

**REVIEW OF
DEVELOPMENTS IN CASSITERITE FLOTATION IN
RESPECT OF PHYSICO-CHEMICAL
CONSIDERATIONS**

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REVIEW OF DEVELOPMENTS IN CASSITERITE FLOTATION IN RESPECT OF PHYSICO-CHEMICAL CONSIDERATIONS

by

P.R.A. Andrews*

Abstract

The development of cassiterite flotation has progressed along a varied and diverse course. Early experimentation was restricted mainly to the use of either alkyl carboxylate or alkyl sulphate collectors, and selectivity depended on an optimum combination of activator, depressant and pH modifier. Current developments are concentrating on either synthesizing selective collectors of the arsonic, phosphonic, sulphosuccinamate and humic acid derivatives, or exploring the possibilities of new techniques such as electroflotation and dissolved air flotation.

A comprehensive review of the main developments of cassiterite flotation by each of the main collector systems is presented. These systems include oleic acid and sodium oleate, alkyl sulphates, sulphonates and sulphosuccinamate derivatives, alkyl hydroxamic acid, aryl arsonic acid, alkyl phosphonic acid derivatives and cationic collectors. Flotation with a variety of miscellaneous collectors is also included.

Flotation with each collector system is discussed in terms of surface charge, point of zero charge, limits of flotation with reference to pH, minimum and maximum collector concentration, depression, activation (including pseudo depression and activation) and collector adsorption mechanisms. When possible, the type and scale of technique are quoted, which can range from contact angle and bubble pick-up to plant-scale investigations.

Cassiterite often occurs with iron oxide and silicate minerals that possess similar flotation characteristics. Differences in flotation behaviour between cassiterite and two commonly occurring minerals, topaz and tourmaline, are discussed where they occur with each collector system.

Most of the major anionic collectors were used in processing plants at different times; the use of styrene phosphonic acid at Altenberg, East Germany, appears to be the most selective.

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The potential of alternative techniques – sulphidization, electrolytic reduction, selective aggregation, two-liquid flotation, carrier flotation and dissolved air flotation – are briefly discussed. Selective aggregation and dissolved air flotation are considered to be potential techniques for the recovery of minus 5 μm cassiterite.

Keywords: Cassiterite, topaz, tourmaline, collector selectivity, depressants, activators, chelating and sequestering agents.

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INTRODUCTION

Finely disseminated cassiterite ores cannot be treated efficiently by gravity concentration, because of the inherent inefficiency of gravity concentration techniques at sizes less than 75 μm . This is partly due to the friable nature of cassiterite, so that much valuable mineral is lost in the tailings as fine slimes. Successful separation by flotation was hindered because of the non-selective nature of some of the earlier collectors that were used to separate cassiterite from commonly occurring silicate minerals, e.g., topaz and tourmaline. Collectors early considered included the alkyl carboxylates and sulphates. More recently attention has focused on the alkyl amines, sulphonates, sulphosuccinamates, hydroxamates and phosphonic, arsonic and hydroxamic acids. In fact, commercial plants have been designed incorporating flotation of cassiterite. Thus, Kirchberg and Wottgen (1964) described the use of para-tolyl arsonic acid, and recently Mosch and Becker (1985), the use of styrene phosphonic acid at Altenberg, East Germany. Styrene phosphonic acid was also reported as concentrating minus 6 μm cassiterite at the Rooiberg Tin mine in South Africa (Owen, 1988). In the United Kingdom, Moncrieff et al. (1973) described the use of octadecyl sulphosuccinamate at the Wheal Jane mine, and in the U.S.S.R., Pol'kin et al. (1973) the plant use of p-nitrobenzeneazosalicylic acid as collectors for cassiterite.

Concurrent with the development of new and more selective collectors was the development of improved flotation techniques. Two such techniques that have been applied to cassiterite flotation are electroflotation, which employs the principle of electrolysis (Mamakov, Sorokina and Avvakumov, 1969; Hogan, Kuhn and Turner, 1979), and dissolved air flotation (DAF). Dissolved air flotation, originally developed for sewage treatment, is based on air dissolved in water under pressure. The air-saturated water is injected through a valve into a flotation cell, and the resultant pressure reduction across the valve causes the formation of a cloud of fine bubbles. DAF has been successfully applied to float 50% <5 μm cassiterite (Gochin and Solari, 1983; Solari, 1983).

Since cassiterite flotation is now becoming so diverse, the variety of phosphonic acid derivatives alone coming onto the market is increasing rapidly, a review of past and present developments is considered necessary to aid those concerned with cassiterite flotation.

CRYSTAL STRUCTURE

Cassiterite has the 6.3 coordination rutile structure, and X-ray diffraction study (Bragg and Claringbull, 1965) has shown that the tin atoms are arranged on a body-centred tetragonal lattice. Each tin atom is surrounded by six oxygen atoms approximately at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle.

Cassiterite shows an imperfect cleavage on the 100 plane, so that fracture will tend to follow in a vertical direction. Fracture will therefore cut across bonds joining tin atoms rather than tin-oxygen bonds, so that tin atoms will be exposed on the surface. The surface exposure of oxygen ions is also possible, since fracture is not necessarily confined to cleavage planes.

Cassiterite is represented by the chemical formula SnO_2 and when pure contains 78.8% Sn, but in practice impurities are normally present. The principal lattice impurity is Fe^{3+} and although usually present in minor amounts, <1% Fe, as much as 7.8% Fe^{3+} can be present as a lattice impurity (Pryor and Wrobel, 1951).

SURFACE PROPERTIES

The double layer surrounding hydrous oxides was postulated by Johnson (1984) as being influenced by surface site density and the standard free energies of adsorption of hydrogen ions and the ions of the supporting electrolyte.

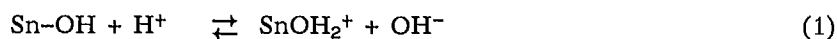
The surfaces of non-metallic oxide minerals are understood by studying the structure of the electrical double layer, which consists of ions that determine the sign of the surface charge (potential-determining ions) and counter ions required for electroneutrality. Only one side of a fracture surface is considered, when attempting to determine which ions are exposed; the other side of the surface being considered to have similar ions exposed due to the alternate arrangement of atoms.

When discussing the surface properties of cassiterite, a distinction is drawn between natural cassiterite and artificially prepared cassiterite or stannic oxide, as this latter form is chemically more active than natural cassiterite. Reported point of zero charge (p.z.c.) data, unless otherwise stated, refer to determinations conducted in the presence of indifferent electrolytes, e.g., perchlorate or chloride ion.

Surface charge and p.z.c.

The surface properties of natural cassiterite were studied by Gaudin and Sun (1946); O'Connor and Buchanan (1953); Ahmed and Maksimov (1969); and using stannic oxide, by Edwards and Ewers (1951); Johansen and Buchanan (1957b); Jaycock, Ottewill and Tar (1964) and by Pol'kin et al. (1973). The results of these investigations indicate that cassiterite has an amphoteric oxide surface of the type proposed for iron oxides (Parks and de Bruyn, 1962; Joy and Watson, 1964) where the hydrated OH^- layer acquires an electrical charge by ionization (Edwards and Ewers, 1951; O'Connor and Buchanan, 1953). Cibulka and Dobias (1963) suggested that the crystal surface is composed of O^{2-} and Sn^{2+} , and that when hydrated, the surface would consist of SnOH species. Evidence supporting this supposition was found from infrared spectra which showed the presence of an OH band.

Edwards and Ewers (1951) state further that the idea of amphoteric OH^- is consistent with the ability of the surface to act as an acid when titrated with alkalis. The mechanism whereby cassiterite acquires a surface charge is represented as follows:



(after Jaycock, Ottewill and Tar, 1964)

The sign of the surface charge is determined by the pH of the medium, i.e., H^+ and OH^- are potential-determining ions, since the pH of the medium controls the extent of surface ionisation. This agrees with the studies of Aplan and Fuerstenau (1962) for other oxide minerals, rutile and corundum.

The point of zero charge (p.z.c.) of cassiterite was reported as occurring between neutral and slightly acid pH values (Abeidu, 1975 at pH 6.9; Ahmed and Maksimov, 1969 at pH 5.6; Degoul, 1969 at pH 4.5; Zambrana, Romero and Gutierrez, 1970 at pH 4.0; Blazy, Degoul and Houot, 1969 at pH 3.4; and Taha et al., 1986 at pH 2.0). The indication is that the p.z.c. occurs in such pH regions if cassiterite is free of impurities. Point of zero charge values have been reported as high as 7.4 (O'Connor and Buchanan, 1953; Johansen and Buchanan, 1957b), which is due to the presence of foreign metal ions in the crystal lattice. In particular, if Fe^{3+} is present the p.z.c. will be shifted to the slightly alkaline pH regions (Cibulka and Dobias, 1963). There is no known data correlating p.z.c. of cassiterite with the concentration of Fe^{3+} in the lattice, but the following data seems to indicate a tentative relationship.

<u>p.z.c.</u>	<u>% Fe^{3+}</u>	<u>Reference</u>
4.2	0.5	Gochin and Solari (1983)
4.5	0.6	Doren, Van Lierde and de Cuyper (1979)
5.5	1.0	Ball, Cox and Yap (1979)

It would be of interest to know the p.z.c. values of the high-iron cassiterite samples reported by Pryor and Wrobel (1951). Nevertheless, even when cassiterite is free of impurities, the p.z.c. varies from 4.0 – 5.6, and a possible reason for this variation is that different techniques were used by the different investigators to obtain these values. Hence, Degoul (1969) used electrophoresis techniques, whilst Ahmed and Maksimov (1969) obtained their results from potentiometric titrations.

Significance of the p.z.c. on adsorption

The importance of determining the sign of the surface charge of cassiterite in order to ascertain whether cassiterite would respond to anionic or cationic collectors, was demonstrated by Blazy, Degoul and Houot (1969). In a study of the flotation of hematite and goethite, Iwaski, Cooke and Choi (1960) found that the point of zero charge was only significant in determining floatability for

low-chain length collectors, for example, amines and alkyl sulphates. As the chain length was increased to 18 carbon atoms, floatability became independent of the p.z.c., e.g., sodium oleate showed strong flotation in pH regions of negative surface charge.

The presence of modifying ions can also determine the adsorption of collectors by surface charge sign reversal on complex species formation with Sn^{4+} . Evidence of specific adsorption on stannic oxide included sulphate and phosphate (Ghosh, 1928); tartrate and oxalate (Aditya and Ghosh, 1952). Adsorption on cassiterite included phosphate and citrate (Johansen and Buchanan, 1957a), oxalate and citrate (Andrews, 1971); arsenate and bisulphite (Ball, Cox and Yap, 1979).

Therefore, modifying ions that act as potential-determining ions significantly alter the p.z.c.; whereas collector ions which function as counter ions in the electrical double layer would not be expected to alter the p.z.c. Thus, for cassiterite, Gaudin and Sun (1946) obtained a value of 5.0 in dodecylamine hydrochloride.

PREVIOUS FLOATABILITY STUDIES

In reviewing published information, only flotation studies that involve adsorption of a collector onto unaltered cassiterite surfaces are considered in detail. The techniques for chemically altering cassiterite, such as sulphidization and electroflotation, and various novel techniques, selective aggregation, two-liquid flotation, carrier flotation and dissolved air flotation are briefly discussed. Skin flotation and flotation of sulphide minerals from cassiterite ores are not included.

The data reported are consistent with successful flotation. Grades and recoveries are not reported, since studies range from batch, pilot-plant and plant-scale flotation of cassiterite ores to flotation studies of pure cassiterite samples; the latter often involving weights of <5g. Important studies are discussed in the text; significant studies for which there is limited information are referenced according to scale of investigation, e.g., Hallimond tube, etc., in Tables 1-4.

Parameter data

The principal parameters, pH and collector concentration, are discussed since they can be related to all studies. Techniques such as bubble pick-up, vacuum flotation and Hallimond tube can determine limits of contact, i.e., flotation or non-flotation at constant collector concentration and variable pH, and constant pH at variable collector concentration. Batch and larger scale techniques are dependent on achieving a tangible recovery before flotation is apparent.

The gradation between no contact and complete recovery in some studies is rapid, while other studies show a gradual rise over several pH units. These differences are not always reported in the various publications. Flotation is stated as being between two pH values and it is inferred to be complete, but the range of contact may extend over wider pH values. In an attempt to standardize, limits of

flotation are reported together with the flotation technique used in a particular investigation, which at least puts the degree of flotation in perspective. When differences between limits of contact and limits of flotation are significantly different in terms of pH, such differences, if known, are reported.

When varying collector concentration at constant pH, flotation recovery increases gradually to a maximum. The maximum remains over a considerable range of collector concentration before decreasing. The reduction in recovery at high collector concentrations is due to the adsorption of a second layer of collector molecules with reversed orientation which causes hydrophilicity. The limits of contact for maximum and minimum collector concentration in the various studies, when known, are stated. This phenomenon is not apparent with larger scale investigations, where the greater surface areas provided by gangue minerals adsorb excess collector. In fact, under plant conditions, this is one of the main causes of non-selectivity. Collector concentrations are quoted as mg/L for small-scale studies and as g/t for larger scale studies; approximate comparison between studies is possible by equating mg/L to g/t.

An important variable that was omitted is size, since the variance of size with flotation performance was not the same for all the techniques employed. The size of cassiterite reported varied from 200 μm to 5 μm ; two distinct ranges, 200 to 50 μm and 50 to 5 μm are related to the scale of technique. The flotation of cassiterite by batch flotation cell, pilot-plant cell and plant-scale cell was best in the 200 to 50 μm range, selectivity diminishing rapidly below 50 μm . Conversely, with smaller scale techniques, there did not appear to be a direct relationship between size and flotation performance, in fact, Gochin and Solari (1983) using dissolved air flotation conducted their studies on cassiterite of size 50% <5 μm .

Secondary data such as flotation times, stirring speed etc. are omitted since they relate only to batch or pilot-plant studies.

Scale of techniques

The various techniques employed all possess inherent features that distinguish them; that none approach the ideal state is axiomatic. The 'static' contact angle method of Taggart and Arbiter (1943) is no longer used because of the difficulty in preparing flat surfaces and producing a clean surface free of abrasive particles remaining from the polishing cloth. Cylinder flotation (as described by Wark, 1938) is no longer used because of the difficulty of controlling bubble size, and the frothing of collectors that possess frothing characteristics. Small-scale techniques that continue to be used for studies include the Hallimond tube (Hallimond, 1944), vacuum flotation (Schuhmann and Prakash, 1950) and bubble pick-up (Cooke and Digre, 1949). Each method has been adequately described elsewhere and has been modified many times. The Hallimond tube is characterized by kinetic rate factors of flotation, and vacuum flotation is characterized by the nucleation of bubbles on mineral surfaces caused by a vacuum. Bubble pick-up has greater sensitivity to high and low collector concentrations over the entire pH scale when compared to the Hallimond tube (Buckenham and Rogers, 1954; Fleming and Robinson, 1960). Large-scale techniques, including batch flotation cell,

pilot-plant and plant scale, are used for the beneficiation of cassiterite ores and are thus closer to practical conditions of operation.

Classification of collectors

The collectors that have been used to float cassiterite are mainly anionic, e.g., the fatty acids and their soaps (largely oleic acid and sodium oleate) and sodium alkyl sulphates. More recent usage has been directed towards the phosphonic acids, hydroxamic acids, para-tolyl arsonic acid and sulphosuccinamate collectors. Flotation by cationic collectors has been mainly restricted to dodecylamine hydrochloride. The flotation properties are therefore discussed under the following headings:

Oleic acid and sodium oleate

Miscellaneous carboxylates

Sodium alkyl sulphates

Alkyl sulphonates

Aryl arsonic acids

Alkyl and aryl phosphonic acids

Alkyl cationic collectors

Flotation nomenclature is written out; the chemical formulae of some of the more important collectors are adequately described in the well-known publications of flotation (Sutherland and Wark, 1955; Gaudin, 1957a; Klassen and Mokrousov, 1963a; Lovell, 1982).

Oleic acid and sodium oleate

The earliest recorded work on the flotation of cassiterite ores was performed by Gaudin et. al. (1928), when it was found that fatty acids (in particular oleic acid) were effective but non-selective collectors. Subsequently, in order to increase selectivity, the role of depressants was investigated, leading to separation of cassiterite from gangue minerals. Depressants such as sodium silicate and sodium hexametaphosphate were also found to have a similar depressing effect upon cassiterite.

Evidence from adsorption studies of oleic acid, indicated that adsorption was little influenced by the sign of the surface charge (Trahar, 1965). Thus, flotation was possible over a wide pH range, 2.0 - 13.0; Taggart and Arbiter (1943) using contact angle; Hergt, Rogers and Sutherland (1946) using cylinder test; Schuhmann and Prakash (1950) using vacuum flotation; Yaksic (1969) using the Hallimond tube and Andrews (1971) using bubble pick-up. Within this pH range, the surface charge passes from a high positive value to a high negative value. Indirect evidence of the adsorption of oleate ions in the diffused portion of the electrical double layer was indicated by a decrease in surface charge (Klassen and Mokrousov, 1963b) from -23 mv to -47 mv. The large range of pH for flotation, however, would suggest that a stronger mechanism of adsorption other than electrostatic is governing the interaction between surface groups and collector ions. Pol'kin (1960), moreover provides evidence to show the irreversible nature of adsorption of oleate ions with the presence of a

tin oleate or oxyoleate phase on the surface, suggesting that the mechanism of adsorption in this case is chemical in nature.

The maximum response to flotation, using various techniques (Oberbillig and Frink, 1941; Gaudin, Schuhmann and Brown, 1946; Mitrofanov and Rozin, 1955; and Abeidu, 1975) was in the vicinity of pH 7.0. The pH range of maximum adsorption was determined by Yaksic (1969) as between pH 4.0 and pH 7.0, and maximum contact angle was developed at pH 7.0 (Taggart and Arbiter, 1943). The decrease in flotation response on the acid side of the maximum is most probably due to collector hydrolysis, and in the alkaline regions to competitive adsorption between collector and hydroxyl ions for the mineral surface; the pKa at 5.5 for oleic acid was determined by Ralston (1948). Apart from the pH range of floatability being dependent on collector concentration, the position of the lower and upper critical pH limits was dependent on whether a particular value was approached from the acid or alkali side. Thus, Taggart and Arbiter (1943) showed that flotation may persist below the normal lower limit if cassiterite is conditioned with collector before the pH is reduced. Schuhmann and Prakash (1950) and Burt (1966) determined the upper critical limit using vacuum flotation by approaching from the acid side. When the approach was made from the alkaline side, non-flotation persisted to a lower pH value. These effects upon flotation limits indicate the presence of non-equilibrium conditions. At constant pH (7.0) and variable collector concentration, cassiterite floats over a wide range of collector concentration 0.02 mg/L (Andrews, 1971) to 300 mg/L (Schuhmann and Prakash, 1950). Burt (1966) reported flotation at even higher collector concentrations (500 mg/L).

Activation by various metal ions was reported in the pH range 8.0–12.0 when oleate ion is the predominant species. Thus, Gaudin and Sun (1946) obtained activation with Ca^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} and Pb^{2+} using cataphoresis techniques; Schuhmann and Prakash (1950) with Ca^{2+} and Ba^{2+} using vacuum flotation; Vainshenker and Khainmann (1964) with Ba^{2+} , Sn^{2+} , Sn^{4+} , Fe^{3+} , Cu^{2+} and Pb^{2+} . Gaudin et al. (1928) obtained activation with the chelating compound Cupferron using the flotation cell.

When metal ion salts are added in large amounts (>500 g/t), pseudo depression occurs through precipitation of the collector as metal oleates. Pseudo depression occurred in the pH range 7.0–10.0, and was reported by Collins (1967) with Ca^{2+} and Fe^{3+} using vacuum flotation; Oberbillig and Frink (1941) with Fe^{3+} , Cu^{2+} , Pb^{2+} and Ca^{2+} ; and Abdel Rehim (1977) with Sn^{2+} using the flotation cell.

Depression of cassiterite was reported in neutral pH ranges by various investigators using the flotation cell. Thus, Oberbillig and Frink (1941) obtained depression by silicate, hexametaphosphate and tannin; Plaksin and Shroder (1965) with silicate, silicofluoride and sulphide; MacDonald (1937) with hexametaphosphate. Gaudin and Sun (1946) obtained depression with hexametaphosphate using cataphoresis. Depression by quinalizarin dyes between pH 2.0 and pH 12.0 was reported by Schuhmann and Prakash (1950) using vacuum flotation.

Studies of oleic acid, for which there is only limited information, are referenced in Table 1.

Miscellaneous carboxylates

Carboxylic and carboxylate derivatives have been assessed with varying success as alternatives to oleic acid and sodium oleate. Thus, the limits of flotation for palmitic acid and sodium palmitate were determined between pH 2.0 and pH 11.0 by Oberbillig and Frink (1941); Orelli (1937) using flotation cell, and Hergt, Rogers and Sutherland (1946) with contact angle. Flotation cell tests of Korzhov and Pol'kin (1970) determined the limits of flotation of tall oil using 25–50 g/t between pH 3.0 and pH 10.0. Duke (1965) used lauric acid; and Gaudin and Sun (1946) used sodium laurate to float cassiterite. A comprehensive study of the collecting properties of lauric acid conducted by Zambrana et. al. (1974a) established the limits of flotation between pH 1.7 and pH 9.5 using Hallimond tube with optimum flotation at pH 3.3, and a minimum collector concentration of 2 mg/L.

Several carboxylate derivatives were synthesized and assessed for their collecting ability. Trahar (1970) obtained selective flotation using 150 g/t of α -sulphocarboxylic acid between pH 3.0 and pH 6.0 using the flotation cell. Baldauf, Schoenherr and Schubert (1985) conducted a comprehensive study of an alkane derivative, undecane-1, 1-dicarboxylic acid. The limits of flotation were established between pH 2.0 and pH 7.0 using 29 mg/L collector concentration by Hallimond tube, with maximum flotation between pH 2.0 and pH 4.0. A minimum collector concentration value was established at 6 mg/L.

A summary of flotation studies by other carboxylate collectors is presented in Table 1.

Table 1 – Cassiterite flotation using miscellaneous carboxylate collectors

Collector type	Method of study	Reference
Oleic acid	Vacuum flotation	152
	Flotation cell	106,136,187
	Electroflotation	109
Nitro benzene-azo salicylate	Not stated	115
p-nitrobenzeneazosalicylic acid coll. conc. 300 g/t	Plant cell	141
α - bromohexadecanoic acid pH 4.6 and pH 5.7 coll. conc. 50 g/t	Flotation cell	159
Tridecane -1,3-dicarboxylic acid coll. conc. 200 g/t	Flotation cell	159
n-3-carboxyacyloyl-n-octadecyl aspartic acid	Not stated	75
n-octadecyl-n-(sulphosuccinoyl) aspartic acid	Not stated	104
Coco-alkylamino-proponic acid pH 5.7 coll. conc. 150 g/t	Flotation cell	39

Sodium alkyl sulphates

Hergt, Rogers and Sutherland (1946), in a comprehensive study of the flotation of cassiterite, first showed that collectors containing the polar groups $-\text{SO}_4$ were selective collectors, and that flotation was best at slightly elevated temperatures, 35°C . Subsequently, the interaction of alkyl sulphates with cassiterite or stannic oxide was the subject of a great deal of attention.

The influence of surface charge is more apparent for alkyl sulphate collectors than for the fatty acids, which suggests that adsorption is of a physical nature where the collector ions are less strongly adsorbed. Thus, O'Connor and Buchanan (1953) found that adsorption of hexadecyl sulphate was easily reversible by washing. It is possible that hexadecyl sulphate ions do not interact directly with the surface tin groups.

Since the electrostatic forces are important in determining the extent of adsorption, it is hardly surprising to find that adsorption is predominant at pH values below the p.z.c. Thus, Edwards and Ewers (1951) using hexadecyl sulphate; Jaycock, Ottewill and Tar (1964); Gutierrez and Pommier (1969); Zambrana, Romero and Gutierrez (1970) and Abeidu (1975) using dodecyl sulphate, showed that collector adsorption increases below pH 5.0. These observations are also in agreement with cell flotation tests where recovery falls rapidly above pH 5.0 (Hergt, Rogers and Sutherland, 1946). The decrease in recovery may also be attributed to the pKa of alkyl sulphuric acid, reported as being 1.99 (Hogfeldt, 1982).

Since adsorption of hexadecyl sulphate increases below the p.z.c., Edwards and Ewers (1951) postulated a collector-hydroxyl ion exchange as they found that when the pH was reduced to 2.5, the adsorption was accompanied by a stoichiometrical increase in hydroxyl ion concentration in solution. Trahar (1965) pointed out that since the adsorption of hexadecyl sulphate on positively charged cassiterite reverses the sign of the surface charge, the titration results of Edwards and Ewers (1951) could be explained in terms of hydrogen ion adsorption into the diffuse double layer.

A second exchange mechanism was postulated whereby hexadecyl sulphate ions are adsorbed by exchange with chloride ions, rather than hydroxyl ions (O'Connor and Buchanan, 1953; Jaycock, Ottewill and Tar, 1964). O'Connor and Buchanan, 1973 argue that initially there is substitution of hydroxyl by chloride ion and that dissociation of the stannic-chloride bond subsequently occurs. Collector ions can then replace chloride and become more firmly held, the surface charge becoming negative. Jaycock et al., 1964 base their conclusions on finding no difference between the adsorption isotherms at pH 2.9 and pH 4.2. These conclusions were questioned by Kitchener (1964), since the adsorption of collector was found to be independent of pH despite the fact that the collector is anionic and the surface potential would not be the same at both values.

In Hallimond tube and cell flotation tests the range of floatability was between pH 1.0 and pH 5.0 (Hergt, Rogers and Sutherland, 1946; Edwards and Ewers, 1951; Mitrofanov and Rozin, 1955 and Evans, Ewers and Meadows, 1962) using hexadecyl sulphate as collector. The range of maximum floatability was between pH 1.5 and pH 3.5. Other studies for which there was only limited

information are referenced in Table 2. On either side of the pH limits of flotation, floatability falls rapidly to zero, although Hergt, Rogers and Sutherland (1946) using the contact angle test obtained contact up to pH 10.5.

At constant pH 7.0 and variable collector concentration, cassiterite floats between 2.0 mg/L and 120 mg/L (Edwards and Ewers, 1951); above the upper limit flotation decreases rapidly until at 200 mg/L flotation virtually ceases (Edwards and Ewers, 1951).

When using dodecyl sulphate collector, the range of flotation was extended up to pH 9 (Gutierrez and Pommier, 1969 using microflotation, and Abeidu, 1975 using Hallimond tube). Extended flotation beyond the p.z.c. is explained by the increased chain length of dodecyl sulphate over hexadecyl sulphate. The region of maximum flotation between pH 2 and pH 6 is below the p.z.c. The upper limit of collector concentration is 200 mg/L (Gutierrez and Pommier, 1969), the lower limit 14 mg/L (Gochin and Solari, 1983).

Metal-ion activation using alkyl sulphate collectors was possible in the alkali pH regions. Thus, Vainshenker and Khainmann (1964) with Fe^{3+} , and Zambrana, Romero and Gutierrez (1970) with Pb^{2+} obtained activation in the pH range 6.8 to 10.2. Presumably, activation was by surface charge sign reversal, since this pH region corresponded to negative surface charge. Evidence of adsorption of La^{3+} (pH 2.9) and Th^{4+} (pH 4.2) on stannic oxide was reported by Jaycock, Ottewill and Tar (1964). It is difficult to interpret this data as activation, since pH 2.9 and pH 4.2 is the region of maximum floatability using dodecyl sulphate without activators. It is possible that these ions were adsorbed as hydroxyl complexes, since it is known that La^{3+} and Th^{4+} have excellent complex formation ability.

Pseudo depression by collector precipitation occurred between pH 2.0 and pH 4.5. Thus, Collins (1967), using vacuum flotation, reported pseudo depression by Ca^{2+} and Fe^{3+} ; Evans, Ewers and Meadows (1962), using flotation cell, by Fe^{2+} ; and Hergt, Rogers and Sutherland (1946), using the cylinder test, by Ba^{2+} , Bi^{3+} , Sn^{4+} and Th^{4+} .

Depression of cassiterite was reported by Hergt, Rogers and Sutherland (1946) using the cylinder test with a range of modifiers: carbonate, arsenate, hexametaphosphate, borate, cyanide, ferro and ferricyanides. Hallimond tube studies by Evans, Ewers and Meadows (1962) extended the range of modifiers to include gum arabic, tragacanth, mimosa, tannin, pectin, dextrin, agar, cobalt sulphate, sodium alginate, sodium polyphosphate, potassium ferricyanide and ferrocyanide.

Alkyl sulphonates

Alkyl sulphonates are characterized by the $-\text{SO}_3$ group, but the term alkyl sulphonate is mainly commercial usage, e.g. the Cyanamid *Aeropromoter 800* series are described as natural and modified petroleum sulphonates. These collectors were used to float cassiterite, but their use was less than the alkyl sulphates. Renewed interest followed the discovery that the alkyl sulphosuccinamate derivatives, specifically *Aerosol 22*, renamed *Aeropromoter 845* (estimated to be a 35% solution of the active alkyl

sulphosuccinamate derivative) were collectors for cassiterite. These reagents are represented as $\text{SO}_3(\text{CH}_2)_2\text{CO}(\text{CH}_2)_2(\text{COO})_3$. Arbiter and Hinn (1968) first patented the use of *Aerosol 22* (n-1,2-dicarboxyethyl-n-octadecyl sulphosuccinamate) as a collector to float cassiterite from Catavi cassiterite tailings, Bolivia, in a 1,000 t.p.d. plant.

The dissociation constant for succinamic acid is 2.89×10^{-5} (Körtum, Vogel and Andrussov, 1961) which indicates that, like oleic acid ($K = 1.5 \times 10^{-5}$), it would not be very effective at low pH values. The sulphonated derivative, however, is more effective at lower pH values. Surfactants of this type possess two functional groups, whereas *Aerosol 22* possesses four, and the reagent is used commercially as the tetra sodium derivative.

Adsorption data for alkyl sulphosuccinamates are limited. The flotation mechanism for these collector types at pH values less than the p.z.c. is possibly related to an initial electrostatic attraction followed by chemical adsorption. Berger, Hoberg and Schneider (1980) also noted that adsorption increased with increasing temperature.

The range of floatability, pH 1.0 and pH 12.0, was established by various investigators using a variety of techniques (Collins, Hollick and Joy, 1969; Gutierrez and Pommier, 1969 using vacuum flotation; Zambrana et al., 1974 using the Hallimond tube; Moncrieff et al., 1973 using the flotation cell; Bunnaul, 1984 using microflotation and Hogan, Kuhn and Turner, 1979 using electroflotation techniques). The upper limit of flotation was determined at 400 g/t (Moncrieff et al., 1973) and the lower limit of flotation at 1.5 mg/L (Collins, Hollick and Joy, 1969; Gutierrez and Pommier, 1969 and Gochin and Solari, 1983).

Activation was possible by Fe^{3+} , Zn^{2+} , Cu^{2+} (Arbiter and Hinn, 1968). The pH range of activation was not reported for these species, but Zambrana, Romero and Gutierrez (1970) and Arbiter and Hinn (1968) report the pH range of activation for Pb^{2+} as 8.2 to 10.2. Within this pH range, PbOH^+ species are present in solution (Latimer, 1952). Adsorption of hydrolyzed PbOH^+ is possible by electrostatic forces, since pH 8.2 and pH 10.2 is in the region of negative surface charge. Since alkyl sulphosuccinamates possess a certain degree of chelating ability, it is not surprising that pseudo-activation was possible by EDTA (Roettig and Breuer, 1980). The chelating ability of citric acid and sodium silicofluoride (Collins, Hollick and Joy, 1969; Gutierrez and Pommier, 1969) was also demonstrated by complexing Fe^{3+} and Ca^{2+} . Citric acid and sodium silicofluoride are known to form stable complex species with Fe^{3+} and Ca^{2+} (Sillén and Martell, 1964). When Fe^{3+} and Ca^{2+} are absent from solution, each modifier can act as a depressant for cassiterite.

Other derivatives in the same series that have been used successfully to float cassiterite include *Aeropromoter 801*, which was used at Renison Ltd., Tasmania, to float cassiterite at pH 2.0 and pH 3.0 (Renison Jin Ltd., 1968). Guzman (1980), using the flotation cell, employed *Aeropromoter 860* at pH 2.5.

When using dodecyl sulphonate with Hallimond tube techniques, Blazy, Degoul and Houot (1969) and Ball, Cox and Yap (1979) established the limits of flotation between pH 1.0 and pH 12.0 with

maximum recovery at pH 3.0. As with the alkyl sulphate collectors, flotation was best below the p.z.c., and adsorption would seem to be governed mainly by electrostatic forces. At constant pH 4.0 and variable collector concentration, cassiterite floats over a narrow range of collector concentration 0.3–29 mg/L (Blazy, Degoul and Houot, 1969). Ball, Cox and Yap (1979) reported flotation up to 33 mg/L.

Other significant studies for which there is only limited information available are reported in Table 2.

Table 2 – Cassiterite flotation using alkyl sulphate, sulphonate and sulphosuccinamate collectors

Collector type	Method of study	Reference
Alkyl sulphate	Flotation cell	135, 152, 177
	Microbubble	166
Stearyl aminosulphonate	Not stated	206
Sulphosuccinamate	Hallimond tube	42
	Flotation cell	84
	Not stated	17
	Not stated	154
Monosulphosuccinate	Not stated	pH 5 and pH 6
		140
Dicarboxy methylamino succinate	Not stated	176

Aryl arsonic acids

Aryl arsonic acids are classified as $R.AsO_3H_2$ and the derivative used most often is para-tolyl arsonic acid. Other derivatives that have been evaluated include benzyl (Zhu and Zhu, 1980); p-methyl benzyl (Zhu, Zhu and Jiang, 1981) and an alkane derivative, heptane arsonic acid (Wottgen and Rosenbaum, 1972).

Para-tolyl arsonic acid first prepared by Neunhöffer (1943), is essentially a compound containing a phenol radical with a nitro group in the o- position and a metal group in the p- position. The acidity at $K_1 = 2 \times 10^{-4}$ (Körtum, Vogel and Andrussov, 1961) indicates that para-tolyl arsonic acid may be used at low pH values. Experimental data using a variety of techniques, confirms this supposition, since cassiterite floats between pH 2.0 and pH 6.0, (Töpfer, 1960; Joy and Kirkup, 1967; Moncrieff et al., 1973 using the flotation cell; Töpfer, 1967 using bubble pick-up; Collins, 1967 using vacuum flotation; Baldauf, Schoenherr and Schubert, 1985 using plant-scale equipment). On either side of this narrow pH range, flotation rapidly decreases to zero, although to a lesser extent on the alkaline side, since contact was reported up to pH 8.5. The pH of maximum flotation was reported as occurring at pH 4.0 and pH 5.0 (Collins, 1967).

The dependence of flotation on pH values below the p.z.c. would suggest electrostatic adsorption forces. Very little infrared spectroscopic data is available regarding adsorption studies, but Dietze (1974), studying the bonding of heptyl arsonic acid on cassiterite, concluded that chemisorption was the dominant mechanism, and that only a small portion of the collector was physically adsorbed.

The upper and lower collector concentration boundary levels differ from the concentration levels of alkyl carboxylate and sulphate collectors. Thus, Collins (1967) reported that there was no flotation until the collector concentration was 150 mg/L, and Moncrieff et al. (1973) reported a collector addition of 350 g/t for flotation in a laboratory batch flotation test.

Activation of cassiterite by Fe^{2+} , Fe^{3+} , Sn^{2+} , Sn^{4+} , Cu^{2+} , Pb^{2+} and Zn^{2+} at low concentrations of benzyl arsonic acid was reported by Zhu and Zhu (1980). At higher concentration levels of these ions, pseudo-depression by collector precipitation occurred. Significantly, Wottgen and Rosenbaum (1972) reported a tolerance for Ca^{2+} and Mg^{2+} . The mechanism of activation is unclear since the pH was not reported.

Depression of cassiterite by a variety of modifiers including phosphate, oxalate, fluoride and silicofluoride ions was reported by Wottgen and Rosenbaum (1972) using heptane arsonic acid with the flotation cell and Hallimond tube techniques.

Alkyl and aryl phosphonic acids

The first reported use of phosphonic acids ($\text{R.PO}_3\text{H}_2$) as collectors for cassiterite was by Wottgen and Lippmann (1963). Extensive studies were subsequently conducted by Kirchberg and Wottgen (1965) and Collins (1967) to establish which derivative was most selective. The work of Collins (1967) indicated that n-heptyl phosphonic acid was most selective.

Since 1967 many alkane, alkyl and alkyl/aryl derivatives have been synthesized and evaluated. The acid phosphates which are synthesized from C_{6-8} alcohols also received some attention. Three derivatives, n-heptyl, p-ethyl benzene and 2-phenyl ethylene phosphonic acid were studied extensively. A summary of other derivatives used to float cassiterite are reported in Table 3.

Adsorption studies conducted using n-heptyl and p-ethyl benzene phosphonic acid (Wottgen, 1969) indicated that maximum adsorption occurred at pH 2.0, which corresponds approximately to the first dissociation constant $\text{pK} = 2.9$. Below pH 2.0, adsorption decreased rapidly to zero at pH 1.0 but decrease above pH 2.0 was gradual, reaching zero at pH 10.0. When studying the adsorption pattern of 2-phenyl ethylene phosphonic acid (styrene phosphonic acid), Kuys and Roberts (1987) found that maximum adsorption occurred between pH 4.5 and pH 5.5. Contact was possible over a wider pH range, between pH 2.3 and pH 7.5, and the monoanion species was dominant in the pH range of 3.0–5.0. The limits of contact for styrene phosphonic acid correspond to the first and second dissociation constants of the dibasic acid ($\text{pK}_{a1} = 2.92$ and $\text{pK}_{a2} = 7.42$). Styrene phosphonic acid is sparingly soluble in water, solubility rising with increasing pH because of the formation of phosphonate ions.

Table 3 – Cassiterite flotation using miscellaneous phosphonic acid derivatives

Collector type	Method of study	Reference
1. <i>Phosphonic acids</i>		
n-butane	Vacuum flotation	89
n-hexane	Plant cell	13
n-heptane	Plant cell	13
	Not stated	203
n-octane	Vacuum flotation	89
n-decane	Not stated	203
n-heptane benzene	Hallimond tube	201
n-dodecane benzene	Hallimond tube	201
n-octyl		
pH 6.0 and pH 7.3	Flotation cell	31
	Pilot-plant cell	32
coll. conc. 220 g/t	Pilot-plant cell	32
Mono-hexyl		
pH 6.2 and pH 6.4	Flotation cell	196
Mono-octyl		
pH 6.2 and pH 6.4	Flotation cell	196
2-ethyl hexyl	Vacuum flotation	34
iso-hexyl	Flotation cell	122
3-indene	Not stated	156
Methyl phenyl	Not stated	91
Ethyl phenyl	Flotation cell	122
pH 4.5 and pH 5.0		122
coll. conc. 330 g/t		
2-phenyl vinyl	Not stated	198
t-amino alkylidene	Not stated	142
1-hydroxy alkylidene	Not stated	100
α -hydroxy benzyl		
pH 4.5		54
coll. conc. 342 g/t	Flotation cell	54
1-hydroxy-1,3-dimethyl butyl	Not stated	209
2. <i>Acid phosphates</i>		
Mono alkyl hydrogen	Not stated	103
2-ethoxy lauryl	Flotation cell	164
2-ethyl hexyl	Flotation cell	47
Decyl phosphite	Not stated	29

Infrared spectrographic investigations by several researchers indicate that adsorption of phosphonic acid was mainly influenced by chemical forces. Wottgen (1969) found that the surface compound formed using *n*-heptyl phosphonic acid has a structure similar to stannic phosphonate. Evidence of chemisorption of other derivatives was obtained by Zhong and Zhu (1985) using methyl phosphonic acid and Kuys and Roberts (1987) using styrene phosphonic acid. Chemical forces govern adsorption, but there is evidence of some dependence of adsorption on the p.z.c., since adsorption increases below the zero point of change. Dietze (1974), using heptyl phosphonic acid, found that while chemisorption was the dominant force, there was a small but distinct amount of physically adsorbed collector. Kuys and Roberts (1987) further claim that the presence of Fe^{3+} , either in solution or as a lattice impurity on the cassiterite surface, did not influence adsorption of styrene phosphonic acid. Identical adsorption characteristics were obtained using natural cassiterite and pure stannic oxide.

Cell flotation tests using *n*-heptyl phosphonic acid show satisfactory correlation with adsorption studies; the limits of floatability were between pH 2.5 and pH 8.0 (Wottgen, 1965), and the region of maximum flotation occurred between pH 5.6 and pH 7.4 (Collins, 1967). Vacuum flotation studies using iso-heptyl phosphonic acid demonstrated a similar range of flotation (Collins, Hollick and Joy, 1969). Significantly, Collins (1967) states that the limits of floatability are defined by the first and second dissociation constants of the dibasic acid ($\text{pK}_1 = 2.9$, $\text{pK}_2 = 8.4$). At constant pH 6.0 and variable collector concentration, cassiterite floats between 30 mg/L (Collins, 1967) to 400 g/t (Joy and Kirkup, 1967), although the latter value was not necessarily an upper limit. Collins, Hollick and Joy (1969) found that when using iso-heptyl phosphonic acid, the lower limit of minimum collector concentration was 2 mg/L.

The range of flotation of *p*-ethyl benzene phosphonic acid was much narrower than *n*-heptyl phosphonic acid. Collins (1967) using vacuum flotation, and Wottgen and Gruner (1966), using Hallimond tube techniques, determined the pH range as 3.5 and pH 5.5. Collins (1967) further determined that no flotation was possible below 500 mg/L collector concentration; Joy and Kirkup (1967) found that cell flotation requirements were 600 g/t. A substituted aminodiphosphonic acid derivative, when used between pH 4.0 and pH 7.5, was claimed to be more selective than styrene phosphonic acid (Collins and Collins, 1987).

The use of styrene phosphonic acid was reported by many investigators (Wottgen, 1975; Wottgen and Töpfer 1976; Warren, (1984); Baldauf, Schoenherr and Schubert, 1985), but only limited data is available concerning flotation behaviour. The cell flotation tests of Warren (1984) indicate maximum floatability at pH 5.0; interestingly, these investigations were related to size. Maximum recovery was reported at 20 μm and maximum grade at 60 μm .

Very few data are available concerning activation and depression studies using phosphonic acid collectors. Collins, Hollick and Joy (1969) report that Fe^{2+} , Fe^{3+} and Ca^{2+} will precipitate iso-heptyl phosphonic acid, but Wottgen (1970) using 2-phenyl vinyl phosphonic acid reported a tolerance for Ca^{2+} and Mg^{2+} up to 2 g/L and 1.2 g/L. Wottgen (1980) reported that when using styrene phosphonic acid, pre-treatment with sodium silicofluoride was beneficial.

A few studies were conducted with acid phosphate collectors; one in particular, 2-ethoxy lauryl acid phosphate was studied in detail. Cell flotation tests performed at pH 4.0 by Smith (1976) were conducted with only 5 mg/L collector concentration; a minimum collector concentration of 1 mg/L was also reported.

Alkyl hydroxamates

Hydroxamic acid and the solubilized hydroxamate salts as collectors for cassiterite were first reported by Gorlovsky (1968), although *cupferron* (ammonium nitroso phenyl hydroxylamine) was used as a collector for cassiterite as early as 1927 (Vivian, 1927). The principal hydroxamate derivatives are sodium octyl hydroxamate and hydroxylamine sulphate.

Adsorption data of potassium hydroxamate on cassiterite by radiometric and infrared spectroscopic studies indicated chemisorption (Bogdanov et al., 1973). Adsorption in acid conditions was easily reversible, indicating that adsorption was also by physical forces. The chelating ability of hydroxamic acids was demonstrated by Golikov et. al. (1975), using pelargon hydroxamic acid.

When cassiterite contains lattice Fe^{3+} , leaching to remove Fe^{3+} results in cassiterite becoming more floatable than cassiterite not containing lattice Fe^{3+} . The mechanism of adsorption is not clear, since flotation of cassiterite previously containing lattice Fe^{3+} is only floatable through activation by Fe^{3+} introduced into solution. Cassiterite containing lattice Fe^{3+} is possibly more active than cassiterite not exhibiting lattice Fe^{3+} . Analogous studies of adsorption of hydroxamate on hematite were reported by Fuerstenau et al. (1970) and Raghavan and Fuerstenau (1975a, 1975b). Ferric hydroxamate was formed in solution from Fe^{3+} which was released by mineral surface dissolution. Chemisorption then occurred on the hematite surface.

Cell flotation studies established the limits of flotation between pH 2.6 and pH 10.0 (Gorlovsky, 1968; Rosenbaum, 1969; Strel'tysn, 1968a; and Golikov et. al. 1975). The wide range of flotation pH confirms the adsorption studies that adsorption is mainly chemisorption and independent of the p.z.c.

Alkyl amines

In comparison with other collector types, cationic collectors have received the least attention, because of the non-selectiveness shown towards oxide and silicate minerals. Selectivity is obtained when specific modifying ions, i.e., activators and depressants, are used. The principal cationic derivative is the amine, RNH_3 , and of the four groups – primary, secondary, tertiary and quarternary – the primary group, specifically dodecylamine or laurylamine, was most successful. Commercial usage of this collector is by either the hydrochloride or acetate radical.

The adsorption of dodecylamine hydrochloride was studied by Gaudin and Sun (1946) and Mukai and Kano (1958), and the results indicate that adsorption occurs above the p.z.c., when the surface is negatively charged. This dependence on the p.z.c. suggests that adsorption is controlled by electrostatic forces. The lower pH limit is controlled by the p.z.c. and the upper limit by collector

hydrolysis. It is possible that two regions of flotation exist corresponding to the existence in solution of two distinct species, as indicated by the adsorption studies of amines on platinum by Zisman and Shafrin (1949). The first region pH 7.0 and pH 9.0 corresponds to the RNH_3^+ species being predominant, whereas the second region pH 9.0 and pH 11.5 corresponds to the RNH_2 species being predominant.

Cassiterite flotation was possible between pH 4.5 and pH 12.5 (Bruce and Yaksic, 1966 using flotation cell; Blazy, Degoul and Houot, 1969 using Hallimond tube; Andrews, 1971 using bubble pick-up techniques), which is in agreement with adsorption studies. Interestingly, Blazy, Degoul and Houot (1969) obtained contact down to pH 3.0 for cassiterite from Zimbabwe which exhibited a p.z.c. of 3.4. Maximum flotation was determined between pH 8.0 and pH 12.0 (Blazy, Degoul and Houot, 1969; Andrews, 1971), and a minimum collector concentration was established at 0.02 mg/L (Andrews, 1971). A similar pH range of floatability was obtained when using dodecylamine acetate by Hallimond tube (de Cuyper and Gutierrez, 1968); flotation cell (Duke, 1965); and vacuum flotation (Rich and Mitsmager, 1966).

Activation studies using dodecylamine hydrochloride are numerous using a variety of techniques. Cell flotation studies included sulphite (Gaudin and Schuhmann, 1946); bisulphate (Trahar, 1968); sulphate (Gaudin and Schuhmann, 1946; Trahar, 1968; Verkholtantsev, 1961) and oxalate (Trahar, 1968). Sulphate activation was also reported using cataphoresis (Gaudin and Sun, 1946) and bubble pick-up techniques (Andrews, 1971). The pH range of sulphate activation for most of the studies was 1.7–5.0, and a possible mechanism of activation was by the formation of the complex species SnSO_4^{2+} , which are known to exist when cassiterite is in contact with sulphuric acid (Brubaker, 1955). An alternate mechanism is electrostatic attraction of sulphate ions onto positively charged cassiterite. Activation is also consistent with the protoned species being the most active, since the pK_{a2} for sulphuric acid is 1.99 (Hogfeldt 1982). Weak activation was obtained by fluoride ion (Andrews, 1971), which is consistent with the evidence of the unstable stannic fluoride species; Trahar (1968), however, reported depression by fluoride ion.

Activation by sequestering and chelating agents was remarkably pronounced. Thus, Trahar (1968) obtained activation by tripolyphosphate, oxalate and citrate; Andrews (1971) by dihydrogen phosphate, oxalate and citrate; Gaudin and Schuhmann (1946) by tartrate. Activation in these cases may possibly be by direct complex formation with Sn^{4+} , or as a result of removal of Fe^{3+} and Cu^{2+} ions which commonly occur in cassiterite flotation pulps. The pick-up studies by Andres, (1971) using phosphate, oxalate and citrate. Some of these anions can act as pseudo-depressants, for example, hexamataphosphate (Gaudin, 1945; Abeidu, 1973) and cyclic polyphosphates (Trahar, 1968). Ball, Cox and Yap (1979) postulated a depression mechanism for phosphate whereby the negative oxygen ion from the phosphate anion interacts with the hydrogen ion from the surface OH^- ; this interaction weakens or breaks the O–H bond.

Depression by Ca^{2+} , Cu^{2+} , Pb^{2+} , Al^{3+} and Fe^{3+} was reported by Gaudin and Sun, 1946; and depression by Cr^{3+} and Fe^{3+} was reported by Gaudin and Schuhmann, 1946. Depression by the action of metal cations is mainly governed by the valency of the inorganic ions, since divalent ions

depress less strongly than do trivalent ions. The mechanism of cation depression is mainly due to the metal cations occupying sites on the mineral surface, thus preventing adsorption of amine ions. Depression by organic compounds, including guar gum, lignin sulphonate and sorghum flour, was reported by Bruce and Yaksic (1966). The depressant mechanism for starches is uncertain, but the basis of their depressant action is the existence of strongly hydrated polar groups. These reagents can adsorb and interact chemically with a mineral surface, and also can combine with a portion of a cationic collector, producing undissociated compounds resulting in mineral depression.

Other collectors

Salicylaldehyde has a specific affinity for Sn^{4+} . The aryl portion of this compound has in the o-position two functional groups, hydroxide and aldehyde. Stannic ions are known to have a strong affinity for these groups by which linkage with an ionic and a covalent bond can produce an inner complex salt. Solution chemical studies by Marabini (1975) demonstrated the existence of a high-stability complex, and it was inferred that chemisorption of salicylaldehyde on cassiterite would produce a similar complex salt $\text{Sn}(\text{CHO} \cdot \text{C}_6\text{H}_4\text{O})_4$. The limits of flotation using the Hallimond tube were established between pH 1.5 and pH 7.5 at 2500 mg/L collector concentration (Marabini, 1975; Rinelli, Marabini and Alesse, 1976). The main disadvantages with this reagent are that flotation was not possible under 500 mg/L (Marabini, 1975), and the high cost of commercial production.

Polyethylene oxide is a nonionic surfactant that successfully flocculates phosphate slimes (Smelley and Scheiner, 1980). Doren, Van Lierde and de Cuyper (1979) established that cassiterite could be floated by this class of surfactant, specifically the alkyl polyoxyethylene and alkyl ethylene oxide, although successful separation seems to depend on the aid of alkyl sulphonates. Hallimond tube studies by Doren, Van Lierde and de Cuyper (1979) indicate the range of floatability between pH 1.5 and pH 5.5 for ethylene oxide, with maximum flotation at pH 4.0. A minimum collector concentration of 20 mg/L was reported, and the presence of only 0.5 mg/L *Aeropromoter 840* improved recovery at pH 5.5. The restriction of flotation to the pH area below the p.z.c. would imply electrostatic adsorption, although flotation was also possible with alkyl polyoxyethylene at pH 8.5.

These reagents are cheap to manufacture, but the restriction of flotation to the area of the p.z.c., and the reliance on other collector types to improve floatability would imply that they are weak non-selective collectors.

The quarternary ammonium and pyridium salts were the only cationic species that were examined in detail (Hergt, Rogers and Sutherland, 1946; Schubert, 1957). The range of contact was between pH 4.0 and pH 12.5, but the air contact was only weakly held, even in the alkaline pH regions above the p.z.c. where flotation with cationic collectors should be stronger.

A recent study (Zhao, 1985) reports that sodium and ammonium humates prepared from coal are collectors for cassiterite and iron ores, but the degree of selectivity is uncertain.

A summary of data for various miscellaneous collectors is presented in Table 4.

Table 4 - Cassiterite flotation using miscellaneous collectors

Collector type	Method of study	Reference
<i>Anionic</i>		
Calcium petronate pH 8.2 and pH 8.6	Flotation cell	117
Oxidised petrolatum	Plant cell	141
Cupferron* pH 7.0 and pH 8.8	Flotation cell	64, 189
Cupferron-Alizarin	Flotation cell	81
Phosphotene pH 4.0 and pH 10.5	Flotation cell	137, 178
Troykyd lecithin pH 4.5 and pH 10.0 coll. conc. 375 g/t	Flotation cell	123
Cataflot KST pH 2.4 coll. conc. 900 g/t	Flotation cell	22
Sodium humate	Not stated	216
Ammonium humate	Not stated	216
Alkyl glucoside/ α -dodecane epoxide/ butyl stannate	Flotation cell	190
<i>Cationic</i>		
Diethanolamine	Flotation cell	118
Octadecylamine	Flotation cell	135
Oxazoline	Flotation cell	28
Amidoamine	Not stated	101

*Ammonium nitroso-phenyl hydroxylamine

COLLECTOR SELECTIVITY

Cassiterite is a readily floatable mineral, but flotation selectivity is hindered because of the mode of occurrence, general friable nature and associated gangue minerals with similar flotation properties.

Commonly, lode tin ores analyze less than 1% SnO₂ and some less than 0.5% SnO₂, which necessitates enrichment ratios as high as 150 to meet concentrate smelter requirements. Cassiterite often occurs in hard siliceous ores, so that it is extremely difficult to prevent the production of slime cassiterite. It was not uncommon to see large gravity concentrator plants with inefficient slime gravity

separators, before the introduction of cone concentrators to recover coarse cassiterite. The loss of cassiterite to the primary cyclone overflow, in one plant, was as much as 40%, from which only 25% was recovered by a combination of vanners, slime tables and Buckman frames (Andrews, 1968). The introduction of cone concentrators improved recovery but the production of slime cassiterite was unavoidable, and for this reason flotation became a possible alternative to inefficient slime-gravity methods.

The number of minerals that can occur with cassiterite are numerous. Gaudin (1957b) states that up to fifteen minerals may occur in a typical ore. The most probable minerals include pyrite, chalcopyrite, pyrrhotite, iron oxides, garnet, rutile, tantalite, wolframite, scheelite, apatite, monazite, barite, fluorite, spodumene, zircon, topaz and tourmaline. These minerals can be classified as base-metal sulphide, magnetic, silicate and semi-soluble salt. The base-metal sulphides are successfully separated by using long-chain xanthates after activation with Pb^{2+} , Zn^{2+} or Cu^{2+} (Michell, 1958; Michell, 1960). Iron and titanium oxides, garnet, wolframite, zircon and pyrrhotite can be separated by high-intensity magnetic separation, using superconducting magnetic cores. Successful separations from the remaining minerals are few, although separation from scheelite (Nedogovorov, 1947; Schranz and van Gathen, 1960) and fluorite (Schuhmann and Prakash, 1950) were reported using oleic acid. Separation from wolframite at pH 2.5 and pH 3.5 using alkyl sulphate (Tham and Pol'kin, 1966), and separation from barite at pH 9.0 and pH 11.0 using stearyl aminosulphonate (Wrobel, 1970) are also reported. The most troublesome minerals are topaz and tourmaline, since not only do these minerals possess identical floatability with cassiterite, but they also occur in significant amounts in cassiterite ores. The only producing cassiterite operation in Canada, at East Kemptville in Nova Scotia, contains significant quantities of topaz in the ore.

The magnitude of this dilemma is best appreciated by discussing the selectivity of each of the major collector systems, in respect of differences or similarities between the flotation behaviour of cassiterite, topaz and tourmaline.

Sodium oleate selectivity

Gerth (1932) first recognized that topaz could be floated using oleic acid, but no pH or collector concentration data were reported. Patek (1934), using dry-ground mineral, established that a specific contact angle was developed when using oleic acid.

The mechanism of adsorption is probably a combination of chemisorption and physical adsorption. Thus, Berger and Bulatova (1969), using infrared spectrographic analysis, obtained evidence indicating the existence of chemisorbed ionic and physically adsorbed molecular species of collector. Infrared spectrographic studies of Vainshenker and Krivekva (1966) indicated that oleate was adsorbed by direct contact with cations in the topaz crystal lattice, and not as free acid or micelles of the sodium salt. Eigelles and Sakharova (1967) have suggested that, in strongly acid media, physical adsorption of the molecular form occurs by displacing surface water molecules.

Laboratory-scale flotation investigations confirm the probable chemical and physical adsorption mechanisms, since topaz floats on either side of the p.z.c., which was determined at 5.6 (Andrews,

1971). Thus, Wyman (1965) using bubble pick-up, and Fergus, Sullivan and Workentine (1968) using Hallimond tube techniques, established that topaz floated between pH 3.0 and pH 10.0 with sodium oleate. These studies, however, were conducted at specific pH values and did not extend to the whole pH range. Thus, Andrews (1971), using bubble pick-up established the limits of contact between pH 2.9 and pH 13.8, using 6 mg/L sodium oleate, with maximum flotation between pH 5.0 and pH 8.0. Contact at pH 7.0 was even obtained at 5×10^{-3} mg/L collector concentration. The vacuum flotation studies of Manser (1973) confirmed the limits of flotation at pH 3.0 and pH 12.0, but at a higher collector concentration of 12 mg/L.

Modifier studies were mostly depression by specific anions. Thus, depression was reported by sodium silicofluoride (Berger and Bulatova, 1969) using flotation cell; by fluoride ion and citric acid at pH 7 (Wyman, 1965), using bubble pick-up; by sodium silicate and calcium lignin sulphonate at pH 8.5, using Hallimond tube techniques (Fergus, Sullivan and Workentine, 1968).

Patek (1934), using dry-ground mineral, first determined that tourmaline developed a specific contact angle when using oleic acid. Bayula (1935) in the U.S.S.R. described the concentration of tourmaline from a tailings deposit.

The mechanism of adsorption is similar to that of topaz as Pol'kin and Najfanow (1964), using desorption collector studies, obtained evidence which indicated the existence of chemisorbed ionic and physically adsorbed molecular species of collector.

Laboratory-scale flotation studies confirm the evidence of adsorption studies, since tourmaline floats on either side of the p.z.c., determined at between 6.6 to 7.0 (Andrews, 1971; Rice 1968). Thus, Kennedy and O'Meara (1948) and Pol'kin and Najfanow (1964) using flotation cell; and Andrews (1971) using bubble pick-up technique, determined the limits of flotation between pH 2.5 and pH 11.5 using 6 mg/L sodium oleate. Maximum flotation occurred at pH 7.0 (Pol'kin and Najfanow, 1964; Andrews, 1971) and at this pH, contact was possible at 10^{-2} mg/L (Andrews 1971). The vacuum flotation studies of Manser (1973) confirmed the limits of flotation between pH 4.0 and pH 12.0 using 12 mg/L sodium oleate, and the Hallimond tube studies of Tice (1968) reported the limits of flotation between pH 2.0 and pH 12.0 using 32 mg/l potassium oleate.

Pol'kin and Najfanow (1964) determined that tourmaline was depressed by sodium silicofluoride and sodium silicate. Strel'tsyn and Vishnerski (1965) compared the depression abilities of oxalic acid and sodium silicofluoride, and determined that the former was the more effective depressant. Strel'tsyn (1968b), in fact, describes a plant operation in which tourmaline was depressed by oxalic acid. Manser (1973) determined that fluoride depressed tourmaline at pH <6.0.

Topaz and tourmaline are floated between pH 3.0 and pH 12.0 and maximum floatability for each is at pH 7.0. Differences in floatability in the presence of either cationic activators or anionic depressants should be treated with caution. The reporting of either mineral as not being activated or depressed by a particular species does not imply selectivity; it only signifies that the mineral was not assessed by that species.

Metal ions, e.g., Fe^{3+} , Al^{3+} and Cu^{2+} , were derived from the ore precipitate collector and activate gangue minerals with similar flotation properties to cassiterite. The use of chelating agents (citric and oxalic acid) and sequestering agents (sodium hexametaphosphate, sodium silicate and sodium silicofluoride) can overcome this problem to some extent if the concentration of interfering cations is small. The removal of larger concentrations of metal ions can only be accomplished by desliming.

Despite the similarities in floatability between cassiterite, topaz and tourmaline, cassiterite was concentrated by oleic acid in some early full-scale operations including those in Altenberg in East Germany (Finn, 1952; Glembotsky, Klassen and Plaksin, 1961).

A combination of anionic and cationic collector flotation was claimed by Bruce and Yaksic (1966) to be selective for concentrating cassiterite. A cassiterite rougher concentrate was obtained using oleic acid at neutral pH. Oleic acid was removed from mineral surfaces by thermal desorption at 300°C , and gangue minerals were removed by a primary amine at pH 11.0; cassiterite was depressed with sorghum flour.

The selectivity of oleic acid was claimed to be improved by the addition of phenol derivative compounds (Matsiev, 1963). More recently, Sun and Xin (1986) reported improved cassiterite flotation after exposure of oleic acid to gamma radiation. Gamma radiation causes the formation of dimers, trimers and peroxide, increasing the size of the adsorbed oleic acid molecules.

Miscellaneous carboxylate selectivity

Tall oil is claimed to be more selective than oleic acid as a collector for cassiterite. Thus, Sukhovdskaya et al. (1965) were able to replace oleic acid by tall oil for floating fine cassiterite from the tailing of a gravity plant. Korzhov and Pol'kin (1970) obtained selective flotation of cassiterite from tourmaline by using a light fraction of tall oil in a pH range of 3.0 to 10.0. Tall oil is much less expensive than oleic acid.

Recently successful separations of cassiterite from topaz were reported by the use of aminonaphenesulphonic acid depressant in undecane 1,1-dicarboxylic acid flotation. Hallimond tube studies of Baldauf, Schoenherr and Schubert (1985) demonstrated that, while undecane 1,1-dicarboxylic acid floats cassiterite, topaz and tourmaline, selectivity was achieved with respect to topaz and tourmaline. Thus, 29 mg/L of collector was sufficient to float cassiterite between pH 2.0 and pH 7.0, but tourmaline did not float at a collector concentration below 288 mg/L at pH 3.5. Topaz, while being floated by this collector at the same collector concentration and pH range as cassiterite, was depressed by aminonaphthene sulphonic acid (Baldauf, Singh and Schubert, 1980; Baldauf, Schoenherr and Schubert, 1985).

Alkyl sulphate selectivity

Hergt, Rogers and Sutherland (1946) first used alkyl sulphate collectors to float topaz. Cylinder flotation tests using hexadecyl sulphate indicated the limits of flotation between pH 1.0 and pH 5.5,

although contact was possible up to pH 9.0. Anomalous behaviour with hexadecyl sulphate was observed by Evans (1953) when fresh-ground topaz was virtually unresponsive; flotation only being obtained after conditioning indicating activation by surface hydration. Hallimond tube studies of Fergus, Sullivan and Workentine (1968) using heptyl sulphate determined similar limits of flotation between pH 2.8 and pH 6.0. The range of maximum flotation for each collector was pH 2.0 and pH 4.5; Hergt, Rogers and Sutherland (1946) obtained a minimum collector concentration of 1 mg/L. Bubble pick-up studies of Wyman (1965) using octyl sulphate and Wyman (1969) using lauryl sulphate indicated similar pH limits of flotation between pH 3.0 and pH 6.0.

The adsorption of alkyl sulphate on topaz is probably governed by electrostatic forces, since flotation is only possible below the p.z.c. Activation and depression studies by Evans (1953) indicated that Fe^{3+} at pH 3.0 and pH 4.0 activates topaz, but Ca^{2+} depressed flotation by collector precipitation at pH 2.5 and pH 5.0. Topaz was similarly depressed by sequestering agents such as polyphosphate.

The limits of flotation of tourmaline are not reported, but Evans, Ewers and Meadows (1962) conducted testwork at pH 3.5 using hexadecyl sulphate, and found that tourmaline exhibited similar flotation properties to cassiterite. Since tourmaline is apparently similar in floatability to cassiterite and topaz, it would be expected that adsorption of hexadecyl sulphate would be governed by charge considerations.

An extensive study of flotation modifiers by the same authors using hexadecyl sulphate and Hallimond tube techniques indicated that tourmaline was activated by gelatin, methyl cellulose and casein. Depression was reported by numerous reagents, including gum arabic, tragacanth, mimosa, tannin, pectin, dextrin, agar, cobalt sulphate, sodium alginate, sodium silicate and sodium polyphosphate. Selective depressants for tourmaline that did not depress cassiterite included potassium alum, sodium fluoride and sodium silicofluoride. Each modifier was assessed at a concentration of 5 and 50 mg/L. Cell flotation tests of Pol'kin and Najfanow (1964) also indicated that sodium silicofluoride was a selective depressant for tourmaline at pH 3.5.

The main disadvantage to the use of alkyl sulphate collectors is that cassiterite is associated with topaz and tourmaline; topaz (Hergt, Rogers and Sutherland, 1946) and tourmaline (Evans, Ewers and Meadows, 1962) markedly reduce selectivity. The unselective effect these minerals have on cassiterite flotation was demonstrated by Trahar (1965), by comparing cassiterite from two different sources. The first sample contained quartz with minor mica, and the second sample a mixture of quartz, topaz, tourmaline and iron oxides. The cassiterite flotation enrichment ratio of the first sample was much higher than the cassiterite flotation enrichment ratio of the second sample.

The presence of slimes in alkyl sulphate flotation is detrimental to selectivity, so too is the presence of metal ions, especially Ca^{2+} , since collector is precipitated. The best tourmaline depressant was sodium silicofluoride, which was confirmed in cell flotation tests, but not pursued further.

The evidence available concerning the flotation behaviour of topaz and tourmaline with alkyl sulphate collectors suggests that there is little possibility of achieving any selectivity in flotation response.

Alkyl sulphonate selectivity

There is only limited information available concerning the flotation response of topaz and tourmaline to this collector group. Bubble pick-up studies of Wyman (1969) indicate excellent flotation between pH 3.0 and pH 6.0 using petroleum sulphonate and fatty acid sulphonate collectors. Furthermore, flotation with these collectors was relatively unaffected by Fe^{3+} , Al^{3+} , fluoride, starch, dextrin and citric acid. The non-selective nature of petroleum sulphonate collectors was demonstrated at Renison Tin in Tasmania, where only low-grade cassiterite concentrates could be obtained (Renison Tin Ltd., 1968).

Alkyl sulphosuccinamate collectors have the advantage of chelating ability, so that a certain tolerance towards Fe^{3+} and Ca^{2+} is possible when using sequestering agents. Thus, Pol'kin, Korzhova and Pis'mennyi (1970) determined that, although cassiterite and tourmaline possessed similar flotation properties when using disodium monoalkyl sulphosuccinate, tannin-based depressants (Sintan-5 and Tanner-3) were excellent depressants for tourmaline between pH 2.0 and pH 10.0. Cassiterite in the pH range 5.0 to 6.0 was unaffected by these depressants. Hallimond tube experiments of Fergus, Sullivan and Workentine (1968) indicated that topaz was floated by sodium sulphosuccinate at pH 4.0.

Aerosol 22 is an excellent collector for cassiterite and tourmaline. Selectivity is possible by the use of either sodium silicate or sodium silicofluoride at pH 2.0 and pH 2.5, which effectively depress tourmaline but not cassiterite (Collins, Hollick and Joy, 1969). Cell flotation studies of Arbiter and Hinn (1968) demonstrated depression of topaz and tourmaline by potassium ferricyanide, and ferrocyanide, sodium silicate and sodium silicofluoride. Citric acid also depresses both topaz and tourmaline.

Arsonic acid selectivity

Several disadvantages limit the effectiveness of arsonic acid collectors: No flotation of cassiterite occurs until the collector concentration is 150 mg/L (Collins, 1967); Moncrieff et al., (1973) further reported a collector addition of 350 g/t necessary for flotation. This, together with the high cost of manufacture, restricts the economic use of arsonic acids, although benzyl arsonic acid is reported to be cheaper than para-tolyl arsonic acid (Zhu and Zhu, 1980). Arsonic acids are also highly toxic and not entirely specific for cassiterite, as other minerals are also floated, including garnet (Grunder, 1955), mica (Bourgeois, 1962), chlorite and tourmaline (Moncrieff et al., 1973), fluorite and topaz (Wottgen and Rosenbaum, 1972) and iron oxide minerals (Glembotsky, Klassen and Plaksin, 1961).

When these various disadvantages are considered, it is not surprising that no systematic studies of the flotation of topaz and tourmaline are reported with any of the aryl derivatives.

Phosphonic acid selectivity

Phosphonic acids are perhaps the most widely used group of collectors judging by the variety of derivatives reported in Table 3. The introduction into commercial operations, however, has been slow because of early purification difficulties in preparing commercial-scale quantities of collector. Mosch and Becker (1985) reported the successful introduction of styrene phosphonic acid at Altenburg, East Germany, replacing the earlier use of para-tolyl arsonic acid.

The flotation response of topaz and tourmaline to phosphonic acids is similar to cassiterite, but selectivity can be achieved through various depressants. Collins, (1967) states that n-heptyl phosphonic acid has a strong affinity for minerals with a high iron content, but that when sodium silicofluoride and citric acid were used, tourmaline was depressed.

The pilot-plant studies of Collins et al. (1968) demonstrated that n-octyl phosphonic acid floats topaz and tourmaline, but that depression of these minerals was possible through the use of sodium silicofluoride.

Cell flotation studies of Pol'kin and Najfanow (1964) determined the limits of flotation of tourmaline using sodium iso-octyl phosphate to be pH 1.0 and pH 9.0 with maximum flotation at pH 3.0 and pH 4.0; depression of tourmaline was effectively induced by sodium silicofluoride. Similarly, Fergus, Sullivan and Workentine (1968), using the Hallimond tube, determined that topaz was floated between pH 3.0 and pH 5.0 using sodium iso-octyl phosphate. Wottgen and Luft (1971), using heptane phosphonic acid, report that cassiterite was selectively separated from topaz.

Recent studies by Ryaboi et al. (1981) report the use of acryloyl hydroxamic acids (polymers with chelating hydroxamate groups) as depressants for tourmaline when using a variety of phosphonic acid collectors. Cassiterite was apparently unaffected by these depressants.

Alkyl hydroxamate selectivity

The use of alkyl hydroxamates has received little attention, outside the U.S.S.R., possibly because of the high cost of commercial production. The lack of research with these collectors is surprising, since the chelating ability of hydroxamates indicates that high concentrations of Fe^{3+} in solution can be tolerated.

In cell flotation studies, Gorlovsky (1968) first discussed the depression of tourmaline by oxalic acid at pH <3.0, using hydroxylamine sulphate. Hydroxylamine sulphate is the soluble salt of hydroxamic acids synthesized from C_7 to C_9 carboxylic acids. Strel'tsyn (1968a) further improved the technique by employing a mixture of hydrochloric and oxalic acid to depress tourmaline.

Large-scale investigations of the depression of topaz and tourmaline by oxalic acid are reported. Thus, Strel'tsyn, Popovich and Yakovlev (1970) in a pilot-plant study, obtained depression of topaz and tourmaline by a mixture of oxalic and sulphuric acid using hydroxamic acid collector. Plant-scale

studies of Bogdanov et al. (1973) reported the depression of tourmaline by oxalic acid at pH 2.5 and pH 5.0.

Alkyl amine selectivity

When using dodecylamine, topaz displays similar flotation properties to cassiterite. Thus, Fergus, Sullivan and Workentine (1968) using the Hallimond tube, and Wyman (1965) and Andrews (1971) using bubble pick-up techniques determined the limits of flotation between pH 5.5 and pH 13.0, with maximum flotation between pH 7.5 and pH 10.0. The dependence of flotation on pH values above the p.z.c. would imply electrostatic adsorption, and it is likely that the amine ion and the undissociated amine species would be adsorbed.

The effect of modifiers on topaz flotation above the p.z.c. is limited. Thus, Wyman (1965) reported depression by Fe^{3+} at pH 10.0, and Fergus, Sullivan and Workentine (1968) reported depression by sodium silicate at pH 11.0. Below the p.z.c. amines become weak collectors, with only insignificant adsorption occurring (Gaudin and Morrow, 1954), so that the effect of modifiers is greater. The influence of sulphate between pH 1.7 and pH 5.0 was to activate cassiterite (Trahar, 1968; Verkholtantsev, 1961; Andrews, 1971), whereas the influence on topaz was insignificant (Andrews, 1971). The best example of activation was obtained with fluoride ion at pH 3.0. Andrews determined that fluoride was an excellent activator for topaz, but the effect on cassiterite was insignificant (Andrews, 1971; Trahar, 1968).

Fluoride as a modifying ion has received much attention in the study of feldspars. Buckenham and Rogers (1954) considered that the mechanism of activation involved first the displacement of hydroxyl ions by fluorine forming an aluminum-fluoride bond, followed by adsorption of RNH_3^+ .

Smith (1965), however, considered that the activation of feldspar by fluoride was based on the formation of silicofluoride ions from the chemical action of hydrofluoric acid with hydrolyzed surface silicic acid. Activation then occurred when silicofluoride ions were adsorbed onto exposed aluminum ions.

Read and Manser (1975) in a study of the action of fluoride on certain silicate minerals suggested the SiF_6^{2-} and AlF_4^- were activating species at low pH values when using dodecylamine collector.

These activation mechanisms can be applied to topaz, since it is likely that exposed ions will include aluminum and silicon. It is also possible that activation is the result of adsorbed fluosilicate ions, which might be expected to be released into solution from the topaz surface, since topaz is chemically aluminum fluosilicate.

The strong adsorption of fluoride ions on topaz can be inferred from the strong covalent bond between aluminum and fluoride ions. The stability constant of AlF_4^- at 17.6 (Matijevic et al. 1969) indicates a very stable covalent bond which does not hydrolyse in water. The weak effect of fluoride ion on tourmaline can be explained qualitatively by the lower stability of the ferric fluoride complex species compared to the aluminofluoride species.

Tourmaline, like cassiterite and topaz displayed similar floatability when using dodecylamine. Thus, Pol'kin and Najfanow (1964), Kennedy and O'Meara (1948) using flotation cell, and Andrews (1971) using bubble pick-up techniques determined the limits of flotation between pH 6.5 and pH 12.5; although Pol'kin and Najfanow (1964), and Rice (1968) using the Hallimond tube obtained contact down to pH 2.0. Maximum flotation was determined between pH 8.0 and pH 11.0 (Andrews, 1971; Rice, 1968).

The dependence of flotation on pH values above the p.z.c. implies electrostatic adsorption, and it is likely that the amine ion and the undissociated amine species would be involved.

The effect of modifiers in the pH region below the p.z.c. is similar to topaz with respect to sulphate ion. The effect of sulphate in activating tourmaline (Kennedy and O'Meara, 1948; Andrews, 1971) was insignificant when compared to cassiterite (Trahar, 1968; Verkholtantsev, 1961; Andrews, 1971). Similarly, fluoride ion was an insignificant activator for tourmaline (Andrews, 1971); in fact, Kennedy and O'Meara, 1948 reported that fluoride ion had a depressing effect.

In comparison with other collectors, cationic collectors have received the least attention because of their non-selective nature towards oxide and silicate minerals in the region above the p.z.c. of each mineral. Selectivity was obtained when specific modifying ions, i.e., activators and depressants, were used. Despite the potential for selectivity in the pH regions below the p.z.c., no studies larger than laboratory scale are reported. A plant-scale study of the flotation of cassiterite from tourmaline, at an undetermined pH, (Eigelles and Ershov, 1967) on the tailings of a gravity concentration plant had limited success.

ALTERNATIVE TECHNIQUES

The development of alternative techniques to concentrate cassiterite is almost as varied as the development of a selective collector system. The techniques considered include sulphidization and electrolytic reduction, selective aggregation, two-liquid flotation, carrier flotation and dissolved air flotation.

Sulphidization

Sulphidization is based on the reduction from the stannic to the stannous state, preferably stannous sulphide, so that sulphydric collectors may then be used to float cassiterite. Two early attempts were reported, one by Reed (1944) and one by Shorsher (1946), but the principal study was by Pryor and Wrobel (1951).

Sulphidization was attempted using either dry gaseous or wet gaseous techniques. Dry gaseous involved using a mixture of H_2S and H_2 at temperatures above $300^\circ C$ (Shorsher, 1946). Pryor and Wrobel (1951) employed wet gaseous methods, which involved bubbling either H_2S alone or H_2S and

H₂ into a warm aqueous suspension of cassiterite, when layers of sulphur were deposited on the cassiterite surfaces. The technique produced encouraging results but several disadvantages became apparent not least of which was the hazard of handling H₂S and H₂ at elevated temperatures. The results were not independent of lattice Fe impurities, and it was necessary to activate with Pb²⁺ before flotation was possible with xanthates. Furthermore, the possibility exists of sulphidizing gangue minerals, particularly iron oxides.

Subsequent attempts at overcoming these difficulties are few. Balberyszski, Cooke and Dorenfeld (1968) established that it was only necessary to obtain 8% conversion to stannous sulphide, and the optimum flotation pH was pH 3.0 and pH 4.0. The various studies are based on the assumption that stannous sulphide was the only active species. It is conceivable that free sulphur derived from the oxidation of H₂S could influence results.

Electrolytic reduction

Reduction to the metallic state was first attempted by chemical (Ralston, 1938) and later electrolytic methods (Klassen, 1947; Plaksin, 1960) but results were inconclusive. A description of successful flotation after electrolytic reduction was first described by Mamakov, Sorokina and Avvakumov (1969). Fine cassiterite was electrolyzed in a two-compartment cell. Cassiterite in the cathodic compartment floated more selectively with oleic acid than conventional flotation with oleic acid. The improved flotation was partly due to the action of nascent hydrogen in reducing the cassiterite surface to SnO₂H. Recently, Hoberg, Breuer and Schneider (1979) were able to selectively reduce cassiterite without co-reduction of oxidized iron minerals, using CO or H₂ at temperatures <300°C. Subsequent flotation was by hexyl xanthate.

A comprehensive comparison between electroflotation and conventional flotation was made by Hogan, Kuhn and Turner (1979). The effects of current density, cell height, pH values, pulp density and temperature on flotation grades and recoveries using a sulphosuccinamate collector indicated that electroflotation was more selective than conventional flotation. The main disadvantage was the high energy requirement, which was estimated to be fifty times greater than the 1 to 3 kWh/t of concentrate value deduced by Arbiter and Harris (1962) for conventional flotation.

Selective aggregation

Early attempts at producing mutual coherence were based on grinding cassiterite ores in an aqueous media of crude oil and a collector (Farnand et al., 1964). Results, however, were inconclusive since each collector produced similar results. Subsequent studies were directed towards agglomeration of 'tinned' cassiterite, which is self-flocculating. A mixture of minus 20 µm cassiterite and quartz were tinned on a zinc block and attempts to separate the flocs were made by elutriation. The flocs were easily ruptured and although high grades were obtained, only low recoveries were reported (Trimlett and Manser, 1972).

The conditions for selective aggregation of ultrafine particles were discussed in great detail by Warren (1984). The conditions were outlined for the formation of flocs to be strong enough to withstand the

turbulent forces usually encountered in mineral processing operations. The degree of hydrophobicity was imparted by choosing reagents usually used in conventional froth flotation separations. Thus, Warren (1982) investigated the selective flocculation of cassiterite from tourmaline.

Selective aggregation is a potential area of research for the selective separation of cassiterite from topaz and tourmaline in complex cassiterite ores.

Two-liquid flotation

Two-liquid flotation is similar to conventional flotation, except that oil drops are used instead of air bubbles to concentrate cassiterite. Thus, Yap (1975), using pure cassiterite, obtained flotation at the oil/water interface in the region below the p.z.c., using dodecyl sulphate as collector. Studies on cassiterite ores were conducted by Zambrana et al. (1974b), and Zambrana and Arguedas (1977), using *Aerosol 22* collector at pH values <3.0, where the highest recoveries were obtained. Marinakis and Shergold (1988), however, using styrene phosphonic acid at pH 6.0, were not able to obtain significant flotation of fine minus 6 μm cassiterite from the Rooiberg, South Africa cassiterite slimes.

Two-liquid flotation has some advantages over conventional flotation in that it is energetically more favourable to disperse oil in water than air in water. The oil/water interfacial area available for particle contact is much greater than in air/water systems. Oil droplets have more momentum than air bubbles, which enables them to overcome repulsive energy barriers on particle drop-collisions.

The excessive reagent concentrations reported by Marinakis and Shergold (1988), and the poor performance on actual plant cassiterite slimes limit the application of this process until further development can improve flotation selectivity.

Carrier flotation

The size range of carrier flotation, also known as ultraflotation or piggy-back flotation, is in the ultrafine range. The principle by which carrier flotation is possible is the formation of slime coatings. The method was originally developed for the removal of fine anatase from kaolin by introducing a coarser size carrier mineral calcite, which collected the anatase as a slime coating (Greene and Duke, 1962). Warren (1975) has suggested that the mechanism by which the hydrophobic anatase was deposited onto the calcite was by shear-flocculation.

An attempt to apply this principle to ultrafine cassiterite recovery was described by Mercade (1967). The method involved removal of sulphide minerals, followed by treatment of the residue with Na_2CO_3 and Na_2SiO_3 at pH 9.0, and 5 μm calcite carrier added. A cassiterite concentrate in calcite carrier froth was obtained using a fatty acid/petroleum sulphonate collector mixture at pH 8.2. Removal of the calcite from the cassiterite concentrate was possible by reconditioning with Na_2SiO_3 at 90°C and pH 9.1 and pH 9.9.

The recovery of ultrafine cassiterite is possible by this method but there are some drawbacks. The high consumption of reagents because of the fine sizes results in high reagent costs, and the disposal of 5 μm calcite on a plant scale could present filtration and handling problems.

Dissolved air flotation

Dissolved air flotation was originally developed for sewage treatment, but has found an application in mineral processing. The method is based on air dissolved in water under pressure. The air-saturated water is injected through a valve in a flotation cell, the resultant pressure reduction across the valve causes the formation of a cloud of fine 50 μm size air bubbles. The bubbles thus produced are much smaller than those produced with conventional flotation aeration systems.

Gochin and Solari (1983), in a comprehensive study, successfully concentrated cassiterite from a 50% <5 μm cassiterite and quartz mixture using sodium dodecyl sulphate and *Aeropromoter 845* collectors. Collector-induced coagulation was considered to be an important factor for flotation rates and selectivity, but of equal importance was the availability of sufficient bubble surface area.

The advantages with this system are that fine particles are floated by fine bubbles, and that the generation of a large number of air bubbles can be adequately controlled through the saturation and venturi devices. The same degree of control is not so apparent in conventional flotation aeration systems. The main disadvantage is the cost of air supply, since the pressurizing of large volumes of water to achieve the level of supersaturation can be costly. The water industry, nevertheless, has found dissolved air flotation to be competitive with other treatment systems (Hyde et al., 1977; Upton and Hale, 1978).

CONCLUSIONS

Cassiterite in common with other oxide minerals floats over a wide pH range using carboxylic and sulphonate collectors. The response to alkyl phosphonic and aryl arsonic collectors is over a more restricted pH range. The flotation behaviour towards collectors governed by electrostatic forces, i.e., the alkyl sulphate and alkyl amines, is dependent on the p.z.c.

The main problem with the flotation of cassiterite is achieving adequate selectivity, which is based not so much on collector response, as rather on the association of cassiterite with minerals possessing similar floatabilities. Selectivity was achieved in part by the use of specific modifying ions, especially with chelating and sequestering ability. Thus, oxalic acid and citric acid, sodium silicate, sodium hexametaphosphate and sodium silicofluoride were used in various plant trials to depress the most troublesome minerals, topaz and tourmaline. Most of the major anionic collectors were used in processing plants at different times; the use of styrene phosphonic acid at Altenberg, East Germany appears to be the most selective.

The results of surface modification techniques, sulphidization and electrolytic reduction are inconclusive, and have not been attempted beyond the laboratory stage. Selective flocculation and dissolved air flotation are areas of potential fruitful research for the recovery of minus 5 μm cassiterite.

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