

A study of some factors influencing the flotation characteristics of cassiterite

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A STUDY OF SOME FACTORS INFLUENCING THE

FLOTATION CHARACTERISTICS OF CASSITERITE

by

P. BUNNAUL, B.ENG. (MINING)

A thesis submitted for the degree of Master of

Engineering of the University of New South Wales.

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School of Mining Engineering Faculty of Applied Science September, 1981. I, the undersigned, certify that the work described herein was carried out by me at The University of New South Wales, and has not been submitted for a higher degree to any other University or Institution.

P. BUNNAUL

September, 1981.

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ABSTRACT

Cassiterite in primary deposits usually occurs as very fine grains. It is difficult to liberate and recover fine-grained cassiterite by conventional gravity concentration methods. An alternative method is flotation. Some aspects of cassiterite flotation including collector systems, effects of associated minerals, and kinetics of flotation processes were studied.

A micro-flotation cell was constructed for the study of the flotation of cassiterite with four collecting agents, being Aerosol-22, Aero-845 Promoter, S-3903 and S-4082, and effects of some associated minerals were established. It was found that S-3093 and S-4082 float cassiterite over a wide range of pH, from pH below 2 to pH10.2 for S-3903 and to pH8.2 for S-4082 while Aerosol-22 and Aero-845 Promoter float cassiterite in the pH range below 2.6 and 2.85 respectively. When galena and pyrite

are present in cassiterite ore galena can be selectively floated with sodium ethyl xanthate leaving cassiterite and pyrite in the nonfloated products. Pyrite can be selectively floated later with potassium amyl xanthate. Fluorite and apatite, when present, will produce a problem when floating cassiterite ore with S-3903 or S-4082 because they respond to both collectors in a manner similar to cassiterite. Suppressing fluorite with citric acid or aluminium chloride was studied but no improvement in selectivity was noted. Selective flotation of cassiterite from quartz and ilmenite with S-3903 was found possible. With S-4082 it was difficult to float cassiterite from quartz.

Kinetics of cassiterite flotation were studied using a 2.6 litre Denver flotation cell. It was found that the influences of the flotation rate and recovery rate controlling variables could be explained by three probabilities, being the probability of bubbleparticle collision, the probability of attachment or adhesion after collision and the probability of bubble-particle aggregate to withstand the disruptive forces. The rate constants of the flotation of cassiterite of various particle sizes were calculated and it was found that the rate constant for 0.0380 + 0.0240 m.m. particle size was maximum, being $55 \times 10^{-3} \text{ sec}^{-1}$ for first order rate constant. The investigation showed that cassiterite flotation is more likely to fit the first order rate equation more than the zero and second order rate equations.

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CHAPTER ONE

TIN MINERALS

1.1 Introduction

There are some 18 known tin-bearing minerals (see Table 1.1.1). The majority of these minerals are rare. Cassiterite or tin stone is the major source of commercial tin metal. It is composed of stannic oxide (SnO_2) . A minor source of commercial tin metal is stannite which consists of tin, copper and iron sulphides (Cu_2SnFeS_4) . It may occur in association with cassiterite as in some deposit such as in Cornwall and also in the tin lodes of Bolivia. Cassiterite is mined from either lode (primary) or alluvial (placer) deposits. In alluvial deposits, cassiterite occurs as free coarse to medium sized grains in sands and gravels. It is normally recovered by dredging and concentrated by gravity separation processes, so that low grade

deposits may be worked economically. Primary tin ore needs more complicated treatment because of the complex mineral associations, very fine grain size of the cassiterite and the necessity for comminution to obtain liberation. However, this kind of deposit is becoming more important while the cassiterite from alluvial deposits is slowly being depleted.

Table 1.1.1 Tin-bearing minerals

	Name	Chemical Formula	Occurrence
1	Native tin	Sn	Rare, in gold placers in Australia
2	Cassiterite	SnO2	World wide; main tin mineral
3	Stannite	Cu ₂ FeSnS ₄	Common, but less important than cassiterite
4	Teallite	PbSnS ₂	Bolivia; rare
5	Herzenbergite	SnS	Bolivia; rare
6	Franckeite	Pb5Sn3Sb2S14	Bolivia; Tasmania; unimportant
7	Cylindrite	$Pb_3Sn_4Sb_2S_{14}$	Bolivia; rare
8	Canfieldite	Ag ₃ SnS	Bolivia, Tasmania; rare
9	Hydrocassiterite	H ₂ SnO ₃	Bolivia, Congo; locally important
10	Thoreaulite	SnTa ₂ O ₇	Congo; locally important
11	Nardenskioldine	CaSn(BO3)2	Norway, South-West Africa; very rare
12	Hocksckildite	PbSnO ₃ nH ₂ O	Bolivia; rare
13	Stokesite	H ₄ CaSnSi ₃ O ₁₁	Cornwall, England; very rare
14	Arandisite) tin silicato	Nigeria; rare
15	Nigerite		South-West Africa; rare
16	Hulsite] complex borates	Seward Peninsula, Alaska; rare
17	Paigeite		Sewand Peninsula, Alaska; rare
18	Malayaite	CaSnSiO ₅	Cornwall, England; rare

(Extracted from C.L. Sainsbury et.al.⁽³⁾)

1.2 Physical and chemical properties of cassiterite

Cassiterite is tin oxide and when pure it contains 78.8 per cent Sn. Sometimes it contains up to 3 per cent of Fe⁺⁺⁺ substituting for Sn and may contain minor quantities of niobium, tantalum, tungsten or manganese⁽³⁾. Its crystals belong to the tetragonal prisms terminated by tetragonal pyramids. Twin crystals are common, both contact and penetration twins⁽¹⁾. Cassiterite also occurs massive or as grains. Its relative density is between 6.8 to $7.1^{(2)}$ and its hardness is 6.5 according Moh's scale⁽¹⁾. Its color is usually brown to black but may vary from white to yellow (wax-tin) or red (ruby-tin)^(1,2). It often shows color zoning⁽²⁾. Luster is adamantine and streak is white, greyish, or brownish⁽¹⁾. Cassiterite has three cleavages. It is brittle with a sub-conchoidal fracture⁽¹⁾.

1.3 Mode of occurence

3.

Cassiterite occurs in both primary (lode) or placer deposits. Placers (or alluvial deposits) are derived from primary deposits by the action of weathering. Because cassiterite is chemically and physically resistant to erosion and its relative density is high, it is often deposited downstream from the weathered origin by streams or river deposition taking place where the velocity of the streams decreases and its accumulation with gravels, sands, silts and clay form placer or alluvial deposit. The particles of cassiterite in this kind of deposit are mostly free. Minerals associated are varied and their nature depends on the geology and drainage pattern of the surrounding area⁽⁴⁾. The associated minerals may be ilmenite, monazite, zircon, topaz, tourmaline, magnetite, columbite-tantalite and silica.

The principal lode tin deposits are closely related to biotite or biotite-muscovite granite except the Bolivian deposits which in the past were considered to be related to subvolcanic dacite or quartz latite⁽³⁾. Cassiterite is commonly accompanied by minerals containing boron and fluorine (fluorite, topaz, danburite and tourmaline) which leads to the beliefs that it is of pneumatolytic origin. The genesis of tin deposits is still not fully understood. However, many investigations have been attempted to ascertain the concentration mechanisms of tin in various geological environments. The prevailing views on the genesis of tin deposits may be concluded as follows:

> a) The classical pneumatolytic theory said that residual liquids rich in "mineralizers" escaped outward from crystallizing magma, and tin was carried as the halide and deposited as cassiterite⁽³⁾. Recently, Eadington and Giblin (1979)⁽⁵⁾ suggested that the transportation

and precipitation of cassiterite occurred through a chloro and fluoro-complexing mechanism.

- b) Burasukov, (1975) and Hesp(1974)⁽⁶⁾ suggested that biotite is the main tin holding mineral. Tin can replace cations of similar atomic radii in biotite lattice. Burasukov⁽⁶⁾ proposed that tin was released from biotite by chemical reaction with NaF vapours during the cooling stage of granitic magma.
- c) The transport of tin may occur as the alkali stannate, e.g. Na_2SnO_3 , in hydrothermal solution⁽³⁾.
- d) Many tin deposits have recently been reexamined and are now considered volcanic exhalative in $origin^{(7,8,9)}$. A model of volcanic exhalative tin deposits has been postulated recently by Plimer⁽¹⁰⁾. He said that this

type of deposit commonly occurred in thick deep water sedimentary sequences. The sequence is intruded by granites with economic Sn or W mineralization. If these sequences are melted as a result of tectonic stress, the association of Sn from sedimentary rocks and granitic rocks will form tin deposits.

1.4 Types of lode tin deposits

Primary tin deposits frequently occur as veins traversing granites, metamorphosed sedimentary rocks or, in some instances, metamorphosed limestone to form lodes, fissure veins, stockworks, and disseminated replacements⁽¹¹⁾. G.L. Sainsbury and J.C. Hamilton⁽³⁾ classified primary tin deposits into 6 types.

1.4.1 Pegmatite

Pegmatites often contain cassiterite in association with columbite-tantalite and other rare minerals⁽³⁾. Most pegmatites containing cassiterite are found in rocks of Pre-Cambrian age such as those in Monano, Congo and Minas Gerais, Brazil where the tin content seldom exceeds 0.3 per cent $\operatorname{Sn}^{(3)}$. Cassiterite in this type of lode is distributed in pockets about 3-4 m.m. in diameter and the grain size is usually medium to coarse (e.g. from 1 m.m. to 2 m.m.)⁽¹¹⁾. Felspars are commonly associated and the following minerals may be present; quartz, lithium-mica, albite, tourmaline, columbite-tantalite, beryl and spodumene⁽¹¹⁾.

1.4.2 Contact-metamorphic deposits

Contact metamorphic deposits are rare and generally consist of cassiterite or malayaite⁽³⁾ in tactites near granites. The cassiterite is associated with garnet, magnetite, pyroxene, fluorite, various sulphide minerals and, sometimes, beryllium minerals. Grades of tin in the lode are generally less than 0.5 per cent tin.

1.4.3 Pneumatolytic-hydrothermal deposits

Tin occurs near or in biotite granite and the orebodies are generally replacement lodes or fissure fillings in diverse type of country rocks. The regional zoning leads to a wide variation in mineralogy within individual deposits⁽³⁾. In or near granite, cassiterite usually occurs in greisen (quartz-mica rock) or quartztopaz-tourmaline rock which may be associated with numerous basemetal sulphides, wolframite and fluorite, while the lodes farther

from the granite contain stannite and other complex tin-bearing minerals⁽³⁾. Apart from cassiterite, base-metal sulphides are usually main products from this type of deposit. Cassiterite is typically finely disseminated (usually 0.001 m.m. or less in grain diameter generally not more than 0.2 m.m. and seldom up to 1 m.m.)⁽¹¹⁾. The main feature of the deposit is the high iron content.

1.4.4 Subvolcanic or tin-silver deposits

Cassiterite occurs in veins in or near subvolcanic masses of dacite, quartz latite, rhyolite or biotite granite. Apart from cassiterite, the deposits may contain a high percentage of sulphide minerals containing Sb, Ag, Bi, As, Pb, and Zn. Strong telescoping of the deposits as a consequence of near-surface deposition has resulted in liberation of the cassiterite and hence in subsequent concentration⁽³⁾. Bolivian deposits belong to this type $^{(3)}$.

1.4.5 Fumarole deposits

Cassiterite occurs in vein fillings in fractures in tertiary lavas and is generally intergrown with specular hematite. The veins are bordered by kaolinized rock in which cassiterite is distributed as minute grains. Such deposits are locally widespread but small.

1.4.6 Disseminated deposits

Cassiterite occurs as disseminated grains in granite. The granite may show various types of alteration such as tourmalinization, formation of topaz or fluoritization, and may contain other rare mineral such as columbite, zircon and rare-earth minerals⁽³⁾. In areas of deep tropical weathering such as South East Asia such deposits are the source of large and rich placers⁽³⁾.

The principal lode deposits are of the pneumatolytichydrothermal and tin-silver types (3).

1.5 Location of world tin deposits

World tin deposits are confined to a comparatively small number of areas and the majority of them are located in South East Asia and Bolivia. The biggest and the most important tin belt of the world is the tin field in South East Asia which is lying from lower Burma to Thailand, Malaysia and Indonesia. Most of tin occurs in alluvial deposits although lode deposits are mined. Bolivian tin field is the world's second largest tin field. All deposits are primary or vein deposits. Other tinfields are in Great Britain (Cornwall), Germany (Erzgebrige deposit), Portugal, Spain, Russia, Finland, Nigeria, Congo, Rhodesia, South Africa, ^{Zaire}, Brazil and Australia. Australian tin deposits occur in New South Wales, Queensland, Victoria and Tasmania. Tin occurs as lodes, in stockworks and alluvial deposits.

1.6 Grade of mineable deposits

The minimum grades of ore which can be profitably worked vary widely depending on exploiting methods, types of the deposits, the size of ore deposits and fluctuations in market price of the metal. The grade limit for gravel pump mining is around 0.01-0.02 per cent Sn. When dredging is employed the ground which contains as little as 0.0066 per cent Sn can be economically mined, such as that in Malaysia⁽¹⁴⁾.

Because of the complexity of liberating associated minerals and the fineness of cassiterite particles produced by comminution, the minimum content of tin for primary deposits is much higher than

that for placer deposits. It is partly controlled by the recovering methods and by the value of by-products, i.e. associated economic minerals. The limit fluctuates between 0.3 and 1.0 per cent Sn and is seldom less than 0.1-0.2 per cent Sn (with cassiterite occuring in pegmatite and quartz-cassiterite deposits). Examples of grade of ore mined in various deposits are shown in Table 1.6.1.

While the easily exploited deposits are becoming exhausted, the large low grade tin deposits tend to be more interesting. With the development of new technology and the fact that prices of tin metal tend to be higher, lower grade tin deposits become more possible to be exploited.

Table 1.6.1

Grade of primary ore mined in various mines.

Mine	Characteristic of ores	Grade of ore mined	References & year of publication
Catavi, Bolivia	Cassiterite occurs as a microcrystalline form and the gangue minerals are a great variety of sulphides, quartz and many silicates.	0.38-0.40%Sn	Rich, P.J.H. ⁽¹⁴⁾ (1980)
Renison, Australia	The feature of the deposit is a minutely disseminated cassiterite-sulphide ore. Sulphides contents may be up to 60 p.c.	0.9-1.1%Sn	Murach, N.N. et al ⁽¹¹⁾ (1967)
Aberfoil, Australia	Cassiterite occurs with tungsten as large crystals in quartz vein and there are some contents of sulphides.	1%Sn 0.5%WO ₃	Murach, N.N. et al ⁽¹¹⁾ (1967)
Mawchi, Burma	Cassiterite is associated with tungstenite, scheelite and occurs as coarsely disseminated in quartz, granite and altered schists.	1%Sn 1.25%WO ₃	Murach, N.N. et al ⁽¹¹⁾ (1967)
Monano, in Katanga; Zaire	The ore belongs to pegmatite type. By-products produced are tantalite, columbite and thoreaulite.	2.2kg/m ³ (0.13%Sn)in 1971, and 1 kg/m ³ (0.06%Sn)in 1974.	Rich, P.J.H. ⁽¹⁴⁾ (1980) The Geo'-Mines Company ⁽¹⁵⁾ (1967)
Kitololo, Congo	The ores belongs to pegmatit types by-products produced are columbite-tantalite, beryl and spodumene.	e In deeply weathered parts may be as low as 0.1%Sn and not more than 0.3%Sn in unweathere parts.	Sainsbury, C.L. (3) and Hamilton, J.C. (1967)

1.7 World tin production

From 1851 to 1978 the Western world has produced 13,254,000 tonnes of tin. More than 79 per cent of this amount came from Malaysia, Bolivia, Indonesia and Thailand⁽¹⁴⁾. (See Table 1.7.1) Malaysia is the largest world tin producer. Most of its tin is produced by gravel pumping or dredging from alluvial deposits. Malaysia produced 4,817,500 tonnes of tin between 1851 and 1976. The annual production reached 76830 tonnes in 1972 and since then it has declined. Bolivia is the second largest tin producer, at about 30,000 tonnes a year. Almost all of Bolivian tin comes from primary The third and the fourth largest tin producers are deposits. Indonesia and Thailand respectively. As in Malaysia, most of their tin is produced from alluvial deposits or off-shore deposits, which are mined by gravel pumping and dredging. The other sources of western world tin are from Zaire, Nigeria, Congo, United Kingdom,

Australia, Brazil and Burma. In Australia tin is produced by underground mining from the primary deposits in Tasmania and New South Wales. Minor tin production comes from alluvials in Queensland, New South Wales and Western Australia. Yearly production of Australian tin since 1972 has been about 10,000 tonnes⁽¹⁴⁾. Tin is also produced in the USSR and China. The USSR yearly production has reached 31,000 tonnes in 1978 and Chinese tin production is about 20,000 tonnes a year⁽¹⁴⁾.

Year	Production, t Zaire	Nigeria	Bolivia	Indonesia	Malaysia	Thailand	Other countries	World
1900			9197	17900	43800	3962	8876	83700
1901			13123	16029	47490	3962	9961	90500
1902			10603	15705	47223	3962	7932	85000
1903		6	12532	15691	50761	3250	9704	92000
1904		5	12901	13961	51782	5199	9410	93000
1905		2	16581	12340	51806	5283	9933	96000
1906		12	17623	16113	47747	5308	11545	98000
1907		145	16606	16220	49251	4380	12988	99500
1908		384	17691	17223	51683	4849	13852	106000
1909		219	21340	20633	51566	4794	14300	112800
1910		582	23128	21746	46652	4974	14741	111800
1911		1046	22433	20254	48257	6024	15103	113100
1912		2125	23025	20046	50607	6690	15870	118300
1913	7	4074	26354	26354	52199	6855	17057	127800
1914	45	4525	22354	19787	51453	6695	14264	119200
1915		5090	21793	20320	50624	9141	15052	122000
1916	93	6030	21143	22197	47978	8905	14126	120500
1917	107	6134	27856	20955	43588	9300	12561	120500
1918	107	6212	29279	20133	40745	8976	11995	117400
1919	160	6017	27387	21235	39868	8458	11742	114900
1920	397	5919	29540	21911	37518	6300	12619	113700

Table 1.7.1 World tin production, 1900-78 (After R.J.H. Rich⁽¹⁴⁾).

to be cont.

Table 1.7.1 cont.

Year	Production, t Zaire	Nigeria	Bolivia	Indonesia	Malaysia	Thailand	Other countries	World
1921	637	5331	28956	25758	36821	6248	7634	111300
1922	908	5390	28127	30004	37820	7090	6205	115500
1923	1001	6167	31126	25356	40012	7745	8234	119700
1924	1008	6523	32057	31963	47668	8079	9522	136800
1925	1107	6582	32739	31827	48917	7987	10486	139600
1926	1155	7803	30541	32360	48555	7089	11743	139300
1927	885	8477	36380	34274	55261	7553	12503	155300
1928	796	9606	42066	35778	65537	7647	12171	173600
1929	1022	11295	47079	36494	73483	10098	12858	192300
1930	662	8767	38756	35461	67964	11236	11579	174400
1931	192	7218	31233	23603	25441	12646	9654	140000
1932	687	4419	20912	17529	29672	9444	11237	93800
1933	1988	3650	14960	13007	25271	10347	12148	81300
1934	4425	5080	20964	19997	38204	10808	14659	114100
1935	6234	6661	27602	20507	43046	10034	16849	131000
1936	7419	9893	24459	31220	67837	12937	19053	172800
1937	9249	10954	25530	38181	78502	16163	19631	198200
1938	9823	9120	25894	30203	44063	15057	19909	154100
1939	8277	9577	27915	27187	48174	15887	20360	157300
1940	12449	12156	38528	41994	84328	17389	19580	226500

to be cont.

Table 1.7.1 cont.

Year	Production, t Zaire	Nigeria	Bolivia	Indonesia	Malaysia	Thailand	Other countries	World
1941	15999	12256	42738	54225	80670	16080	20826	242800
1942	16049	12601	38904	10056	15999	79 58	14955	116500
1943	15746	12863	40958	19390	26416	5933	15235	136500
1944	15998	12712	39339	7120	9457	3348	10893	98800
1945	15991	11403	43165	1066	3202	1803	10664	87300
1946	13299	10498	38219	6525	8566	1072	10003	88100
1947	11200	9279	33798	16190	27458	1423	10312	109600
1948	11684	9384	37933	31102	45532	4307	8755	148700
1949	12315	8964	34659	29497	56086	7940	10466	160000
1950	11946	8390	31712	32616	58691	10529	11017	164900
1951	11956	8675	33662	31481	58314	9655	11342	165100
1952	12065	8448	32470	35563	57978	9630	11795	167900
1953	13440	8346	35382	34363	57306	10288	13709	172800
1954	13357	8053	29285	36434	61907	9932	12781	171700
1955	13263	8288	28367	33900	62223	11199	13408	170600
1956	13037	9313	27271	30535	63292	12680	12963	169000
1957	12677	9765	28240	28166	60241	13744	12852	165700
1958	9844	6329	18012	23571	39073	7841	12931	117600
1959	9337	5611	24191	21958	38125	9838	12045	121100
1960	9349	7797	20542	23346	52810	12274	12915	138700

Table 1.7.1 cont.

Year	Production, t Zaire	Nigeria	Bolivia	Indonesia	Malaysia	Thailand	Other countires	World
1961	6675	7903	20994	18871	56924	13483	13809	138600
1962	7312	8341	22148	17586	59540	14913	14053	143800
1963	7166	8869	22669	13154	60908	15834	15095	143200
1964	6596	8861	24586	16607	60964	15847	16254	148700
1965	6311	9700	23406	14934	64689	19352	16383	154400
1966	9832	9687	25930	12726	69986	22926	18714	166300
1967	7111	9489	27720	13819	73275	22850	20514	172800
1968	6264	9803	29567	16898	76270	23979	21487	183200
1969	6647	8741	30045	16541	73322	21091	23435	178100
1970	6458	7959	30100	19092	73794	21779	27252	185700
1971	6440	7326	30290	19767	75445	21689	25496	187100
1972	5960	6731	32405	21766	76830	22072	29679	195900
1973	5442	5828	28568	22648	72260	20921	28451	188800
1974	4675	5455	29151	25630	68122	20339	28380	184100
1975	4574	4652	31958	25346	64364	16406	32410	181200
1976	3950	3710	30315	23418	63401	20453	34789	179900
1977	3900	3267	33624	25921	58703	24205	39294	188600
1978	3450	2751	30881	27410	62650	30186	40416	198200
Sub-total	L							
1900-78 1851-99	438660	521244	$2191521 \\ 46560$	1838694 429454	4133967 804884	874550 105075	1225424 653749	11214600 2039700
Total	438660	521244	2238148	2268148	4938851	979625	1879173	13254300

14.

Fig. 1.8.1 Annual tin prices and buffer stock floor and ceiling prices, 1957 - 1972 (after Taylor, R.G.⁽¹⁷⁾)



1.8 World tin market

There are four major tin markets which are Penang Market in Malaysia, London Metal Exchange (LME), New York dealer market and G.S.A. (General Services Administration). The last two markets are located in New York, U.S.A.. Penang Market and LME are the key markets for tin. Their prices are quoted to reflect the world market for tin. New York dealer market quotes daily tin prices which are often based on LME and Penang prices, and their prices will reflect only local market factors.

Tin prices are rather stable. This is partly because of an activity of an organisation called ITC (The International Tin Council). ITC was established in 1956⁽¹⁸⁾. It is composed of both producing and comsuming nations. The producer group includes the six major producing nations; Malaysia, Bolivia, Indonesia, Thailand, Nigeria and Zaire⁽¹⁸⁾. Two of its objectives are to provide for

adjustment between world production and consumption and to prevent excessive prices fluctuations (16,18). To carry out its objectives, two key instruments, buffer stock operation and export controls are employed. The buffer stock's function is to maintain the prices of tin within a prescribed ceiling and floor price (according to the fifth tin agreement, the market prices for considering being the Penang prices (16)). Export controls are operable when the market prices are below the floor price due to the fact that world production is more than consumption and the buffer stock cannot afford to buy the excess amount into the stock. Fig.1.8.1 shows the annual tin prices and buffer stock prices.

U.S.A. has a significant size of tin stockpile, over 200 thousand tonnes as of December, $1977^{(16)}$. The sale of tin from this stockpile through GSA has a considerably effect on the world tin

prices and is claimed to have a greater stabilizing forces than ITC buffer stocks. (U.S.A. has just been included in ITC in June, $1975^{(16)}$).

1.9 Uses of tin

The properties of tin supporting its position in technology are low melting point, alloy forming characteristics, resistance to corrosion, non-toxicity and good appearance⁽²⁰⁾. There are two major uses for tin which are: ^(18,19,20)

- a) for tin plate, principally for containers, and
- b) for alloying with lead to make solder, babbitt metal, and other so-called white metal products.

Tin plate consumes the major part of tin production. Most of the tin plate is used for containers especially for food and drink. The factors for increasing demand for tin plate are the increases in population and better living standard, although there are the competitions

by aluminium, glass, plastic and tin-free metal⁽¹⁸⁾.

Solder is another major use of tin. In all joint-forming operations, particularly for electrical circuits, the concept of reliability is very important. Mass soldering with tin-lead alloys can ensure this concept. The important competitors which have replaced solder in many applications are silver brazing alloys and epoxy resin⁽¹⁸⁾.

Tin alloys for the automotive industry are another important use of tin. Most bearings have been made of tin-rich alloy (babbitt), but due to the increased power and speed of modern engines some tinrich alloy bearings have been replaced by copper-lead alloy which gives higher fatigue strength. After the invention of aluminium-tin bearings with higher fatigue strength than that of copper-lead alloys, tin use for bearings has increased⁽¹⁹⁾. Cast iron, when it contains about 0.1 per cent of tin has improved wear resistance, with greater uniformity of hardness and better retention of shape on heating. This kind of cast iron is used for cylinder blocks, cylinder heads, piston rings, clutch plates, etc., in the automotive industry, and for a wide range of uses including tool beds and dieblanks for press tools.

Tin alloying with copper to make bronze and brass, the high strength and corrosion-resistant metal is another use of tin. Bronze which contains some amounts of magnesium gives very useful age-hardening properties coupled with relatively high electrical conductivity. This alloy could well be used for such components as springs and electrical contacts (20).
CHAPTER TWO

REVIEW ON CONCENTRATION METHODS FOR CASSITERITE

2.1 Introduction

Methods of cassiterite beneficiation depend on the type of deposit especially the mineralogical composition of the ore. Because of its high relative density, cassiterite can be separated from gangue minerals by gravity concentration. This has been the basis of tin dressing. However, most of gravity concentrators are most effective for cassiterite coarser than 0.074 m.m. For finer cassiterite its efficiency decreases and when treating cassiterite finer than 0.010 m.m. recovery is $low^{(21)}$.

Cassiterite from placer deposits is amenable to gravity concentration since it has been liberated from gangue minerals and its

particle size is relatively coarse, possibly above 3 m.m. in diameter⁽²²⁾. Comminution is not necessary. Simple gravity concentration can be employed efficiently and other heavy minerals contained in the gravity concentrate can be removed later by magnetic, electrostatic separator or froth flotation.

In primary deposits, the ore must be comminuted to liberate the economic minerals. Some cassiterite may be slimed during comminution due to its brittle property. This causes serious problems in concentration by gravity processes. In many primary deposits, cassiterite grains are very fine, for example the Renison mine⁽¹¹⁾ where cassiterite occurs finely disseminated in sulphides. Its grain size is finer than 0.074 m.m. and about 19-40 per cent of cassiterite is finer than 0.020 m.m. This results in serious losses of fine cassiterite in the tailing when gravity concentration is employed. Classification and desliming processes are necessary prior to concentration in order to reduce slime and thus improve the efficiency of concentration.

Slimes are a major problem in treatment of primary cassiterite ores. Its presence in gravity concentration feed influences the results due to an increased viscosity of the pulp⁽²⁹⁾ and this also increases losses of cassiterite to the tailing. When floating sulphides from cassiterite, slimes and fines of cassiterite tend to be lost to the sulphides concentrate such as that in Renison mine⁽²²⁾ where about 53 per cent of losses of tin occurs in the sulphides flotation process.

One of the problems that makes primary cassiterite ore treatment difficult is the complexity of the association of cassiterite and gangue or other value minerals. The associated minerals are generally heavy metal sulphides or arsenides, silicates and other oxide minerals. Since they are difficult to remove they reduce the grade of the concentrate. Further, the presence of Ca⁺⁺, Fe⁺⁺ and Fe⁺⁺⁺ ions

in the pulp affect the flotation of cassiterite (31, 32, 33).

Due to the problems described above, concentrate grade from treatment of primary ore may be low. Any attempt to further upgrade the concentrate reduces overall percentage recovery. This is very different from placer mining where the concentrate grade may be as high as 65 per cent Sn or more at about 80 per cent recovery while the concentrate grade from the treatment of primary ore may be as low as 20 per cent Sn or less at a recovery below 50 per cent (24).

2.2 Mining and dressing alluvial cassiterite ore

Two major mining methods employed for mining alluvial (or placer) cassiterite ore are dredging and hydraulic mining.

2.2.1 Dredging

Dredging is used for mining large low grade deposits. An area for dredging is preferable relatively flat, however offshore operation are practicable. A dredge represents a high capital investment. After mining has been finished the dredge has limited salvage value because it is normally not practicable to move the dredge from one place to another place especially in-land dredges. This means that reserves must have a mine life that is sufficient to recover the high investment cost and is usually more than 15 years⁽²⁴⁾.

A common type of dredge is the bucket chain dredge where ground is dug by a number of buckets attached on the chain or ladder. Bucket size may be as large as 0.4-0.5 cubic meters⁽²²⁾. Digging efficiency of bucket chain dredges is relatively high but when the bed rock contains deep gullies which are usually rich in tin, the buckets cannot reach and recover cassiterite in the bottom of the gullies⁽²⁴⁾.

Furthermore, when dredging the deeper bed, it needs more power for driving the bucket chain or ladder. To mine such deposits, suction dredging is introduced. With the suction dredge, the ground is broken or loosened by high pressure water jets or cutters mounted at the end of suction pipe and is pumped to the dressing plant on the dredge. The limitation of using a suction dredge is that when a large amount of timber or grass is present in the deposit they often block the suction pipe or pump or cutter especially when using an in-land dredge⁽²⁵⁾.

The dressing plant on the dredge usually does not produce a final concentrate. The concentrate from here needs further upgrading in the plant on the shore. Tailing from the dredge is discharged directly to the rear of the dredge. This may cause some problems when the difference between water surface and bed rock level is not high, especially in in-land dredging. Excessive content of slime and/or clay in the tailing makes it settle slowly. This not only leads to tailing disposal problems $^{(25)}$, but also makes a problem in the dressing plant if the water in the pond is used.

2.2.2 Hydraulic mining

Hydraulic mining is suitable for mining hill-side deposits and small deposits in flat plains. Ground is broken or loosened by high pressure water jet from the monitor. The loosened material is carried by water flowing along the ditch to the sump where the gravel pump is situated for pumping the pulp to the dressing plant. Where the ground contains high contents of clay or is too compact, earth moving equipments or explosives are employed to break the ground prior to using the monitor⁽²⁷⁾. Large stone and boulders are picked up at the boulder trap at the sump. Common size of gravel pump, especially that used in Thailand, is 203 m.m. (or 8 inches) in diameter of both suction and delivery pipe⁽²⁷⁾. In some areas where the topography allows building a water reservoir at the top of the hill, the power from this high static head water is used in pumping material from the sump to the dressing plant. This is called an "hydraulic elevator".

2.2.3 Primary concentration

Before World War II, simple concentration was employed for treating tin ore because high grade deposits containing coarse grains of cassiterite were still available. Primary concentration was usually done in palongs or sluices (28). Later, jigs were introduced and they are widely used now in place of palongs and sluices. However, palongs are still widely employed in Thailand and Malaysia due to lower capital investment and no need of special skill to control the equipment as is required for jigs (4,26). A palong is a wood or cement channel. Its size is generally 55-60 metres long and 4.9-5.5 metres wide for single or 3-3.7 metres for twin palong. Its slope varies from 1:12 to 1:24. Along the length of palong, there are riffle boards 50 x 75 m.m. in size placed transversely at every 1.8 to 3.0 metres intervals in order to trap the heavier particles. Pulp density of feed is controlled by dewatering box or "kui" mounted at the head end of the palong⁽²⁶⁾. Palongs work satisfactorily when treating coarse tin ores, but for ores where the particles to be recovered are less than 0.100 m.m. the recovery is seldom over 50 per cent⁽²⁸⁾ and it seems to be very difficult to recover tin ore finer than 0.075 m.m. Sometimes coarse cassiterite particles are lost to the tailing due to careless control of water flow or raking the sand bed during the cleaning period. After studying tin losses in palong tailings, Suwanpradip⁽²⁶⁾ noted that even the particles of cassiterite up to 1.00 m.m. (16 B.S. mesh) in size were still found in the tailing. He explained that it was

probably because the sand on the floor of palong was too compact and the flow of water was too strong so that the cassiterite did not have enough time to settle.

Jigs are widely used on dredges. The separation is controlled by the pulsation of water through the screen and suction of water on the return stroke. The heavier minerals such as cassiterite settle quicker than the lighter gangue and stratify in the jig bed passing through the screen into the hutch. The lighter gangue remaining in the upper zone of the jig is carried over the top of the jig by the water stream.

Conventional jigs are usually rectangular. A horizontal screen is mounted near the top of the tank and the section below the screen is called the "hutch". The mechanism for inducing pulsion may be a plunger or pulsating diaphragm. On the jig screen is a layer of material which is called "ragging layer" and is coarser than the screen aperture. Common jig bed material is hematite which has been roughly rounded in a ball mill or cement mixer. Thickness of ragging layer for primary jigs is approximately 80 millimetres⁽²³⁾.

The first type of jig used in place of palong was the Harz jig. When the scale of production increased it was developed into a 4-cell diaphragm Harz jig. Other units include 4-cell Rouss jig, 4-cell Bendelari jig, 4-cell Pan-American jig and the Yuba jig⁽²⁸⁾. A recent type of jig is the I.H.C. Cleaveland jig. It is a radial jig in which the water pulsation is made by an hydraulically driven diaphragm. It is claimed that its efficiency and capacity per unit area is greater than for conventional jigs. Even more important is that the water consumption for hutch water is less or none and it can recover finer cassiterite than a conventional jig. Another advantage is that it requires less space which is good for using on a dredge ^(22,23,28,29) Due to the fact that cassiterite in alluvial deposits is usually finer than 3 m.m.⁽²⁸⁾ the coarser particles are rejected before concentration. In gravel pump mining, when palongs are employed, bar grizzlies are used to screen off coarse particles. The slope of bar grizzlies is generally 45° and the set between steel bars ranges from 6 m.m. to 2.5 m.m. Overall size of bar grizzlies is about 1 m. wide and 2 m. long⁽²²⁾. Grass and gravels which are often stuck between the bars are forked out by a man working there. A revolving screen may be employed in some gravel pump mines. Most dredges usually use revolving screens. The screen holes range from 9 m.m. to 12 m.m. in diameter (24). The common size of the revolving screen is about 2 m.-3 m. in diameter and 12 m. -21 m. long (overall length). The screen length is about 9 m. to 12 m. $^{(28)}$. Its slope is about 1:12 and it turns at around 6 to 8 $\text{RPM}^{(23)}$. A number

of nozzles are mounted inside along the revolving screen for spraying water with high pressure up to 700,000 kg/m² (1000 psi)⁽²⁸⁾ for disintegrating clay which normally tends to form clay balls. If clay balls are formed, cassiterite contained in them will be lost to the tailing.

Undersize from the revolving screen is pumped to the distributor for feeding into each jig. The pulp from a revolving screen is low in per cent of solids. Therefore it needs thickening prior to being fed into the jig. The optimum value for primary jig feed is around 30 per cent solids⁽²⁵⁾ but it usually varies from 10 to 50 per cent depending on the feed preparation method. Feed preparation will be mentioned later in this chapter.

Tailings from primary jigs are rejected as is the oversize from revolving screens. In case the tailing contains high contents of fine cassiterite, it is screened to reject coarse particles, such as at $1.0 \text{ m.m.}^{(28)}$, and the undersize is treated in another jig. Cassiterite recovered from this is usually finer than 0.150 m.m.

The concentration ratio for primary jigs when a 4-cell conventional jig is used is generally about 20:1 but when a 2-cell jig is used the concentration ratio at least 10:1 is needed to obtain as high a recovery as obtained when using a 4-cell jig⁽²⁸⁾.

The concentrate from a primary jig is further upgraded in secondary and tertiary jigs. Tailing from each stage is recycled to the former stage.

The principal objective of primary concentration is to reject a major portion of the gangue with maximum tin recovery producing tailings with a minimum content of tin. Therefore the primary concentrate grade is still low and needs further upgrading to achieve a saleable grade. Primary concentrate grade from palongs and jigs varies from 15 to 25 per cent $\operatorname{Sn}^{(24)}$.

2.2.4 Secondary concentration

Lanchute has been used for cleaning primary concentrates for a long time. Its efficiency depends mainly upon the skill of the operator. It is suitable only for treating coarse particles and for small scale production. When treating cassiterite finer than 0.252 m.m. the losses are severe $^{(26)}$. Shaking tables give higher efficiency and produce less losses. Shaking tables can work satisfactorily when treating cassiterite ranging from 1.670 m.m. to 0.050 m.m. $^{(28)}$. (That stated by J.E. Denyer $^{(24)}$ is from 0.297 m.m. to 0.074 m.m.) The Humphrey spiral is also employed but not widely.

In some gravel pump mines concentrate from the palong is preconcentrated in a jig prior to being upgraded in a lanchute or

on a shaking table.

2.2.5 Feed preparation

Per cent solid and uniformity of feed are the important factors for jig and shaking table performances. Per cent solid of undersize from a revolving screen is too low and not uniform depending on the characteristics of the ground being dug by the dredge or loosened by the monitor. Thickening for increasing per cent solid and making uniform feed is needed and it is usually done by a classifier. Another reason is that when the ground being mined contains a high clay content, not only low in per cent solid but the pulp also contains a lot of slime which lowers the jig efficiency⁽³⁰⁾. The common classifiers used for primary jig feed preparation are hydrocyclones or dewatering cones or boxes. Hydraulic classifiers such as the Willoughby and Stokes classifier are common for feed preparation for shaking tables (28). Dewatering cones are also used.

Because conventional hydrocyclones operating at high pressure have low capacities but high pumping costs, high-capacity low-pressure hydrocyclone (apex angle may be as large as 120°) may be used. The head of feed can be as low as 3 m. when separating at a particle size of minus 0.050 m.m. (25, 30).

If the overflow of hydrocyclone still contains a high content of fine cassiterite it may be reclassified by higher-pressure hydrocyclone and the underflow is treated in separate jig to recover fine cassiterite (28).

Feed preparation for lanchute is usually done in a Willoughby classifier. It is also used for shaking table feed preparation in some mines where the scale of production is small. For large scale operation a Stokes type of classifier is preferable because it works continuously and can produce several ranges of sized particles for feeding shaking tables separately.

2.2.6 Magnetic and electrostatic separation

Concentrate from gravity concentration still contains other heavy minerals such as ilmenite, monazite, columbite-tantalite, wolframite, magnetite, siderite, zircon, scheelite, garnet, etc. These are separated from cassiterite by means of the different properties in magnetic suseptibility and electrical conductivity. Some of these minerals are produced as by-products when their contents in the ore are large.

Cassiterite is non-magnetic mineral. It can be separated from magnetic or slightly magnetic minerals, such as magnetite, siderite, ilmentite, garnet and monazite, etc. in magnetic separators. Common and well-known magnetic separators are Rapid belt type and McClean which are pick-up types and the Carpco high intensity induced roll magnetic separator. All of these are dry magnetic separators. Selection of machine depends on mineral composition of the ore to be treated. McClean is a high intensity and single disc type. It is generally used for separating small amounts of cassiterite from large amounts of high magnetic minerals such as ilmenite and magnetite. McClean is not suitable when the ore contains minerals having a variety of magnetic properties, such as cassiterite mixed with ilmenite, monazite, columbite-tantalite, because its magnetic intensity cannot be adjusted. To treat this kind of ore a magnetic separator such as the Rapid is employed. Rapid magnetic separator is multi disc type. Its magnetic intensity on each

pole is adjustable. Therefore it can treat lower magnetic minerals (4,28)

Carpco induced roll is less popular than the pick-up type. In cases where there is no strongly magnetic mineral it can be used for separating medium magnetic minerals such as monazite from cassiterite when the medium magnetic minerals are finer than cassiterite.

Feed to the magnetic separator should be closely sized. The size limit of magnetic separators ranges from 1.680 m.m. to 0.074 m.m. for pick-up type and 0.841 m.m. to 0.149 m.m. for induced roll. Treating the ores finer than this usually encounters dust loss problems especially when induced roll is used⁽²⁸⁾.

Since cassiterite is a relatively good electrical conductor, it can be separated from non-conductor minerals such as zircon, monazite, scheelite, silica in high tension or electrostatic separators. It usually treats the ores ranging from 0.500 m.m. to 0.105 m.m. in size.

When treating finer ore, there are dust losses and the fines, especially non-conducting particles, adhere to the drum or agglomerate.

2.3 Dressing primary tin ore

Both open pit mining and underground mining are employed for winning primary tin ore. Run-of-mine ore may be blended before feeding to the treatment plant because of variations of the ore characteristics and composition from different areas of the mine.

Cassiterite is friable. Slime is normally produced during the liberation process. Design of comminution circuit is important including blasting at the mining faces. Blasting patterns must be designed to produce minimum overbreak and minimise the formation of primary slimes. As cassiterite usually occurs minutely disseminated or intergrown with other minerals, several stages of comminution are required. This leads to more chance of slime forming. To prevent overgrinding of cassiterite during grinding stage, stage grinding followed by gravity concentration is preferable in order to recover free cassiterite at as coarse a particle size as possible. Tailings and middlings are further ground before further concentration⁽²²⁾. At South Crofty mine⁽³⁴⁾ the products from fine crushing are screened in double deck screen (20 m.m. and 2 m.m.). The minus 2 m.m. fraction is treated in a jig to recover coarse free cassiterite and the tailings are reground. Most of treatment plants for primary ore include a crushing unit, preconcentration unit, grinding unit, tin recovery unit (for sand-size cassiterite) and fines and slimes recovery unit.

2.3.1 Crushing unit

Primary crushing is usually done in a jaw crusher or a gyratory crusher installed underground. Primary crushing products

may range from 100 per cent minus 75 m.m. to 230 m.m. $^{(4,34)}$. Further reduction is done in secondary and/or tertiary crushing stages using gyratory crushers or cone crushers in closed circuit with roll grizzlies or vibrating screen. Product sizes may range from 100 per cent minus 10 m.m. to 20 m.m.. Secondary crushing is usually followed by agitation in drum washers before entering the tertiary stage to remove slimes and fines. In some mines such as Wheal Jane $^{(34)}$ wet crushing is employed. The secondary stage is in closed circuit with a vibrating screen and screw classifier.

2.3.2 Preconcentration unit

Preconcentration after fine crushing is employed in many mines. This is to reject gangue minerals before the grinding stage, thus reducing the load for grinding units. At South Crofty mine and Geevor mine in Cornwall⁽³⁴⁾, about 30 to 40 per cent of gangue minerals in

the ores is rejected in preconcentration processes.

Heavy media separation (HMS) is widely used for this stage. There are two main types of HMS, static type and dynamic type $^{(29,35)}$. Cones separator which belong to the static type are used in South Crofty and Geevor mine $^{(34)}$. The feed size at South Crofty is -20 m.m. + 2 m.m. and that at Geevor is -16 m.m. + 6 m.m.. Units of the dynamic type are heavy media cyclones and the Dynawhirlpool (D.W.P.). Heavy media cyclones are used for small tonnages and the feed size usually ranges from 25 m.m. to 0.85 m.m. $^{(35)}$. Feed size for DWP ranges from 0.85 m.m. to 25 - 30 m.m. $^{(29)}$. D.W.P. has some advantages compared with heavy media cyclones. It need less pumping power because only medium and water need pumping into the inlet pipe at the lower end of D.W.P. Feed material is fed into the top of D.W.P. by gravity $^{(29,35)}$. When using D.W.P., a two stage system is usually needed. Tailing from the first unit is retreated in the second one in order to recover the fines lost in tailing.

Ferrosilicon is commonly used as a medium and the relative density of the medium pulp if of the order of 2.78 as used in South Crofty mine⁽³⁴⁾. Ferros-silicon can be recovered by wet drum magnetic separators and is demagnetised before being recycled to the HMS machine.

2.3.3 Grinding and tin-recovery unit

Stage grinding followed by gravity concentration is usually employed in this stage. By this method, overgrinding is reduced and thus losses of cassiterite as fines and slimes are minimised. Grinding is done in ball mill or rod mill. Ball mill or vibrating mill is used for regrinding of middlings (secondary grinding). Regrinding of middlings with a vibrating mill is practiced at Wheal Jane⁽³⁴⁾.

In spite of not being widely used, it is suggested by D.J. Ottley⁽²⁹⁾ that, with control of ball size and amplitude of vibrator the mill can reduce overgrinding of cassiterite and other brittle minerals.

Products from each grinding stage, including those from fine crushing, are usually cycloned to remove fines and slimes which are treated separately in fines and slimes recovery units. Primary grinding products, after removing fines and slimes by hydrocyclones, are classified into several fractions in hydrosizers or screens. Each fraction is concentrated separately on shaking tables. Tailings and middlings from the coarsest fraction are recycled to the previous grinding stage. Tailing from all of the finer fractions are discarded. Middlings are further ground and treated by tabling, the middlings produced being recycled to the secondary grinding unit.

As the capacity of shaking table is low (about 1 dry tonne per hour of feed⁽²²⁾), a large number of tables are required. Preconcentration of primary grinding products in jigs, spirals or the Reichert cones before upgrading by tabling is practiced in many mines. These concentrators are used also for scavenging the table tailings as well⁽²²⁾.

The Reichert cone was developed by Mineral Deposits Ltd. in Australia⁽²⁹⁾. It treats cassiterite effectively when the particle size ranges from 1 m.m. to 0.053 m.m.⁽²⁹⁾. Reichert cones are used at Ardlethan Tin N.L. in New South Wales, Australia for preconcentrating rod mill products, after screening at 1.190 m.m. size particles and removing minus 0.044 m.m. by cyclones⁽³⁶⁾. The reported recovery of tin in this unit is at about 80 per cent. Concentrate from Reichert cones is further upgraded by tabling.

2.3.4 Fines and slimes recovery unit

Cassiterite in primary deposits is often finely disseminated and when comminuted, slime is produced during the liberation process. The presence of slimes results in low recoveries. Slimes are removed and treated in separated units. Hydrocyclones and hydrosizers are used to remove fines and slimes (-0.076 m.m. and 0.053 m.m. such as at South Crofty mine⁽³⁴⁾). Fines and slimes recovery unit feed is usually recycloned at higher pressure $(34,500 \text{ kg per m}^2 \text{ or } 50 \text{ psi as at Wheal}$ Jane⁽³⁴⁾) to reject ultrafines (minus 0.005 or 0.010 m.m. depending on the type of concentrator used). Besides the recovery of ultrafines is very low, its presence results in bad separation because of its increasing viscosity of the $pulp^{(37)}$.

Fines and slimes treatment usually involves flowing film concentrators. Before Bartles-Mozley concentrators and crossbelt concentrators had been introduced, vanners, round frames and slime tables were used. The capacity of these concentrators is low. Attempts to develop flowing film concentrators had been made in order to improve the recovery of finer particles (or slimes) with as high efficiency as possible and to increase the capacity of the units. C. Mills and C.R. Burt⁽³⁷⁾ made an excellent review on the development of the gravity concentrator for treating fines and slimes using flowing film principles. According to this article, shear rate is the most important for producing separation forces. When using round frames, buddles, strakes and Denver Buckman tilting frames, where shear rate depends on the velocity of the flowing film, fines are normally lost due to excessive turbulence. Frue vanners and shaking tables produce rapid shear rate but fines are still lost due to excessive turbulence. In 1958, Burch, C.R. introduced shaken helicoid where an orbital shear was produced. However, this unit still had a low capacity. Using the principles from shaken helicoid, Mozley developed

the Mozley frame concentrator and, after that, joined Bartles to develop this concentrator commercially. This unit can recover cassiterite down to 0.005 m.m.. Bartles crossbelt concentrator was developed later which can produce higher grade concentrates.

2.3.4.1 Bartles-Mozley concentrator (B-M concentrator)

On other flowing film concentrators, except Burch's shaken helicoid, only forward flow action is present. To obtain more shear rate, which depends on flowing film velocity, steeper inclination of surfaces is needed. This produces turbulence which causes losses of fines. B-M concentrator combines forward flow action together with orbital motion in the plane of collecting surfaces. Orbital shear produced by orbital motion allows the lower deck angle used on B-M concentrator, thus less or no turbulence is present. This

Fig. 2.3.4.1 Schematic plan of Bartles-Crossbelt concentrator



improves its ability to recover finer particles. Cassiterite down to 0.005 m.m. in size is claimed to be recoverable by B-M concentrator (34,37,38)

The construction of B-M concentrators comprises a number of shallow channels supported on the subframes which hang from the main frame. Mounted at the middle of the subframe is an out-of-balance weight for producing orbital movement. The channels are slightly inclined to induce pulp flow. Shear, principally due to orbital motion, induces separation. According to the separation forces, the relatively large light particles (gangue) are held in suspension while the fine heavy particles remain on the surfaces of the channels. After a predetermined period feeding is stopped. The channels are tilted 45° for washing off the particles collected on the surfaces (34, 38).

2.3.4.2 Bartles crossbelt concentrator

As on the B-M concentrator, an orbital motion is applied on the Bartles crossbelt concentrator. The concentration on the unit is based upon the use of a PVC surface thin endless belt. Both sides of the top surface of the belt incline transversely from a longitudinal ridge. The belt itself is longitudinally level and moves slowly on the Filon covered aluminium framework deck. The transverse inclination is adjustable at both head and drive pulleys. Pulleys and deck assembly are supported on the subframe which is supported by wires from the main frame. Orbital shear motion is produced by an out-of-balance weight. Both orbital motion and forward speed of the belt can be adjusted.

Pulp is fed over one half of the central longitudinal ridge. The concentration zone on the deck is divided into 3 zones; feed, middling and cleaning zone (37, 39) (see Fig. 2.3.4.1). At the feed zone, heavier minerals deposit on the deck while the lighter gangue is maintained in the suspension and flows to the side of the belt. At the middling zone, transverse water flow is applied in order to wash waste particles entrained in the bed out to the side of the belt and this is collected as a middling. At the cleaning zone heavier minerals in the bed are further cleaned by drip water washing across the width of the belt. The concentrate on the belt is discharged over the head pulley. The minerals washed off at this zone combined with the middling are recycled to the concentrator but are fed at the middling zone (37, 39).

In the Bartles Crossbelt concentrator, particles as fine as 0.005 or 0.010 m.m. can be recovered (29,37). According to R.O. Burt(39), the advantage of the Bartles Crossbelt concentrator compared with other flowing film concentrators is that, besides its ability to recover finer particles, it can produce higher grade concentrates with high percentage

recovery especially when treating particles between 0.020 to 0.010 m.m.. This is shown in his comparison test between Bartles Crossbelt concentrator, round frame and slime tables. He also indicated that when using Bartles Crossbelt concentrator, the recovery is very high when treating cassiterite between 0.150 to 0.020 m.m. and decreases in the range of 0.020 to 0.010 m.m..

Bartles-Mozley concentrator is usually used for preconcentration of tabling or Crossbelt concentrator feed. At Hydraulic Tin and Mt. Willington mines⁽³⁴⁾ B-M concentrators are used to preconcentrate fine cassiterite after removing minus 0.010 m.m. material by hydrocycloning. This concentrate is further upgraded using slime tables.

A Bartles Crossbelt concentrator is usually used in conjunction with B-M concentrator such as at Geevor mine (40). The concentrate from B-M concentrator is upgraded on a Bartles Crossbelt concentrator. These

units are now used as slime recovery units in many mines in Bolivia, Canada, Cornwall, South Africa and the Soviet Union⁽³⁵⁾. They are used for treating cassiterite ranging from 0.100 to 0.010 or 0.005 m.m.. According to R.O. Burt⁽³⁹⁾ using B-M concentrators in series with Bartles Crossbelt concentrators, a double enrichment ratio is produced comparable to using round frames in series with slime tables, while both give nearly equal percentage recovery.

The comparison among a number of gravity concentrators for both fine and coarse cassiterite regarding to capital cost per unit capacity literature⁽²²⁾ and size range of feed was reported in (See Table 2.3.4.1). This table shows relatively low cost for using Bartles Crossbelt concentrator compared with table and vanner. Lower cost of Reichert cone used for preconcentration is also notable.

Sulphides are commonly associated in primary tin ore. They are separated from cassiterite by flotation. Sulphides flotation is usually done after fine grinding. The sink products are fed to tin recovery units such as at Mt. Willington mine⁽³⁴⁾. In some mines such as South Crofty and Geevor⁽³⁴⁾ flotation of sulphides is practised in tin recovery and fines and slimes recovery unit. Where cassiterite flotation is employed, sulphides flotation is done first after fine grinding prior to the flotation of cassiterite such as at Wheal Jane $^{(34)}$ and Renison mine (22).

Table 2.3.4.1 Capital cost per unit capacity of gravity concentration equipment.

Equipment	Size Range of Feed (m.m.)	Average Capacity (dry tonne/hr.)	Capital Cost including Ancillaries	Capital Cost per tonne/hr. of New Feed
Pre-concentration				
Jig (coarse roughing:24 by 36 inch, two hutch)	6.350 to 1.675	12	玉 4,970	玉 414
Jig (fine roughing: 24 by 36 inch, two hutch)	1.675 to .600	6	4 ,970	玉 828
Spiral (double start)	.600 to .075	4	も 1,380	≞ 345
Spiral (single start)	.600 to .075	2	5 930	E 465
Reichert cone (Type 4 DSV)*	.500 to .050	70	玉 17,775	玉 254
Bartles-Mozley table	.100 to .005	2.25	五 5,760	五 2,560
Finishing				
Jig (coarse cleaning 12 by 18 inch, one hutch)	6.350 to 1.675	0.5	_毛 1,650	玉 3,300
Table (sand)	.500 to .075	1	≞ 3,490	击 3 , 490
Table (slime)	.100 to .010	0.25	≣ 3,490	≞ 13,960
Vanner (field house)*	.100 to .010	0.25	± 5,445	五 21,780
Vanner (Bartles crossbelt)	.100 to .010	0.45	≞ 4, 475	垂 9,950

1. Costs quoted are for equipment ex-works and include feed and product launders, but exclude freight and installation costs. Those marked* have been converted from Australian dollars at an exchange rate of A 1.35 = E. All prices effective October/November 1976.

(After World Mining, Feb.

2.3.6 Flotation of cassiterite

Flotation is an alternative method for recovering fine cassiterite. It is used effectively for cassiterite at particular size ranges from $0.030 \text{ to } 0.007 \text{ m.m.}^{(22)}$. Cassiterite finer than 0.007 m.m. which is often regarded as slimes is usually removed prior to the flotation because it is difficult to recover and it influences the flotation results. Collectors used are usually sulphosuccinamate, phosphonic acid and arsonic acid. Pulp pH for the flotation is usually acidic or slightly acidic pH. Reagent consumption used in various mines are shown in Table 2.3.6.1.

Mine	Reagent	Reagent Consumption (kilogram per tonne section feed)	
Wheal Jane (Sulphosucci- namate collector)	Procol CA540 (collector) D.A. 811 (silicate depressant) Sodium silicate	0.18 0.26 0.36	
	Sodium silicofluoride Sulphuric acid Fuel oil	0.04 0.42 0.04	
Union Tin (Phosphonic acid collector)	E.P.P.A. (collector) Sodium silicate Sodium silicofluoride sulphuric acid Caustic soda	0.28 0.24 0.08 0.58 0.08	
Rooiberg "A" mine (Phosphonic acid collector)	E.P.P. A. (collector) Sodium silicate Sodium silicofluoride Sulphuric acid	0.26 0.40 0.40 1.34	
Renison	Arsonic acid (collector)	0.67	

Table 2.3.6.1 Cassiterite flotation reagent consumption.

Renison (Arsonic acid collector)	Arsonic acid (collector) Sulphuric acid Caustic soda MIBC frother	0.67 1.31 0.16 0.006
Altenberg East Germany	Phosphonic acid collector	no detail
Cleveland Tin N.L.	Arsonic acid collector	no detail

(Extracted from World Mining, Feb. 1977⁽¹⁴⁾)

Tasmania

CHAPTER 3

SURFACE CHEMICAL PROPERTIES OF CASSITERITE

3.1 Introduction

The study of the interface between mineral surfaces and solution (or water) is very important for flotation studies. Knowledge of interfacial phenomena assists in the prediction of the influences of various ionic species of surfactants on the floatability of minerals. Thus controlling of the environmental conditions for flotation processes is possible, for example, pH control, collector selection, minimising or preventing depression effects of some ions of soluble salt present in the flotation pulp and other conditions for selective flotation.

3.2 Surface potential and electrical double layer

A solid immersed in water carries an electrical charge on its

surface. This may result from one of the following (41.42):

- surface discontinuities in the crystal lattice, leaving an excess of positive or negative ions on the surfaces.
- transferring of certain ions from solid surface into the solution, leaving a charge on the surface.
- adsorption of charged ions from the solution, such as H^{+} , metal cations or anions.

Those ions which are chemisorbed onto the surfaces and establish the surface charge are called "potential-determining ions" $^{(42)}$.

When a solid surface is charged (e.g., negatively), owing to Coulombic interaction, cations in the solution will be attracted to the surface in order to balance its charge and anions will be repelled. This gives rise to the formation of an electrical double layer at the interface between the solution and the solid surface. In the electrical double layer, the concentration gradient of cations and anions occurs in such a



- **9** Potential-determining ions
- + Hydrated counter ions
- Θ Negative counter ions



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 Ψ_0 = surface potential Ψ_8 = potential at the stern plane

distance from solid surface

Fig. 3.2.1 Schematic representation of an electrical double layer and potential drop ocross the double layer An electrical double layer is divided into two parts - compact layer "a" or stern layer - diffuse layer "b" Plane A-A is called "stern plane" which is the plane of closest approach of the electrical centres of the hydrated counter ions.
(Simplified from D.J. Shaw⁽⁵³⁾ and M.C. Fuerstenau and B.R. Palmer⁽⁴²⁾). way that more cations and less anions are present near the solid surface than those in the bulk solution. This is followed by ionic diffusion in which anions diffuse towards the solid surface to equalize their concentration throughout the solution while cations diffuse away from the solid surface $^{(43)}$. The schematic representation of an electrical double layer is shown in Fig. 3.2.1.

When a solid particle moves in the solution, shear takes place in such a way that the counter-ions next to the surface move with the particle while other ions become diffused $^{(41,44)}$. The potential existing between the shear plane and the diffused layer is known as the zetapotential of the solid surface. The value of the zeta-potential is normally slightly lower than the potential at the Stern plane $^{(45)}$ and thus, can be used to represent the ionic charge of solid surfaces $^{(32, 46)}$. A high positive zeta-potential means that the solid surfaces are dominated by cations. Alternatively a high negative zeta-potential means that anions

dominate at the solid surfaces $^{(46)}$. Value and sign of the zeta-potential may be altered by the adsorption of ions or their products onto the solid surfaces or by the condensation of the electrical double layer due to the increase of ionic strength in the solution $^{(32)}$.

At a certain concentration of potential-determining ions there is no net transfer of charged ions to the solid or to the solution, no electrical double layer is present and there is no excess charge on the solid surface. This critical point is known as "zero point of charge, ZPC" $^{(43)}$. In other words, if there is no specific adsorption, it is the concentration (or pH when H⁺ and OH⁻ are the potential-determining ions) where the zeta-potential changes its sign $^{(45)}$.

When specific adsorption of some ions onto the surfaces occurs, the concentration where the zeta-potential changes its sign does not indicate the zero charge on the surfaces. The zeta-potential is zero but the surface potential may not be zero. This critical concentration is known as "the point of zeta reversal, ZRP". It depends on the surfactant concentration in the system (45).

3.3 Electrokinetic properties of cassiterite

3.3.1 Origin of surface charge

When oxide minerals are immersed in a liquid, the surface charge is brought about by surface hydration followed by dissociation of the surface hydroxide $^{(45)}$. The potential-determining ions for mineral oxides have been claimed to be H⁺ and OH⁻ ions $^{(45, 48)}$ and thus the surface charge is controlled by the pH of the solution.

For cassiterite, E. Wottgen $^{(49)}$ has confirmed by infrared spectra of cassiterite samples that water-wetted cassiterite surfaces carry (OH) groups. The dissociation of surface hydroxides brought about by pH conditions results in the variation of surface charges as shown





3.3.2 Zeta-potential of cassiterite

The zeta-potential of cassiterite has been reported by many investigators. Gaudin, in $1946^{(46)}$, measured the zeta-potential of cassiterite in distilled water at pH7.0 and reported that it was a negative value of 23 millivolts. Increase of hydrogen ion concentration made the zeta-potential less negative whilst increase of hydroxyl ion concentration made it more negative.

In 1953, O'Connor and Buchanan⁽⁵⁰⁾, using the streaming potential method, found that the zeta-potential of cassiterite was negative at pH6-6.5. When HCl solution was added the negative zetapotential was reduced to zero and became positive when the concentration of HCl was greater than 1×10^{-5} N. In alkaline solution, it was more negative than that at pH6-6.5.

In 1968, Ahmed and Maksimor $^{(51)}$ studied the electrical double layer of cassiterite and rutile and reported that the Z.P.C. of

cassiterite existed at pH5.5 and 5.4 in 0.1 M and 1.0 M KNO₃ respectively. The increase of ionic strength (concentration of KNO₃) from 0.001 M to 1.0 M reduced the pH of ZPC in the order of 0.3⁺ 0.05 units of pH. Blazy, Degoul and Houot⁽³¹⁾, in 1969, studied the zeta-potential of cassiterite by potentiometric method using potassium chloride for control the ionic strength. Cassiterite samples investigated were from three different deposits. One was from a primary deposit (Rhodesian ore) and the others were from placer deposits (Maniema-Congo D.R. and Brittany-France). The ZPC reported were

Rhodesian c	assiterite	ZPC at pH	3.40
Congolese	11		3.92
French	11	"	4.45.

The different pH of ZPC might be due to the slightly different surface composition of cassiterite in different deposits. However, the ZPC was around pH 4.0. The ZPC of some silicate minerals were also noted by them as shown in Table 3.3.2.1.

Table 3.3.2.1 ZPC of some silicate minerals and cassiterite (after Blazy, Degoul and Houot⁽³¹⁾)

Mineral	ZPC
Cassiterite	3.4 - 4.45
Quartz	1.30
Feldspar	1.50
Muscovite	0.95
Biotite	0.41

In the same year, Guturrez and Pommier⁽³²⁾ reported that the ZPC of cassiterite from Bolivia (Catovi, Colquiri and Machacamarca mine) was around pH4.0. They investigated by potentiometric methods and used potassium chloride for control the ionic strength.

3.3.3 Effects of metal ions on the zeta-potential of cassiterite

Metal cations which effect the zeta-potential of cassiterite, and thus selective flotation of cassiterite are Fe⁺⁺⁺, Fe⁺⁺ and Ca⁺⁺. These ions are usually present in cassiterite ore, either as an associated mineral or derived from the grinding units.

The presence of Fe⁺⁺⁺ ions shifts the pH of ZPC of cassiterite from around pH4.0 to the neutral pH (around pH6.5) $^{(32, 33)}$. If the ionic species of ferric ions in the solution are considered, the possible ionic species are $\operatorname{Fe}_2(\operatorname{OH})_2^{4+}$, Fe^{+++} , $\operatorname{Fe}(\operatorname{OH})_2^{++}$, $\operatorname{Fe}(\operatorname{OH})_2^+$ and $\operatorname{Fe}(\operatorname{OH})_4^{-(43,52)}$. The total concentration of the four positive ionic species decreases when the pH of the solution increases from pH 2 to 5 due to the precipitation of colloidal ferric hydroxide (Fe (OH)₃). Positive ferric ionic species may be adsorbed on the negatively charged surface of cassiterite by Coulombic forces and hydrogen bonding forces as explained by J.M.W. Mackenzie in the case of the adsorption of ferric ions on quartz surfaces ⁽⁵²⁾. Mackenzie also explained that colloidal ferric hydroxide had the i.e.p. at pH6.7 and thus it might be adsorbed onto negatively charged quartz surfaces by Coulombic forces and/or hydrogen bonding between OH groups of the colloidal ferric hydroxides and OH group at the quartz surfaces. This explanation may be possible in the case of cassiterite because wet cassiterite surfaces also bear (OH) groups as stated before in 3.3.1.

The adsorption of colloidal ferric hydroxides on the cassiterite surface was also noted by Gutirrez and Pommier (32). The adsorption of

positive ferric ions and/or positively charged colloidal ferric hydroxides may cause the shifting of the ZPC of cassiterite from around pH4.0 to the neutral pH region. The effects of Fe^{+++} ion on the zeta-potential of cassiterite increases with increasing Fe^{+++} concentration. Fe^{++} and Ca^{+++} ions have less effect than Fe^{+++} ions. The

effects of Fe⁺⁺ is independent of the concentration $(^{32})$. Gutierrez and Pommier $(^{32})$ noted that the change in ZPC might not be due to Fe⁺⁺ ion itself but it might be due to other phenomena such as oxidation to Fe⁺⁺⁺ when contacted with oxygen of the atmosphere. Ca⁺⁺ affects the zetapotential of cassiterite only at high pH, around pH9.0, where the Ca(OH)⁺ species start to form.

3.4 Correlation between electrokinetic properties and adsorption mechanism of anionic collector on cassiterite surfaces

As in 3.3, the ZPC of cassiterite exists around pH4.0. The adsorption of collector anions onto the surfaces is possible in the pH range lower than ZPC where cassiterite is charged positively. The mechanism of the adsorption has been claimed by many investigators to be the exchange of OH^- ions on the cassiterite surface for collector anions (49, 54).

Regarding to the pH range where the adsorption occurs, the following collectors have been investigated.

Boris Yaksic⁽¹⁹⁾ has shown that the adsorption of oleic acid occurs in the pH range of 2 to 10. The maximum adsorption exists between pH4-7.

G.R. Edwards and W.E. Ewers (54) investigated the adsorption of sodium cetyl sulphate on cassiterite and reported that no adsorption

occurred at the pH value above 5.0. When the pH value decreased the adsorption increased and reached the maximum at pH2.6.

The investigation of E. Wottgen $^{(49)}$ showed that the adsorption of phosphonic acid on cassiterite surfaces increased with the rising pH and reached a maximum at pH2.0. With further increase in pH up to pH4.0 there is a sharp drop of the adsorption. Above pH4.0 the adsorption decreased slightly with increasing pH value until pH10.0.

Considering these investigations, the maximum adsorption usually exists in the pH range below the ZPC, except the case of oleic acid. The shift of the maximum adsorption of oleic acid to the higher pH value may be due to the dissociation of the oleic acid and its chemical behavior as explained by E. Wottgen⁽⁴⁹⁾. Above the ZPC (around pH4 or 5.6 in the case of E. Wottgen) where cassiterite is charged negatively the adsorption of collector is difficult because of the electrostatic repulsion between the negatively charged surface and collector anions. The existence of the adsorption above the ZPC, though it is a small amount, indicates that the adsorption is not solely of electrostatic origin but partly by chemical reaction between the cassiterite surface and collector. This is described by Blazy and his colleagues⁽³¹⁾ in the case of sodium lauryl sulphonate that the adsorption of the collector on a negatively charged cassiterite surface could occur if the chemical reaction between the collector and cassiterite was strong enough to inhibit the electrostatic repulsion, especially when the surface charge was not too high.

CHAPTER 4

CASSITERITE FLOTATION AND FLOTATION KINETICS

4.1 Introduction

Flotation is an alternative method for treating fine-sized cassiterite. It has been examined by many investigators and has been used in a commercial scale in some mine such as Altenberg in Germany, Renison mine, Cleveland Tin N.L. in Australia and Wheal Jane in the United Kingdom⁽²²⁾.

4.2 Collectors for cassiterite flotation

Most of the collectors studied by investigators belong to the anionic collector group. These includes fatty acid and soap, sodium cetyl sulphate, alkyl and lauryl sulphonate, phosphonic acid and arsonic ٦ Cationic collectors such as the hydrochloride of dodecyclamine have acid. been studied by P. Blazy and his colleagues⁽³¹⁾ in comparison with anionic collector (sodium dodecyl sulphonate). They concluded that sodium dodecyl sulphonate was a more active collector. Furthermore, when siliceous gangue minerals were present, selective flotation of cassiterite with amionic collector in acid pH range was improved because of their differences of the ZPC. (See Table 3.3.2.1). At pH around 3.0, cassiterite surfaces are charged positively while the siliceous gangue minerals are charged negatively.

Early research work involved fatty acid and soap flotation. Oberbilig and Frink⁽⁵⁵⁾, in 1941 indicated that emulsified oleic acid could float cassiterite at pH 7. A fair selective flotation of cassiterite from hematite and silicate minerals could be achieved with the addition of a certain amount of sodium silicate. They also found that metallic salts depressed cassiterite at high concentration. Ferric chloride, lead acetate and aluminium nitrate showed cassiterite depression even at their low concentrations.

Gaudin and co-worker, between 1946-47, studied the flotation of cassiterite from Bolivia (56, 57, 58, 59) using oleic acid as a collector. They noted that soluble salt problems could be minimized by grinding cassiterite in a porcelain mill instead of a steel mill and by the addition of small amounts of calgon. They postulated that calgon might be a sequester for residual cations which formed complexes of polyvalent ions with calgon. Treating cassiterite with hot, dilute aqua regia and washing to remove dissolved iron before flotation was also found useful (57).

The disadvantages of oleic acid are that it is heavily consumed by hydrophobic surfaces, strongly depressed by Fe^{+++} ions, partially depressed by Ca^{++} ions and the concentrate produced is difficult to disperse^(61,62). However, the fact that it can float

cassiterite at neutral pH may be the only advantage of oleic acid (the flotation of cassiterite with oleic acid take places in the pH region of 4-7.0⁽²¹⁾ while other anionic collectors will float cassiterite at slightly acidic or acidic $pH^{(62)}$.

Sodium cetyl sulphate was introduced in 1946 by Hergt and his colleagues $^{(63)}$. They claimed that, at 35° C, cetyl sulphate could float cassiterite in a wide pH range from 2 to 9. The recovery was low in the pH range of 5 to 9 and increased rapidly when the pH was below 5.0. This was supported by the works of Edwards and Ewers $^{(54)}$. They investigated the adsorption of sodium cetyl sulphate on cassiterite and showed that no adsorption occured at the pH above 5.0. At the pH lower than 5.0 the adsorption increased and reached the maximum value at pH2.6. Uses of sodium cetyl sulphate are limited by the fact that it is strongly depressed by Ca⁺⁺ ions and that the recovery and selectivity is poor

unless the pulp temperature is elevated to $30-35^{\circ}C^{(61,62)}$. When ferric ions are present cassiterite is depressed due to slime coating by colloidal ferric hydroxide and due to the precipitation of cetyl sulphate by ferric ions (54,62,63). Elevation of pulp temperature improves the flotation because it increases the solubility of ferric cetyl sulphate.

Lauryl sulphate was also found to be a collector for cassiterite. It can float cassiterite in the pH range from 2.0 to $4.5^{(33)}$. When small amounts of Fe⁺⁺⁺ ions are present (10mg/litre) the range of maximum recovery extends to pH6.5. This was explained by Gutierrez⁽³²⁾ as a result of the fact that the ZPC of cassiterite in the presence of Fe⁺⁺⁺ ions shifted from pH4.0 to pH around 6.0, thus the surface being charged positively. However, higher concentration of Fe⁺⁺⁺ ions depresses cassiterite.

Alkyl phosphonic acids and arsonic acids are claimed to be higher

selective collectors than those stated above ⁽⁶²⁾. The difficulty of using arsonic acid is that a high concentration is needed and it is very expensive⁽⁶²⁾. Use of the emulsion of arsonic acid together with non-polar oil and emulsifiers (such as alkyl sulphates or sulphonates or soaps), in order to increase the speed and stability of cassiteriteair bubble attachment, can reduce the concentration of arsonic acid required for satisfactory flotation, thus reducing collector cost as suggested by Topfer $^{(64)}$. However, its toxicity and the effects from Ca⁺⁺ and Fe^{+++} ions when present ⁽⁶²⁾, hinder its use. Flotation of cassiterite with phosphonic acid is more economical because it can be used in low concentration and its cost is lower⁽⁶²⁾. Regarding the effects from metal cations, phosphonic acid has lower sensitivity to Ca⁺⁺ ions depression when compared to other collectors (53,54). The pH where the flotation occurs ranges from slightly acidic to meutral $pH^{(62)}$.

Aerosol-22 was found to be a collector for cassiterite.

Cassiterite responds to aerosol-22 in the pH range from 1.5 to $10.0^{(32)}$. In the presence of Fe⁺⁺, Fe⁺⁺⁺ and Ca⁺⁺ ions the flotation response was considerably reduced and was only satisfactory in the very acid region (pH1-2) as noted by Gutierrez⁽³²⁾.

Cassiterite flotation with chelating agents such as chelate compounds of salicylaldehide (SA) was introduced by A.M. Marabini⁽⁶⁵⁾ and G. Rinelli and his colleagues⁽⁶⁶⁾ in 1975 and 1976 respectively. ${\rm Sn}^{+4}$ of cassiterite had a strong affinity for the aromatic ring of this compound and could form an inner complex salt or a chelate with it⁽⁶⁵⁾. G. Rinelli⁽⁵⁸⁾ had shown that the reaction of this chelating agent with ${\rm Sn}^{+4}$ occurred in a very short time and induced rapid flotation of cassiterite so that the prior conditioning was not needed. The only problem was the high concentration of chelating agent needed⁽⁶⁵⁾.

4.3 Flotation kinetics

Flotation kinetics is the study of variation in the rate of recovery of froth and quantitative identification of all rate controlling variables including rate of aeration, intensity of agitation, pulp density, frother, and particle size. The rate of removal of minerals to the froth product when all rate controlling variables are constant is called "the rate of flotation". Factors determining the rate of flotation and rate of recovery may be explained in the term of probability (P) $^{(67,68,69)}$.

- $P = Pc \cdot Pa \cdot Ps$
- Pc = the probability of collision between bubbles and particles
- Pa = the probability of attachment or adhesion after collision
- Ps = the probability of the stability in particle-bubble attachment.

When particles come into contact with bubbles by collision they are attached to each other provided the intervening wetting layer between them becomes thinner and ruptures. If the attachment is stable enough, they can pass into the froth overflow $^{(67)}$.

Pc is the function of particle size, bubble size, a number of bubbles in a unit volume of the pulp and the velocity of bubbles relative to particles $^{(69,70,71)}$. Pc increases with increasing particle size, bubble size and the number of bubbles per unit volume of the pulp or rate of aeration.

Pa is influenced by contact time and induction time (or period). Contact time is the time that the particle is in contact with the bubble. There are three models of contact time.

Sutherland (74) wrote his model of contact time as:

$$t_{C} = \frac{4R}{3v} \frac{\operatorname{sech}^{-1} E}{-1}$$

- √ 3rR
- E = perpendicular distance of the particle at infinity from the path of the centre of the bubble
- r = radius of the particle
- R = radius of the bubble
- v = the velocity of the bubble relative to the liquid at rest.

In his model the phenomena when an elastic bubble was pressed by the particle was not considered. Phillipoff⁽⁷⁶⁾ and Evans⁽⁷⁵⁾ introduced "bounce theory". They assumed that when a particle collided with a bubble it deformed the bubble until the kinetic energy of the particle was transformed into potential energy of the deformed surface. After that the bubble recovered its shape and ejected the particle and
water from the deformed region. This process was like a simple harmonic. Thus the particle may have a very short time in contact with the bubble. Phillipoff⁽⁷⁶⁾ expressed his model of contact time as:

$$t_{c} = \frac{4.67 \text{ m}^{\frac{1}{2}}}{\emptyset}$$

when
$$\emptyset = \frac{D}{4L^2} + \frac{1}{\ln \frac{L}{D} + 0.4625}$$

m = mass of the particle (mg)

D = diameter of the particle

L =
$$\sqrt{\frac{2\chi}{\rho g}}$$
 (Laplace constant)
= 3.85 m.m. for water

$$\delta$$
 = surface tension

$$\rho$$
 = density of the particle

g = acceleration due to gravity.

Evans⁽⁷⁵⁾ made more simple expression as:

$$t_{c} = \sqrt{\frac{\pi m}{2\chi}}$$

In this equation, t_c is directly proportional to square root of mass of particle. Thus, contact time, according to Evans, decreases with particle size.

Induction period (or time) is defined as the elapsed time between the apparent contact (considered to be when the bubble deformation commences) to true contact (formation of solid-liquid-gas interfaces)⁽⁷²⁾. If disruptive agencies such as shearing forces are not important, adhesion between bubbles and particles (true contact) occurs when the induction period is less than contact time⁽⁷²⁾. Induction period is a function of particle size and shape and the relative motion of the particles and the bubbles. When the particles and the relative velocity are smaller, the induction period decreases. Eigeles and Volova⁽⁷⁷⁾ postulated the expression of the induction period as:

$$\ln ti = \frac{A}{T} + B$$

ti = induction period

A and B = experimental constant

T = temperature.

A depends on the mineral and B increases with particle size and degree of acceleration employed in withdrawing the particle from contact with the bubble. Both A and B are affected by collector concentration.

The function of collector concentration on the induction period studied by E. Topfer⁽⁶⁴⁾ indicated that the induction period

decreased with increasing collector concentration. He also showed experimentally that collector-non-polar oil emulsion could increase the speed of attachment between bubbles and cassiterite particles (or in other words, reduce the induction period) and increase the stability of the attachment. The collector he studied was arsonic acid. He explained that it was due to the fact that non-polar oil contained in the interface displaced liquid between the particle and bubble faster. Frother also affects induction period. Lekki and Laskowski⁽⁶⁷⁾ showed experimentally that the induction period decreased rapidly with increases in the concentration of frother.

The stability of particle-bubble attachment (or adhesion) depends on the disruptive forces. When a bubble and its load is moving in a fluid, there is frictional drag. If the frictional drag exceeds adhesion forces, the particle will be detached from the bubble. The frictional drag increases rapidly with particle size (70,72). Thus, the smaller the particle, the greater is the probability of particle-bubble aggregate withstanding disruptive forces.

Cell turbulence affects "Ps" hence the turbulence in the cell increases the disruptive forces (73).

So far, it can be concluded that;

a) factors determining the flotation rate and recovery may be explained in a term of probability, P;

 $P = Pc \cdot Pa \cdot Ps$.

- b) Pc increases with particle size, bubble size and aeration rate,
- c) Pa is determined by contact time and induction period. If induction period is less than contact time the bubbleparticle adhesion can occur. Contact time decreases with

particle size and induction period decreases with particle size and relative velocity of particles to bubbles. Increases in the concentration of collector reduce the induction period,

d) Ps decreases with frictional drag and cell turbulence.
 Frictional drag increases rapidly with particle size.
 Cell turbulence is caused by excessive aeration rate.

4.3.1 Flotation rate equation

Attempts to express the rate of flotation equation were made by a number of investigators in order to predict theoretically what was happening in the flotation process. Schuhmann⁽⁷⁸⁾ considered the probability of collision between bubbles and particles, the probability of adhesion after the collision and the froth stability in his proposed equation. The equation is;

 $Rx = Pc \cdot Pa \cdot c(x) \cdot V \cdot F$ (4.3.1)

when Pc = Probability of collision in a given time interval,

Pa = Probability of adhesion (or attachment) after collision,

$$c(x) = concentration of particles of average size x in the$$

flotation cell in weight per volume of the pulp,

$$V = total volume of the pulp,$$

and F = the froth stability factor.

Sutherland $(^{74})$ transformed the Schuhmann equation into terms of physical variables as:

Rx =
$$[3\pi x \chi v N]$$
 [sech² $(3v\lambda/4\chi)$] $\theta c(x)V$ (4.3.2)

or

$$W = Wo [1 - e^{-3\pi\phi x\chi vNt} \operatorname{sech}^2 3v\lambda/4\chi]$$
 (4.3.3)

when X = particle radius,

- χ = bubble radius,
- v = velocity of bubbles relative to particles,
- N = number of bubbles per unit volume of the pulp,
- λ = induction period necessary for air-mineral adhesion,
- θ = proportions of particles retained in the froth after fruitful collision. (It has the same significances as F in equation 4.3.1),
- Wo = initial weight of particles in unit volume of the pulp,
- W = weight of particles floated at unit volume of the pulp in a time t.

When compared with Schuhmann equation;

 $3\pi x \chi v N$ is equivalent to Pc sech²($3v\lambda/4\chi$) is equivalent to Pa and θ is equivalent to F. In Sutherland equation, it can be seen that the flotation rate is linearly proportional to the number of bubbles per unit volume and the radii of bubbles and particles and it is affected by the induction period. The rate constant according to the Sutherland equation is;

K =
$$3\pi\phi x\chi vN$$
 sech² (3vλ/4χ) (4.3.4)

For the bubble radius finer than 0.1 cm which is usual in flotation Allen (1900) showed experimentally that

$$v = 229 (\chi - 0.0034)$$
 (4.3.5)

and the unit of χ and v being cm and cm-sec⁻¹ respectively. Thus, the rate constant in equation 4.3.4 will be

$$K = 2170 \ \phi x N \chi^2 sech^2 \ (173\lambda) \tag{4.3.6}$$

Another flotation rate equation was proposed by Plaksin, Klassen and Berger (79) which is

$$\frac{dn}{dt} = Z\phi'(N) (no-n) \qquad (4.3.7)$$

when n = number of particles per unit volume of the pulp floated in t seconds,

no = number of particles per unit volume of the pulp at time,
$$t = 0$$
,

- Z = constant related to the probability of collision between bubbles and particles,
- N = number of bubbles per unit volume of the pulp at time,
 t,

$$\varphi^{\, \prime}$$
 = proportion of effective collision and is related to
 Pa . Pe . Pf ,

Pa = probability of adhesion of a particle to a bubble,

- Pe = probability that the particle will remain attached to the bubble and be carried to the pulp surface,
- Pf = probability that the particle will survive the cleaning action in the froth column and appear in the concentrate.

In general, the flotation rate equation may be written in the form analogous to chemical rate reaction but instead of the interaction between atoms, molecules or ions it is concerned with the interaction between bubbles and particles⁽⁷²⁾.

It is possible to write;

$$\frac{dc}{dt} = -K'Ca^{na}C^{n} \qquad (4.3.8)$$

when Ca = concentration of air bubbles in the pulp,

C = concentration of particles in the pulp,

t = time,

na, n = exponents

K' = a complex rate constant involving reagent concentration, particle and bubble size, induction period, flotation cell design, rate of froth removal, previous treatment and power input.

The order of the process is said to be (na + n). Under the circumstances when the air supply is constant, which is usual in most flotation processes, equation 4.3.8 can be rewritten as:

$$\frac{dc}{dt} = -Kc^n \tag{4.3.9}$$

K = flotation rate constant

n = exponent or order of the flotation process.

First order rate equation.

$$\frac{dc}{dt} = -Kc$$
or
$$-\frac{dc}{c} = Kt$$
or
$$\ln \frac{c_0}{c} = Kt$$
(4.3.10)
where
$$C_0 = \text{initial residual concentration}$$

Zero order rate equation.

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}\mathbf{t}} = -\mathbf{K}$$

or dc = -Kdt

or $c_0 - c = Kt$ (4.3.11)

Second order rate equation.

$$\frac{dc}{dt} = -Kc^2$$
or $\frac{1}{c} - \frac{1}{c_0} = Kt$
(4.3.12)

When the concentration of nonfloatable particle (c $_\infty$) is considered, equation 4.3.10 and 4.3.12 become

First order;
$$\ln \frac{c_0 - c_\infty}{c - c_\infty} = Kt$$
 (4.3.13)

Second order;
$$\frac{1}{c-c_{\infty}} - \frac{1}{c_{o}-c_{\infty}} = Kt$$
 (4.3.14)

If the values on the left hand side of equation 4.3.11, 4.3.13 and 4.3.14 are plotted against time, time being on x-axis, the slope of the linear line represents the value of the rate constant of the flotation process (K).

CHAPTER 5

PROGRAMME OF WORK

As described in Chapter 2, flotation is an alternative method for treating fine-grained cassiterite from primary deposits. Where the gravity concentration fails to recover fine-grained cassiterite, the flotation method becomes more important. The aim of the present work was to study some aspects of cassiterite flotation including effects of associated minerals, collecting agents and kinetics of flotation processes.

Because limited cassiterite and associated minerals samples were available, it was decided to use a micro-flotation cell, which required only a small sample of less than 1 gm. One of the advantages of using a micro-flotation cell is that it saves time in sample preparation and experimentation. However, there are limits when

using the micro-flotation cell. It cannot be used in the study of flotation kinetics which involves the rate of mineral passing into the froth because it is dealing with a small sample and the collecting of froth products at time intervals is not possible. So, a 2.6 litre Denver flotation cell was used for kinetic studies.

The experimental work was divided into two main parts:

5.1 Study of cassiterite flotation in micro-flotation cell. This includes the flotation of cassiterite with various collecting agents and flotation of cassiterite and associated minerals in the presence and absence of suppressing agents.

5.2 Study of flotation kinetics of cassiterite. This includes the effects of collecting agent concentration, conditioning time, frother concentration, rate of aeration, intensity of agitation and particle sizes.





Fig. 6.2.1 Hallimond tube (earlier developed by A.F. Hallimond⁽¹⁾)

CHAPTER 6

STUDY OF CASSITERITE FLOTATION IN MICRO-FLOTATION CELL

6.1 Introduction

The purpose of this series of experiments was to study the flotation of cassiterite using various collectors and to examine the effects of associated minerals. The associated minerals studied included galena, pyrite, fluorite, apatite, quartz and ilmenite.

6.2 Micro-flotation cell

6.2.1 Reviews on the micro-flotation cell types

Various types of small flotation cells have been used. A.F. Hallimond $(^{80,81})$ introduced one known as the Hallimond tube. The cell consisted of a glass tube about 220 m.m. long and 18 m.m. wide

(see Fig. 6.2.1). The lower end of the tube was constricted to about 1.6 m.m. where the elongated cotton wool pad was placed. (In the present Hallimond tube a sintered glass disc was used instead of the cotton wool pad). Air bubbles were produced by introducing air through the pad. When bubbles carried mineral particles to the top surface and broke, the particles were discharged into the side tube. A very small sample of the order of 0.5 gm. was needed. In 1957, D.W. Fuerstenau, P.H. Metzger and G.D. Seele⁽⁸²⁾ modified the Hallimond tube by using a single glass capillary for gas inlet, a magnetic stirrer for keeping particles moving and a ground glass joint at the bottom end for ease in handling (see Fig. 6.2.2). In 1964, M.C. Fuerstenau⁽⁸³⁾ introduced a small glass cell developed from a 150 c.c. Buchner funnel (coarse fritted glass filter) by removing its stem and placing another small stem parallel to the glass filter for nitrogen introduction.



Fig. 6.2.2 Modified hallimond tube by Fuerstenau, D.W.; Metzger, P.H; and Seele, G.D.⁽⁸²⁾



Fig. 6.2.3 Small flotation cell developed by Partridge, A.C. and Smith, G.W. ⁽³⁴⁾

The lip was shaped at the top of the cell to discharge the froth. He used a magnetic stirrer to keep the particles in the cell in suspension. With this cell, conditioning could be done in the cell. In 1971, A.C. Partridge and G.W. Smith⁽⁸⁴⁾ developed a small cell for the study of the flotation characteristics of iron ore. The principle was similar to the Hallimond tube. They used a variablespeed mechanical stirrer instead of a magnetic stirrer. The cell was composed of two different-sized cylinders assembled as shown in Fig. 6.2.3. On the stirrer rod above the top of the lower cylinder, a conical buffle was mounted. Bubbles were produced by introducing air through the glass fritt. Mineral particles carried by the bubbles to the surface were deflected by the conical buffle and deposited on the floor of the upper cylinder and subsequently recovered by washing out through the side tube at the end of the experiments.

The cell volume was about 150 ml. The advantages of this cell were that the level of the impeller could be adjusted and it was easy to operate. So this type of flotation cell was chosen for the present study. However, for the period for the construction of the cell, which will be referred as "micro-flotation cell", a Hallimond tube was used.

6.2.2 Micro-flotation cell construction

The cell was made of perspex and the stirrer rod and its impeller were made of stainless-steel. The reason for using perspex and stainless-steel was to reduce the possibility of metal ions from the cell affecting the flotation process. The cell construction and drawings are shown in Fig. 6.2.4 - 6.2.5.

Mineral particles are initially contained in the column A and kept in suspension by the variable-speed mechanical stirrer C



Fig. 6.2.4 Micro-flotation cell





Plate 1 Arrangement of micro-flotation cell and ancillary

- A Micro-flotation cell
- B Gas-washing bottle
- C Air controlling valve
- D Air Flow meter
- E Electrical motor
- F Nitrogen tank
- G Water trap



- A Air controlling valve
- B Gas-washing bottle
- C Air flow meter
- D Flotation cell
- E Water trap

Fig. 6.2.6 Experimental circuit diagram for the flotation in micro-flotation cell

which is driven by an electrical motor. Air bubbles are produced by introducing nitrogen gas through the glass fritt D at the required flow rate. The particles carried by the bubbles are deflected outwards by the conical baffle E before reaching the surface and deposit on the floor of the upper column B, and are washed through the side tube F, or through the top of the cell after inserting a plug into the top end of the lower column A at the end of the experiment.

The arrangement of the experimental circuit is shown in Plate 1 and Fig. 6.2.6. Air flow rate is adjusted by by-passing excess nitrogen gas through a ball valve. Nitrogen is kept CO, free by passing it through a gas-washing bottle containing saturated sodium hydroxide solution.

6.3.1 Cassiterite

High grade cassiterite from an alluvial deposit was used in the investigation in order to eliminate the assaying of tin content in the flotation products. The ore was first screened to a size range of -0.500 + 0.250 m.m. Gangue minerals and impurities were eliminated by using a high-tension separator and a Frantz isodynamic separator and recleaned many times followed by examination under a microscope. Staining samples with dilute hydrochloric acid in a zinc plate was used as a method of identifying cassiterite particles. The cleaned cassiterite was ground in a porcelain vibratory mill and wet screened to the size range of -0.125 + 0.075 m.m. The reason of using wet screening is to maximise the screening accuracy. Using wet screen, the possibility of mineral particles coating with

slime is minimised thus reducing the possibility of the particles retained in a larger sized screen. Samples of 0.7 gm. were weighed and stored in sealed plastic bags.

6.3.2 Galena

Very pure galena was used in the study of galena flotation in the Hallimond tube. The hand selected mineral was ground in a porcelain vibratory mill followed by wet screening into the size range of -0.075 + 0.038 m.m. and drying in open air. Samples of 0.3 gm. were weighed and stored in sealed plastic bags after gently blowing nitrogen into the bags in order to prevent oxidation during the storage. However, samples for the study of a function of collector concentration and pH were freshly prepared just before the experiments so as to minimise any possibility of oxidation occurring on the surface of freshly ground galena during drying and storage. To estimate the weight of wet samples approximately equivalent to 0.3 gm. of dry galena, a known weight sample of wet galena was dried in the oven at low temperature and weighed again to determine the moisture content of wet samples. By this method, the weight of wet sample equivalent to 0.3 gm. of dry galena could be estimated.

Galena samples of other size ranges were also prepared. All samples were wet screened over a size range of $\sqrt{2}$ series from -0.300 m.m. to +0.038 m.m. Samples of sizes below 0.038 m.m. were sized in a cyclosizer into 5 fractions. The selected sizes were 0.0235, 0.0179, 0.0126, 0.0087 and 0.0064 m.m. The coarsest fraction was elutriated again by beaker decantation with the selected size of 0.0300 m.m..

6.3.3 Pyrite, apatite and fluorite

Samples of these minerals were prepared from high grade lump samples. The ore was crushed by hand in a porcelain mortar. The ground ore was wet screened into the size range of -0.125 +0.075 m.m. and air dried. Dry samples of 0.7 gm. were weighed and stored in sealed plastic bags. For pyrite, nitrogen was gently blown into the bags before sealing.

6.3.4 Ilmenite

Ilmenite samples were prepared from high grade samples. The preparation procedure was the same as in 6.3.3..

6.3.5 Quartz

Quartz was prepared from high grade mineral sand. Contaminant

minerals were removed by means of a Frantz isodynamic separator and recleaned many times particularly to remove any iron bearing minerals. Preparation procedure was the same as in 6.3.3..

6.4 Reagent preparation

All reagents were diluted with distilled water to the required concentration. Warming of the solution was required to dissolve S-3903, S-4082 and Aero-845 Promoter. All collectors were prepared just before starting each experiment in order to eliminate any effect of changing properties of collectors due to the storage. However, suppressing agents were prepared once and stored.

6.5 Experimental procedure

The method adopted for flotation in the micro-flotation cell was as follows:-

- adjust the pH of 200 ml. of the collector solution in a beaker at the selected pH using sulphuric acid or sodium hydroxide solution as required,
- put 0.7 gm. of mineral into the beaker and stir with a magnetic stirrer for the required conditioning time,
- transfer the pulp into the cell by pipetting,
- adjust the water level,
- lower the mechanical stirrer into the cell with the impeller positioned about 5 m.m. above the glass fritt,
- switch on the stirrer and introduce nitrogen into the cell at 0.4 1/min. flow rate using the ball value to control the rate of flow,
- float for 5 minutes,
- stop nitrogen flow and the stirrer, take the stirrer out

- and put a plug into the top end of the lower column A (see Fig. 6.2.4),
- wash and collect the float product,
- take the plug off and wash and collect the sink product, and
- filter, dry and weigh both products.

6.6 Study of the collector system for cassiterite flotation

Many collector systems such as fatty acid, soap, sodium cetyl sulphate, alkyl and lauryl sulphonate, phosphonic acid, arsonic acid and chelating agents of salicylaldehide have been studied by a number of investigators as described in Chapter 4. In the present study, flotation of cassiterite with collectors other than those



1 × 100 mg/l Aerosol-22

- 2 0 100 mg/l Aerosol-22, 108 mg/l citric acid
- 3 🛛 100 mg/l Aero 845 Promoter
- 4 Δ 100 mg/l S-3903

.

5 0 100 mg/l S-4082

Fig. 6.6.1 Flotation of cassiterite of - 0.125 + 0.075 m.m. particle size with various collecting agents

mentioned above were studied. These included Aerosol-22, Aero-845 Promoter, S-3903 and S-4082. All were supplied by the American Cyanamid Company. Each collector was used to float cassiterite at various pH values while keeping other variables constant. The conditions for flotation with each collector was compared and subsequently the collector which floated cassiterite over the widest range of pH was selected for all later experiments. The controlling variables were;

- collector concentration 100 mg/l,
- conditioning time 10 min.,
- flotation time 5 min.,
- aeration rate 0.4 l/min.,
- agitation rate 1180 RPM.

The experimental results are shown in Table 6.6.1 - 6.6.5 and Fig.

6.6.1.

6.6.1 Discussion of the results

<u>6.6.1.1 Aerosol-22</u> The maximum flotation occurs in the pH range below 2.6 (see Table 6.6.1 and Fig. 6.6.1 curve 1). This is the pH range below the ZPC of cassiterite which has been reported to exist around pH4.0 as described in Chapter 3. The recovery at a pH higher than 2.6 falls rapidly to less than 30 per cent recovery at pH4.4. For further increases in pH value the recovery decreases slowly. The pulp was checked for the presence of Fe⁺⁺ and Fe⁺⁺⁺ ions but they were not detected. This assures that there was no effect of Fe⁺⁺ and Fe⁺⁺⁺ ions on the flotation system. It can be postulated that the collecting mechanism of Aerosol 22 on cassiterite surfaces may solely result from the adsorption of collector anion onto cassiterite surfaces as counterions in the electrical double layer. No specific chemical affinity between cassiterite and Aerosol-22 is present.

Preconditioning with citric acid did not improve the flotation results (see Fig. 6.6.1 curve 2 and Table 6.6.2). Preconditioning with sulphate ions was also tried at pH2.7 and 3.4. The results which are not shown here indicated no improvement in flotation.

<u>6.6.1.2 Aero 845 Promoter</u> The maximum flotation exists in the pH range below 2.85. At a pH above this range the recovery falls rapidly (see Fig. 6.6.1 curve 3 and Table 6.6.3). Like Aerosol-22, the pH range of the maximum flotation is also below the ZPC of cassiterite. The collecting mechanisms may be similar to Aerosol-22.

6.6.1.3 S-3903 and S-4082 The maximum flotation exists

in the pH range from highly acidic to pH 10.2 for S-3903 and pH8.2 for S-4082. (See Table 6.6.4, 6.6.5 and Fig. 6.6.1 curve 4 and 5). This is far above the ZPC of cassiterite. Above the ZPC cassiterite surfaces are charged negatively. In this pH region there is the electrostatic repulsion between the negatively charged cassiterite surfaces and collector anions so that the adsorption of collector anions should be difficult. The fact that maximum flotation exists even in alkali pH which is brought about by the adsorption of collector anions onto the negatively charged cassiterite surfaces may indicate that the adsorption is not solely of electrostatic origin but partly by chemical reaction. S-3903 and S-4082 may have specific chemical affinity to cassiterite surfaces. When the negative surface charge is not too high the chemical reaction may be strong enough to inhibit the electrostatic repulsion and thus result in the adsorption. When the pH increases the negative surface charge and the electrostatic repulsion increases. It can be seen from Fig. 6.6.1 curve 4 and 5 that at pH range above 8.2 for S-4082 and 10.2 for S-3903 the recovery falls rapidly. This can be described by the increases in negative charge and the electrostatic repulsion which becomes higher than the attractive forces due to chemical reaction and thus the adsorption drops quickly. Another reason for the existence of the maximum flotation in alkali pH region may be the high degree of dissociation of the collectors. Unfortunately, their dissociation constants are not known.

6.6.2 Conclusion

Regarding the pH range of maximum flotation, S-3903 and S-4082

show better collecting properties than Aerosol-22 and Aero-845 Promoter do. The collecting mechanisms of Aerosol-22 and Aero-845 Promoter are nearly the same. The maximum flotation or, in turn, the adsorption of collector anions onto cassiterite surfaces occurs in the pH region below the ZPC (below pH2.6 for Aerosol 22 and pH2.85 for Aero-845 Promoter). It may be possible to postulate that the collecting mechanism solely results from the adsorption of collector anion onto cassiterite surfaces as counter-ions in the electrical double layer. As cassiterite surfaces bear (OH) group (as described before in Chapter 4) the adsorption of collector anions may occur through the process of the exchange of OH⁻ ions at the surfaces for collector anions. Thus for the pH range between 2.6 for Aerosol-22 and 2.85 for Aero845 Promoter and the pH of the ZPC (around pH4.0) the recovery drops sharply although the cassiterite surfaces are still charged positively. This phenomena may be described as the liberation of hydroxyl ions at the cassiterite surfaces. In this range of pH the liberation of hydroxyl ions might be masked by cation exchange in the electrical double layer which H^+ ions are replaced by collector cations. Another possible explanation is that the precipitation of the collectors with some impurities from cassiterite surfaces may cause reduced recovery before the ZPC. Unfortunately, the detection of the precipitation has not been completed.

The collecting mechanisms of S-3903 and S-4082 are very different from those of Aerosol-22 and Aero845 Promoter. Because they can float cassiterite well even in the pH range above the ZPC (up to pH10.2 for S-3903 and pH8.2 for S-4082) it is possible to say that S-3903 and S-4082 have specific chemical affinity to cassiterite surfaces and thus the chemical reaction or specific adsorption play a large role in the adsorption mechanism of these collectors. Above the ZPC the electrostatic repulsion between negatively charged cassiterite surfaces, which increases with pH, and collector anions is not high enough to overcome the attractive forces due to the chemical reaction between cassiterite surfaces and collectors until pH10.2 for S-3903 and pH8.2 for S-4082 so that the adsorption and consequently the flotation is possible in this pH range.

So far, these conclusions may be made:

- Regarding to the area of maximum flotation, S-3903 and S-4082 show better collecting properties than Aerosol-22 and Aero-845 Promoter do and they were selected for use as the collectors in all later experiments.
- The collecting mechanisms of Aerosol-22 and Aero-845 Promoter are solely of electrostatic origin.

- The collecting mechanisms of S-3903 and S-4082 are not solely of electrostatic origin but chemical reaction or specific adsorption also plays a large role.

Table 6.6.1 Flotation of cassiterite of -0.125 +0.075 m.m. particle size with 100 mg/l Aerosol-22

pН	Floats %	Non-floats %
1.6	98.22	1.78
2.2	100.00	0.00
2.6	97.64	2.36
2.9	55.72	44.28
3.3	55.25	44.75
4.4	29.01	70.99
6.1	29.24	70.76
8.2	22.10	77.90

Table 6.6.2 Flotation of cassiterite of -0.125 +0.075 m.m. particle size with 100 mg/l Aerosol-22, preconditioned with 108 mg/l citric acid for 5 minutes

pН	Floats %	Non-floats %
2.1	97.44	2.56
3.0	72.99	27.01
4.1	27.86	72.14
5.0	8.08	91.92

Table 6.6.3 Flotation of cassiterite of -0.125 +0.075 m.m.

рH	Floats %	Non-floats %
2.6	98.58	1.42
2.8	97.86	2.14
3.0	72.51	27.49
3.4	38.42	38.42

particle size with 100 mg/l Aero-845 Promoter

Table 6.6.4 Flotation of cassiterite of -0.125 +0.075 m.m.

particle size with 100 mg/l S-3903

рH	Floats %	Non-floats %
2.3	95.48	4.52
3.9	95.59	4.41
5.9	93.83	6.17
8.1	94.24	5.76
10.2	94.35	5.65
11.8	4.00	96.00

Table 6.6.5 Flotation of cassiterite of -0.125 +0.075 m.m. particle size with 100 mg/l S-4082

рH	Floats %	Non-floats %
2.2	95.47	4.53
4.2	98.94	1.06
6.2	94.12	5.88
8.2	97.33	2.67
10.3	36.74	63.26
11.6	1.03	98.97

.



Fig. 6.7.1 Experimental circuit diagram for the flotation in Hallimond tube

6.7 Flotation and suppressing of associated minerals

As described in Chapter 1 and 2 other economic minerals, apart from cassiterite may occur in primary deposits including sulphides of lead, zinc, copper and silver, and oxides such as wolframite, scheelite. The following gangue minerals may be present, quartz, micas, tournaline, pyrite, topaz, fluorite, apatite, zircon, some carbonate minerals, rutile and siderite. Some gangue minerals such as tournaline, topaz, siderite and iron oxide have similar flotation properties to cassiterite ^(4, 62). Furthermore, sulphides appear to be more readily floatable than cassiterite ⁽⁶²⁾ so that they should be floated from cassiterite first before the flotation of cassiterite.

In the present study, galena, pyrite, fluorite, apatite, quartz and ilmenite are included.

6.7.1 Flotation of galena

In some mines, e.g. Renison mines in Tasmania, sulphides are the main associated minerals. The recovery of sulphides such as galena may be important when the quantity present makes the recovery economically viable. Some factors influencing galena flotation were studied including flotation time, conditioning time, rate of aeration, collector concentration, pulp pH and particle size. The collector used was sodium ethyl xanthate. All experiments were done in the Hallimond tube. The diagram of an experimental circuit is shown in Fig. 6.7.1. The experimental procedure was as follows:-

- Put 0.3 gm. galena and water into a beaker and adjust the volume of the pulp to 100 ml,



1

Flotation time (sec)







Conditioning time (min.)





•

- adjust the pH to 7.5 by adding sodium hydroxide solution and add required amount of sodium ethyl xanthate,
- condition the pulp for 8 minutes,
- transfer the pulp into the Hallimond tube by pipetting and adjust the water level,
- introduce nitrogen gas into the cell at required flow rate and float for the selected time. Gently knocking of the cell with a plastic or rubber stick may be necessary in order to prevent the particles from being trapped in the bubble-free region around the edge of the bottom of the cell,
- stop the nitrogen flow and collect float product,
- collect sink product,
- filter, dry and weigh both products.

The experimental results are presented in Table 6.7.1 - 6.7.7 and Fig. 6.7.2 - 6.7.7.

<u>6.7.1.1</u> Discussion of the results The recovery in most experiments, as shown in Fig. 6.7.2 - 6.7.4, is very high. This is due to the very good floatability of galena. In some experiments it was observed that some particles were mechanically lifted to the surface by the flow of bubbles eventhough attachment were not obtained. This factor was examined and attempts were made to reduce its effects, however, complete elimination was not possible under the condition of the tests. Consequently consideration was given to this factor in assessing the results of the experiments.

Fig. 6.7.2 and 6.7.4 indicate that the flotation time and conditioning time required for complete flotation of galena is around 75 seconds and 8 minutes respectively. The recovery increases rapidly


Sodium ethyl xanthate concentration (mg/l)



6

with the increase in the rate of aeration (see Fig. 6.7.3) until reaching about 0.125 litre/min. At higher rates of aeration the recovery is approximately constant. According to the observation, at the rate of aeration of 0.175 litre/min and higher the influence of mechanical entrainment is too great for effective flotation testing. Some bubbles generated in the cell are very large, bubble dispersion not being achieved and due to the small cross-sectional area of the cell, the bubbles of this size tend to push galena particles upwards.

As referred in Chapter 4, a number of bubbles generated in the cell is one of the factors influencing flotation of minerals. At a rate of aeration lower than 0.125 litre/min the probability of collision between bubbles and galena particles is reduced. This results in the lower recovery. When the rate of aeration increases, the probability of collision increases and consequently, the recovery increases.

A function of the concentration of sodium ethyl xanthate is shown in Table 6.7.4 and Fig. 6.7.5. It can be seen that some flotation of galena occurs in the absence of collector. This may be the influence of one or combination of these possible factors;

- Contamination from the cell. The cell might not be a) clean enough so that some amount of collector from the former experiment might be left on the cell surface which made galena float.
- b) Oxidation of galena sample by oxygen from the atmosphere or in the water during preparation or during pH adjusting is another probable factor because slightly oxidised galena can float to some extent.





Geometric mean size of galena particles (m.m.)

c) Mechanically entrainment as described before.

With only a small amount of sodium ethyl xanthate present (0.04 mg/l) the recovery rises rapidly to about 63 per cent but rises slowly with increasing concentration of the collector until reaching about 3 mg/l. After that the recovery is nearly constant.

Particle size affects the floatability of galena. The recovery of galena 0.252 m.m. in size is only 54 per cent (see Fig. 6.7.6 and Table 6.7.5). The recovery increases to 90 per cent when the particle size decreases to about 0.165 m.m. and to nearly 100 per cent for the particle size of 0.080 m.m. For the particles finer than 0.040 m.m. the recovery decreases. This phenomena can be explained by the probability of collision and adhesion between mineral particles and bubbles and the stability of the attachment as described in Chapter 4. The flotation of coarse particles depends

largely on the probability of adhesion and the stability of the attachment. Although the adhesional force increases with the increase in particle size, the disruptive forces experienced to the bubbleparticle adhesion due to the frictional drag from the liquid increases with particle size at the faster rate. This results in the higher probability of the particles to be detached from the bubbles for the coarser particles and consequently, less flotation occurs. For galena finer than 0.040 m.m., the decrease in the recovery could be considered to result from the lower probability of collision with the bubbles. As described in Chapter 4 the probability of collision decreases with decreasing particle size, provided the number and size of bubbles remains constant.

Regarding the pH range, the maximum flotation occurs in a wide pH range of 4.0 to 9.0 (see Table 6.7.6 and Fig. 6.7.7). At the pH higher than 9.0 and lower than 4.0 the recovery falls rapidly.



Fig. 6.7.7 Flotation of galena of -0.075 + 0.038 m.m. particle size with 8 mg/l sodium ethyl xanthate as a function of pH

6.7.1.2 Conclusion Some characteristics and kinetics of galena flotation has been discussed. The experiments indicate that galena floats well with NaEx (sodium ethyl xanthate) in the pH range from 4.0 to 9.0. Unless cassiterite floats in this condition galena can be selectively floated from cassiterite ore. Studies on these aspects will be described in 6.7.2.

> Table 6.7.1 Flotation of galena of -0.075 +0.038 m.m. particle size as a function of flotation time Collector: 8 mg/l sodium ethyl xanthate Conditioning time: 10 min. 7.5 pH;

0.125 1/min. Aeration rate:

Flotation time sec.	Floats %	Non-floats %
30	88.26	11.76
45	88.51	11.49
60	95.31	4.69
90	94.72	5.28
150	95.60	4.40
300	95.96	4.04
600	95.03	4.97

Table 6.7.2 Flotation of galena of -0.075 +0.038 m.m. particle size as a function of aeration rate

Collector: 8 mg/l sodium ethyl xanthate

Conditioning time: 10 min.

Flotation time: 75 sec.

pH: 7.5

Aeration rate 1/min	Floats %	Non-floats %
0.075	89.54	10.46
0.100	95.85	4.15
0.125	98.74	1.26
0.150	99.46	0.54
0.175	98.57	1.43
0.225	98.57	1.43
0.350	99.47	0.53

	Table 6.7.3	Flotation	of	galena	of	-0.075	+0.038	m.m.
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particle size as a function of conditioning time

Collector:	8 m	g/1	sodium	ethyl	xanthate
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- Flotation time: 75 sec.
- pH: 7.5
- Aeration rate: 0.150 l/min.

Conditioning time min.	Floats %	Non-floats %
1	95.77	4.23
2	96.55	3.45
3	97.01	2.99
5	97.06	2.94
8	97.49	2.51
12	97.62	2.38
20	97.22	2.78
30	97.27	2.73

Table 6.7.4 Flotation of galena of -0.075 +0.038 m.m. particle size as a function of collector concentration

Collector:	sodium ethyl xanthate
Conditioning time:	8 min.
Flotation time:	75 sec.
pH:	7.5
Aeration rate:	0.150 1/min.

Sodium ethyl xanthate concentration mg/l	Floats %	Non-floats %
0.00	36.50	63.50
0.04	62.25	37.75
0.09	67.50	32.50
0.92	76.35	23.65
2.76	89.40	10.60
4.26	90.64	9.36
6.00	91.50	8.50

Table 6.7.5	Flotation of galena as a function of				
	particle size				
Collector:		8 mg/l sodium ethyl xanthate			
Conditioning time: 8 min.					
Flotation tim	e:	5 min.			
pH:		7.5			
Aeration rate: 0.150 l/min.					

Particle size m.m.	Geometric means size m.m.	Floats %	Non-floats %
-0.3000 +0.2120	0.2522	53.78	46.22
-0.2120 +0.1500	0.1783	87.09	12.91
-0.1500 +0.1250	0.1369	94.18	5.82
-0.1250 +0.1060	0.1151	94.96	5.04
-0.1060 +0.0900	0.0977	97.88	2.12
-0.0900 +0.0750	0.0822	99.99	0.01
-0.0750 +0.0630	0.0687	99.13	0.87
-0.0630 +0.0530	0.0578	99.86	0.14
-0.0530 +0.0450	0.0488	99.77	0.23
-0.0450 +0.0380	0.0414	99.60	0.40
-0.0380 +0.0300	0.0338	98.91	1.09
-0.0300 +0.0235	0.0266	97.22	2.78
-0.0235 +0.0179	0.0205	98.18	1.82
-0.0179 +0.0126	0.0150	97.60	2.40
-0.0126 +0.0087	0.0105	94.38	5.62
-0.0087 +0.0064	0.0075	95.44	4.56

Table 6.7.6	Flotation of galena of $-0.075 + 0.038$ m.m.		
	part	icle size as a function of pH	
Collector:		8 mg/l sodium ethyl xanthate	
Conditioning tim	e:	8 min.	
Flotation time:		75 sec.	
Aeration rate:		0.150 l/min.	

рH	Floats %	Non-floats %
2.7	90.78	9.22
3.9	96.77	3.23
4.9	97.91	2.09
5.9	97.78	2.22
6.5	96.80	3.20
7.7	97.31	2.69
8.4	98.10	1.90
9.4	95.14	4.86
10.3	82.56	17.44
11.4	58.76	41.24
13.1	31.61	68.39

Fig. 6.7.8 Flotation of galena, pyrite and cassiterite with 8 mg/l sodium ethyl xanthate

- + Galena (- 0.075 + 0.038 m.m., from Fig. 6.7.7)
- ▲ Pyrite (- 0.125 + 0.075 m.m.)
- O Cassiterite (- 0.125 + 0.075 m.m.)



Fig. 6.7.9 Flotation of pyrite and cassiterite of - 0.125 + 0.075 m.m. particle size with 35 mg/l potassium amyl xanthate



рН

6.7.2 Separation of galena and pyrite from cassiterite

The flotation of galena with sodium ethyl xanthate in the Hallimond tube has been discussed. To examine the floatability of cassiterite and pyrite in the presence of 8 mg/l. sodium ethyl xanthate the following experiments were done in the micro-flotation cell. The experiments included the flotation of pyrite and cassiterite with 8 mg/l. sodium ethyl xanthate and with 35 mg/l. potassium amyl xanthate. In all experiments the pulp pH was varied while other factors were kept constant. The experimental results are presented in Table 6.7.7-6.7.8 and Fig. 6.7.8-6.7.9.

<u>6.7.2.1</u> Discussion of the results Fig. 6.7.8 shows that, with sodium ethyl xanthate no flotation of cassiterite occurs and only a small amount of pyrite floats with a recovery up to 28 per cent. With potassium amyl xanthate, the longer chain collector, pyrite floats well from pH2 to pH9.7 (see Fig. 6.7.9). Above pH9.7 recovery falls. No flotation of cassiterite was observed with potassium amyl xanthate.

<u>6.7.2.2 Conclusion</u> Previous flotation results showed that galena floats well with sodium ethyl xanthate between pH4-9 while cassiterite does not float in this pH range. This indicates that galena can be selectively floated from cassiterite with sodium ethyl xanthate. To achieve high recovery of galena the effective pH range should be between 4.0 - 9.0.

With sodium ethyl xanthate a small amount of pyrite floats. It floats well with the longer chain xanthate, potassium amyl xanthate, below pH9.7. No cassiterite floats with potassium amyl xanthate so that

Table 6.7.7	Flotation of cassiterite,	and pyrite of - $0.125 + 0.075$ m.m.
	particle size with 8 mg/l	sodium ethyl xanthate
	Conditioning time	10 min.
	Flotation time	5 min.
	Aeration rate	0.4 l/min.
	Agitation rate	1180 RPM.

6.7.7.a Cassiterite

pH	Floats %	Non-floats %
1.9	1.37	98.63
4.5	1.49	98.51
6.6	3.06	96.94
8.5	1.70	98.30
10.8	2.52	97.48

12.9	2.04	97.96

6.7.7.b Pyrite

рН	Floats %	Non-floats %
7.1	27.65	72.35
9.0	21.78	78.22
11.1	12.37	12.37

Table 6.7.8 Flotation of cassiterite and pyrite of - 0.125 + 0.075 m.m. particle size with 35 mg/l potassium amyl xanthate (controlling variables are the same as in Table 6.7.7)

6.7.8.a Cassiterite

рH	Floats %	Non-floats %
2.0	6.75	93.25
4.6	3.62	96.38
7.5	3.11	96.89
10.3	1.95	98.05

6.7.8.b Pyrite

рH	Floats %	Non-floats %
2.0	93.91	6.09
4.1	94.86	5.14
6.0	97.93	12.07
7.7	84.80	15.20
9.7	84.44	15.56
11.7	48.04	51.96

pyrite can be selectively floated from cassiterite with this collector. As described before cassiterite ore in many primary deposits contains galena and/or pyrite. These minerals should be selectively floated from cassiterite before the flotation of cassiterite. When only galena is present high grade galena concentrate can be produced by the flotation with sodium ethyl xanthate. Where both galena and pyrite are present certain amount of pyrite will be present in the galena concentrate. Suitable depressants for pyrite are required to obtain a high grade galena concentrate. This was not included in the present work because it extends beyond the scope of the present study. However, possible depressants are lime and sodium cyanide⁽⁸⁵⁾.

In flotation with sodium ethyl xanthate, the non-floated products will contain, apart from cassiterite, certain amount of pyrite so a second stage flotation with potassium amyl xanthate may be used when pyrite can be selectively floated from cassiterite. When galena is present in a small amounts in cassiterite ore it may not be economical to produce a galena concentrate so a one stage flotation with potassium amyl xanthate can be employed to float both galena and pyrite from the cassiterite.

6.7.3 Flotation of fluorite, apatite, quartz and ilmenite with S-3903 and S-4082

In primary tin deposits, quartz occurs as a gangue mineral, particularly in pegmatite type deposits. Flourite and ilmenite are found in many deposits in Australia⁽⁸⁶⁾. Apatite has been reported as an associated mineral in cassiterite lodes in Yeuralba in Northern Territory in Australia⁽⁸⁶⁾. When a large content of these minerals are present in the cassiterite ore they may produce some difficulties



- 1 × Cassiterite
- 2 ^O Fluorite
- 3 🔺 Apatite
- 4 0 Quartz
- 5 🛛 Ilmenite
- Fig. 6.7.10 Flotation of cassiterite, apatite, fluorite, ilmenite and quartz of - 0.125 + 0.075 m.m. particle size with 100 mg/l S-3903

in the flotation of cassiterite if the collector used can float them In the present work, each mineral was floated separately as well. both with S-3903 and with S-4082 in the micro-flotation cell in order to study their response to these collectors. Pulp pH was varied while other factors were kept the same for all experiments:

Collector concentration	100 mg/1.
Conditioning time	10 min.
Flotation time	5 min.
Rate of aeration	0.4 l/min.
Rate of agitation	1180 RPM.

Sample preparation has been described in 6.3. The experimental results are presented in Table 6.7.9 and Fig. 6.7.10 for S-3903 and in Table 6.7.10 and Fig. 6.7.11 for S-4082.

6.7.3.1.1 Fluorite Fluorite floats well with both collectors (see Fig. 6.7.10 - 6.7.11 and Table 6.7.9.b and 6.7.10.b). Its recovery is a little below that obtained for flotation of cassiterite. The maximum recovery exists between pH2.2 and pH11.2 for S-3903 and between pH2 and pH9.0 for S-4082. Considering the electrokinetic potential of fluorite, the pH-electrokinetic potential diagram reported by A. Rihar $^{(40)}$ indicated the ZPC of fluorite to exist around pH9.7. Below pH9.7 fluorite surfaces are charged positively so that the adsorption of collector anions onto fluorite surfaces is possible in this pH range. With S-3903, maximum flotation of fluorite extends to above the pH of the ZPC. The explanation to this phenomenon may be similar to that described before in 6.6.1.3 for cassiterite flotation. S-3903 may have special chemical affinity for fluorite so that the adsorption of these collector anions by chemical reaction is possible. The adsorption

Fig. 6.7.11 Flotation of cassiterite, apatite, fluorite and quartz of - 0.125 + 0.075 m.m. particle size with 100 mg/1 S-4082



mechanism may be the combination role of both the electrical double layer and the specific adsorption due to chemical reaction. The decreases in the recovery of fluorite below pH2.2 (see Fig. 6.7.10) may be due to one or a combination of the following factors:

- a) When the pH decreases the dissociation of S-3903 may decrease and consequently the concentration of collector anions decrease.
- b) When fluorite is charged positively its surface is dominated by Ca^{++} ions ⁽⁴⁸⁾. When the pH decreases, the chemical salt of calcium and collector anions at the surface may be more soluble and thus reduce the adsorption.
- c) Precipitation of S-3903 with impurities on fluorite surfaces may cause decreases in per cent recovery below pH2.2.

Probably, "a" is the least probable cause because at pH below 2.2 quartz still floats well (see Fig. 6.7.10) which might be the indicator that the collector anions concentration might not decrease. In case of S4082, the maximum recovery exists below the ZPC

(see Fig. 6.7.10). At the pH of the ZPC (pH9.7) the recovery is 70 per cent compared to 89 per cent at pH9.0. It may be said that the adsorption mechanism is the role of the electrical double layer only. No specific adsorption of S-4082 on fluorite surfaces occurs.

<u>6.7.3.1.2 Apatite</u> The recovery of apatite was in excess of 50 per cent for the conditions used with both collectors. The pH range where maximum flotation exists is between 2.0 - 10.0 for S-4082 and 2.0 - 11.0 for S-3903 (see Fig. 6.7.10 - 6.7.11). S.K. Mishra⁽⁸⁷⁾ reported the ZPC of apatite from different deposits to vary between pH3.5 and pH6.7. The flotation results show that either collector can float apatite even in the pH range higher than the ZPC. This may indicate the occurence of specific adsorption of the collectors onto apatite surfaces. At pH lower than the ZPC the adsorption may be the role of electrical double layer alone or in combination with specific adsorption. In the pH range higher than the ZPC specific adsorption is important. It was noted that at pH10.0 apatite recovery with S-4082 increases to about 75 per cent compared with about 61 per cent at pH8.2. At a pH above 10.0 the recovery decreases rapidly.

6.7.3.1.3 Quartz The recovery of quartz when floated with S-3903 is of the order of 70 per cent at pH1.2 but decreases rapidly with further increases in pH value reaching a minimum at pH4.3 (see Table 6.7.9.d and Fig. 6.7.10). Above this pH the recovery increases slightly and falls again at pH above 7.6. When floated with S-4082 the pH-recovery curve is different from that obtained when floated with S-3903 (see Table 6.7.10.c and Fig. 6.7.11). The recovery is around 45 to 50 per cent in the pH range of 2.0 to 8.0 and rises rapidly to about 92 per cent at pH10.2. Above pH10.2 it drops sharply to about 32 per cent at pH11.5. It can be noted that S-3903 shows a more selective flotaion property for cassiterite from quartz than S-4082, particularly at pH4.3 where the recovery of quartz is about 20 per cent compared with 50 per cent when floated with S-4082.

Considering the electrokinetic properties of quartz, the ZPC of quartz varies between pH1.3 - $2.8^{(31, 48, 88)}$. Above

the ZPC quartz surfaces hold negative charges. For S-3903 collector, at pH1.2 high recovery (71 per cent) is obtained because quartz surfaces are charged positively so that the adsorption



рН

Fig. 6.7.12 Electrokinetic potential of

quartz

(After Rihar, A.⁽⁴⁸⁾)

of collector anions in the electrical double layer is possible. After pH1.2 the positive charges decrease, with a decrease in the adsorption and consequently recovery decreases. It can be seen in Fig. 6.7.10 that the flotation of quartz at a pH above the ZPC still exists even though recovery is low (about 20-30 per cent). There are two possible explanations. Firstly, S-3903 may have specific chemical affinity to quartz, but not as high as for cassiterite, fluorite and apatite. S-3903 may be specifically adsorbed onto negatively charged quartz surfaces to some extent which brings about the flotation. Secondly, there may be some area among the negatively charged surfaces holding positive charges where collector anions are adsorbed.

For S-4082, the explanation for the existence of some flotation (about 40 - 50 per cent recovery) between pH2.0 and 8.2 may be the same as described for S-3903. It was noted that the recovery increased rapidly after pH8.2 to about 92 per cent at pH10.3 and decreased rapidly for further increases in pH value. This may be described in terms of hemi-micelle formation and the ionization of the collector. Unfortunately, the ionization of S-4082 was not investigated in the present work. However, it is likely that the ionization of S-4082 has not been completed below pH10.3. Some amount of collectors are Rihar⁽⁴⁸⁾ still in the form of molecules instead of all free anions. reported that, apart from the pH below 2.7 (the ZPC), there is another pH region where the electrokinetic potential of quartz is positive i.e. between pH9.2 and 10.3 (see Fig. 6.7.12). Consequently, with higher concentrations of collector anions due to nearly complete ionization of the collector, hemi-micelle formation may be possible with a high recovery of quartz at pH10.3. Flotation tests at lower concentrations to support this postulation were not completed.

The rapid decrease in recovery at a pH higher than 10.3 may be due to the increases in ionic competition between OH⁻ ions and S-4082 anions which reduce the adsorption of S-4082 anions.

<u>6.7.3.1.4 Ilmenite</u> Maximum recovery of ilmenite with S-3903 is about 85 per cent at a pH below 2.0. At above pH2.0 the recovery curve falls sharply to about 26 per cent at pH3.8 and slowly falls to nearly zero at pH11.5 (see Table 6.7.9.c and Fig. 6.7.10). Because the ZPC of ilmenite was not known, its flotation mechanisms are not discussed here.

<u>6.7.3.2 Conclusion</u> Flotation mechanisms of fluorite, apatite and quartz both with S-3903 and S-4082 have been discussed. Both collectors seem to have specific chemical affinities for cassiterite, fluorite and apatite so that specific adsorption onto

those minerals' surfaces is possible and consequently, the existence of maximum flotation of the minerals with S-3903 and S-4082 occur in nearly the same pH region. This could be a problem when fluorite and apatite are present in cassiterite ores because they would float with cassiterite. Suitable depressants or conditions are required for suppressing them. For apatite the flotation results indicate that less apatite floats with S-4082 (60 per cent recovery) compared to about 70 per cent recovery with S-3903.

In the case of quartz, selective flotation of cassiterite from quartz with S-3903 at pH4.3 is possible although some amounts of quartz floats (about 20 per cent recovery). With S-4082, selective flotation of cassiterite is difficult because nearly fifty per cent of the quartz content will float with cassiterite. The existence of some flotation of quartz with both S-4082 and S-3903 may indicate that both collectors, particularly S-4082, have specific chemical affinities (but not as high as cassiterite) to quartz. The role of specific adsorption of collector onto quartz surfaces may result in the flotation. It is interesting to note that at pHl0.2 selective flotation of quartz from cassiterite with S-4082 could be possible privided a proper depressant for cassiterite is available (see Fig. 6.7.11).

When ilmenite is present in cassiterite ores cassiterite can be selectively floated from ilmenite above pH4.0. The higher the pH, the less ilmenite floats.

Table 6.7.9 Flotation of apatite, fluorite, ilmenite and quartz of 0.125 +0.075 m.m. particle size with 100 mg/l S-3903 Conditioning time 10 min. Flotation time 5 min. Aeration rate 0.4 1/min. Agitation rate 1180 RPM.

6.7.9.a Apatite

PH	Floats %	Non-floats %
1.7	84.61	15.39
2.3	80.07	19.93
3.5	76.08	23.92
6.2	71.90	28.10
9.8	69.06	30.94
11.3	64.76	35.24
12.2	13.94	86.06

6.7.9.b Fluorite

рH	Floats %	Non-floats %
1.6	78.37	21.63
2.2	87.68	12.32
6.6	86.63	13.37
11.1	81.30	18.70
12.2	27.60	72.40

6.7.9.c Ilmenite

рH	Floats %	Non-floats %
1.6	85.68	14.32
2.1	84.38	15.62
2.9	46.77	53.23
3.8	26.09	73.91
6.4	11.01	88.99
8.5	5.96	94.04
11.6	0.84	99.16

6.7.9.d Quartz

рH	Floats %	Non-floats %
1.2	71.02	28.98
1.9	47.98	52.02
2.4	52.82	47.18
3.2	35.64	64.36
4.3	20.95	79.05
6.3	25.20	74.80
7.6	31.14	68.86
9.6	24.95	75.05
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Table 6.7.10 Flotation of apatite, fluorite, and quartz of -0.125 +0.075 m.m. particle size with 100 mg/l S-4082 Conditioning time 10 min. Flotation time 5 min. Aeration rate 0.4 l/min. Agitation rate 1180 RPM.

6.7.10.a Apatite

рH	Floats %	Non-floats %
2.2	62.24	37.76
4.2	58.73	41.27
6.3	64.01	35.99
8.2	61.78	38.22
10.1	75.86	24.14
11.7	20.50	79.50

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6.7.10.b Fluorite

рH	Floats %	Non-floats %
2.0	87.48	12.52
4.0	86.11	13.89
6.4	90.18	9.82
9.0	88.87	11.13
11.6	15.98	84.02

6.7.10.c Quartz

рH	Floats %	Non-floats %
2.0	45.28	54.74
4.2	50.68	49.32
6.3	49.47	50.53
8.2	42.75	57.25
10.3	91.88	8.12
10.6	84.19	15.81
11.6	32.49	67.51



рН

- 1 x Cassiterite (- 0.125 + 0.075 m.m.), 100 mg/1 S-3903
- 2 o Fluorite (-0.125 + 0.075 m.m.), 100 mg/1 S-3903
- 3 ^Δ Cassiterite (- 0.125 + 0.075 m.m.), 100 mg/l S-3903, 80 mg/l citric acid
- 4 □ Fluorite (- 0.125 + 0.075 m.m.), 100 mg/l S-3903, 80 mg/l citric acid
- 5 0 Cassiterite (- 0.125 + 0.075 m.m.), 100 mg/l S-3903, 80 mg/l AlCl₃
- 6 + Fluorite (- 0.075 + 0.038 m.m.), 100 mg/l S-3903, 80 mg/l AlCl₃
- Fig. 6.7.13 Flotation of cassiterite and fluorite with 100 mg/l S-3903 in the presence and absence of suppressing agents.

6.7.4 Suppressing fluorite

The results described in 6.7.3 indicate that cassiterite cannot be selectively floated from fluorite with S-3903, S-4082 without the aid of a selective depressant. The possible suppressing agents for fluorite as suggested by the American Cyanamid Company⁽⁸⁵⁾ are citric acid, barium chloride and aluminium salts. Barium chloride cannot be used for this purpose because it depresses cassiterite⁽⁸⁵⁾. Citric acid and aluminium chloride were considered in the present work. Fluorite and cassiterite were floated in the micro-flotation cell separately in the presence of a suppressing agent with S-3903 as a collector. Flotation with S-4082 in the presence of aluminium chloride was examined. The pH value was varied in all experiments while other factors were kept the same as follows:

Conditioning time	10 min.
Flotation time	5 min.

Rate of aeration0.4 l/min.Rate of agitation1180 RPM.Collector concentration100 mg/l.

Suppressing agent concentration 80 mg/1.

The experimental results are presented in Table 6.7.11 - 6.7.13 and Fig. 6.7.13 - 6.7.14.

6.7.4.1 Discussion of the results

<u>6.7.4.1.1 Citric acid</u> Citric acid was ineffective as a suppressing agent for fluorite when floated with S-3903 (see Table 6.7.11.b and Fig. 6.7.13). At pH4.2 the recovery of fluorite was reduced from about 87 to 64 per cent when citric acid was present. At this pH value the recovery of cassiterite was about 91 per cent in the presence of citric acid compared with 96 per cent when no citric



рH

- 1 × Cassiterite, 100 mg/l S-4082
- 2 o Fluorite, 100 mg/l S-4082
- 3 \triangle Cassiterite, 100 mg/l S-4082, 80 mg/l AlCl₃
- 4 D Fluorite, 100 mg/l S-4082, 80 mg/l AlCl₃

Fig. 6.7.14 Flotation of cassiterite and fluorite of 0.125 + 0.075 m.m. particle size with 100 mg/l S-4082, in the presence and absence of AlCl₃ acid was added (see Table 6.7.11.a and Fig. 6.7.13). At higher pH value the recovery of cassiterite decreased. Below pH4.0 citric acid had no effect on cassiterite flotation which indicated no adsorbtion of citric acid onto cassiterite surfaces. An ionic competition between S-3903 anions and citric acid anions for the site in the electrical double layer may be responsible for this phenomena. S-3903 anions may be preferentially adsorbed onto cassiterite surfaces. Above pH4.0 cassiterite surfaces were charged negatively so that an ionic adsorbtion of both citric acid and S-3903 anions due to coulombic forces was eliminated due to electrostatic repulsion between negatively charged surfaces and both reagent anions. In this pH range depressing effects from citric acid increased with pH. This may be due to the specific adsorption of citric acid onto cassiterite surfaces in preference to S-3903.

In the case of fluorite flotation, the presence of citric

acid lowered the recovery to about 70 per cent compared with about 87 per cent in the absence of citric acid. This indicated that the adsorbtion of S-3903 still occurred and resulted in the flotation. However, some citric acid was adsorbed onto the fluorite surfaces replacing some S-3903 anions and reducing the recovery.

<u>6.7.4.1.2 Aluminium chloride</u> In cassiterite-S-3903 system, aluminium chloride reduced the recovery of cassiterite from about 94 per cent at pH2.2 to about 5 per cent at pH3.1. Above pH4.0 the recovery increased from 4 per cent to about 77 per cent at pH8.0 (see Fig. 6.7.13). In the flotation of fluorite with S-3903,

aluminium chloride reduced the recovery of fluorite from 80 per cent at pH2.0 to about 45 per cent at pH3.1. The recovery increased above pH3.9 (46 per cent) to about 78 per cent at pH5.9 and it was nearly



Fig. 6.7.15 Logarithmic concentration diagram for 1×10^{-4} M Al⁺⁺⁺ (After Fuerstenau, M.C. and Palmer, B.R.⁽⁴²⁾)

constant at the pH value above this pH. It should be noted here that the fluorite samples used were of a finer particle size range than the cassiterite samples (-0.075 +0.038 m.m. compared with -0.125 +0.075 m.m. of cassiterite) (insufficient fluorite sample of -0.125 +0.075 m.m. being available). Therefore the less suppressing effect from aluminium chloride on fluorite may be due to the better floatability of the finer particles and/or the mechanical entrainment which was more for finer particles. If fluorite and cassiterite samples used were of the same particle size the results may be nearly similar to each other as happened in S-4082 system (see Fig. 6.7.13 and 6.7.14).

In S-4082 system the maximum suppressing effect from aluminium chloride on both cassiterite and fluorite occurred in approximately the same pH region, i.e. between pH3.0-5.1. Because aluminium chloride is a stable compound⁽⁸⁹⁾, it may

be in the form of neutral molecules at the highly acidic pH, i.e. pH2.2 so that it has no effect on the adsorption of collector anions (both S-3903 and S-4082) on cassiterite surfaces which are carrying a high magnitude of positive charges. When the pH increases aluminium chloride may start to hydrolise (90);

 $AlCl_3 + H_2O \longrightarrow Al (OH)_3 + HCl.$

When aluminium chloride hydrolises, the possible ionic species of aluminium may be Al^{+3} , $Al(OH)_{2}^{+1}$, $Al(OH)_{4}^{-1}$ and $Al(OH)_{3}$ (solid)⁽⁴²⁾ (see Fig. 6.7.15). Below pH4.0, Al^{+3} ions are the major ionic species while $Al(OH)_{2}^{+1}$ and $Al(OH)^{+2}$ ions are present in a minor concentration. The decrease in per cent recovery of cassiterite, when floated with S-3903, is probably due to the masking effect of Al^{+3} ions which reduce the amount of S-3903 to be adsorbed onto cassiterite surfaces. Al^{+3} ions may have stronger chemical affinity for S-3903 than cassiterite
does and may form a complex salt with the collector anions, thus reducing the amount of the collector available to be adsorbed onto cassiterite. Above pH4.0 the concentration of Al^{+3} decreases so that the amount of collector left to be adsorbed by cassiterite surfaces increases and consequently the recovery increases. When Al^{+3} ions concentration decreases to a minimum at about pH5.6 (see Fig. 6.7.15) the increase in the recovery of cassiterite is low (to about 25 per cent compared with 4 per cent at pH4.0 or with 94 per cent at pH5.6 when floated with S-3903 alone). This may indicate that $Al(OH)_2^{+1}$ ions have the same masking effects, but not as high as Al^{+3} ions because between pH4.0 and pH5.6 $Al(OH)_2^{+1}$ is the dominant ionic species of aluminium. Above pH5.1 the positive ionic species of aluminium ions decreases while the colloidal $Al(OH)_3$ starts to form quickly and results in less effects on the adsorbtion of the collector on cassiterite surfaces and consequently

the recovery increases.

The effect of aluminium chloride on the flotation of cassiterite with S-4082 may be described in the same way as in S-3903 system. However, $Al(OH)_2^{+1}$ ions may not have an effect on cassiterite-S-4082 system because the recovery suddenly increases when the pH is higher than 5.1 (to above 90 per cent at pH5.2 compared with 13 per cent at pH5.1). At this pH the major ionic species of aluminium, apart from colloidal $Al(OH)_3$, is $Al(OH)_2^{+1}$ ions (where its concentration is a maximum). The high recovery obtained at this pH indicates no effect of $Al(OH)_2^{+1}$ on the flotation process.

In the flotation of fluorite, the results are approximately similar to the flotation of cassiterite. So the explanation of the suppressing phenomena may be the same as described for cassiterite flotation. <u>6.7.4.2 Conclusion</u> The possible mechanism of citric acid and aluminium chloride on the flotation of cassiterite or fluorite with S-3903 or S-4082 has been discussed. The results indicate that neither citric acid nor aluminium chloride improve the selectivity of cassiterite flotation from fluorite. Aluminium chloride reacts to fluorite flotation in the same way as it does to cassiterite flotation. Although the recovery of fluorite decreases a little in the presence of citric acid, the recovery of cassiterite also decreases. The suppressing effect of citric acid on cassiterite flotation increases with pH increases above 2.2.

Therefore, it may be concluded that cassiterite cannot be selectively floated from fluorite under the conditions used here. The presence of fluorite at high concentration in cassiterite ores could produce problems because the cassiterite concentrate will contain a considerable amount of fluorite. Considering the pH of the ZPC of both minerals, the ZPC of cassiterite exists around pH 4.0 while that of fluorite is around pH9.7. A possible comment here is to find an anionic collecting agent which has no specific affinity for cassiterite and float fluorite from cassiterite above pH4.0. Another alternative is selective flotation of cassiterite from fluorite with a cationic collector above pH4.0 where cassiterite surfaces are charged negatively but fluorite is charged positively, provided the collector has no specific affinity for fluorite.

Table 6.7.11	Flotation of cassiterite and fluorite of	
	-0.125 +0.075 m.m. p	article size with
	100 mg/1 S-3903, precon	ditioned with 80 mg/1
	citric acid for 5 minut	es
	Conditioning time	10 min.
	Flotation time	5 min.
	Aeration rate	0.4 l/min.
	Agitation rate	1180 RPM.

6.7.11.a Cassiterite

pH	Floats %	Non-floats %
2.0	94.38	5.62
4.2	91.18	8.82
6.1	82.93	17.07
8.1	63.25	36.75

6.7.11.b Fluorite

рH	Floats %	Non-floats %
1.9	75.11	24.89
4.2	63.94	36.06
6.2	71.96	28.04
8.2	75.11	24.89

Table 6.7.12 Flotation of cassiterite and fluorite with 100 mg/l S-3903, preconditioning with 80 mg/l aluminium chloride for 5 minutes. (Controlling variables are as same as in Table 6.7.11)

6.7.12.a Cassiterite (-0.125 +0.075 m.m.)

рH	Floats %	Non-floats %
2.2	93.64	6.36
3.1	5.61	94.39
3.9	4.49	95.51
5.6	25.00	75.00
6.2	48.51	51.49

8.1	76.94	18.06	

6.7.12.b Fluorite (-0.075 +0.038 m.m.)

рH	Floats %	Non-floats %
2.0	80.61	19.39
3.1	45.10	54.90
3.9	46.19	53.81
5.9	78.97	21.03
8.1	75.26	20.64

Table 6.7.13Flotation of cassiterite and fluorite of

-0.125 +0.075 m.m. particle size with 100 mg/1

S-4032, preconditioned with aluminium chloride for 5 minutes. (Controlling variables are as same as in Table 6.7.11)

6.7.13.a Cassiterite

рH	Floats %	Non-floats %
2.0	92.25	7.75
3.2	1.93	98.07
4.0	7.15	92.85
5.1	13.17	86.83
5.2	88.19	11.81
5.4	92.13	7.87
5.9	92.91	7.09
6.5	89.79	10.21
8.7	96.44	3.56

рH	Floats %	Non-floats %
1.9	92.53	7.47
2.9	12.60	87.40
4.2	17.88	82.12
5.3	79.68	20.32
5.5	86.24	13.76
6.0	80.88	19.12
6.5	86.29	13.71
7.4	84.44	15.56
8.5	85.80	14.20
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Plate 2 Denver flotation cell

A Flotation cell

- B Air controlling valve
- C Air flow meter
- D Add-water hose
- E pH meter

CHAPTER 7

STUDY ON CASSITERITE FLOTATION KINETICS

7.1 Introduction

The purpose of the following work is to study the flotation kinetics of cassiterite. The factors influencing the kinetics of flotation studied included collector concentration (S-3903), conditioning time, frother concentration, rate of agitation, rate of aeration and particle size. The rate of flotation as a function of particle size was included.

7.2 Instruments

All flotation experiments were done in a 2.6-litre Denver flotation cell as shown in Plate 2. An air flowmeter was connected to the air-inlet of the cell for reading the rate of flow. The air

flow rate was adjusted by a value at the air-inlet of the cell. Above the flotation cell a small plastic hose was connected to a tap-water value for adding water into the cell in order to keep the level of the pulp in the cell approximately the same during the experiment. The level of the cell impeller was positioned about 10 mm. above the bottom of the cell in all experiments.

7.3 Sample preparation

Cassiterite ore used was from the same alluvial deposit as used in the study of cassiterite flotation in the micro-flotation cell. The ore was first screened into 3 fractions; +1.000 m.m., -1.000 + 0.500 m.m. and -0.500 m.m. Each fraction was cleaned on a Wilfley shaking table separately to eliminate major gangue minerals. The tabling products were divided into concentrate, middlings and tailing. Tailing was rejected and the concentrate was collected. The middlings was recleaned on the shaking table. An examination of products by use of a microscope was used as a guide for setting the shaking table. Heavy minerals other than cassiterite contained in the tabling concentrate of each fraction were eliminated by a Carp-co high-tension separator and Rapid magnetic separator. The high-tension separator was adjusted to produce a very high grade cassiterite. Examination of cassiterite content under a microscope was used as a guide for separator adjusting. More than 50 per cent of the feed was produced as a middlings and was returned to the separator. For the magnetic separator, the products were divided into 5 groups. The first two products which were highly magnetic were rejected. The third and fourth products which were medium and low magnetic were returned to the separator. The non-magnetic product was collected and recleaned many times followed by an examination of cassiterite content under a microscope in order to achieve a very high grade cassiterite.

Great care was taken to eliminate iron-bearing minerals. The average grade of cassiterite samples as examined under a microscope was above 95 per cent SnO_2 . The major impurity present was quartz (SiO₂). No iron-bearing minerals were observed in the final cassiterite samples.

A roll crusher was used for sample grinding. In order to minimise overgrinding, stage grinding in a closed circuit with screening was employed. Ground products of +1.000 m.m. and -1.000 +0.500 m.m. fractions were screened on 0.500 m.m. and 0.250 m.m. sieves. Oversized material was reground and the -0.250 m.m. products stored. The -0.500 +0.250 m.m. material combined with the -500 m.m. shaking table concentrate were ground in closed circuit with a 0.250 m.m. sieve and the oversizes reground. All -0.250 m.m. products were combined together and screened

on 4 sieves; 0.125, 0.090, 0.063 and 0.038 m.m. sieves. Oversized material was reground. Approximately 4 kg. of each size fraction were obtained. The remaining -0.250 m.m. material was screened using a set of sieves from 0.125 to 0.038 m.m. The products were stored for a study of the function of particle size on the cassiterite flotation kinetics. The minus 0.038 m.m. material was classified by a cyclosizer into 5 fractions, the selected sizes being 0.0240, 0.0177, 0.0126, 0.0086 and 0.0070 m.m. The two coarsest fractions were combined together in order to make about 4 kg. of cassiterite of particle size -0.0380 +0.0177 m.m. Approximately 400 gm. of each cyclosizer fraction were also stored separately.

A splitting riffle was used for dividing the samples for use in the experiment.

7.4 Reagents

The collector used was S-3903. The frother was MIBC. Dilute sulphuric acid and sodium hydroxide were used as pH regulators. S-3903 was prepared just before each experiment. It was diluted to the required concentration before use.

7.5 Experimental procedure

The method adopted for the flotation in Denver flotation cell was as follows:

- a) adjust water level in the cell and adjust the pulp pH within the range of 3.8 to 4.0,
- b) turn on the machine and adjust the agitation rate as required,
- add a prepared cassiterite sample into the cell, C) measure the pulp pH again and condition for 5 minutes,

- d) add required amount of S-3903, measure the pulp pH and readjust the pH unless it is in the range of 4.2 4.6,
- e) condition for 10 minutes,
- f) add required amount of MIBC as a frother,
- g) condition for 5 minutes,
- h) turn on the add-water value and air-inlet value and adjust the flow rate of air as required,
- i) float for 5 minutes,
- j) stop air flow (turn off the air-inlet valve) and stop the add-water,
- k) stop the machine,
- 1) weigh the floated product,
- m) filter both products and dry in the oven,
- n) weigh both dried products.

For the experiments in which the rate of flotation was

studied seven froth products were collected at the following time intervals; 0 - 20, 20 - 40, 40 - 60, 60 - 80, 80 - 120, 120 - 180 and 180 - 300 seconds. In some experiments when the flotation was slow the last time interval was divided into 180 - 240 and 240 - 300 seconds.

7.6 Study on the minimum concentration of S-3903 for cassiterite flotation

Collector concentration is one of the factors influencing the flotation of mineral particles. A certain minimum collector concentration is required for the particles to obtain enough surface coverages so that the adhesion between them and bubbles after collision is possible. Particles of different size need different minimum collector concentration. For finer particles, the surface area increases and so more collector is required in order to obtain the same surface coverages per unit of the surface area. On the other hand, when the particles are coarser the stability of particlebubble adhesion (or aggregates) becomes involved. As described in Chapter 4 on the topic of "Flotation Kinetics", for coarser particles the frictional drags or disruptive forces experiencing to the particle-bubble aggregates increases and thus the stability of the attachment decreases. Higher collector concentration may be required in order to increase the adhesion forces between the particles and the bubbles due to increases in surface coverages and consequently increases in the probability of the particles staying in contact with bubbles and being lifted to the froth. In the present investigation, in order to study a function of collector concentration (S-3903) on cassiterite flotation and an effect of particle size on the minimum collector concentration required for flotation, cassiterite of different size ranges were floated separately in a Denver-flotation cell in the presence of various S-3903 concentrations. The size ranges

selected were -0.1250 + 0.0900 m.m., -0.090 + 0.0630 m.m., -0.0630 + 0.0380 m.m., -0.0380 + 0.0177 m.m., and -0.0177 + 0.0126 m.m. and -0.0126 + 0.0086 m.m., the last three size ranges being the combination of the first and second, the third and the fourth fraction of cyclosizer products respectively. In each experiment an 80 gm. cassiterite sample was used. The controlling conditions were:

- conditioning time 10) min.
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- pH 4.2 4.6
- frother MIBC 0.15 kg/tonne
- rate of aeration 2.0 l/min.
- rate of agitation 1200 RPM.
- flotation time 5 min.

The experimental results are presented in Table 7.6.1.a -

7.6.1.f and Fig. 7.6.1 and 7.6.2.



- - 2 Ō - 0.0177 + 0.0126 m.m.
 - 0.0380 + 0.0177 m.m. 3 Δ
 - 4 🗆 - 0.0630 + 0.0380 m.m.
 - 5 × - 0.0900 + 0.0630 m.m.
 - $6 \quad 0 \quad 0.1250 + 0.0900 \text{ m.m.}$
- Fig. 7.6.1 Flotation of cassiterite of various particle sizes as a function of collector (S-3903) concentration

7.6.1 Discussion of the results

a) Particle size, -0.0126 + 0.0086 m.m.

The recovery of cassiterite increases as S-3903 concentration increases and reaches 84 per cent at the concentration of 0.17 kg/tonne. For further increases in the collector concentration, the recovery increases slightly to about 94 per cent when the collector concentration is 1.0 kg/tonne.

b) Particle size, -0.0177 + 0.0126 m.m.

Cassiterite of this particle size range responds to the increasing collector concentration in the same manner as the -0.0126 + 0.0086 size. The recovery at 0.17 kg/tonne is about 87 per cent and at 1.0 kg/tonne is about 97 per cent.

c) Particle size, -0.038 + 0.0177 m.m.

Cassiterite of this particle size range responds to the increasing collector concentration similarly. However, at

lower collector concentration (below 0.14 kg/tonne) its recovery is less but the maximum recovery at 0.17 kg/tonne collector concentration is higher than those obtained for cassiterite of the other two particle size ranges. At this concentration the recovery is about 94 per cent and at 1 kg/tonne the recovery is 99 per cent.

d) Particle size, -0.063 + 0.038 m.m.

The recovery increases with collector concentration and reaches 81 per cent at the concentration of 0.33 kg/tonne. At higher collector concentration, the recovery increases slowly to 99 per cent at the concentration of 1.0 kg/tonne.

e) Particle size, -0.090 + 0.063 m.m.

Increases in the collector concentration increase the recovery of cassiterite for this particle size range.



The recovery reaches 94 per cent at the collector concentration of 0.83 kg/tonne and 96 per cent at 1.0 kg/tonne.

f) Particle size, -0.125 + 0.090 m.m.

The recovery is very poor. At 1.0 kg/tonne collector concentration it is 53 per cent. Further increases in the collector concentration were not studied.

7.6.2 Conclusion

The results show that for a recovery of 90 per cent, the flotation of cassiterite of -0.125 + 0.090 m.m. particle size will not be achieved for the conditions studied here. This is due to poor floatability of cassiterite of this particle size. The influences of particle size on the flotation of cassiterite was studied and discussed in 7.8. For finer particle size ranges a high recovery can be achieved at the following concentration of S-3903 (see Fig. 7.6.1).

Particle size (mm)	S-3903 concentration (kg/tonne)
- 0.0900 + 0.0630	0.79
- 0.0630 + 0.0380	0.72
- 0.0380 + 0.0177	0.16
- 0.0177 + 0.0126	0.38
- 0.0126 + 0.0086	0.47

This may indicate that for satisfactory flotation, the collector concentration required for cassiterite of -0.038 + 0.0177 m.m. particle size is the lowest. Higher concentration is required for the finer and coarser particle size. This can be seen clearly in Fig. 6.7.2 where the per cent recovery is plotted against the particle size with

various collector concentrations. It may be said that the critical particle size ranges for the optimum in the cassiterite-S-3903 The increases in the minimum system is -0.038 + 0.0177 m.m. collector concentration required for the flotation of cassiterite coarser than this critical particle size range may be explained in terms of the stability of cassiterite-bubble adhesion in the flotation To explain this two published reports are referred, T.M. Morris⁽⁹¹⁾ system. and A.M. Gaudin and K. Vincent⁽⁹²⁾. Morris⁽⁹¹⁾ introduced a term of the degree of flexibility of the bubble-particle attachment which was defined as the difference between the maximum contact angle possible for the collector system and static contact angle required for the equilibrium between bubble and particle system. The greater the degree of the flexibility of the system, the greater is the ability of the bubbleparticle adhesion forces to withstand disruption. Gaudin and Vincent reported that the maximum contact angle increased as the collector

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concentration increased. Thus the degree of flexibility increases and the probability of the system to withstand the disruptive forces increases. Therefore the recovery increases as a result of high probability of particles being lifted up to the surface by bubbles. When the particle size increases, the disruptive force increases so that it requires greater static contact angle for the equilibrium of bubble-particle system. By this, the degree of flexibility decreases and consequently the recovery decreases as well. To obtain the same degree of flexibility, a higher collector concentration is required to increase the value of the maximum contact angle. This means that the minimum collector concentration for cassiterite coarser than the critical size range (-0.038 + 0.0177 m.m.) must be higher.

For cassiterite finer than -0.038 + 0.0177 m.m., the increases in the collector concentration required for the flotation may be due to the increases in the surface area of the particles. The finer the particle the more is the surface area. For a given collector concentration, starvation condition may occur when the surface area increases to a critical limit. Some particles may not obtain enough surface coverages for equilibrium of bubble-particle attachment and a decrease in the per cent recovery occurs. Thus, higher concentration of collector is required for the finer cassiterite to obtain a satisfied flotaion.

So far, the following conclusions may be made.

a) The minimum collector concentration required for the flotation of cassiterite is a function of particle size.

b) Cassiterite of -0.038 + 0.0177 m.m. in size requires the lowest S-3903 concentration. Higher collector concentration is required for finer or coarser cassiterite.

c) If 90 per cent recovery is required for the flotation of

mixed-size cassiterite, the minimum concentration of S-3903 should be

about 0.8 kg/tonne.

Table 7.6.1 Flotation of cassiterite of various particle size

ranges as a function of S-3903 concentration

Conditioning time	10	min.
рН	4.2-4.6	
Frother, MIBC	0.15	kg/tonne
Aeration rate	2.0	l/min.
Agitation rate	1200	RPM.
Flotation time	5	min.

7.6.1.a - 0.1250 + 0.0900 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.00	0.13	99.87
0.17	8.88	91.12
0.33	15.88	84.12
0.50	31.25	68.75
0.67	36.75	63.25
0.82	42.12	57.88
1.00	53.50	46.50

7.6.1.b - 0.0900 + 0.0630 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.00	2.62	97.38
0.17	44.00	56.00
0.33	55.80	44.20
0.67	78.60	21.40
0.82	94.12	5.88
1.00	95.88	4.12

Table 7.6.1 cont.

7.6.1.c - 0.0630 + 0.0380 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.00	2.41	97.59
0.05	12.88	87.12
0.17	37.38	62.62
0.33	81.12	18.88
0.50	81.88	18.12
0.67	88.50	11.50
0.82	94.13	5.87
1.00	98.88	1.12

7.6.1.d - 0.0380 + 0.0177 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.00	5.38	94.62
0.05	21.38	78.62
0.17	93.75	6.25
0.33	95.62	4.38
0.67	97.62	2.38
1.00	98.75	1.25

Table 7.6.1 cont.

7.6.l.e - 0.0177 + 0.0126 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.05	71.88	28.12
0.17	87.38	12.62
0.33	89.25	10.75
0.67	95.75	4.25
1.00	96.75	3.25

7.6.1.f - 0.0126 + 0.0086 m.m.

S-3903 concn. kg/tonne	Floats %	Non-floats %
0.05	53.75	46.25
0.17	84.38	15.62
0.33	88.25	11.75
0.67	92.75	7.25
1.00	94.62	5.38

7.7 Function of frother, agitation rate, aeration rate and conditioning time on the flotation of different particle sizes of cassiterite

In the flotation system, the adsorption of a collector onto mineral surfaces needs a period of time to reach the equilibrium between mineral surfaces and collector ions in the pulp. If this period of time is not achieved the adsorption will not be complete and as a result, the surfaces will be less hydrophobic and consequently their floatability is less. So the conditioning time is one of the important factors influencing the flotation of minerals. Frothers influence the flotation in such a way that they make the froth tougher so that the bubbles do not break easily during the collision or after adhesion with mineral particles. The presence of a frother affects the adhesion between bubbles and particles by decreasing the induction time required for the adhesion⁽⁶⁷⁾. The rate of air applied to the flotation cell affects the flotation system. Higher rates of air input produce a larger number of bubbles and increase the probability of the collision between bubbles and particles. Extremely high rates of aeration may cause turbulence in the cell and increase the disruptive forces. By this the probability of particles staying in contact with bubbles may be less and the per cent recovery may decrease.

Agitation rate influences the flotation. Sufficient intensity of agitation is required in order to obtain complete dispersion of mineral particles in the flotation cell.

In the present work, the influences of the factors mentioned above on the recovery of cassiterite of four different particle size ranges were studied using a 2.6 litre Denver flotation cell. The four particle size ranges of cassiterite studied were - 0.125 + 0.090 mm, - 0.090 + 0.063 mm, - 0.063 + 0.038 mm and - 0.038 + 0.0177 mm.



- 1 □ 0.0630 + 0.0380 m.m.
- 2 ° 0.0900 + 0.0630 m.m.
- 3 × 0.1250 + 0.0900 m.m.
- Fig. 7.7.1 Flotation of cassiterite of various particle sizes as a function of frother (MIBC) concentration

The finest particle size fraction is the combination of cyclosizer fraction one and two.

The influences of a frother were studied first followed by agitation rate, rate of aeration, and conditioning time respectively. The controlling factors used in the study of a frother were the same as that in 7.6 but the collector concentration (S-3903) was selected at 1.0 kg of S-3903/tonne of cassiterite because at this concentration maximum recovery was obtained for cassiterite of all particle size ranges studied in 7.6. The frother used was MIBC. The optimum value found in each study was used for the later studies. For example, an amount of frother used in the study of agitation rate was selected from the optimum value found in the study of frother.

The experimental results are presented in Table 7.7.1 - 7.7.4 and Fig. 7.7.1 - 7.7.4.

7.7.1 Discussion of the results

7.7.1.1 Effects of MIBC concentration on cassiterite recovery

No flotation of cassiterite occurs without MIBC. According to the observation, very few bubbles can reach the surface of the cell and their sizes were very large. When MIBC is present the recovery increases quickly and reaches a maximum at 0.09 kg/tonne concentration. (see Fig. 7.7.1) For further increases in frother addition the recovery remains approximately constant.

The increases in per cent recovery in the presence of MIBC may be explained by 3 possible factors, namely the induction period, size of the bubbles and toughness of the froth. As indicated by Lekki and Laskowski⁽⁵⁹⁾, the induction time required for the bubble-particle attachment decreases rapidly with increasing frother concentration. This may be due to the presence of the frother in the bubble-particle interfaces which displaces water between the bubble and particle faster. As a result, the probability of bubble-particle adhesion after collision increases.

As the frother concentration increases, it was observed that the bubble size became smaller. For a given air input, the number of bubbles must increase when the bubble size is reduced. Therefore the probability of collision between bubbles and particles, which is in a function of the number of bubbles, increases.

The toughness of the froth increases with the increase of frother concentration so that the tendency of the bubbles to break during collision with mineral particles or coalesce with other bubbles is reduced.

Combination of the three factors described above may lead to increases in the recovery of cassiterite as the frother concentration

increases unless the bubbles generated are too small. (If so, the bubbles will reduce "lifting" ability). Flotation of cassiterite in the presence of MIBC without S-3903 was studied but no flotation occured. This indicates that MIBC has no collecting property for cassiterite.

It can be seen from Fig. 7.7.1 that the recovery of cassiterite of - 0.125 + 0.090 m.m. in size tends to decrease for MIBC concentration above 0.21 kg/tonne. Above this concentration the bubble size was very small (as observed). These very small bubbles may not have enough bouyancy to carry the attached particles up to the surface and consequently, the recovery is lower. The recovery of cassiterite of - 0.090 + 0.063 m.m. particle size does not decrease at the concentration of MIBC above 0.21 kg/tonne as compared to - 0.125 + 0.090 m.m. particle size fraction since the particle is smaller and the bubble bouyancy is sufficient to lift particles of this size. It may be possible to postulate that an excess of MIBC may decrease recovery. Unfortunately the flotation in the presence of MIBC higher than 0.27 kg/tonne was not studied to confirm this postulation.

Frother concentration of 0.09 kg/tonne was selected for the later investigations.

Table 7.7.1 Flotation of cassiterite of various particle sizes as a function of MIBC concentration Collector 1.0 kg/tonne S-3903 Conditioning time 10 min. Flotation time 5 min. pH 4.2 - 4.6 Aeration rate 2.0 1/min. Agitation rate 1200 RPM.

7.7.1.a - 0.1250 + 0.0900 m.m.

MIBC concn. kg/tonne	Floats %	Non-floats %
0.00	0.00	100.00
0.03	41.12	58.88
0.09	53.50	46.50
0.15	53.50	46.50
0.21	54.12	45.88
0.27	51.12	48.88

120.

Table 7.7.1 cont.

7.7.1.b - 0.0900 + 0.0630 m.m.

MIBC concn. kg/tonne	Floats %	Non-floats %
0.00	0.00	100.00
0.03	87.12	12.88
0.09	95.25	4.75
0.15	95.88	4.12
0.21	96.38	3.62
0.27	95.25	4.75

7.7.1.c - 0.0630 + 0.0380 m.m.

MIBC concn. kg/tonne	Floats %	Non-floats %
0.00	0.00	100.00
0.03	91.75	8.25
0.09	98.38	1.62
0.15	98.88	1.12
0.21	99.25	0.75



7.7.1.2 Effects of agitation rate

The optimum agitation rate for the flotation of cassiterite of the size ranges of - 0.038 + 0.0177, 0.063 + 0.038 and 0.090 + 0.063 m.m. exists between 1200 - 1450 RPM. At the agitation rate lower or higher than this range the recovery decreases. The lower limit for the flotation of cassiterite of - 0.125 + 0.090 m.m. in size is higher than those three size fractions, being at 1300 RPM. This may be due to their larger size of particles which need more agitation intensity in order to keep them in suspension.

The rate of agitation necessary for complete suspension was indicated by Foust (93) to increase with particle size. This supports the above explanation.

The variation of per cent recovery with agitation rate may be explained by the variation of bubble size generated in the flotation cell. With a given air input, it was found by Foust (93) that bubble

dispersion varied with the square root of power intensity. Because power intensity is a function of agitation rate, it can be said that bubble dispersion increases with agitation rate. This means that when the agitation rate increases the bubble size decreases, thus the number of bubbles increases. As a result, the probability of collision between bubbles and particles increases. Furthermore, as the number of bubbles increases, the surface area of bubbles in a unit volume of pulp increases which increases the surface area for the attachment. Coupled with the increases in the probability of collision, the probability of cassiterite particles being lifted to the surface is greater, thus the recovery increases. This explanation can be applied in the case of the lower agitation rate (1100 - 1200 RPM). When the agitation rate eventually increases to above this critical value the bubble size generated may be too small to levitate the attached particles. This results in a decrease in the recovery as occurs in the present investigation at an agitation rate higher than 1450 RPM. Another reason may be due to changes in bubble-particle attachment stability. As the agitation rate increases the centrifugal forces increases so that the disruptive forces are higher and consequently, the probability of particles to be detached from bubbles is greater which results in the lower per cent recovery.

It can be seen from Fig. 7.7.2 that the rate of decrease in per cent recovery varies with particle size. For the coarser particles (say - 0.125 + 0.090) the disruptive forces are higher due to higher relative mass so that the effect of the agitation rate is greater than that for the finer particles. The decreases in per cent recovery for cassiterite of - 0.038 + 0.0177 m.m. in size is very small.

Table 7.7.2Flotation of cassiterite of various particle

sizes as a function of agitation rate

Collector 1.0 kg/tonne S-3903

Conditioning time 10 min.

Flotation time 5 min.

рН 4.2 - 4.6

Aeration rate 2.0 1/min.

Frother 0.09 kg/tonne MIBC

7.7.2.a - 0.1250 + 0.0900 m.m.

Agitation rate RPM	Floats %	Non-floats %
1200	53.50	46.50
1300	66.25	33.75
1400	61.75	38.25

1500	61.75	38.25
1600	55.25	44.75
1800	41.25	58.75

7.7.2.b - 0.0900 + 0.0630 m.m.

Agitation rate RPM	Floats %	Non-floats %
1100	75.00	25.00
1200	95.25	4.75
1300	91.50	8.50
1450	92.62	7.38
1600	85.88	14.12
1800	80.38	19.62

Table 7.7.2 cont.

7.7.2.c - 0.0630 + 0.0380 m.m.

Agitation rate RPM	Floats %	Non-floats %
1100	94.50	5.50
1200	98.38	1.62
1300	98.38	1.62
1450	97.25	2.75
1600	92.12	7.88
1800	88.25	11.75

7.7.2.d - 0.0380 + 0.0177 m.m.

Agitation rate RPM	Floats %	Non-floats %
1100	95.38	4.62
1200	98.20	1.80
1300	97.88	2.12
1500	97.50	2.50
1750	96.00	4.00

Fig. 7.7.3 Flotation of cassiterite of various particle size ranges as a function of aeration rate

$$1 \times -0.1250 + 0.0900 \text{ m.m.}$$

$$2 \circ -0.0900 + 0.0630 \text{ m.m.}$$

$$3 \square -0.0630 + 0.0380 \text{ m.m.}$$

$$4 \triangle -0.0380 + 0.0177 \text{ m.m.}$$



7.7.1.3 Effects of the rate of aeration

The experimental conditions used here were the same as used in the study of agitation rate. Optimum agitation rate of 1300 RPM. was used. For the present experimental conditions the maximum rate of aeration the machine could produce was limited to 2.5 l/min. The variation of air flow rate studied was from 1.0 to 2.5 l/min. The experimental results are given in Table 7.7.3 and Fig. 7.7.3. The recovery of -0.090 + 0.063, -0.063 + 0.038 and -0.038 + 0.0177 mm fraction increases when the air flow rate increases from 1.0 to 1.5 l/min. After that it is nearly constant. The air flow rate-recovery curve of -0.063 + 0.038 mm fraction and -0.038 + 0.0177 mm fraction are approximately similar to each other while that of -0.090 + 0.063 mm fraction is different. Its rate of increase of recovery (or slope) is higher than that for the two finer fractions. The influences of air flow rate on -0.125 + 0.090 mm fraction differ from those on the

other three fractions. Its recovery increases with air flow rate and reached a maximum at 2.0 1/min. (67 per cent recovery). After that the recovery decreases.

The increases in per cent recovery when the air flow rate increases may be explained by the increases in the number of bubbles generated in the flotation cell. The greater the number of bubbles, the higher is the probability of bubble-particle collision, hence the higher is the per cent recovery. At 1.5 1/min. air flow rate, the recovery of - 0.125 + 0.090 mm fraction has not reached a maximum while those of the three finer fraction have. (See Fig. 7.7.3). This phenomenon is not clearly understood. However, it may be explained that cassiterite particles of this size may be so large and heavy that they require combination of more than a single bubble to lift them to the surface. Hence, they may require a greater number of bubbles.

The decreases in per cent recovery of - 0.125 + 0.090 m.m. fraction at the air flow rate higher than 2.0 l/min. may result from the turbulence condition of the pulp due to too high a rate of aeration (as described in Chapter 4). Therefore the disruptive forces increase so that the stability of bubble-particle attachment decreases and thus, the recovery is lower. In case of the three finer fractions, the recovery does not decrease at this rate of aeration. It may be due to smaller-sized particles which the increasing disruptive forces under the present turbulence condition may be still lower than the critical value to overcome the attractive (adhesion) forces between bubbles and particles. It was expected that the recovery might decrease for further increases in the air flow rate when the disruptive forces due to turbulence condition increased to above the critical limit of the adhesion forces between bubbles and cassiterite particles.

Table 7.7.3 Flotation of cassiterite of various particle sizes

as a function of aeration rate

Collector	1.0 kg/tonne	S-3903
Conditioning time	10 min.	
Flotation time	5 min.	
рН	4.2 - 4.6	
Agitation rate	1300 RPM.	
Frother	0.09 kg/tonne M	IIBC

7.7.3.a - 0.1250 + 0.0900 m.m.

Aeration rate l/min.	Floats %	Non-floats %
1.0	39.75	60.25
1.5	54.00	46.00
2.0	66.25	33.75

2.0	00.23	55.15
2.5	46.38	53.62

7.7.3.b - 0.0900 + 0.0630 m.m.

Aeration rate l/min.	Floats %	Non-floats %
1.0	79.25	20.75
1.5	94.62	5.38
2.0	91.50	8.50
2.5	97.00	3.00

7.7.3.c - 0.0630 + 0.0380 m.m.

Aeration rate 1/min.	Floats %	Non-floats %
1.0	96.25	3.75
1.5	98.50	1.50
2.0	98.38	1.62
2.5	99.62	0.38

7.7.3.d - 0.0380 + 0.0177 m.m.

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Aeration rate l/min.	Floats %	Non-floats %
1.0	95.12	4.88
1.5	98.12	1.88
2.0	97.88	2.12
2.5	99.25	0.75


- 1 × 0.0380 + 0.0177 m.m.
- 2 o 0.0630 + 0.0380 m.m.
 - 3 □ 0.0900 + 0.0630 m.m.
 - 4 \triangle 0.1250 + 0.0900 m.m.
- Fig. 7.7.4 Flotation of cassiterite of various particle sizes as a function of conditioning time

- $\theta d = Dynamic contact angle$ $\Theta s = Static contact angle$
 - R = Bubble radius



Particle diameter (m.m.)

Fig. 7.7.5 Minimum contact angles which permit fruitful contact (After Robinson, A.J.⁽⁹⁴⁾)

7.7.1.4 Effects of conditioning time

The control conditions used here were the same as used in 7.7.1.3. The optimum rate of aeration of 2.0 l/min. was selected. The experimental results are given in Table 7.7.4 and Fig. 7.7.4.

The results show that the conditioning time required for the flotation of cassiterite of - 0.125 + 0.090 and - 0.090 + 0.063 m.m. in size is about 3 minutes. Further conditioning does not increase the recovery. In the flotation of -0.063 + 0.038 m.m. fraction, conditioning time of one minute is enough. For the finest fraction (- 0.038 + 0.0177 m.m.), the conditioning time required increases again. These phenomena may be described in terms of the contact angle. The required minimum contact angle for the flotation of different size particles was described by A.J. Robinson⁽⁹⁴⁾. He calculated the minimum contact angle for the levitation of a particle by bubbles under static condition (static contact angle) after Morris⁽⁹¹⁾ and the minimum dynamic contact angle which permitted rupture of the fluid phase during the time of first contact (or for particle-bubble adhesion) under dynamic condition after Philippoff⁽⁷⁶⁾ (see Fig. 7.7.5). The dynamic contact angle decreases with increasing particle size while static contact angle increases with particle size. As seen from Fig. 7.7.5, for a given bubble size there is an optimum size of particle at the point of intersection of the static and dynamic contact angle. For finer or coarser particles a larger contact angle is required. As a certain period of time is required to obtain the maximum contact angle, during this period Seidler⁽⁹⁵⁾ showed that the contact angle increased with conditioning time until a maximum was obtained. According to the above explanation, it is now possible to discuss the results of the present investigation. The optimum particle size (as in the explanation of

Robinson) may be in the range of -0.063 + 0.038 m.m. For finer (- 0.038 + 0.0177) or coarser (- 0.090 + 0.063 and 0.125 + 0.090 m.m.) cassiterite the maximum contact angle required is higher so that they need longer conditioning times in order to achieve more surface coverage and improved contact angle.

Table 7.7.4 Flotation of cassiterite of various particle sizes

as a function of conditioning time

Collector	1.0 kg/tonne S-3903
Flotation time	5 min.
Frother	0.09 kg/tonne MIBC
рH	4.2 - 4.6
Aeration rate	2.0 1/min.
Agitation rate	1300 RPM.

7.7.4.a - 0.1250 + 0.0900 m.m.

Conditioning time min.	Floats %	Non-floats %
1.0	39.62	60.38
3.00	51.12	48.88
6.00	46.38	53.62
10.50	54.00	46.00
16.00	52.75	47.25

7.7.4.b - 0.0900 + 0.0630 m.m.

Conditioning time min.	Floats %	Non-floats
1.00	54.48	45.52
3.00	93.38	6.62
6.00	95.50	4.50
10.00	92.50	7.50
15.00	95.62	4.38

Table 7.7.4 cont.

7.7.4.c - 0.0630 + 0.0380 m.m.

Conditioning time min.	Floats %	Non-floats %
1.00	98.00	2.00
3.00	98.12	1.88
6.00	98.75	1.25
10.00	98.38	1.62
16.00	98.38	1.62

7.7.4.d
$$- 0.0380 + 0.0177$$
 m.m.

Conditioning time min.	Floats %	Non-floats %
1.75	94.75	5.25
3.50	96.88	3.12
6.00	98.25	1.75
10.00	97.88	2.12
15.00	98.62	1.38

7.7.2 Conclusion

The influences of MIBC (frother), agitation rate, aeration rate and conditioning time on the recovery of cassiterite have been discussed. The following conclusion may be made.

> a) No flotation of cassiterite with S-3903 occurs in the absence of MIBC. The minimum concentration of 0.09 kg/tonne of MIBC is required. The influences of MIBC concentration are determined by the reduction in induction time required for bubble-particle attachment, the reduction in bubble size and hence increases in the number of bubbles, and the increases in toughness of the froth. With the extremely high concentration of MIBC (0.27 kg/tonne), the recovery of - 0.125 + 0.090 m.m. fraction decreases. It was expected that further increases in MIBC concentration might reduce the recovery of the other two finer

fractions.

b) At the agitation rate below 1450 RPM, the recovery of cassiterite increases when the agitation rate increases. Above 1450 RPM the recovery decreases. The optimum value was found to be at 1300 RPM. The rate of decrease of the per cent recovery at the agitation rate above the 1450 RPM varied with particle size, being less for finer cassiterite. The influences of agitation rate on the recovery of cassiterite are determined by the degree of dispersion of cassiterite in the flotation system, bubble size and the number of bubbles, and centrifugal forces induced by the agitation.

- The optimum rate of aeration was found to be at 2.0 1/min. C) for the present condition. Below 2.0 1/min. the recovery increases when the rate of aeration increases. Above this rate the recovery of - 0.125 + 0.0900 m.m. fraction decreases while those for the three finer fractions remain nearly the same. It was expected that further increases in the aeration rate might decrease the recovery of all fractions due to more turbulence in the flotation The influences of the rate of aeration on the system. recovery of cassiterite are determined by the increases in the number of bubbles in the system which increase the probability of bubble-particle collision, and the turbulence condition in the system when extremely high rates of aeration are introduced into the flotation
 - system.

d) The conditioning time required for the flotation of different size fractions is different. Cassiterite of - 0.063 + 0.038 m.m. fraction requires the least conditioning time, being less than one minute while longer conditioning time is required for the finer or coarser fraction. The influences of conditioning time on the recovery of cassiterite are determined by the degree of surface coverage necessary to produce the minimum contact angle required for bubbleparticle attachment which depends on the conditioning time available.



Fig. 7.8.1.a Time - cum % recovery curves of cassiterite of several particle sizes (- 0.0450 m.m. to + 0.0070 m.m.)



Fig. 7.8.1.b Time - cum % recovery curves of cassiterite of various particle sizes (- 0.1250 m.m. to + 0.0450 m.m.)

7.8 Study on the influences of particle size on the rate of flotation and recovery of cassiterite

In the flotation system, particle size is one of the important factors influencing flotation kinetics of minerals. The maximum flotation of a mineral occurs in a certain range of particle sizes. The recovery and rate of flotation decreases for finer or coarser particles. In the present work the influences of particle size on the rate of recovery and rate of flotation of cassiterite were investigated. Samples of cassiterite of different particle sizes were floated separately in a 2.6 litre Denver flotation cell. The following variables were maintained constant:-

Collector	l kg/tonne S-3903
Frother	0.09 kg/tonne MIBC
Conditioning time	10 minutes
pH of the pulp	4.2 - 4.6

Agitation rate 1300 RPM

Aeration rate 2.0 l/min.

Froth products were collected at several time intervals in order to study the rate of the flotation process. Zero, first and second order rate of flotation (or rate constant) were calculated.

7.8.1 Experimental results and discussion

7.8.1.1 Recovery of cassiterite

The experimental results are tabulated in Table 7.8.1. The cumulative per cent recovery of cassiterite for each particle size range was plotted against time in Fig. 7.8.1.a and 7.8.1.b. The influences of particle size on the recovery of cassiterite is shown in Fig. 7.8.6. In this figure the value of per cent recovery is the cumulative per cent recovery after 300 seconds flotation as shown in Table 7.8.1. Fig. 7.8.1 shows that the maximum recovery exist for cassiterite of particle size ranging from 0.015 - 0.068 m.m. and its value is around 95 per cent. For finer or coarser cassiterite the recovery decreases. The recovery of finer particles of cassiterite decreases to about 90 per cent for cassiterite of 0.0070 m.m. in size. For coarser particles of cassiterite the recovery decreases remarkedly and is less than 10 per cent for cassiterite of - 0.1250 + 0.1060 m.m. in size (see also Fig. 7.8.1.b., curve 6).

Table 7.8.1	Experimental results	of the flotation rate study
	of cassiterite of va	rious particle sizes
	Collector	1.0 kg/tonne S-3903
	Conditioning time	10 min.
	Frother	0.09 kg/tonne MIBC
	pH	4.2 - 4.6
	Aeration rate	2.0 l/min.
	Agitation rate	1300 RPM
	Pulp volume	2.6 litre
	Weight of feed	140 gm.

7.8.1.a - 0.1250 + 0.1060 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	2.8	2.00	2.00	52.77
40	2.7	1.93	3.93	51.73
60	1.2	0.86	4.79	51.27
80	1.6	1.14	5.93	50.65
120	1.2	0.86	6.79	50.19
180	0.3	0.21	7.00	50.08
300	2.1	1.50	8.50	49.27
Total floats	11.9	8.50		<u></u>
Non-floats	128.1	91.50		
Total	140.0	100.00		

7.8.1.b - 0.1060 + 0.0900 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	13.9	9.93	9.93	48.50
40	9.6	6.86	16.79	44.81
60	8.2	5.86	22.65	41.65
80	4.4	3.14	25.79	39.96
120	6.8	4.86	30.65	37.35
180	5.4	3.86	34.51	35.27
300	7.6	5.43	39.94	32.35
Total floats	55.9	39.94		
Non-floats	84.1	60.06		
Total	140.0	100.00		

137.

7.8.1.c - 0.0900 + 0.0750 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	14.3	10.25	10.25	48.33
40	14.2	10.14	20.39	42.87
60	8.2	5.88	26.25	39.71
80	9.3	6.64	32.89	36.14
120	13.0	9.29	42.18	31.14
180	19.3	13.79	55.97	23.71
240	9.8	7.00	62.97	19.94
300	2.7	1.93	64.90	18.90
Total floats	90.9	64.90		
Non-floats	49.1	35.10		
Total	140.0	100.0		

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7.8.1.d - 0.0750 + 0.0630 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	11.1	7.93	7.93	49.58
40	29.5	21.07	29.00	38.23
60	17.8	12.71	41.71	31.38
80	10.6	7.57	49.28	27.31
120	23.9	17.07	66.35	18.12
180	31.6	22.57	88.92	5.96
300	11.0	7.80	96.78	1.73
Total floats	135.5	96.78		
Non-floats	4.5	3.22		
Total	140.00	100.00		

Table 7.8.1 cont.

7.8.1.e - 0.0630 + 0.0530 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	48.0	34.29	34.29	35.38
40	43.4	31.00	65.29	18.69
60	25.0	17.86	83.15	9.08
80	9.6	6.88	90.01	5.38
120	6.0	4.29	94.30	3.03
180	2.2	1.57	95.87	2.23
300	1.4	1.00	96.87	0.54
Total floats	135.6	96.87		
Non-floats	4.4	3.13		
Total	140.0	100.00		

Table 7.8.1 cont.

7.8.1.f -0.0530 + 0.0450 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0	0.00	0.00	53.85
20	51.6	36.86	36.86	34.00
40	58.0	41.43	78.29	11.69
60	16.3	11.64	89.93	5.42
80	3.9	2.79	92.72	3.92
120	3.3	2.36	95.08	2.65
180	3.0	2.14	97.22	1.50
240	0.7	0.50	97.72	1.23
300	0.7	0.50	98.22	0.90
Total floats	137.5	98.22		
Non-floats	2.5	1.78		
Total	140.0	100.00		

Table 7.8.1 cont.

7.8.1.g - 0.0450 + 0.0380 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	53.2	38.00	38.00	33.38
40	59.9	42.79	80.79	10.35
60	16.2	11.57	92.36	4.12
80	3.2	2.29	94.65	2.88
120	2.8	2.00	96.65	1.81
180	1.9	1.36	98.00	1.08
240	0.3	0.21	98.21	0.96
300	0.1	0.07	98.28	0.92
Total floats	137.6	98.28		-
Non -floats	2.4	1.72		
Total	140.0	100.00		

Table 7.8.1 cont.

7.8.1.h - 0.0380 + 0.0240 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	79.9	57.07	57.07	23.16
40	41.1	29.36	86.43	7.31
60	11.1	7.93	94.36	3.04
80	3.3	2.36	96.72	1.77
120	1.4	1.00	97.72	1.23
180	0.1	0.07	97.79	1.19
300	0.1	0.07	97.86	1.15
Total floats	137.0	97.86		
Non-floats	3.0	2.14		
Total	140.0	100.00		

7.8.1.i - 0.0240 + 0.0177 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	74.4	53.14	53.14	25.23
40	37.4	26.71	79.85	10.85
60	13.7	9.79	89.64	5.58
80	4.4	3.14	92.78	3.88
120	2.7	1.93	94.71	2.85
180	0.7	0.50	95.21	2.58
300	0.1	0.07	95.28	2.54
Total floats	136.4	95.28		
Non-floats	3.6	4.72		
Total	140.0	100.00		

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Table 7.8.1 cont.

7.8.1.j - 0.0177 + 0.0126 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	71.8	51.29	51.29	26.23
40	31.8	22.71	74.00	14.00
60	14.8	10.57	84.57	8.31
80	5.8	4.14	88.71	6.08
120	6.7	4.79	93.50	3.50
180	5.4	3.86	97.36	1.42
300	2.7	1.93	99.29	0.38
Total floats	139.0	99.29		
Non-floats	1.0	0.71		
Total	140.0	100.00		

Table 7.8.1 cont.

7.8.1.k - 0.0126 + 0.0086 m.m.

Time sec.	Weight of floats gm.	Weight %	Cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	37.3	26.64	26.64	39.50
40	38.2	27.29	53.93	24.81
60	9.0	6.43	60.36	21.35
80	8.4	6.00	66.36	18.12
120	14.9	10.64	77.00	12.38
180	14.4	10.27	87.27	6.35
300	9.5	6.79	94.06	3.19
Total floats	131.7	94.06		
Non-floats	8.3	5.94		
Total	140.0	100.00		

Table 7.8.1 cont.

7.8.1.1 - 0.0086 + 0.0070 m.m.

Time sec.	Weight of floats gm.	Weight %	cum. recovery %	Residual concentration gm/l
0	0.0	0.00	0.00	53.85
20	23.5	16.79	16.79	44.81
40	33.4	23.86	40.65	31.96
60	21.1	15.07	55.72	23.85
80	8.4	6.00	61.72	20.62
120	18.6	13.29	75.01	13.46
180	11.7	8.36	83.37	8.96
300	10.5	7.50	90.87	4.92
Total floats	127.2	90.87		
Non-floats	12.8	9.13		
Total	140.0	100.00		

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- 1 + -0.0086 + 0.0070 m.m.
- 2 o 0.0126 + 0.0086 m.m.
- 3 △ 0.0177 + 0.0126 m.m.
- $4 \times -0.0240 + 0.0177$ m.m.
- 5 🗆 0.0380 + 0.0240 m.m.
- $6_0 0.0450 + 0.0380$ m.m.
- Fig. 7.8.2.a Time residual concentration curves of cassiterite of several particle sizes (- 0.0450 m.m. to + 0.0070 m.m.)



Time (sec)

1 '+ - 0.0530 + 0.0450 m.m.

2 <u>-</u> - 0.0630 + 0.0530 m.m.

3 ▲ - 0.0750 + 0.0630 m.m.

4 × - 0.0900 + 0.0750 m.m.

5 ° - 0.1060 + 0.0900 m.m.

6 0 - 0.1250 + 0.1060 m.m.

Fig. 7.8.2.b Time - residual concentration curves of cassiterite of various particle sizes (- 0.1250 m.m. to 0.0450 m.m.)

7.8.1.2 Flotation rate

The determination of the rate of flotation was based on equation 4.3.11, 4.3.13 and 4.3.14 (in Chapter 4) for zero, first and second order rate constant respectively. The calculations are tabulated in Tables 7.8.2.a - 7.8.2.1. The residual concentration was determined by dividing the weight of cassiterite remaining in the flotation pulp by the pulp volume, of 2.6 litre.

According to Fig. 7.8.2.a - 7.8.2.b where the residual concentration of various particle size is plotted against time, the residual concentration at time, 300 seconds can be considered to be approximately the concentration of non-floatable fraction (C_{m}) . The zero, first and second order plot of various particle size are shown in Fig. 7.8.3.a - 7.8.3.c, 7.8.4.a - 7.8.4.c, and 7.8.5.a - 7.8.5.c respectively. These plots indicate that the flotation of cassiterite is likely to correspond well to the first order rate equation. The rate constant represented by the slope of the graph was determined using linear regression method. The rate constants of various particle size are tabulated in Table 7.8.3. The influence of particle size on the rate of flotation are shown in block diagram in the same figure as per cent recovery (Fig. 7.8.6), the rate of flotation being the first order rate constant. It can be seen that the rate constant is a maximum for cassiterite of - 0.0380 + 0.0240 m.m. in size, being about $55 \times 10^{-3} \text{ sec}^{-1}$. The rate constant of finer or coarser cassiterite decreases.



1, 2, 3, 4 Values from experimentsa, b, c, d Values from linear regression

Fig. 7.8.3.a Zero order plot of the flotation of cassiterite of various particle sizes





- 1, 2, 3, 4 Values from experiments
- a, b, c, d Values from linear regression
- Fig. 7.8.3.b Zero order plot of the flotation of cassiterite of various particle sizes







1, 2, 3, 4 Values from experiments

a, b, c, d Values from linear regression

Fig. 7.8.3.c Zero order plot of the flotation of cassiterite of various particle sizes



- 1, 2, 3, 4 Values from experiments
- a, b, c, d Values from linear regression
- Fig. 7.8.4.a First order plot of the flotation of cassiterite of various particle sizes



- 1, 2, 3, 4 Values from experiments
- a, b, c, d Values from linear regression
- Fig. 7.8.4.b First order plot of the flotation of cassiterite of various particle sizes







Fig. 7.8.5.a Second order plot of

the flotation of cassiterite of

various particle sizes





Time (sec) 1, 2, 3, 4 Values from experiments

a, b, c, d Values from linear regression

Fig. 7.8.5.c Second order plot of the flotation of cassiterite of various particle sizes
Table 7.8.2 Calculation of first order, second order and zero order rate constant

Assumption: $\mathrm{C}_{_{\!\!\infty}}$ = the residual concentration at time = 300 sec.

7.8.2.a particle size - 0.1250 + 0.1060 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C_{o} - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C _o - C
0	53.85	4.58	0.0000	0.0000	0.00
20	52.77	3.50	0.2689	0.0674	1.08
40	51.73	2.46	0.6215	0.1882	2.12
60	51.27	2.00	0.8286	0.2817	2.58
80	50.65	1.38	1.1996	0.5063	3.20
120	50.19	0.92	1.6051	0.8686	3.66
180	50.08	0.81	1.7324	1.0162	3.77
300	49.27				

150.

Table 7.8.2 cont.

7.8.2.b particle size - 0.1060 + 0.0900 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{0}-C_{\infty}}$	Zero order C _o - C
0	53.85	21.50	0.0000	0.0000	0.00
20	48.50	16.15	0.2861	0.0154	5.35
40	44.81	12.46	0.5455	0.0337	9.04
60	41.65	9.30	0.8380	0.0610	12.20
80	39.96	7.61	1.0386	0.0849	13.89
120	37.35	5.00	1.4586	0.1535	16.50
180	35.27	2.92	1.9965	0.2960	18.58

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7.8.2.c particle size - 0.0900 + 0.0750 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{0}-C_{\infty}}$	Zero order C ₀ - C
0	53.85	34.95	0.0000	0.0000	0.00
20	48.33	29.43	0.1719	0.0054	5.52
40	42.87	23.97	0.3881	0.0131	10.98
60	39.71	20.81	0.5185	0.0194	14.14
80	36.14	17.24	0.7067	0.0294	17.71
120	31.14	12.24	1.0492	0.0531	19.71
180	23.71	4.81	1.9832	0.1793	30.14
240	19.94	1.04	3.5147	0.9329	33.91
300	18.90		: 1		
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151.

152.

Table 7.8.2 cont.

7.8.2.d particle size - 0.0750 + 0.0630 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C _o - C
0	53.85	52.12	0.0000	0.0000	0.00
20	49.58	47.85	0.0860	0.0017	4.42
40	38.23	36.50	0.3568	0.0082	15.62
60	31.38	29.65	0.5647	0.0147	22.47
80	27.31	25.58	0.7123	0.0199	26.54
120	18.12	16.39	1.1574	0.0418	35.73
180	5.96	4.25	2.5072	0.2161	47.89
300	1.73				

1			1	
1				
	1		1	1
	1	•	1	1
			1	
				1
1			5	
	4		1	1
			1	

7.8.2.e particle size - 0.0630 + 0.0530 m.m.

Time sec.	C gm/l	C - C gm/1	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C _o - C
0	53.85	53.31	0.0000	0.0000	0.00
20	35.38	34.84	0.4254	0.0099	18.47
40	18.69	18.15	1.0774	0.0363	35.16
60	9.08	8.54	1.8314	0.0983	44.77
80	5.38	4.84	2.3992	0.1873	48.47
120	3.08	2.54	3.0440	0.3749	50.77
180	2.23	1.69	3.4514	0.5230	51.62
	1		1		

153.

300	0.54		

7.8.2.f particle size - 0.0530 + 0.0450 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C ₀ - C
0	53.85	52.89	0.0000	0.0000	0.00
20	34.00	33.04	0.4705	0.0114	19.85
40	11.69	10.73	1.5952	0.0743	42.16
60	5.42	4.46	2.4731	0.2053	48.43
80	3.92	2.96	2.8830	0.3189	49.93
120	2.65	1.69	3.4435	0.5728	51.20
180	1.50	0.54	4.5844	1.8329	52.35

154.

240	1.23	0.27	5.2776	3.6848	52.62
300	0.96				

7.8.2.g particle size - 0.0450 + 0.0380 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_o - C_{\infty}}{C - C_{\infty}}$	Second order 1 - 1 $C-C_{\infty} C_{0}-C_{\infty}$	Zero order C _o - C
0	53.85	52.93	0.0000	0.0000	0.00
20	33.38	32.46	0.4890	0.0119	20.47
40	10.35	9.43	1.7251	0.0872	43.50
60	4.12	3.20	2.8058	0.2936	49.63
80	2.88	1.96	3.2960	0.4913	51.57
120	1.81	0.89	4.0855	1.1047	52.04
180	1.08	0.16	5.8016	6.2311	52.77
240	0.96	0.04	7.1879	24.8911	52.89
300	0.92				

156.

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Table 7.8.2 cont.

7.8.2.h particle size - 0.0380 + 0.0240 m.m.

Time sec.	C gm/l	$C - C_{\infty}$ gm/1	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C ₀ - C
0	53.85	52.70	0.0000	0.0000	0.00
20	23.16	22.01	0.8731	0.0265	30.69
40	7.31	6.16	2.1465	0.1434	46.54
60	3.04	1.89	3.3280	0.5101	50.81
80	1.77	0.62	4.4426	1.5939	52.08
120	1.23	0.08	6.4903	12.4810	52.62
180	1.19	0.04	7.1835	24.9810	52.66
300	1.15				

Table 7.8.2 cont.

7.8.2.i	particle size	- 0.0240 +	0.0177 m.m.
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Time sec.	C gm/l	C – C gm/l	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C ₀ - C
0	53.85	51.31	0.0000	0.0000	0.00
20	25.23	22.69	0.8160	0.0246	28.62
40	10.85	8.31	1.8204	0.1008	43.00
60	5.58	3.04	2.8260	0.3095	48.27
80	3.88	1.34	3.6452	0.7268	49.97
120	2.85	0.31	5.1091	3.2063	51.00
180	2.58	0.04	7.1568	24.9805	51.27

100	2.50	0.04	00C1.1	24.9003	J1.27	
300	2.54					

7.8.2.j particle size - 0.0177 + 0.0126 m.m.

Time sec.	C gm/l	C - C gm/1	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C _o - C
0	53.85	53.47	0.0000	0.0000	0.00
20	26.23	25.85	0.7268	0.0200	27.62
40	14.00	13.62	1.3676	0.0547	39.85
60	8.31	7.93	1.9085	0.1074	45.54
80	6.08	5.70	2.2386	0.1567	47.77
120	3.50	3.12	2.8413	0.3018	50.35
180	1.42	1.04	3.9399	0.9428	52.43

158.

300	0.38		

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Table 7.8.2 cont.

7.8.2.k particle size - 0.0126 + 0.0086 m.m.

Time sec.	C gm/l	C - C gm/1 [∞]	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order $\frac{1}{C-C_{\infty}} - \frac{1}{C_{O}-C_{\infty}}$	Zero order C _o - C
0	53.85	50.66	0.0000	0.0000	0.00
20	39.50	36.31	0.3330	0.0078	14.35
40	24.81	21.62	0.8515	0.0265	19.04
60	21.35	18.16	1.0259	0.0353	32.50
80	18.12	14.93	1.2218	0.0472	35.73
120	12.38	9.19	1.7070	0.0891	41.47
180	6.85	3.66	2.6277	0.2535	47.00
300	3.19				

160.

Table 7.8.2 cont.

7.8.2.1 particle size - 0.0086 + 0.0070 m.m.

	Time sec.	C gm/l	C - C gm/1	First order $\ln \frac{C_{o} - C_{\infty}}{C - C_{\infty}}$	Second order 1 - 1 $C-C_{\infty} - C_{0} - C_{\infty}$	Zero order C _o - C
	0	53.85	48.93	0.0000	0.0000	0.00
	20	44.81	39.89	0.2043	0.0046	9.04
	40	31.96	27.04	0.5931	0.0165	21.89
	60	23.85	18.93	0.9496	0.0324	30.00
	80	20.62	15.70	1.1367	0.0432	33.23
	120	13.46	8.54	1.7456	0.0967	40.39
	180	8.96	4.04	2.4942	0.2271	44.89
1			1			

300	4.92		

7.8.2 Conclusion

7.8.2.1 The order of the rate equation of the flotation process

The order of the rate equation has been proposed by many investigators to vary between first and second order. Some investigators indicated that the flotation process could be described by first order rate equation $^{(71, 96, 97, 98, 99)}$ while the others indicated the second order rate equation $^{(100)}$.

In the present work, there is evidence showing that the flotation of cassiterite conforms well to the first order rate equation. The first order rate equation fits the experimental data more than does a zero or second order rate equation (see Fig. 7.8.3 - 7.8.5). The deviation of the experimental data from the best-fit linear line was postulated by the author to be due to the decreases in the pulp concentration when the flotation proceeds because no addition of new cassiterite into the cell to compensate the cassiterite particle

being removed to the froth products. This is a common problem in the batch flotation study.

7.8.2.2 Influences of particle size on the rate constant and per cent recovery of cassiterite

Cassiterite of -0.0380 + 0.0240 m.m. has the highest rate of recovery. The rate constant decreases for coarser or finer cassiterite. The decreases of the rate constant for finer particles agree with the prediction of K.L. Sutherland⁽⁷⁴⁾ and the work of Gaudin, Schuhmann and Schlechten⁽¹⁰¹⁾ that the rate constant varies with particle size. This is the role of the probability of particlebubble collision which decreases when the particle is finer as discussed in the previous part of this chapter. When the probability of particle-



Geometric mean of particle size (m.m.)

bubble collision decreases, the rate of flotation decreases. The behaviour of the particle of cassiterite coarser than 0.0380 m.m. in size opposes this explanation. However, it agrees with T.M. Morris⁽⁹¹⁾ who noted that the probability of the bubble-particle system to withstand the disruptive forces decreases when the particle is coarser so that the particles tend to be detached from the bubbles. As a result the rate of flotation decreases.

As can be seen in Fig. 7.8.6, while the rate of flotation decreases for cassiterite finer than 0.0240 m.m., as well as that coarser than 0.0380 m.m., the recovery remains approximately constant. The recovery decreases when the particle of cassiterite is finer than 0.0086 m.m. or coarser than 0.0750 m.m. This indicates that high recovery of cassiterite of this size range (- 0.0240 + 0.0086 m.m. and - 0.075 + 0.038 m.m.) can be achieved if enough time is available for the flotation although they float slowly. This can be seen clearly in

Fig. 7.8.1.a and 7.8.1.b.

So far it can be concluded that:-

a) regarding to the maximum per cent recovery of cassiterite, the optimum particle size ranges from 0.0086 m.m. to 0.0750 m.m.,

b) the rate constant is a maximum for cassiterite of

- 0.0380 + 0.0240 m.m., being 55 x 10^{-3} sec⁻¹ for first order rate flotation,

- c) for finer or coarser cassiterite the rate constant decreases,
- d) the present data of the flotation of cassiterite fit

the first order rate equation than zero and second order rate equation.

Table 7.8.3 Flotation rate constant of various particle size

Particle size mm	Zero order rate constant x10 ⁻² (gm.1 ⁻¹ sec ⁻¹)	First order rate constant x10 ⁻³ (sec ⁻¹)	Second order rate constant $x10^{-5}$ (1.gm ⁻¹ sec ⁻¹)
-0.1250+0.1060	0.0302	13.6	610
-0.1060+0.0900	0.1342	12.2	110
-0.0900+0.0750	0.1661	8.7	40
-0.0750+0.0630	0.3090	9.9	30
-0.0630+0.0530	0.6162	26.8	230
-0.0530+0.0450	0.6422	30.6	420
-0.0450+0.0380	0.6620	36.4	630
-0.0380+0.0240	0.8414	55.2	1840
-0.0240+0.0177	0.7960	43.4	870
-0.0177+0.0126	0.7442	23.5	200
-0.0126+0.0086	0.3431	14.0	60
-0.0086+0.0070	0.3413	14.8	60

CHAPTER 8

GENERAL DISCUSSION AND CONCLUSION

Mineralogy and geological occurence, general concentration methods and surface properties of cassiterite including early works in the flotation of cassiterite and flotation kinetics have been reviewed. A micro-flotation cell was constructed for the study of the collector systems for cassiterite flotation and the influences of associated minerals. Kinetic flotation of cassiterite was studied using a 2.6 litre Denver flotation cell. The topics studied included the influences of frother (MIBC), conditioning time, rate of agitation and rate of aeration on the recovery of cassiterite. The influences of particle size on the flotation rate and recovery of cassiterite was also included.

8.1 The collector system for cassiterite flotation

Four collecting agents were studied, being Aerosol-22, Aero-845 Promoter, S-3903 and S-4082. S-3903 and S-4082 float cassiterite over a wide range of pH, from highly acidic pH to pH10.2 for S-3903 and pH8.2 for S-4082 while Aerosol-22 floats cassiterite in the pH range below pH2.6 and Aero-845 Promoter in the pH range below pH2.85. It was postulated that the collecting mechanism of Aerosol-22 and Aero-845 Promoter were solely of electrostatic origin. The adsorption of these collectors onto cassiterite surfaces occurs in the pH region below the pH of the ZPC of cassiterite (the ZPC being around pH4.0) where the surfaces are charged positively. No specific adsorption is present. For S-3903 and S-4082, the collecting mechanisms are not solely of electrostatic origin but chemical reaction or specific adsorption also plays a large role. Below the pH of the ZPC, the adsorption of these collectors is due to the electrostatic attraction between positively charged surfaces and collector anions. Above the pH of the ZPC, the adsorption still occurs. This was postulated to be due to the specific adsorption of collector owing to the strong chemical affinity of these collectors for cassiterite. The attractive forces due to chemical affinity may be higher than the repulsion between negatively charged surfaces and collector anions so that adsorption occurs. Above pH10.2 for S-3903 and 8.2 for S-4082 the repulsion becomes higher because of higher negatively charge at the surface so that the adsorption decreases, hence the recovery decreases.

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The influences of galena, pyrite, fluorite, apatite, quartz and ilmenite on the flotation of cassiterite in the presence of S-3903 and S-4082 were studied.

a) Galena and pyrite Both minerals may occur in cassiterite ores espeically in pneumatolytic type deposits. In some mine where galena is present in large amounts its concentrate is produced economically. Galena and pyrite are more floatable than cassiterite. Therefore it is necessary to float them from cassiterite prior to the flotation of cassiterite.

In the present work, galena floated well with sodium ethyl xanthate between pH4.0-9.0 while cassiterite did not. So galena can be selectively floated from cassiterite by sodium ethyl xanthate. Pyrite

floats to some degree with sodium ethyl xanthate but better recoveries were obtained at a pH less than 9.7 with potassium amyl xanthate which is the longer chain xanthate. No flotation of cassiterite occurs with potassium amyl xanthate at any pH values. When both galena and pyrite are present two-stage flotation is required to remove them from cassiterite ores. Galena was floated first by sodium ethyl xanthate followed by the flotation of pyrite with potassium amyl xanthate. When galena is present in small amounts it may not be economical to produce its concentrate, so a one-stage flotation with potassium amyl xanthate can be employed to float both galena and pyrite from cassiterite ore.

b) Fluorite and apatite The maximum flotation of fluorite and apatite with S-3903 and S-4082 occurs in nearly the same pH range as that of cassiterite. The collecting mechanism of S-3903 on cassiterite, fluorite and apatite flotation are nearly similar.

The specific adsorption of the collector is important. The maximum recovery of fluorite and apatite when floated with S-3903 are around 85 and 70 per cent respectively compared with 95 per cent recovery for cassiterite. For flotation with S-4082, specific adsorption is important for apatite flotation while only the adsorption due to electrostatic forces occurs in collector-fluorite system. With both collectors apatite and fluorite tend to float with cassiterite. This indicates that cassiterite cannot be selectively floated from apatite and fluorite with S-4082 or S-3903 alone.

Suppressing fluorite with citric acid and aluminium chloride was investigated. No improvement of the selectivity was achieved. Aluminium chloride suppresses both cassiterite and fluorite in nearly the same pH range. Citric acid suppresses fluorite to some degree but it suppresses cassiterite also at the pH value above 4.0. So the selective flotation of cassiterite from fluorite is not improved.

Suppressing apatite was not studied. More detail involving the flotation and suppression of apatite may be seen in the work by $Mishra^{(87)}$.

<u>c)</u> Quartz The present work indicates that cassiterite can be fairly selectively floated from quartz by S-3903 at pH4.3 although quartz floats to some extent with this collector (about 20 per cent recovery). It is difficult to float cassiterite from quartz with S-4082 because nearly 50 per cent of quartz content floats. However, it is noted that at pH10.2 selective flotation of quartz from cassiterite with S-4082 could be possible if a proper depressant for cassiterite is available.

d) Ilmenite The presence of ilmenite in cassiterite

ores does not affect the results of cassiterite flotation. Cassiterite can be selectively floated from ilmenite by S-3903 above pH4.0. The higher the pH, the less does ilmenite float .

8.3 Flotation kinetics

8.3.1 Influences of collector concentration

It was found that the minimum collector concentration required for the flotation of cassiterite is a function of particle size. Cassiterite of - 0.0380 + 0.0177 m.m. particle size requires the lowest collector concentration. Higher concentration is required for coarser or finer cassiterite. The degree of flexibility of bubbleparticle attachment describes the higher collector concentration required for coarser cassiterite. The higher the collector concentration,

the larger is the maximum contact angle and the greater is the degree of flexibility. As a result, the probability of bubble-particle system to withstand the disruptive forces increases. When particle size increases, higher collector concentration is needed to increase the flexibility so that the stability of bubble-particle attachment increases. For finer cassiterite, the surface area of cassiterite particles is important. Higher concentration of collector is required for finer cassiterite in order to obtain the necessary surface coverages for an equilibrium of bubble-particle attachment. The minimum concentration of S-3903 required for 90 per cent recovery of mixed particle sized cassiterite was found to be around 0.8 kg/tonne.

Influences of frother, agitation rate, aeration rate, 8.3.2

conditioning time and particle size

The rate of flotation and rate of recovery of cassiterite is determined by 3 probabilities,

- the probability of collision between bubbles and particles, a.
- the probability of attachment or adhesion after collision, b.
- the probability of bubble-particle system to withstand and c. the disruptive forces.

Frothers influence the flotation of cassiterite by all three above probabilities. Increases in concentration of frother reduce bubble size, hence increase the number of bubbles in the cell which result in an increase in the probability of the collision. Decreases in the induction period with increasing frother concentration increases the probability of adhesion. Toughness of the froth increases with frother concentration so that the probability of bubble-particle system to withstand the disruptive forces increases. As a result, the recovery of cassiterite increases when frother concentration increases. However,

excess amounts of the frother (MIBC) reduce the recovery because the bubbles produced are too small to carry the attached particles. The minimum concentration of frother (MIBC) required was found to be 0.09 kg/tonne. Without MIBC cassiterite flotation with S-3903 does not occur.

Agitation rate influences the flotation of cassiterite by the degree of dispersion of cassiterite in the flotation system, bubble size and centrifugal forces induced by the agitation. The dispersion of cassiterite in the cell varies directly with agitation rate and inversely with particle size. Coarser cassiterite needs higher rates of agitation. The increases in agitation rate also reduces the bubble size and hence increases the number of bubbles in the cell which result in greater probability of bubble-particle collision. However, extremely high rates of agitation increase the centrifugal forces so that the stability of bubble-particle system decreases. The optimum agitation

rate for cassiterite flotation for the present conditions was found to be about 1300 R.P.M. The influences of agitation rate on the recovery of cassiterite varies directly with particle size.

The rate of aeration influences the flotation of cassiterite by increasing the probability of collision when the rate of aeration increases. However, extremely high rates of aeration cause turbulent conditions which reduce the stability of bubble-particle system. The optimum rate of aeration was found to be around 2.0 l/min.

Conditioning time required for the flotation of different particle sizes of cassiterite increases at the finer and coarser end of particle size. Cassiterite of - 0.063 + 0.038 m.m. required the lowest conditioning time, being only one minute. The influences of conditioning time on the recovery of cassiterite are determined by the degree of surface coverage for producing the minimum contact angle which depends directly on the time available for conditioning. Particle size influences the rate of flotation and rate of recovery of cassiterite. At the coarser end the rate of flotation and recovery decreases with increasing particle size since the disruptive forces increase and consequently the stability of bubble-particle system decreases. At the finer end, the probability of collision is important. The finer the particles, the less is the probability of collision so that the rate constant and recovery decreases.

The optimum particle size, regarding to the recovery, was found to range from 0.0086 m.m. to 0.0750 m.m. The rate constant of cassiterite of 0.0380 + 0.0240 m.m. particle size is maximum, being $55 \times 10^{-3} \text{sec}^{-1}$ for first order rate constant. The flotation of cassiterite (as in the present work) is likely to fit the first order rate equation more than the zero and second order rate equation.

8.4 Recommendation for further work

It has been shown that S-3903 floats cassiterite over a wide range of pH. Selective flotation of cassiterite from quartz and ilmenite is possible but selective flotation of cassiterite from fluorite and apatite with this collector is difficult. The cassiterite samples used were from an alluvial deposit and its properties may differ from cassiterite from other sources. Therefore, it is recommended that further work be done to study the flotation of other gangue minerals with S-3903, the use of other collecting agents and cassiterite from other sources.

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