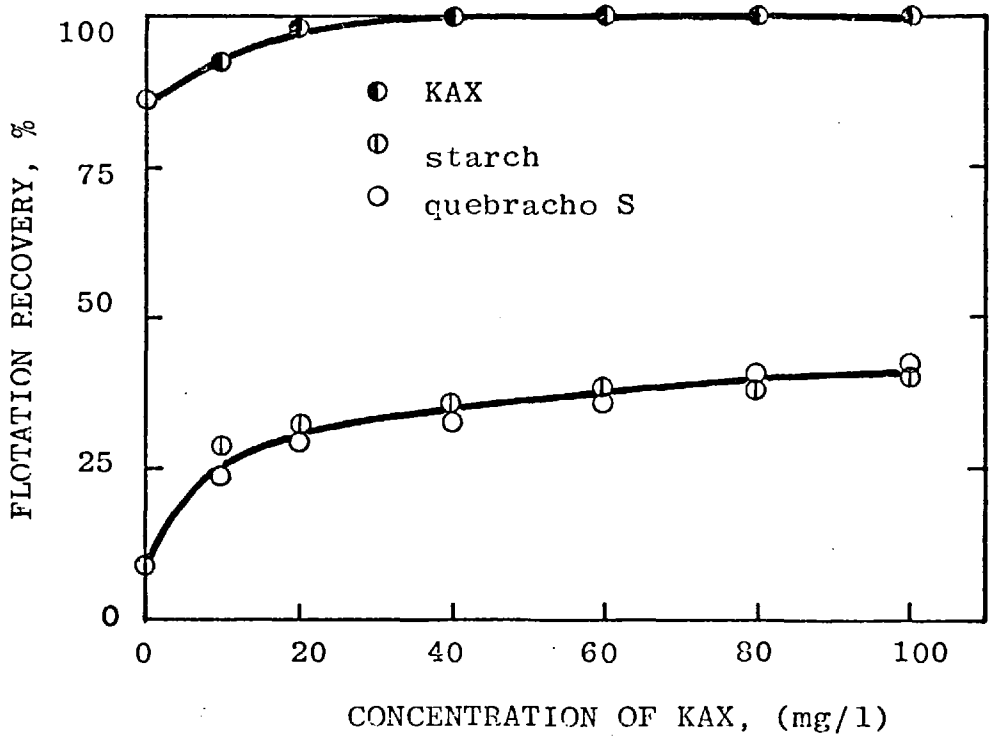


Fig.6.3 Flotation of synthetic graphite at various KAX concentrations in the presence of 40 mg/l starch or quebracho S at pH 9.

are similar. About 10 mg/l of these depressants reduced the flotation recovery of graphite from 85% to 12%. This effect of starch on graphite is similar to the depression of calcite with starch reported by Somasundaran[204].

It was also observed that at starch concentrations greater than 60 mg/l, some graphite particles appeared to have been flocculated (starch being a bridging polymer), whilst quebracho S at similar concentrations behaved more like a dispersant. Account should be taken therefore of the concentration of starch to be used for depressing graphite to avoid flocculation which is undesirable in practical flotation system, as flocculation causes entrainment of values.

The effects of xanthates on the flotation of graphite in the presence and absence of starch and quebracho S are shown in Figs.6.7 and 6.8. The results clearly show that xanthate improves the flotation of graphite in the presence or absence of these depressants. In general, the flotation recovery increased with increase in xanthate concentration. A similar trend would occur, though in reverse sense, if the depressant concentration had been increased while keeping the concentration of xanthate fixed. Such trends would be consistent with the results of co-adsorption of xanthate and starch on graphite from xanthate + starch solutions discussed in Chapter 5.

The adsorbed xanthate species responsible for improving the flotation recovery of graphite can only be dixanthogen which was identified. But it should be noted that the contact angles on graphite in xanthate solutions determined

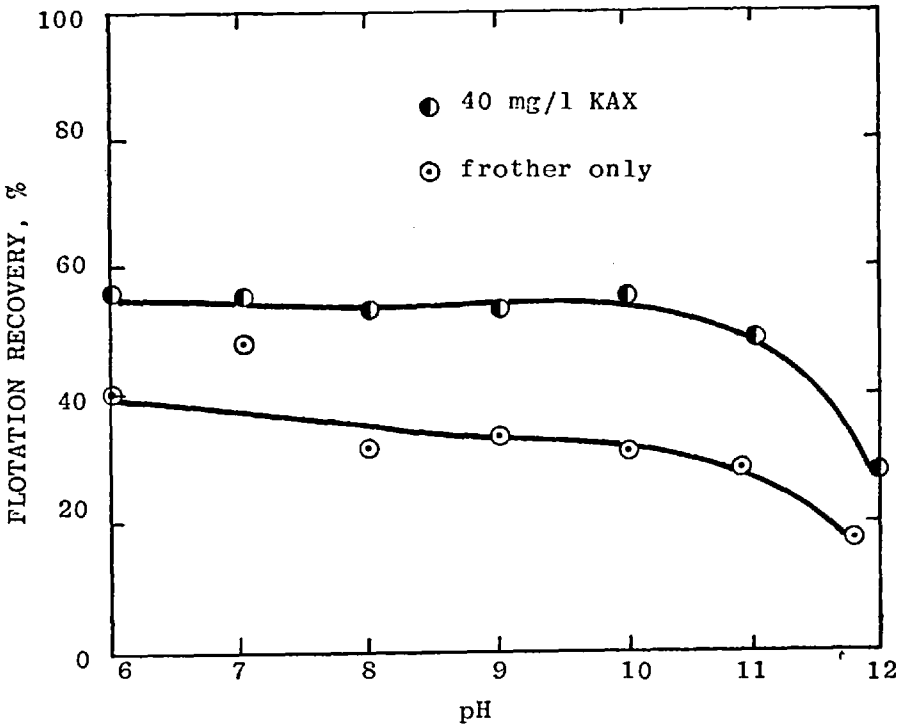


Fig.6.9 Flotation of Prestea Carbonaceous matter with and without xanthate at various pH values.

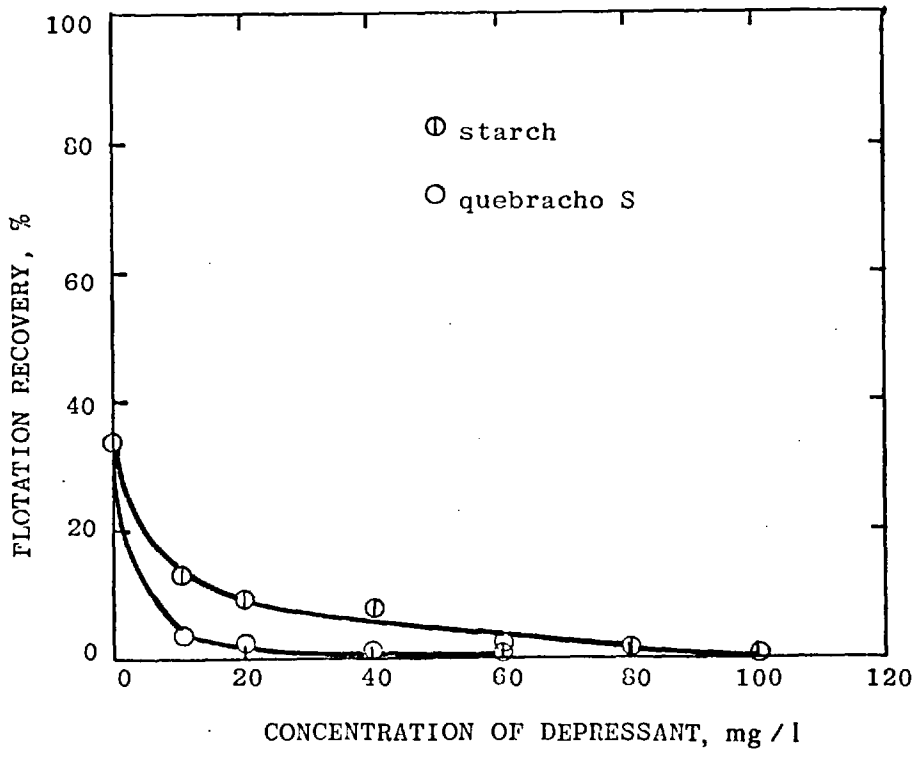


Fig.6.10 Flotation of Prestea carbonaceous matter at various concentrations of starch and quebracho S at pH 9.

earlier, did not indicate that an improvement in the flotation recovery could be made.

The difference between the flotation recoveries of graphite conditioned with KEX + starch solution and, KEX + quebracho S (Fig.6.7) as compared with the recoveries for KAX + starch and KAX + quebracho S (Fig.6.8) is beyond experimental error, but the explanation is not clear.

6.3.3 Flotation of Prestea carbonaceous matter.

The flotation recovery of Prestea carbonaceous matter (Fig.6.9) is about half of the flotation recovery of the synthetic graphite under similar conditions. The effect of pH on the flotation recovery is comparable to that of synthetic graphite (Fig.6.5a). In the presence of 40 mg/l KAX, the flotation recovery of the carbonaceous matter increased by about 20%; this increase corresponds to about 50% improvement in the flotation recovery. The lower recovery as compared with that of synthetic graphite might be attributed to the impurities in the carbonaceous matter, which consist mostly of aluminium silicates of which sericite and chlorite predominate. These impurities, being hydrophilic, would inhibit the flotation of the carbonaceous matter and would not catalyse the oxidation of xanthate to dixanthogen (a species which enhances carbon flotation); hence the lower flotation recovery.

Fig.6.10 shows the results of the flotation recovery at different concentrations of starch and quebracho S. The results show that starch and quebracho S strongly depressed the carbonaceous material and that the effect of quebracho S is slightly stronger than that of starch. The difference

in the flotation recoveries between that for starch and quebracho S cannot be satisfactorily explained because of the impurities in the carbonaceous material. The results show, however, that the carbonaceous material is depressed just as readily as the synthetic graphite.

6.3.4 Flotation of the Prestea carbonaceous gold ore.

Table 6.1 shows that the pH for maximum gold recovery (about 94%) is at 9.5. The percentage weight of the concentrate at this pH is 28.7%. The results show that in general, the weight of flotation concentrate decreased with increase in pH, but the gold recovery did not quite follow a similar pattern. Although the ore is complex and the conditions of flotation were different from those for the flotation of metallic gold described earlier, nevertheless there is a similarity in the trend of the flotation of the gold in the carbonaceous ore and the metallic gold. For instance, the recovery of gold in the carbonaceous ore was between 90% and 94% for pH values 7 to 9.5, but decreased from 94% to 84% from pH 9.5 to 11.5. This trend is consistent with the flotation recovery of metallic gold shown in Fig.6.2a and with the recovery of some sulphide minerals (e.g. galena as reported by Langtry[217]).

The results of flotation recovery for different sizes are summarised in Table 6.2. The results show that the gold recovery did not appear to differ markedly at particle sizes below 67.8% -75 μm. Nevertheless, the size at which the flotation recovery appeared maximum (i.e. 80% -75 μm)

Table 6.1 Flotation of Prestea carbonaceous gold ore with KAX at different pH values.

pH	Flotation concentrate			Flotation tailing		
	% Wt.	Grade g Au/t	% Recovery	% Wt.	Grade g Au/t	% of Au not recovered
7.0	33.2	28.46	90.0	66.8	1.57	10.0
8.5	31.0	30.92	91.3	69.0	1.32	8.7
9.5	28.7	34.54	94.4	71.3	0.71	5.6
10.5	24.5	37.84	88.3	75.5	1.68	11.7
11.5	22.7	38.85	84.0	77.3	2.17	16.0

Table 6.2 Flotation of Prestea carbonaceous gold ore at different sizes at pH 9.5.

Size	Flotation concentrate			Flotation tailing		
	% Wt.	Grade g Au/t	% Recovery	% Wt.	Grade g Au/t	% of Au not recovered
67.8% -75 µm	18.6	49.21	87.2	81.4	1.67	12.8
70.0% -75 µm	20.0	50.13	88.0	80.0	1.55	12.0
80.0% -75 µm	20.0	48.56	92.5	80.0	0.98	7.5
86.0% -75 µm	21.9	43.15	90.0	78.1	1.36	10.0
90.0% -75 µm	24.5	38.23	89.1	75.5	1.50	10.9
100% -75 µm (60% -53 µm)	30.8	28.73	84.4	69.2	2.36	15.6

Table 6.3 Flotation of Prestea carbonaceous gold ore with 40 mg/l KAX in the presence of various concentrations of starch (80% -75 µm size of ore.)

Starch concentration	Flotation concentrate			Flotation tailing			
	% Wt.	Grade g Au/t	% Recovery	% Wt.	Grade g Au/t	% not recovered	% carbon depressed
20 mg/l	15.5	61.98	91.5	84.5	1.05	8.5	82.1
30 mg/l	12.8	81.7	99.6	87.2	0.48	0.48	87.0
50 mg/l	12.0	63.2	72.2	88.0	1.46	27.8	90.3
80 mg/l	11.5	51.68	56.6	88.5	5.15	43.4	91.1

was accepted as the possible size to which the ore should be ground for maximum flotation recovery. One significant trend is the general increase of the weight of the flotation concentrate with decrease in particle size, and consequently a decrease in concentrate grade with decrease in particle size. The flotation recovery also fell as the particle sizes became finer. Such a trend in flotation recovery is a common feature in flotation practice.

The results in Table 5.3 indicate that only low concentrations of starch (<40 mg/l) should be used in depressing the carbonaceous matter. Concentrations of starch >40 mg/l would result in substantial loss of gold to the tailing. At starch concentration of 20 mg/l, the weight of the concentrate was 15.5% as compared with 20% in Table 6.2 which corresponds to 22% decrease in the weight of the flotation concentrate, and loss of 1% of the total gold. The results also show that more gold was depressed as the concentration of the starch increased, but there was not much decrease in the weight of the flotation concentrate.

The depression of gold at the relatively low starch concentrations of 40 - 80 mg/l as compared with its negligible depression when pure gold was floated in the presence of starch concentration of 10 - 1000 mg/l cannot be adequately explained on account of the complexity of the ore. These preliminary tests are not sufficient to reveal the optimum conditions for the flotation recovery of the gold. Even so, the flotation results show that starch at low concentrations can be used for depressing a substantial amount of the carbonaceous matter whilst floating

the gold with xanthate without much loss of gold. (Some of the factors which might influence the flotation of this ore are discussed in Chapter 8.)

6.4 Conclusions

1. Gold is readily floated with xanthate at pH 6 - 11, but considerably less so at higher pH values. The presence of starch at low concentrations (100 mg/l) hardly reduces the flotation recovery of gold. Even at higher concentration up to 1 g/l, the depressing effect of starch is not very strong.

2. Quebracho , on the other hand, is an effective depressant for gold in the presence of xanthate at all pH values greater than 5, except at pH>9 where because of the ionization (i.e. destruction) of quebracho by hydroxyl ions, gold can be partially floated.

3. Starch and quebracho have strong and similar depressing effects on graphite. But in the presence of xanthate, their depressing power is reduced.

4. In the flotation of gold in a graphitic ore with xanthate, starch (and possibly its derivative e.g. dextrin) can be used to depress graphite whilst gold can be floated. But although quebracho is a strong depressant for graphite, it should not be used in the flotation system in which gold has to be floated, because it is a strong depressant for gold.

5. The flotation recovery of Prestea carbonaceous matter is in general, lower than that of the synthetic graphite used. But the influence of pH on the flotation

recoveries for both minerals are similar.

6. Prestea carbonaceous gold ore can be treated successfully by floating the gold and sulphide minerals with xanthate whilst depressing the carbonaceous matter with low concentration of starch without much loss of gold.

CHAPTER 7

7. FLOCCULATION AND FILTRATION OF PRESTEA ORE AND FLOTATION CONCENTRATE.

7.1 Introduction

7.1.1 Some basic concepts about flocculation.

The filtration and de-watering of suspension of finely-divided minerals commonly presents difficulties. If the "slimes" fraction is "stable" in the colloidal sense (i.e. the particles remain separate), the suspension is not only extremely slow to settle but is particularly unfilterable. In practice, such suspensions have to be caused to aggregate by coagulation with electrolytes or flocculation with polymeric flocculants before they can be conveniently de-watered. De-watering is commonly needed for re-use of the water, or its clarification before discharge to a stream or for recovery of the solids for use or for land-fill.

It has been known that particles in a stable aqueous suspension are electrically charged either positively or negatively: the electrical double layers produce electrostatic forces of repulsion which (if strong enough) prevent coagulation. The surface charges may arise in several ways:

(1) Ionisation of the surface groups of the particle as weak acids (or bases).

(2) Unequal dissolution of the ions in a crystal lattice.

(3) The adsorption of ions from the solution.

The particles will coagulate or be flocculated if the magnitude of the van der Waals attractive forces between particles is stronger than repulsive forces. This may occur on the addition of coagulants (inorganic electrolytes)

or by the adsorption of polymeric flocculants.

In the present investigation attention has been directed to the effects of polymeric flocculants on the flocculation and filtration of particles. Much work has been done in the field of flocculation of minerals. The mechanism of polymeric flocculation is generally accepted to be by "polymer bridging". This phenomenon is basically the result of polymer adsorption onto the solid surface by the following means:

1. Non-specific electrostatic interaction between the solid particles carrying electrical double layer and the polymer ions of opposite sign. There may also be electrostatic interaction between delocalised areas of a charge in a heterogeneous surface and the polymer ions.

2. Electrostatic site interaction resulting in the formation of chemical bonds between specific ions on the particle and the functional groups on the polymer e.g. as in the formation of calcium acrylate through the interaction of calcite and polyacrylic acid.

3. Hydrogen-bonding between polymer and substrate. This type of bonding arises between molecules which have hydrogen atom attached directly to a strongly electronegative atom such as O, N and S. The hydrogen is shared between such electronegative atoms, one of the atoms being on the particle.

4. The adsorption of non-ionic polymer on hydrophobic minerals e.g. graphite, is believed to occur by hydrophobic association with the hydrophobic sites on the particle.

5. Dipole-dipole interaction has been evoked where the interaction is between non-ionic groups of the polymer

and the electrostatic field of the particle, e.g. the adsorption of polyacrylamide on CaF_2[218].

7.1.2 Factors affecting flocculation.

The flocculation of particles by polymers is dependent on adsorption, and the degree of polymer adsorption determines the type of flocs produced. It has been shown that the proportion of segments attached to the solid is generally small and that the adsorption does not attain a close packed monolayer coverage. Indeed the optimum polymer adsorption is found to be usually less than 50% coverage (e.g. the adsorption of polymethymethacrylates on silica[219]).

A definite relationship is known to exist when similar polymeric flocculants of different molecular weights adsorb onto a solid. For instance, flocculation is improved with increase molecular weight of a flocculant because of increased molecular size (i.e. increased segments and chains), the bridging property of the polymer is enhanced. But the kinetic rate of adsorption of the polymer decreases with increased molecular weight as a result of slower rate of diffusion.

For higher molecular weight polymers, the greater end-to-end distance of a molecule improves the flocculation as there is a greater chance of bridging the inter-particle distances in the system. For a similar molecule, linear polymers are often more effective than highly branched chains[220]. But it has been observed that the more branched starch (amylopectin) improved the efficiency of flocculation[221].

The following factors are also known to affect the flocculation of particles, namely, substitution of groups into the segments of the polymers, viscosity and pH, particularly when the polymer has ionic groups.

Flocculation does not improve indefinitely with addition of the polymer. Beyond the optimum dosage deflocculation occurs by increased electrical repulsion or by steric stabilisation (i.e. non-adsorbed segments of the polymer behaving as a hydrophilic "protective" colloid). A coating of hydrated polymers effectively reduces the van der Waals attraction between the particles at their point of adhesion.

For this reason, flocculation is generally improved if a polymer is added in stages and in very dilute form. "Haze", the suspended particles with excess adsorbed polymer left in the supernatant liquid, can be avoided by this procedure.

As the kinetics of flocculant adsorption involves diffusion to the particles, agitation of the suspension is essential for efficient flocculation. However, excessive mechanical agitation destroys the flocs, particularly if the solid content is low.

Increased solid content enhances the frequency of particle collision and should lead to improved flocculation since the inter-particle distance is decreased and this favours inter-particle bridging with polymers. At low solid content (e.g. <0.1% by weight of solids), a linear relationship has been found to exist between solid content and optimum polymer concentration. Similar relationships have been found to exist for solid contents up to 50% for the polyacrylamide-silica system[222].

7.1.3 Coagulation by inorganic electrolytes.

It was not necessary in the present investigation to study the effects of inorganic electrolytes on the instability of the mineral suspensions. However, application of inorganic electrolytes for slime clarification is common in mineral industries.

The mechanism of coagulation of particles by reducing the surface potentials, the reduction of the zeta-potential, the collapse of the electrical double layer and the formation of ionic-bridge between particles by use of inorganic electrolytes have been described by many works and will not be considered here. For economic reasons, it is usual to employ some degree of electrolytic coagulation prior to using a polymeric flocculant as the dosage of polymer needed to attain a useful degree of aggregation is thereby reduced. (In some cases, anionic polymers are not appreciably adsorbed by negatively charged particles, unless the surface potential is first reduced by means of electrolytes).

7.1.4 Filtration.

It is generally accepted that flocculation improves the filtration properties of minerals[223]. The relationship between permeability of a filter-cake of flocculated material and the concentration of the flocculant has been developed by La Mer and Smellie[224-227]. Details of their equation which was modified by Healy[228] have been reported by Slater[229] and the assumptions on which the equation was based were discussed.

According to La Mer and Smellie's theoretical derivation, the permeability of unflocculated material which is generally

low, improves with increase in polymer dosage until a maximum was attained at optimum dosage and maximum floc size and then the permeability decreases with increased polymer dosage because of deflocculation. Slater and Kitchener[218] have however, shown that the floc size and the strength continue to increase at dosage in excess of the permeability optimum.

The work to be described has shown results which are contrary to the assumption that increased permeability necessarily accompanies increased floc size.

7.1.5 Aim of this work.

In the preceding chapter the flotation of Prestea carbonaceous ore was reported on. For the subsequent process (roasting) it is considered essential to prepare easily filterable flotation concentrate for roasting since efficient roasting is partly dependent on the porosity and low moisture content of the feed. Poor filtration often results in poor roasting and lower cyanide recovery.

It is intended here to study the effect of polymeric flocculants on the flocculation and the filtration properties of the carbonaceous matter and the flotation concentrate of the ore. Attention was directed mainly to effect of flocculation of these materials on their filtrability.

7.2 Experimental

7.2.1 Materials. (1) Hand-picked Prestea carbonaceous material with the composition similar to that described in PartII Chapter 4, which had been ground to -53 μm size, flotation concentrate of Prestea ore and synthetic graphite of -53 μm size, used in the previous experiments, were used for these experiments.

(2) The following polymeric flocculants were employed. (a) Non-ionic polymers: namely "Separan NP10" which is a non-ionic polyacrylamide of molecular weight of about 1×10^6; "Superfloc 16" which is of the same chemical nature as Separan NP10 but of higher molecular weight ($3 - 5 \times 10^6$), produced by Cyanamid of Great Britain, and "Polyox", polyethylene oxide of 5×10^6 molecular weight, made by the Union Carbide Ltd.
(b) Cationic polyacrylamides, namely "Magnafloc R365" of molecular weight of about 12×10^6, from Allied Colloids Co., Ltd. and B.T.I. C110.

Non-ionic and cationic polymers were selected because the minerals to be flocculated would be negatively charged i.e. would have negative zeta-potentials. Nevertheless, some anionic polyacrylamides were also employed in the preliminary tests but were found to be less efficient as flocculants for the material.

7.2.2 Methods of flocculation and filtration.

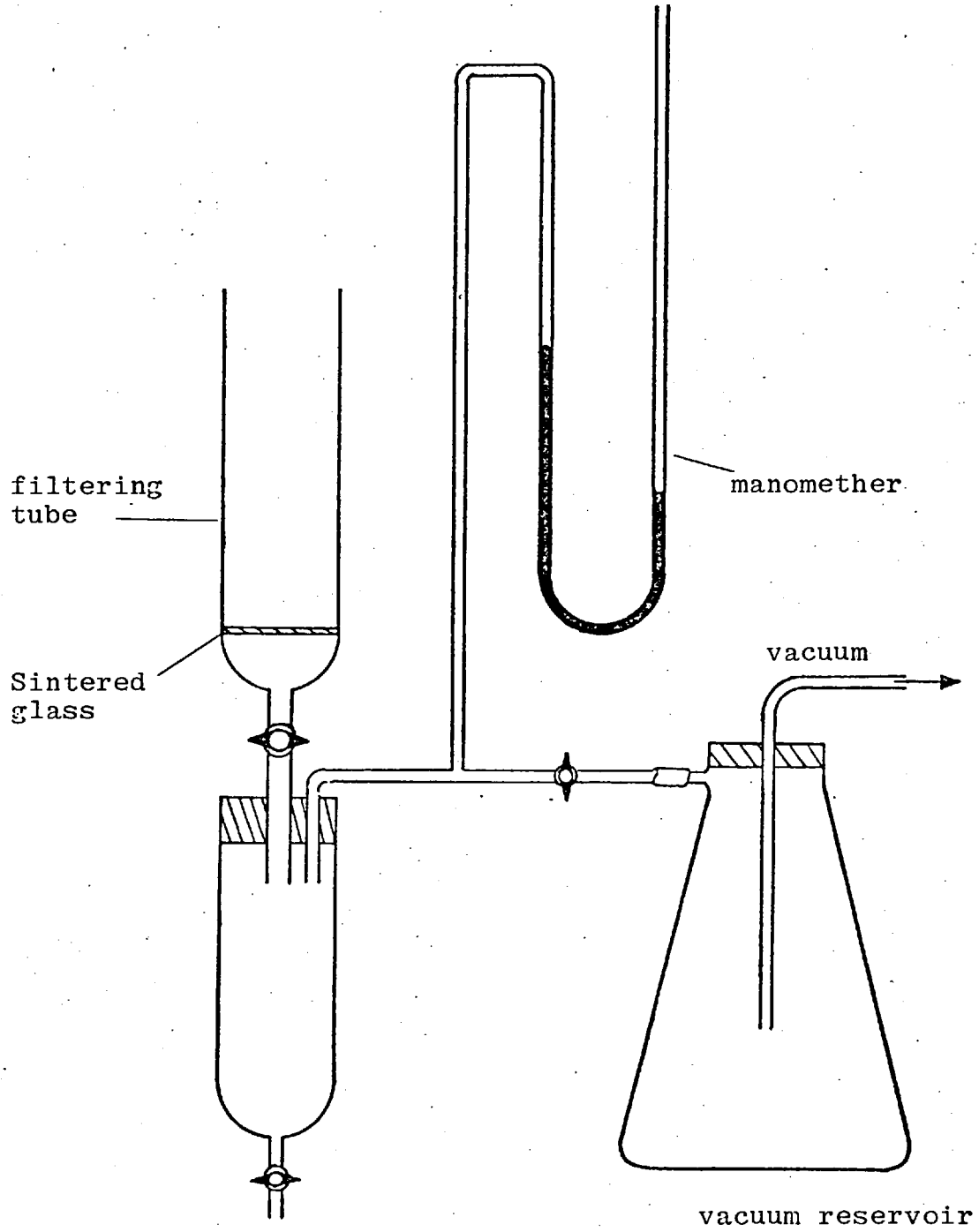
7.2.2.1 Flocculation.

(a) Flocculation tests were carried out in a specially designed glass tube of 3.5 cm diameter by 30 cm long which has two side outlets spaced about 5 cm above each other from the bottom of the tube.

1 g of the carbonaceous matter was dispersed in 100 ml distilled water by stirring the solution with a glass stirrer at 300 r.p.m., and the pH adjusted with NaOH to 9, because in the plant the pH of the floated ore is about 9. A given amount of 0.1% polymer solution was added dropwise to the solution and stirred at the same speed for 5 minutes and the flocs were allowed to settle for 30 seconds when the stirrer was removed. The lower solution outlet was opened and supernatant solution drained into a beaker. The solution was later decanted and the solid dried and weighed. A similar test was carried out without the addition of a polymer and the weight of solid in the supernatant determined. Flocculation was carried out at different polymer dosages.

The degree of flocculation was determined by expressing the weight of solid in the supernatant solution of a flocculated material as a percentage of the weight of solid in the supernatant solution of the material not treated with a polymer. Thus, low solid percentage is an indication of efficient flocculation. The results are represented graphically in Fig.7.2.

(b) Similarly, 1% solid of dispersed suspension of the carbonaceous matter was prepared; 200 ml of the suspension was flocculated in a beaker with a given polymer



Fg.7.1 Apparatus for filtration.

dosage. The flocs were transferred into a 100 ml graduated cylinder and allowed to settle for 24 hours. A series of such tests were carried out with polymer dosages of 0-20 p.p.m. and the heights of the settled beds were measured after 24 hours. The heights of the settled beds are related to the polymer dosages in Fig.7.3.

7.2.2.2 Filtration

The apparatus used was similar in principle to that employed by Slater[229] (Fig.7.1). The object is to determine the "refiltration" rate of a filter-cake.

2 g of the sample was dispersed in 200 ml distilled water and the pH adjusted to 9 with NaOH. The suspension was flocculated as before with Separan NP10, Magnafloc P365 or Polyox for 5 minutes and the flocs transferred into the filtration tube. The solution was then filtered through Whatman No.542 filter-paper under 15 cm Hg vacuum pressure produced by a water-pump. The filtration time for collecting 100 ml of the filtrate was recorded. The filtrate was returned into the filtration tube and the refiltration time recorded. The refiltration time was reproducible and always greater than the first filtration time.

Refiltration tests were carried out on the carbonaceous matter, the flotation concentrate and the synthetic graphite. Only the results of the refiltration rates for the carbonaceous matter and the synthetic graphite were represented (Figs.7.5 and 7.6) because those for the flotation concentrate were similar to those for the carbonaceous matter.

7.3 Results and Discussion

7.3.1 Flocculation

The results of flocculating the carbonaceous matter with cationic and non-ionic polymers are represented in Figs.7.2 and 7.3.

Fig.7.2 shows the percentage of solid in the supernatant solution of the flocculated Prestea carbonaceous material as a function of polymer dosage. The polymers used can be divided into three according to their efficiency of flocculation. Magnafloc R365 was most effective in flocculating the carbonaceous material. Its optimum dosage was about 5 p.p.m. Even at a dosage of 1 p.p.m. the flocculation was comparatively well marked and consequently it may be unnecessary to use a dosage of 5 p.p.m. in flocculating this carbonaceous material.

The flocs produced with Polyox (PEO) belong to the second group. The flocs produced were relatively smaller than those produced with Magnafloc R365 and more easily destroyed e.g. by gentle agitation in distilled water. The optimum dosage was also found to be around 5 p.p.m.

In the third group belong the flocs produced with Separan NP10 , Superfloc 16, and B.T.I. C110, which have settling rates between those produced with Magnafloc R365 and Polyox. Their flocs appeared to be stable as those produced with Magnafloc. There appeared to be not much to choose between the efficiencies of flocculation with Separan NP10 and Superfloc 16, although Superfloc 16 is a higher molecular weight polymer. Edwards[230] working

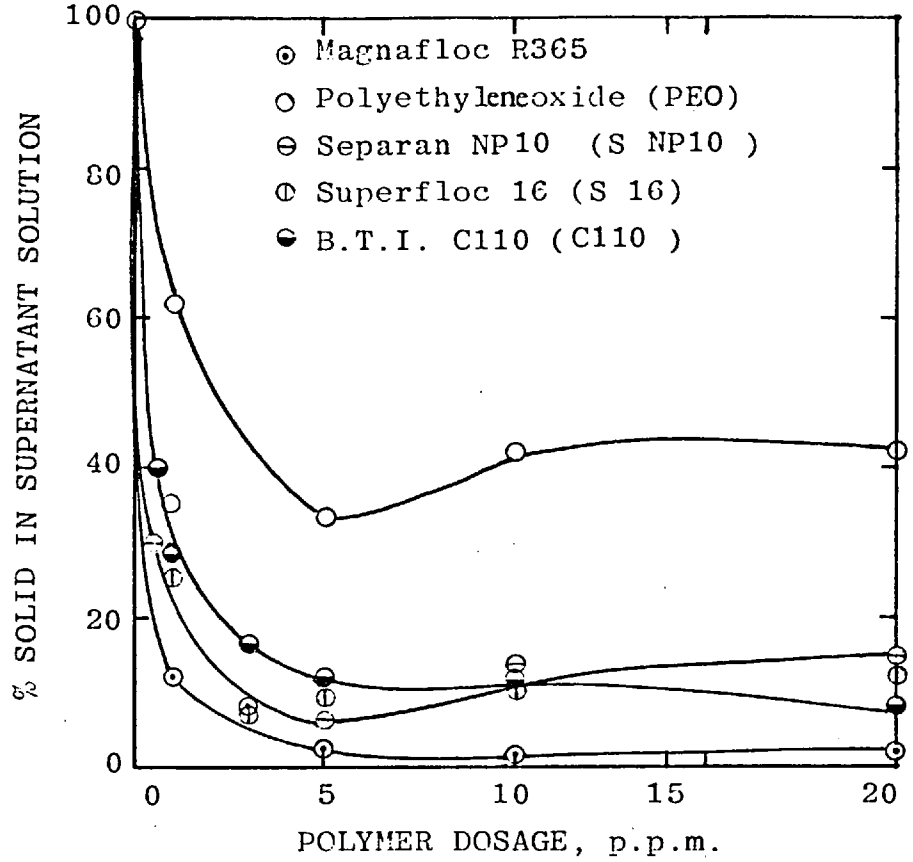


Fig.7.2 Flocculation of Prestea carbonaceous material as related to polymer dosage. (solid content= 1%)

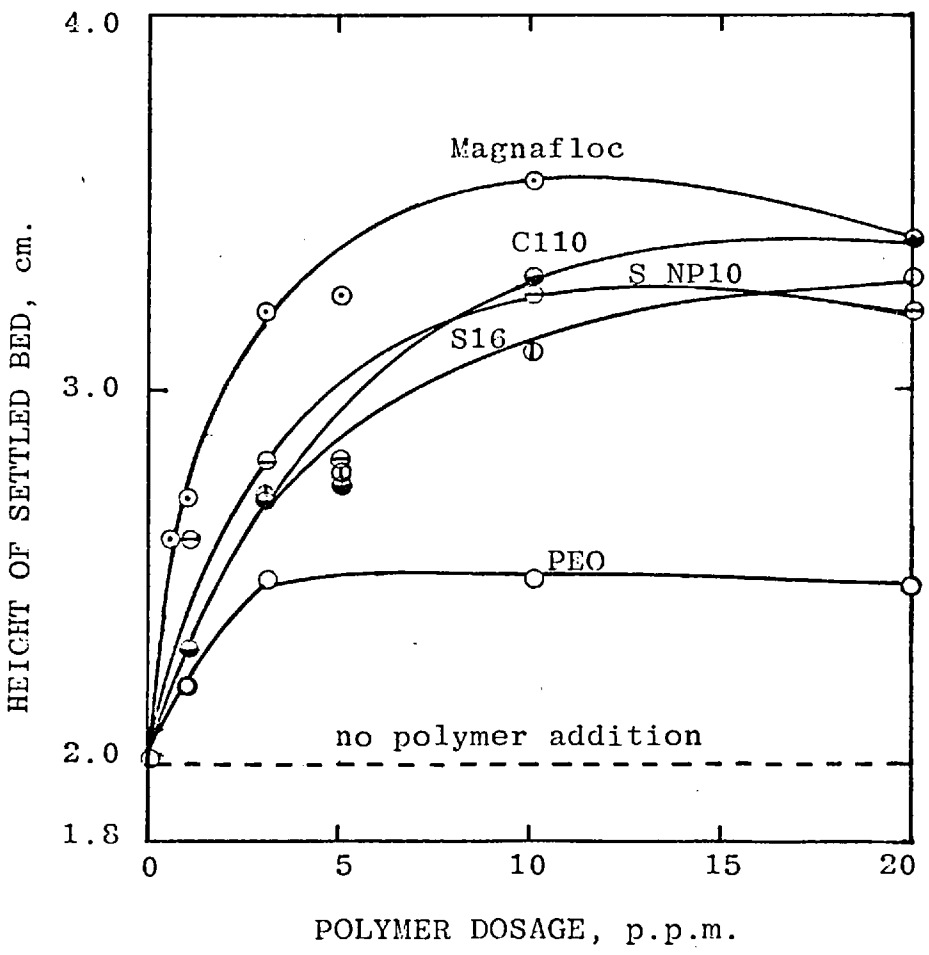


Fig.7.3 Height of the settled bed of the flocculated carbonaceous matter as a function of polymer dosage. (solid content=1%)

on Thames mud observed that while the polymer:solid ratios for Separan NP10 and Superfloc 16 were about the same, Separan NP10 produced floc sizes which were twice as large as those produced with Superfloc 16 for the same dosage.

The optimum dosage of these polymers for flocculating this material was about 5 p.p.m. From the results it would appear that in flocculating this material with Separan NP10 , Superfloc 16 and B.T.I. C110 a dosage of 3 p.p.m. or less would produce adequate flocculation to facilitate settling and thickening.

The results in Fig.7.3 confirm those in Fig.7.2. As expected, the height of the settled bed for flocs produced with the Magnafloc was the greatest followed by those produced with Seperan NP10 , B.T.I. C110 and Superfloc 16, assigned to group three and those produced with PEO in a descending order of floc size. Fig.7.3 also shows that even beyond 5 p.p.m. (optimum dosage) the heights of the settled beds continued to increase, indicating that the flocs were stronger.

From Fig.7.2 it would appear that the permeability of the flocs should be greatest at about polymer dosage of 5 p.p.m. where the settling rates of the flocs appeared to be fastest. This expectation would have been realised if the theory of La Mer and Smellie[224-227] is applicable to this system. From Fig.7.2 it would also be expected that maximum height of the settled flocs should coincide with the optimum dosage. The present results, however, show that the heights of the settled flocs increased beyond the polymer dosage of 5 p.p.m. In the work of Slater[229] it

was observed that when fluorite was flocculated with polyacrylamide (P 250), the height of the settled bed of the flocs did not coincide with the optimum polymer dosage or with maximum permeability since different factors were measured in determining the optimum conditions.

In particular, a small "over-dose" of flocculant leads to re-stabilisation of some of the particles, because the flocculant cannot be perfectly mixed with the slurry. This leads to some residual suspended solid and also to a reduced refiltration rate (because of blockage). On the other hand, flocs once formed are further strengthened by a moderate excess of flocculant, provided the thinning is gentle. Hence, the product of a small over-dose is often large, cohesive flocs, accompanied by some residual turbidity.

7.3.2 Filtration

It has been generally accepted that flocculation improves filtration. The explanation of the relationship between the settling rate of the floc and the floc size, and the rate of flow of fluid through the floc bed follows from the Stokes's law of free fall in a viscous medium and Poiseuille's law of flow through capillaries. The rate of free fall of the effective sphere (i.e. the floc shape) depends primarily upon r^2 for the flocs of constant density, where r is the effective radius of a sphere equivalent to the floc. According to Poiseuille's law, the rate of liquid through a capillary is proportional to R^4, where R is the effective radius of the capillaries in the cake, or the spaces between flocs. In general, the filtration rate is proportional to R^4.

A more explicit theoretical relationship between permeability of a filter-cake and polymer dosage was derived by La Mer and Smellie[224-227] and modified by Healy[228]. It is represented graphically as shown in Fig.7.4, where P_m is the concentration of polymer required

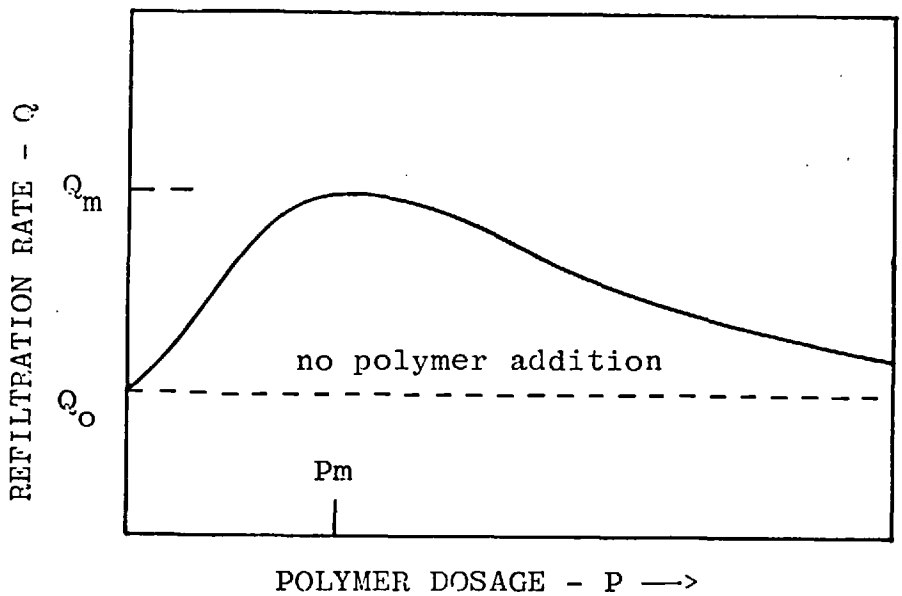


Fig.7.4 Theoretical form of the refiltration rate against dosage curve, according to the theory of La Mer and Smellie.

to give optimum refiltration rate (i.e. highest permeability), Q_o is the refiltration rate with no polymer addition and Q_m, the optimum refiltration rate. The theory thus predicts an optimum permeability with increase polymer dosage at maximum degree of flocculation. As it was assumed that the poor flocculation at high surface coverage is associated with the reduced bridging capacity of the adsorbed polymer, the right hand side of the curve in Fig.7.4 is the result of decreasing floc size.

This theory was checked by Slater[229] who obtained a similar trend of permeability of a filter-cake with polymer dosage and besides observed that the permeability

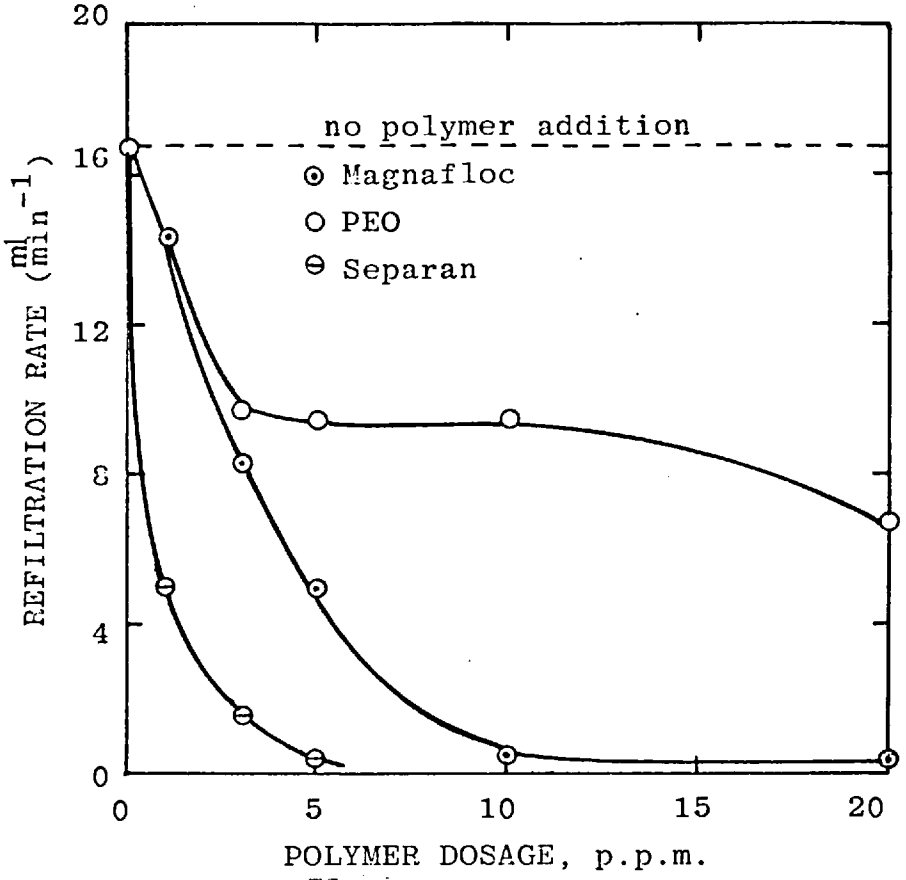


Fig.7.5 Effect of flocculation on refiltration rate of Prestea carbonaceous material. (solid content= 1%)

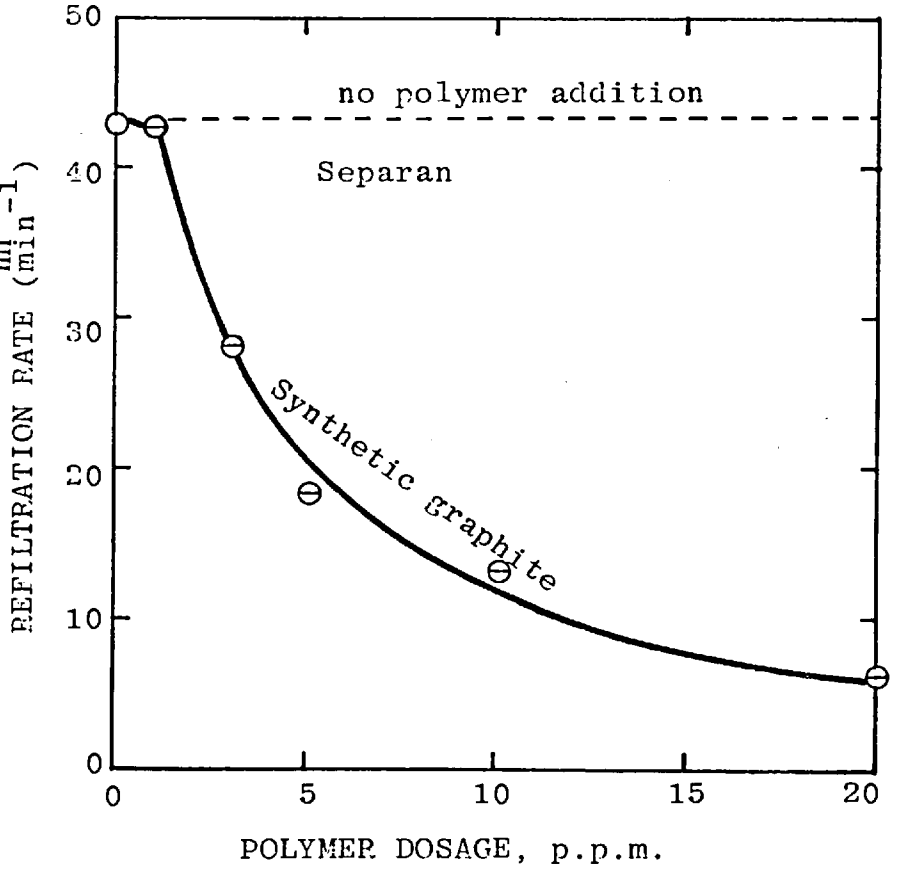


Fig.7.6 Effect of flocculation on refiltration rate of synthetic graphite. (solid content= 1%)

can be lower than that for a filter-cake which had not been treated with a polymer. It is thus anticipated that the permeability of the filter-cakes in this present investigation should behave similarly.

However, contrary to expectation the refiltration rates (i.e. permeability) of the filter-cake of the carbonaceous matter (Fig.7.5), the flotation concentrate and that of synthetic graphite (Fig.7.6) produced with all polymers used did not obey La Mer and Smellie's theoretical prediction. Instead the refiltration rates of all filter-cakes were consistently lower than those not treated with polymers. The polymer (PEO) which produced the smallest flocs rather gave the most easily filterable filter-cakes.

These observations are entirely contrary to the theory and the accepted view on the filtration of flocculated materials. One possible explanation might be that some minerals in the sample have different properties with respect to flocculation.

Since the carbonaceous matter is not mono-minerallic similar tests were carried out on synthetic graphite. The results shown in Fig.7.6 are in agreement with the earlier results shown in Fig.7.5. Similar observations (i.e. reduction in the rate of filtration of materials treated with polymer dosage from 0 - 25 p.m.m.) were noted by La Mer and Smellie[224] in certain conditions in the filtration of leached zone phosphate rock slime with potato starch in the absence of an electrolyte, but no explanations were given.

Further work will be needed before any adequate explanations for this phenomenon can be given. But the possible explanations for the filtration behaviour of the carbonaceous matter and the synthetic graphite treated with the above polymers may be given as follows:

Flocs may remain as discrete spheres if each floc is charged (i.e. carries an electrical double layer). Conversely, flocs may adhere to each other more readily under filtration pressure, if the forces of repulsion between them can be overcome by the forces of attraction once the energy barrier of the "floc stability" is exceeded.

It is possible that for this carbonaceous matter and graphite which are predominantly hydrophobic materials which have the tendency for hydrophobic association, the presence of adsorbed polymer bridges the inter-particle distances and facilitates the adhesion of the floc . Thus under pressure flocs collapse irreversibly and once a certain inter-floc distance is exceeded, the carbon particles could adhere to each other more strongly. Besides, the polymers can adsorb on the walls of the capillaries of the settled bed.

Fine suspensions can also reduce the pore spaces between the flocs. But under efficient flocculation conditions fine suspensions should be eliminated. In fact, clear supernatant liquid was obtained with proper conditions. It may therefore appear that the factors most likely to be responsible for poor permeability would be the increased forces of adhesion between flocs enhanced by polymer adsorption and natural hydrophobic association of the carbon particles.

Examination of the filter-cake showed that the material which was not treated with a polymer tended to "blind" the filter paper whereas the flocculated material carpeted it. The adhesion between the flocs was strongest among the flocs in immediate contact with the filter paper. This may mean that the flocs under pressure did not behave as discrete spheres so as to improve filtration, but collapsed into a tight coating.

If this theory is correct, the problem could be overcome in principle by finding a different flocculant that gave stronger flocs. Unfortunately, none of those examined - which included all the usual types - was satisfactory in this respect.

The ultimate aim of this filtration test is to produce a filter-cake with low moisture content for roasting. As the relationship between the moisture content of the filter-cake and polymer dosage has not been studied, further work may be necessary to provide this information. With this ore, it may be that only a small amount of polymer dosage (e.g. 1 p.p.m.) which gives a clear supernatant liquid may be necessary to give a satisfactorily low moisture content.

7.4 Conclusion

Filtration of well flocculated Prestea carbonaceous material or the flotation concentrate or synthetic graphite at polymer (cationic and non-ionic) dosages between 0 - 20 p.p.m. did not conform to La Mer and Smellie's theoretical model. Although the use of the above polymeric flocculants produced large flocs, accelerating the settling, this did not lead to improved filtration. On this account a lower polymer dosage than the optimum dosage (5 p.p.m.) should be employed in flocculating Prestea ore. Flocculation, however, prevented the blinding of the filter paper although it did not seem to improve the filtration rate.

CHAPTER 8

8. THE IMPLICATIONS OF PROCESSING PRESTEA CARBONACEOUS GOLD ORE.

8.1 Introduction

The results of the mineralogical investigation of Prestea carbonaceous gold ore had been described in Part I of this thesis where it was pointed out that the gold in the ore was associated with nearly all other minerals and occurred in microscopic and sub-microscopic sizes and that the presence of "activate" carbon and sulphides was responsible for the refractoriness of the ore.

Because of the complexity of the ore it may be necessary to employ a combination of several processes in treating the ore to recover the gold. Consequently, this chapter will be devoted to the possible processes which can be used. The processes to be considered are, comminution, gravity concentration, flotation, oxidation (i.e. aqueous oxidation and roasting), cyanidation and the recovery of the gold from the leach solution. Emphasis will be laid on the effects of the mineralogy and the chemistry of the minerals in the ore on the processes. Since the ore is being economically processed, the economic implication of processing the ore will only be dealt with when necessary. The processes which can be improved, abandoned or introduced will be suggested.

8.2 Possible processes.

8.2.1 Comminution

The exact nature of the problems which will be encountered in the crushing of this ore is difficult to predict. However, on account of the preponderance of quartz (about 67%) it will be expected that the ore will be abrasive and would rapidly wear the crusher liners and mantles and would cause high consumption of power. The effect of the carbonaceous material should be to reduce the efficiency of size reduction of the harder minerals. But as the amount of the carbonaceous matter is about 4% of the total ore, its effect on the crushing efficiency may not be noticeable. However, if mining is not properly controlled and, as a consequence, the amount of the carbonaceous matter is high, it may have considerable effect on crushing efficiency.

During the grinding of this ore it is possible that the carbonaceous matter will act as a lubricant and a surface coating material. The extent of the coating of freshly formed particles will depend on the type of minerals and their surface properties (e.g. charge and energies). The coating of other mineral surfaces by the carbon can affect the flotation recovery of the gold. For this reason it could be suggested that the run-of-mine ore should be washed to remove the carbon prior to crushing. But the washing of the ore can only partly remove the carbon whilst at the same time fine free gold may be washed along with the carbon and cause gold loss if it is not recovered from the carbon. The extent of the coating of minerals by the carbon and its effect on the

efficiency of grinding can only be known by detailed investigation. The indication is that the ore should be ground to about 80% -75 μm size for satisfactory liberation of gold and for high flotation recovery.

8.2.2 Gravity concentration.

On account of the refractoriness of the ore and the fact that a considerable proportion of the gold is coarse, it would be reasonable to attempt to employ a gravity concentration process in recovering the gold just after grinding. This process may recover the greater part of the gold liberated during comminution and so reduce the gold in the circuit. The advantage of this process is that, regardless of whether the gold surface is coated by carbon or not, it can be recovered readily since the criterion for concentration depends on the density differences.

Perhaps the gravity concentration is the most profitable single process in terms of ease and low cost of operation and the amount of gold recovered. (Indeed, about 60% of the total gold is recovered with gravity concentration alone by the present plant for processing this ore).

Jigs, which have been used for concentrating such an ore, have been completely replaced in some plants by strakes, presumably on account of the lower maintenance cost of the latter. Shaking tables can be used for further concentration of the strake concentrate and the final concentrate can either be calcined or amalgamated.

For this type of ore which will have high proportion of sulphide minerals in the table concentrate, it would be preferable to amalgamate the concentrate rather than calcine it. However, to avoid the danger of mercury poisoning, the table concentrate can be calcined rather than amalgamated, but it will mean the acceptance of the fact that the fineness of the bullion so produced will be lower than that produced by amalgamation.

8.2.3 Flotation.

When a gold ore is not refractory the use of flotation to recover the gold is unnecessary, and in such a case direct cyanidation is often employed after the ore has been finely ground. But because of the refractoriness of this ore it is considered essential to use flotation in concentrating the gold. The presence of the carbonaceous matter, which is known to have coated some of the minerals, will complicate the flotation of the ore. In general, the carbonaceous material will float readily under normal sulphide flotation conditions. When the sulphide minerals are activated, for example with $CuSO_4$, and conditioned with long-chain xanthates as collectors, the sulphide minerals and gold can be successfully floated.

Two possible methods can be adopted in the flotation of gold in this ore. These are:

(1) The flotation of gold together with the sulphide minerals with simultaneous depression of the carbonaceous matter.

(2) Bulk flotation of gold and the sulphide minerals together with the carbonaceous matter.

Each method has its advantages and disadvantages which have to be taken into account in deciding which method should be finally adopted in practice.

In the flotation of gold with simultaneous depression of the carbonaceous matter, the major problem would be that of the depression of gold and sulphide minerals which had been coated by carbon. However, the depression of the carbonaceous matter will reduce the amount of such gangue minerals which had also been coated by carbon and could otherwise have floated. The result would be the production of a high concentrate grade coupled with small weight of flotation concentrate, and a flotation concentrate which is sufficiently free of carbonaceous matter which would adversely affect the efficiency of subsequent processes, for instance oxidation and cyanidation.

If the carbon is floated together with gold and the sulphide minerals, it is likely that, in general, the gold recovery will be greater than when the carbon is depressed. This, as a rule, will be coupled with low grade of the flotation concentrate as more gangues particularly those particles which had been coated with carbon, will be floated. The result would be a lower sulphide to gangue ratio than that if carbon had been depressed. With carbon as a reducing agent in the flotation concentrate in addition to lower sulphide to gangue ratio, the roasting will be expected to be less efficient.

As the carbon is very finely divided (a source of slime), the filtration of the concentrate prior to roasting may also be poor. Thus it is essential to prepare readily filterable cake (Chapter 7) for roasting.

(a) Flotation of the gold in the ore.

As mentioned earlier, gold in the ore is alloyed with Ag, Cu, Zn, and Pb. Most of these metals are easily oxidised in water under normal atmospheric conditions. Consequently the gold will have differently oxidised surface sites under normal flotation conditions. It will be expected, therefore, that this gold should be more hydrophilic than high purity gold, and react more readily with xanthate on account of its less noble metallic impurities. Its reaction with xanthate in a flotation circuit may be that of chemisorption of xanthate onto some of the surface sites of the gold, coupled with some catalytic oxidation of xanthate to dixanthogen. Thus it would appear that the Prestea gold would react faster with xanthate and probably float more readily than pure gold used in the previous experiments.

(b) Sulphide mineral flotation.

Although it is known that many of the types of the sulphide mineral in this ore float readily with xanthates, their rate of flotation will nevertheless differ. From the critical OH^- ion concentrations for the sulphides in Table 8.1, (determined by Wark and Cox[231]) it can be seen that the flotation of the sulphide minerals in the ore will proceed in the order of decreasing pH as follows;

tetrahedrite > chalcopyrite > pyrite > galena > arsenopyrite > pyrrhotite.

Table 8.1 Critical hydroxyl ion concentrations at room temperature in 25 mg/l KEX solution for sulphide minerals. (after Wark and Cox[231])

Mineral	$\{OH^-\}$	pH
tetrahedrite	10^0	14
chalcopyrite	9×10^{-3}	12
pyrite	7×10^{-4}	10.8
galena	6×10^{-4}	10.8
arsenopyrite	6×10^{-6}	8.8
pyrrhotite	10^{-8}	6.0

By taking the critical pH for gold to be 12, those for bournonite and boulangerite to be between 9 - 11, it is apparent that the pyrrhotite and arsenopyrite will be most readily depressed by increasing the pH, while sphalerite (also present in the Prestea ore) may not be floated without activation with $CuSO_4$. The flotation of these sulphide minerals in the ore will therefore require the use of activators e.g. $CuSO_4$ in addition to long-chain xanthate collectors. The use of these reagents will shift the critical pH of the minerals to the higher pH values. Thus, in the flotation of the sulphide minerals in the ore, $CuSO_4$ and long-chain xanthate collectors are required for successful recovery of the gold since many of the sulphides contain gold.

Although clean pyrite may be expected to float readily at pH 9.5 (the pH for maximum gold flotation recovery for this ore), there is a possibility of oxidised pyrite being less successfully floated, it being the most oxidised

sulphide mineral observed. It may therefore follow that, on the whole, oxidised pyrite, arsenopyrite and pyrrhotite may be lost to the flotation tailing more readily than the other sulphide minerals. The work of Chant[232] on the flotation tailing of this ore showed that pyrite and arsenopyrite are indeed the most common sulphide minerals lost to the tailing. It is to be realised, however, that the above factors cannot account adequately for the loss of pyrite and arsenopyrite noting also that these two sulphides form over 90% of the total sulphide minerals. Other possible reasons for inefficiency in the flotation of the ore will be discussed later.

pH regulators. It is well known that NaOH, NaOH + Na_2CO_3, and Na_2CO_3 and CaO are used to regulate pH of flotation pulps. It has been shown[233] that NaOH and NaOH + Na_2CO_3 solutions are better pH regulators than lime (CaO) for the flotation of gold. In practical gold flotation, however, the economics dictates the use of lime rather than NaOH or NaOH + Na_2CO_3. As lime can depress gold when used in high concentration, judicious use of it is always required. Lime has also the ability of enhancing the rate of settlement of slimes, a property caustic soda and soda ash do not have.

(c) Some aspects of the flotation of Prestea ore.

If gravity concentration is used to recover part of the gold, the grade of the flotation feed will be less than 10.5 g Au/t, the head grade of this ore. Assuming 60% for the gravity concentration recovery of gold, the grade of the flotation feed will be about 4.2 g Au/t. A rather lower flotation feed grade should be more suited, in general, to the production of a higher total recovery of gold than when the feed grade is 10.5 g Au/t under similar flotation concentrations assuming the same level of flotation recovery.

In practice, the flotation concentrate produced is between 2 - 3% of the total weight of ore and gives about 70 - 75% recovery of the remaining 40% of the gold. But from the mineralogical investigation it was found that the sulphide minerals form about 2.4% of the total ore. By taking into account the fact that some gangues will float even in the flotation system where the carbonaceous matter is depressed, it appears that a substantial amount of sulphide minerals might have been lost to the tailing. Since the sulphides carry gold, the loss of gold to the tailing in the plant may be attributed also to the incomplete recovery of the sulphides. Consequently it may seem advantageous to produce a greater quantity of flotation concentrate with lower grade and higher gold recovery. Unfortunately the amount of the flotation concentrate that the plant can produce at present is also controlled by the throughput of the roasters. Thus it may seem that the

inability to improve the plant flotation recovery of gold is due to some extent to the lack of qualitative and quantitative data on the mineralogy of the ore and the acceptance of the constraints imposed by the roasters.

To obtain conditions of maximum flotation of gold, detailed investigation of the flotation system needs to be carried out to find whether the present practice of depressing the carbonaceous matter should be retained or improved. The preliminary flotation tests on the ore (Chapter 6), suggest that the depression of the carbonaceous matter whilst floating the gold could give a higher recovery than the present plant gold recovery.

8.2.4 Leaching of the ore with oxidising reagents.

1. Leaching with $Ca(OCl)_2$ or NaOCl.

Advantage can be taken of the reaction of calcium or sodium hypochlorite with this type of carbon, to leach the carbon in the ore or the flotation concentrate. For instance, $Ca(OCl)_2$ can be produced in situ by the introduction of Cl_2 gas into the aqueous pulp of the ore at low temperatures to react with limestone which had been mixed with the ore. The $Ca(OCl)_2$ so produced will react slowly with the carbonaceous matter to produce $CaCl_2$, CO and CO_2. A temperature of more than 60^oC is needed, as reported by Scheiner[234].

A direct leach of the carbonaceous matter with $Ca(OCl)_2$ may be useful if the gold in the ore were associated almost exclusively with the carbon and the ore

contained little or no sulphide minerals. Because of the presence of sulphide minerals in this ore, other oxidising reagents would have to be used to oxidise them. Hot concentrated HNO_3 acid can be used to leach the sulphides after $Ca(OCl)_2$ treatment. The subsequent processing of the ore could be by cyanidation. (This process may not be economic because of the high cost of acid and the great oxidising conditions under which it will operate).

It will be necessary to neutralise the acidic solution before cyanidation. Such a neutralisation process will be expensive and therefore the logical process after acid treatment should be the chlorination of the material instead of cyanidation. Because of the highly dangerous oxidising conditions of the acid and chlorine treatment coupled with problems of corrosion of the reactors, and high cost of the reagents it may be less economically attractive to use these processes.

2. Treatment with oxidising acids.

Direct leaching of the gold in the ore with concentrated nitric acid followed by aqua regia is feasible. But under such conditions some of the dissolved gold will be adsorbed by the carbon. The acidic solution will have to be neutralised and the carbon floated off and calcined to recover the gold. These methods of extracting gold are less practicable.

8.2.5 Roasting

The purpose of roasting this ore is to liberate the gold particles locked up in the sulphide minerals and oxidise the carbon. Possibly the best approach to the roasting of the flotation concentrate is to know the step by step reactions of the sulphide minerals to form products with structures that will allow a ready attack of the gold in them by cyanide. This will need a systematic study of the decomposition, dissociation, reduction and the oxidation reactions of the sulphides. When the pattern of the sulphide reactions in the presence of the carbon and air is understood then a suitable roaster can be chosen to roast the flotation concentrate.

In the absence of such information on this ore, data for similar types of ore together with the data obtained during the present mineralogical investigation will be used to propose possible conditions for roasting the flotation concentrate.

(a) Roasting in air.

Although direct roasting of the ore can be carried out, it will be more economically attractive to roast the flotation concentrate. It will therefore be assumed that the material to be roasted is a flotation concentrate consisting mainly of the carbonaceous matter and the sulphide minerals. (It is to be realised that some of the carbonaceous matter will still be floated even if an attempt was made to depress it.)

The oxidation of these minerals will be considered individually. The oxidation reactions of the sulphides will be predominantly due to those of pyrite and arseno-

pyrite because they constitute over 90% of the total sulphide minerals.

It had been stated earlier (Part I) that the carbonaceous material roasts readily in air above 600°C. According to Norwood[235], pyrite forms Fe_3O_4 between 450° - 550°C and at temperatures greater than 650°C Fe_2O_3 is formed and any $FeSO_4$ formed at a lower temperature would have been eliminated. In excess air pyrrhotite is said to oxidise to Fe_2O_3 between 430° - 590°C.[236] For arsenopyrite, the liberation of total arsenic occurs at about 700°C. The oxidation of pyrite, pyrrhotite and arsenopyrite is expected to be complete at temperatures where Fe_2O_3 is the final product. This Fe_2O_3 is the most favourable oxidation product as it may give higher cyanide gold recovery than FeO or Fe_3O_4[237].

To achieve the formation of Fe_2O_3, full oxidation of the sulphides is necessary. It was suggested that the oxidation roast of arsenopyrite should be carried out in two stages - the first stage being the partial oxidation which will ensure the elimination of As in the arsenious state and the final stage should be the full oxidation.

The work of Lodeishchikov et al[238] on Au - As concentrate showed that the most suitable temperature for the oxidation of arsenopyrite to form the most porous product favourable for cyanide gold extraction was 600 - 700°C and they suggested that FeAsS oxidation occurred in these stages,

$$FeAsS \longrightarrow FeS \longrightarrow Fe_3O_4 \longrightarrow Fe_2O_3$$

Kolesnikov et al[239] also investigated the roasting of Au - As concentrate containing carbon and found that at 650°C the elimination of As was maximal in excess air whilst that of carbon was complete. They also observed that As removal depended on the air supply and that by increasing the air, the liberation of As was increased, but when the amount of carbon was increased, the liberation of As and desulphurisation were reduced.

Zhuchkov and his co-workers[240] found that during the oxidation roasting of carbonaceous Au - As concentrate, the presence of carbon in intimate contact with As led to almost entirely dearsenised products by preventing the formation of non-volatile arsenates. Lodeishchikov and his co-workers[241] reported 89 - 93% recovery of gold from gold-bearing sulphide concentrate containing pyrite between 500 - 800°C. Above this temperature the particles were fused and the gold recovery fell as a result of non-porosity of the particles containing embedded gold.

The general behaviour of oxidation roasting of chalcopyrite, $CuFeS_2$, in air is similar to that of pyrrhotite except that besides Fe_xO_y and $FeSO_4$, Cu_xO_y and $CuSO_4$ are formed[236]. The $FeSO_4$ can be converted to the oxide and SO_2 below the decomposition temperature of $CuSO_4$ which is 653 - 670°C[242]. The decomposition and the oxidation of tetrahedrite is said to be less satisfactory than that of chalcopyrite under similar conditions. In the present ore, the complex nature of

tetrahedrite makes it difficult to predict its oxidation temperature. It will therefore be assumed to be between the oxidation temperature range for chalcopyrite and arsenopyrite (i.e. 600 - 670°C). The mineral is known to be still refractory even after roasting.

In the oxidation of sphalerite, ZnS, in air the reaction products are often ZnO, SO_2 and $ZnSO_4$. The maximum roasting temperatures are about 650°C for complex zinc concentrates and about 750°C for concentrates which are very high in zinc. The decomposition temperature for $ZnSO_4$ ranges from 702 - 720°C.(242)

The remaining sulphide minerals, namely, galena, bournonite, $PbCuSb_3S$ and boulangerite, $Pb_5Sb_4S_{11}$, are likely to be oxidised to their respective oxides at temperatures less than 720°C. These sulphides being not greater than 1.6% of the total sulphides may not significantly influence the oxidation roasting of the sulphide concentrate.

From the foregoing it can be suggested that the possible suitable temperature for roasting of the flotation concentrate of this ore may be between 600° - 700°C. Within this temperature range it should be possible to oxidise all the sulphide minerals to their respective oxides which are not inert. But the possibility of the formation of ferrites ($M_xO_y \cdot Fe_2O_3$) (M is a metal other than Fe), insoluble compounds which could retain gold may remain. There is also a possibility of iron oxides coating the surface of gold. Besides these problems it

is difficult to tell exactly what will happen when all these sulphides and the carbonaceous matter in the ore are roasted together at temperatures up to between 600 - 700°C. In spite of some uncertainties about the types of the reaction products, it is reasonable to suppose that careful roasting of the flotation concentrate in excess air up to 600 - 700°C will lead to high liberation of gold and consequently high extraction of gold from the calcine.

The following factors should also be taken into account in roasting the concentrate; the preparation of the roaster feed, the throughput for the roaster, the residence time, air and heat distribution in the concentrate during roasting. The type of roaster will determine to a great extent the efficiency of roasting.

The trend in recent times is to use fluosolids reactors for roasting ores because of their efficient heat exchange system, air distribution and better temperature control. But because of the fine particle sizes (i.e. 80% -75 μm) of this flotation concentrate, fluosolids reactor may not be suitable for it. Fluosolids reactors are best suited for relatively coarse size materials. Furthermore gold loss to the dust might be high and, in addition, controlling of the dust in such a system is always a problem. It also needs highly skilled personnel to run and maintain it. On the other hand the horizontal multi-spindle roaster which is being used for roasting the flotation concentrate of this ore, is simple, more trouble-free, has less dust problems and can be run and maintained by less skilled personnel. For these reasons

the Edwards horizontal multi-spindle type roaster should be preferred to the fluosolids roasters. The other types of roasters, namely, the rotary kiln and the vertical, multiple-hearths have generally not been used for roasting gold ores[237].

(b) Roasting with inorganic compounds in air.

The flotation concentrate of the ore can alternatively be roasted when an adequate amount of Na_2CO_3 has been mixed with it to temperatures lower than 700°C, and the calcine quenched with water and finally cyanided. MacKay[237] reported gold recovery of 94% after roasting of Au - As concentrate with Na_2CO_3 in absence of air. The improvement in the gold extraction was thought to be due to the formation of a new compound of gold.

The concentrate can also be roasted with NaCl. Although the exact nature of the chemical reactions with NaCl is not clear, it had been observed that the reaction of NaCl with some refractory ores has beneficial effects on the cyanidation of such calcine.

For this ore it may seem desirable to roast the flotation concentrate in air and, if economically advantageous, to add inorganic salts to the concentrate prior to roasting.

(c) Pollution problems.

Up to the present time the practice in the Prestea mine is to release the roaster fumes of the flotation concentrate direct into the atmosphere, a practice which is undoubtedly objectionable because of the danger of arsenic poisoning. It will be necessary, therefore, to find an alternative method which is not hazardous of disposing of the roaster fumes, e.g. by wet scrabbing.

8.2.6 Cyanidation

Since the invention of the gold cyanidation process (in 1887), many theoretical and practical developments have taken place. The classical dissolution of gold in cyanide solution in the presence of oxygen as expressed by Elsner's equation

$$4Au + 8KCN + O_2 + 2H_2O \longrightarrow 4KAu(CN)_2 + 4KOH \quad (1)$$

has been changed and is now based on the electrochemical theory suggested by several investigators[243-245]. According to the electrochemical theory, the gold will dissolve from the anodic areas of the surface as follows:

$$4Au + 8CN^- \longrightarrow 4Au(CN)_2^- + 4e \quad (2)$$

and at the cathodic sites, O_2 is reduced by electrons given out by the gold according to the reaction

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \quad (3)$$

Both theories recognise that O_2 is the primary agent in the dissolution of gold in cyanide solution. It is also known that high alkalinity is essential for efficient dissolution of gold. The alkali prevents the hydrolysis of cyanide, expressed as

$$KCN + H_2O \rightleftharpoons HCN + KOH \quad (4)$$

and also reacts with other agents which might react with the cyanide and reduce its concentration in solution[12,246,247] and consequently the efficiency of dissolution of gold. In practice, therefore, gold is cyanided at high pH in the presence of excess air. (The chemistry of the cyanidation of gold has been dealt with by Hedley and Tabachnick[246].

(a) The effect of cyanide on some of the minerals in the ore.

Data so far obtained about this ore suggest that direct cyanidation of gold in the ore may not satisfactorily recover the gold because of the presence of

(1) sulphide minerals which have locked-up gold and which are not readily dissolved by cyanide,

(2) carbonaceous matter which is an active adsorbent of dissolved gold.

In the subsequent discussion, the reactions of cyanide with the sulphide minerals in the ore and the adsorption of dissolved gold by the carbon in cyanide solution will be considered to show the possible reasons why the ore needs to be oxidised before cyanidation.

(b) Interference of the sulphide minerals in cyanide leaching.

Pyrite[246] is said to be easily oxidised in alkaline solution under atmospheric conditions to give soluble sulphides, thiosulphates and minor amounts of colloidal sulphur. The dissolved O_2 reacts with the soluble sulphides to produce thiosulphate and sulphate ions. A prolonged oxygenation of pyrite in lime solution results in the formation of reducing agents, calcium sulphide and calcium thiosulphate at about pH 8. In a normal cyanidation process, the oxygen required for the dissolution of gold may be consumed by pyrite and the oxidation products of pyrite whilst at the same time the products will react with cyanide to form cyanates. At high alkali concentration the pyrite surface adsorbs OH^- ions and thereby inhibits any further reaction. Thus the reaction products of pyrite will act as "cyanicides" and reduce the efficiency of gold dissolution.

Pyrrhotite[248,249] decomposes more rapidly than pyrite in air-water systems to form H_2SO_4, ferrous sulphate, basic iron sulphates and ferrous carbonates and hydrates. It reacts with cyanide to form NaCNS and the decomposition products also react with cyanide to form cyanates. Thus pyrrhotite also acts as cyanicide.

Arsenopyrite, FeAsS[12,249,250] dissolves very slowly in cyanide solution in the presence of air. In high lime cyanide solution containing air, arsenopyrite reacts slowly with $Ca(OH)_2$ as follows;

$$4FeAsS + 4Ca(OH)_2 + 11O_2 \longrightarrow 4FeSO_4 + 4CaHAsO_3 + 2H_2O \qquad (5)$$

and reduces the O_2 in solution required for the oxidation of gold. Hedley and Tabachnick[246] found that the dissolution of arsenopyrite at ordinary temperatures in the presence of air is very slow and has no apparent effect on the dissolution of gold. It, therefore, means that gold locked up in arsenopyrite, as in the present ore, cannot be leached out by cyanidation except after oxidation of the arsenopyrite.

Copper Minerals. Tetrahedrite and chalcopyrite, the predominant copper minerals in the ore, react with cyanide at different rates. Leaver and Woolf[251] showed that about 21.9% of tetrahedrite and 5.6% of chalcopyrite (as compared with 90% dissolution of metallic copper) were dissolved in 0.1% NaCN at 23°C in 24 hours. It follows that these sulphides in the ore will not readily dissolve in cyanide. Gold locked up in chalcopyrite will be less readily attacked by cyanide.

Sphalerite. Leaver and Woolf[251] also reported the dissolution of ZnS in cyanide solution and that the reaction products also react with oxygen. The reactions are represented as,

$$ZnS + 4NaCN \rightleftharpoons Na_2Zn(CN)_4 + Na_2S \quad (6)$$

$$Na_2S + H_2O \rightleftharpoons NaSH + NaOH \quad (7)$$

$$2NaSH + 2O_2 + H_2O \rightleftharpoons Na_2S_2O_3 + 2NaOH \quad (8)$$

The remaining sulphide minerals in the ore, which are galena, bournonite and boulangerite, will also react similarly with cyanide.

(c) Adsorption of dissolved gold by carbon.

The gold accessible to the cyanide will be dissolved in a normal cyanidation system. The dissolved gold in the form of aurocyanide may be adsorbed by the available carbon in the ore, thus depleting the cyanide solution of gold.

From these considerations it can be concluded that,
(1) the sulphide minerals in the ore will react with cyanide and oxygen and reduce their concentrations in cyanide solution and thus decrease the efficiency of the dissolution of gold,
(2) the rates of dissolution of many of the sulphide minerals will be so slow that gold locked up in the sulphides may not be readily dissolved,
(3) even if there were no sulphide minerals in the ore, the presence of the active carbon would warrant the oxidation of the ore prior to cyanidation.

8.2.7 Extraction of gold from cyanide solution.

A cyanide solution of the leached calcine of the flotation concentrate will contain cyanide complexes of Au, Ag, Cu, Zn, Pb, Fe and various other metallic cyanide complexes. To extract the gold from such a solution the following methods can be employed,

(1) "Precipitation" of gold from solution,

(2) Ion-exchange methods,

(3) Solvent-extraction (liquid - liquid extraction) method.

1. "Precipitation" method.

This method is the most widely used for extracting gold from cyanide solutions. Zinc dust or shavings, charcoal, aluminium and electrodeposition are used.

(a) Zinc precipitation[21,30,31] of gold is by far the most common way of extracting gold from alkaline cyanide solution. The precipitation reaction is said to proceed as follows:

$$NaAu(CN)_2 + Zn + 2NaCN + H_2O \longrightarrow Na_2Zn(CN)_4 + Au + H^+ + NaOH$$

The precipitation proceeds well when the pregnant cyanide solution has sufficient "free cyanide" , the pH is between 11 - 13, the solution is free from impurities (often in the forms of metallic cyanide complexes) and the solution is oxygen-free. Although the zinc precipitation is reasonably selective, other metallic cyanide compounds will be precipitated from a cyanide solution

of the present type. The result will be a general lowering of the grade of the precipitated gold. Part of these impurities (i.e. Zn, Cu, Fe, Pb, etc) can be removed during the smelting of the precipitate with suitable flux, but a substantial amount of the metals will still remain alloyed with the gold. Copper with a m.p. of 1083°C, (compared with that of gold at 1064°C) will hardly be removed while silver as a rule will remain alloyed with gold and be removed by electrowinning.

(b) Charcoal as a "precipitant" for gold[252,253]

Activated charcoal can be used to extract the aurocyanide complex from a leached calcine pulp or from clarified pregnant aurocyanide solution. The use of activated charcoal is particularly useful for its selectivity for gold and silver. The result is a high bullion grade.

After gold has been adsorbed from a cyanide pulp, it has to be stripped with hot alkaline cyanide solution and the gold recovered from solution by electrodeposition in a manner similar to the practice in Homestake mine, U.S.A.[24]. When the gold is extracted from the pregnant solution with activated charcoal, the "precipitate" is calcined and the charcoal is removed. The gold so produced may be of higher grade than that produced by zinc precipitation.

The use of charcoal to replace zinc for gold recovery, which is already practised in Prestea, needs to be fully investigated and the economics assessed before any decision can be made about the use of activated charcoal although this might appear to produce a higher grade gold.

The mechanism of the adsorption of aurocyanide by charcoal is still not clear. However, the present trend is to favour the suggestion made by Allen[252] and Gross and Scott[253] that the adsorbed gold on charcoal is not in the form of metallic gold as thought by some investigators but as an adsorbed aurocyanide complex.

(c) Electrodeposition and aluminium precipitation methods.

Direct electrodeposition of gold from the pregnant solution of this ore can be done but at high cost. This method does not seem to have any economic benefits over the present method of gold precipitation with zinc.

The precipitation of gold with aluminium from alkaline cyanide solution is less effective than that with zinc and will not be considered any further.

2. Ion-exchange methods.

The trend in the research into the extraction of gold from cyanide solution is towards finding a suitable ion-exchange resin for the recovery of gold. As the pregnant cyanide solution has the impurities mentioned earlier which will reduce the fineness of zinc-precipitated gold, an ion-exchange purification technique can be a reasonable alternative method.

The literature shows that much work has been done using (a) strong-base ion-exchange resins[254,255], (b) weak-base ion-exchange resins.

The strong-base ion exchange resins so far used in various investigations were not selective and, in addition, the selective elutions for gold from the resins have not been totally successful. Weak-base ion-exchange resins were

found to be more selective than strong-base resins. Even so, in using weak-base ion-exchange resins, the recovery of gold was often less than that for zinc precipitation, whilst there was loss of resin and cyanide.

3. Liquid - liquid extraction of gold.

The liquid - liquid systems can be divided into three, namely, solvating solvents, liquid cation- and liquid anion-exchangers. The work of Zryagintse et al[256] demonstrated that solvating solvents (e.g. alcohol and ketone) can be used to extract gold from cyanide solution. Of the two ion-exchangers, anion-exchange method is said to have some future. The work of Zryagintsev and co-workers[257] indicated that nearly all the gold in a cyanide leach was removed with a kerosene solution of trioctylamine and that the gold was free from impurity metals e.g. Pb, Cu, Zn, As and Ag, but a small amount of iron was present.

The ion-exchange and liquid-liquid methods for gold extraction are still at the experimental stages. In addition, the technical difficulties involved in operating such plants may be greater than the conventional Zn precipitation.

It can be concluded that the Zn precipitation method being used in the plant for processing this ore should be retained but studies should be made about the extraction of the gold with charcoal and the economic benefits assessed to see if it could replace the Zn precipitation method.

8.2.8 Direct cyanidation of the flotation concentrate.

Cyanidation of the flotation concentrate of this ore appears unsuitable for reasons stated already. But the present high cost of fuel makes roasting expensive. If this trend of energy cost continues, roasting may become so expensive that attention may be directed to the direct leaching of the flotation concentrate produced by depressing the carbonaceous material. This process may not be as efficient as the present one, but may be economically viable on account of the high price of gold. The use of this process will eliminate the processes for preparing the flotation concentrate for roasting, the roasting process and the environmental problems associated with roasting this ore.

The initial flotation concentrate can be conditioned at high pH (probably not less than 12) with a suitable organic reagent to float any carbon which might have been previously floated whilst depressing the gold and the sulphides. The carbon recovered may be calcined and cyanided. The flotation tailing will be finely ground in cyanide solution and the solution filtered, clarified and the gold precipitated with zinc or activated carbon.

8.2.9 Proposed flow-sheet for processing Prestea carbonaceous gold ore.

The proposed flow-sheets for processing this ore are shown in Figs.8.1 and 8.2. The first flow-sheet (Fig.8.1) comprises all the processes being used at present in processing the ore. In addition to these processes, a grinding process has been incorporated in the flow-sheet to grind the calcine before cyanidation.

It has been proposed that

(1) the flotation feed should be ground to 80% -75 μm size as compared with 62% -75 μm, the size at present obtained in the plant.

(2) a lower flotation concentrate grade with a higher gold recovery should be produced. This may require that the flotation concentrate weight produced be more than 2.4%, the weight of the total sulphide minerals.

(3) the carbonaceous matter can be depressed or floated.

(4) the flotation concentrate should be roasted up to temperatures between 600 - 700^{o}C.

(5) the calcine should be finely ground prior to cyanidation.

The second method of processing the ore is shown by the second flow-sheet, Fig.8.2. It shows the processes to be used under conditions of direct cyanidation of the flotation concentrate already described.

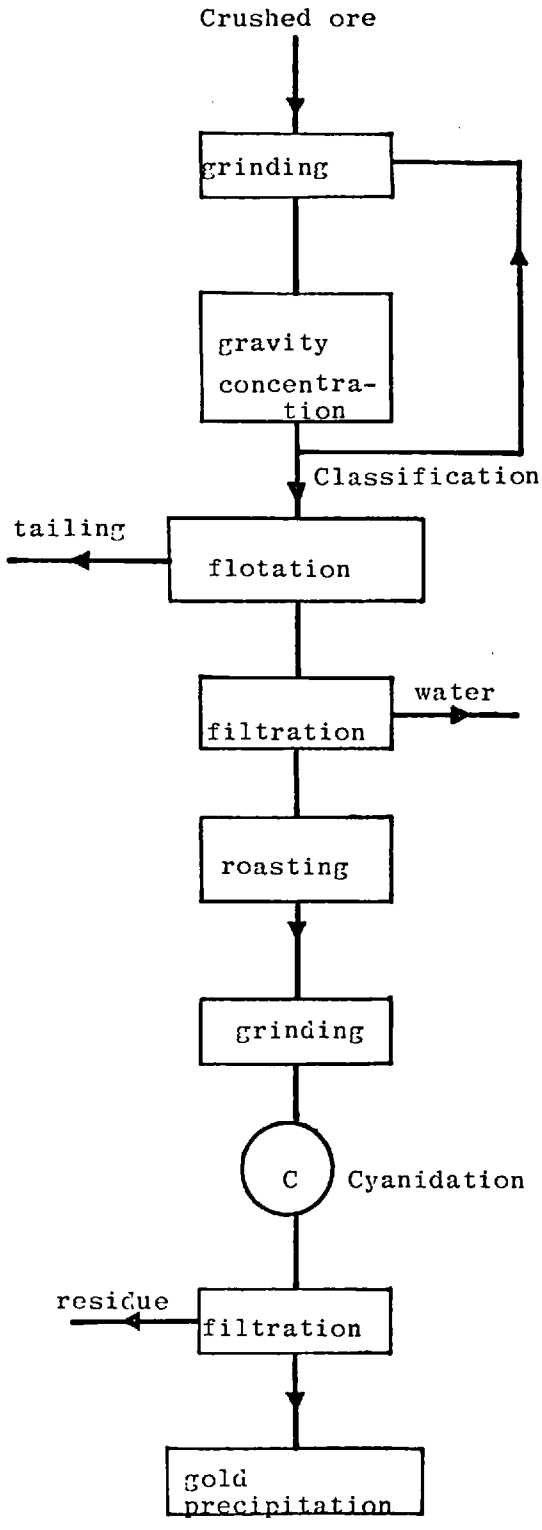


Fig.C.1 Proposed flow-sheet for processing Prestea carbonaceous gold ore.

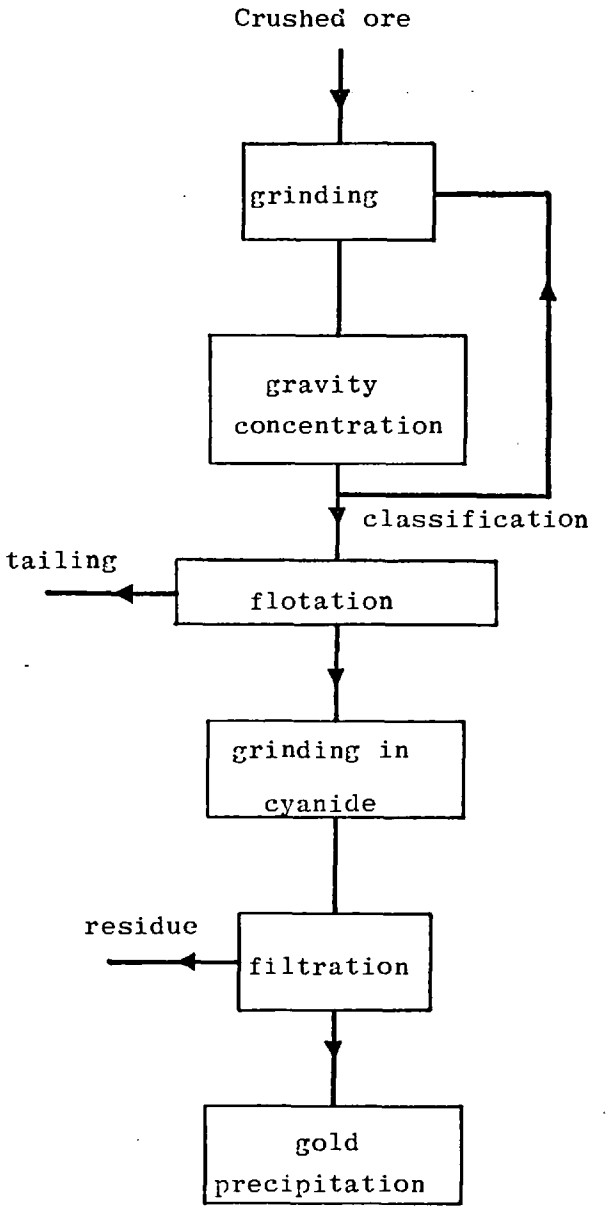


Fig.3.2 Proposed flow-sheet for processing Prestea carbonaceous gold ore.

8.2.10 Economic assessment of the proposed processes.

In Table 8.2 very approximate estimated operation costs of the proposed processes are shown in columns 3 and 4 and compared with the present operation costs of the processes shown column 2. The figures for the operation costs are the monthly averages for the present year (1975). The price of gold was taken to be US$130 per oz.

In column 3 the proposed processes are similar to those in use in processing the ore at present, except that a new grinding process has been incorporated in the circuit between the roasting and cyanidation processes. The estimated operating cost of this grinding mill (ball-mill) has been taken to be about 1/5 of the operating cost of the existing ball-mills. This fraction of the operation cost of the ball-mill was taken because 5 ball-mills usually operate, when the plant is working at full capacity, and treat 33 times the tonnage produced for roasting. Assuming that the cost of operating other processes remain the same as they are at present, there would be an increase of 1.07% in operating cost by adding the new ball-mill. But if the total gold recovery has been increased by 1% as a result, the profit would be about 16.3%. This would be about 0.3% increase in profit over the present profit and would correspond to $1,240 increase in the monthly profit.

The operating costs of the second proposed processes are shown tabulated in column 4. These processes excluded roasting but include fine grinding process instead. The cost of the fine grinding of the flotation concentrate was

Table 8.2 The operation costs of Prestea gold extraction plant and the estimated operation costs of the proposed methods for processing Prestea ore. (* The figures for the operation costs of Prestea processing plant (1975) were kindly supplied by Prestea Goldfields, Ghana).

Column	1	2	3
Processes	*Operation cost of Prestea plant $/t (1975)	Estimated operation cost Flow-sheet 1 $/t	Flow-sheet 2 $/t
Crushing	0.281	0.281	0.281
Grinding, Gravity concentration	1.435	1.435	1.435
Flotation, Cyanidation	0.602	0.602	0.602
Fine grinding	--	--	0.667
Roasting	0.288	0.288	--
Calcine grinding	--	0.267	--
Total electricity, Water	0.551	0.551	0.667
Total Operation Cost	3.157	3.424	3.652
Total income	30.756	31.064	28.960
Total mine expenditure	26.486	26.753	26.976
Profit	4.270	4.311	1.984
% profit	16.0	16.3	7.5

estimated at about half the present operating cost of the ball-milling because this grinding will consume a lot of energy. The cost of power has also been increased by 20%. Assuming that the operating costs of other processes are same as indicated for the present plant, this method would lead to about 1.83% increase in operating costs. But if it is assumed that the total gold recovery is 80%, the total profit would fall from 16% to 7.5%. This decrease corresponds to about $70,000 fall in profit per month.

Thus from an economic point of view it would appear that the method which incorporates roasting in the processing circuit would be preferable. But the profit margin of this method would decrease when the cost of controlling environmental pollution is taken into account. Even so it seems that roasting of the flotation concentrate (under the present conditions) and grinding the calcine before cyanidation may be still more economic than direct leaching of the flotation concentrate, as $70,000 per month may be much more than the amount to be spent on pollution control.

8.3 Summary

Considerations of the possible methods of processing Prestea carbonaceous gold ore have led to the conclusion that there is no one simple and straightforward way of processing this refractory ore, and that only a combination of processes can be employed to recover the gold. Two main ways of processing the ore have been suggested.

1. The choice of the first set of processes for treating the ore has been based on the nature of the ore and on economic consideration but with more emphasis on the former .These proposed processes for treating the ore are similar to those already employed in the plant in Prestea. The proposed processes are comminution, gravity concentration, flotation, roasting, grinding of the calcine, cyanidation and precipitation of the gold with zinc or carbon. The processes which need to be improved have been pointed out.

Because of the complexity of the ore and the occurrence of gold in coarse and fine sizes, it is considered advantageous to use gravity concentration method to recover the coarse gold liberated during grinding and that the final particle sizes of the ground ore should be about 80% -75 μm.

It appears necessary that the gravity concentration process should be followed by flotation. The flotation of gold can be carried out by floating the sulphide minerals together with the carbonaceous matter or by floating of gold together with the sulphide minerals whilst the

carbonaceous material is depressed. In both cases it would be advantageous to produce flotation concentrate weight in excess of 2.4% of the total weight of the ore since the total weight of the sulphide minerals which contain gold is about 2.4%, as loss of the sulphide may mean loss of gold.

The roasting of the flotation concentrate in excess air up to 600°C - 700°C may be required to oxidise the sulphides and the carbon and liberate the locked-up gold. It is therefore proposed that the roasting process should be retained but improved.

The roasted flotation concentrate should be finely ground prior to cyanidation since it is likely to increase the cyanide extraction.

2. The second method of processing the ore is that of direct cyanidation of the flotation concentrate in which the carbonaceous matter had been depressed and the concentrate finely ground in alkaline cyanide solution to leach the gold. This process has the advantage of eliminating the roasting process which can be expensive, and is responsible for environmental pollution.

The economic considerations of the two methods for processing the ore indicate that the method incorporating the roasting process appears to be more economically viable than that of direct cyanidation of the flotation concentrate.

9. SUMMARY OF CONCLUSIONS

9.1 Mineralogical investigation of Prestea carbonaceous gold ore.

The study of the refractory Prestea carbonaceous gold ore which has been carried out has shown that the ore contains quartz (forming about 67% of the ore), silicates comprising sericite, chlorite and feldspar, and carbonates (ankerite, siderite, calcite) forming about 26%, active carbon containing alkanes and carboxylic acids forming 2.47% of the ore. Sulphide minerals form about 2.4% and comprise pyrite and arsenopyrite, which are the most abundant sulphide minerals, accounting for more than 90% of the sulphides. Other sulphide minerals include chalcopyrite, bournonite ($PbCuSb_3S$), boulangerite ($Pb_5Sb_4S_{11}$), sphalerite, galena and tetrahedrite.

Because of the presence of carbon, which is an active adsorbent of dissolved gold, and the sulphide minerals, the ore is rendered "refractory" to cyanidation. Processing the ore is made worse by the occurrence of gold not only in the quartz but also in the sulphides and in the carbonaceous matter in various forms and sizes from coarse to sub-microscopic sizes.

The native gold is alloyed with silver which is the most abundant minor mineral, and with Pb, Cu, Zn, and in some cases with Te and Hg.

On account of the mineralogical data it has been suggested that the following processes could be employed in treating the ore. These include gravity concentration, flotation, oxidation (roasting or chemical oxidation), leaching and precipitation of the gold.

9.2 The wettability of gold.

The results of the studies of the wettability of gold show that very pure clean gold is hydrophilic but only weakly so. However, it loses its hydrophilicity readily in ordinary water or when exposed to the air as a result of adsorbing organic contamination. Thus large contact angles (50^{o} - 80^{o}) obtained on gold by some investigators can only be due to the adsorption of organic impurities.

The stable hydrophilic surface exhibited by gold when treated with oxidising reagents such as sodium hypochlorite, aqua regia, chromic acid, sulphuric acid and nitric acid is probably due to the formation of an oxidised surface.

The contact angle of an air bubble on gold in air- and oxygen-saturated solutions of KEX ranged from 52^{o} to 62^{o}. With a longer chain xanthate, KAX, the contact angle was about 10^{o} greater for comparable concentrations of 20 - 1000 mg/l. But the hydrophobicity of gold in xanthate solution was developed only in the presence of dissolved oxygen. Thus dixanthogen is considered the main species responsible for the enhanced hydrophobicity of gold in the xanthate-oxygen system.

It was observed that a starch concentration lower than 300 mg/l had no great effect on the hydrophobicity of gold in the starch-xanthate-oxygen system.

9.3 The wettability of graphite.

Contact angles on pure graphite were found by some investigators to be 85.7°. In the present investigation with synthetic graphite, it was found to be 65°± 2° and was not strongly affected by pH except, by a strongly alkaline solution of pH >9.

In pure xanthate solution the contact angle tended to decrease in high concentration of xanthate solution, presumably because of hydrophobic association of xanthate with the hydrophobic sites on graphite. The effect of the expected catalytic oxidation of xanthate to dixanthogen in the presence of air on the contact angle was not apparent.

Starch, however, easily adsorbed on graphite reducing the contact angle and rendering it hydrophilic.

9.4 Adsorption of xanthate and starch on gold.

In the adsorption of xanthate on gold it was found that the presence of oxygen was prerequisite for the uptake of xanthate. The xanthate uptake is mainly by catalytic oxidation. The adsorbed species detected was mainly dixanthogen; although gold xanthate might form as an additional species, it was not detected. The adsorbed species (dixanthogen) readily decomposed in strongly alkaline medium giving xanthate and another species which was unidentified. It was therefore concluded that the species responsible for rendering gold hydrophobic in xanthate-oxygen system is mainly dixanthogen.

At equilibrium at pH 7, xanthate appeared to be adsorbed on gold in the presence of air to form a monolayer and a double layer in the presence of oxygen.

The adsorption of xanthate by gold is markedly influenced by pH with the maximum uptake being reached around pH 7 and decreasing with increase or decrease of pH.

Starch, on the other hand, does not appear to be adsorbed at all on gold.

9.5 Adsorption of xanthate, starch and dextrin on synthetic graphite.

The results of the adsorption of xanthate on graphite indicate that the uptake of xanthate proceeds mainly by catalytic oxidation of xanthate to dixanthogen in the presence of air. The xanthate uptake, however, was initially by physical adsorption i.e. hydrophobic association of the non-polar groups of xanthate with the hydrophobic sites on graphite.

As in the case of gold, the adsorption of xanthate on graphite is strongly influenced by pH, being greatest around pH 7, but decreasing as the pH increases. The adsorption of starch on the other hand is not strongly dependent on pH. Its rate of adsorption is faster than that of xanthate.

The adsorption isotherm of starch (and possible dextrin) apparently obeys the Langmuir type of isotherm. Starch, being of higher molecular weight than dextrin, adsorbs on graphite to form a thicker layer.

In the co-adsorption of xanthate and starch from starch-xanthate solution, the xanthate uptake is more inhibited than that of starch. It was concluded that starch and xanthate appeared to be adsorbed partly on the same sites or adjoining sites on graphite.

9.6 Flotation of gold and graphite, Prestea carbonaceous matter and Prestea ore.

The results of the flotation of gold with xanthate show that gold readily floated at pH 6 - 11 but poorly above pH 11. Even in the presence of starch of concentration up to 1 g/l, the flotation of gold is not inhibited in the pH range of 6 - 11. Quebracho, however, acts as an effective depressant for gold, particularly at pH <9, but less so at pH >9.

Starch and quebracho are strong depressants for graphite in pure water, but in the presence of xanthate their effectiveness is reduced. Similar effects were obtained when Prestea carbonaceous material was depressed with starch and quebracho.

From these results it is concluded that starch rather than quebracho should be used as a depressant for the Prestea carbonaceous material in the flotation of the Prestea carbonaceous gold ore.

Preliminary flotation tests on the Prestea carbonaceous gold ore using starch as a depressant showed that the gold could be recovered successfully by use of xanthate in the presence of low starch concentration (<40 mg/l) at about pH 9.5 if the ore is ground to about 80% -75 μm size.

9.7 Flocculation and Filtration of Prestea ore

Contrary to La Mer and Smellie's theoretical model of re-filtration rate as a function of polymer dosage, the flocculation of Prestea carbonaceous matter and the flotation concentrate did not appear to improve the filtration rate at polymer dosage of 0 - 20 p.p.m. In fact, the permeability of the filter-cake was actually reduced. This does not, however, mean that flocculation of the ore is not advantageous. Flocculation is still needed to assist the settlement of slimes and filtration, not to reduce the rate of filtration but rather to produce flocs which will prevent the blinding of the filter cloth. As the filtration rate decreases with polymer dosage it would be beneficial to use the lowest polymer dosage necessary (e.g. 1 p.p.m.) for flocculating the flotation concentrate prior to filtration when using the polymers used in the present tests.

9.8 The implications of processing Prestea carbonaceous gold ore.

The implications of this work for the processing of Prestea carbonaceous gold ore have been considered from the mineralogical and economic point of view. Upon these considerations two general methods for processing the ore have been proposed as follows:

1. That the ore should be processed by employing comminution, followed by gravity concentration, flotation, roasting of the flotation concentrate, grinding and cyanidation of the calcine, filtration and precipitation of the gold with zinc or carbon.

2. That after flotation, when the carbon is depressed, the flotation concentrate should be finely ground in an alkaline cyanide medium. The product should be cyanided further before filtration and precipitation of the gold.

The above two methods have been approximately evaluated and it was found that in terms of suitability of processes for treating this ore and for economic viability, the first method (i.e. processes incorporating roasting) appears to be more attractive even though roasting is a source of environmental pollution. The preference for the second method, the direct cyanidation of the flotation concentrate would depend largely on the cost of roasting and the degree of the environmental pollution caused by the former method. Even so it would appear that the cost of incorporating roasting fume control process would not make the method less economically viable.

It is, therefore, proposed that the method which includes flotation and the roasting of the flotation concentrate is most suitable for processing the ore. Thus the improvement in the total recovery of the gold will depend mainly on the improvement of the flotation and roasting techniques.

REFERENCES

1. Goldschmidt, V. M., Geochemistry. Oxford University Press, (1954).

2. Rankana, K. and Sahama, J. G., Geochemistry. University of Chicago Press, Chicago,(1950).

3. Mason, H. B., Principles of Geochemistry. 2nd edn. John Wiley & Sons., Inc., New York, (1958).

4. Lindgren, W., Mineral Deposits. McGraw-Hill Book Co., Inc., New York, (1933) .

5. Bateman, A. M., Economic Mineral Deposits, 6th edn. John Wiley & Sons, Inc., New York, (1949).

6. Emmons, W. H., Gold Deposits of the World. McGraw-Hill Book Co., Inc., New York, (1937) .

7. Wise, E. M.(ed.), Gold, Recovery, Properties and Applications. D. van Nostrand Co., Inc., New York,(1964).

8. Fells, P. D., Gold 1975. Consolidated Goldfields Ltd. London,(1975).

9. Johnson, E. H., Concentration and selective regrinding. J. Chem. Met. & Min. Soc. S. Africa, 215-220 (1927).

10. MacArthur, J. S., Forrest, R. W. and Forrest, W., British Patents Nos 14,174, October 19, 1887; and 10,223, July 14,(1888).

11. Barsky, G., Swainson, S. J., Hedley, N., Chemistry of Cyanidation, Am. Cyanamid Co., Tech. Paper 21. New York, 1955.

12. Barsky, G., Swainson, S. J. and Hedley, N., Dissolution of gold and silver in cyanide solutions. Trans. Am. Inst. Min.-Metall. Engrs. 112, 660 (1934).

13. Bernewitz, M. W., Roasting gold-silver ores and concentrates. Parts I to V. Can. Min. J., (1940).

14. Archbald, F. R., Roasting of arsenical gold ores and concentrates. Trans. Can. Inst. Min. Metall. 42, 129 (1949).

15. Djingeluzian, L. E., Theory and practice of roasting sulphide concentrates. Can. Min. & Metall. Bull. 55, 238-252 (1952).

16. Putman, G. L. Chlorine as solvent in gold hydrometallurgy. Eng. Min. J. 145,(3)70 (1944).

17, Walker, G. A. The chemical treatment of gold slime for the recovery of high purity gold and silver. Australas.Inst.Min. Metall. Proc. 180, 21 (1956).

18. Le Blanc, R., Precipitation of gold from cyanide solution by zinc dust. Can. Min. J., April, May, June 1942.

19. Dorr, J. V. N. & Bosqui, F. L., Cyanidation and Concentration of gold and silver ores. McGraw-Hill Book Co., New York, 184 (1950).

20. Dorr, J. V. N. & Bosqui, F. L., op. cit. 186.

21. Crowe, T. B., and Victor, E. M., Effect of oxygen on precipitation of metals from cyanide solutions. Trans. Am. Ins. Min. Engrs. 60, 116 (1919).

22. Allen, A. W. Early history of the cyanide process. Engng. Min. J., 371-374 (1927).

23. Dorr, J. V. N. & Bosqui, F. L., op. cit. 137-200.

24. Howell, F. M., Homestake's new process helps save environment. The Northern Miner, Apr. 20 (1972).

25. Junner, N. R., Progress in geological and mineral investigations in the Gold Coast. G.S. Gold Coast Bulletin 16, (1946).

26. Cooper, W. G. G., The geology of the Prestea goldfields. G. S. Gold Coast Memoir No.3, (1934).

27. Feldtmann, W. R., The precipitation action of carbon in contact with auriferous cyanide solutions. Trans. Inst. Min. Metall. 24, 229-343 (1915).

28. Barko, A. B., Mining geology of the Prestea goldfields. Ph.D. Thesis, University of Cagliari, Italy, (1972).

29. Howat, D. D., Ariston Gold Mines (1929) Ltd. Mine and Quarry Engng. 5, 191-3 (1940).

30. Chamber of mines of South Africa, Eleventh annual research review. pp 32-39 (1973).

31. Gy, P., "Poids à donner à un echantillon Abaques d'échantillonnage", Note Technique No. 4-55. Laboratoire de Minerais et Métaux, Paris (1953).

32. Carlson, G. G. and van Loon, J. C., Determination of gold in solution containing high concentration of other salts. Adsorp. Newsl. 9, No. 4, 90-1 (1970).

33. Mikhailova, T. P. and Rezepina, V. A., Determination of Au and Ag in plant liquors and electrolytes by A. A. Spectrophotometer. Analyst (London) 95, No. 1134 (1970).

34. Vogel, A. I., A Text Book of Quantitative Inorganic Analysis 3rd edn. Longmans, Green & Co., London, 581 (1961).

35. Cohen, E. and Schloegl, I., The application of micrography in mineral dressing. 2nd International Symposium on X-ray microscopy. Stockholm, (1959).

36. Hallbauer, D. K., The plant origin of the Witwatersrand 'carbon'. Minerals Sci. Engng. 7, (2) 111-129 (1975).

37. Skeat, J. 'Association of gold with green sericite' 1903, quoted by Cooper, W. G. G., The geology of the Prestea goldfields. Gold Coast Memoir No.3, (1934).

38. Uytenbogaardt, W. and Burke, E. A. J., Tables for microscopic identification of ore minerals. 2nd revised edn. Elsevier Pub. Co., Amsterdam, (1971).

39. Feather, C. E. and Koen, G. M., The mineralogy of the Witwatersrand reefs. Minerals Sci. Engng.7, (3), 200-201 (1975).

40. Merwin, R. W., Gold resources in the oxidised ores and carbonaceous material in the sedimentary beds of Northeastern Nevada. Bureau of Mines Heavy metal program. Technical Progress Report, March 1968.

41. Sheiner, B. J., Lindstrom, R. E. and Henrie, T. A., Investigation of oxidation systems for improving gold recovery from carbonaceous materials. Bureau of Mines Technical Report, July 1968.

42. Fowkes, F. M., Attractive forces at solid-liquid interfaces. "Wetting" Soc. Chem. Industry, Monograph No. 25, 4, (1967).

43. Fowkes, F. M. I., Chemistry and Physics of Interfaces, American Chem. Soc. Publication, Washington, D. C., 1-12, (1965).

44. London, F., The general theory of molecular forces. Trans. Faraday Soc. 33, 8-26 (1937).

45. Hamaker, H. C., The London-Van der Waal's attraction between spherical particles. Physica 4, 1058-72 (1937).

46. Visser, J., On Hamaker constants: A comparison between Hamaker constants and Lifshitz - van der Waals constants. Advan. Colloid Interface Sci. 3, 331-363 (1972).

47. Kitchener, J. A., Discussion of the paper, "Surface forces in flotation" Minerals Sci. Engng. Vol.6, No. 4, 245-6 (1974).

48. Reerink, H. and Overbeek, J. Th. G., The rate of coagulation as a measure of the stability of silver iodide sols. Discuss. Faraday Soc. 18, 74 (1954).

49. Krupp, H., Schnabel, W. and Walter, G., Computation of the Lifshitz - van der Waals constant on the basis of optical data. J. Colloid Interface Sci. 39, 421 (1972).

50. Harrison, J. H. and Elton, G. A. H., Electrophoresis of gold and silver particles. J. Chem. Soc., 3838-43 (1959).

51. Laskowski, J. and Kitchener, J. A., The hydrophilic - hydrophobic transition on silica. J. Colloid Interface Sci. 29, 670-679 (1969).

52. Hurd, R. M. and Hackerman, N., Electrokinetic potentials on bulk metals by streaming current measurements. J. Electrochem. Soc. 103, 316-9 (1956).

53. Benton, D.P. and Sparks, B. D., Adsorption from aqueous solutions of ionic surface-active agents on gold. Trans. Faraday Soc. 62, 3244-52 (1966).

54. de Boer, J. and Verwey, E. J., Surface oxide films. Rec. Tran. Chem. 55, 675 (1936).

55. Adam, N. K., "The Physics and Chemistry of Surfaces" (Oxford University Press, London) (1941).

56. Sutherland, K. L. and Wark, I. W., "Principles of Flotation". Australasian Institute of Mining and Metallurgy, Melbourne, (1955).

57. Gaudin, A. M., "Flotation" 2nd ed. McGraw-Hill Book Co., New York ,(1957).

58. Fox, H. W., Hare, E. F. and Zisman, W. A., Wetting properties of organic liquids on high energy surfaces. J. Phys. Chem. 59, 1097-1106 (1955).

59. Bewig, K. W. and Zisman, N. A., Surface potentials and induced polarisation in non-polar liquids on metals. J. Phys. Chem. 68, 1804 (1964).

60. Bartell, F. E. and Smith, J. T., Alteration of surface properties of gold and silver as indicated by contact angle measurements. J. Phys. Chem. 57, 165-172 (1953).

61. Fowkes, F. M., Determination of the contribution to surface and interfacial tensions of dispersion forces in various liquids. J. Phys. Chem. 67, 2538-43 (1963).

62. White, M. L., The wetting of gold surfaces by water. J. Phys. Chem. 68, 3083-85 (1964).

63. Erb, R. A., Wettability of metals under continuous condensing conditions. J. Phys. Chem. 69, 1306-9 (1965).

64. Bewig, K. W. and Zisman, W. A., The wetting of gold and platinum by water. J. Phys. Chem. 69, 4238-42 (1965).

65. White, M. L. and Drobek, J., The effect of residual abrasives on the wettability of polished gold surfaces. J. Phys. Chem. 70, 3432-36 (1966).

66. Plaksin, I. N. and Bessonev, S. V., The effect of adsorption and chemical reaction of oxygen on the flotation properties of gold, silver, and copper. Doklady Akad. Nauk. S.S.S.R. 60, 637-9 (1948).

67. Johns, J. W., Further test in flotation of free gold. Engng. and Min. Journal 136,No. 10, 498 (1935).

68. Benton, D. P. and Sparks, B. D, Adsorption from aqueous solutions of ionic surface-active agents by gold. Trans. Faraday Soc. 537, 63, 2270-4 (1967).

69. Gardner, J. W. and Woods, R., The use of a particulate bed electrode for the electrochemical investigation of metal and sulphide flotation. Aust. J. Chem., 1635-44, (1973).

70. Wark, I. W. and Cox, A. B., Principles of Flotation. Trans. Am. Inst. Min. Met. Engrs. 112, 189-193 (1934).

71. Hoare, J. P., A study of the rest potentials in the gold-oxygen-acid system. J. Electrochem. Soc. 110,245 (1963).

72. Allmand, A. J., The Principles of Applied Electrochemistry. Eward Arnold, London, 271 (1972).

73. Adam, N. K., Advances in Chemistry Series, No. 43, Chapter 2. American Chemical Society, Washington, 1964.

74. Holmes, P. T.,"The electrochemistry of semi-conductors" Academic Press, London, 1962.

75. Derjaguin, B. V. and Zorin, Z. M., Optical study of the adsorption and surface condensation of vapours in the vicinity of saturation on a smooth surface. 2nd International Congress of Surface Activity, London, Vol. 13, BM 270-7 (1957).

76. Frumkin, A. J. Phys. Chem, Moscow 12,337 (1938), quoted by Derjaguin, B. V. and Zorin, Z. M., 2nd International Congress of Surface Activity, London, Vol. 13 1957.

77. Gardner, J. R. and Woods, R., An electrochemical investigation of contact angle and the flotation in the presence of alkylxanthates. I. Platinum and gold surfaces. Aust. J. Chem. 27, 2139-48 (1974).

78. Hoare, J. P. "The electrochemistry of oxygen" Intersciences Publishers. John Wiley and Sons (Inc.)., 47-53 (1968).

79. Young, L., "Anodic oxide films" Academic Press, London , 297-302 (1961).

80. Ogura, K., Haruyama, S. and Nagasaki, K.,The electrochemical oxidation and reduction of gold. J. Electrochem. Soc. 118, (4) 531-5 (1971).

81. Brummer, S. B. and Makrides, A. C., Surface oxidation of gold electrodes. J. Electrochem. Soc. 111, 1122 (1964).

82. Brummer, S. B., Ageing effects in thin oxide films on gold in $HClO_4$ J. Electrochem. Soc. 112, (6), 633-6 (1965).

83. Dickinson, T., Povey, A. F. and Sherwood, P. M. A., X-ray photoelectron spectroscopic studies of oxide films on platinum and gold electrodes. Trans.Faraday Soc., 298-311 (1974).

84. Trasatti, S., Work function, electronegativity and electrochemical behaviour of metals II. Potentials of zero charge and electrochemical work functions. J. Electroanalytic.Chem. 33, 351 (1971).

85. Frumkin, A., Damaski, B., Grigoryev, N. and Bagotskaya, I., Potentials of zero charge, interaction of metals with water and adsorption of organic substances.I Potentials of zero charge and hydrophilicity of metals. Electrochem. Acta 19, 69-74 (1974).

86. Smolders, C. A., Contact angles; Wetting and de-wetting of mercury. Part III. Contact angles on mercury Recueil des travaux chimiques des pays-bas, The Hague T80, 8 699-72 (1961).

87. Kostelitz, de MM. M. and Oudar, J., Reversible chemical adsorption of sulphur on the (111), (100) and (110) faces of gold. C. R. Acad. Sc. Paris t. 271, 1205-7 (1970).

88. Eigeles, M. A. and Volova, M. L., Kinetic investigation of effect of contact time, temperature and surface condition on the adhesion of bubbles to mineral surfaces. International Mineral Processing Congress No. 14, London,(1960).

89. Klassen, V. I. and Mokrousov, V. A., An introduction to the theory of flotation. London, Butterworths, 210 (1963).

90. Majima, H. and Takeda, M., Electrochemical studies of xanthate-dixanthogen system on pyrite. Trans.A.I.M.E. Soc. Min. Eng. 241, 431-6 (1968).

91. Tulon, R. and Kitchener, J. A., Electrochemical study of the galena-xanthate-oxygen flotation system. Trans.Inst. Min. Metal. 72, 313-322, (1964).

92. Golikov, A. A., Interaction of xanthogenate type collectors on sulphide mineral surfaces. Sov. J. non-ferr. Metals 2, 19-24 (1961).

93. Blackman, L. C. F. (ed.), Modern Aspects of Graphite Technology. Academic Press, London, 79-80 (1970).

94. Campbell, J. A., Chemical Systems, Energetics, Dynamics and Structures. W. H. Freeman and Co., U.S.A., 385-6 1970.

95. Donohue, J., The structures of the elements. John Wiley and Sons, London, 254-61 (1974).

96. Coughlin, R. W., Esra, F. S. and Tan, R. N. Influence of chemisorbed oxygen in adsorption onto carbon from aqueous solution, in 'Hydrophobic Surfaces'. ed. Fowkes, F. M. Academic Press, London, 44 (1969).

97. Kiselev, A. V., Adsorption properties of hydrophobic surfaces in 'Hydrophobic surfaces'. ed. Fowkes, F. M., Academic Press, London, 88 (1969).

98. Kerr, R. W., Chemistry and Industry of Starch. 2nd. Edn. Revised and Enlarged. Academic Press, Inc., New York, 179-213 (1950).

99. Honeyman, J., Chemistry of Carbohydrates. Clarendon Press, Oxford, 125-131 (1948).

100. Rehbinder, V. P., Selective wettability through the adsorption of surface active agents. Koll.Zeit. 65, 269 (1933).

101. Majumdar, K. K., Contact angle of natural graphite. J. Sci. Int. Res.8B,No. 12 232-4 India, (1949).

102. Sun, S. C., Hypothesis for different floatabilities of coals, carbons and hydrocarbon minerals. Trans.Am. Inst. Min. Met. Engrs. 199, 67 (1954).

103. Saleeb, F. Z. and Kitchener, J. A., The effect of graphitization on the adsorption of surfactants by carbon blacks. J. Chem. Soc. 167, 911-17 (1965).

104. Groszek, A. J., Adsorption of polycyclic aromatic hydrocarbons onto graphite. Faraday Soc. Discussion 59, No. 10 (1975.).

105. Arbiter, N., Fuji, V., Hansen, B. and Raja, A., Surface properties of hydrophobic solids. Private communication of Professor Arbiter to Dr. Kitchener.

106. Fowkes, F. M. and Harkins, W. D., The state of monolayers adsorbed at the interface solid-aqueous solution. J. Am. Chem. Soc. 62, 3377 (1940).

107 Isirikyan,A.A. and Kiselev,A.V., Adsorption isotherms of N_2, benzene and n-hexane and heats of adsorption of benzene and n-hexane on graphitised carbon blacks. The thermodynamic characteristics of adsorption equilibria. J. Phys. Chem. 66, 210 (1962).

108. Fedorov, G. G., Zarif'yant, Yu. A. and Kiselev, V. F., Properties of the surface of freshly cleaved graphite. Adsorption and differential heat of adsorption for oxygen. Zh. Fiz. Khim. 37, (7), 1619-22 (1963).

109. Harkins, W. D., Physical chemistry of surface films. (New York: Reinhold), (1952).

110. Young, G. J., Chessick, J. J., Healey, F. H. and Zettlemoyer, A. C., Thermodynamics of the adsorption of Water on graphon from the heats of immersion and adsorption data. J. Phys. Chem. 58, 313 (1954).

111. Campbell, J. A. L. and Sun, S. C., Butiminous coal electrokinetics. Soc. Min. Engrs. A.I.M.E. 247, 113 (1970).

112. Aplan, F. F. and Fuerstenau, D. W., Principles of nonmetallic mineral flotation. Froth Flotation, 50th anniversary volume. A.I.M.M. and Petr.Engrs. Inc., 191 (1962).

113. Campbell, J. A. L. and Sun, S. C., Anthracite and electrokinetics. Soc. Min. Engrgs. A.I.M.E. 247, 120-22 (1970).

114. Horsley, R. M., El-Sinbawy, H. and Smith, H. G., Xanthates in coal flotation. J. Fuel Sci. 31, 301-11 (1952).

115. Balajee, S. R. and Iwasaki, I., Adsorption mechanism of starches in flotation and flocculation of iron ores. Trans. Amer. Inst. Min. Engrs. 244, 401-6 (1969).

116. Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press Ltd, (1966).

117. Finkelstein, N. P. and Hancock, R. D., A new approach to the chemistry of gold. Gold Bulletin 7, 72-7, July, 1974.

118. Johnson, B. F. G., The chemistry of gold. Gold Bulletin. 9-11, Jan. 1971.

119. Sato, M., Oxidation of sulphide ore bodies. 1. Geochemical environments in terms of Eh and pH. Economic Geo. 55, 928-961 (1960).

120. Latimer, W. H., "Oxidation Potentials" Prentice-Hall, Inc., New York, (1952).

121. Allgeir, R. J. Hafford, B. C. and Juday, C., Oxidation-reduction potentials and pH of lake waters and of lake sediments. Wisconsin Academy Science Trans. V33, 115-133 (1941).

122. Bockris, J. O'M and Oldfield, L. F., The oxidation-reduction reactions of hydrogen peroxide at inert metal electrodes and mercury cathodes. Trans.Faraday Soc. 51, 249-58 (1955).

123. MacDonald, W. R. and Hayes, K. E., A comparative study of the rapid adsorption of oxygen by silver and gold. J. Catalysis 18, 115-118, (1970).

124. Dickinson, C. D. T. and Mair, W. N., The interaction of oxygen and hot gold.(Electron diffraction, X-ray and electrochemical studies). Trans. Faraday Soc. 55, 1937 (1959).

125. Banta, M. C. and Hackerman, N., The effect of acidity on the differential capacity of polarised platinum electrodes. J. Electrochem. Soc. 111, 114 (1964).

126. Hoare, J. P., Some effects of alternating current polarization on the surface of noble metal electrodes. Electrochem. Acta 9, 599 (1964).

127. Schmid,G.M.&Hackerman, N., Electrical double layer capacities and adsorption of alcohol on gold. J. Electrochem. Soc. 110, 440 (1963).

128. Schmid, G. M. and O'Brien, R. N.,"Oxygen" adsorption and double layer capacities; Gold in perchloric acid. J. Electrochem. Soc. 111, 832 (1964).

129. Rao, M. L. B. A., Damjanovic and Bockris, J. O'M., Oxygen adsorption related to the unpaired d-electrons in transition metals. J. Phys. Chem.67, 2508 (1963).

130. Plaksin, I. N. and Shafeev , R. Sh., On properties of distribution of xanthate on the surface of sulphide minerals. J. Mines, Metals & Fuels, 1-8 July, 1960.

131. Trapnell, B. W. M., The activities of evaporated metal films in gas chemisorption. Proc. Roy. Soc. A 218, 566, (1953).

132. Hinshelwood, C. N., and Prichard, C. R.; The catalytic decomposition of nitrous oxide on the surface of gold: a comparison with the homogeneous reaction. Proc. Roy. Soc. ; A 108, 211 (1925).

133. Eley, D. D. and Knights, C. F., The decomposition of nitrous oxide catalysed by palladium-gold alloy wires. Proc. Roy. Soc. A 294, 1 (1966).

134. Carpenter, L. G. and Mair, W. N., The interaction of oxygen and hot gold. Trans. Faraday Soc. 55, 1924 (1959).

135. Patterson, W. R. and Kemball, C., The catalytic oxidation of olefins on metal films. J. Catal. 2, 465 (1963).

136. Kul'Kova, N. V. and Levchenko, L. L., Adsorption of oxygen on gold. Kinet. Katal. 6, 688 (1965).

137. Hondros, E. D. and Gladman, D., Surface energy and impurity adsorption on gold heated in air. Surface Sci. 9, 471 (1968).

138. Murgulescu, I. G. and Vass, M. I., Gas adsorption on thin metallic films, Surface potential variation in oxygen-gold system. Rev. Roum. Chim. 13, 373 (1968).

139. Ford, R. R. and Pritchard, J., Chemisorption of oxygen on gold. Chem. Commun., 362 (1962).

140. Rao, S. R., Xanthates and related compounds. (Marcel Dekker, New York), 1971.

141. Pomianowski, A. and Leja, J., Spectrophotometric study of xanthates and dixanthogen solutions. Can. J. Chem. 41, 2219-30 (1963).

142. Rao, S. R. and Patel, C. C., Kinetic decomposition of xanthates. J. Mines, Metal & Fuels, 9-14 (1960).

143. Iwasaki I. and Cooke, S. R. B., The decomposition of xanthate in acid solution. J. Am. Chem. Soc. 80, 285-8 (1958).

144. Cooke, M. A., Hydrophobicity control of metal surfaces by hydrolytic adsorption. J. Colloid and Interface Sci. 28, No. 3/4, 547-55, (1968).

145. Finkelstein, N. P., Kinetic and thermodynamic aspects of the interaction between potassium ethyl xanthate and oxygen in aqueous solutions. Trans. Inst. Min. Metall. (Sec. C. Mineral Process Extra. Metall.) 76, C51-9 (1967).

146. Tipman, R. N. and Leja, J., Reactivity of xanthate and dixanthogen in aqueous solutions of different pH. Colloid and Polymer Sci. 253, 4-10 (1975).

147. Harris, P. J. and Finkelstein, N. P., The formation of mono-thiocarbonates during the reaction between xanthates and sulphide minerals in flotation systems. Processings 11th. International Miner. Proc. Congr., 1975.

148. Kakovskii, I. A., Flotation of native metals. Proc. Sci. Tech. Inst. Metal, (U.S.S.R.), 1955.

149. Leonov, S. B. and Matiskin, O. D., Thermodynamic properties of xanthate acids, from 'Some questions of the theory of flotation and spiral conveying apparatus'. Irkutsk, 32-44 (1972).

150. Plaksin, I. N. and Tyurnikova, V. I., Radiographic methods of analysis of interaction of reagents with minerals (In Russian) 1960, quoted by Zelenov, V. I. and Yavorskaya, E. V., Tr. Tsent. Nauch. Issled Gornorazved, Inst. (U.S.S.R.) 82, 22-27 (1969).

151. Mitrofanov, S. I., Selective flotation, Nyedra 1967 (in Russian) 1960, quoted by Zelenov, V. I. and Yavorskaya, E. V., Tr. Tsent. Nauch. Issled Gornorazved, Inst. (U.S.S.R.) 82, 22-27 (1969).

152. Zelenov, V. I. and Yavorskaya, E. V., On the question of the interaction of sulphydryl collectors with gold. Tr. Tsent. Nauch. Issled Gornorazved; Inst. (U.S.S.R.) 82, 22-27 (1969).

153. Plaksin, I. N. and Zaitseva, S. P., The influence of oxygen, nitrogen and hydrogen on the potassium ethyl xanthate adsorption on gold, silver, copper and their alloys. Doklady Akad. Nauk. (U.S.S.R.) 101, 727-30 (1955).

154. Lopatin, A. G. and Plaksin, I. N., Investigation of xanthate layers adsorbed on gold by means of radio-isotopes. Izvest. Vysshikh Ucheb, Zavedenii, Tsvemaya Met. 3, No. 1 35-41 (1960).

155. Woods, R., The oxidation of ethyl xanthate on platinum, gold, copper and galena electrodes. J. Phys. Chem. 75, 3, 357 (1971).

156. Nikulin, A. I. Shafeev, R. Sh. and Chanturiya, V. A., Adsorption of flotation reagents on natural and chemically pure gold. Tr. Tsent. Nauch Issled Gornorazved; Inst. 82, 16-22 , (1969).

157. Gaudin, A. M., de Bruyn, P. L. and Mellgren, O., Adsorption of ethyl xanthate on pyrite. Trans. Amer. Inst. Min. Engrs. 205, 65-70 (1956).

158. Iwasaki, I. and Lai, R. W., Starches and starch products as depressants in soap flotation of activated silica from iron ores. Trans. Soc. Min. Engrs. 364-71 (1965).

159. Block, B. P., Gold powder. Inorganic Synthesis Vol. IV, McGraw-Hill Book, N.Y., 15 (1963).

160. Bushell, C. H. G. and Malnarich, M., Reagent control in flotation. Min. Engng. 203, 734-7 (1956).

161. Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A. and Smith, F., Calometric method for determination of sugars and related substances. Anal. Chem. 28, 350 1956.

162. Finkelstein, N. P. and Ashurts, K. G., Influence of sulphydryl and cationic flotation reagents on the cyanidation of native gold. Nat. Inst. Metal., S. Afr. Res. Report No. 515, (1969).

163. Granville, A., Finkelstein, N. P. and Allison, S. A., Review of reactions in the flotation system, galena-xanthate-oxygen. Trans. Inst. Min. Metal. C11, 1972.

164. Mellgren, O. and Lwakatare, S. L., Desorption of xanthate ions from galena with sodium sulphide. Trans. Inst. Min. Metall. (Sect. C: Mineral Process. Extr. Metall) 77, C101-4 (1968).

165. Woods, R., Private communication 1973.

166. Aplan, F. F. and de Bruyn, P. L., Adsorption of hexyl mercaptan on gold. Trans. Soc. Min. Engrs. 228, 235-242 (1963).

167. Popova, V. S., Popov, R. L., Solozhenkin, P. M., Kopitsya, N. I., Shvengler, F. V., Form in which xanthate is fastened to a gold surface. Dokl. Akad. Nauch. Tadzh. U.S.S.R. 17, (5) 37-9 (1974).

168. Lewis, J. B., Modern Aspects of Graphite Technology Blackman, L. C. F. (ed.) Academic Press, London & New York, 134 (1970).

169. Thomas, J. M. and Hughes, E. E. G., Localized oxidation rates on graphite surfaces by optical microscopy. Carbon 1, 209 (1964).

170. Roscoe, C. and Thomas, J. M., The identification and some physico-chemical consequences of non-basal edge and screw dislocations in graphite. Proc. Roy. Soc. A 297, 397 (1967).

171. Thomas, J. M. and Evans, E. L., Enhanced reactivity at dislocations in layer structures. Nature, London, 214, 167 (1967).

172. Roscoe, C., Catalytic oxidation of Ticonderoga graphite crystals. Carbon 6, 365 (1968).

173. Volkov, G. M., Anisotropy of chemical activity with oxidising agents of graphite Teor. 1 Eksp. Ihim. 5, 66 (1969).

174. Hennig, G. R., The decoration of individual lattice vacancies in graphite. Proceedings 2nd Ind. Carbon and Graphite Conf. London, 109 (Pub. 1966).

175. Hennig, G. R., Electron microscopy of reactivity changes near lattice defects in graphite. Chem. Phys. Carbon 2, 1. (1966).

176. Lang, F. M., Specific rate of oxidation of various purified graphites in air and in carbon dioxide. C. r. hebd. Seanc. Acad. Sci., Paris 225, 1511 (1962).

177. Hennig, G. R., Catalysis of graphite oxidation. Proceedings 3rd Conf. Carbon, Buffalo, N.Y., 265 (1957) (Pub. 1959).

178. Boehm, H. P., Chemical identification of surface groups. Adv. Catalysis 16, 179 (1966).

179. Zarif'yants, Yu. A., Kiselev, V. F., Lezhnev, N. N. and Nikitina, O. V., Interaction of graphite fresh surface with different gases and vapours. Carbon 5, 127 (1967).

180. Démidovitch, G. B., Kiselev, V. F., Lejnev, N. N. and Nikitina, O. V., Nature la surface du graphite fraichement broyé et mécanisme de l'interaction de cette surface avec l'oxygène et l'hydrogène. J. Chim. Phys. 65, 1072 (1968).

181. Walker, P. L., Austin, L. G. and Tietjen, J. J., Oxygen chemisorption effects on graphite thermoelectric power. Chem. Phys. Carbon 1, 328 (1966).

182. Vastola, F. J., Hart, P. J. and Walker, P. L., Study of the mechanism of the carbon-oxygen reaction using O^{18} as a tracer. Paper presented at 7th Conf. Carbon, Cleveland; abstract Carbon 3 , 350 (1965).

183. Walker, P. L., Vastola, F. J. and Hart, P. J., Fundamentals of Gas-Surface Interactions, (Symposium San Diego, California, 1966, Saltburg, H. ed.) Academic Press, New York , 307 (1967).

184. Walker, P. L., Bansal, R. C. and Vastola, F. J., Paper presented at Carbon and Graphite Symposium; Newcastle. Chem. Phys. Carbon 4, 287 (1968b).

185. Lang, F. M. and de Noblet, M., Surface complexes formed by contact with air on Spheron 6 treated at high temperature. Carbon 6, 210 (1968).

186. Wynne-Jones, W. F. K., The structure and Properties of porous materials. (Everett and Stone, ed.) Butterworths, London, 35 (1958).

187. Kipling, J. J., The properties and nature of adsorbent carbons. Quart. Rev. 13, 287 (1959).

188. Smith, R. N., The chemistry of carbon-oxygen surface compounds. Quart. Rev. 13, 287 (1959).

189. Kipling, J. J., Adsorption from solutions of non-electrolytes. Academic Press, London & New York, (1965).

190. Smith, W. R. and Schaefer, W. D., The nature and activity of carbon black surfaces. Proceedings of the second Rubber Technology conference, London, 403 1948.

191. Gasser, C. G. and Kipling, J. J., The effect of surface complexes on adsorption from the liquid phase by carbon black. Proceedings of the 4th Conference on Carbon, Pergamon Press, London & New York, 55 (1960).

192. Iwasaki, I., Takahasi, and Kahata, H., Extraction of nickel from iron laterite and oxidised nickel ores by a segregation process. Trans. Am. Inst. Min. Engrs. 235, 308-20 (1966).

193. Mellgren, O. and Wallum, P. F., Consumption of potassium ethyl xanthate in graphite suspension. Trans. Inst. Min. Metall. 79, Section C, C62-C64 (1970).

194. Schultz, N. F. and Cooke, S.R.B., Froth Flotation of Iron Ores. Adsorption of starch products and acetate. Ind. Engng. Chem. 45, (12), 2769 (1953).

195. Wie, J. M. and Fuerstenau, D. W., The effect of dextrin on surface properties and the flotation of molybdenite Intern. J. Miner. Proc. 1, 17-32 (1974).

196. Golikov, A. A., "Chemism of the interaction of sulfhydryl collectors on sulphide mineral surfaces", Tsvetn. Metal. 37, 16-22 (1964).

197. Salemy, S. G. and Nixon, J. C., Recent Development in Mineral Dressing, Inst. Min. Metall., London, 503-16 (1953).

198. Salemy, S. G. and Nixon, J. C., Reaction between a mercury surface and some flotation reagents: An electrochemical study. Aust. J. Chem. 7, 146 (1954).

199. Nixon, J. C., Discussion. Role of gases in flotation reactions. (by Plaksin, I. N. & Bessonov, S. V.) Proc. 2nd Int. Congr. Surface Activ. 3, 369 (1957).

200. Peterson, C. and Kwei, T. K., The kinetics of polymer adsorption onto solid surfaces. J. Phys. Chem. 65, 1330 (1961).

201. Kawecka, J., Klesinska-Drwalowa, J. and Lason, A. K. M., Chem. Stosowana, 7, 441 (1963) Quoted by Kipling, J. J. Adsorption from Solutions of Non-Electrolytes. Academic Press, London, 233 (1965).

202. Iskra, J., Depressant properties of quebracho in flotation Min. Tech. Research Progress Report, No. 45, 1-4 (1973).

203. Iskra, J., Gutierrez, C. and Kitchener, J. A., Influence of quebracho on the flotation of fluorite, calcite, hematite and quartz with oleate as collector. Trans. Inst. Min. Metall. 82, C73-C78 (1973).

204. Somasundaran, P, Adsorption of starch and oleate and interaction between them on calcite in aqueous solutions. J. Colloid Int. Sci. 31, 557-565 (1969).

205. Arbiter, N. and Harris, C. C., Froth Flotation-50th Anniversary Volume. D. W. Fuerstenau (ed.), New York, A.I.M.E., 219-20 (1962).

206. De Bruyn, P. L., Overbeek, J. Th. G. and Schuhmann, R., Flotation and Gibbs adsorption equation. Min. Engng. N.Y. Vol. 6, 519-23 (1954).

207. De Bruyn, P. L. and Agar, G. E., Surface chemistry of flotation. Froth flotation - 50th Anniversary Volume. D. W. Fuerstenau (ed.), New York, A.I.M.E., 91-138 (1962).

208. Somasundaran, P., The relationship between adsorption at different interfaces and flotation behaviour. Trans. Soc. Min. Engrs. AIME., 241, 105-108 (1968).

209. Scheludko, A., Zur Theorie der Flotation. Kolloid Z. 191, 52-8 (1963).

210. Laskowski, J. and Iskra, J., Role of capillary effects in bubble-particle collision. Trans. Inst. Min. Metall. 79, C6-C10 (1970).

211. Tait, R. J. C., Giant Yellowknife Gold Mines, Ltd. The milling of Canadian ores - 6th Commonwealth Min. Metall. Congress, 135-38 (1957).

212. Leaver, E. S. and Woolf, J. A., Flotation of metallic gold - Relation of particle size to floatibility. Engng. Min. J. 136, i-ii (1934).

213. Zelenov, V. I., New reagent for the flotation of gold and copper. Tsvetnye Metal 6, 85-7 (1973) (Russian).

214. Brown, D. J., Coal flotation. Froth Flotation - 50th Anniversary volume. D. W. Fuerstenau (ed.), New York, AIME., 518-38 (1962).

215. Instituto del Quebracho Ideq., The Chemistry of Quebracho. Buenos Aires, Argentina.

216. Furstenau, M. C., Kuhn, M. C. Elgillani, D. A., The role of dixanthogen in xanthate flotation of pyrite. Trans. Soc. Min. Engrs., 148-156 (1968).

217. Langtry, D. A., Analysis of flotation cell performance in a continuous flow system. Ph. D. thesis, University of London, (1971).

218. Slater, R. W. and Kitchener, J. A., Characteristics of flocculation of mineral suspension by polymers. Discussion Faraday Soc. 42, 267-75 (1966).

219. Fontana, B. J. and Thomas, J. R., The configuration of adsorbed alkyl methacrylate polymers by infrared and sedimentation studies. J. Phys. Chem. 65, 480-7 (1961).

220. Jones, G. D. and Goetz, S. J., p-Vinylbenzyltrilkyl ammonium salts in vinyl polymerization. J. Polymer Sci. 25, 201 (1957).

221. Whistler, R. L., Industrial Gums, Academic Press, New York, 1959.

222. Linke, W. F. and Booth, D. R., Physical chemical aspects of flocculation by polymers. Trans. Am. Inst. Min. Engrs. 217, 364 (1960).

223. Drexler, F. X., Presented to the Coal Preparation Society, North Eastern Section, Newcastle-upon-Tyne, September, (1960).

224. La Mer, V. K. & Smellie, R. H., Flocculation, subsidence and filtration of phosphate slimes. J. Coll. Sci. 11, 710 (1956).

225. ibid 11, 720 (1956).

226. ibid 12, 230 (1957).

227. ibid 12, 566 (1957).

228. Healy, T. W., Ph.D. Thesis, Columbia University.

229. Slater, R. W., A study of the mineral suspensions by polymers. Ph.D. Thesis, University of London, (1967).

230. Edwards, B. C., Investigation of some electrochemical and colloidal properties of polymeric flocculants. Ph.D. Thesis, University of London, (1967).

231. Wark, L. W. and Cox, A. B., Principles of Flotation, IV - An experimental study of influence of sodium sulfide, alkalies and copper sulfate on effect of xanthates at mineral surfaces. Trans. Am. Inst. Min. Engrs. 134, 14 (1939).

232. Chant, K., Study of gold loss in flotation of Prestea carbonaceous gold ore. (Unpublished work) (1962).

233. Plaksin, I. N. and Lopatin, A. G., Effects of alkalies on the flotation of gold. Nauch Dohlady Vysshei Shkoly, Gornoe Delo No.1., 209-13 (1959).

234. Scheiner, B. J., Lindstrom, R. E., Guay, W. J., and Peterson, D. G. Extraction of gold from carbonaceous ores: Pilot plant studies. U.S. Dept. of the Interior. Bureau of Mines Report of Investigations, 7597, (1972).

235. Norwood, A. F. B. Roasting and treatment of auriferous flotation concentrate. Australas. Inst. Min. and Met., Proc. No. 116, 391-412 (1939).

236. Butts, A., Copper, the metal, its alloys and compounds. Reinhold Publ. Co., New York, N.Y., (1954).

237. Dorr, J. V. N. and Bosqui, F. L., Cyanidation and Concentration of Gold and Silver Ores. McGraw-Hill Book Co., Inc. New York , 158-176 (1950).

238. Lodeishchikov, V. V., Zhuchkov, I. A.; Skobeev, I. K., Smagunov, V. N., Oxidation roasting of Au-As concentrates. Tsvet. Metal 41(1), 24-5 (1968) (Russ.).

239. Kolesnikov, N. A., Larin, V. F., Panteleeva, A. P. and Bakhtina, I. I., Roasting of treatment-resistant Au-As concentrates in a fluidized bed with maximum volatilisation of arsenic. Tsvet. Metal 40(6), 44-6 (1967) (Russ.).

240. Zhuchkov, I. A., Lodeishchikov, V. V. and Skobeev, I. K., Behavior of carbon during the oxidising roasting of carbonaceous Au-As concentrate. Tsvet. Metal. 41 (9), 25-6 (1968) (Russ.)

241. Lodeishchikov, V. V., Skobeev, I. K., Khramchenko, S. I, Behavior of pyrite during roasting of gold-bearing sulphide concentrates. Tsvet. Metal. 33 (10), 44-51 (1960) .

242. Van Arsdale (ed.) , Hydrometallurgy of base metals. McGraw-Hill Book Co., Inc., New York, 1-6 (1953).

243. Christy, S. R., The electromotive force of metals in cyanide solutions. Trans. Am. Inst. Min. Engrs. 30, 864 1900.

244. Thompson, P. E., The dissolution of gold in cyanide solutions. Trans Electrochem. Soc. 91, 41 (1947).

245. Kudryk, V. and Kellog, H. H., Mechanism and Rate-controlling factors in the dissolution of Gold in cyanide solution. J. Metals 6 , 541 (1954)

246. Hedley, N. and Tabachnick, H., Chemistry of Cyanidation American Cyanamid Co. New York · Mineral Dressing Notes No. 23 (1958) .

247. Kakovskii, I. A. and Kholmanskikh, N. B., A study of the kinetics of the cyaniding process of copper and gold. Izv. Akad. Nauk. S.S.S.R., Metallurgia i Toplivo, 5 , 207-218 (1960).

248. Gardiner, B. L.,Discussion of the paper "Reduction Works Practice at Morro Velho, Brazil - by French, J. H. and Jones, H. Trans. Inst. Min. Met. 42, 251 (1933).

249. Lemmon, R. J, Discussion by French, J. H. and Jones, H. Reduction works Practice at Morro Velho, Brazil. Trans. Inst. Min. Met., 42, 247-251 (1933).

250. Ageenkov, V. G. and Svestonov, N. V., Extraction of gold and arsenic from other ores. Izv. Vyss. Ucheb. Zaved., Tsvet. Metal., 2, (4) 88-96 (1959).

251. Leaver, E. S. and Woolf, J. A., Copper and zinc cyanidation U.S. Bur. Mines Technical Paper No. 494, (1931).

252. Allen, A. W., The Moore-Edmunds process of precipitating gold with charcoal. Eng. Min. J. 106, (6) 256 (1918).

253. Gross, J. and Scott, J. W, Precipitation of gold and silver from cyanide solutions on charcoal. U.S., Bureau of Mines Tech. Paper., 378 (1927).

254. Burstall, F. H., Forrest, P. J., Kember, N. F. and Wells, R. A., Ion-exchange process for recovery of gold from cyanide solution. Ind. Engng. Chem. 45, (8) 1648-58 (1953).

255. Davison, J., Read, F. O., Noakes, F. D. L., and Arden, T. V., Ion-exchange for gold recovery. Trans. Inst. Min. Met. 70 (1961).

256. Kuznesov, V. I., Chemical theoretical bases of the extractional isolation of metals. Us. Khim. 23, 654 (1954).

257. Plaksin, I. N. and Shivrin, G. N., Liquid extraction of complex gold and silver cyanides from cyanide solutions. Tsvet. Metal. 34, (9) , 20 (1961).

APPENDIX 1

REACTION OF GOLD WITH COMMON ACIDS.

Introduction

Because of the well-known inertness of gold and its slow rate of reaction with many common acids, it is often assumed that gold does not react with the common acids. In the course of the investigation into the wettability of gold, it was observed that gold reacted the acids used. This has necessitated further investigation into the reactions of gold with HCl, HNO_3, H_2SO_4 and aqua regia.

Experimental

Material

"Specpure" sheet gold and spongy gold, each of grade 99.99% were used in the experiments. All reagents were of Analar grade.

Methods

(a) Reactions of gold with aqua regia and nitric acid.

A piece of sheet gold (1 cm^2 by 0.1 cm thick) was immersed in aqua regia for 1 minute at 22°C and removed, washed thoroughly with distilled water to remove the acid and examined under the Zeiss Ultraphot microscope. Brown patches which were probably residual reaction products remained on the surface. On treating the gold in hot concentrated HCl, the brown coating was removed.

The reaction of boiling nitric acid with gold also produced etched surface which appeared brownish yellow. Prolonged washing of the gold with water did not clean the surface. The tarnished surface was, however, removed when treated with hot concentrated HCl. The HNO_3 solution

containing dissolved gold was scanned with u.v. spectrophotometry, through the wavelengths of 300 - 400 nm, and the u.v. spectra showed an adsorption peak at 340 nm. On diluting the solution, dark brown finely aggregated particles of gold were precipitated.

(b) Reaction of hydrochloric acid with gold.

(1) Reaction with 5 M HCl. 1.73 g of gold of 0.7 - 0.3 mm size was shaken in a 50 ml conical flask with 30 ml 5 M HCl at room temperature for 112 hours with air being bubbled through the solution. After 22.5 hours, 2 ml of the solution was taken and analysed for gold with the atomic absorption spectrophotometer. The solution was filtered after 112 hours. The filtrate was scanned with u.v. spectrophotometry and finally analysed for gold. The characteristic u.v. absorption spectra are shown in Fig. 1.1 and the results for gold analysis are tabulated in Table 1.1.

(2) Reaction of gold with concentrated HCl.

1.55 g of the same size of gold (as in (1)) was used. The tests were carried out at room temperature with 35 ml of concentrated HCl in the presence of air as before for 13 hours. Further tests were also carried out with boiling HCl.

Similar tests were run with 35 ml concentrated HCl at room temperature for 13 hours in the presence of nitrogen gas. The dissolved gold was also analysed.

(c) Reaction with concentrated H_2SO_4.

1.56 g of the same size of gold was heated in to 240°C in 35 ml concentrated H_2SO_4. At temperatures above 200°C the gold particles aggregated.Heating of the acid was continued for 1 hour at 240°C. On cooling to room temperature, the gold particles dispersed. The solution was also analysed for gold.

Results of all the above tests are summarised in Table 1.1.

Results and Discussion.

Reaction with aqua regia and nitric acid.

The dissolution of gold by aqua regia is well known and will not be discussed here. The reaction of nitric acid with gold, however, has not been given much attention. For both acids, the possible residual reaction products appear not to have been considered by investigators.

In this work, the microscopic examination of the gold surface after aqua regia and nitric acid treatments showed definite changes in the surface properties due presumably to the oxidation of the surface. This led to the idea that the gold surface might retain residual intermediate reaction product which might be an oxide layer. Possible support for this idea is the fact that aqua regia and nitric acid react with gold and produce a surface which is definitely hydrophilic in contrast to the surface produced when gold is annealed. This surface is rather weakly hydrophilic.

This work has also shown conclusively that gold dissolved in hot concentrated HNO_3 to form probably $HAu(NO_3)_4$ with an u.v. absorption spectral peak at 340 nm.

Reaction with HCl

The results in Table 1.1 and Fig. 1.1 show that gold dissolves slowly in dilute and concentrated HCl in the presence of air at normal atmospheric conditions. The reaction can be represented as follows:

$$Au + 3/20_2 + 8HCl \longrightarrow 2HAuCl_4 + 3H_2O$$

The reaction product is probably tetrachloroauric acid with u.v. absorption peaks at 226 nm and 312 - 315 nm, because these u.v. spectral peaks are similar to those for standard gold chloride solution (Fig.1.1c) and those for tetrachloroauric acid produced by reacting aqua regia with gold (Fig.1.1b).

The results in Table 1.1 also show that the dissolution of gold in HCl in the presence of air increases with increase in the concentration of HCl and temperature. But the amount of gold dissolved by HCl in the presence of nitrogen appears to be negligible. It is possible that the gold dissolved by HCl in the presence of nitrogen was due to the presence of previously dissolved air in the HCl used. In that case, the dissolution of the gold would continue until all the oxygen in the system is replaced with N_2. In the absence of oxygen, therefore, gold might not dissolve in HCl under normal atmospheric conditions. The dissolution of gold in HCl solution of ferric chloride in absence of air has been reported[1]. In that system, ferric ion was the oxidising species.

Table 1.1 Reaction of sulphuric acid and hydrochloric acid with gold.

reagent	wt. of gold, g.	size (mm)	temp. of reaction	time for reaction (h)	amount leached (mg)	Vol. of reagent (ml)
Conc. H_2SO_4	1.56	0.7 - 0.4	240°C	1	0.1	35
5 M HCl	1.73	0.7 - 0.4	22°C	22.5	0.010	30
aerated				112	0.048	28
Conc. HCl aerated	1.55	0.7 - 0.4	22°C	13	1.4	35
Conc. HCl nitrogenated	1.55	0.7 - 0.4	22°C	13	0.010	35
Conc. HCl	1.564	0.7 - 0.4	boiling	5 min.	0.21	35
	1.563	"	"	5 min.	0.55	35
	"	"	"	10 min.	0.098	35
	"	"	"	10 min.	0.100	35
	"	"	"	10 min.	0.090	35

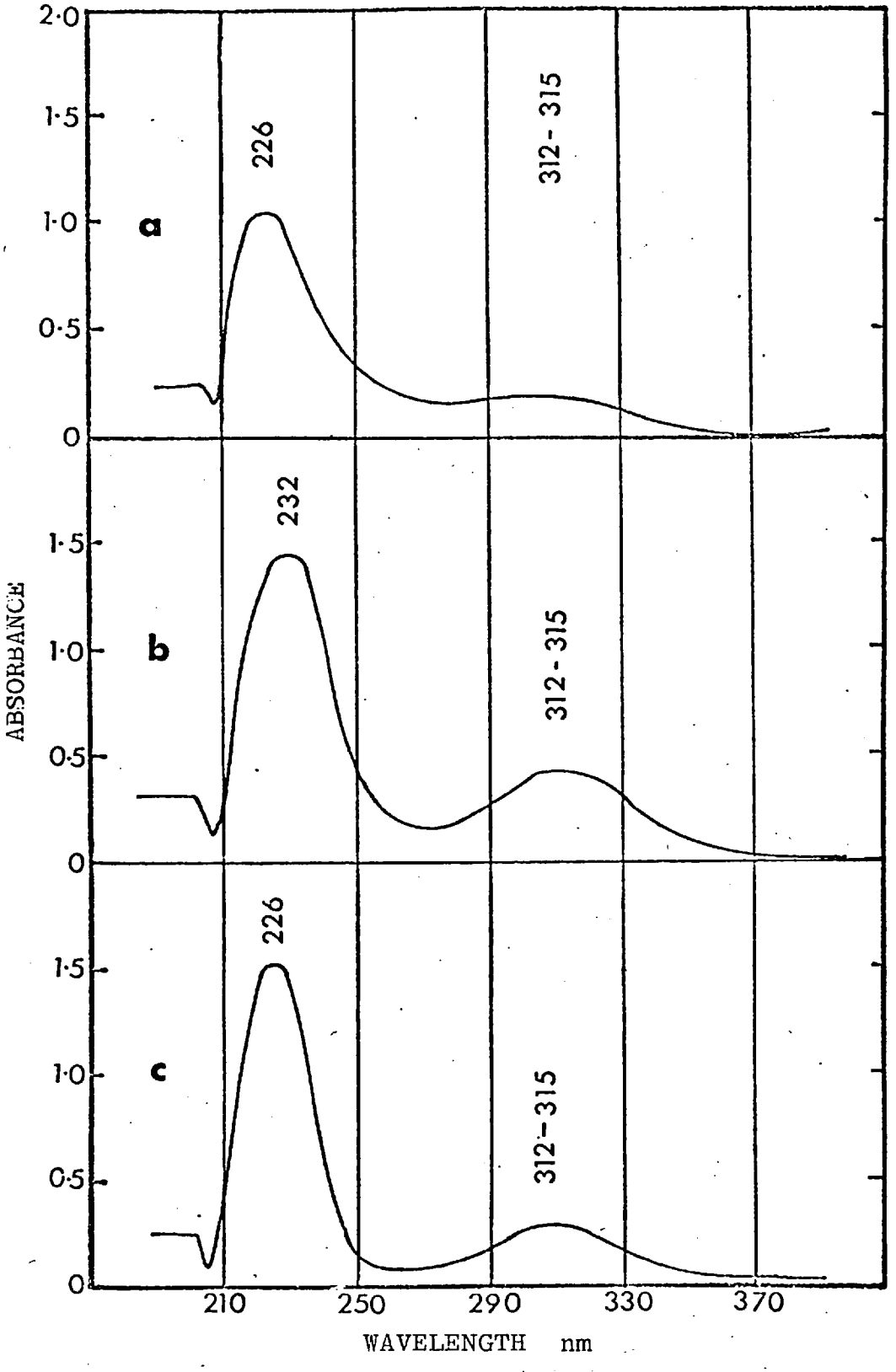


Fig.1.1 u.v.spectrum of gold chloride solutions.
(a) dissolved gold in 1 M HCl.
(b) gold chloride solution prepared with aqua regia.
(c) gold chloride solution for standard A.A. Spec. work. (10 p.p.m.)

Reaction with H_2SO_4

Table 1.1 also shows that gold dissolves in concentrated H_2SO_4 at elevated temperatures. The reaction product may be $HAu(SO_4)_2$[1]. The sintering behaviour of gold in H_2SO_4 at temperature >200°C is considered not unusual since gold is a perfect metal and could sinter far below its melting point of 1064°C. Jeffries and Archer[2] also observed that gold was annealed in air at 200°C and even at 80°C after 100 hours of heating.

1. It can be concluded that besides aqua regia, gold dissolves slowly in other oxidising acids, namely, nitric and sulphuric acids at elevated temperatures but hardly dissolves in these acids at ordinary temperature and pressure.

2. Dilute and concentrated HCl reacts with gold at normal atmospheric conditions to form tetrachloroauric acid but does not appear to dissolve in HCl in absence of oxidising species at ordinary temperature.

References

1. Wise, E.M. (ed) Gold, Recovery, Properties and Applications. D. Van Nostrand Company, Inc. New York. 1964.

2. Jeffries, and Archer, Met. Chem. Eng. 26, 343 (1922)

APPENDIX 2

Thermodynamic data of thio-analogues of carbonic acids. (after Leonov, S.B. and Matiskiv, O.D.[149])

Compound	state	$-\Delta H^0_{298}$ kcal mol^{-1}	$-\Delta G^0_{298}$ kcal mol^{-1}	S^0_{298}
$C_2H_5OCSS^-$	solution	37.43	17.42	54.5
$C_3H_7OCSS^-$	"	43.85	16.85	63.9
$C_4H_9OCSS^-$	"	49.88	15.98	73.3
$C_5H_{11}OCSS^-$	"	55.08	14.28	82.7
$(C_2H_5OCSS)_2$	liquid	--	33.14	--
$(C_3H_7OCSS)_2$	"	--	30.56	--
$(C_4H_9OCSS)_2$	"	--	27.34	--
$(C_5H_{11}OCSS)_2$	"	--	22.48	--
$C_2H_5OCSSAu$	crystal	46.9	18.16	--
$C_4H_9OCSSAu$	"	66.2	18.28	--
$C_5H_9OCSSAu$	"	74.9	17.48	--

(1) The calculation of the free energy change of the reaction

$$2Au + 2C_2H_5OCSS^- + 1/2O_2 + H_2O \longrightarrow 2C_2H_5OCSSAu + 2OH^-$$

$$0 + 2(-17.42) + 1/2(3.95) + (-56.69)$$

$$\longrightarrow 2(-18.16) + 2(-37.595)$$

$$\therefore \Delta G = \underline{-21.96} \text{ kcal mol}^{-1}$$

(2) The calculation of the free energy change of the reaction

$$Au + 3C_2H_5OCSS^- + 1/2O_2 + H_2O$$

$$\longrightarrow C_2H_5OCSSAu + (C_2H_5OCSS)_2 + 2OH^-$$

$$0 + 3(-17.42) + 1/2(3.95) + -56.69$$

$$\longrightarrow -18.16 - 33.14 + 2(-37.595)$$

$$\therefore \Delta G = -19.52 \text{ kcal mol}^{-1}$$

APPENDIX 3

PREPARATION AND CHARACTERISATION OF AUROUS XANTHATE

Preparation of aurous xanthate.

Gold xanthate was prepared by adding 15 ml of weakly acidic solution of 1 g/l auric chloride dropwise to 50 ml of 1 g/l solution of potassium ethyl xanthate. The precipitate was allowed to settle; the solution was pipetted off and gold xanthate was washed thoroughly with ether to remove the dixanthogen which was formed simultaneously. The reaction can be represented as follows:

$$AuCl_3 + 3ROCSS^-K^+ \longrightarrow (ROCSS)_3Au + 3K^+Cl^-$$

$$(ROCSS)_3Au \longrightarrow ROCSSAu + (ROCSS)_2$$

The solution was made acidic to prevent the hydrolysis of the auric chloride. U.v. spectrophotometric analysis of the ether extract confirmed the presence of dixanthogen and that of the solution showed the presence of carbon disulphide and dixanthogen.

Characterisation of gold xanthate.

The gold xanthate produced was a pale yellow crystalline powder. Under crossed Nicols gold xanthate showed oblique extinction and exhibited multiple twinning similar to those of the orthoclase (Plate 3.1). Its crystal properties are similar to those of the monoclinic system. Gold xanthate appears to exhibit habits of the basal pinacoid and combinations which are probably

a = (a:∞b:∞c)

b = (∞a:b:∞c)

c = (∞a:∞b:c)

(See Plate 3.1 for gold xanthate under plane polarised light).

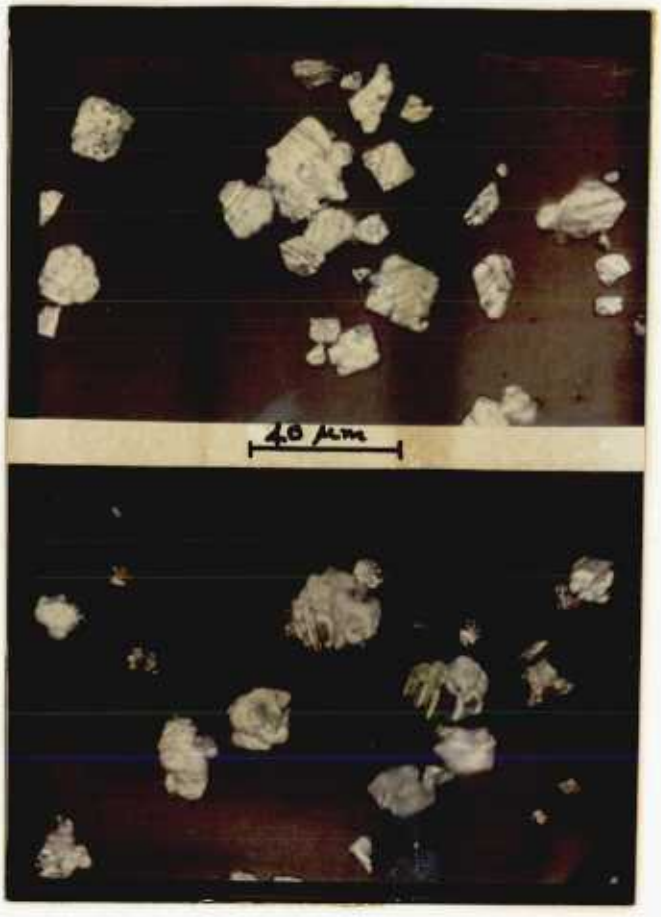


Plate 3.1 Gold xanthate under plane polarised light.

Infra-red data.

Pellets of gold xanthate in KBr for i.r. analysis were prepared as follows: 4 mg of gold xanthate was added to 400 mg of KBr and mixed thoroughly, ground and 180 mg of the mixture was made into a disc under pressure. A reference disc of KBr was similarly made. The i.r. scan of the gold xanthate was carried out with a Grubb

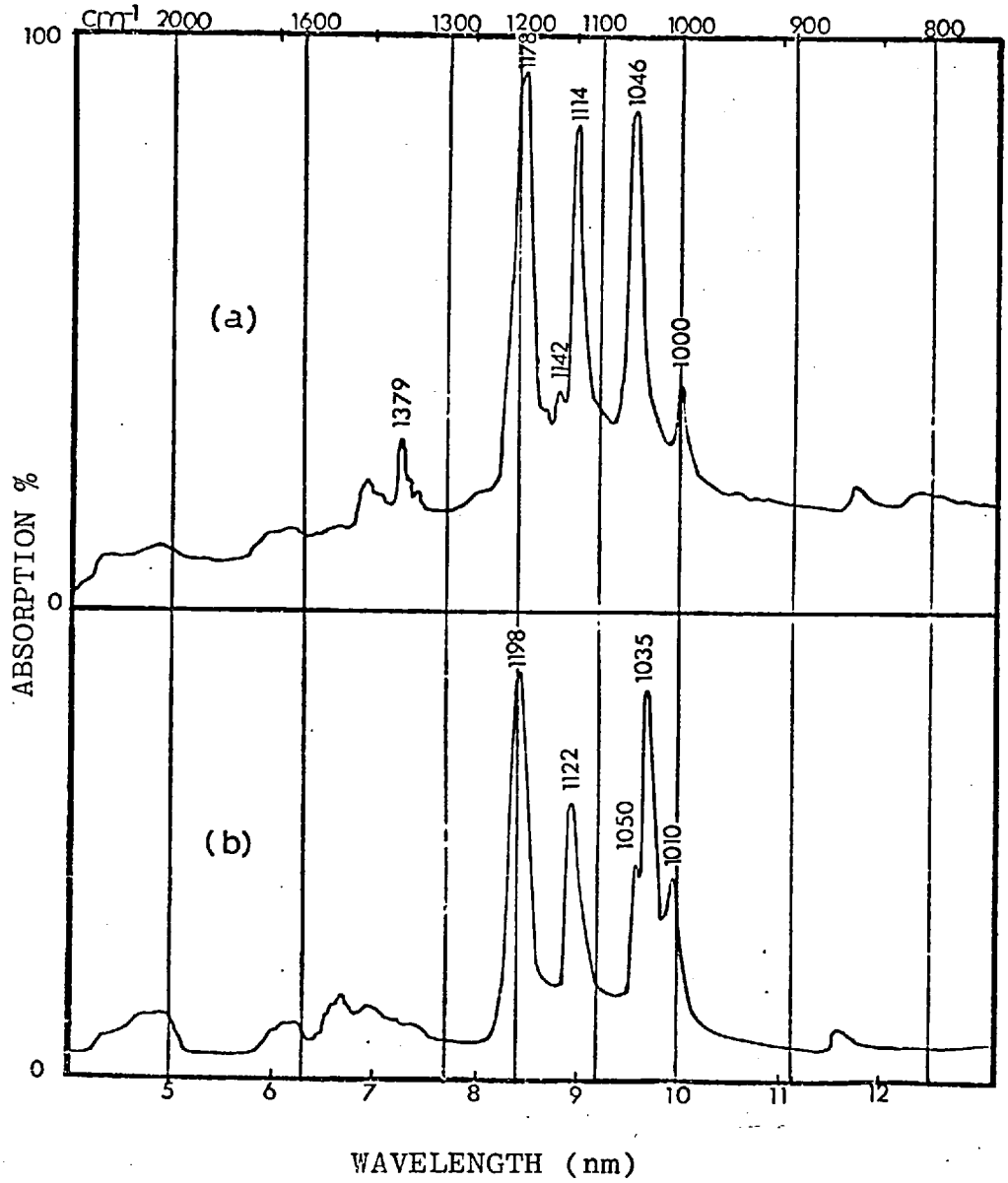


Fig.3.1 Infrared spectrum of
(a) aurous ethyl xanthate.
(b) cuprous ethyl xanthate.

Table 3.1 X-ray diffraction data for aurous ethyl xanthate.

I/I_o	Co-K_α radiation d(Å)	Cu-K_α radiation d (Å)
100	11.60	11.526
11	5.801	5.75
6	5.494	--
8	5.051	4.93
10	4.885	4.85
6	3.902	3.88
7	3.749	--
10	3.330	3.30
16	3.251	3.24
13	3.177	3.18
11	3.059	3.04
7	2.998	2.97
9	2.942	--
10	2.879	2.88
6	2.490	2.49
4	2.149	2.15
6	2.102	2.09

Parsons Spectromaster No.2 and the spectra are shown in Fig.3.1 and compared with the i.r. scan for cuprous xanthate. The spectra for AuX and Cu_2X are similar. The four major absorption peaks for gold xanthate are 1178, 1114, 1046, 1000 cm^{-1}, which compare well with the absorption peaks of 1198, 1122, 1035, and 1010 cm^{-1} for cuprous xanthate.

X-ray diffraction data.

X-ray diffraction data for gold xanthate were obtained from a smear mount scan using Co-K_α and Cu-K_α radiations. Silica was used as the standard. The results are shown in Table 3.1. The most characteristic intensity peak is at

d_{Co} = 11,60 Å or d_{Cu} = 11.526 Å .