

Chapter 6

THE SHEET SILICATES

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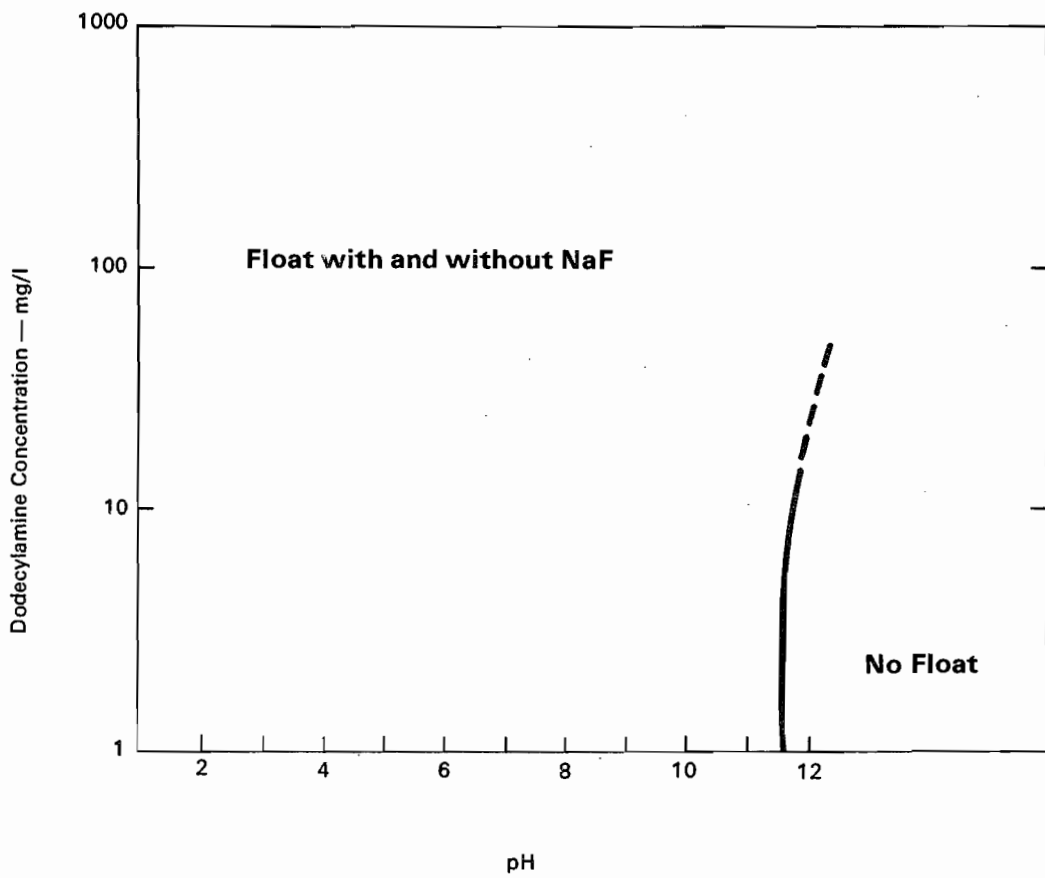
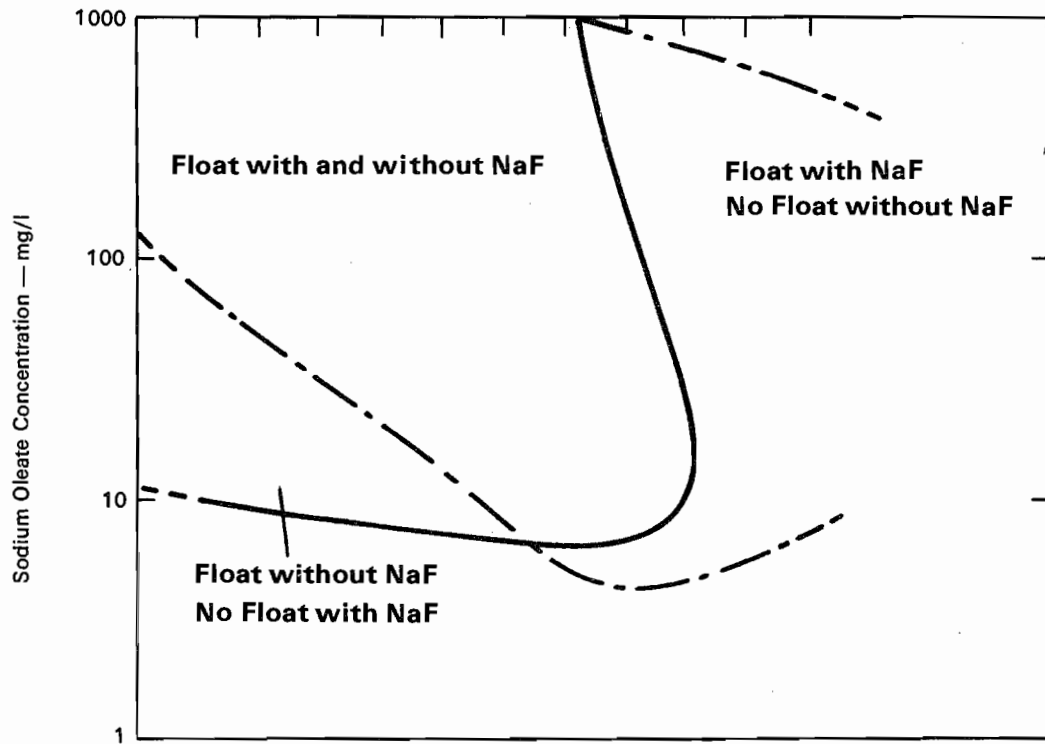


Fig 6.1 Chlorite

COMPOSITION $(\text{Mg,Al,Fe})_{12} [(\text{Si,Al})_8\text{O}_{20}] (\text{OH})_{16}$, hydrated layer silicate.

PHYSICAL PROPERTIES

Hardness 1.5 to 3.0. Specific gravity 2.6 to 3.3.
Green, white, yellow or brown monoclinic crystals.

CHEMISTRY

Chlorite is attacked by strong acids and will release magnesium, aluminium and iron ions. The existence of these in solution will cause activation of most negatively charged minerals with anionic collectors.

FLOTATION CHARACTERISTICS

Of all the silicate minerals studied at Warren Spring Laboratory, chlorite was found to have the greatest flotation areas both with the cationic and the anionic collector. No lower pH limit was found with either collector. An upper limit at pH 8.0 to 10.0 was found for the anionic collector. This limit disappeared on the addition of fluoride. At low concentrations of cationic collector a limiting pH of 11.5 was shown to exist, but at higher amine concentrations this disappeared. Fluoride used in combination with this collector had no measurable effect on chloride flotation. The flotation diagram appears as Fig 6.1.

SEPARATION OF ILMENITE AND CHLORITE

With a view to concentrating ilmenite from an ore containing chlorite, garnet and hornblende, Lyubimov and Shokhin¹ have studied the flotation properties of these minerals with tall oil collector. They found that the optimum pH for flotation was for ilmenite 5.0 to 6.5, for garnet 3.5 to 5.0 and for chlorite 6.0 to 7.0. As would be expected from the properties of hornblendes, determined at Warren Spring Laboratory and reported in Chapter 5, no flotation of this was found at any pH with the tall oil collector.

Other Russian workers² have made an extensive study of the surface properties of ilmenite and chlorite and have found considerable differences between mineral samples derived from a number of ore bodies. They suggest that these differences may be related to minute variations in the surface layers and show that they disappear when the minerals are treated with 5 per cent sulphuric acid followed by water washing. Flotation recoveries using tall oil collector after this acid treatment show an increase for the ilmenite and a decrease for

the chlorite from 44 per cent down to 12 per cent. Although sodium fluoride modifier was adsorbed equally by both minerals its effect on the adsorption of the anionic collector sodium tridecylate was quite different, with reduced adsorption occurring on ilmenite but no change being observed with chlorite. Subsequent flotation experiments reflected these results to a limited extent in that although fluoride did not depress ilmenite it did in fact activate chlorite. Again this is verified by work carried out at Warren Spring Laboratory where the fluoride ion was shown to activate chlorite when using anionic collectors. Conversely the Russian workers found that sodium silicofluoride had little or no effect on the ilmenite flotation but acted as a strong depressant for chlorite in mildly alkaline conditions.

SEPARATION OF CHLORITE AND SERICITE FROM SULPHIDE ORES

A comprehensive investigation of the flotation properties of chlorite with sericite (a variety of muscovite) has been made by Abramov^{3,4} who has shown sodium oleate to be a superior collector to the alkyl sulphate. Both minerals studied floated within the pH range 4.5 to 12.0, with maximum flotation being favoured below pH 7.0. (c.f. pH 6.0 to 7.0 quoted above²).

The effects of sodium silicate, hexametaphosphate, and fluorosilicate as well as such colloids as starch and carboxymethylcellulose have also been investigated using cationic collectors and the anionic collectors referred to in the previous publication⁴. No results have been quoted for specific effects of these modifiers on the two minerals but each was found to be depressed in the pH range 2.7 to 7.5 when using the anionic collectors. Again this confirms substantially the results obtained above² with sodium silicofluoride. The depressant action of the same modifiers with the cationic collectors dodecyl acetate and tetradecyltrimethylammonium chloride was only observed when used at very high concentrations. Abramov concludes that in order to obtain good quality concentrates of metals from ores containing sericite and chlorite, these minerals either have to be removed as a preliminary concentrate, or they must be refloatated from a bulk concentrate whilst depressing the valuable constituents.

The latter approach has been successfully accomplished by Kudryakova⁶, who, by conditioning a bulk sulphide concentrate for five minutes with sodium sulphide, removed the chlorite and sericite to leave a bulk sulphide tailings product containing copper, lead, zinc and iron. He showed that the sodium sulphide had the effect of desorbing xanthate from the sulphide minerals whilst leaving sufficient on the silicate surfaces to enable refloatation to be carried out.

The similarities in the properties of the various mica minerals is so marked that a somewhat different approach has been adopted in this Section in describing their flotation behaviour. Many of the references found in the literature survey did not name the mica type studied so these have been only briefly described in this introduction. The two mica minerals studied at Warren Spring Laboratory, lepidolite and muscovite behaved in such a similar manner that none of the other major micas have been included in the experimental work. Details of the flotation of biotite are, however, given as this mineral is widely reported upon in the literature.

Comparisons between the behaviour of various micas have only been made by a few authors. Kakorin⁷, for example studied the flotation properties of the ANP cationic collector of the group; biotite, margarite, muscovite, and lepidolite. He found that all of these micas had two flotation maxima, one under strongly acid conditions between pH 1.5 and 3.0, and another under alkaline conditions of pH 10.0 to 11.0. (This rather unusual aspect is further discussed in Section 6.2.1 dealing with biotite.) The effects of various multivalent cations on the flotation of margarite and muscovite was further studied by this author. It was shown that, despite the presence of many divalent cations, the floatability of these two minerals remained unchanged over the whole pH range; in the presence of ferric or aluminium cations under alkaline conditions, muscovite was depressed whilst floating margarite. Some depression of margarite could also be achieved after the addition of ferrous ions under these conditions. Norman and O'Meara⁸ found that biotite was slightly less floatable than muscovite when using an amine collector in the presence of aluminium cations under acid conditions. The difference became more pronounced in the cleaning circuits where, in spite of the addition of further collector, very much more biotite remained in the tailing product. This order of flotation is somewhat surprising in view of the results obtained by Mackintosh and Lewis⁹ who, when measuring the rate of displacement of potassium ions on mica surfaces by dodecylamine hydrochloride, found this to increase in the order, lepidolite, muscovite, phlogopite, biotite. In various American patents on mica flotation the use of petroleum sulphonate¹⁰, sodium resinate^{11,12}, naphthenic acids¹², fatty acids¹², and a mixture of both anionic and cationic collectors¹³ is claimed. One also describes the use of alkaline earth salts as activators for soap flotation¹².

Michell¹⁴ has described the separation of micas from other silicate minerals by using either anionic or cationic collectors. With the former either lead nitrate or alkaline earth salts were added as activators, alkaline resinates being shown to act as the best collectors. Cationic flotation of mica was carried out by this author using short-chain amines as collectors in an acid circuit in conjunction with aluminium sulphate to depress the other silicate minerals present. A similar flotation circuit is described by Ralston^{15,16} who used starvation quantities of dodecylamine with the aluminium sulphate to separate micas from feldspar and quartz.

Tallow amine acetate collector was used by Bhappu and Fuerstenau¹⁷ to float micas from beryl-containing pegmatites. At a pH of 2.5 the collector addition for optimum flotation was found to be just over 300 g/t. This collector is also recommended in a patent¹⁸ for the removal of mica from a mixed spodumene/mica concentrate. Here pine oil was also added as a frother and the range of pH suggested was from 3.0 to 5.0. A similar separation has been referred to in Chapter 4 where between 25 and 50 g/t of cationic collector in acid medium was used¹⁹. Tallow amine acetate was again used by Eddy²⁰ and his co-workers but this time at a concentration of 250 g/t and in combination with 230 g/t kerosene and 60 g/t methyl isobutanol frother. The addition of 1 kg/t sulphuric acid reduced the pH value to 2.2 for this flotation.

A Russian study²¹ of pegmatite flotation describes a preliminary separation of iron-containing minerals with an anionic collector under neutral or weakly alkaline conditions followed by mica flotation in acid circuit using IM 11, or at pH 5.0 using ANP collectors.

By very careful control of pH, Bring²² has succeeded in separating apatite, haematite and mica by using oleic acid together with sodium silicate modifier. Under the conditions described haematite floated between pH 5.0 and 6.0, apatite between pH 7.0 and 9.0, and mica between pH 10.0 and 11.0.

The adsorption of C-14 labelled dodecylamine on a number of silicate minerals and the resultant froth flotation properties has been studied by Yanis²³. He showed that, with biotite, two flotation optima existed with this collector, one under very acid conditions and the other under mildly alkaline conditions. When studying the effects of various modifiers he also found that both sodium fluoride and calcium salts activated this flotation. The addition of iron or aluminium salts, however, was found to decrease the collector adsorption and depress flotation. The modifying effects of calcium and iron salts confirmed earlier work carried out by other Russian workers²⁴ which had shown that calcium activation of biotite increased the subsequent amine adsorption. These earlier workers also suggested that the iron salts depressed biotite by increasing the positive surface charge but did not explain why the same effect is not caused by calcium ions.

This existence of two flotation maxima is not confirmed in the results of work by Cases²⁵ who showed that the maximum recovery of biotite with amine collectors was obtained at all pH values above 4.0, this dropping to less than 10 per cent below pH 1.0. The disparity between the work of Yanis and that of Cases is probably explained in a recent publication by Koibash and Rukosueva²⁶. These authors have shown that the flotation of biotite is dependant upon the extent of weathering that has occurred so that when using the cationic collector ANP 14 the highly weathered mineral was floated with a maximum at pH 1.0 and the unweathered part with a maximum at pH 7.0. It was postulated that during the weathering of this mica, potassium, magnesium, and aluminium ions were replaced by both ferrous and ferric ions to such an extent that $[\text{FeO}_4]^{-5}$ tetrahedra are formed within the mica structure. In highly acid conditions these tetrahedra in the exposed layers dissolve to leave chemically active centres on which the collector cations are adsorbed. This postulate was confirmed by infra-red analysis of the biotite flotation products.

Later work published by Cases²⁷ showed that biotite floated well with dodecylammonium chloride over the pH range 3.0 to 10.0 but recoveries dropped to 15 per cent at pH 1.0. With the anionic collector sodium dodecyl sulphate no flotation occurred over the pH range tested from 0.5 to 10.0. This confirms that the mineral samples used by that author are not contaminated by iron to an extent which would have caused anionic activation under mildly acidic or basic conditions. Other Russian works have found it necessary to add depressants such as sodium fluorosilicate²⁸ or pyrogallol²⁹ in order to prevent biotite flotation with anionic-type collectors.

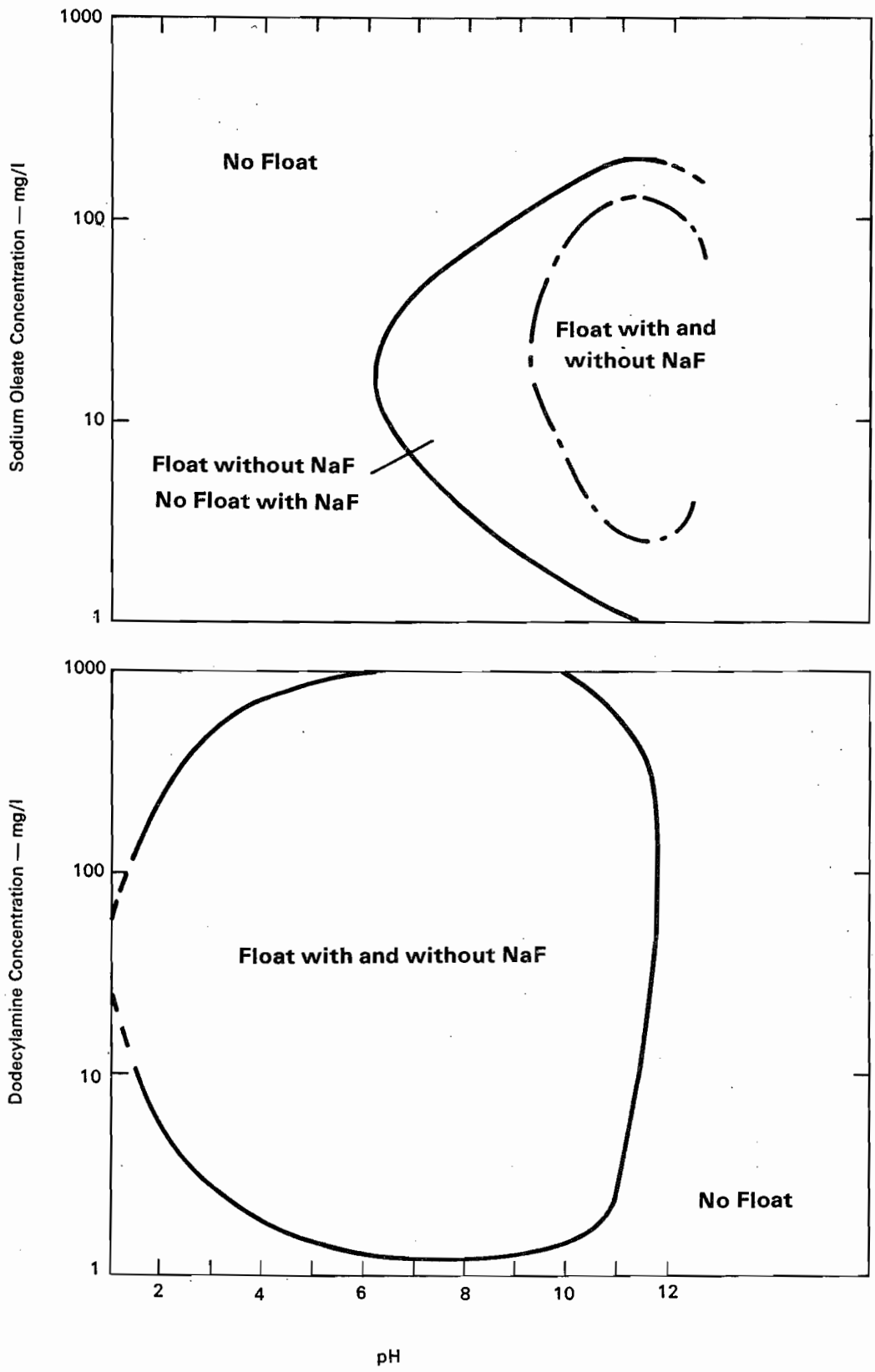


Fig 6.2.2 Lepidolite

6.2.2

Lepidolite

COMPOSITION $K_2(Li,Al)_6 [Si_6 Al_2 O_{20}] (OH,F)_4$, lithium mica.

PHYSICAL PROPERTIES

Hardness 2.5 to 4. Specific gravity 2.8 to 3.2. Colourless, pink or violet monoclinic crystals. Occurs as both cleavable plates and as massive granular material.

CHEMISTRY

The pure mineral is attacked but not decomposed by acids. The inter-layer potassium is capable of ion exchange which as with other micas, frequently occurs with iron salts. This can lead to anionic activation of the mica and could, under acid leaching conditions lead to activation of other minerals in a flotation pulp.

FLOTATION CHARACTERISTICS

Lepidolite has a massive flotation area with the cationic collector dodecylamine, which starts at very low collector concentrations and extends over the pH range from below 2.0 to above pH 11.0. The anionic flotation area is typical of that obtained when cation activation has taken place, with sodium fluoride causing depression probably by reaction with these cation sites and making them unavailable to collector ions. The flotation diagram appears as Fig 6.2.2.

LABORATORY FLOTATION TESTS

The Korean geological survey has made a study of a lepidolite ore from their Ulchin mine. The head ore consists of 1.7 per cent lithia in a quartz/feldspar gangue which also contains some calcite and muscovite.

In the initial tests³⁰ the run-of-mine ore was ground, with the addition of 1 kg/t soda ash, to minus 208 μ m and then deslimed at 30 μ m. This pulp was then conditioned for 10 minutes with 60 g/t dodecylamine acetate and floated at neutral pH to give a rougher concentrate. This was cleaned twice under either neutral or acid conditions in an attempt to improve the product grade. When operating under the neutral conditions a concentrate containing 2.5 per cent lithia was obtained with a recovery of 67 per cent. (Lepidolite analyses may vary³¹, for the pure mineral, between 3.3 and 7 per cent Li_2O). Although

recovery dropped to 63 per cent when the acid cleaning circuit was used, the grade increased to 2.9 per cent lithia.

In the second series of tests³² on this ore which were carried out to determine optimum grinding conditions, only the neutral cleaning circuit was used. Three tests were made in this series after grinding to minus 290 μm , 208 μm and 147 μm with, this time, 0.5 kg/t soda ash. As in the previous tests, each of these samples was deslimed at 30 μm or floated at neutral pH, although the collector addition on this occasion had been increased to 80 g/t. The results obtained after two cleaning stages are given in Table 6.2.2.1.

Table 6.2.2.1 Variation of Lepidolite Grade and Recovery with Size of Grind

Size of grind μm	Weight of concentrate %	Concentrate grade %Li ₂ O	Recovery %
290	45.5	2.7	68.3
208	52.6	2.8	78.5
147	56.7	2.8	83.9

In the first test, over 35 per cent of the head weight had been discarded as a slime containing only 15 per cent of the lithia. The results of the second series of tests suggest that by careful grinding and sizing, a product containing at least 2.5 per cent lithia could be obtained without the use of the flotation stage. This, however, was not the case in an extensive investigation carried out by Madhavan, Viswanathan, and Majumdar³³ on an ore containing 1.2 per cent lithia.

Of various cationic collectors tested by these authors under acid conditions, Armac 16D (hexadecyl amine acetate) proved to be the most satisfactory. Maximum grades and recoveries were obtained with this at about pH 3.5. When the effect of pulp density on lepidolite flotation was studied, these authors found that although grades of 5 per cent lithia could be obtained at low pulp density, the recoveries were only in the 70 per cent range. By increasing the pulp density, recovery was also increased to over 90 per cent with a grade of 4.65 per cent lithia on the cleaned product, or 99 per cent recovery at 4.5 per cent grade on the uncleaned product. Final conditions used to obtain these concentrates were as follows: grind to liberation size, condition 5 minutes with 1.5 kg/t Armac 16D, and float at pH 3.4 at 23 per cent solids. The success of this flotation system is somewhat surprising as the main gangue constituents were quartz and feldspar, both of which would be expected also to float readily at this pH using such a large quantity of cationic collector. A second set of tests, however, was carried out by the same authors on a hand-picked lepidolite concentrate containing 9.5 per cent quartz and feldspar and assaying 2.7 per cent lithia. This was again upgraded by

flotation with the same collector at pH 3.5 to give a 95 per cent recovery with a 3.05 per cent grade. The lower grade obtained from this second series of tests is claimed to be due to the lower lithium content of the lepidolite mica in that ore sample.

Work at the South African National Institute of Metals³⁴ on a dump material containing lepidolite, muscovite, quartz and feldspar has produced a concentrate of 3.4 per cent lithia from a head material assaying 1.75 per cent using an electrostatic separator. Subsequent flotation tests were made after grinding the feed material to 200 μm and desliming. With a cationic collector in acid circuit or a cationic collector in conjunction with a fatty acid in an alkaline circuit, very low yields were obtained. However, when a mixed amine/petroleum sulphonate collector system was used at pH 9.0, grades from 3.6 to 3.8 per cent were obtained with recoveries near to 80 per cent.

Polkin³⁵ claims that a bulk mica concentrate consisting of muscovite and lepidolite, obtained by cationic flotation at pH 4.0, may be separated. The concentrate is first conditioned with 350 g/t hydrofluoric acid and then refloated with oleic acid at pH 8.0 after a washing stage to remove excess acid. Under these conditions it is claimed that the muscovite is concentrated as a froth product leaving the lepidolite in the tailings. This de-activation of lepidolite by fluoride at pH 8.0 is in agreement with the results obtained on this mineral at Warren Spring Laboratory, but flotation of muscovite under the same conditions would not appear to be likely. However the flotation of all micas with anionic collectors almost certainly depends on cation activation and results obtained by different workers will consequently vary greatly with both the extent of cation exchange that has taken place in the ore body as well as the cation environment in the flotation cell.

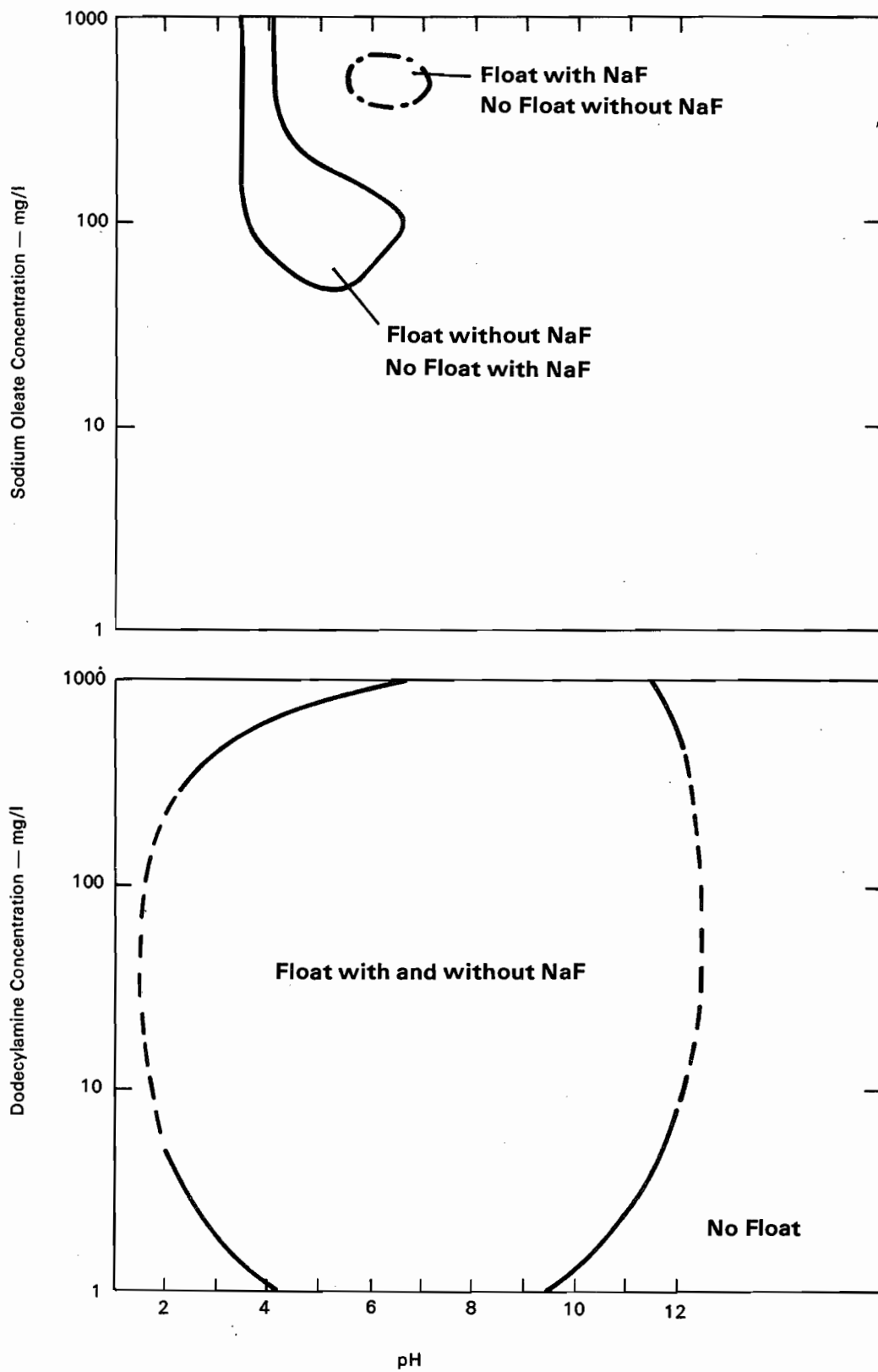


Fig 6.2.3 Muscovite

6.2.3

Muscovite

COMPOSITION $K Al_2 [AlSi_3 O_{10}] (OH,F)_2$, potassium mica

PHYSICAL PROPERTIES

Hardness 2 to 3. Specific gravity 2.7 to 3.0. White, light brown or yellow monoclinic crystals. z.p.c. 0.95³⁶.

CHEMISTRY

The pure mineral is insoluble in acids. Ion exchange frequently occurs with the interlayer potassium so that, under acid conditions, muscovite could yield cations and cause activation of other minerals in a flotation pulp.

FLOTATION CHARACTERISTICS

The cationic flotation area of muscovite is very similar to lepidolite, the other mica mineral studied at Warren Spring Laboratory. Flotation starts at very low collector concentrations and extends from below pH 2.0 to above pH 12.0.

The small area of flotation found with the anionic collector, oleic acid, is typical of the type found when activating cations are present and is almost certainly due to this cause. The flotation diagram appears as Fig 6.2.3.

PRACTICAL FLOTATION SYSTEMS

A major contribution to the knowledge of muscovite flotation processes over the past 8 to 10 years has been made by Browning and his co-workers at the US Bureau of Mines. They have developed two flotation processes through laboratory experimentation and pilot-scale tests up to full-scale commercial plant operation.

The first of these techniques uses cationic collectors under acid conditions. For example,³⁷ an ore from Alabama which contained 16.5 per cent muscovite, 77 per cent quartz, 4.5 per cent kaolin, together with minor amounts of limonite, garnet etc was ground to 590 μm size and deslimed at 53 μm . After reducing the pH by adding 0.7 kg/t sulphuric acid, the pulp was conditioned at 40 per cent solids with 200 g/t kerosene and 140 g/t coco-amine acetate. Flotation was carried out between pH 4.0 and 4.5 and, after cleaning the rougher concentrate three times, a grade of 98 per cent with a recovery of 96 per cent on the deslimed material was achieved. Similar grades and recoveries

were also obtained on a pilot-scale study. In another series of tests³⁸ on a Californian mica ore containing 43 per cent muscovite, the deslimed ore was conditioned with the same quantity of sulphuric acid but on this occasion the kerosene was replaced by 0.5 kg/t No 5 fuel oil and the rougher float carried out at pH 3.9 using 250 g/t tallow amine acetate collector. The results of this test were inferior to the previous one with a 92 per cent grade at an overall recovery of 63 per cent.

The final acid-cationic circuit developed involved grinding the ore with 0.75 kg/t sodium hydroxide, hydrocycloning to remove the minus 75 μm slimes and then conditioning with sulphuric acid as before. The flotation was carried out, using only 150 g/t of a mixture of stearyl and oleyl amines, at pH 4.0. Grades of 98 per cent with recoveries of 62 per cent were obtained after the three-stage cleaning process.

The use of a combination of anionic and cationic collectors under alkaline conditions is the basis of the second of the techniques tested by Browning³⁹. One ore tested under continuous plant conditions was that from Alabama, the analysis of which is given above. This was conditioned for 7 minutes with 350 g/t sodium silicate at a pH of 9.8 adjusted by adding 1 kg/t of sodium carbonate. A second conditioning over a similar period was then carried out with 400 g/t oleic acid or a mixture of this with linoleic acid. Finally 150 g/t tallow amine acetate was added and the flotation carried out at pH 9.7, gave an 84 per cent recovery with a concentrate grade of 98 per cent after three recleaning stages. In order to obtain similar results with a North Carolina ore which contained 13.5 per cent muscovite, 70 per cent quartz and 10.5 per cent kaolin together with other minor minerals, the tallow amine acetate addition had to be increased to 200 g/t. With little to choose between the products obtained from the two methods of treatment of the Alabama ore, the fatty acid cationic flotation system was tested on the Californian ore³⁸. This time the first conditioning time was reduced to five minutes duration and the sodium silicate addition increased to 450 g/t. A little less than that quantity of the fatty acid mixture was then added and, after a further five minutes, 230 g/t tallow amine acetate. The flotation in this case yielded a 96.5 per cent grade product with 70 per cent recovery. Both grade and recovery were thus improved on that obtained previously when using the acid amine flotation system on this ore, although part of the gain in recovery was due to an additional scavenging stage when a further 70 g/t amine collector was added.

A further improvement in the mixed-collector alkaline flotation of muscovite was shown in some testwork⁴⁰ carried out on a Georgian pegmatite. This mineral contained 15 per cent muscovite, 73 per cent quartz, 8.5 per cent clay minerals, 2 per cent biotite and 1.5 per cent limonite. Stage grinding of this ore took place in tap water with the addition of 0.7 kg/t sodium hydroxide added to disperse the clay slimes. These were removed before conditioning the sands with 1 kg/t calcium lignin sulphonate at a pH of 9.2 obtained by adding an equal quantity of calcium carbonate. The collector

combination again was a mixture of oleic and linoleic acids, added at a dose rate of 350 g/t with 5 minutes conditioning time, followed by 200 g/t of the amine. Continuous pilot-plant tests showed that slightly superior results could be obtained by the use of calcium lignin sulphonate rather than sodium silicate in the first conditioning stage. This system of conditioning with lignin sulphonate, then with mixed fatty acids and finally floating with amine collectors at an alkaline pH has also been tested on the Alabama mica sample⁴¹.

A summary⁴² of the final test results has been published outlining the various successful circuits developed and comparing the alkaline mixed anionic/cationic system with the acid cationic system. A summary of the advantages and disadvantages of the two methods as given by Browning is reproduced in Table 6.2.3.1. It is a credit to this research team that both flotation processes developed by them are currently being operated on a commercial scale by the United States mica industry.

Table 6.2.3.1* Comparison of the Two Mica Flotation Processes Developed by USBM

Alkaline (anionic + cationic)		Acid (cationic)	
1	Does not require acid-proof equipment	1	Requires acid-proof equipment
2	Recovers mica from ore-pulps containing slimes	2	Will not tolerate slimes
3	Depresses limonite and biotite	3	Does not effectively depress limonite and biotite
4	Will float finer-size material than acid circuit	4	Will float coarser-size material than alkaline circuit
5	When coarse mica is recovered by differential grinding and screening prior to alkaline flotation, the coarse mica is not coated with reagents	5	Requires more desliming equipment than alkaline circuit, thus increasing operating costs, and losses in fine mica
6	Overall recovery is higher because a large percentage of mica is subject to recovery by screening and flotation		

Other collectors used for muscovite flotation under acid conditions include Azamine F 10A (ref 43), which is a mixture of amine with pine oil frother, and the Russian reagent ANP (ref 44). The latter, which is a mixture of amines of chain length C₇ to C₉, produced from naphthenic acids, was shown to float muscovite from pH 2.5 to 10.5 and thus compares favourably with dodecylamine and IM 11 reagent.

*From Browning, J.S. Mica Process Development, *Trans Soc Min Engrs, (AIME)* 1970, 247(3), 269-273.

Yampol'skaya and Polkin have investigated the separation of muscovite, fluorite and the beryllium orthosilicate phenacite. They showed⁴⁵ that the adsorption of cationic collectors such as dodecylamine and ANP 14 decreased in the order muscovite, fluorite, phenacite and that although the maximum adsorption occurred on these minerals at pH 9.0 to 10.0, the maximum flotation took place between pH 3.0 and 7.0. The separation of muscovite and phenacite with these collectors was, however, found⁴⁶ to be optimum under neutral or slightly acid conditions. Using low concentrations of the anionic collector oleic acid⁴⁷, the phenacite floated well with a maximum recovery of 85 per cent between pH 5.0 and 7.0, and the fluorite with a maximum of 95 per cent between pH 6.0 and 12.0. Under the same conditions the muscovite remained in the tailings product. With this collector it was also shown that sodium silicate depressed all three minerals, sodium sulphide depressed the phenacite but activated the fluorite, calcium chloride had a greater depressant effect on the phenacite and aluminium chloride had a greater depressant effect on the fluorite.

Wyman⁴⁸ has shown that with no modifiers present, muscovite floats most readily under alkaline conditions with cationic collectors, diamines giving the most favourable results. However, the recoveries obtained with primary amines were considerably improved by the addition of activators. Under acid conditions aluminium salts, fluoride, dextrin and citric acid caused activation, under neutral conditions iron salts, fluoride and citric acid were effective, and under alkaline conditions aluminium and dextrin were again useful activators.

Sericite The flotation properties of this mineral with particular reference to its separation from chlorite have been dealt with in Section 6.1 under chlorite flotation.

Zinnwaldite Dobias and his co-workers⁴⁹ have studied the flotation properties of this mica with both cationic and anionic collectors. They have shown that multivalent inorganic ions depress cationic flotation of this mineral but activate anionic flotation by promoting the bond between the negative surface of zinnwaldite and the collector ions. They also demonstrated that sulphuric acid and potassium hydroxide were the most suitable pH regulators for this mineral.

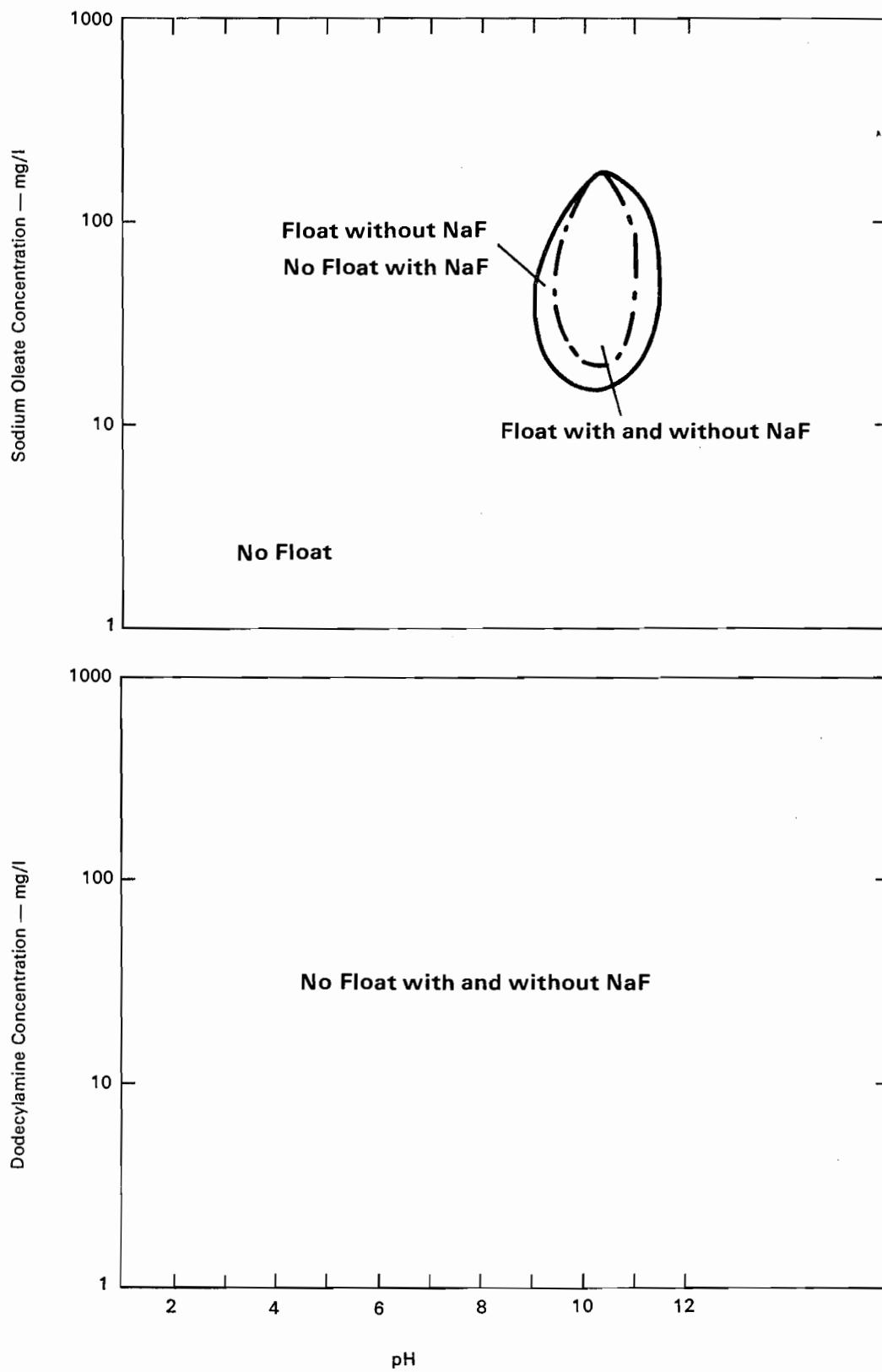


Fig 6.3 Serpentine

COMPOSITION $Mg_3 [Si_2O_5](OH)_4$, hydrated magnesium silicate.

PHYSICAL PROPERTIES

Hardness 2.5 to 4. Specific gravity 2.5 to 2.6. Shades of green, red, or yellow monoclinic crystals. Can also have a fibrous structure as in chrysotile.

CHEMISTRY

Readily attacked by acids to release magnesium ions, serpentine is capable of activating other minerals when using anionic collectors.

FLOTATION CHARACTERISTICS

The only area in which flotation of serpentine occurred lies between pH 9.0 and 11.5 when using the sodium oleate collector. This small area is typical of that obtained when metal-ion activation of anionic collectors occurs. Fluoride has a very small depressant effect most probably due to magnesium-fluoride complex formation making some cation sites unavailable for collector adsorption. The flotation diagram appears as Fig 6.3.

FUNDAMENTAL FLOTATION STUDIES

Indian workers⁵⁰ have shown that, at pH 5.0, a 40 per cent flotation recovery of serpentine can be obtained by using 1 kg/t cotton-seed collector. (This collector consists of 48 per cent linoleic, 23 per cent oleic and 23 per cent palmitic acids together with minor quantities of other saturated and unsaturated fatty acids.) Using additions of 1 kg/t barium chloride the serpentine could be activated and 75 per cent recoveries were obtained when using 2.5 kg/t collector. Although both collector and activator additions were shown to be optimum for the pH conditions tested, both appear to be rather excessive. By considering the anionic flotation area of serpentine derived at Warren Spring Laboratory, as well as the fact that barium salts are known to activate silicate minerals at alkaline pH values, it would appear that flotation at a pH between 9.0 and 12.0 should produce increased recoveries with less collector and very much less activator.

SEPARATION OF CHROMITE AND SERPENTINE

The main interest in the flotation properties of serpentine arises from the fact that it is a common accessory mineral of chromite (FeCr_2O_4).

A German patent⁵¹ of 1957 suggests the use of cationic collectors at pH values in excess of 9.0 to float not only serpentine but also other gangue silicates from chromite. Russian workers⁵² have also shown that the cationic collector ANP 14 at an addition of 0.9 kg/t gives an 80 per cent recovery of serpentine.

However, the same team tested a variety of anionic collectors in conjunction with some typical silicate depressants in an attempt to float the chromite from the serpentine. Of the depressants tested, sodium silicofluoride and a sulphited cellulose liquor were found to be the most effective and good chromite separations were achieved using either of these modifiers together with either tall oil or a still residue collector. Further work by Kurochkin⁵³ has confirmed the effectiveness of silicofluoride in depressing serpentine during anionic flotation of chromite. He has shown that the fluoride ion formed, attacks the serpentine, removing surface magnesium cations, this causing collector desorption. Alizarin Red S at a concentration of 0.25 kg/t has also been shown⁵⁰ to depress serpentine flotation with anionic collectors.

A detailed comparison of the flotation characteristics of chromite and serpentine has been made by Sagheer⁵⁴ who has shown that chromite floats very well over the pH range 3.0 to 11.0 with sodium oleate collector. Although serpentine was also shown to be rendered partially hydrophobic over the same pH range, a hundred-fold increase in collector concentration was necessary to produce similar results to those obtained with chromite. The effect of magnesium, calcium, and ferric ions on the flotation of both minerals was also determined and the importance of cations in solution when attempting to separate these two minerals was demonstrated. Each of the cations depressed the flotation of chromite but had little effect on the flotation of serpentine. Sodium fluoride and various phosphates were tested as agents to counter this effect without success. Of the metal-chelating compounds tested – oxalic, citric, salicylic and ethylene diamine tetra-acetic acids – only the sodium salt of EDTA was effective in partially restoring the flotation properties of chromite and even this had to be used at economically prohibitive dose levels.

In recent pilot-plant operations Malygin⁵⁵ and his co-workers have obtained a 92 to 96 per cent chromium recovery at a grade of over 85 per cent chromite (58% Cr_2O_3) from a mixed chromite/serpentine ore. The collector used was a distilled tall oil soap at a dosage of 1 kg/t together with 20 to 40 g/t of frother OP 7 or OP 8 (polyglycol esters). The addition of these non-ionic esters is claimed to have improved chromite recovery in hard water by up to 30 per cent.

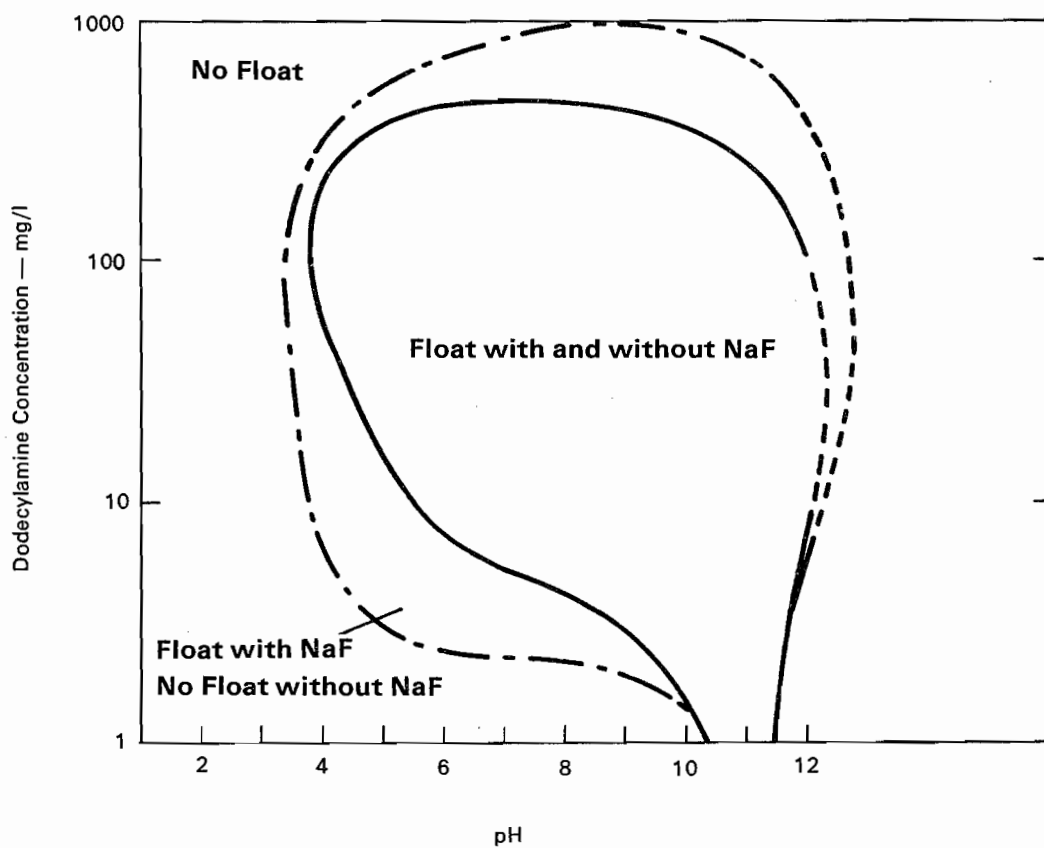
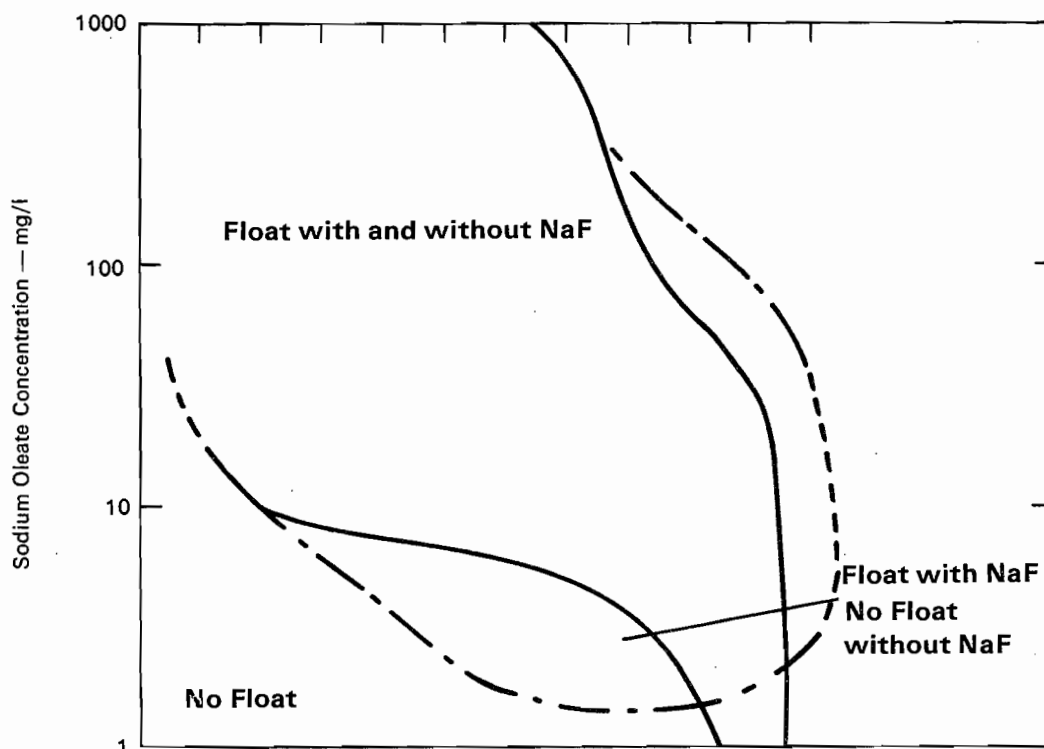


Fig 6.4 Talc

COMPOSITION $Mg_3 [Si_4 O_{10}] (OH)_2$, hydrated layer silicate of magnesium.

PHYSICAL PROPERTIES

Hardness 1. Specific gravity 2.6 to 2.8. White or pale green monoclinic crystals. *z.p.c.* 3.5⁵⁶.

CHEMISTRY

Unlike serpentine and chlorite the other hydrated layer silicates of magnesium, talc is insoluble in acids. However the natural hydrophobic character of the talc combined with its softness can frequently cause activation of other minerals by slime coating.

FLOTATION CHARACTERISTICS

The natural hydrophobicity of talc was demonstrated in the flotation diagrams of this mineral. Not only did fluoride cause activation when using either collector, but the area of flotation with both the anionic and the cationic collector were found to be very similar. The diagrams indicated that alkaline pH conditions are probably the most favourable for cationic flotation but that if the other minerals present make it necessary to work in an acid circuit then anionic collectors would be preferred. The flotation diagram appears as Fig 6.4.

FUNDAMENTAL FLOTATION STUDIES AND PRACTICAL FLOTATION SYSTEMS

Gottlieb⁵⁷ in the year 1943 summarized the main factors controlling the beneficiation of talc saying:

'Talc has an inherent floatability so great that it will be floated by any of the frothing or collecting agents ordinarily used. Consequently the only reagent necessary is a frothing agent to aid in bubble formation. Pine oil is excellent for this purpose. Other good frothers are cresylic acid and many of the alcohols. The amount of frother must be regulated because a deficiency permits loss of talc in the tailings and an excess tends to produce low-grade concentrates. Usually pine oil froths are voluminous and may be modified with kerosene for easier handling as well as increased carrying power. Proper balance of the two must be maintained.

'Many talcs contain accessory minerals that may be depressed automatically. Those that are carried over mechanically in the rougher flotation can be dropped by recleaning the froth. In other talcs, depression of the gangue minerals must be emphasized. Dispersion agents such as sodium silicate or some of the complex sodium phosphates are effective depressants when their need is indicated. The quantity used need not be as precisely controlled as the frother, as an excess does not depress the talc and the resulting change in pH does not affect the flotation. Talc floats readily with pine oil through the pH range of 5.0 to 12.0.

'The quantities of reagent necessary are small; two or three tenths of a pound of pine oil per ton of feed (100 to 150 g/t) is usually sufficient. An equal amount of kerosene will also suffice. If a depressant is used 2.0 lb of sodium silicate per ton (1 kg/t) would be a typical amount.

'Pulp densities in the flotation machine range as high as 25 per cent solids. A lower pulp density may give higher-grade concentration but, of course, at the expense of decreased plant capacity. The froth from the rougher flotation often required recleaning, the number of cleaners depending upon the quality of the feed and the product desired. Lower pulp densities in the cleaners than in the rougher cells are usually helpful. There is no escaping the fact that each deposit is an individual mineral dressing problem and must be treated as such.'

Not surprisingly, it has been shown⁵⁸ that a 40 per cent recovery of talc could be obtained with no collector addition at the natural pH of the pulp (8.2). This area of natural flotation of talc was found to exist under rather more alkaline conditions at Warren Spring Laboratory. An article by Ralston⁵⁹ published as long ago as 1937 pointed out that talc would float almost without collector addition but also added that it could contaminate the surfaces of other minerals rendering them floatable as well. Hence modifiers frequently become necessary to prevent flotation of gangue minerals.

Both pine oil and cresylic acid have been used by Polish workers⁶⁰ on a talc-chlorite ore, but only mediocre concentrates were obtained. However, recoveries exceeding 85 per cent were obtained from an Australian⁶¹ ore containing albite as the major gangue constituent together with minor quantities of apatite, rutile, pyrite and iron-containing minerals. Using pine oil with two cleaning operations a grade of more than 98 per cent was obtained. Similar grades were obtained with only one cleaning stage when Dupont B22 frother (a mixture of aliphatic alcohols and ketones) was employed. In both cases it was claimed that grades were limited by mechanical entrapment of gangue minerals.

Over 70 different reagents for floating talc from quartz, tremolite, or dolomite have been tested by various American workers^{62, 63} who classify them in four grades of collecting power: very powerful, powerful, weak and none. These authors differentiate

between foliated and fibrous talc types, and conclude that pine oil is the most suitable reagent for the former. For the flotation of the fibrous talcs amine-type reagents were preferred. Their tests further showed that quartz was depressed without the need for any additional reagent but both tremolite and dolomite required additional basic or acidic reagents in the cleaning stages. Sodium carbonate was found to be very effective in some cases if added to the grinding stage at a dosage of 1 kg/t. The amines found most selective for the talc/tremolite mixtures were di-n-butylamine and diamylamine. Michell⁶⁴ has also tested a number of reagents for talc flotation in a neutral circuit. Of those tested, he found that pine oil alone was sufficient to float foliated talcs but, in common with the previous authors, concluded that short-chain amines are preferable for the fibrous varieties.

Other collections used for talc flotation include sodium alkyl sulphates⁶⁵ in combination with sodium silicate as a slime dispersant, cotton-seed oil⁶⁶, and ⁶⁷ Du Pont reagent B23. The latter was claimed to produce a talc concentrate of commercial grade by floating at pH 7.0 to 8.0 and cleaning up to seven times, this treatment being preceded by desliming and magnetic separation.

The variation in flotation properties has been shown by Frommer and Fine⁶⁸ who were only able to obtain low-grade concentrates when using a variety of collectors. Better results were obtained by using a combination of collectors. For example 150 g/t petroleum sulphonate collector under acid conditions gave a product grade of 96 per cent after two cleaning stages in which 40 g/t of methyl amyl alcohol frother were added. Recovery under these conditions, however, was only just over 50 per cent. Similar results were obtained by these authors using 500 g/t sodium silicofluoride modifier with a mixed collector comprised of cresylic acid and tributyl amine in equal quantities added at a dose rate of 160 g/t. Again it was necessary to add small quantities of amine in the cleaning stages. Lidstrom⁵⁸ obtained a 70 per cent flotation recovery using only 50 g/t dodecylamine collector, but found that more than four times this quantity was necessary to achieve 100 per cent recoveries.

TALC-MAGNESITE SEPARATIONS

Clemmer and Cooke⁶⁹ have shown that talc can be floated from a magnesite gangue by using a frothing agent only. Pine oil, cresylic acid and a number of alcohols used in very small amounts were all found to be satisfactory, the main problem being to retain selectivity and prevent gangue flotation. Talc grades of up to 95 per cent were obtained with a recovery of 82 per cent by recleaning the rougher concentrate. Better selectivity could be obtained by using emulsions of pine oil with kerosine over the pH range 5.5 to 12.0. The addition of sodium silicate as a gangue depressant was also found to be advantageous.

Buckenham, Rogers and White⁷⁰ demonstrated the differences that exist between the flotation properties of talc and magnesite when using the collector Armeen 10D (mainly decylamine). Although the flotation areas of the two minerals coincided over the pH range 6.0 to 14.0, under acid conditions they showed that it was possible to float the talc only. With a collector concentration of 25 mg/l at pH 5.6 however, the recovery was only 71 per cent with a grade of 90 per cent. The use of pine oil collector was thus investigated. At an addition of 50 g/t and at the natural pH of the ore, 8.2, recoveries were increased to 88 per cent although only at an 82 per cent grade. By cleaning with no further addition of reagent, this could be increased to over 90 per cent although in this case the recovery fell to under 60 per cent. A concentrate grade of 98 per cent was obtained by multiple cleaning but under these conditions further recovery losses were experienced. The authors acknowledge that to attain good concentrate grades, recoveries are necessarily low but suggest that this may be improved by regrinding the combined cleaner tailings products and adding these back to the rougher circuit.

The head ore treated by Sheiko⁷¹ contained talc 40, magnesite 25, dolomite 10, serpentine 10, actinolite 10, and magnetite 5 per cent. A separation of between 90 and 95 per cent of the talc was accomplished by fine grinding to 70 μm size. The pH was lowered by adding 0.6 kg/t sulphuric acid and flotation carried out using 60 g/t pine oil. Further products were obtained by either floating the magnesite with an anionic collector or by removing the remaining silicate minerals with a cationic collector. Magnetite was removed by wet magnetic separation resulting in a magnesite product of between 75 and 80 per cent grade at around 60 per cent recovery. Other Russian workers⁷² have carried out a preliminary talc separation on a similar ore using olive oil collector at 60 g/t in the rougher and 20 g/t in the cleaner circuits.

An American⁷³ patent describes the use of pine oil to carry out a similar talc separation. Barium chloride is then added to the tailings product and the pH adjusted to 9.5. On adding 200 g/t oleic acid the magnesite is activated and may be floated to give a 50 per cent grade concentrate.

TALC-SULPHIDE SEPARATION

A preliminary removal of talc gangue from a copper-zinc-lead deposit was successfully carried out at Stirling mine⁷⁴ by grinding to 70 per cent less than 75 μm . After the addition of 400 g/t soda ash the pulp was diluted to 30 per cent solids and the talc floated with cresylic acid. This removal of most of the talc enabled a successful sulphide flotation to be subsequently carried out.

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