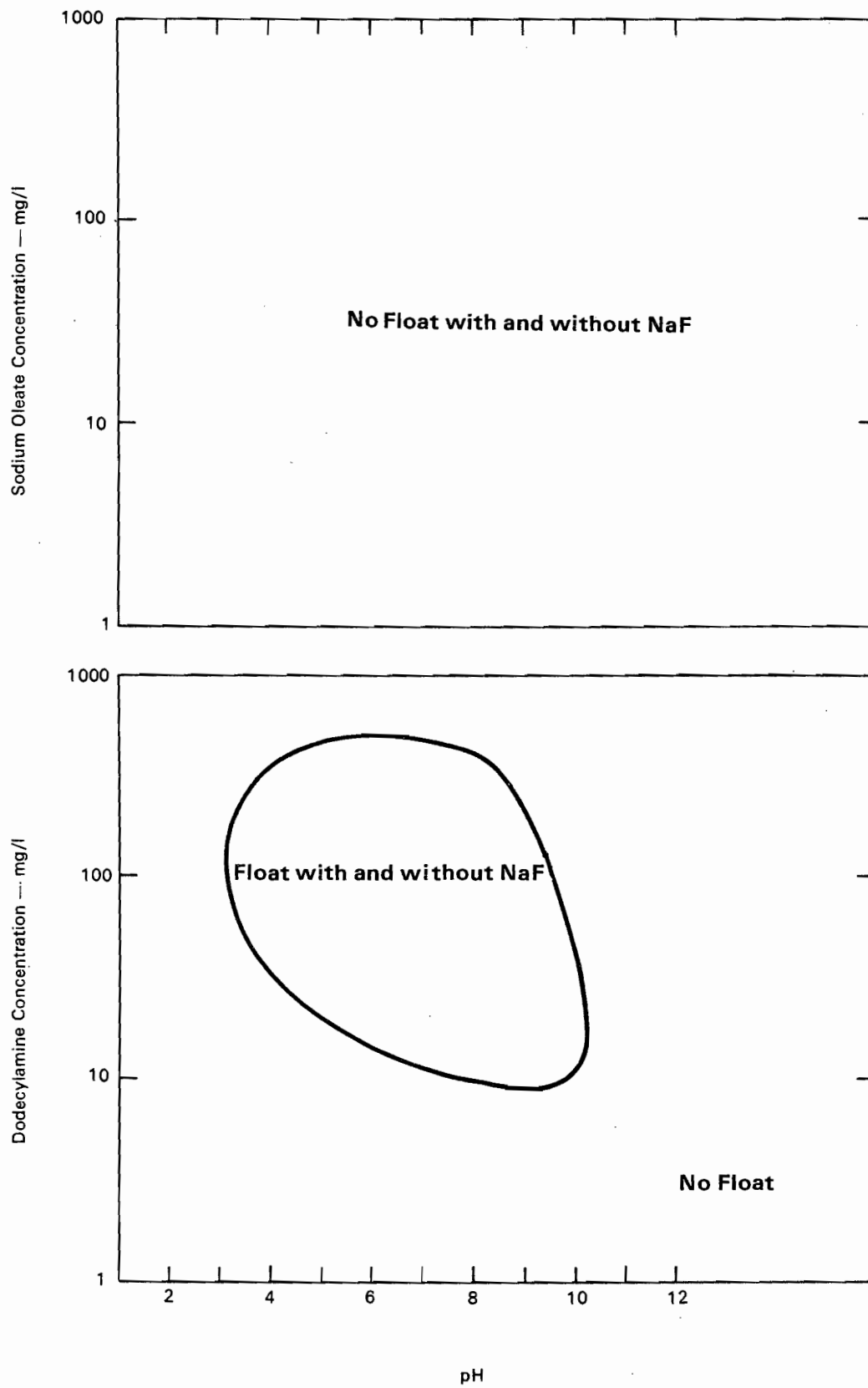# Chapter 4

# THE PYROXENES

Contents:

**Fig 4.1      Aegirine - Augite**

COMPOSITION   (Na, Ca) (Fe$^{II}$, Fe$^{III}$, Mg, Al) [Si$_2$O$_6$], transitional series between augite and
aegirine.
Aegirine NaFe$^{III}$[Si$_2$O$_6$] sodium ferric silicate.
Augite (Ca, Mg, Fe, Al)$_2$ [(Al, Si)$_2$O$_6$] calcium, magnesium, iron, aluminium
silicate.

PHYSICAL PROPERTIES

Hardness 5 to 6.5, augite being the softer material.
Specific gravity 3.4 to 3.6. Colour is variable between
the very dark greens of pure aegirine, through greens,
browns and yellows of aegirine-augite, to more pale
shades in augite.
Monoclinic crystals.   z.p.c. 3.8[1].

CHEMISTRY

Although the pure mineral is insoluble in acids it
has been shown[2] that a weathered surface can give
rise to calcium ions in solution at acid pH values.
Such ions would be capable of activating other
mineral surfaces for anionic flotation.

FLOTATION CHARACTERISTICS

Using the anionic sodium oleate collector, no flota-
tion was found with this mineral over the full pH
range either in the presence or in the absence of
the fluoride modifier.
With the cationic collector poor to moderate flota-
tion was observed over the pH range from 3.0 to
10.0.  The flotation area shows sensitivity to pH-
change as observed within the orthosilicate group
of minerals, with optimum flotation under mod-
erately alkaline conditions between pH 8.0 and
10.0.  No changes were observed in the area or
shape of the diagram when determined in the
presence of the sodium fluoride modifier.  The
flotation diagram appears as Fig 4.1.

OTHER FLOTATION STUDIES

A considerable volume of research has been carried out by Russian workers on the flotation
of ores containing aegirine as a gangue constituent.  The main aim of this work has been either

to depress the aegirine when floating other minerals or the separation of it from flotation products. As there are no clear-cut distinctions throughout this work between fundamental and practical processes, no division is attempted here.

One of two ore types treated contain apatite, nepheline, and a variety of titanium-containing minerals, (sphene, lopartite and titanomagnetite) as well as aegirine. Flotation of the apatite[3] was found to be possible by utilizing Synthapone CP reagent (sodium cetyl and oleyl sulphates) or sodium lauryl sulphonate under acid conditions. Flotation of nepheline was possible only with the former collector with aegirine present and the titanium minerals remained in the tailings with both collectors over the whole pH range. Other authors[4], however, have shown that it is possible to float aegirine from titanium minerals using a sulphate soap collector under alkaline conditions. The use of lead acetate as a silicate depressant when collecting apatite is reported[5] to be successful with a number of different collector types. For example the minerals sphene, aegirine, titanomagnetite and nepheline were all depressed with this modifier using both tall oil and fatty acids at pH 6.5 to 7.2. Similar results were obtained with the ANP collectors (amine hydrochlorides) at pH 7.5, and at pH 9.5 with reagent IM 50 (hydroxamic acid salts synthesized from $C_7$ to $C_9$ carboxylic acids).

Elsewhere[6] a mixed concentrate of sphene and aegirine has been obtained from nepheline using a variety of anionic collectors as well as IM 50. The cationic ANP was found to collect nepheline as well, although a secondary flotation stage on the combined sphene + aegirine-concentrate with ANP at pH 6.5 to 7.0 recovered 70 per cent of the titanium minerals together with only six per cent of the aegirine. A selective separation of sphene and aegirine from the tailings of a similar plant[7] was only partially successful when using a tall oil soap collector in a weakly acid medium (pH 6.5). The dark green aegirine floated with the sphene and the light green variety remained in the tailings. Both the carbonate and the sulphite of sodium have been shown[8] to be effective depressants during aegirine flotation with sodium oleate by virtue of their action in removing the adsorbed collector from the mineral surface.

Anomalies in the flotation behaviour of aegirine are apparent when one author reports no flotation with sulphate soap collectors, and another satisfactory collection under closely similar conditions. Again the flotation diagram presented for this mineral (Fig 4.1) shows no flotation with sodium oleate although other work has shown aegirine to float with tall oil soap which itself has a large content of sodium oleate. Two points of major importance in silicate flotation are illustrated here. The first is that aegirine-augite is a continually varying series of minerals rather than a pure compound, and, as such, small changes in the cations present in the lattice may give rise to considerable changes in flotation properties, (see, for example, those changes observed with the olivine series of minerals Section 3.6). The second effect to note is even more important. This is, that in all the work reported above, the aegirine was associated with the mineral apatite in the original ore assemblage. Apatite is an acid-soluble phosphate of calcium which would certainly give rise to calcium ions in solution, resulting in the activation of surfaces towards anionic collector species.

A second ore type, containing aegirine amongst its gangue minerals, that has been investigated by Russian workers is concentrated mainly for its pyrochlore content.

It is possible here to identify as fundamental the work of Shapovalov and Polkin[9] who have investigated the flotation properties of pyrochlore, zircon, ilmenite, aegirine-augite, limonite and microcline. They found that it was possible to selectively float pyrochlore and zircon with sodium oleate as the collector using a sodium sulphide modifier. The use of sodium carbonate with the sulphide improved selectivity, and preliminary treatment of the minerals with ferric chloride solution increased the adsorption of the sulphide. Sodium alkyl sulphate was also found to act as a selective collector if employed at pH values less than 2.0, but above this value ferric chloride activated the aegirine-augite and the microcline, the latter particularly if the pH rose above neutrality. With the same collector, sodium silicate was found to depress only the pyrochlore, but a mixture of copper sulphate with the sodium silicate also depressed the limonite, microcline and the aegirine-augite. Later work by the same authors[10] on the effects of various multivalent cations on the same suite of minerals using sodium alkyl sulphate collector showed that if the pulp pH was maintained at a value less than 2.0, then ionic concentrations up to 500 ppm of iron, aluminium, copper, calcium and barium could be tolerated with no significant changes in mineral floatabilities. At pH values above 2.0 the minerals are activated by these metal salts with the exception of ferric chloride, which depresses both pyrochlore and zircon whilst activating aegirine-augite.

The effects of sodium hexametaphosphate (Calgon) and of sodium pyrophosphate on similar pyrochlore-containing ores have also been investigated[11]. Trace additions of Calgon (50 g/t) were found to have a beneficial effect in depressing the flotation of the gangue minerals, including aegirine, whilst nearly doubling the niobium content of the froth product. However, if this quantity of Calgon was significantly increased, then the pyrochlore also was depressed. The use of radiotracer techniques showed that both phosphates tested had this effect by decreasing the adsorption of labelled sodium oleate on the minerals surfaces.

A study[12] of the use of the hydroxamate collector IM 50 for the flotation of a pyrochlore ore containing nepheline, calcite, and aegirine-augite as the major gangue minerals has also been carried out in Russia. With this ore a preliminary flotation employing both fatty acid and xanthate collectors removed both calcite and minor sulphide minerals whilst using water glass as a silicate depressant. This was followed by a rougher flotation of the pyrochlore at pH 6.5 to 7.0 using 0.6 kg/t of IM 50. The product from this was subsequently repulped and the pH reduced to below 2.0 by addition of oxalic acid. A cleaning step at this stage using ANP collector gave a four-fold increase in the niobium grade by leaving the nepheline and the aegirine in the tailings product.
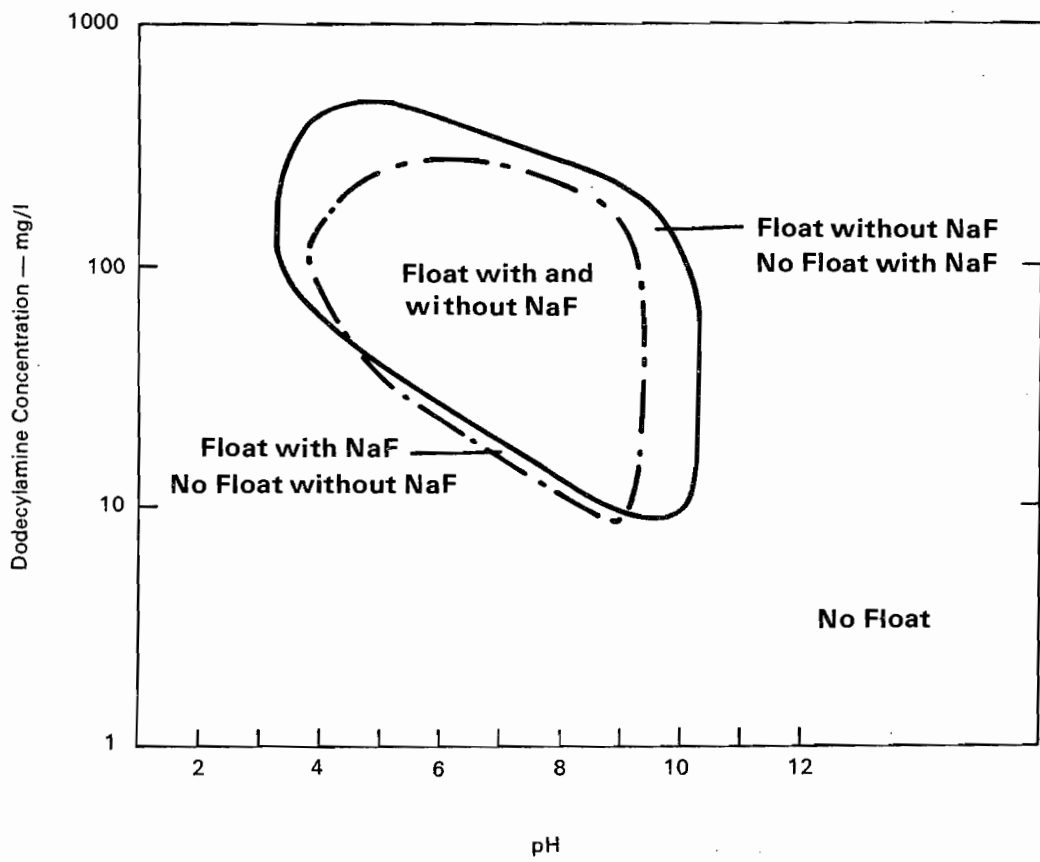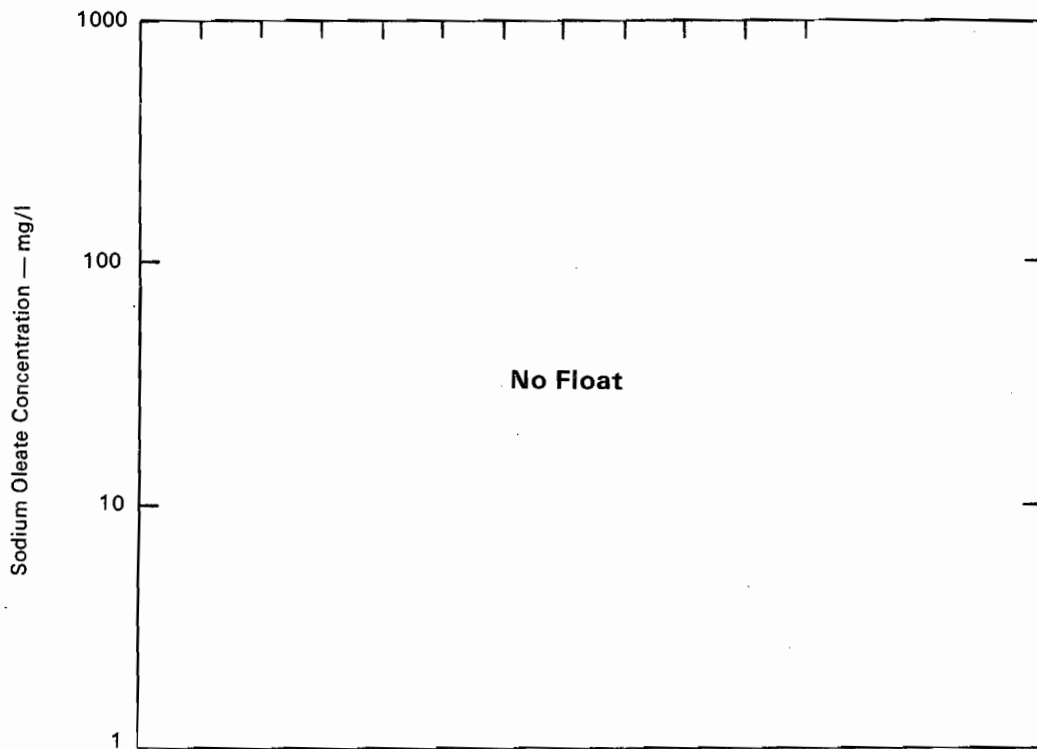
**Fig 4.2      Diopside**

COMPOSITION   Ca $Mg[Si_2O_6]$, calcium magnesium silicate.

PHYSICAL PROPERTIES

Hardness 5.5–6.5. Specific gravity 3.2 to 3.4. Pale green, white or colourless monoclinic crystals.

CHEMISTRY

Diopside is an end member of the diopside-hedenbergite series in which the magnesium is replaced by ferrous cations. Although it is stated in some texts to be insoluble in hydrochloric acid, Burger[2] has shown that calcium is released during artificial weathering in dilute sulphuric acid. Hence, under acid conditions particularly, this mineral could give rise to calcium ions and interfere with anionic flotation systems.

FLOTATION CHARACTERISTICS

No flotation of diopside was found at any pH value with the anionic collector oleic acid either in the presence or absence of fluoride modifier. An area of flotation with the amine collector was found between pH 3.0 and 10.0, this being sensitive to changes in pH with optimum conditions prevailing at alkaline values. With this cationic reagent, fluoride was found to cause mild depression at both ends of the pH scale, but the general shape of the diagram was unchanged with flotation again being favoured at alkaline pH. The flotation diagram appears as Fig 4.2.
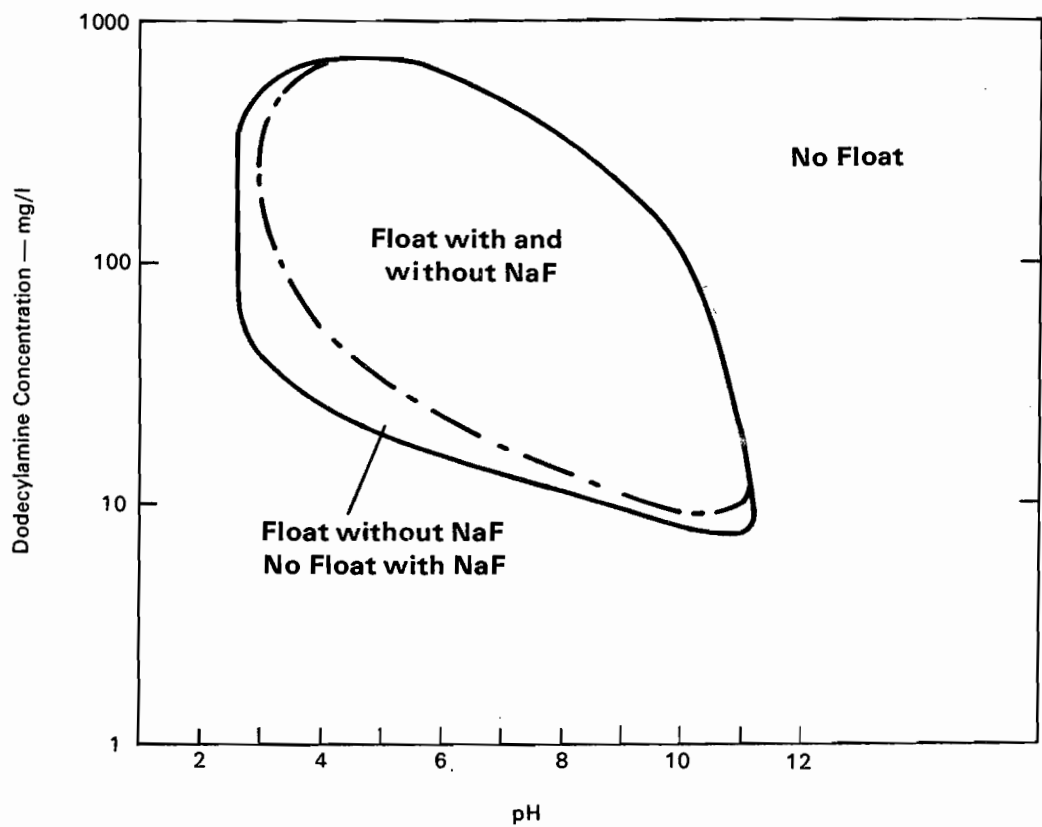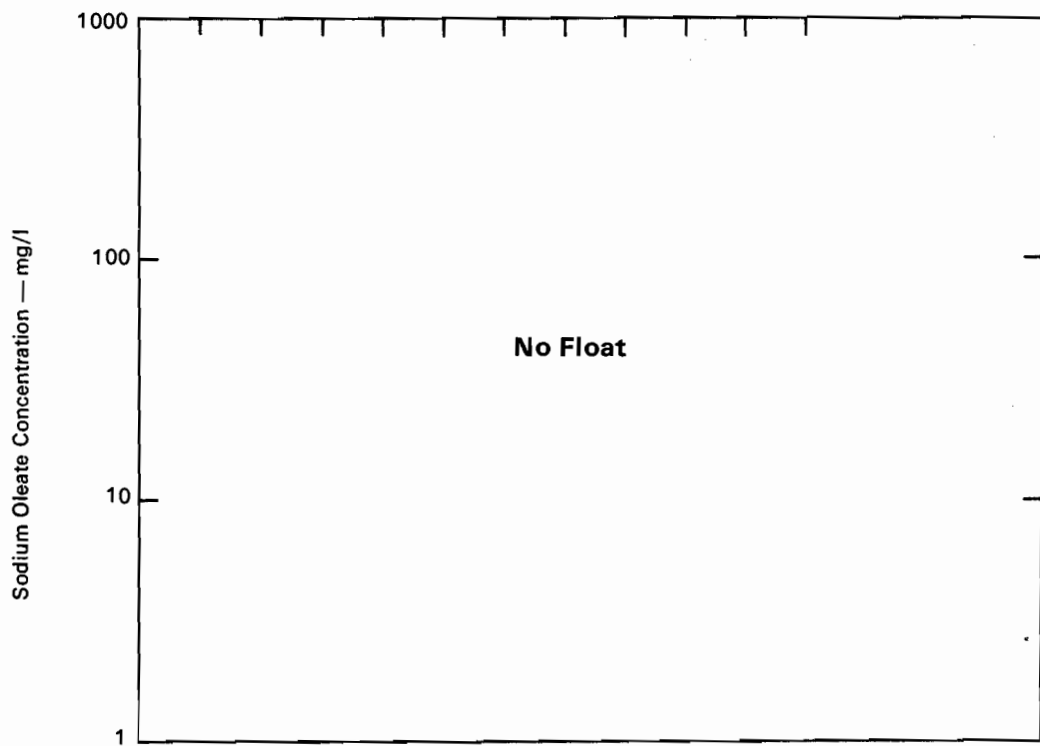
**Fig 4.3    Hedenbergite**

COMPOSITION $CaFe^{II}[Si_2O_6]$, calcium ferrous silicate.

PHYSICAL PROPERTIES

Hardness 6.      Specific gravity 3.5 to 3.7. Various shades of green up to almost black monoclinic crystals.

CHEMISTRY

Hedenbergite is the end member of the diopside-hedenbergite series. The comments on the solubility of diopside will apply equally to this mineral.

FLOTATION CHARACTERISTICS

No flotation of this mineral was found over the range of oleate collector concentrations tested at any pH value. The addition of sodium fluoride to this system caused no change in this situation. With the cationic collector dodecylamine, an area of flotation between pH 2.5 and pH 11.0 was found which, in common with other pyroxenes studied at Warren Spring Laboratory, was sensitive to changes in pH with an optimum flotation occurring in an alkaline medium. The addition of sodium fluoride caused only slight depression of flotation using this collector, this being more marked at acid pH values and at low concentrations. The flotation diagram appears as Fig 4.3.

**Top graph:**

Y-axis: Sodium Oleate Concentration — mg/l (1, 10, 100, 1000)

Float without NaF
No Float with NaF

No Float

**Bottom graph:**

Y-axis: Dodecylamine Concentration — mg/l (1, 10, 100, 1000)

Float with and without NaF

No Float

X-axis: pH (2, 4, 6, 8, 10, 12)

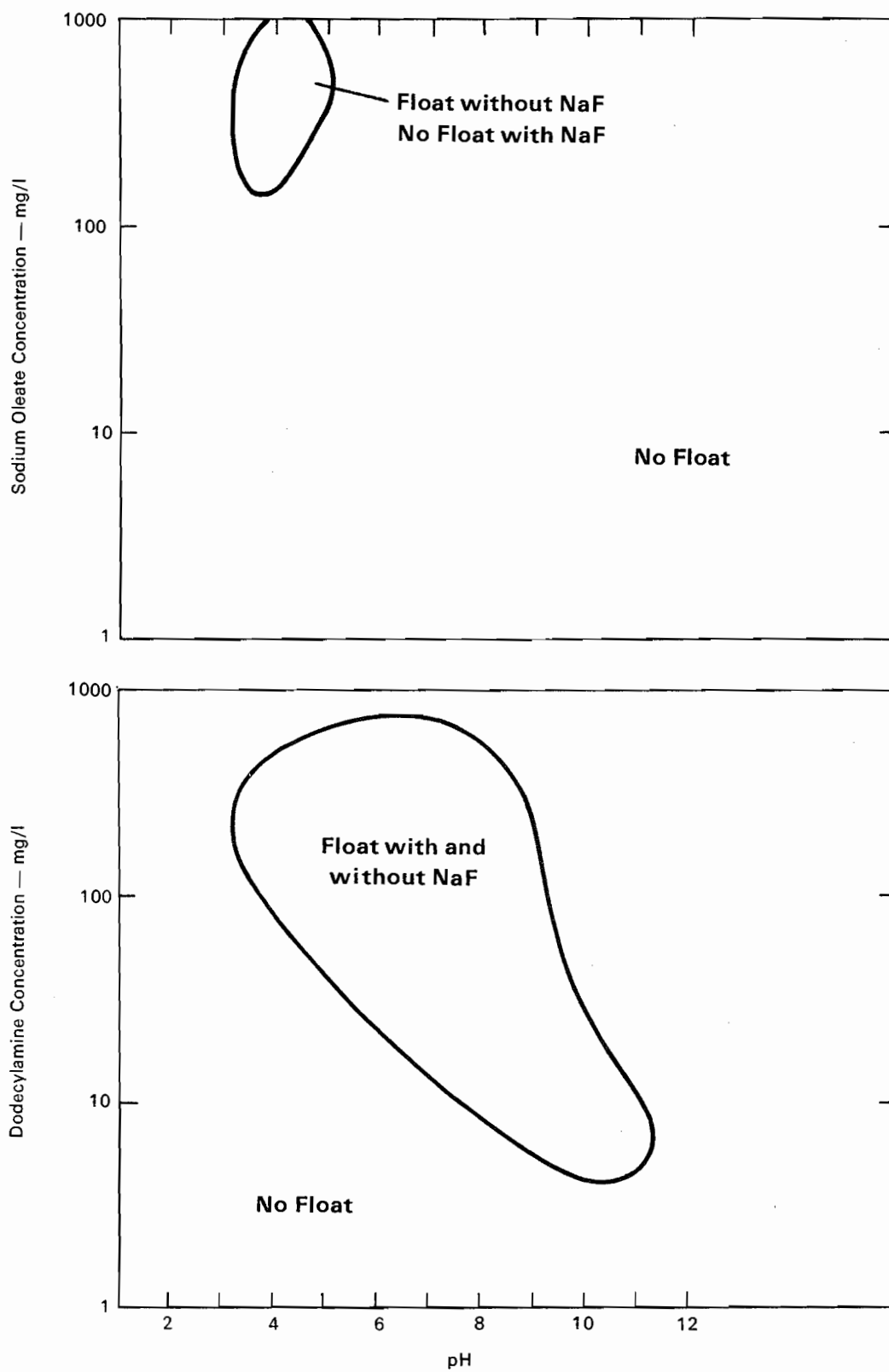**Fig 4.4    Jadeite**

COMPOSITION   Na Al$[Si_2 O_6]$, sodium aluminium silicate.

**PHYSICAL PROPERTIES**

Hardness 6-7. Specific gravity 3.2 to 3.4. White or light green monoclinic crystals.

**CHEMISTRY**

Pure crystalline jadeite is highly stable to acid attack[13] and, although the analysis of some samples has shown partial replacement of sodium with calcium, this occurs to such a limited extent that activation of other minerals in anionic flotation systems would be unlikely.

**FLOTATION CHARACTERISTICS**

With the anionic collector sodium oleate, jadeite has a very small area of flotation between pH 3.5 and 5.0 at high concentrations only. On addition of sodium fluoride the area is eliminated. Such an area of flotation occurring over a limited pH range is typical of that obtained when cation activation has taken place, and the area obtained in this case is almost certainly due to trace quantities of ferrous or ferric ions present as an impurity on the mineral surface or in the lattice.

With its dependence on pH, the cationic flotation area is typical of those obtained with other pyroxene minerals. The flotation area extends from a little above pH 3.0 right down to pH 11.5, less collector being necessary for good flotation in an alkaline medium. The addition of fluoride had no measurable effect on the flotation properties of this mineral when using the dodecylamine collector. The flotation diagram appears as Fig 4.4.
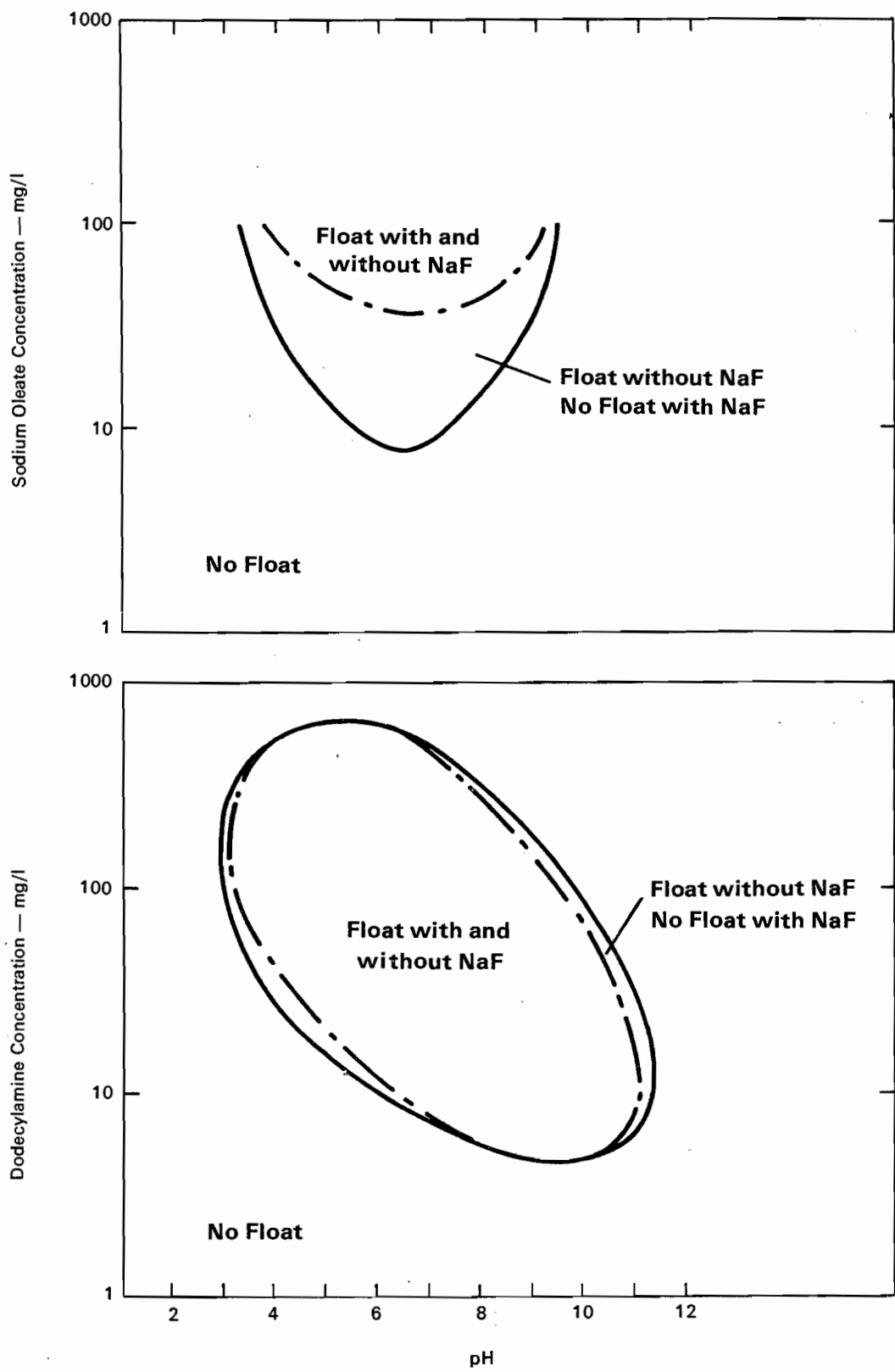
Fig 4.5      Spodumene

COMPOSITION   Li Al[$Si_2O_6$], lithium aluminium silicate.

PHYSICAL PROPERTIES                 Hardness 6.5-7.  Specific gravity 3.0 to 3.2.
                                    White, grey or pale green, sometimes yellow or
                                    purple monoclinic crystals.  z.p.c. 2.5 to 4[14-16].

CHEMISTRY                           The pure mineral is insoluble in dilute acids.  It
                                    is however, frequently found with an iron oxide
                                    coating and analysis of mineral specimens show as
                                    much as one per cent iron.  The removal of surface
                                    coatings, if present, is a necessary preliminary to
                                    selective flotation of this mineral.

FLOTATION CHARACTERISTICS           The anionic flotation area of spodumene extends
                                    from below pH 4.0 up to pH 9.0 with an optimum
                                    value in slightly acid to neutral conditions.  Although
                                    fluoride has a depressant effect, the extent of this is
                                    not marked as with other orthosilicates and pyroxenes.
                                    This could be due to the presence of surface iron
                                    species that are being complexed by the fluoride and
                                    making it unavailable for other surface action.
                                    The area of flotation with the cationic collector is
                                    more typical of the pyroxenes, this mineral floating
                                    from pH 3.0 to above pH 11.0 with a very strong
                                    sensitivity to changes in environment and optimum
                                    conditions occurring at alkaline pH values.  With
                                    this collector the fluoride modifier has caused very
                                    slight depression but the extent of this is of academic
                                    interest only.  The flotation diagram appears as
                                    Fig 4.5.

## FUNDAMENTAL FLOTATION STUDIES

Extensive studies have been made by Yanis on some fundamental considerations of beryl-
spodumene ore flotation.  As well as investigating the two major economic minerals present,
the gangue minerals mica and feldspar were also considered.  In the first of two papers[17] the
reactions with dodecylamine were studied using carbon-14 labelled collector and radioactive

calcium and ferric chlorides. Collector adsorption on all minerals was shown to be predominantly molecular and it occurred equally in both acid and alkaline media, but optimum flotation of spodumene, albite (feldspar) and beryl was found to take place between pH 9.0 and 9.5. The addition of a limited quantity of hydrofluoric acid was shown to reduce the collector adsorption and adversely affected the beryl and albite flotation. However, if this quantity was exceeded then the interaction was reversed and these minerals became activated. Sodium fluoride was found to activate spodumene, beryl and biotite with the amine collector, conditions which have been confirmed by work at Warren Spring Laboratory and shown elsewhere in this publication (page 45 ). A high reactivity of spodumene surfaces towards multivalent cations was shown. This is confirmed by other workers (see below). With the cationic collector this had, as expected, a depressant effect.

The second paper by Yanis[18] reports on flotation testwork using oleic acid in particular for the separation of beryl and spodumene. The method developed comprised of pretreatment of the mixed pulp with sodium hydroxide followed by a washing stage before addition of the oleate collector. (Practical applications of this surface pretreatment are given in the section following). The collector-coated pulp was then thickened and conditioned for an unspecified period at a temperature between 80 and 85 °C. This stage was shown to have caused selective desorption of oleate from the beryl surface making possible the subsequent selective flotation of the spodumene. The effects of sodium fluoride on this process were also investigated and it was shown that this modifier increased the collector desorption from both minerals during the hot conditioning period. However, by increasing collector addition, the separation of the two minerals was still possible. An earlier study[19], using radioactive tracers, of the action of sodium oleate and certain modifiers on beryl and spodumene flotation, showed that optimum flotation of spodumene took place in a weakly alkaline medium whilst that of beryl was favoured when the medium was neutral.

A comparison[20] of the adsorptions of multivalent heavy metal ions on to beryl, quartz and spodumene surfaces has shown a maximum adsorption to occur on to the spodumene surface. It may be deduced from this that under plant conditions such variables as grinding media, water hardness and the presence of minor minerals capable of giving rise to multivalent cations under these conditions, will have considerable effect on the flotation properties of spodumene and particularly when anionic collectors are employed.

The effect of ferric cations on the flotation of spodumene has been investigated by Fuerstenau[21] and his co-workers who compared the flotation of two similar samples of spodumene with sodium alkyl aryl sulphonate over a range of pH values using a cell specially constructed to eliminate possibility of contamination. One sample was dry ground with a pestle and mortar whilst the second was wet-ground in a steel mill. The iron-free sample showed a maximum flotation recovery at pH 1.0, which fell rapidly as the pH was increased, while the portion wet-ground in the steel mill gave a 30 per cent greater recovery with the same concentration of collector over the range pH 1.0 to 4.0. The recovery then dropped as

the pH was increased but even at pH 5.0 had only just fallen below the maximum obtained with the clean sample at pH 1.0. Lai and Smith[22] also showed that a clean sample of spodumene was not floated with the anionic collector sodium dodecyl sulphate at any pH value.

Little or no flotation of spodumene is reported by Wyman[23] when using a wide range of different anionic collectors. Surprisingly, modifiers were also shown to have little effect with no apparent improvement when iron cations were added and only moderate flotation occurred with oleic acid under neutral conditions when aluminium ions were added. These results are difficult to comprehend in the light of those reported by other workers but a highly probable explanation lies in the hydrochloric acid pretreatment given to all mineral samples by this author before any flotation testwork was carried out. Acid leaching has been shown at Warren Spring Laboratory[24] to cause irreversible changes on the surface and completely alter the reactivity of minerals towards flotation reagents. An investigation by a Russian worker[25] of the effects of hydrofluoric acid on spodumene flotation has shown that after treatment with this acid and subsequent water washing, no flotation occurred with sodium oleate if the pulp contained no activating ions. The addition of multivalent cations ($Fe^{+3}$, $Ca^{++}$) after this acid treatment caused activation and good flotation recoveries were obtained with oleic acid.

The reported effects of irradiating oleic acid with high-energy $\beta$-emitters and using the resultant product in a beryl/spodumene flotation separation are the subject of an interesting paper by Plaksin and his co-workers[26]. Use of this irradiated collector increases the extraction of spodumene whilst simultaneously decreasing the beryl recovery. Optimum effects were reached after the oleic acid had been irradiated for a period of 20 hours when, for example, using a collector dosage of 1 kg/t, 50 per cent of the spodumene was recovered in the froth product together with only 10 per cent of the beryl. Corresponding extractions using a similar collector but without irradiation, were 35 per cent spodumene together with 27 per cent beryl. The authors suggest that the collecting properties of oleic acid have been altered in three possible ways, partial conversion to the isomer elaidic acid, partial production of stearic acid, and polymerization to form a less soluble but more hydrophobic homologue.


PRACTICAL FLOTATION SYSTEMS

The importance of surface treatment prior to spodumene flotation has been demonstrated by many workers, particularly in the United States of America, and as early as 1938 Ralston[27] reported that it was possible to obtain selective flotation of spodumene by dry grinding followed by attrition scrubbing and desliming to remove surface iron. Either cationic collectors or anionic collectors together with multivalent cationic activators were used in the flotation stages. Two years later the same author[28] reported on a number of methods for spodumene flotation, in particular for surface-weathered ores. All methods

involved surface treatment by blunging which was carried out at 50 per cent solids for periods of between 20 minutes and one hour adding 0.5 kg/t sodium hydroxide at 10-minute intervals. Blunging for one hour with 1 kg/t sodium sulphide was also tested with success. Flotation after these surface treatments followed by desliming, was carried out using between 400 and 750 g/t oleic acid together with 50 g/t pine oil frother.

Oleic acid was also found to be the best collector for spodumene by Norman and Gieseke[29], who used attrition conditioning with sodium hydroxide dispersant as a flotation pretreatment. These authors, however, had less success when treating weathered rocks and found it necessary to clean the mineral surfaces with 5 per cent hydrofluoric acid before flotation. As well as using sodium hydroxide in the scrubbing stage, silicofluoride, phosphate, and sulphide were tested. Sodium hydroxide and sodium sulphide used either separately or together were found to be the most effective, with the time of treatment necessary varying with the extent of contamination of the mineral surfaces. Quantities of collector similar to those used by Ralston were added at a pH between 6.5 and 8.5. Sulphates and sulphonate collectors were also successfully used under acid conditions. All tests by these authors were made on a feed that had been deslimed at 20 $\mu$m.

A grade of 90 per cent spodumene with a 75 per cent recovery was obtained in laboratory flotation tests[30] on a South Dakota ore after pretreating the surface by scrubbing for 15 minutes with 2.5 kg/t sodium hydroxide. After decantation of the slimes and two washes with soft water the pulp density was diluted to 25 per cent solids and flotation was carried out at pH 7.3 using in this instance only 400 g/t oleic acid collector.

Two methods of treating a pegmatite ore containing spodumene, mica, feldspar, and quartz have been developed[31] by the ore testing section of the American Cyanamid Company. In both methods the ground ore was scrubbed at 22 per cent solids with 2 kg/t sodium hydroxide for 20 minutes. The resulting pulp was washed and deslimed. In one method an initial removal of the mica fraction was carried out using trace quantities — about 25 g/t — of a cationic collector under acid conditions. (The ease with which micas float under these conditions is discussed in Chapter 6.) The mica tailings were then dewatered and conditioned with 0.5 kg/t oleic acid at 50 per cent solids. After dilution of the pulp a rougher spodumene flotation was carried out at natural pH and the resultant concentrate cleaned three times by refloating under acid conditions with further addition of frother only. The spodumene rougher and cleaner tailings were combined and conditioned with 2 kg/t hydrofluoric acid before floating the feldspar with 300 g/t cationic collector. The cleaned spodumene product obtained by this method had a grade of 88 per cent but a recovery of only 47 per cent. The second method examined was more successful, involving the immediate flotation of the spodumene following acid conditioning of the deslimed pulp at 64 per cent solids with 0.5 kg/t oleic acid. The rougher float carried out at 21 per cent solids was in this case cleaned only two times, again in an acid circuit.

This was followed by a mica float using small quantities of a cationic collector and then a feldspar float using hydrofluoric acid and the same collector. In this second test on the same ore, a 93 per cent spodumene product was obtained with an overall recovery of 90 per cent on the head ore.

Attritioning and conditioning in the flotation of spodumene ores is the subject of a paper published by Arbiter and his co-workers[32]. The ore treated was a weathered pegmatite from North Carolina. Sodium fluoride, Aero depressant 610 (American Cyanamid Co), and sodium carbonate were added to the ball mill and the deslimed solids were attritioned at 60 per cent pulp density with further additions of fluoride and depressant 610. After a second desliming stage the pulp was conditioned with further additions of sodium fluoride and depressant 610 together with sodium carbonate, Aero promoter 765 (a mixture of refined fatty acids consisting mainly of oleic and linoleic acids), and a neutral oil. After two cleaning stages recoveries in the pilot plant were in the range of 80 per cent with grades of 4 to 5 per cent lithia. This paper is of importance in that a careful study of scale-up factors from laboratory to pilot plant is made with particular reference to power demands required by the necessary surface treatment. Horst[33] experienced difficulties when attempting to scale-up from pilot-plant to full-scale operation. A mathematical approach showed that cell retention time was a rate-determining step in spodumene flotation and improved results could be obtained by lengthening this time.

A modification of the above attritioning pretreatments was used during tests[34] on spodumene ores from the Edison mine in South Dakota. The ore here was ground in the presence of sodium hydroxide and followed by a deslime and wash before conditioning at 50 per cent solids with 0.6 kg/t oleic acid at pH 8.0 for a period of 10 minutes. After dilution to 25 per cent solids the flotation carried out at pH 7.0 gave a spodumene grade of 60 per cent with a recovery of 80 per cent.

The flotation of spodumene from North Carolina beryl-containing pegmatite[35-8] was successfully accomplished by a milder surface treatment involving conditioning for 5 minutes with 1 kg/t sodium fluoride together with 1 kg/t lignin sulphonate followed by washing and desliming. Five minutes conditioning with 0.5 kg/t oleic acid followed by flotation between pH 6.5 and 8.0 gave more than 80 per cent recoveries of a concentrate containing 6.5 per cent lithia. Batch test-work was later extended to pilot-plant tests in which it was found necessary to make a further addition of 100 g/t quebracho before conditioning with the collector, in order to obtain similar grades and recoveries. An identical system was also tested at the Foote Mineral Company's Kings Mountain deposit. The report[39] on this work gives the pH as 6.9 for both the pretreatment and the flotation stages.

Laboratory and pilot-plant flotation tests[40] have also been made on an Australian ore using the methods of McVay and Browning[38] described above. Concentrates obtained

contained more than 6.5 per cent lithia with recoveries on the deslimed feed in excess of 75 per cent. However, in the pilot-plant tests it was found necessary to make a further addition of tannic acid in order to suppress the activating effects of iron salts arising during the milling stage.

A reagent dosage of 2 kg/t of a mixture comprising 18 per cent sulphonated whale oil, 29 per cent linseed fatty acids, 47 per cent diesel fuel oil and 6 per cent cresylic acid was used on another Australian spodumene ore[41]. This ore was deslimed at 20 $\mu$m and then conditioned with the reagent for 20 minutes at 60 per cent solids in an attritioner. After reducing the solids content to about 15 per cent the spodumene was floated at pH 8.2. A cleaned concentrate from such laboratory tests contained 6.7 per cent lithia with a spodumene recovery of 72 per cent, but pilot-plant tests were not as successful, probably due to undergrinding and inefficient desliming, giving concentrates containing only 6.1 per cent lithia at recoveries of 65 per cent. Although this method of spodumene concentration has attractions in view of both the low-cost collector and the absence of need of further conditioning reagents, similar results were obtained by the same authors on a beryl ore using the identical system so that the two minerals occurring simultaneously in an ore would make it unworkable.

Ores containing quartz, feldspar and micas have been tested on a laboratory scale by Wyman[42] who initially tried a direct flotation of spodumene using sodium silicate as a gangue depressant with a variety of anionic collectors. Only limited success was achieved with any of these systems and the degree of success varied with the source of the mineral used. Subsequent testwork was directed towards floating the gangue minerals and leaving a spodumene-enriched tailings product. Of the cationic collectors investigated, Armac T (Armour Hess Chemicals Ltd) proved to be the most successful when used in conjunction with sodium hydroxide, dextrin, and pine oil. Using this combination, most of the mica and quartz together with part of the feldspar was removed by floating at a low solids content (15-20 per cent), and products containing about 6 per cent lithia at recoveries of 80 per cent or more in the flotation stage were obtained.

Spodumene was depressed with either starch or dextrin whilst floating mica, feldspar and quartz with cationic collectors in the flowsheet outlined by Thom and Gisler[43]. Iron minerals are subsequently removed in an acid circuit using sodium resinate as collector together with hydrofluoric acid as a spodumene inhibitor. A more recent publication[44] describes a reverse-flotation technique for spodumene using the Armour reagent Armeen L9 (2-amine nonane) to float feldspar, mica and quartz and leave a 6 per cent lithia tailings product with a low iron content.

An early patent by Bunge[45] for separating spodumene present in pegmatites uses a petroleum sulphonate collector which, it claims, floats the spodumene together with part of the mica.

A second flotation stage on the acid-deslimed concentrate obtained uses tallow amine acetate (e.g. Armac T) at pH 3.0 to 5.0 with pine oil frother to remove the mica fraction.

The separation of spodumene and beryl by flotation is the subject of a patent by Browning and Clemmons[46] where the spodumene is floated at between pH 6.5 and 9.0 using 450 g/t oleic acid together with 1 kg/t each of magnesium ligno-sulphonate and sodium fluoride to depress the beryl. It is also claimed the beryl may be depressed alternatively using starch, quebracho, or sodium sulphide in place of some or all of the ligno-sulphonate or sodium fluoride.
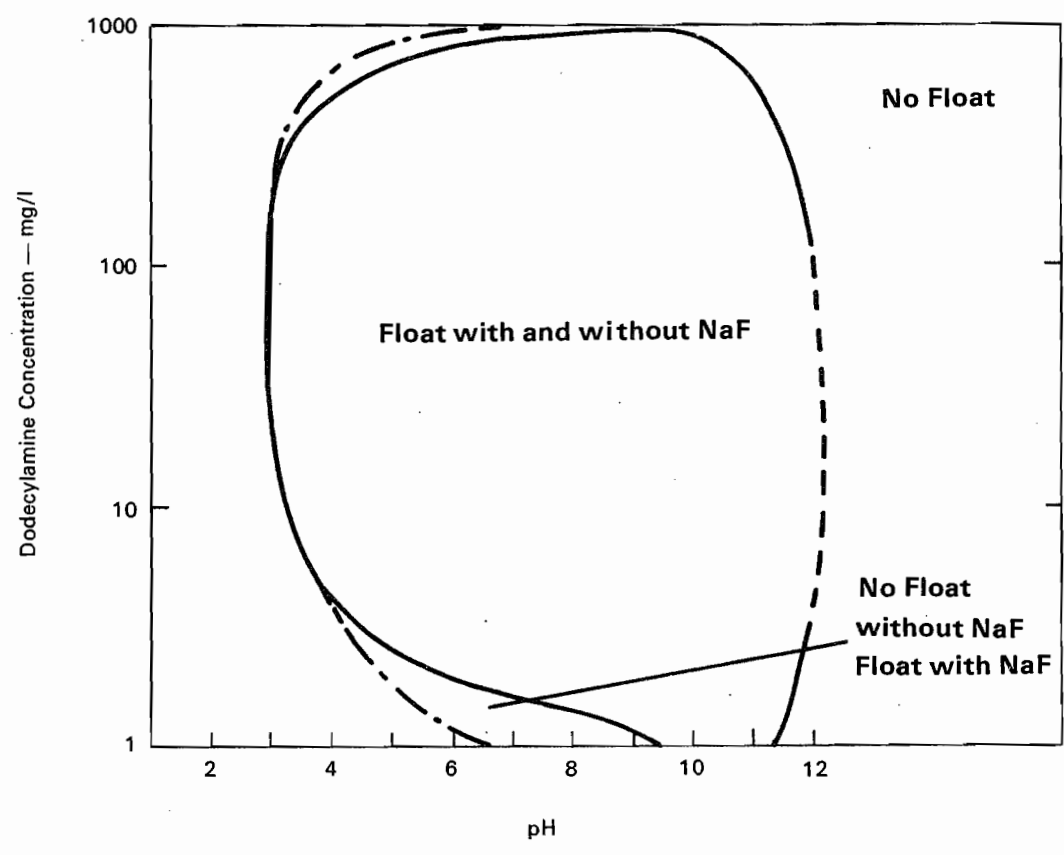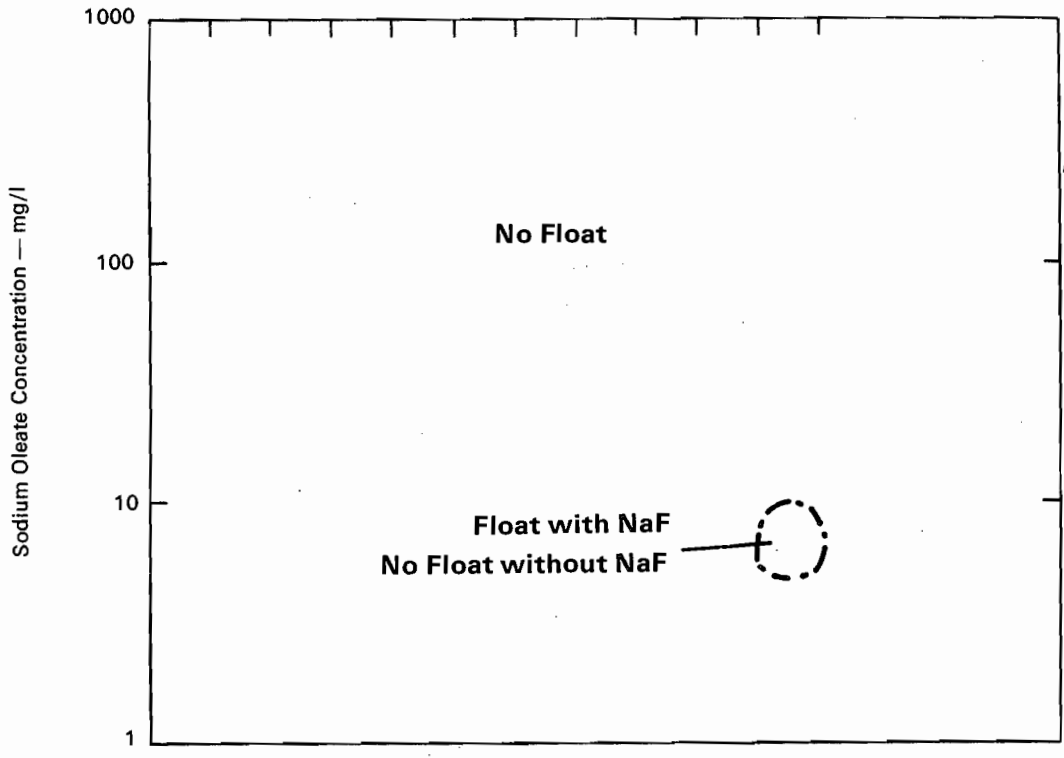
Fig 4.6.1     Wollastonite

COMPOSITION    $Ca[SiO_3]$, calcium metasilicate

Although wollastonite contains $[SiO_3]_n$ chains running parallel to the 'b' crystallographic axis, the shape of these chains is different from that found in the pyroxene series, with the unit being repeated every three tetrahedra with the wollastonite and every two tetrahedra with the pyroxenes[47,48].

PHYSICAL PROPERTIES                          Hardness 4.5 to 5.0. Specific gravity 2.8 to 3.1. White, grey or very pale green, triclinic crystals.

CHEMISTRY                                       Calcium in the wollastonite crystal can be replaced by iron, manganese and magnesium. The mineral is decomposed by concentrated hydrochloric acid, and in flotation circuits may give rise to calcium and iron ions capable of activating other minerals in the present of anionic collectors.

FLOTATION CHARACTERISTICS             No flotation area with sodium oleate was found for wollastonite at any concentration over the whole pH range. The very small area found with this collector in the presence of the fluoride modifier is of academic interest only and has no practical significance. Unlike the true pyroxenes wollastonite has a very large flotation area with the cationic dodecylamine reagent. Floating over a wide range of collector concentrations it shows little sensitivity to pH change from 3.0 to beyond 12.0. The slight activating effect of sodium fluoride is more significant under acid conditions but again, with such a large total area of flotation, has little practical importance. The flotation diagram appears as Fig 4.6.1.

## PRACTICAL FLOTATION SYSTEMS

The beneficiation of wollastonite ores is carried out with the purpose of reducing the portion of calcite present or eliminating harmful iron-containing minerals. Either one or, in some instances, both gangue materials may be present in the head ore and are generally removed as froth products using anionic collectors, thus leaving the wollastonite concentrated in the non-floatable tailings. Although from structural considerations the flotation characteristics of wollastonite shown above are anomalous (it would be expected, for example, to be self activating in anionic flotation with such a large portion of calcium ions present) the correlation between this and accepted plant flotation practice is indeed close.

In Rumania, Stoian and his coworkers[49] have investigated the concentration of ores containing 56 per cent wollastonite occurring with iron-containing gangue minerals. After initial crushing the 25 to 88 mm fraction of head ore was hand picked to remove part of the garnet and pyroxene before further grinding. Three concentration routes were then investigated. The first utilized a two-stage high-intensity magnetic separation and yielded a 95 per cent grade wollastonite product with 70 per cent overall recovery. The second method tested involved a single-stage magnetic separation followed by flotation of the iron-containing minerals and yielded a similar grade product but with 83 per cent overall recovery. The final method tested dispensed entirely with magnetic separation, feeding the ground hand-picked material directly to the flotation cells. Again a product containing 95 per cent wollastonite was obtained but in this case overall recovery had increased to 86 per cent. Clearly the two methods involving flotation were superior to magnetic separation alone but from a head assay of 5.5 per cent $Fe_2O_3$ the concentrate obtained in the third method contained 0.48 per cent $Fe_2O_3$ whereas the combined magnetic separation and flotation treatment of the second method reduced the $Fe_2O_3$ content to 0.37 per cent.

In the flotation stage of the above tests both sodium oleate and sulphate soaps were tested as collectors under acid and alkaline conditions. The use of a silicofluoride modifier was also investigated, but optimum conditions for the flotation of the iron-containing minerals were found to prevail when using 0.75 kg/t sulphuric acid with between 0.75 and 1.0 kg/t of sulphate soap collector, (e.g. sodium dodecyl sulphate). A second publication by the same author[50] on the reverse flotation of similar wollastonite ores containing garnet, diopside, epidote, etc uses a mixed-collector system comprising sulphate soaps and sodium oleate together with a soap product derived from the residual products of the purification of sunflower seed oil. This test was again carried out under acid conditions using 1 kg/t sulphuric acid to give a pH between 6.0 and 6.5. The concentration of wollastonite from such ores using the reverse flotation process is the subject of a Rumanian patent[51] which in addition to giving ranges of collector and pH modifier dosages, also recommends that grinding of the head ore should be carried out in non-metallic mills.

The ease with which wollastonite is floated with amine collectors is exploited at the Finnish plant at Lappeenranta[48] where it is removed together with accompanying silicate minerals from the calcite present in that deposit. In a second stage of the operation, cationic and anionic collectors are used together to remove other silicate impurities to leave 'the wollastonite again as a tailings product.

At the Central Asiatic Scientific Research Institute for Geology and Minerals (SAIGIMS) in the Soviet Union, Shvetsov[52] and his co-workers have studied the concentration of wollastonite by reverse flotation methods. They showed that the separation of wollastonite from gangue minerals presented considerable problems due to marked similarities in flotation properties. After grinding and classification, the weakly magnetic mineral fraction was removed before conditioning the pulp with 1.7 kg/t of sodium silicate. A sulphate soap flotation under alkaline conditions was then used to remove the 25 per cent calcite present leaving a 97-98 per cent grade wollastonite product in the tailings. Recovery by this method was 88 per cent. With a second sample treated in a similar manner, the concentrate grade was reduced to 93 per cent wollastonite due to the higher quartz and feldspar content of the head ore. An attempt to up-grade this concentrate by floating these gangue minerals with ANP-14 at pH 6.0 using fluoride modifier caused an increase in the wollastonite grade of between 1 and 2 per cent and gave an overall recovery of 82-83 per cent.

A further ore tested[53] at SAIGIMS contained 70 per cent wollastonite, 18 per cent mixed feldspars, 7 per cent pyroxenes, various minor silicate minerals, and only 2 per cent calcite. The flotation flowsheet which was used successfully on this ore is shown in Fig 4.6.2. The calcite flotation stage was carried out under alkaline conditions using tallow soap or saponified napthenic acid as collector. After reducing the pH of the pulp with sulphuric and hydrofluoric acids the main feldspar concentrate was removed using ANP-14 collector together with pine oil frother. Further feldspar was removed in a scavenger stage by the addition of 20 g/t fuel oil and a second quantity of ANP-14. The final stage to remove pyroxenes was carried out using a soap collector together with 600 g/t lead nitrate modifier. The concentrate produced in this manner contained 92 per cent wollastonite with an overall recovery of 81 per cent whilst also producing a feldspar product of 65-70 grade at a 70 per cent recovery.

A wollastonite ore containing both calcite and iron minerals has also been successfully concentrated by Yugoslav workers[54]. Reducing the $Fe_2O_3$ content to less than 0.5 per cent in a high-intensity magnetic separator, the non-magnetic fraction was subjected to flotation when the greater portion of the calcite was removed as a froth product to give a wollastonite tailing containing less than 1 per cent carbonate.

A further batch-scale separation of calcite from wollastonite was reported by Grosman[55] is based on a half-hour pretreatment of the ground pulp at 50 per cent solids with a 1 per cent sodium silicate solution at 90 °C. This pulp was then acidified to pH 2.0 and the calcite floated with sodium alkyl sulphate collector. It must be assumed in this case that the larger part of the calcite surface had been converted to the silicate otherwise the acid consumption would have been prohibitive.

Feed

Crushing

Grinding

Classification

+0·15mm

−0·15mm

Calcite Flotation
3 min

Calcite
Product

Tailings

+10 μm

Deslime

−10 μm

Tailings
Dump

1st Feldspar Flotation
5 min

Tailings

2nd Feldspar Flotation
3 min

Feldspar
Product

Tailings

Pyroxene Flotation
5 min

Wollastonite
Concentrate

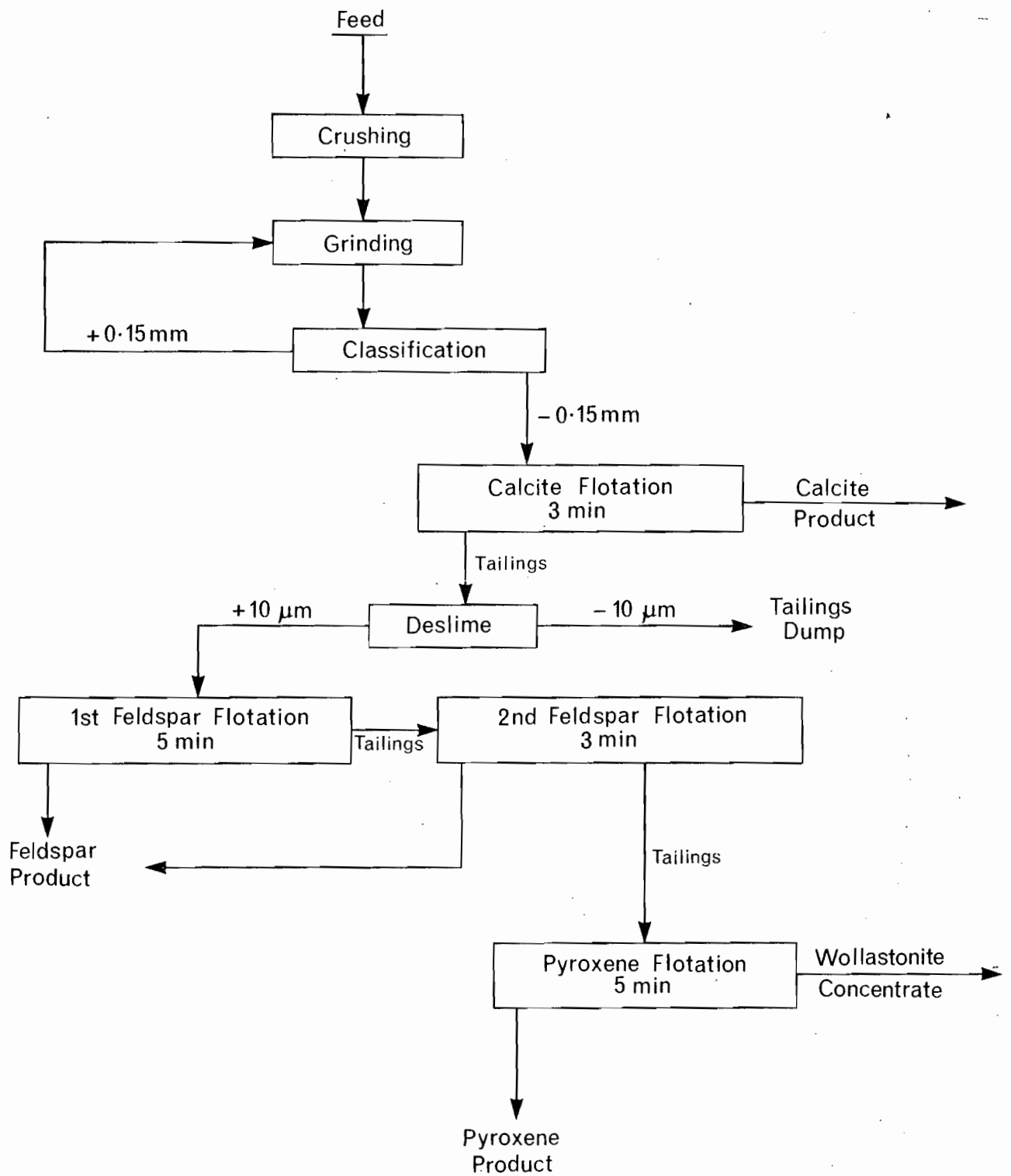Pyroxene
Product

**Fig 4.6.2    Flow-sheet for Wollastonite
concentration developed at SAIGIMS**

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# Chapter 5

# THE AMPHIBOLES

Contents:

No Float

Sodium Oleate Concentration — mg/l

100

Float without NaF
No Float with NaF

10

1

Dodecylamine Concentration — mg/l

1000

No Float with NaF
Float without NaF

No Float

100

Float with and without NaF

10

1

2    4    6    8    10    12

pH
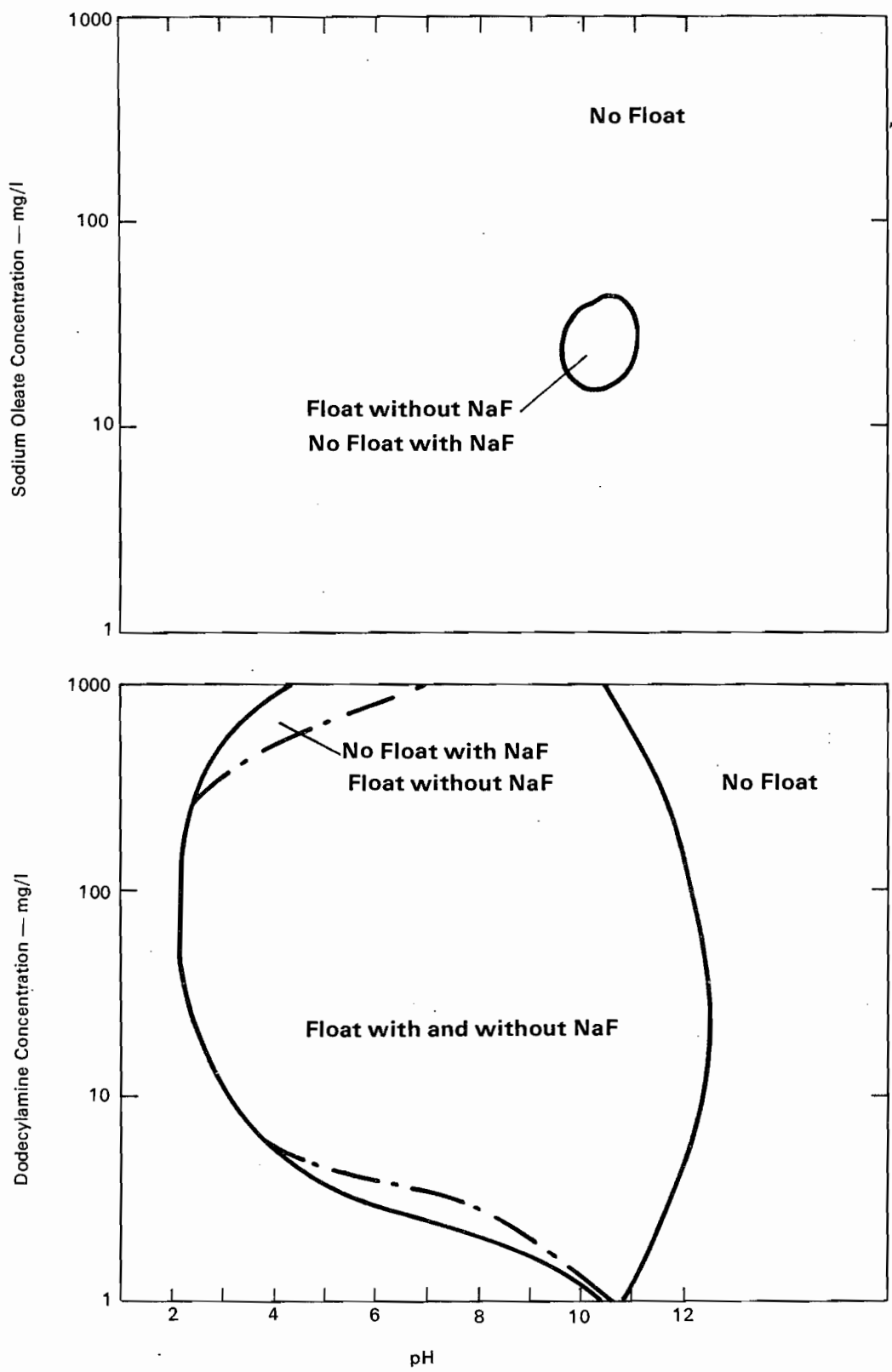
**Fig 5.1        Actinolite**

COMPOSITION   $Ca_2(Mg,Fe^{II})_5[Si_8O_{22}](OH,F)_2$, calcium, magnesium/iron silicate. An intermediate member of the tremolite-ferroactinolite series which has end members of calcium magnesium silicate and calcium iron silicate respectively i.e. Tremolite $Ca_2Mg_5[Si_8O_{22}](OH,F)_2$, ferroactinolite $Ca_2Fe^{II}_5[Si_8O_{22}](OH,F)_2$

PHYSICAL PROPERTIES

Hardness 5-6. Specific gravity 2.9 to 3.4. Pale to dark green monoclinic crystals, but may also exist as a fibrous asbestos-like material. Only the crystalline form is considered within the confines of froth flotation separations.

CHEMISTRY

The pure crystalline material is reported to be insoluble in dilute acids. It is thus unlikely to give rise to interfering cations when present in an ore which has to be concentrated by flotation with anionic collectors.

FLOTATION CHARACTERISTICS

A very small area of flotation with sodium oleate collector was found between pH 10.0 and 11.0 which was reduced to zero on adding fluoride modifier to the system. The area found has no practical importance and is almost certainly due to the presence of an interfering cation arising from an impurity existing in the sample as tested. Such activation under basic conditions is consistent with the existence of alkaline-earth cations in the pulp.

Actinolite was found to have a very large area of flotation with the amine collector from a pH of less than 3.0 to well above pH 11.0. Although a slight preference for alkaline conditions is shown at low concentrations of collector, this would be insignificant in plant conditions. Addition of sodium fluoride modifier to the cationic flotation system caused very mild depression at both extremes of collector concentrations but did not alter the range over which the mineral floated. The flotation diagram appears as Fig 5.1.
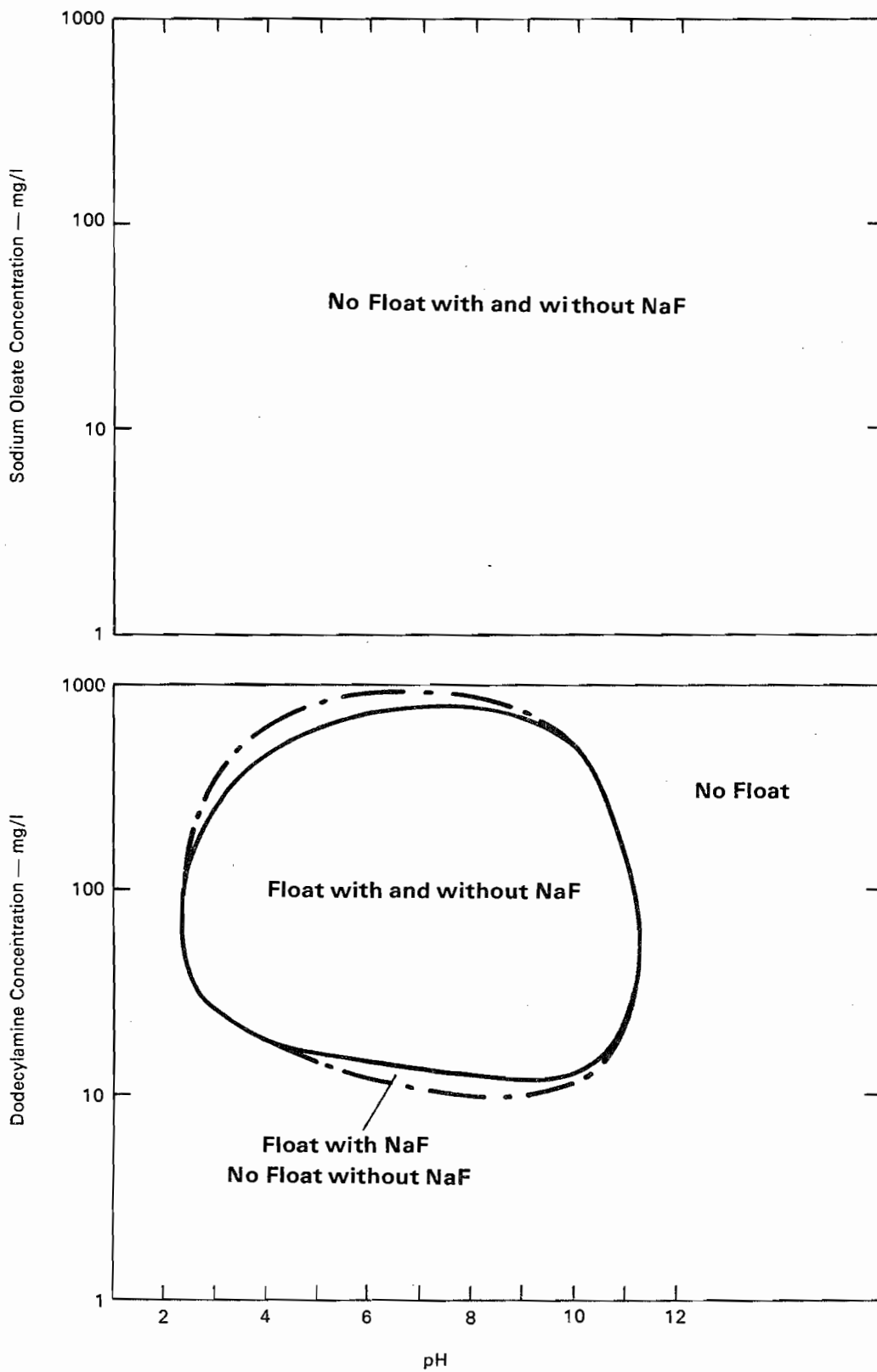
Fig 5.2    Hornblende

**COMPOSITION**       The title hornblende includes a group of amphibole silicates in which up to two silicon atoms in the ribbon structure have been replaced by aluminium. The general anion formula becomes $[Si_6(Si,Al)_2O_{22}](OH,F)_2$ with a net negative charge of between 14 and 16 depending on the extent of aluminium replacement. Cation balance is made up by alkali and alkaline earth metals, ferrous and ferric iron, and aluminium. The general formula for common hornblende may be written,

$$(Ca,Na,K)_{2-3}(Mg,Fe^{II},Fe^{III},Al)_5[Si_6(Si,Al)_2O_{22}](OH,F)_2.$$

**PHYSICAL PROPERTIES**          Hardness 5-6. Specific gravity 3 to 3.5. Shades of green from yellow-green through dark greens to black monoclinic crystals.

**CHEMISTRY**          Burger[1] found that it was possible to leach calcium from hornblende with sulphuric acid at pH 3.0. Although the extent of attack was slight and only occurred over long periods of contact, it is possible that hornblende (particularly if partially weathered) could give rise to interfering ions such as calcium, iron or magnesium which would seriously effect a flotation system employing anionic collectors.

**FLOTATION CHARACTERISTICS**      No area of flotation was found with sodium oleate either in the presence or absence of the fluoride modifier. With the cationic collector, dodecylamine, the hornblende tested had an extensive area of flotation between pH 2.5 and 11.0 with little or no sensitivity to pH change between these limits. The addition of sodium fluoride to the cationic flotation system had a barely perceptible activating effect at low collector concentrations but did not extend the pH range over which the mineral floated. The flotation diagram appears as Fig 5.2.

## PRACTICAL FLOTATION SYSTEMS

Russian workers[2] have investigated the flotation properties of various silicate minerals occurring in an ilmenite deposit. Using a tall oil collector, ilmenite, garnet and chlorite were successfully floated from hornblende over a range of pH values from 3.5 to 7.0. The removal of silicate minerals from ilmenite concentrates is also the subject of a patent[3] which describes the cationic flotation of garnet, feldspar, hornblende and augite whilst depressing ilmenite. This is accomplished by pretreating the concentrate with hydrofluoric acid and following this with a period of conditioning with potato starch before the addition of 170 g/t amine acetate for flotation. Presumably the fluoride treatment activates the silicate minerals and the starch acts as an ilmenite depressant. A removal of 80 per cent of the silicate minerals is claimed by the authors using this method. These two references are in complete accord with the fundamental flotation properties of hornblende described in the previous paragraph.
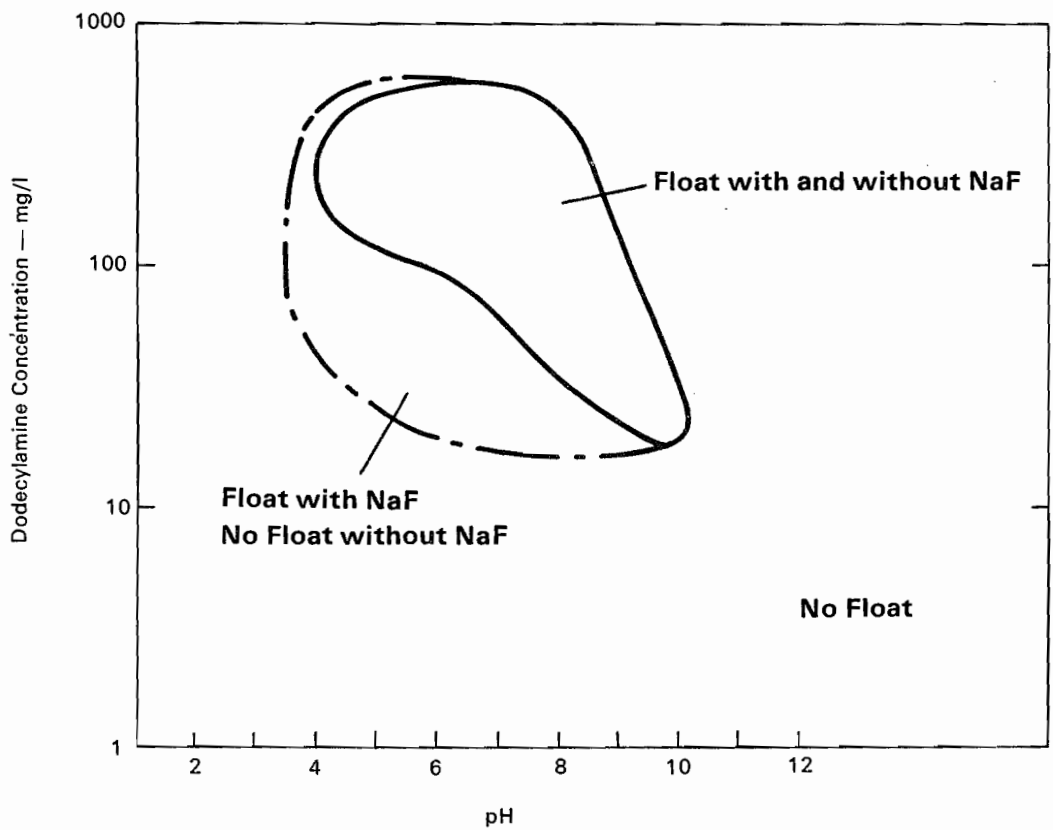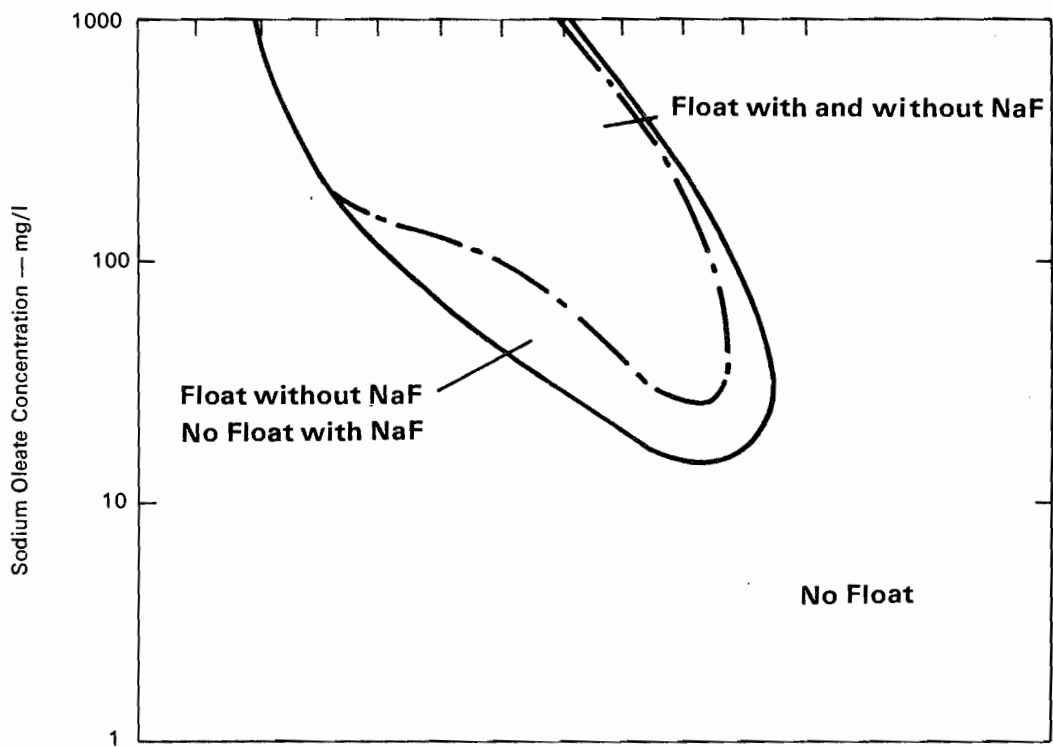
Fig 5.3    Riebeckite

## 5.3             RIEBECKITE

COMPOSITION        $Na_2 Fe^{II}_3 Fe_2^{III} [Si_8 O_{22}] (OH,F)_2$, sodium iron silicate.

PHYSICAL PROPERTIES

Hardness 4-5. Specific gravity 3 to 3.45. Dark blue or black monoclinic crystals. Riebeckite is the crystalline form of the fibrous asbestos crocidolite.

CHEMISTRY

Although there is no reference in the literature to the solubility of riebeckite, the flotation of this mineral with anionic collectors (see below) is markedly different from that of the other amphiboles studied at Warren Spring Laboratory. It is possible that this arises from the presence of ferrous or ferric ions, and that if riebeckite were present in an anionic flotation system then other minerals could likewise be activated.

FLOTATION CHARACTERISTICS

Using the anionic collector sodium oleate, a considerable area of flotation was found with riebeckite between the limits of pH 3.0 and pH 11.0. Unlike any other silicate tested with this collector, this area was found to be very dependant on changes in pH, with alkaline media favouring flotation at low collector concentrations, and acid conditions yielding better flotation at higher concentrations. Although the area of flotation was reduced on adding the fluoride modifier, the extent of depression was less than that observed with many other silicate minerals. The general shape of the flotation area remained similar but the minimum concentration of collector for the onset of flotation occurred at a slightly higher value.

The area of flotation of riebeckite with the cationic collector again appears to be rather different from that of other amphibole silicates. The sensitivity to pH change with optimum flotation occurring under alkaline conditions is more typical of the type of flotation found with pyroxene chain silicates. However, the extent of

the increase in area obtained on adding fluoride modifier to the dodecylamine flotation system of this mineral is more typical of that obtained with orthosilicates. The flotation diagram àppears as Fig 5.3.
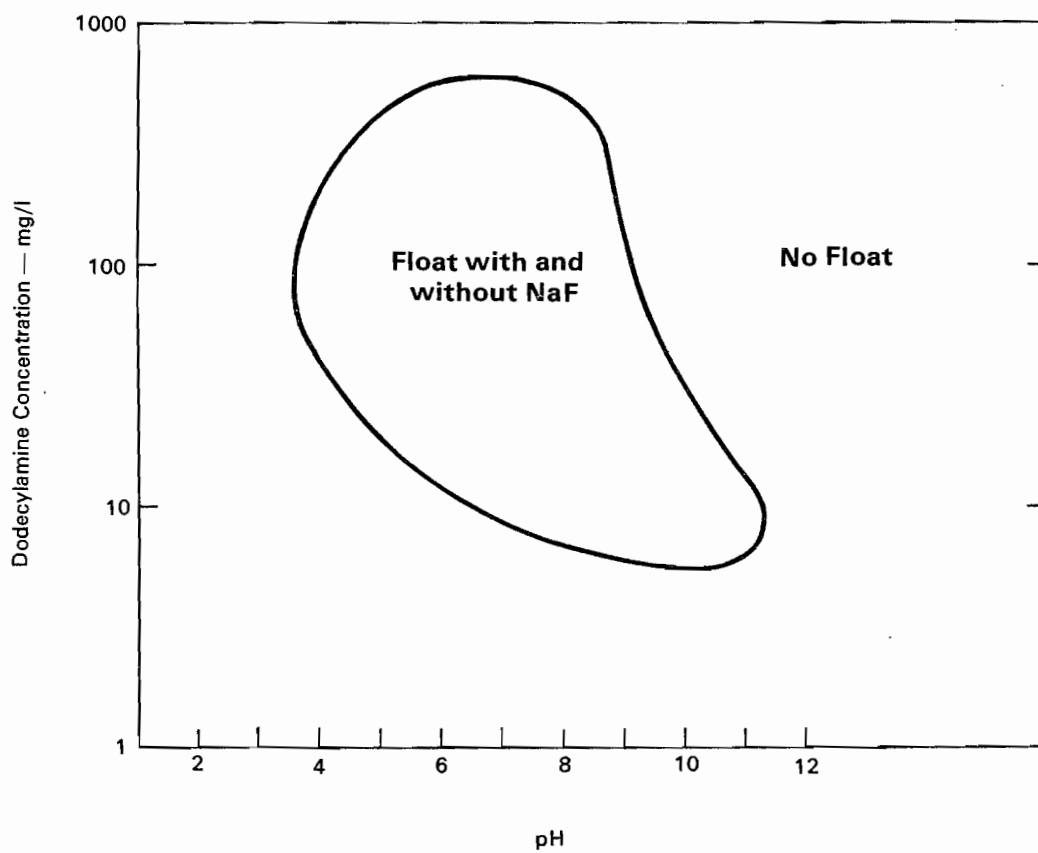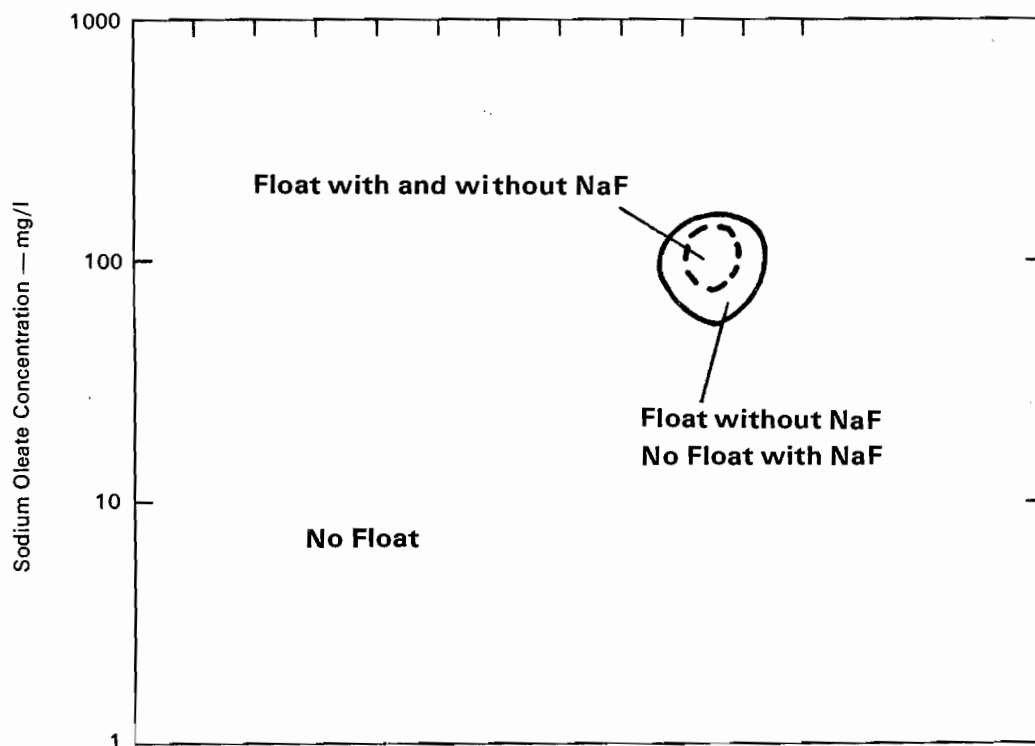
**Fig 5.4**       **Tremolite**

## 5.4        TREMOLITE

COMPOSITION    $Ca_2Mg_5[Si_8O_{22}](OH,F)_2$, calcium magnesium silicate. The end member of the ferroactinolite-tremolite series in which actinolite occurs.

PHYSICAL PROPERTIES

Hardness 5-6. Specific gravity 2.9 to 3.2. Colourless, white or dark grey monoclinic crystals.

CHEMISTRY

The pure crystalline mineral is reported to be insoluble in dilute acids and as such is unlikely to give rise to interfering cations in flotation circuits. If this mineral is at all weathered, however, it could give rise to both magnesium and calcium cations which would cause considerable activation if floating with anionic type collectors. The first sample of tremolite studied at Warren Spring Laboratory and reported in a previous publication[4] had a very considerable area of flotation with sodium oleate which was caused by this type of activation.

FLOTATION CHARACTERISTICS

The very small area of flotation found between pH 10.0 and 11.0 is consistent with calcium ion activation and is of no practical significance in anionic flotation systems. The possibility of this area increasing with activation is however very real as mentioned in the previous paragraph. The flotation area of tremolite with the cationic collector dodecylamine was found to lie between pH 3.0 and 11.0 with some sensitivity to pH change at low concentrations. The addition of fluoride modifier to this system had no measurable effect of this flotation area. The flotation diagram appears as Fig 5.4

**5.5**          **REFERENCES**

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