

Chapter 3

THE ORTHOSILICATES

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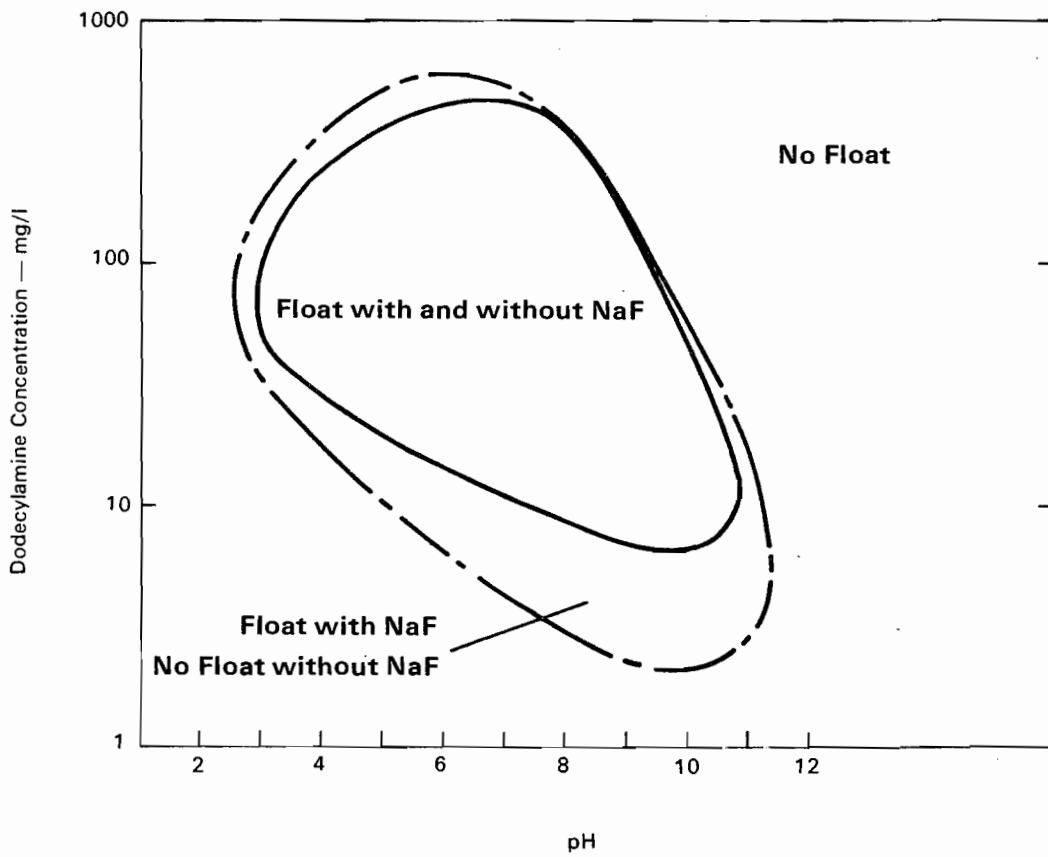
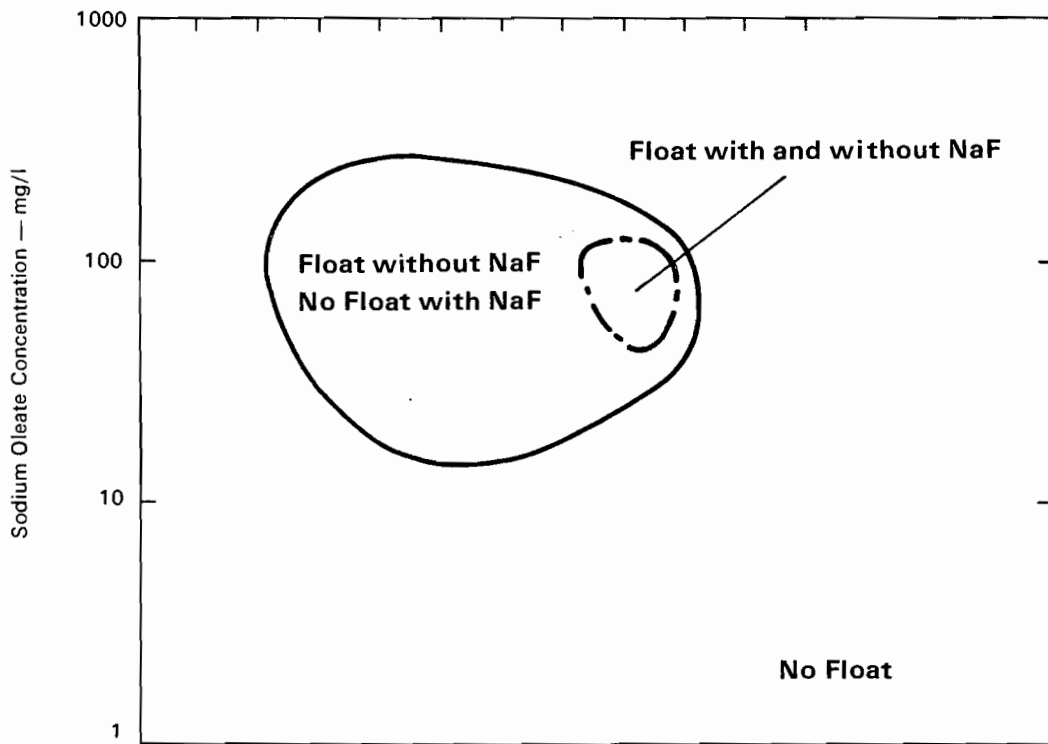


Fig 3.1 Andalusite

COMPOSITION $Al_2O[SiO_4]$, aluminium orthosilicate.

PHYSICAL PROPERTIES

Hardness 7.5. Specific gravity 3.1 to 3.3. Grey, purplish-red, red-pink, but may exist as white, yellow or even green orthorhombic crystals. z.p.c. 5.2 to 7.5¹⁻³.

CHEMISTRY

The pure mineral is insoluble in dilute acids, including hydrofluoric acid, although it has been shown that the zero point of charge is reduced by washing in dilute acid³. Some aluminium in the lattice may be replaced by iron. It is frequently found in association with cordierite and may thus give rise to ferric ions in flotation pulps.

FLOTATION CHARACTERISTICS

Andalusite shows moderate flotation with both anionic and cationic collectors. The oleate flotation shows little sensitivity to change in pH between 3.0 and 10.0, but fluoride has a very marked depressant action. Cationic flotation is favoured at alkaline pH values and is promoted by the addition of the fluoride ion. The flotation diagram appears as Fig 3.1.

FUNDAMENTAL FLOTATION STUDIES

Choi and Oh^{1,2} have made a detailed investigation and comparison of the surface properties of andalusite and kyanite and correlated these with simple flotation tests. They found good flotation of andalusite with oleic acid between pH 4.0 and pH 9.0 with rapid decline outside this range. Linoleic and linolenic acids also act as collectors but with these the fall in flotation occurs at pH 8.0. Lauric acid was found to be a very poor collector for these minerals.

In a comparison of the flotation behaviour and surface characteristics of andalusite, kyanite and sillimanite, Smolik, Harman and Fuerstenau³ have shown that by dissolving surface aluminium ions with dilute acid it is possible to cause a shift in the z.p.c. of these minerals. This change in the z.p.c. to a more acid value leads to increased flotation recoveries at lower pH values with the cationic collector dodecylamine acetate.

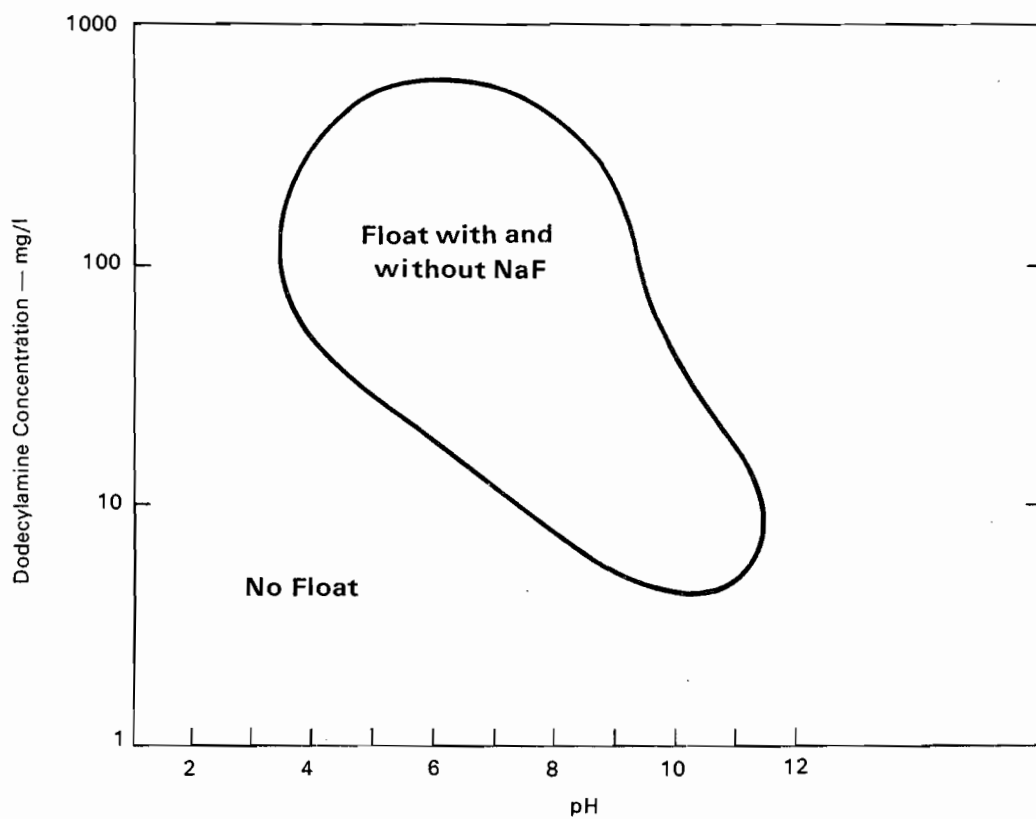
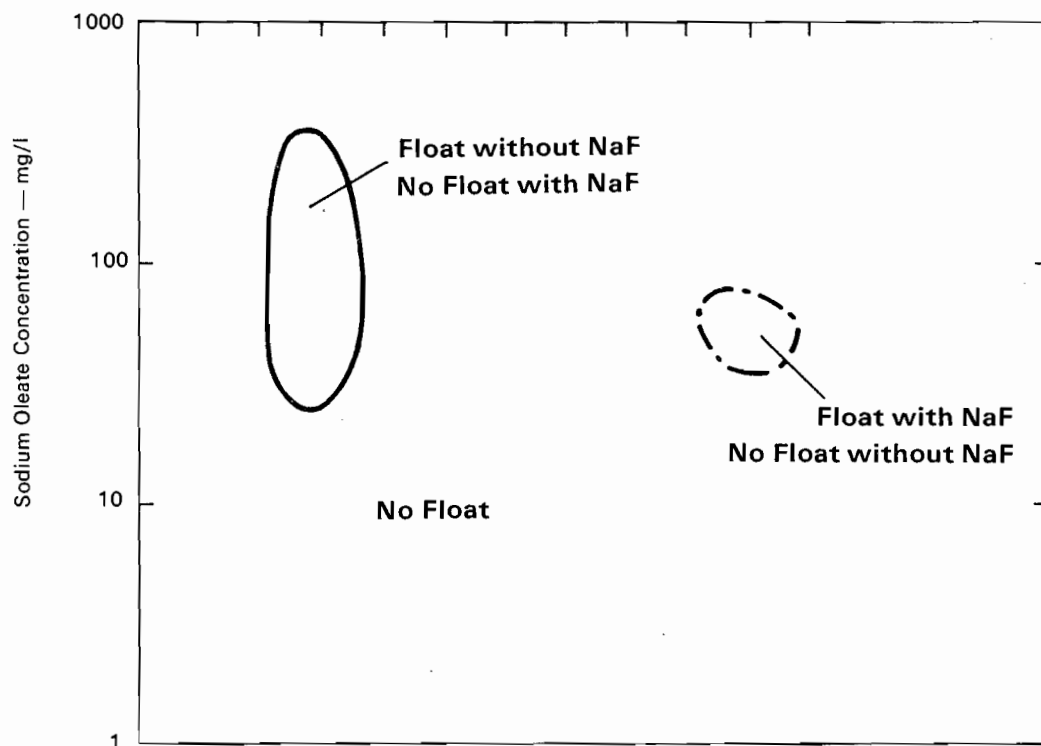


Fig 3.2 Axinite

COMPOSITION $(\text{Ca, Mn, Fe}^{\text{II}})_3 \text{Al}_2\text{BO}_3[\text{Si}_4\text{O}_{12}]\text{OH}$, calcium aluminium borosilicate.

PHYSICAL PROPERTIES

Hardness 6.5 - 7. Specific gravity 3.28. Blue, brown or light grey triclinic crystals.

CHEMISTRY

Acid insoluble.

FLOTATION CHARACTERISTICS

The flotation of this mineral with the anionic collector (sodium oleate) is very poor indeed. It shows great sensitivity to pH change having its small area of flotation between pH 3.0 and 4.5. The effect of fluoride is to shift this small area of flotation to the alkaline region around pH 11.0.

The cationic flotation properties are more conventional showing moderate flotation with dodecylamine and sensitivity to pH change with an optimum pH for flotation occurring between 8.0 and 9.0. No change could be found in the flotation area on adding sodium fluoride modifier. The flotation diagram appears as Fig 3.2.

FUNDAMENTAL FLOTATION STUDIES

The floatability of axinite with anionic collectors⁴ has been compared with other borosilicates and the order found was: garnet > datoline > danburite > axinite. The maximum adsorption of sodium oleate⁵ was found to occur in neutral solution for datoline, at pH 4.5 to 5.5 for axinite and garnet, and at pH 2.0 for danburite. It was also shown that the flotation maximum in this weak acid medium could be related to the leaching of aluminium from the mineral surface. An infra-red study⁶ showed that the oleic acid under these conditions was adsorbing on axinite in both the ionic and the molecular forms.

The effects of sodium silicate and potassium silicofluoride modifiers were also studied⁵. No effects on the flotation are reported but the silicate was found to decrease the adsorption, and the silicofluoride to increase the adsorption of oleate.

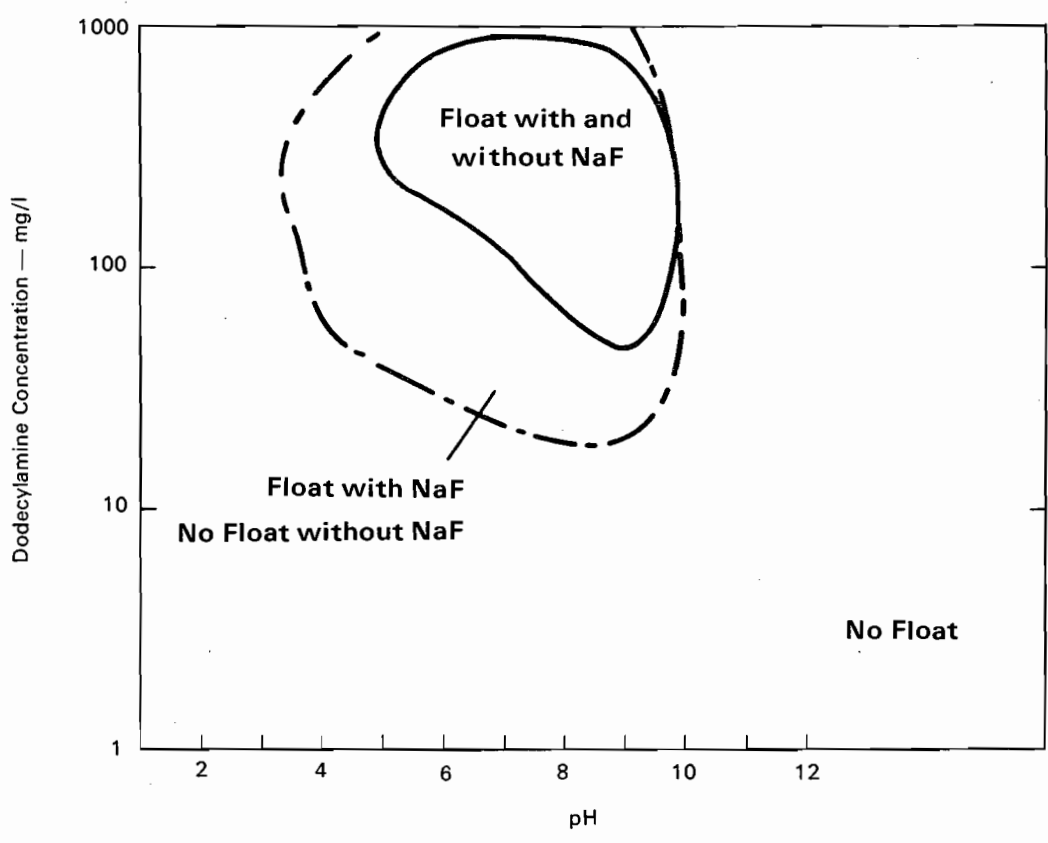
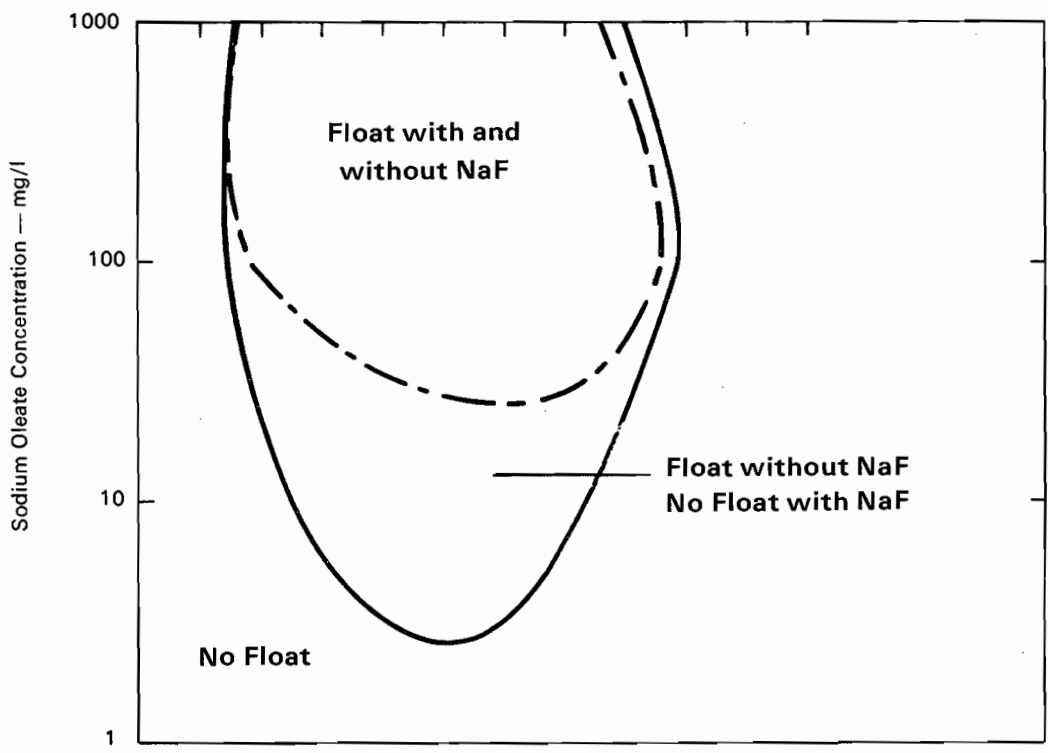


Fig 3.3.1 Beryl

COMPOSITION $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$ beryllium aluminium silicate.

PHYSICAL PROPERTIES

Hardness 7.5 to 8.0. Specific gravity 2.6 to 2.9. White or green shades, hexagonal crystals. z.p.c. 2.5 to 4.1⁷⁻¹³.

CHEMISTRY

The mineral is insoluble in dilute acids including HF. However, surface impurities may well be leached in acid or alkaline circuits causing a very marked alteration in the flotation properties¹⁴.

FLOTATION CHARACTERISTICS

Beryl floats well with the anionic collector sodium oleate between pH 3.0 and 10.0. Unlike many orthosilicates it is quite sensitive to pH change with an optimum value for flotation at pH 6.0. Fluoride causes considerable depression with this collector but the sensitivity to change in pH is considerably reduced with the optimum changing to pH 7.5.

Flotation of beryl with the amine collector is only moderate with less than normal sensitivity to pH change. Activation occurs on adding fluoride. Alkaline conditions are favoured with this collector both with and without the fluoride modifier. The flotation diagram appears as Fig 3.3.1.

FUNDAMENTAL FLOTATION STUDIES

The volume of work that has been carried out on fundamental flotation testing of beryl and associated ores exceeds by several times that on any other silicate mineral with perhaps the exception of quartz. It would be beyond the scope of this publication to critically review each and every contribution that has been made towards the understanding of not only the flotation properties of the pure mineral but also the action of certain depressants for which this mineral has been chosen as a model. For the reader with special interest

in a particular aspect of beryl flotation a selected bibliography is given at the end of this chapter (page 78).

PRACTICAL FLOTATION SYSTEMS

The mineral beryl commonly occurs in granitic pegmatites in association with micas, quartz and feldspars. Minor minerals also present in a beryl ore may include, apatite, spodumene, garnets, amblygonite, actinolite, tourmaline, cassiterite, topaz, etc. As each of these minor minerals will float to some degree with both anionic and cationic collectors the successful flotation separation of beryl from its ores is highly dependent on the extent of their co-occurrence.

Direct flotation with oleic acid or other fatty acids¹⁵ at neutral pH has been successful on certain ores but is usually preceded by a surface treatment, the most common of which is a conditioning with hydrofluoric acid or sodium fluoride at a pH between 2.0 and 4.0. After washing and removal of slimes, the beryl is normally floated with the oleic acid under neutral conditions. Pine oil as a frother¹⁶⁻¹⁸ may also be employed as may an emulsifying agent¹⁹⁻²² in some cases. If economically attractive quantities of spodumene are present in the ore, a preconcentrate of this may be made^{23-25,30} by an oleic acid flotation using lignin sulphonate together with sodium fluoride as depressants for the beryl. Other techniques employed in conjunction with the fluoride pretreatment/oleic acid concentration include: pre-separation of magnetic constituents, pre-separation of mica by screening or by flotation^{20,21} with an amine in acid circuit, and an apatite flotation^{21,26} with very low quantities of oleic acid. Surface scrubbing with sodium hydroxide has also been used both before²⁷ as well as in place of¹⁹ the fluoride treatment.

An alternative to the acid fluoride surface treatment was originally proposed by Eigeles and Leviush²⁸ where the pulp was pretreated with sodium sulphide under alkaline conditions. Subsequently a further conditioning period was carried out with oleic acid at 80-85°C before flotation at pH 9.5 to 11.0. A very similar process is the subject of an American patent²⁹.

The other major group of collectors that has been employed for beryl flotation is the sulphonated petroleum products. Using these under acid conditions it is necessary at some stage to remove mica. The method that has received the most attention involves a preliminary removal of mica by flotation with an amine collector (usually dodecylamine) at pH 1.5 to 2.5. This is followed by the addition of further amine together with a fluoride modifier (sodium fluoride³¹, silico-fluoride³², or hydrofluoric acid³³) in order to float a bulk beryl/feldspar concentrate again at an acid pH. This stage leaves a clean quartz tailing product. The amine is then removed from the surface of the beryl/feldspar concentrate, by washing with calcium hypochlorite^{34,35} solution, before the addition of

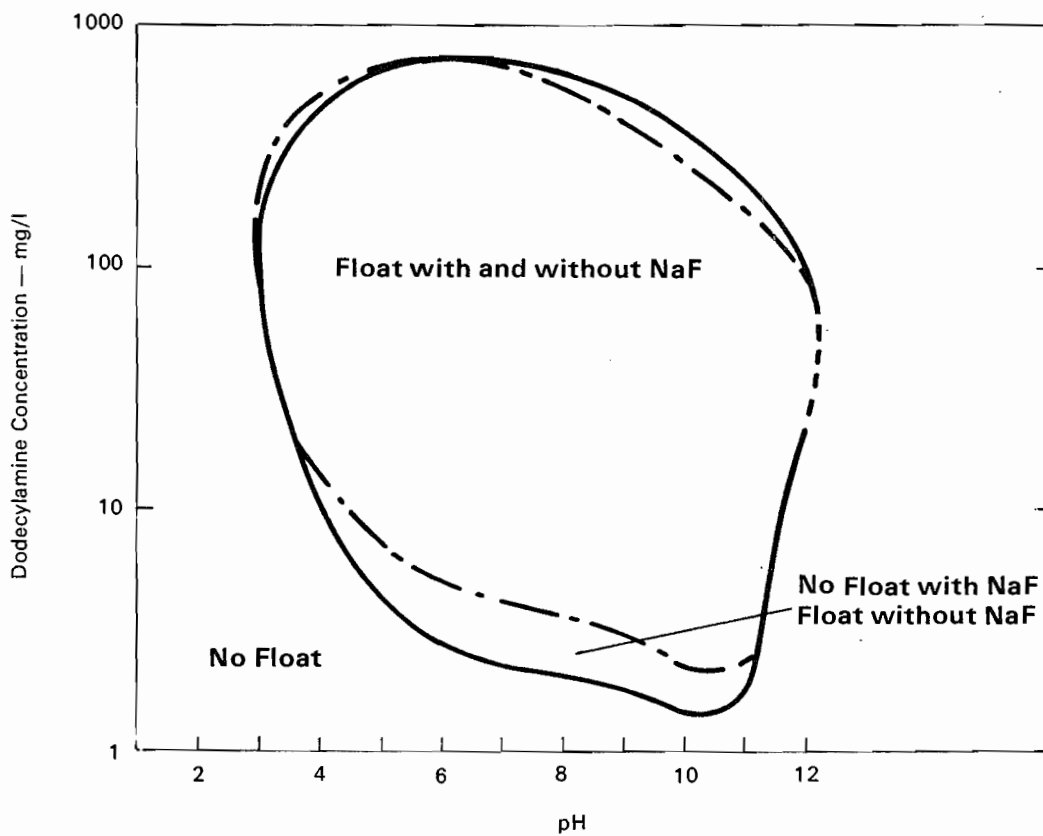
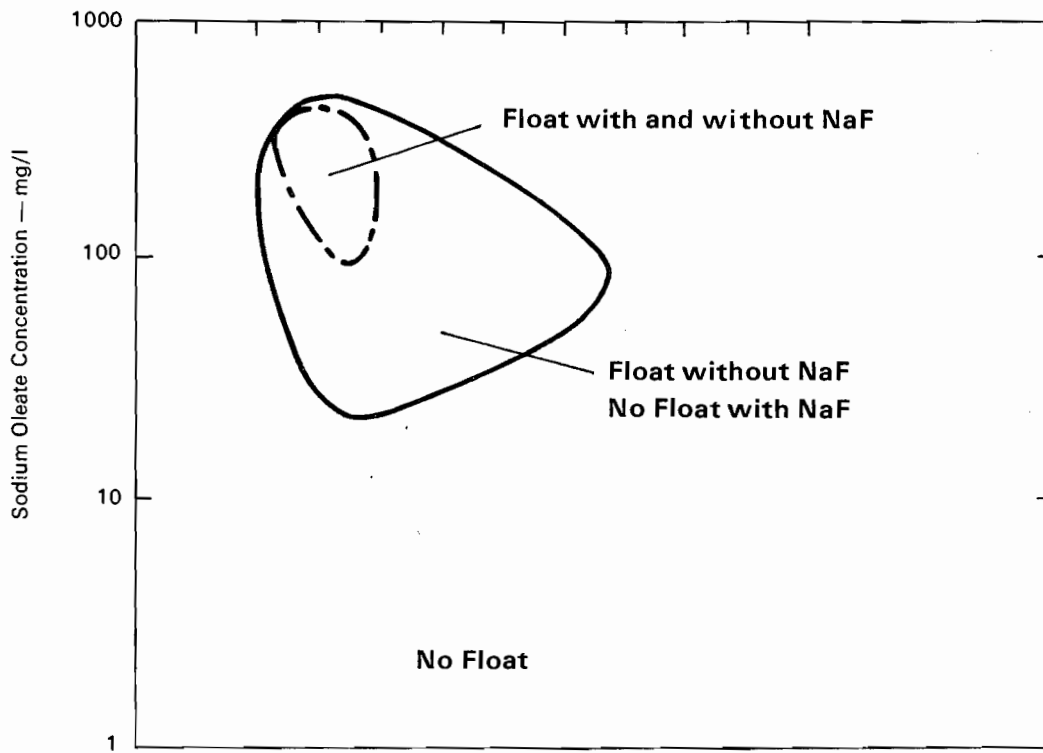


Fig 3.4 Epidote

COMPOSITION $\text{Ca}_2\text{Fe}^{\text{III}}\text{Al}_2\text{O.OH}[\text{Si}_2\text{O}_7] [\text{SiO}_4]$, basic silicate of calcium, aluminium and iron.

PHYSICAL PROPERTIES

Hardness 6 to 7. Specific gravity 3.25 to 3.50. Shades of green from yellowish green through to greenish black. Mainly monoclinic but can be orthorhombic crystals (eg Zoisite).

CHEMISTRY

Some members of the epidote series are partially soluble in hydrochloric acid and thus may give rise to iron or calcium ions in solution.

FLOTATION CHARACTERISTICS

Epidote floats moderately well with sodium oleate at acid pH values only. The optimum pH seems to be between 3.0 and 4.0 after which flotation rapidly ceases. Except for a very small area sodium fluoride causes depression of the anionic flotation.

With the cationic collector dodecylamine, epidote floats very well over a range of pH between 3.0 and 12.0 having a very slight preference to alkaline values. The fluoride modifier has very little effect on this diagram except at low concentrations where slight depression is caused. The flotation diagram appears as Fig 3.4.

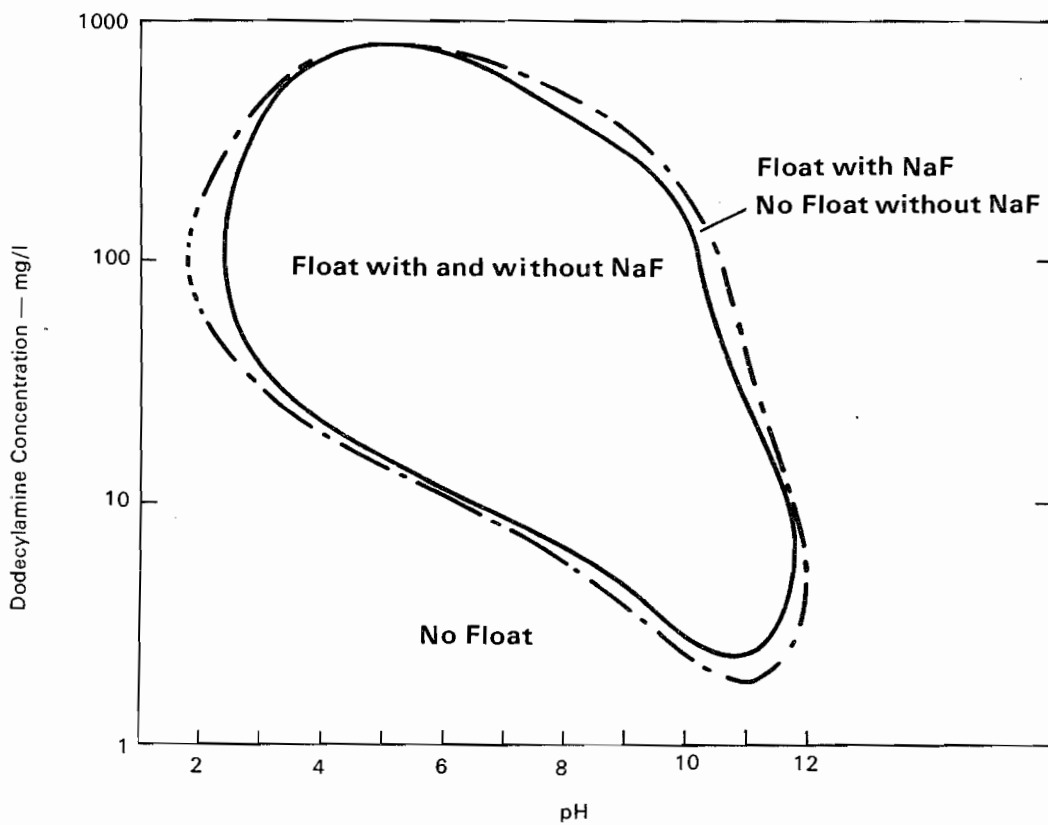
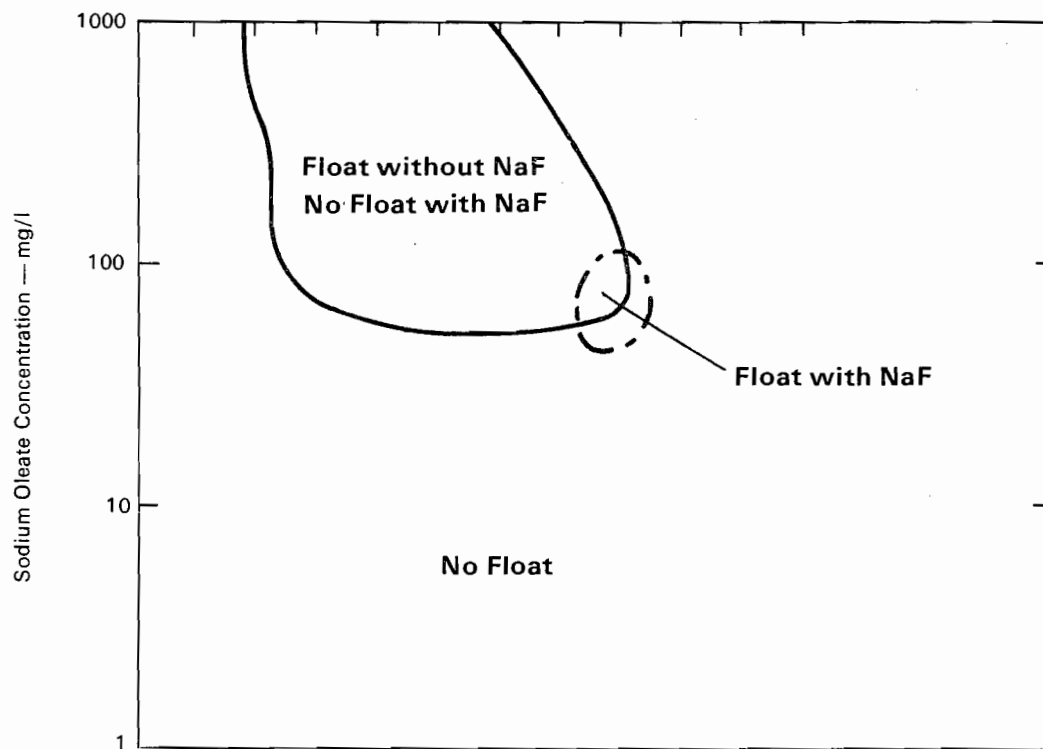


Fig 3.5 Kyanite

COMPOSITION $\text{Al}_2[\text{SiO}_4]$ aluminium orthosilicate

PHYSICAL PROPERTIES

Hardness: Variable between 4 and 7 dependent on crystal face. Specific gravity 3.6 to 3.7. Light-blue, white, grey-green, grey, pink or black triclinic crystals. z.p.c. 6.2 to 7.9^{1-3,37}

CHEMISTRY

The pure mineral is insoluble in dilute acids including HF, although, like andalusite, it has been shown that the point of zero charge is reduced by washing in dilute acid³. Kyanite is commonly found in gneisses and schists associated with iron minerals such as staurolite, limonite and cordierite. Each of these may be partially soluble in an acid medium and thus give rise to ferric ions.

FLOTATION CHARACTERISTICS

With the anionic collector sodium oleate, kyanite floats with little sensitivity to pH change between pH 3.0 and 8.5. Higher collector concentrations are required for this mineral than for its polymorph andalusite. Like andalusite, however, it is very sensitive to the fluoride ion which causes almost complete depression of flotation with oleate. Although the flotation diagram shows that it is sensitive to pH change favouring alkaline conditions, kyanite floats extremely well with the cationic collector dodecylamine over the range from pH 3.0 to 12.0. The fluoride modifier has only a slight activating effect on this mineral under the above conditions. The flotation diagram appears as Fig 3.5.

FUNDAMENTAL FLOTATION STUDIES

Choi and Oh^{1,2} have made a detailed investigation and comparison of the surface properties of andalusite and kyanite and correlated these with simple flotation tests. They found that kyanite floated well between pH 2.0 and 10.0 with oleic acid and between pH 2.0 and 9.5 with linoleic and linolenic acids. A satisfactory recovery was also obtained between pH 4.0 and 7.0 when using lauric acid as a collector, showing that kyanite is far more amenable to flotation than andalusite.

PRACTICAL FLOTATION SYSTEMS

The flotation of kyanite is the subject of a number of United States patents,³⁸⁻⁴⁰ dating from before the 1939-45 war, in which the ores were pretreated with either caustic soda or acids such as sulphuric, nitric or hydrochloric, and then subsequently washed with water before floating with oleic acid. One patent⁴¹ uses cationic collectors (C_{12} - C_{19}) with a fluoride modifier to effect simultaneous separation of both kyanite and feldspar from quartz.

Because of its frequent occurrence with quartz, anionic collectors are generally favoured for kyanite flotation. Workers in both the United States⁴² and Australia⁴³ used oleic acid as the collector together with sodium carbonate, to control the pulp pH to a value of 7.5, and citric acid to act as a quartz depressant. It was also found necessary to employ conditioning times of ten minutes⁴³ in order to obtain high-grade concentrates. After four cleaning stages, grades of 95 per cent with recoveries of 85 per cent were obtained by Wyman⁴⁴ on a Canadian kyanite ore. He used up to 1kg/t oleic acid modified with sodium carbonate to a pH of 9.2 using 100g/t sodium silicate to depress quartz flotation.

Desliming the flotation feed and conditioning at high pulp density with sulphonated petroleum collectors, followed by flotation at pH 3.0 using an alcohol frother, is reported by Thom and Gisler⁴⁵. Very similar conditions were found to be the most favourable during pilot-plant studies carried out on behalf of the US Bureau of Mines^{46,47}. Here the pulp pH was held between 3.0 and 4.0 with sulphuric acid and 0.6 kg/t petroleum sulphonate was used. It is of interest to note that the conditioning times found necessary with this collector were of the order of 15 minutes confirming the previous finding with oleic acid⁴³.

Improved sensitivity, together with the avoidance of the use of depressants is claimed in a Russian patent⁴⁸ based on high-molecular-weight alkyl benzene sulphonate collectors. More details of this process are given in a paper by Alekseev⁴⁹ and his co-workers who use 4-600 g/t of this collector (molecular weight 400, predominantly n-chains) at pH 4.0 to 4.5.

The use of hydrocarbon emulsions for kyanite flotation has also been reported^{50,51} to be advantageous for certain ores where the more common modifiers (Na_2SiO_3 , Na_2S , fluosilicate, etc) have been found to be ineffective. One such emulsion consisted of 30 parts distilled tall oil, 30 parts synthetic carboxylic acids (C_{10} - C_{16}), 40 parts of a neutral oil together with 10 per cent alkyl sulphate. Maximum recoveries with this type of collector were obtained when operating at pH 6.0 to 7.0 with a collector dose of 1.5 kg/t.

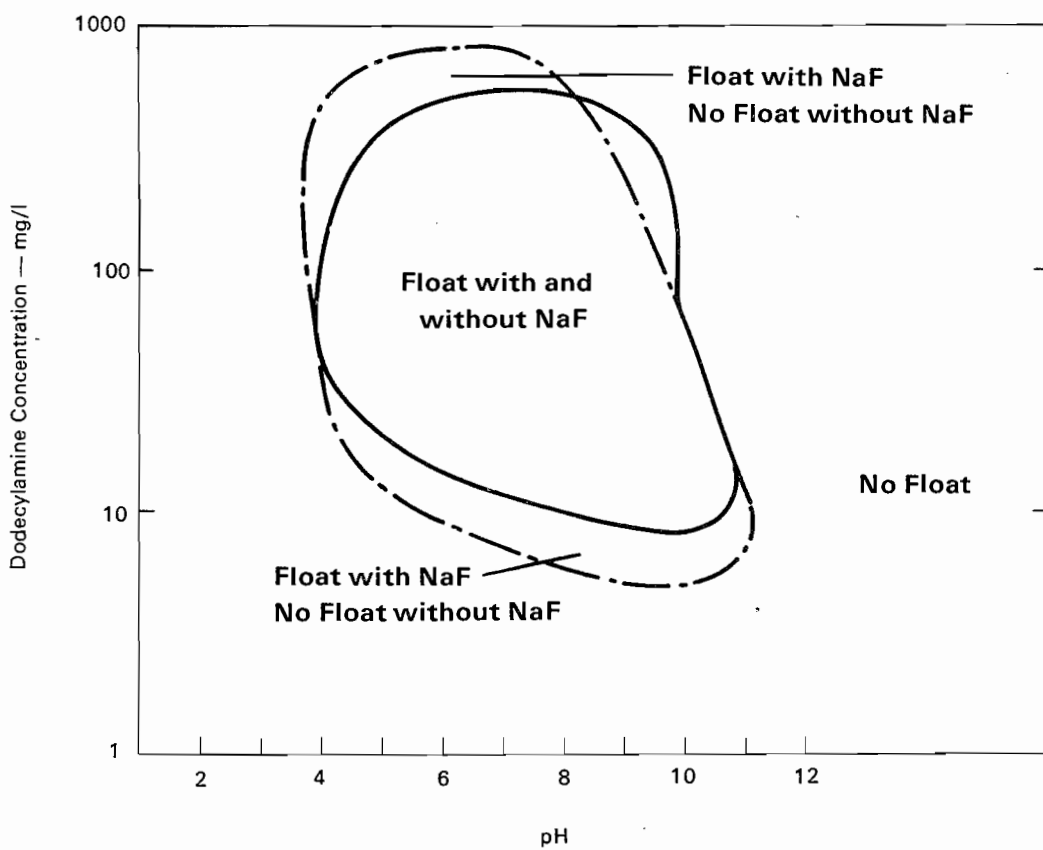
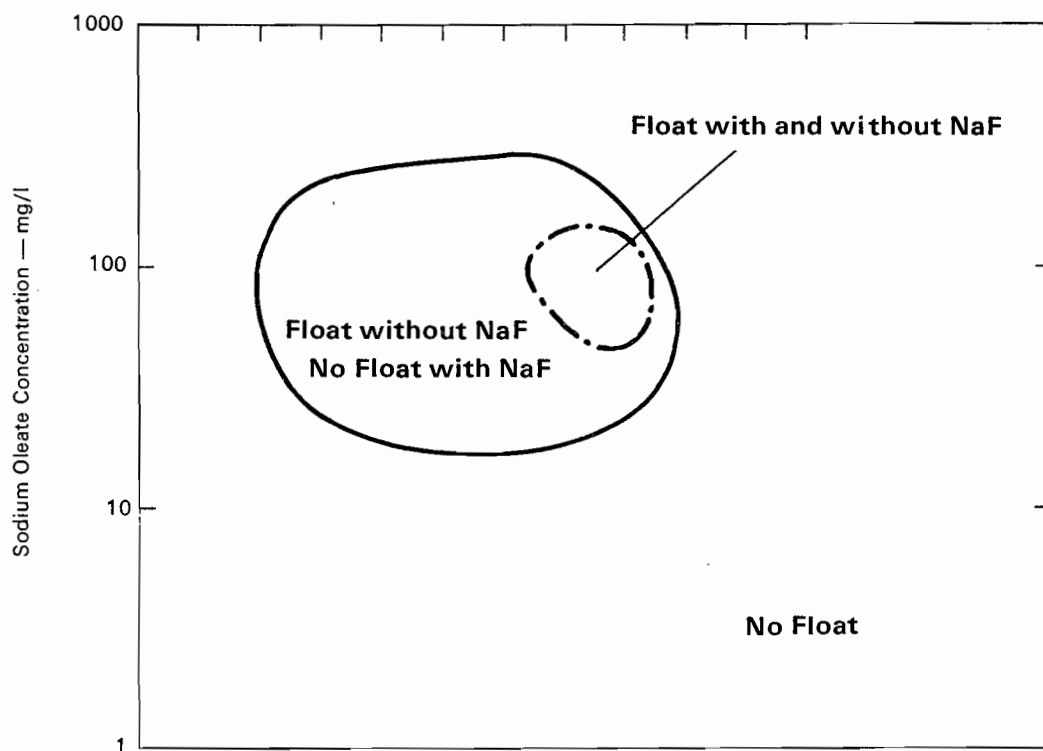


Fig 3.6.1. Olivine - Forsterite

COMPOSITION

The mineral olivine is an intermediate between forsterite and fayalite $(\text{Mg,Fe})_2 [\text{SiO}_4]$ – magnesium iron orthosilicate. The olivines are an isomorphous series with the general formula $\text{R}_2 [\text{SiO}_4]$ where $\text{R} =$

Magnesium (Mg)	Iron (Fe)	Manganese (Mn)
FORSTERITE	FAYALITE	TEPHROITE

PHYSICAL PROPERTIES

Hardness	7	6.5	6
Specific gravity	3.2	4.3	3.8 - 4
Colour	Yellow to green orthorhombic	Yellow-green to light brown orthorhombic	Dark green to grey-red orthorhombic
z.p.c.	4.0 - 4.1 (6.7 after acid treatment) ^{52,53}	5.7 ⁵³	6.0 ⁵³
CHEMISTRY	Partially soluble in acid to yield a gelatinous residue.	Acid insoluble	Soluble in acid as for forsterite.

FLOTATION CHARACTERISTICS

Of the olivine minerals considered here, the forsterite-fayalite series is the more important as these are common rock-forming minerals. The magnesium-rich forsterite is more commonly found in basic rock formations with fayalite occurring in rocks of volcanic origin. The flotation diagram appears as Fig 3.6.1. As the mineral tephroite is comparatively rare, it will not be considered in detail, but its flotation diagram is reproduced in Fig 3.6.2 for reference. Both forsterite and fayalite float moderately well with sodium oleate, neither showing sensitivity to pH change between 3.5 and 10.0. Each of these minerals is hypersensitive to the fluoride ion with

this collector, the flotation being reduced to an area around pH 9.0 that is so small as to have no practical significance.

The flotation of forsterite with dodecylamine is typical of that found with orthosilicate minerals: moderate to good flotation favoured by alkaline conditions and activated by fluoride. That of fayalite, however, having a small area of flotation between pH 6.0 and 10.0 and with fluoride having a slight depressant effect, is anomalous.

FUNDAMENTAL FLOTATION STUDIES

Russian authors⁵⁴ have investigated the flotation properties of olivine and ludwigite $[(\text{Mg}, \text{Fe}^{\text{III}})_2 \text{Fe}^{\text{III}}\text{BO}_5]$ with both anionic and cationic collectors. Sodium oleate, tall oil and the cationic collector ANP-14 were all found to be highly effective, but sodium alkyl sulphate was found to be a poor collector for these minerals. Radioisotope and infra-red investigations⁵⁵ showed that the oleate was attached both in the ionic form as magnesium and iron oleates and in the molecular form as oleic acid. Each mineral was found to be depressed by sodium silicate if this was introduced before the collector, but, if treated with sodium oleate or tall oil before the addition of silicate, then it was found possible to float the ludwigite in a weakly acid medium⁵⁶.

PRACTICAL FLOTATION SYSTEMS

Sodium silicate⁵⁷ and aluminium silicate⁵⁸ have been shown both to act as suitable depressants for olivine when floating apatite ores with tall oil.

A German patent⁵⁹ dealing with the flotation of chromite ores containing serpentine and olivine employs a two-stage process using a cationic collector. The primary stage is the removal of serpentine by flotation above pH 9.0 followed by reduction of the pH below 5.0 to float the chromite, leaving the olivine as a tailings product. The extent to which this can be interpreted in the light of an interpolation of the forsterite and fayalite flotation diagrams with these collectors is questionable. If the fayalite diagram is considered then flotation would not be expected below pH 5.0 but it would appear that a considerably higher pH than 9.0 would have to be reached before olivine would no longer float under alkaline conditions.

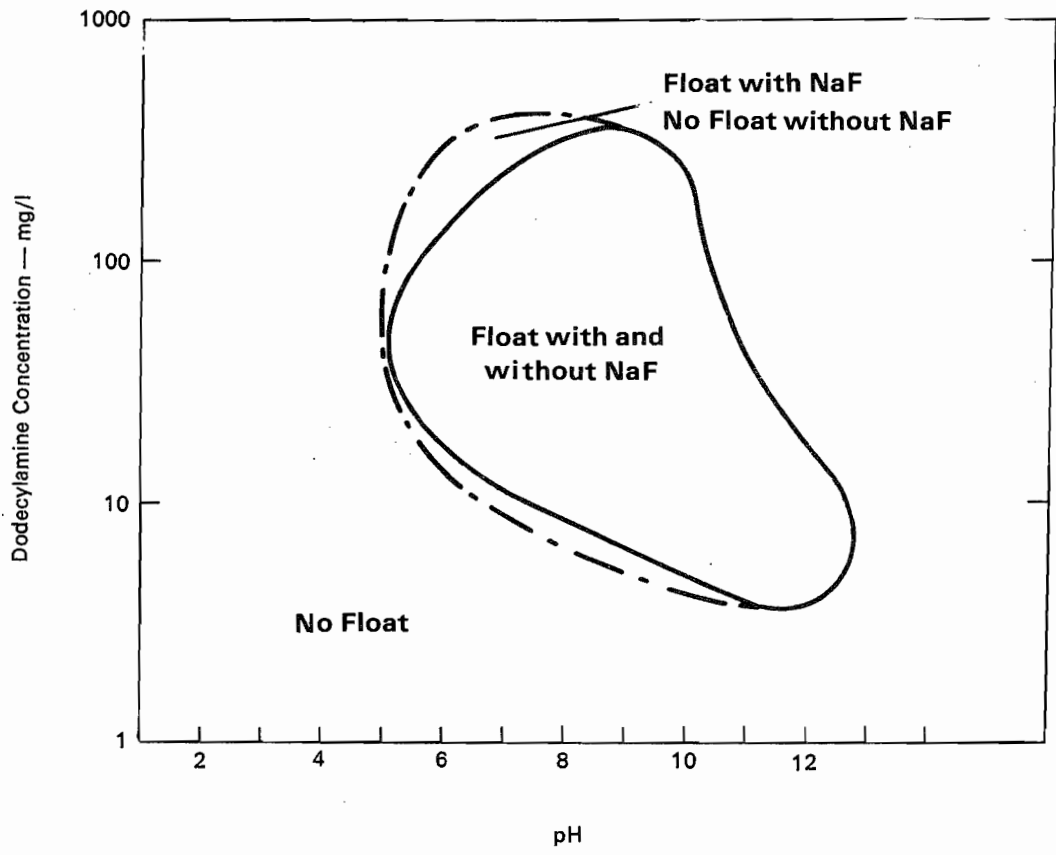
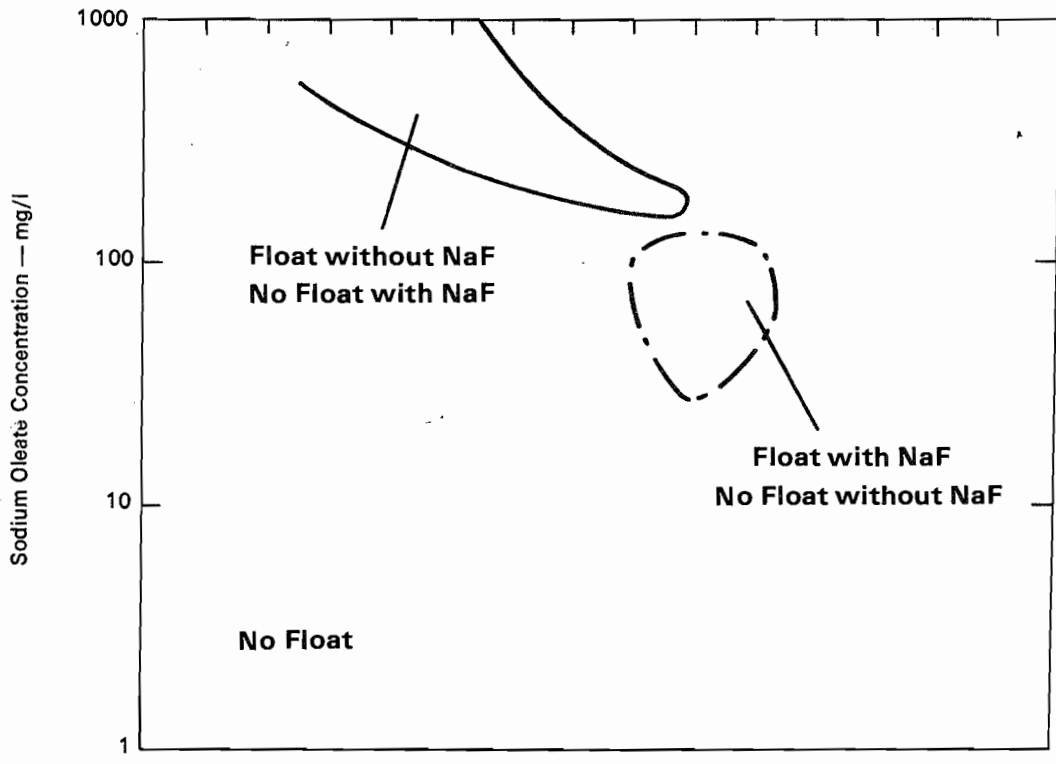


Fig 3.6.2 Olivine - Tephroite

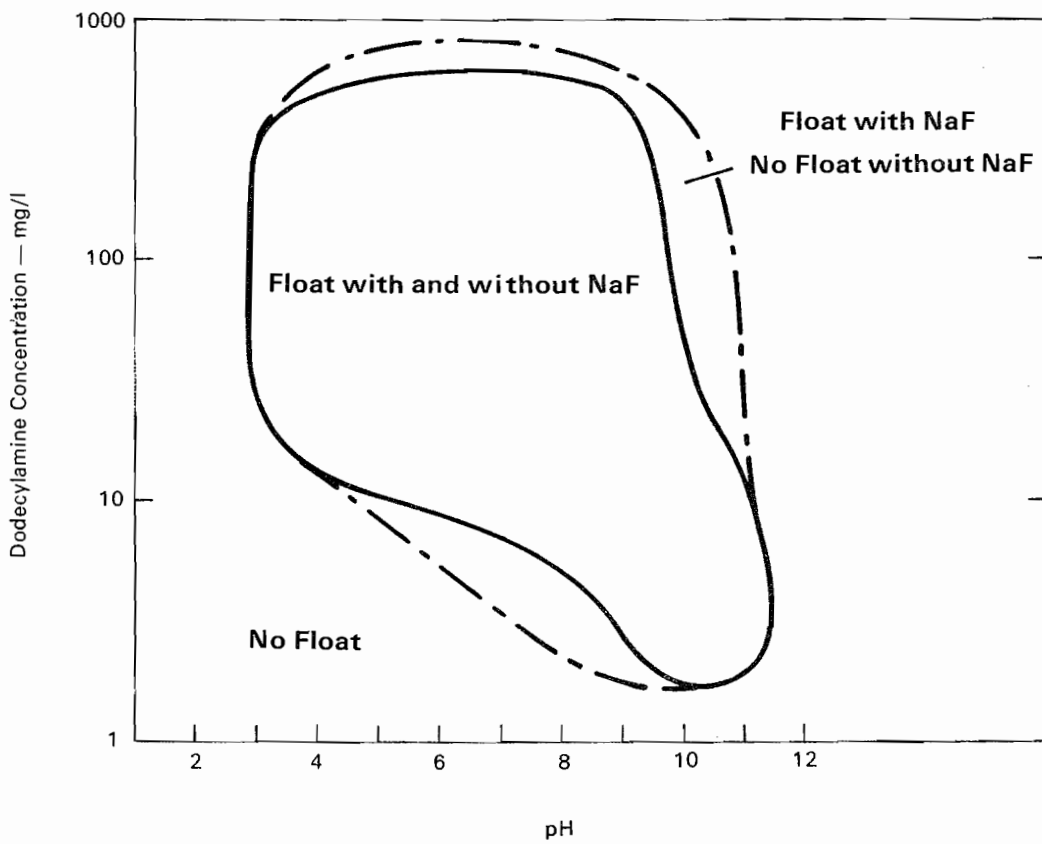
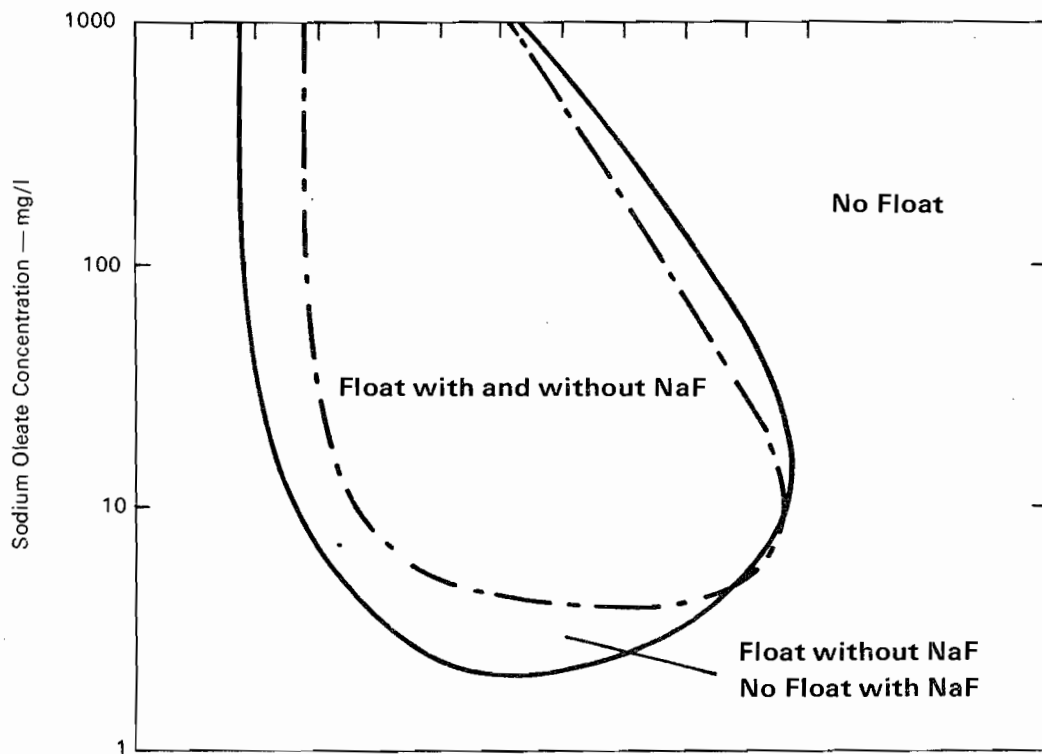


Fig 3.7 Topaz

COMPOSITION $\text{Al}_2[\text{SiO}_4](\text{OH},\text{F})_2$ aluminium fluosilicate.

PHYSICAL PROPERTIES

Hardness 8. Specific gravity 3.4 to 3.6.
White, yellow, light grey, light blue or pink orthorhombic crystals.

CHEMISTRY

This mineral is partially soluble in sulphuric acid and may give rise to aluminium ions in very acid flotation circuits.

FLOTATION CHARACTERISTICS

With the exception of chlorite and talc, topaz was the most readily floatable silicate tested with the anionic collector sodium oleate. It floated well over the range from pH 3.0 to 12.0 with little sensitivity to pH change between 4.0 and 11.0. The effect of fluoride on this flotation was the least marked of any of the orthosilicate group leaving an extensive area of flotation between pH 4.0 and 12.0 at a slightly higher reagent concentration than was necessary in the absence of fluoride.

The flotation area obtained with the amine collector is far more typical of previous orthosilicates showing sensitivity to pH change and an increase in flotation area on the addition of fluoride. Again, alkaline conditions favour the flotation of this mineral with the cationic collector. The flotation diagram appears as Fig 3.7.

FUNDAMENTAL FLOTATION STUDIES

The anionic sodium hexadecyl sulphate was found to be a poor collector for freshly ground topaz but improved with conditioning time⁶⁰. Activation with multivalent cations (Fe^{III} or Pb^{II}) improved recovery but it was found to be depressed by calcium which precipitated the collector.

Infra-red studies⁶¹ have indicated that oleate is adsorbed by reacting with cations in the

crystal lattice and not as the free acid or as micelles of the sodium salt, although Eigeles and Sakhorava⁶² suggest that it is adsorbed in a molecular form by displacing water molecules from the surface in a strongly acid medium. The latter author has investigated the effects of acid treatment on topaz, beryl and microcline that have been previously conditioned with oleate collector. He found that the topaz was readily floated after a mild acid treatment, beryl after vigorous treatment and microcline not at all. Topaz may be separated from microlite and columbite/tantalite concentrates^{63,64} by removing surface iron staining of the minerals with dilute sulphuric or hydrochloric acid before floating with an anionic collector at pH 9.5 (adjusted with sodium carbonate) and using a pine oil frother.

The separation of beryllium minerals from their associated gangue is the subject of a US Bureau of Mines report⁶⁵ in which are reported the effects of various modifiers on both cationic and anionic flotation of topaz in the Hallimond tube. For example, at 20 mg/l sodium oleate at pH 8.5, a concentration of 300 mg/l sodium silicate was required to reduce topaz recovery from 100 per cent down to 15 per cent. Ammonium carbonate, dextrin and tapioca starch had no depressant effect but 100 mg/l calcium lignin sulphonate reduced the recovery by one third. When the same modifiers were tested using C₁₂ - amine collector (at a concentration of 4 mg/l at pH 11.0) 25 mg/l of tapioca starch reduced the recovery to 60 per cent and 300 mg/l sodium silicate reduced it to 1 per cent. Again the dextrin and ammonium carbonate had no effect.

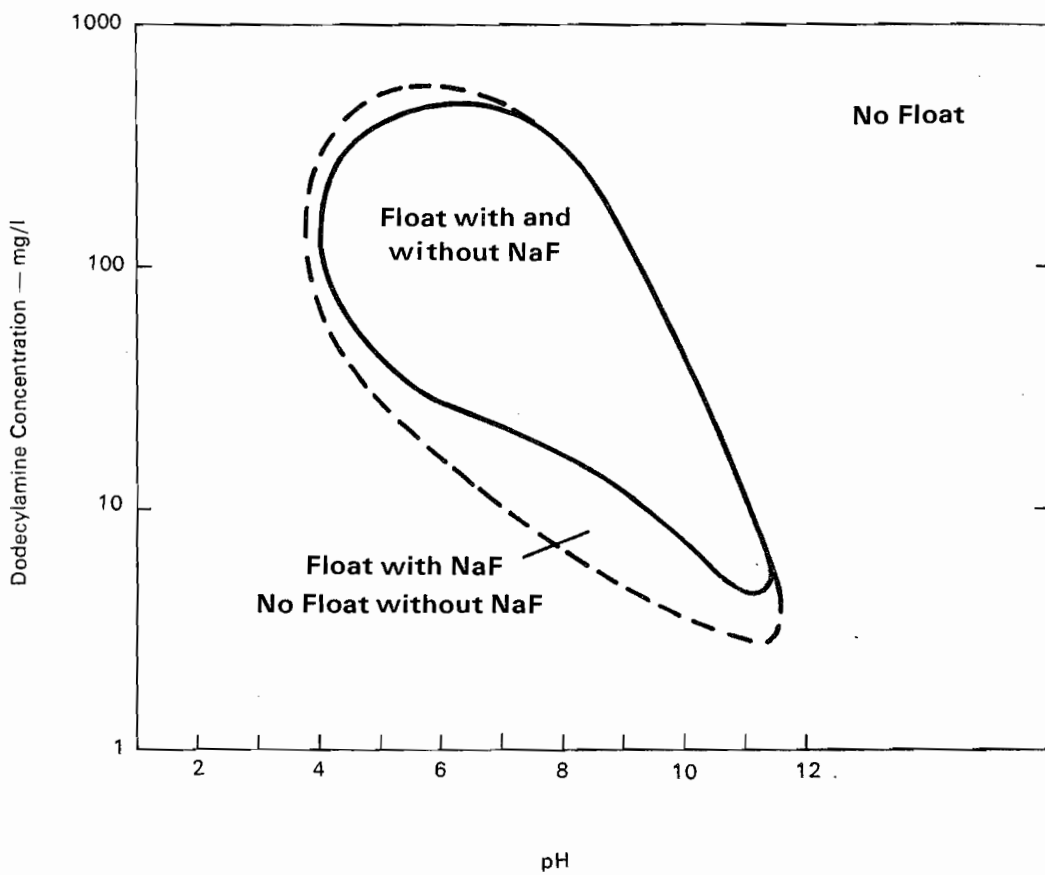
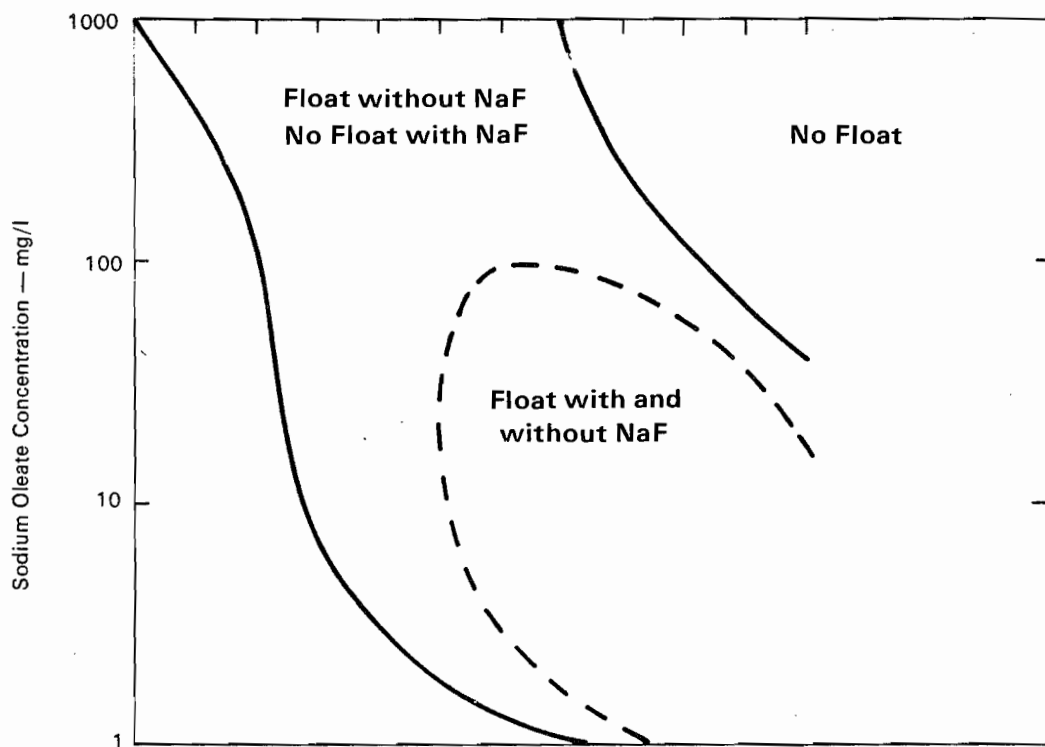


Fig 3.8 Tourmaline

COMPOSITION $XY_3Al_6(BO_3)_3[Si_6O_{18}](OH,F)_4$ – a complex borosilicate based on a six-membered silicate ring.

X = Na, Ca. Y = Mg, Fe, Mn, Li, Al.

Tourmalines can be divided into two compositional series, the first with end members dravite – $NaMg_3Al_6(BO_3)_3[Si_6O_{18}](OH,F)_4$, and schorl – $Na(Fe,Mn)_3Al_6(BO_3)_3[Si_6O_{18}](OH,F)_4$ and the second with end members schorl and elbaite – $Na(Li,Al)_3Al_6(BO_3)_3[Si_6O_{18}](OH,F)_4$. There is no series between elbaite and dravite.

PHYSICAL PROPERTIES

Hardness 7 to 7.5. Specific gravity 3 to 3.25. Colour: variable, schorl is normally black, dravite brown to black, elbaite dark red, blues and greens. Trigonal crystals. z.p.c. 6.2⁶⁶.

CHEMISTRY

Slightly attacked by HF

FLOTATION CHARACTERISTICS

Three species of tourmaline were investigated; the first was a sample of black schorl and the other two were members of the elbaite/schorl series. Of these one was the red-pink variety rubellite, which was low in iron and high in lithium content and the other blue variety containing approximately equimolar amounts of iron and lithium. Differences between flotation diagrams as determined on each mineral were so small that an average diagram Fig 3.8 is reproduced for the sodium oleate float and the schorl diagram is given for the flotation with dodecylamine collector.

With the exceptions of talc, chlorite, and topaz, the three tourmalines tested here gave larger flotation areas with the fatty acid collector than any other silicate investigated. Excellent flotation between pH 4.0 and pH 12.0 was observed with little sensitivity to changes except at high

reagent concentrations. Here the range of flotation shifted towards the acid side, floating now between pH 2.0 and 8.0. The only mineral to show similar characteristics that has been investigated at Warren Spring Laboratory is topaz. As with the other ortho- and ring-silicates the fluoride ion modifier had a depressant effect, although in this case not to the same marked extent in that flotation was restricted to pH values above 6.0.

Smaller areas of flotation were found with dodecylamine and, in common with the flotation areas of many other silicates with this cationic collector, these were found to be sensitive to pH change. Flotation was favoured under acidic conditions at the higher collector concentrations and under alkaline conditions at lower concentrations. The only significant difference in the flotation diagrams of the three tourmalines was noted here in that the lower edge of the schorl diagram was found to be slightly more sensitive to changes in pH than that of the other two tourmalines tested.

PRACTICAL FLOTATION SYSTEMS

Published work on the flotation properties of tourmalines may be classified according to the economic mineral from which it is desired to make a separation. For convenience only, these will be discussed in three sections which should be regarded as complementary rather than independent, as all information available on any one mineral should be considered when flotation problems are encountered.

Separation of cassiterite from tourmaline

Both sodium oleate and sodium alkyl sulphate have been tested⁶⁷ for cassiterite flotation from martite and tourmaline using silicate, fluoride, silicofluoride, sulphide and oxalate modifiers. With a very high iron concentration in the pulp no satisfactory separation was obtained with any collector-modifier combination. Tests using hydroxamic-acid-based collector IM50 produced a 6 to 7 per cent tin concentrate at 80 per cent recovery whilst depressing the iron minerals with a mixture of hydrochloric and oxalic acids. Further

details of this separation of cassiterite from tourmaline were published in the proceedings of the Leningrad mineral processing congress⁶⁸.

A comparison⁶⁹ made between the action of oxalic acid and of sodium silicofluoride on the flotation of tourmaline with oleic acid showed the former to be the more effective depressant. The same author⁷⁰ later describes an industrial development based on tourmaline depression with oxalic acid. When attempting to recover fine tin from the tailing of a gravity plant it was found to be possible⁷¹ to replace oleic acid with tall oil. A 70 per cent recovery with a grade of 2.2 per cent tin was obtained while depressing the tourmaline with silicofluoride rather than oxalic acid.

A comprehensive study of flotation modifiers has been made by Evans and his co-workers⁷² when employing sodium hexadecyl sulphate as a collector to separate cassiterite from tourmaline. The modifiers were placed into one of the following groups according to their effects:

- (a) No effect on tourmaline: magnesium sulphate, copper sulphate, lead acetate, thorium nitrate, sodium borate, gallic acid, a number of proprietary surface-active agents.
- (b) Activated tourmaline: gelatin, methyl cellulose, casein.
- (c) Depressed both tourmaline and cassiterite equally: gum arabic, tragacanth, mimosa, tannin, pectin, dextrin, agar, cobalt sulphate, sodium alginate, sodium silicate, carboxymethyl cellulose, sodium polyphosphate.
- (d) Depressed cassiterite but not tourmaline: potassium ferrocyanide, potassium ferricyanide.
- (e) Selective depressants for tourmaline: potash alum, sodium fluoride, sodium silicofluoride.

Each of the above modifiers was tested at concentrations of 5 and 50 mg/l when floating with a constant quantity of the collector at pH 3.5. The best results were obtained using the silicofluoride modifier at an elevated temperature (35°C).

The cationic collector ANP 14 (C_{14} - amine) was found to selectively float cassiterite from tourmaline and limonite⁷³ when employing a synthetic mixture of the three pure minerals. However further tests with this collector on the tailings from a gravity concentration plant for cassiterite had very limited success.

Other authors⁷⁴ have shown the flotation properties of tourmaline and cassiterite to be identical with oleic acid and disodium monoalkylsulphosuccinate collectors. The latter, however, was found to be advantageous due to both its lower cost and its higher activity resulting in lower consumption. With this collector, tannin-based regulators were found to be selective depressants for tourmaline over the pH range from 2.0 to 10.0 and flotation of cassiterite was found to be successful with these reagents at an optimum pH value between 5.0 and 6.0.

Isoheptyl phosphonic acid and 'Aerosol 22' (American Cyanamid Co.) have been investigated as differential collectors for cassiterite from tourmaline on Bolivian tin ores. When used alone neither collector was sufficiently selective but both silicofluoride and citric acid modifiers had a pronounced depressant effect on the tourmaline.

Separation of columbite-tantalite from tourmaline

The separation of tantalite from a gravity concentrate⁷⁶ containing tourmaline, feldspar, quartz and garnet has been successfully carried out using anionic collectors at pH 6.0 to 7.5 to produce a mixed concentrate of tourmaline, tantalite and garnet. A reverse flotation of this product under acid conditions, using sodium silicate modifier, enabled the tourmaline and garnet to be removed leaving the tantalite as a tailings product.

Sodium oleate, alkyl phosphate, and isooctyl phosphate, as well as ANP 14 have been investigated⁷⁷ as possible collectors for columbite-tantalite, tourmaline and garnet, from quartz and albite. With the anionic collectors, low concentrations were necessary to achieve selectivity. Pretreatment of the minerals, with sulphuric and hydrofluoric acids activated the heavy minerals whilst depressing muscovite, quartz and albite.

In investigating the fundamental properties of tantalite, tourmaline and garnet with respect to the adsorption of C_{12} and C_{14} amines, Naifanov⁷⁸ showed that two modes of attachment could be defined. The first was where amine ions were adsorbed on the mineral surface and the second where amine molecules were adsorbed in the double layer. On the basis of these observations a separation of tantalite was made by first carrying out a bulk separation of the three minerals with the C_{14} amine, and following this by a thorough water wash and then selectively floating the tantalite with an anionic collector.

Naifanov and Polkin⁷⁹ claim that the same three minerals are floated with oleic acid by virtue of multivalent metal soaps being formed on the mineral surfaces. A preliminary

treatment of these minerals with sulphuric acid at 200 g/t dissolves iron and manganese ions from the lattice and improves the floatability of both tantalite and garnet. Although this work may appear to have little immediate practical application, it does emphasize the effects that surface treatment can have on the anionic flotation properties of many of the silicate minerals particularly those in the ortho- and ring-silicate group. This is demonstrated in a separate publication⁸⁰ where the adsorption of iron and calcium ions and their effects are determined. Here a three-to-five-fold increase in collector adsorption was obtained for tridecylic and oleic acids on tantalite-columbite, tourmaline and garnet after pretreating with iron or calcium salts. The sequence of addition of such salts was shown to be of vital importance as an excess of ions present in the pulp when the collector is added will lead to insoluble soap precipitation causing poor flotation or even complete depression.

Separation of other minerals from tourmaline

Although the use of oleic acid as a collector for tourmaline was recommended⁸¹ as long ago as 1935, no details are given in an abstract of the Russian paper. It is, however, used in the separation methods for beryl, tourmaline and garnet described by Chipanin⁸². Three methods for their concentration were developed. The first was a direct flotation of tourmaline and garnet with no activator under alkaline conditions. A pretreatment of the pulp for one hour at 80 to 90°C with sodium carbonate before floating the tourmaline and garnet with oleic acid at room temperature was the basis of the second method. In the third a cationic collector was used at pH 2.0 following pretreatment of the pulp with the anionic collector. The selectivity of this method was inferior to the other two in that it extracted tourmaline together with mica whilst leaving the beryl and garnet in the tailings.

The effect of treating microcline, beryl, wolframite, tourmaline, topaz and fluorite with sulphuric acid before floating with sodium alkyl sulphate or fatty acid has also been determined⁸³. Enhanced flotation of topaz and beryl is reported but, again, no details are given in the available abstract of the effects on tourmaline.

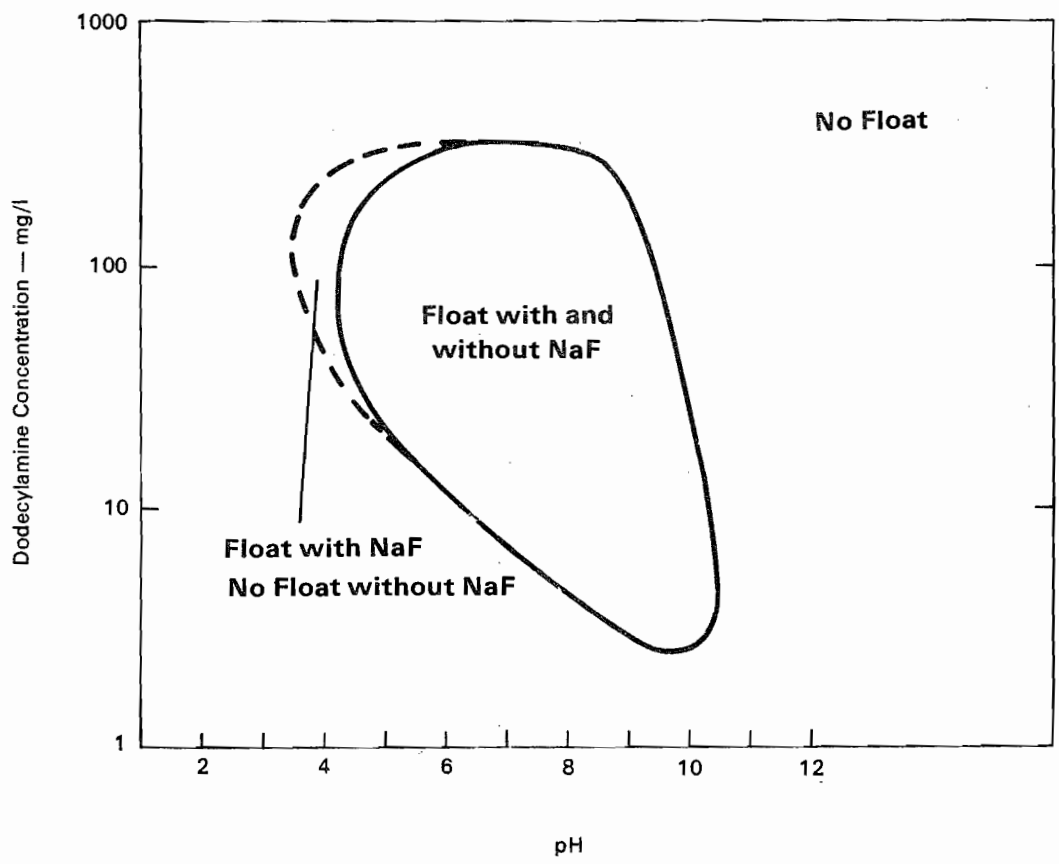
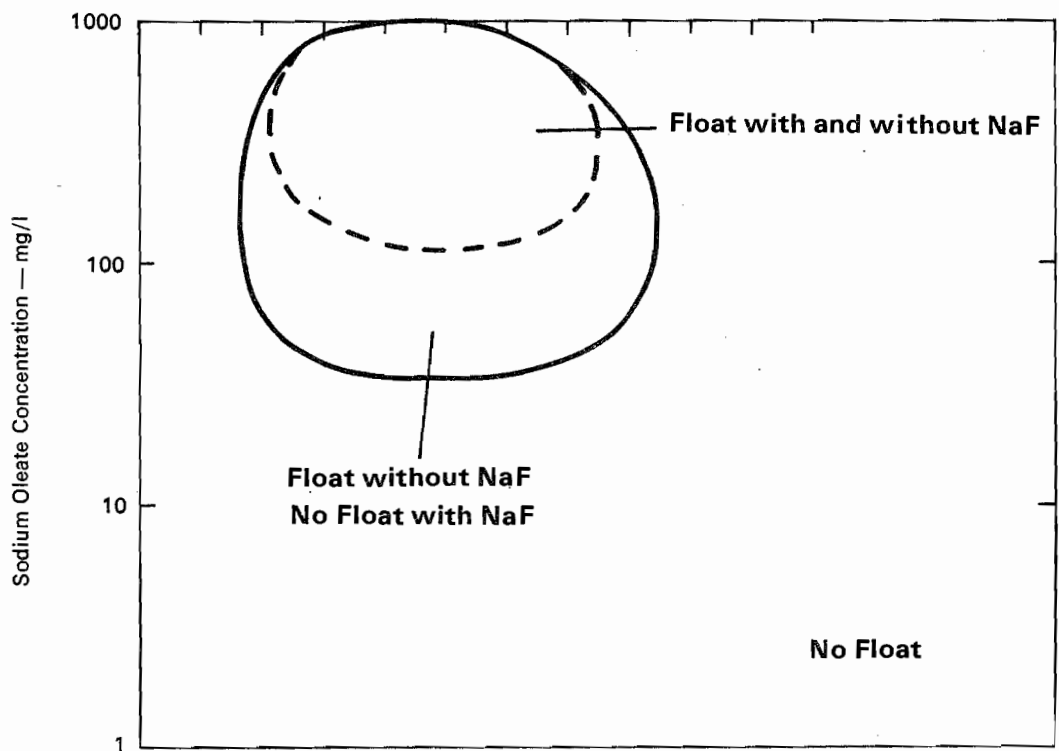


Fig 3.9 Zircon

COMPOSITION $Zr[SiO_4]$ · zirconium orthosilicate

PHYSICAL PROPERTIES

Hardness 7.5. Specific gravity 4.7.
Pale yellow, green or red brown tetragonal crystals. z.p.c. 5 to 6.05⁸⁴⁻⁸⁸ (2.5 in one case)⁸⁹

CHEMISTRY

Acid insoluble, normally associated with trace amounts of hafnium. Zirconium in the lattice may be replaced by iron and/or calcium.

FLOTATION CHARACTERISTICS

This mineral floats moderately well with both anionic and cationic collectors. Anionic flotation shows very little sensitivity to pH change between 3.0 and 9.5. Cationic flotation of zircon shows some sensitivity to pH change with alkaline conditions being favoured. Although sodium fluoride depresses flotation with oleic acid, the extent of this is very much less than that found with other orthosilicates. Again the effect of fluoride on the amine flotation is less marked than with other members of this class in showing only very slight activation at high collector concentrations in acid media. The flotation diagram appears as Fig 3.9.

FUNDAMENTAL FLOTATION STUDIES

A very thorough investigation of the surface properties and floatability of zircon has been made by Choi and Whang⁸⁴ who determined the electrophoretic mobility, the adsorption and the flotation recovery of an anionic and a cationic collector over a wide range of pH values. The collector adsorption density as a function of pH showed that the adsorption of sodium dodecyl sulphate at pH 2.5 and the adsorption of dodecylamine chloride at pH 10.0 was ten times that occurring at the cross-over point of pH 5.8. These authors also determined the flotation recovery of zircon with C_{18} -fatty acids and found that the range of flotation could be extended from pH 4.0 to 9.0 with oleic acid and from 4.0 to 7.5 with linoleic acid. Other authors⁹⁰ have shown that the hydroxyl ion acts as a depressant for zircon and Preiningerova⁸⁹ found the optimum flotation of this mineral with sodium oleate to occur at pH 8.0.

It has also been shown⁹¹ that this mineral is activated by sulphate, phosphate, and oxalate anions in the acidic pH range with amine collectors, and by ferric iron when floating with sodium oleate⁸² in the alkaline range.

PRACTICAL FLOTATION SYSTEMS

At Byron Bay in Australia, Zircon Rutile Ltd use a froth flotation process to separate zircon from the non-magnetic product in a beach-sand separation. This process is based upon that of Dunkin and Blaskett⁹³ and involves a preliminary treatment of the mineral mixture at 30 per cent solids for 20 minutes at 95°C with a mixture of equal quantities of oleic and stearic acids at a controlled alkaline pH. This is followed by three water washes and an acid wash at room temperature with the final flotation being carried out at pH 1.9 with a eucalyptus oil frother. With this method zircon recoveries of over 95 per cent, with grades in the same order, have been obtained. Subramanya⁹⁴ has obtained 80 per cent recoveries of zircon at 95 per cent grade by using the above method of pre-treatment but with a final flotation at pH 11.5 to avoid the use of a highly acid circuit.

The use of sodium silicate as a modifier for zircon flotation is reported by many workers^{92,96,97}. When used at low concentrations (eg 0.1 kg/t) with anionic collectors it is a useful gangue depressant, and also may have a mild activating effect on the zircon. At higher concentrations (1.0 kg/t) it depresses the flotation of zircon as well⁹⁵.

One system⁹² uses pretreatment with sodium sulphide followed by washing and then activation with sodium silicate. Simple treatment with sulphide but omitting the washing stage caused complete depression.

Sodium silicofluoride has also been used⁹⁸ as an effective modifier at acid pH values when employing a mixed (anionic plus cationic) collector. Using this system zircon has been successfully floated from pyrochlore at the pilot-plant scale. The separation of rutile-zircon concentrates is the subject of a Russian patent⁹⁹ which uses oleic acid together with a neutral oil as the promoter, with sodium silicofluoride as a depressant for the zircon. These two systems would appear to be contradictory but it will be appreciated that in the first example the pyrochlore is more sensitive to the modifier than the zircon, whereas in the patent the zircon is the more sensitive mineral.

- 1 Choi, H.S. and Oh, J.H.
Surface properties and floatability of kyanite and andalusite.
J. Inst. Min Metall. Japan, 1965, **81** (927), 614-620
- 2 Choi, H.S. and Oh, J.H.
Effect of the weighted average charge of surface metallic atoms on the isoelectric point of kyanite, andalusite and sillimanite.
Ibid; 1966, **82** (941), 755-762
- 3 Smolik, T.J. Harman and Fuerstenau, D.W.
Surface characteristics and flotation behaviour of aluminosilicates.
Trans. Soc. Min Engrs(AIME), 1966, **235**, 367-375
- 4 Gaitsintova K.V. et al.
Sorption of ^{14}C -labelled sodium tridecylate by boron silicates.
Dokl. Akad. Nauk. Tadzh. SSR, 1964, **7** (11), 18-21. CA,63, 12712e
- 5 Glembotskii, V.A. et al.
Sorption of sodium oleate on the surface of borosilicates.
Ibid, 1965, **8** (3), 16-19. CA,63, 7672h
- 6 Rakitina, E.V. and Solozhenkin, R.M.
Infra-red spectroscopic study of the sodium oleate reaction with some borosilicates and garnet.
Ibid, 1967, **10** (4), 32-34. CA,67, 68931t
- 7 Fuerstenau, M.C. et al
Metal ion hydrolysis and surface change in beryl flotation.
Trans. Inst. Min. Metall., 1964, **74**, 381-391.
- 8 Moir, D.N. and Stevens, J.R.
Studies relating to the flotation of beryl.
Trans. Inst. Min. Metall., 1964, **73**, 373-391.
- 9 Fuerstenau, M.C. et al.
The role of iron in the flotation of some silicates.
Trans. Soc. Min. Engrs (AIME), 1966, **235** (4), 321-328.
- 10 Avotins, P.V.
Use of a modified Hallimond cell in investigation of flotation properties of beryl.
Proc. S. D. Acad Sci., 1963, **XLII**, 84.

- 11 Beaudoin, P.
Flotation of silicates. Flotation of beryl.
Sci. Terre, 1967, Mem. No 8.
- 12 Plaksin, I.N. et al
Study of the influence of alkaline modifiers on beryl flotation by means of electrokinetic potential measurement.
Izv. Vysshikh. Uchebn. Zavedenii, Gorn. Zh., 1962, 5 (7), 132-136. CA,58, 6472h
- 13 Deju, R.A. and Bhappu, R.B.
A chemical interpretation of surface phenomena in silicate minerals.
Trans. Soc. Min. Engrs (AIME), 1966, 235 (4), 329-332.
- 14 Troitsky, V.V.
Effect of iron on the electrokinetic potential of beryllium and its floatability.
Tsvet. Met., 1960, 33 (8), 73-74.
- 15 Weir, L.J.
Flotation of beryl from pegmatite.
Min. Rev., (Dept. Mines S. Australia), 1967, (123), 22-32.
- 16 Kennedy, J.S. and O'Meara, R.G.
Flotation of beryllium ores.
USBM Rept Invest., 1948, 4166.
- 17 Srinivasan, N.R. and Aswath, H.S.
The beneficiation of low-grade beryl ores by flotation.
J. Indian Inst. Sci., 1956, 135-142.
- 18 Kennedy, J.S. and O'Meara, R.G.
Beneficiation of beryllium ores.
US Pat. 2,414,815 /1947.
- 19 Lamb, F.D. and Banning, L.
Beneficiation of beryllium ores.
US Pat. 2,385,819/1945.
- 20 Gibbs, H.L. and Snedden, H.D.
Beneficiation of beryllium ores.
US Pat. 2,395,475 /1946.
- 21 Snedden, H.D. and Gibbs, H.L.
Beneficiation of Western beryl ores.
USBM Rept. Invest, 1947, 4071.

- 22 Weir, L.J. and Moskovits, E.E.
Flotation of lithium and beryllium pegatites.
Aust. Inst. Min. Metall., 1963, (206), 143-152.
- 23 Browning, J.S. and Clemmons, B.H.
Separation of spodumene and beryl by flotation.
US Pat. 3,028,008/1962.
- 24 Browning, J.S., Clemmons, B.H. and McVay, T.L.
Beneficiating North Carolina spodumene-beryl ores.
USBM Rept. Invest., 1961, 5750.
- 25 Hegarty, A.
Tests on spodumene-beryl ores in America.
Mining Mag., 1963, 108 (4), 202-207.
- 26 Soule, J.H.
Exploration of Harding tantalum-lithium deposits, Taos County, N. Mexico.
USBM Rept. Invest., 1946, 3986.
- 27 Karve, V.M. et al.
Improved process for flotation of beryl from Doddakadanur (Mysore State).
Trans. Indian Inst. Metals, 1968, 21(4), 57-59.
- 28 Eigeles, M.A. and Leviush, I.T.
Floatability of beryl.
Proc. UN Intern. Conf. Peaceful Uses At. Energy, 2nd Geneva 1958, 3, 162-166.
- 29 Johnston, T.L.
Concentration of beryllium ores.
US Pat. 3,300,147/1967.
- 30 Browning, J.S.
Flotation of spodumene-beryl ores.
Trans. Soc. Min. Engrs (AIME), 1961, 220, 420-423.
- 31 Runke, S.M. and Riley, J.M.
Progress report on pegmatite investigations in South Dakota for fiscal years 1954-56.
USBM Rept. Invest., 1957, 5339.
- 32 Shelton, J.E.
Flotation of beryl from north-eastern pegmatites: A progress report.
USBM Rept. Invest., 1961, 5767.
- 33 Anon
Flotation
Deco Trefoil, 1958, 22 (4), 15-16.

- 34 Runke, S.M.
Petroleum sulphonate flotation of beryl.
USBM Rept. Invest., 1964, 6466.
- 35 Browning, J.S., McVay T.L. and Bennett, P.E.
Continuous flotation of beryl from spodumene mill tailing, Foote Mineral Company,
Kings Mountain, N.C.
USBM Rept. Invest., 1964, 6466.
- 36 Moir, D.N. et al.
The concentration of beryl from pegmatite ores.
In Proceedings of 6th International Mineral Processing Congress, Cannes.
London: Pergamon Press, 1965, pp 651-67.
- 37 Cases, J.
Determination of zero point of charge of cyanite in aqueous medium.
Compt. Rend., 1965, 261 (1), 183-186.
- 38 *US Pat.* 2,289,741/1942.
- 39 *US Pat.* 2,305,502/1942.
- 40 *US Pat.* 2,326,807/1943.
- 41 *US Pat.* 2,297,689/1942.
- 42 McVay. T.L. and Browning, J.S.
Flotation of kyanite-quartzite rock, Graves Mountain, Lincoln County, Georgia.
USBM Rept. Invest., 1963, 6268.
- 43 Muskatt, G.H. et al.
Flotation of kyanite-quartz mica schist.
Aust. CSIRO Sch. Mines West Australia, Kalgoorlie Ore Dressing Invest., 1968.
Rep. No 747.
- 44 Wyman, R.A.
Flotation of Canadian kyanite.
Min. Engr 10 (1), 111-12, *Trans AIME*, 211 Tech. Pub. No 4510 (1958).
- 45 Thom, C. and Gisler, H.J.
Flotation of non-metallics.
Trans. Can. Inst. Min. Metall. 57 in *Can. Min. metall. Bull.*, 1954, (504), 240-250.
- 46 Browning. J.S.
Flotation of south-eastern kyanite ores.
Trans. Soc. Min. Engrs. (AIME), 1969, 244 (3), 283-287.

- 47 Browning, J.S. and Bennett, P.E.
Beneficiation of Georgia kyanite ore.
USBM Rep. Invest., 1970, 7376.
- 48 *USSR Pat.* 202,804/1966.
- 49 Alekseev, V.S. et al.
Preparation of high-alumina kyanite concentrates from 'Novaya Shuvrurta' deposit ores.
Tsvet. Metall, 1968, 41 (3), 44-46.
- 50 Alekseev, V.S.
Application of hydrocarbon emulsions in the flotation of finely intergrown calcite/apatite and kyanite aggregates.
Freiburg Forschungsh., 1967, A 415, 171-190.
- 51 Alekseev, V.S.
Enrichment of kyanite ore from the Chervurt deposit.
Obogashch. Apatitovykh, Vermikulitovykh, Perovskovykh Rud, Akad. Nauk S.S.S.R. Kol'sk Filial. 1967, 69-81 CA,69, 4030g
- 52 Deju, R.A. and Bhappu, R.B.
A chemical interpretation of surface phenomena in silicate minerals.
Trans. Soc. Min. Engrs (AIME), 1966, 235 (4), 329-332.
- 53 Read, A.D., Manser, R.M., and Robinson, R.
To be published.
- 54 Komlev, A.M., and Polkin, S.I.
The floatability of ludwigite and olivine with different collectors.
Izv. Vysshikh Uchebn. Zavedenii, Isvetn. Met. 1964, 7 (3), 32-36.
- 55 Komlev, A.M. and Korobkov, B.S.
Reaction of sodium oleate with olivine and ludwigite.
Izv. Sibirsk. Otd. Akad. Nauk. S.S.S.R., Ser Khim Nauk, 1964, (3), 44-47.
CA,63, 2419c
- 56 Polkin, S.I. and Komlov, A.M.
Effect of water glass on flotation of ludwigite and olivine.
Obogashch Rud., 1964, 9(5), 12-15. CA,62, 8716f
- 57 Pavlova, K.S. and Sorokina, T.P.
Flotation of apatite from residues of magnetic separation of Ena-Kovdor ore.
Obogashch Rud, 1965, 10(4), 11-14, CA,64, 12235e
- 58 Efremov, A.G. et al.
Flotation of apatite from ore of the upper horizon of the Ena-Kovdor iron deposit.
Obogashch, Kompleksn Rud, Akad. Nauk SSSR, Kolsk Filial, Gornomet Inst., 1964, 35-43. CA,62, 1355e

- 59 Flotation of chromite ores containing serpentine and olivine.
German Pat. 1,021,302/1957.
- 60 Evans, L.F.
The flotation of topaz using sodium hexadecyl sulphate as collector.
Australian J. App. Sci., 1953, 4, 163-173.
- 61 Vainsheuker, I.A. and Krivekva, E.D.
Interaction of topaz with sodium oleate and oleic acid.
Obogashch Rud, 1966, 11 (6), 53-56. CA,67, 85300d
- 62 Eigeles, M.A. and Sakharova, E.P.
Flotation properties of some silicates in an acid medium and after sulphuric acid treatment.
Tr. Vses. Nauch-Issled. Inst. Miner. Syr'ya, 1967, (18), 82-101. CA,70, 13575m
- 63 Chipanin, I.V. and Kozhukhovskaya, A.N.
Flotation separation of microlite and columbite-tantalite from topaz.
Nauch. Tr., Irkutsk. Gos. Nauch-Issled. Inst. Redk. Metal, 1965, (13) 251-256.
CA,66, 21195v
- 64 Chipanin, I.V. et al.
Finishing of coarse microlite-containing concentrates.
Ibid. 1967, (16), 190-205. CA,70, 70350h
- 65 Fergus, A.J. Sullivan, G.V. and Workentine, G.F.
Flotation characteristics of some beryllium minerals and associated gangue minerals.
USBM Rep. Invest., 1968, 7188.
- 66 Naifonov, T.B. et al.
The condition of the electrical double layer of tantalite and some accompanying minerals during flotation.
Izv. Vysshikh Uchebn. Zavedenii, Tsvet Met., 1963, 6 (3), 40-46. CA,60, 1363e
- 67 Strel'tsyn, V.G.
Flotation of cassiterite in the presence of iron-containing minerals.
Obogashch Rud., 1968, 13 (1), 3-6. CA,71, 15223g
- 68 Gorlovsky, S.I. et al.
Improvement in concentration technology of some rare metal ores based on the action of hydroxamic acids.
Paper D3, VIII International Mineral Processing Congress, Leningrad 1968.
- 69 Strel'tsyn, V.G. and Vishnerski, E.N.
Industrial tests on the flotation of cassiterite from pulps.
Tr. Nauch-Tekh. Sess Inst Mekhanobr 1965, 1967, 1, 658-665. CA,70, 5952s

- 70 Strel'tsyn, V.G.
Development of the selective flotation technique for cassiterite.
Tr. Nauch. Tekh. Konf. Inst. Mekh. Posvyashch 50-Letiya Velikoi Okt. Sots Revolyutsii,
1968, 1, 59-69. CA,72, 817A62
- 71 Sukhovdskaya, S.D. et al.
The flotation of cassiterite from sludges of gravity enrichment.
Obogashch Rud., 1965, 10 (3), 6-8. CA,64, 342d
- 72 Evans, L.F. et al.
The flotation of cassiterite.
Australian J. Appl. Sci. 1962, 13 (2), 113-146.
- 73 Eigeles, M.A. and Ershov, V.I.
Flotation of cassiterite from a cassiterite-tourmaline-limonite complex.
Obogashch Rud., 1967, 12 (3), 7-8. CA,68, 71367q
- 74 Polkin, S.I. et al.
Selective flotation of cassiterite and tourmaline using the disodium salt of monoalkylsulphosuccinic acid and high molecular weight tanning agents.
Izv. vyssh ucheb Zaved Tsvet Met, 1970, 13, 10-13.
- 75 Collins, D.N., Hollick, C.T. and Joy, A.S.
The recovery of fine tin by flotation. Recent developments.
Paper to 2nd Technical Conference on Tin, Bangkok, 1969.
- 76 Naifonov, T.B. and Polkin, S.I.
Flotation finishing of tantalite from the fine fraction of bulk gravity concentrates.
Obogashch Polez Iskop Kol'sk Poluostrova Akad Nauk SSSR Kol'sk Filial, 1966, 46-55.
CA,67, 46100u
- 77 Gladkikh, Yu.F. and Polkin, S.I.
Columbite-tantalite flotation.
Tr. Irkutskogo Politekhy Inst., 1963, (20), 44-60. CA,61, 9203e
- 78 Naifonov, T.B.
Reaction of cationic collectors with tantalite and some associated minerals.
Obogashch Polez Iskop Kol'sk Poluostrova Akad Nauk SSSR, Kol'sk Filial, 1966, 41-45.
CA,67, 46099a
- 79 Naifonov, T.B. and Polkin, S.I.
Reaction of oleic acid with tantalite and with some concurrent minerals.
Izv Vyssh Uchebn Zavedeniü, Tsvet Met, 1965, 8 (3) 22-30. CA,64, 342c
- 80 Gladkikh, Yu. F. and Polkin, S.I.
Effect of salts of multivalent metals on floatability of tantalite-columbite, tourmaline and garnet.
Ibid., 1963, 6 (5), 33-37. CA,60,3760g

- 81 Bayula, A.G.
Concentration of tourmaline from the tailings of Kluchevskii ores
Novosti Tekh., Ser. Gorn. Prom., 1935, (22), 11-12. CA,30, 7917
- 82 Chipanin, I.V.
Methods for the flotation separation of beryl, tourmaline, and garnet.
Nauch. Tr., Irkutsk. Gos. Nauch-Issled. Inst. Redk., Tsvet. Met., 1967, (16), 186-190.
CA,70, 21961z
- 83 Eigeles, M.A. and Sakharova, E.P.
Flotation properties of some silicates in an acid medium and after sulphuric acid treatment.
Tr. Vses Nauch-Issled. Inst. Míner. Syr'ya, 1967, (18), 82-101 CA,70, 12575m
- 84 Choi, H.S. and Whang, K.U.
Surface properties and floatability of zircon.
Can. Min. Metall. Bull., 1963, 56, 466-468.
- 85 Smith, G.W. and Salman, T.
Zero point of charge of hematite and zirconia.
Can. Met. Q. 1966, 5, 93-107.
- 86 Cases, J.M.
La détermination du point du charge nulle des nesosilicates en milieu aqueau.
J. Chim. Phys., 1967, 64, 1101-1107.
- 87 Ahmed, S.M. and Maksimov, D.
Studies of the double layer at the oxide/solution interface.
Dept. of Mines, Ottawa, 1968, Report R196. 104 pp.
- 88 Salatic, D.V.
Floatability of monazite and zircon related to electrochemical charges on their surfaces.
Trans. Inst. Min. Metall., 1967, 76, C231-237.
- 89 Preiningerova, B.
Surface properties of zircon.
Rudy, 1965, 13, 409-411. CA,65, 67h
- 90 Dixit, S.G. and Biswas, A.K.
pH dependance of the flotation and adsorption properties of some beach-sand minerals.
Trans. Soc. Min. Engrs (AIME), 1969, 244, 173-178.
- 91 Nakatsuka K. et al.
On the activation of multivalent ions in the amine flotation of oxide minerals.
J. Min. Metall. Inst. Japan, 1968, 84, 27-30.

- 92 Ilie, P.
Effect of modifying agents on the flotation of some rare metal minerals by sodium oleate.
Rev. Roumaine Sci. Tech. Ser. Met., 1966, 11 (1) 5-19. CA,65, 8416e
- 93 Dunkin, H.H. and Blaskett, K.S.
Ore dressing investigations: Investigation No 303.
CSIRO and University of Melbourne Ore Dressing Laboratory, 1949.
- 94 Subramanya, G.V.
Selective flotation of zircon from beach sands.
J. Mines Metals Fuels, 1960, 8, 47-48.
- 95 Lyushnya, L.M. et al.
Selective flotation of pyrochlore from rough pyrochlore-zircon concentrates.
*Moscow. Izd. Nauka, 1967 Sovrem. Sostoyanie, Zadachi Selek Flotatii Rud*161-165.
CA,69, 108832m
- 96 Akopova, K.S. and Romanovskaya, N.E.
Flotation separation of rutile and zircon.
Tr. Vses. Nauchn-Issled Inst Mineral Syr'ya, 1961, 6, 167-172. CA,57, 3079b
- 97 Khonina, O.I. and Eigeles, M.A.
Effect of soda and sodium silicate on the flotation of zircon by oleic acid.
Ibid, p 147-157. CA,57, 3079f
- 98 Eigeles, M.A. and Kuznetsov, V.P.
Selective flotation of a pyrochlore-sphene-zircon mineral complex.
Ibid, 1967, 18 126-139.
- 99 Separation of rutile-zirconium concentrates.
USSR Pat. 107,421/1967.

A. FLOTATION USING FATTY ACIDS

- 1 Fergus, A.J., Sullivan, G.V. and Workentine, G.F.
Flotation characteristics of some beryllium minerals and associated gangue minerals.
USBM Rep. Invest., 1968, 7188.
- 2 Peck, A.S. and Wadsworth, M.E.
An infra-red study of the activation and flotation of beryl with hydrofluoric and oleic acid.
Trans. Soc. Min. Engrs. (AIME), 1967, 238 (3), 264-268.
- 3 Fuerstenau, M.C. et al.
The role of iron in the flotation of some silicates.
Trans. Soc. Min. Engrs. (AIME), 1966, 235 (4), 321-328.
- 4 Viswanathan, K.V. et al.
The role of inorganic ions in the flotation of beryl.
Trans. Soc. Min. Engrs. (AIME), 1965, 232 (3), 282-286.
- 5 Nutt, C.W. and Bromley, K.
Conditions for the flotation of beryl – Part 1. Fatty acids.
Trans. Inst. Min. Metall., 1963, 72 (12), 793-806.
- 6 Khazhinskaya, G.N. and Maksimov, D.V.
Influence of some factors on the reaction of beryl with flotation agents.
Materialy 2-oi [Vtoroi] Leningr. Kong. po Primeneniyu Radiokt. Izotopov v Ugol'n Gornorudn. Prom., Leningrad-Moscow, 1961, (1), 60-73. CA,61, 5240d
- 7 Bogdanov, O.S. et al
The action of sodium oleate and modifiers during flotation of beryl, spodumene and feldspar.
Trud. vses. Nauch-Issled. Proekt. Inst. Mekh. Obrab. Polez. Iskop., 1961, (128), 26-36.
CA,57, 4393b
- 8 Eigeles, M.A. and Fuki, I.V.
Effect of sodium sulphide on the flotation of some oxides and silicates by a fatty acid collector.
Tr. vses. Nauch-Issled. Inst. Miner. Syr'ya, 1967, (18), 62-82. CA,70, 13,570f
- 9 Dolzhenkova, A.N.
Effect of treatment of beryl and spodumene with hydrofluoric and sulphuric acid on their surface activity.
Trud. vses. Nauch-Issled Proekt. Inst. Mekh. Obrab. Polez. Iskop., 1964, (134), 121-132
CA,64, 7736d

- 10 Yanis, N.A.
Distribution of amine during the separation of binary mixtures of minerals.
Tr. Nauch-Telsh. Sess. Inst. Mekh, 5th 1965, 1967, 1, 551-573. CA,69, 98,551e
- 11 Yanis, N.A.
Mechanism of the action of modifiers in the separation of spodumene and beryl.
Tr. vses. Nauchn-Issled. i Prok. Inst. Mekh. Obrab. Polez. Iskop. 1965, (135), 127-138. CA,64, 9298h
- 12 Yanis, N.A.
Effect of modifying agents on flotation of silicate minerals.
Tr. IV-oi [Chelvertoi] Nauchn-Tekjn. Sessii. Inst. Mekh. Obrab. Polez. Iskop. Leningrad, 1958, 254-273. CA,59, 4823e
- 13 Beaudoin, P.
Flotation of silicates. Flotation of beryl.
Sci. Terre, 1967, Mem. No 8.
- 14 Leviush, I.T. and Eigeles, M.A.
Flotation of beryl.
Tr. vses. Nauch-Issled. Inst. Mineral'n Syr'ya. 1961, (6), 106-122. CA,57, 144771f
- 15 Razumov, K.A. and Wei-Chung-Hsing.
Effect of sulphuric acid on flotation of beryl with sodium oleate.
Izv. Vysshikh. Uchebn. Zavedenii. Gorn. Zh., 1962, 5 (6), 178-181. CA,57, 16,218b
- 16 Plaksin, I.N. et al.
Study of the influence of alkaline modifiers on beryl flotation by means of electrokinetic potential measurement.
Isv. Vysshikh. Uchebn. Zavedenii, Gorn. Zh., 1962, 5 (7), 132-136. CA,58, 6472h
- 17 Troitsky, V.V.
Effect of iron on the electrokinetic potential of beryllium and its floatability.
Tsvet. Met, 1960, 33 (8), 73-74.
- 18 Eigeles, M.A. and Sakharova, E.P.
Flotation properties of some silicates in an acid medium and after sulphuric acid treatment.
Tr. vses. Nauch-Issled Inst. Miner. Syr'ya, 1967, (18), 82-101. CA,70, 13575m
- 19 Kuzkin, S.F. and Golov, V.M.
Action of iron compounds in flotation of beryl.
Sborn. Nauch. Trudov. Moskov. Inst. Tsvet Metal. i Zolta i Vsesoyuz. Nauch. Izhener-Tekh. Obshch Tsvet. Met., 1957, (26), 7-20. CA,53, 15,894i

B. FLOTATION USING AMINE COLLECTORS

- 20 Trahar, W.J.
Flotation of beryl and feldspar with amine.
CSIRO and University of Melbourne. Ore Dress. Invest. No 645, 1963.
- 21 Moir, D.N. and Stevens, J.R.
Studies relating to the flotation of beryl.
Trans. Inst. Min. Metall., 1964, 73 (3), 373-391.
- 22 Plaksin, I.N. and Maksimov, D.V.
The action of cationic collectors on the flotation of beryl, quartz, and feldspar.
Izv. Vysshikh. Uchebn. Zavedenii, Gorn. Zh, 1962, 5 (5), 187-190. CA,57, 12099c
- 23 Razumov, K.H. et al.
The effects of cations of calcium and iron on the flotation of beryllium and biotite by a cationic collector.
Obogash Rud, 1962, 7 (3), 3-5.
- 24 Yanis, N.A.
Interaction of a cationic reagent with aluminosilicates.
Tr. vses. Nauchn-Issled. Proek. Inst. Mekhan. Obrab. Polez. Iskop, 1965, (125), 89-126. CA,64, 9296e
- 25 Chipinin, I.V. et al.
Methods for the flotation separation of beryl, tourmaline and garnet.
Nauch. Tr. Irkutsk. Gos. Nauch-Issled Inst. Redk. Tsvet. Metal, 1967, (16), 186-190. CA,70, 21961z
- 26 Sullin, M.S. and Smith, R.W.
Hallimond tube investigation of fluoride activation of beryl and feldspars in cationic collector systems
Trans. Inst. Min. Metall., 1966, 75, C333-336.
- 27 Smith, R.W. and Smolik, T.J.
Infra-red and X-ray diffraction studies of the activation of beryl and feldspars by fluorides in cationic collector systems.
Trans. Soc. Min. Engrs. (AIME), 1965, 233, 196-204.
- 28 Avotins, P.
Use of a modified Hallimond cell in investigation of flotation properties of beryl.
Proc. S. Dakota Acad. Sci., 1963, 42 (26), 84-88.

See also references: 1,3,10 and 19.

C. FLOTATION USING SULPHONATE COLLECTORS

- 29 Matar, J.A.J. and Rudolph, C.G.
The mechanism of activation and flotation of beryl with sodium hexadecyl sulphonate.
Paper S10 to VIII Intern. Min. Proc. Congress Leningrad 1968.
- 30 Fuerstenau, M.C. and Bhappu, R.B.
Sulphonate flotation of beryl.
Trans. Soc. Min. Engrs. (AIME), 1963, 226 (2), 164-174.
- 31 Fuerstenau, M.C. et al.
Metal ion hydrolysis and surface charge in beryl flotation.
Trans. Inst. Min. Metall., 1964, 74, 381-391.
- 32 Trahar, W.J. and Heyes, G.W.
The flotation of beryl and some associated minerals.
CSIRO and University of Melbourne Ore Dress. Invest. No 638, 1963.
- 33 Nutt, C.W. and Kemp, M.
Conditions for the flotation of beryl. Part 2 petroleum sulphonate.
Trans. Inst. Min. Metall., 1963, 72 (12), 806-816.

See also references: 3,13 and 28.

D. FLOTATION USING COLLECTORS OTHER THAN THOSE ABOVE

- 34 Polkin, S.I.
Study of the mechanism of the reaction of reagents with minerals of rare metals by using radioactive isotopes.
Materialy 2-oi [Vtoroi] Leningr. Konf. po Primneniya Radioakt. Izotopov v. Ugol'n i Gorn. Prom., Leningrad-Moscow Sb, 1961, (1), 3-21 CA,61, 5249h
- 35 Lai, R.W.M. and Smith, R.W.
Flotation of beryl, spodumene, and quartz with anionic collectors in the absence of multivalent metal activators.
Paper to *Soc. Min. Engrs, AIME Annual Meeting, New York, Feb-March 1966.*

See also references: 1,18 and 21.

E. EFFECT OF IRON ON SURFACE PROPERTIES AND FLOTATION

- 36 Collins, D.N. and Manser, R.M.
Contribution to discussion on paper ref 31.
Trans. Inst. Min. Metall., 1966, 75, C194.

See also references: 3, 4, 7, 9, 12, 14, 17, 19, 21, 23, 24, 29, 30 and 31.

F. EFFECT OF CATIONS OTHER THAN IRON

- 37 Chipinin, I.V. et al.
Sorption of certain ions on spodumene and beryl and their effect on adsorption of a collector.
(Sborn) Nauch. Trud. Irkuts. Nauch-Issled. Inst. Red. Metallov, 1961, (10), 244-254.

See also references: 4, 12, 23, 24, 29, 31, 32 and 36.

G. EFFECT OF THE FLUORIDE ION ON BERYL FLOTATION

See references: 2, 5, 7, 9, 10, 11, 12, 20, 24, 25, 26, 27, 28, 32 and 36.

H. EFFECT OF THE SULPHIDE ION ON BERYL FLOTATION

See references: 5, 7, 8, 13 and 37.

I. STUDIES OF SURFACE POTENTIAL

- 38 Deju, R.A. and Bhappu, R.B.

A chemical interpretation of surface phenomena in silicate minerals.
Trans. Soc. Min. Engrs (AIME) 1966, 235 (4), 329-332.

See also references: 3, 5, 13, 16, 17, 21, 28, 31 and 36.