handbook of SILICATE FLOTATION

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PREFACE

World interest in the froth flotation properties of non-sulphide minerals has expanded considerably over the past decade. This interest stems from the increasing use of the so-called 'space age' metals – beryllium, lithium, titanium, zirconium, niobium etc – and from the growing need to recover economic minerals from lower grade but more widely distributed ores. In general these ores, in which the minerals exist as, or are associated with, complex silicates, do not respond to the concentration methods used in the past to treat higher-grade less complex mineral occurrences.

Since the formation of the Mineral Processing Division of Warren Spring Laboratory in 1959, the development of processes for the selective recovery of silicate minerals from their ores has been a continuing and important activity. Over the past six years Mr R M Manser of the physical-chemistry section of the Division has been investigating the basic froth flotation properties of these silicate minerals to provide a firmer foundation for applied studies and to assist other research investigations. The results of this work have been published in a number of Laboratory reports as well as in the scientific literature. During the course of these studies extensive contacts have been made with research workers in other countries and the world literature has been surveyed both for fundamental investigations and for practical applications of silicate flotation.

This handbook contains details of the practical work carried out at Warren Spring as well as the very considerable information gained from world-wide sources. Its aim is to provide the practical mineral processor, faced with a problem of separating a mixture of minerals, with a digest of the information available on each constituent, thus enabling him to carry out his test-work in a more systematic manner, and to assist him in controlling flotation plants.

I believe that this book will also provide a fund of background information for research workers operating in this area, containing as it does, a critical and comprehensive survey of world literature on silicate flotation.

The main sections of this book are devoted to the individual silicate minerals, grouped according to their structural class. The areas of flotation of each mineral with both cationic and anionic collectors that have been determined at this Laboratory are given, together with information on the influence of fluoride modifier. Fluoride in various forms (sodium fluoride, hydrofluoric acid, sodium silico-fluoride) is one of the most widely used modifiers in silicate flotation and certainly the most versatile.

The basic physical characteristics (density, hardness, z.p.c., solubility etc) are included and, where known, the fundamental flotation characteristics and practical flotation plant procedures for each mineral are described.

With past experience in mind, and as an engineer then deeply involved in the selective recovery and treatment of a variety of silicate minerals, a handbook such as this would have saved me many days and nights of bewildered anxiety and fruitless testwork resulting from lack of knowledge and resources and time to acquire it.

I have no doubt that others, similarly placed today, will be grateful to Mr R M Manser for the dedication and care which has gone into the preparation of this work.

A J Robinson
Director
Warren Spring Laboratory
Stevenage, Herts
November 1973

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INTRODUCTION

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1.1 GENERAL INTRODUCTION

Over twentyfive per cent of the earth's crust consists of silicon which is second in abundance only to oxygen. Its main occurence is as silica and the various silicates which are widely disseminated in nature. Generally, silicates respond poorly to gravity separation techniques and also present considerable problems of selectivity in froth flotation. The investigation of those basic physico-chemical properties of silicates which affect their flotation response would appear to offer good prospects of obtaining technically useful information, because in the flotation of low-grade ores which are now being more widely exploited, silicate minerals are encountered in increasing quantity and variety.

The usual physico-chemical approach has been to take a simple flotation system consisting of one or two minerals and to discuss in detail the surface chemistry of this system. While this method has provided considerable information on particular minerals, few generalized facts on silicate flotation have resulted.

The purpose of this book is to present the work that has been carried out at Warren Spring Laboratory on the flotation of silicate minerals and to discuss at the same time the research that has been carried out by others in this field. The author has attempted primarily to meet some of the needs of the practical mineral dresser but has also indicated the directions which fundamental research is taking. It is thus hoped that this information will be of use to all those that are involved with silicate flotation problems in the widest sense.

After a description of some of the practical techniques used in this Laboratory the main part of the book is devoted to the silicate minerals, each chapter dealing with groups of minerals with similar crystal structure. Each chapter is further sub-divided so that there is a section devoted to each mineral that has been investigated within that structural group.

In these sections the composition and physical properties are given and these are followed by any known information on the chemistry of that mineral that may affect its flotation properties or the flotation properties of other minerals that occur with it. The flotation characteristics with anionic and cationic collectors both in the presence and absence of the fluoride modifier are those determined at Warren Spring Laboratory using the vacuum flotation test technique. This is followed by a brief discussion of any fundamental studies that have been carried out on the mineral, and finally by a description of practical flotation systems. These practical systems may include laboratory batch-scale testwork, pilot-plant testwork or continuous full-scale production plant results. If particular separation problems have become apparent involving the silicate mineral under discussion, then these are highlighted individually. It will be seen that the sections on some of the minerals are short and terminate with the description of the flotation characteristics as determined at Warren Spring Laboratory. This indicates that the author is unaware of any other work that has been carried out on these species. Conversely the quantity of research and development that has been carried out on the flotation of some of the minerals included in this book is very great indeed. Notably, the work on beryl and quartz, if fully discussed, could well lead to separate books on each of these minerals. Here, the author has attempted to outline some of the main areas of research and particularly those that have a direct bearing on specific separation problems. It is suggested that the reader makes full use of the literature references given in these cases.

1.2 SILICATE STRUCTURE

The fundamental unit in all silicate structures is the orthosilicate ion $[SiO_4]^{-4}$. In this unit, four electrons are drawn from four oxygen atoms to the silicon Si^{+4} ion, the central silicon atom becomes neutral, and each oxygen atom takes on unit negative charge and is positioned tetrahedrally around the central silicon atom, as shown in Fig 1.2.1

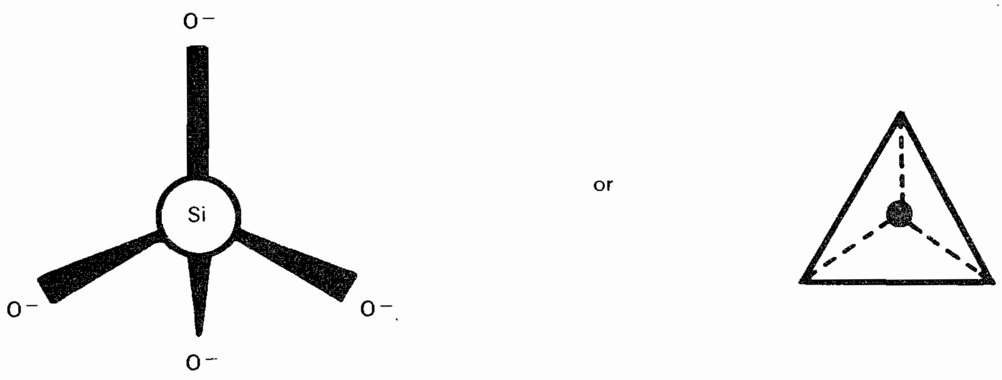


Fig 1.2.1 The orthosilicate ion

This tetrahedral arrangement is represented as shown with the oxygen atoms situated at the points of the tetrahedron which has been completed to show the geometry although no oxygen-oxygen linkage is present.

ORTHOSILICATES

The simplest of the silicates are known as orthosilicates where the $[SiO_4]^{-4}$ ions are independent and the negative charges on them are balanced by the positive charges of multivalent cations present in the lattice between the silicate ions. For example, in forsterite, $Mg_2[SiO_4]$, the $[SiO_4]^{-4}$ tetrahedra are arranged in parallel rows with Mg^{+2} ions interposed as shown in Fig 1.2.2.

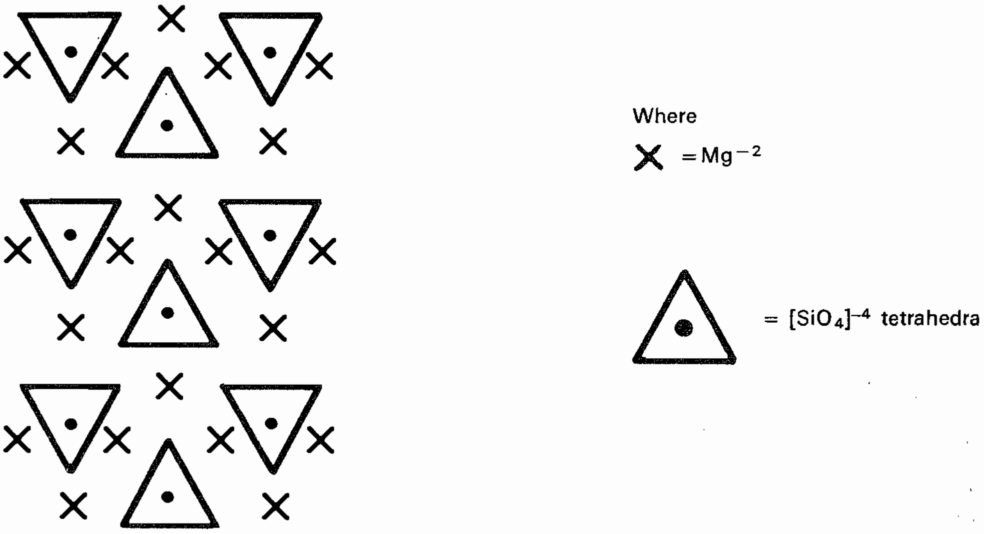
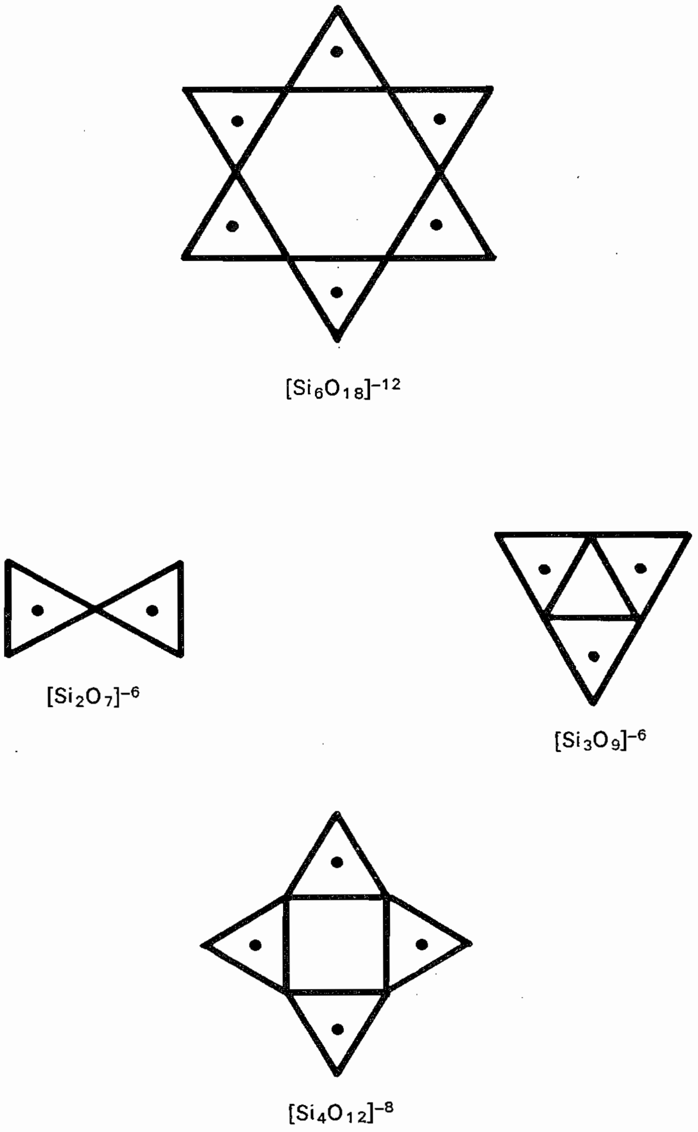


Fig 1.2.2 Orthosilicate structure

DISILICATES AND RING STRUCTURES

The more complex silicates are built from this fundamental orthosilicate $[SiO_4]^{-4}$ ion by silicon-oxygen-silicon (siloxan) bonding leaving a net negative charge on the complex ion. According to the complexity of the ion this negative charge is satisfied by either a simple cation or, in some cases, a complex ion having a net positive charge.



$[Si_6O_{18}]^{-12}$

$[Si_2O_7]^{-6}$

$[Si_3O_9]^{-6}$

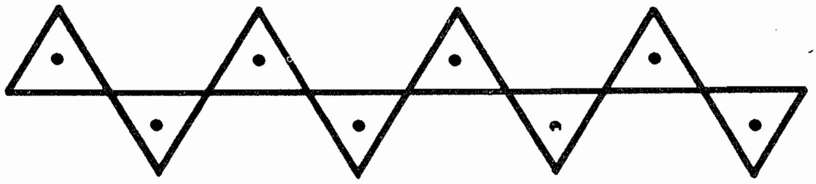
$[Si_4O_{12}]^{-8}$

Fig 1.2.3 Disilicate and ring structures

The structures shown in Fig 1.2.3 contain a finite number of silicate tetrahedra and form an intermediate between the orthosilicates and the macromolecules containing siloxan bonds extending infinitely in one, two or three dimensions.

METASILICATES OR PYROXENES

Metasilicates, or pyroxenes, contain single chains of silicate tetrahedra having an infinite length. The type illustrated in Fig 1.2.4 is a simple idealized structure but more complex examples are known to exist. These, however, lie outside a general treatment of silicate structure necessary for the purposes of this book.

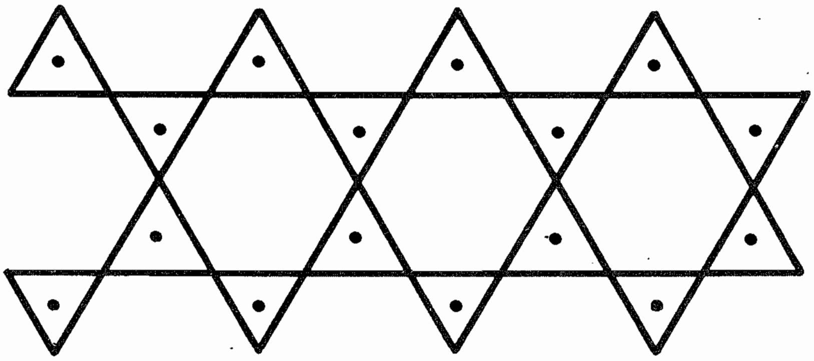


$[SiO_3]_n^{-2n}$

Fig 1.2.4 Metasilicate or Pyroxene structure

AMPHIBOLES

The combination of two pyroxene chains leads to a ribbon-like structure known as an amphibole or metatetrasilicate, illustrated in Fig 1.2.5.

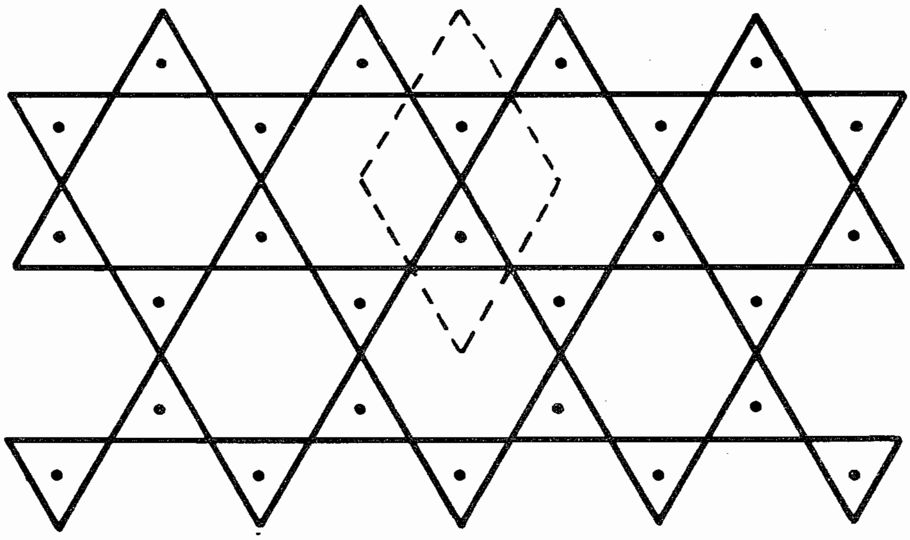


$[Si_4O_{11}]_n^{-6n}$

Fig 1.2.5 Amphibole or metatetrasilicate structure

SHEET SILICATE STRUCTURES

Sheets extending infinitely in two dimensions may be considered as being formed by the linking of many amphibole ribbons. The idealized structure is shown in Fig 1.2.6.



$[Si_2O_5]_n^{-2n}$

Fig 1.2.6 Sheet silicate structure

The basic unit shown with a dotted outline in the Fig 1.2.6 contains two silicon atoms in combination with three oxygen atoms and sharing a further four oxygen atoms with neighbouring units. This gives a total of 3 + 4 (½) = 5 oxygen atoms of which all but two are bridging oxygen atoms, and the net charge is thus minus 2. The unit may be written $[Si_2O_5]^{-2}$.

Although by definition all sheet silicates contain these infinite two-dimensional hexagonal networks, the minerals formed differ considerably according to the proportion of silicon that has been replaced by aluminium to give the sheet additional negative charge. The Si-O-Si (siloxan) bonds that bind the tetrahedra together are particularly strong and hence all of the minerals in this group tend to cleave along these sheets rather than across them to give the group its characteristic platelet form when crushed.

The simplest example of a mineral in this group containing no replacement of silicon by aluminium is serpentine, $Mg_3[Si_2O_5](OH)_4$. In this structure each sheet consists of one layer of silica tetrahedra with just one excess negative charge per unit that is neutralized by a 'brucite' type of layer as shown in Fig 1.2.7.

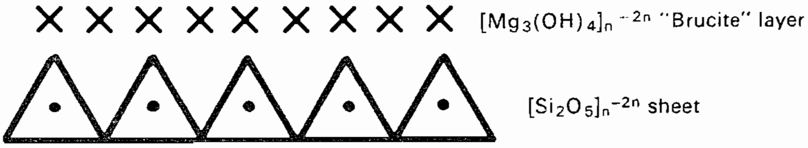


Fig 1.2.7 Serpentine structure

There is no valency linkage between one sheet and the next, so, being linked only by van der Waals forces, this mineral is very soft and when it shears it produces platelets that have no resultant surface charge.

The structure of the mineral talc, shown in Fig 1.2.8 is only slightly more complex than that of serpentine. With two less hydroxyl ions to each of the three magnesium ions, the brucite layer attains extra positive charge so that another hexagonal network of silica tetrahedra is added to the serpentine type of structure to give the crystal the sandwich construction shown. Once again there is no net charge on the sheets, which are held together only by van der Waals forces, so that the layers are capable of slipping easily over one another, this giving rise to the characteristic soft properties of talc.

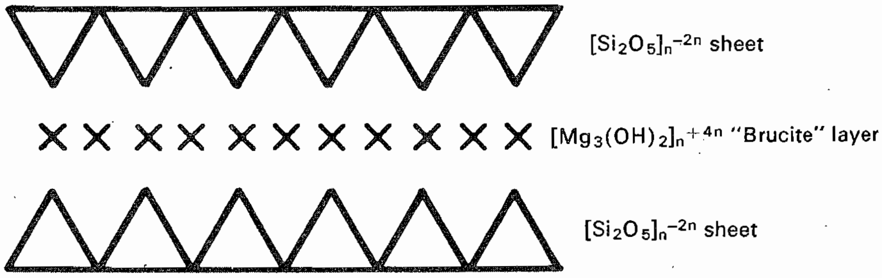


Fig 1.2.8 Talc structure

If one in every eight of the silicon ions $[Si]^{+4}$ in the hexagonal silica network is replaced by an aluminium ion $[Al]^{+3}$ then an extra unit charge on that sheet is created. This is the situation in the mica group of sheet silicate minerals. In this group the bases of the tetrahedra are symmetrically opposed so that two opposite hexagonal rings outline a large cavity into which a potassium (or sodium) atom is situated with twelve-fold co-ordination. Thus a mica may be regarded as a series of charged talc-like sandwiches connected by an alkali metal ion as illustrated in Fig 1.2.9. Cleavage in mica takes place between one double sheet and the next by breaking the weak bonds between the potassium (or sodium) ions and the oxygen atoms in the sheets. This alkali metal ion, once exposed, becomes extremely labile so that the exposed mica surface develops what is, in effect, a negative charge.

A further increase in the aluminium-to-silicon ratio in the silicate sheets creates sufficient charge density to accommodate rather more than the co-ordination type of linkage found between mica sheets. In the chlorite group of minerals the linkage between these sheets is another brucite layer in which one third of the magnesium ions has been replaced by aluminium ions to give a positively charged layer of composition $[Mg_2Al(OH)_6]^+$, as illustrated in Fig 1.2.10. The cleavage of these minerals involves breaking the bonds between the mica-type layers and the brucite layer, leaving alternately charged patches on the surfaces so created.

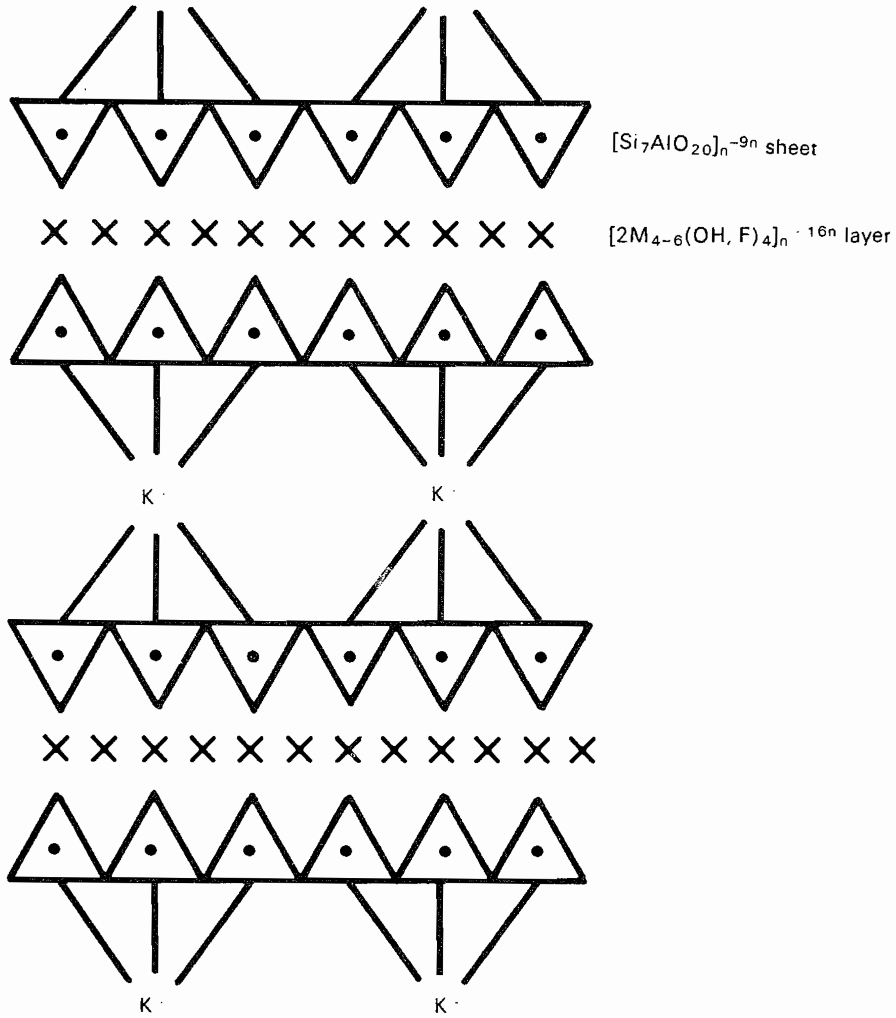


Fig 1.2.9 Mica structure

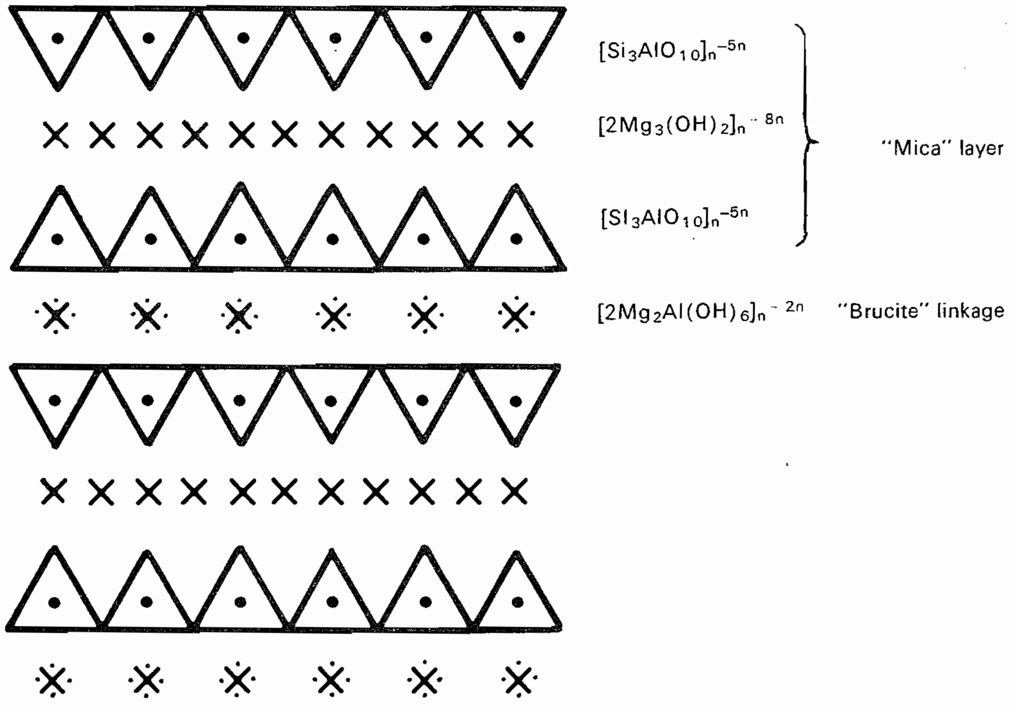


Fig 1.2.10 Chlorite structure

FRAMEWORK SILICATES

An extension of the $[SiO_4]^{-4}$ tetrahedra in three dimensions produces the macromolecule known as silica which is the simplest of the framework silicates. Fig 1.2.11 shows that each silicon atom is surrounded by four oxygen atoms, each of which is linked to another silicon atom.

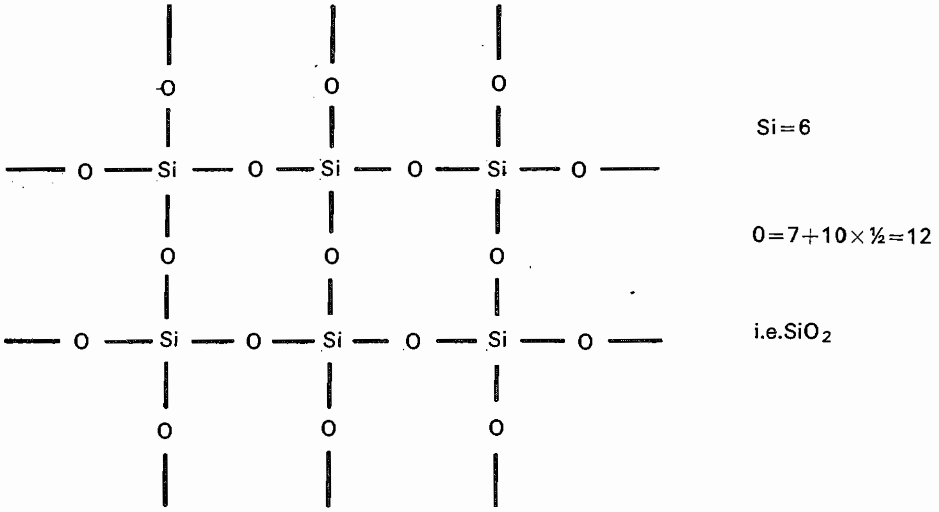


Fig 1.2.11 Framework silicate structure

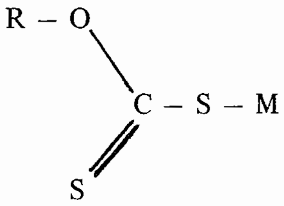
As in the sheet silicates, some of the silicon atoms may be replaced by aluminium atoms giving rise to a net negative charge. The replacement of approximately 25 per cent of silicon by aluminium and the introduction into the lattice of alkali metal ions gives rise to the feldspar minerals. If 50 per cent of the silicon is replaced by aluminium then a feldspathoid results.

1.3 FLOTATION REAGENTS

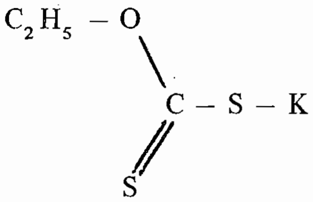
This section is only intended to be a simple introduction to the principal types of collector available for silicate flotation and to the general concept of modifier use. For more detailed accounts the reader is referred to the many excellent standard texts on the subject.

With a few notable exceptions – talc, sulphur, graphite– minerals are readily wetted by water and are said to be hydrophilic. The collector used in the froth flotation process has the purpose of altering the mineral/water interface in such a manner as to reverse this position. Thus the coated mineral now prefers an environment of air rather than water and it is said to have become hydrophobic or aerophilic.

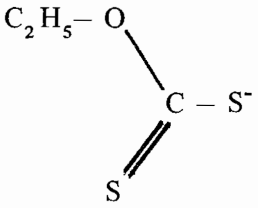
The requirements of a collector are that part of the molecule is in itself hydrophobic, whilst part will interact selectively with mineral surfaces. This interaction may be purely physical adsorption or a surface chemical reaction may take place, but commonly a combination of both processes is involved. When floating sulphide ore minerals the collector frequently used is a member of the xanthate group that have the general formula:



where M is an alkali metal ion usually potassium or sodium, and R is a non-polar group with the general formula C_nH_{2n+1} with a value of n between 2 and 7. For example when n = 2, M = potassium then the xanthate obtained is potassium ethyl xanthate:



which ionizes in solution to give the negatively charged xanthate radical:



This readily reacts with the metal sulphide surface to give a hydrophobic coating.

Oxide and silicate minerals are generally far more naturally hydrophilic than sulphide minerals. As a consequence, they require a collector that has a strongly hydrophobic character. This is achieved by using a collector that has a proportionally longer hydrocarbon chain in the molecule. The majority of collectors for this type of mineral may be classified into one of two groups. The first ionizes in solution to give a negatively charged radical and the second ionizes to give a positively charged radical. These are known respectively as anionic and cationic collectors.

ANIONIC COLLECTORS

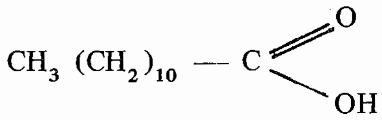
Anionic collectors have the general structure:

$$\mathrm{R — A}$$

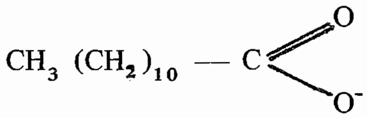
where R is a hydrocarbon chain containing eight or more carbon atoms and A is hydrogen or an alkali metal. This type of collector is partially or totally ionized in solution to give a negatively charged hydrophobic part and a hydrophilic residue:

$$\mathrm{R — A} \xrightarrow{\text{solution}} \mathrm{R^- + A^+}$$

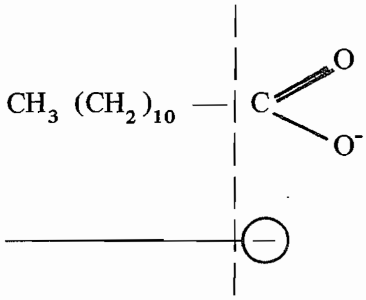
Simple examples in this group are the high molecular weight fatty acids of which lauric acid is typical:



This, being virtually insoluble in water, is either added to the flotation pulp as a soap (sodium laurate) which readily ionizes, or is used under alkaline pH conditions. The resultant situation in solution is the same, the following radical being formed:

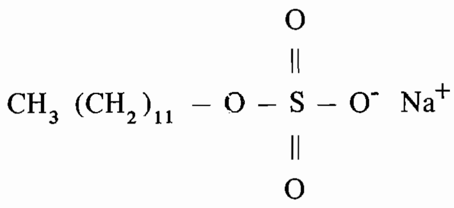


which may be regarded as a radical with a negatively charged 'head group' capable of reaction with the mineral surface, and a long hydrophobic 'tail' which will rapidly interact with air bubbles in a flotation froth. The anionic type of collector is frequently shown in texts as a tadpole with a negative head.



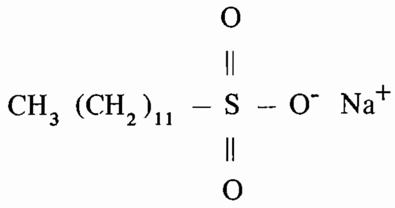
Among the anionic collectors that are commonly used in non-sulphide flotation practice are:

(a) sulphates – e.g. sodium dodecyl (lauryl) sulphate



$$CH_3\,(CH_2)_{11}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-\ Na^+$$

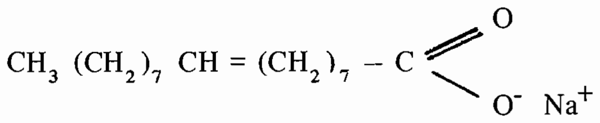
(b) sulphonates – e.g. sodium dodecyl sulphonate



$$CH_3\,(CH_2)_{11}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-\ Na^+$$

(c) unsaturated fatty acids

Unsaturated fatty acids have a deficiency of two or more hydrogen atoms in the hydrocarbon chain, which gives rise to one or more double bonds. The presence of a double bond affects the adsorption properties of a collector as well as making it more soluble in water. The most common example in this group is oleic acid, or its salt sodium oleate:



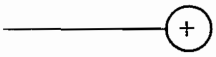
The closely related linoleic, linolenic and ricinoleic acids that frequently occur as minor constituents of the commercial oleic acids used in froth flotation are also used on their own for certain specific applications.

CATIONIC COLLECTORS

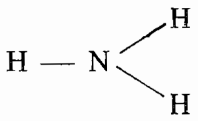
Cationic collectors have the general structure:

R — C

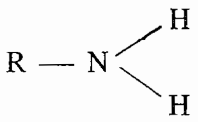
which ionize in solution in a manner similar to that described in the section dealing with anionic collectors (page 13). Cationic collectors give rise to a positively charged hydrophobic ion which is conveniently shown as a 'tadpole' with a positive head:



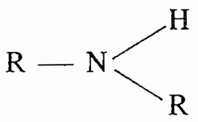
Most collectors in this group may be regarded as ammonia which has one or more of the hydrogen atoms replaced by a hydrocarbon chain. The extent of this replacement classifies them into groups:



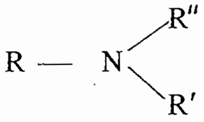
Ammonia



Primary amine

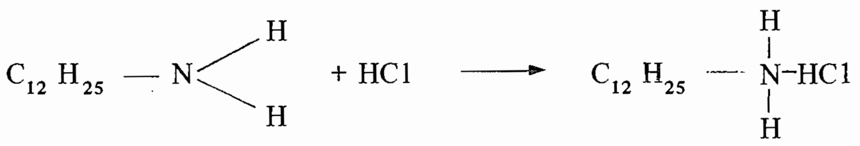


Secondary amine



Tertiary amine

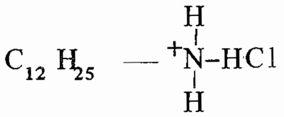
The most common type of cationic collecter used in froth flotation is the primary amine containing between 12 and 18 carbon atoms in the chain. Laurylamine (dodecylamine, $C_{12}H_{25}NH_2$) may be taken as a typical example of this group. Like the anionic collectors these are almost totally insoluble in water and are generally converted to the hydrochlorides or acetates before addition to the flotation circuit:



dodecylamine

dodecylamine hydrochloride

which ionizes to give:



$$C_{12}H_{25}-\overset{\displaystyle H}{\underset{\displaystyle H}{{}^{+}N}}-HCl$$

This reaction may be compared with:

$$NH_3 + HCl \longrightarrow NH_4Cl \longrightarrow NH_4^+ + Cl$$

Again, unsaturated hydrocarbon chains may also be present to increase the solubility of the higher molecular weight collectors. Secondary and tertiary amines are used when a greater surface activity is required and even quaternary salts, such as cetyl trimethyl ammonium bromide, have found some uses in certain specialized flotation circuits.

MODIFIERS

Because of the surface-collector reaction that occurs with sulphide minerals, these rarely present any difficulties in separation from their gangue. Non-sulphide minerals, however, frequently require surface modification before, during, or after addition of the collector. A surface modifier that increases the hydrophilic character of a mineral is known as a depressant, and one which increases the hydrophobic character an activator. Some materials may act as both activator and depressant depending on the conditions under which they are used. For example, the fluoride ion which is used as a modifier on each of the mineral species that are considered in this book, behaves as a depressant if used in conjunction with anionic collectors but as an activator if used in conjunction with cationic collectors.

Other depressants act by reducing or eliminating the adsorption of the collector on to the mineral surface, as well as, in some cases, increasing its hydrophilic character. To be effective a modifier of any type must be selective by accentuating differences between mineral species.

The most common inorganic modifiers include acids and alkalis for pH regulation; various multivalent cations, especially calcium and ferric ions; numerous anions of which fluoride, silicofluoride, sulphide, phosphate, chromate, cyanide and ferricyanide are among the most common.

Organic modifiers include various complexing agents such as the citrate ion but the largest group of organic modifiers are the colloids. This group contains, for example, various tannin products, especially quebracho; starch products derived from various sources and their degradation products such as dextrin, gums and glues.

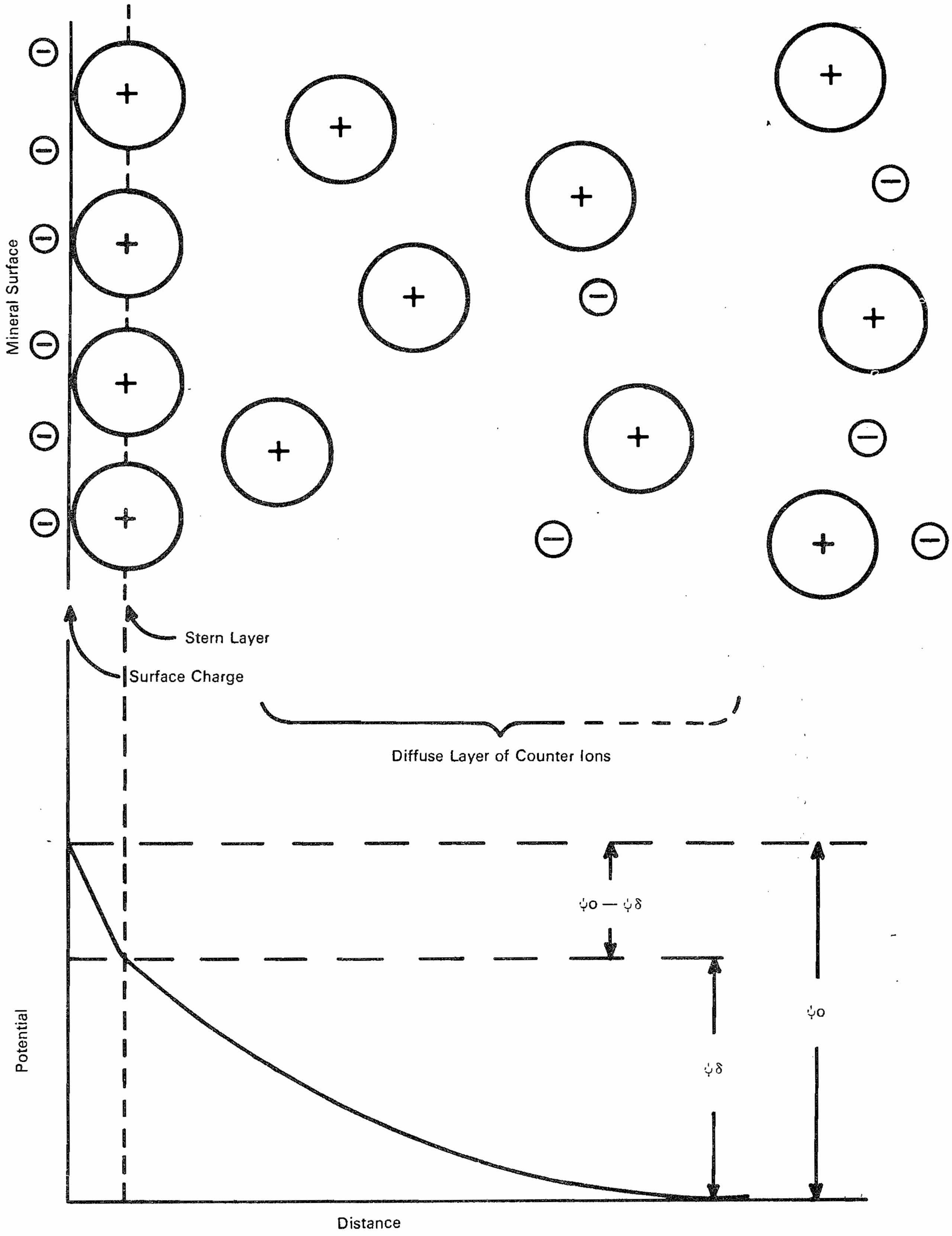


Fig 1.4.1 Diagram of Double Layer and Graph Showing the Potential Drop at a Mineral Surface

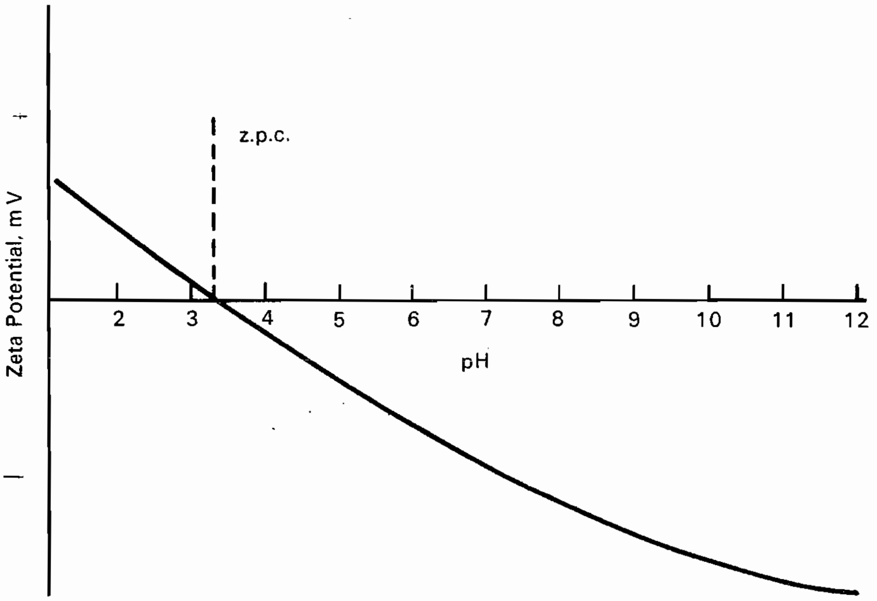


Fig 1.4.2 Effect of pH change on zeta potential

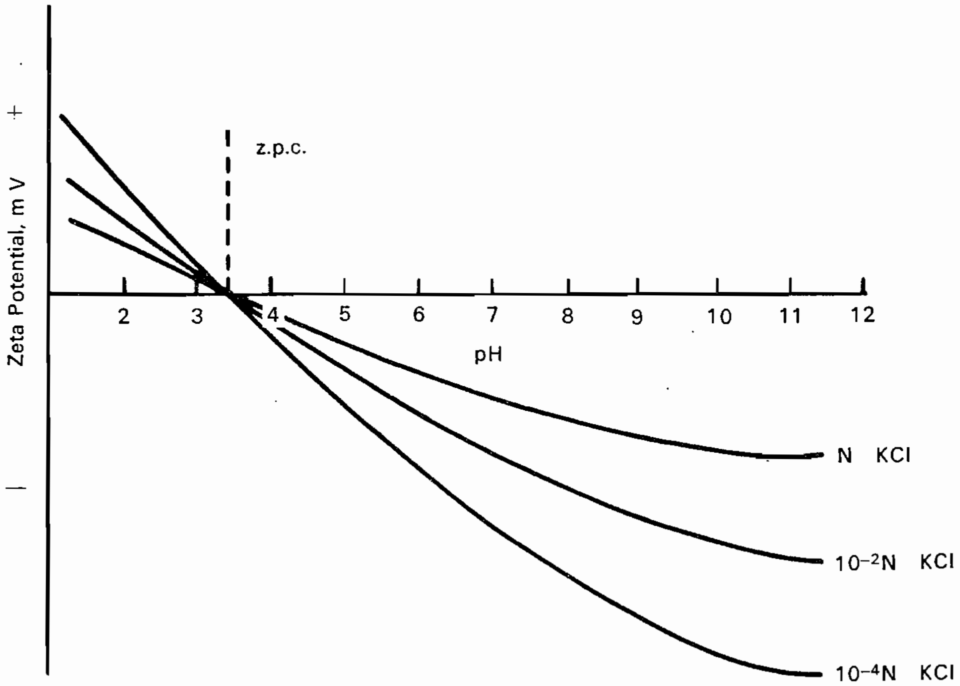


Fig 1.4.3 Effect of ionic strength on magnitude of zeta potential

1.4 ZETA POTENTIAL

When a mineral is crushed and ground to a size suitable for flotation, bonds in the crystal lattice are broken and give rise to a surface excess or deficiency of electrons. The charge created on the surface is neutralized by counter ions from the environment. A diagrammatic representation of the resultant electrical double layer formed is shown in Fig 1.4.1. The fall in potential between the Stern layer and the diffuse layer ($\psi\delta$) is known as the zeta potential (ζ).

Hydrogen and hydroxyl ions are potential determining for silicate minerals, and consequently any change in pH will cause changes in magnitude of the zeta potential. An idealized plot of pH against zeta potential is shown in Fig 1.4.2. At one pH value only, the net charge on the surface will be zero, this value being defined as the zero point of charge or z.p.c. The position of this zero point of charge varies from mineral to mineral but with most it lies well below pH 7.0. When they are available, values of the z.p.c. will be quoted in the introductions to the text dealing with the individual mineral species. As a general rule those minerals with a higher zero point of charge are more favourably floated with anionic (negatively charged) collectors particularly under acid conditions, whereas those with a low z.p.c. are more likely to be floated with oppositely signed collectors (cationic). However, the measured potential is an idealized figure which is an average value determined for a particular mineral and areas of different charge density or even opposite charge are thought to exist simultaneously on the same surfaces. The adsorption of anionic collectors at pH values above the z.p.c. and cationic collectors below, with consequent flotation is therefore not ruled out.

The presence of multivalent cations in the pulp can frequently change the apparent polarity of a mineral. For example, quartz has a very low z.p.c. and thus has a high negative charge on its surface at alkaline pH values. As a consequence it cannot be floated with anionic collectors but the presence of even 5 p.p.m. of calcium ions is sufficient to reverse this charge enabling anionic flotation to be carried out.

If the ionic strength of an indifferent electrolyte (i.e. a non-potential-determining electrolyte) is increased, then the double layer thickness around the particle becomes compressed. This results in a decrease in the magnitude of the zeta potential as is illustrated in Fig 1.4.3. The magnitude of the effect of this indifferent electrolyte is increased dramatically as the valency of the electrolyte is increased according to the Schultz-Hardy rule. Thus a divalent ion will have approximately ten times the effect of a monovalent ion and a trivalent ion approximately 100 times the effect.

1.5 STRUCTURE/FLOTATION RELATIONSHIPS

The flotation diagrams given in the later chapters of this book were originally determined in order to ascertain whether a relationship existed between the structure of silicate minerals and their flotation properties. This work was first outlined[1] in 1966 by the physical-chemistry group at Warren Spring Laboratory and some of the results obtained since have also been published[2-5]. Some general flotation properties of each silicate structural group are described in this section.

ORTHOSILICATES

A full description of the flotation properties of each orthosilicate studied is given in Chapter 3. By referring to the flotation diagrams given in that chapter it will be seen that all the orthosilicates containing the isolated $[SiO_4]^{-4}$ tetrahedra float moderately well with the cationic collector dodecylamine. They are sensitive to changes in pH as well as being promoted by the addition of the fluoride ion modifier.

Although, by comparison, the area of flotation with the anionic sodium oleate is perhaps a little inferior, it will be seen that of all the silicate structures investigated, the orthosilicates show the greatest tendency to float with this collector. The sensitivity to changes in pH when floating orthosilicates with this anionic collector is not as marked as that shown with the cationic collector, but small additions of the fluoride ion are seen to cause very marked depression.

Those silicate minerals investigated that contained pairs, four-membered, and six-membered rings of tetrahedral silicate groups generally showed similar flotation properties to the orthosilicates and have therefore not been grouped in a separate chapter in this book.

PYROXENES

A full description of the flotation properties of each pyroxene or chain-silicate mineral studied is given in Chapter 4. Again, reference to the flotation diagrams of the minerals in that chapter shows that the cationic flotation areas closely resemble those obtained with the orthosilicate type; that is, they have moderately good flotation properties with high sensitivity to pH change. A noticeable difference between the flotation properties of pyroxenes and the orthosilicates is evident when the effects of the fluoride modifier are studied. Under these conditions the orthosilicate minerals are activated to a considerable extent whereas the pyroxene minerals are hardly, if at all, affected by this modifier.

Larger differences in flotation properties become apparent when the flotation areas obtained with the anionic collector are compared. It will be seen here that pyroxenes do not float nearly as well with this collector. A combination of the fluoride modifier with the oleate collector produced no flotation with any of the pyroxene minerals except spodumene.

AMPHIBOLES

A full description of the flotation properties of each amphibole studied is given in Chapter 5. Although only a limited number of crystalline minerals in this group were available for investigation, the flotation properties of actinolite, hornblende and tremolite show marked similarities. No significant area of flotation was found with any of these three minerals when using the anionic collector either with or without fluoride present. However, the areas of flotation obtained when using the cationic collector were very much greater than those obtained with either the orthosilicate or the pyroxene minerals. Unlike those previous classes, the cationic flotation properties of the amphibole silicates were very much less sensitive to change in pH, each floating very well in the range from pH 3.0 to 11.0. The effect of fluoride on these cationic flotation areas was very small, causing minor activation or depression which was slightly more marked under acid conditions. The flotation properties of the fourth amphibole studied, riebeckite, appear to be anomalous under both anionic and cationic flotation conditions. This is discussed further in Chapter 5 (page 121).

SHEET SILICATES

A full description of the flotation properties of each of the sheet silicates studied is given in Chapter 6. An initial inspection of the flotation diagrams given in that chapter will lead the reader to the conclusion that there is no sensible correlation between the flotation properties of this structural class of silicate minerals and those other classes previously discussed. Further, it might be concluded that this is the point at which the silicate structure has no longer any influence on its flotation properties. However, by referring back to the description of sheet silicate structures in section 2 of this chapter (pages 7-10) and considering the methods by which the sheets within this class of minerals are attached to one another, the following relationships become apparent.

There is no valency linkage between individual sheets of serpentine, one being linked to the next only by van der Waals forces. Because of this, the mineral is very soft and when it shears it produces platelets that have no resultant surface charge, and are thus incapable of reacting with ionic surface-active agents. The flotation properties of this mineral are to a great extent in agreement with this analysis, the small area of flotation being probably due to soap formation on edges of the broken platelets.

Likewise the individual sheets in the mineral talc are joined only by van der Waals forces. Therefore, from the analysis of the properties of serpentine given above, talc also would be expected to have a poor flotation response. The flotation areas obtained, however, do not confirm this but indicate that this mineral has a 'natural floatability'. The similarities between the flotation areas obtained, and the unique effect that the fluoride modifier has of activating flotation with both anionic and cationic collectors, both indicate that there is a massive and non-specific adsorption of collector on to this mineral surface which causes flotation. The natural floatability of this mineral is further demonstrated in flotation practice when the use of frothers only is sufficient to enable good flotation recoveries to be obtained.

Common flotation practice with mica minerals rarely differentiates between the particular species of this class being treated. The flotation properties of the two micas tested at Warren Spring Laboratory show considerable similarities when the cationic collector is used. The large areas of cationic flotation with little sensitivity to change in pH again reflect the mode of attachment of the individual sheets to one another. In the case of the micas this attachment is ionic through a 12-fold coordination with an alkali metal ion. Due to the weak bonding and hence the mobility of this ion, high negative charges are created on the exposed surfaces when the mineral is sheared. These lead to good adsorption of positively charged cationic collectors.

The areas of flotation obtained when using anionic collectors with mica minerals occur only under very limited pH conditions. This is indicative of multivalent cation activation. The mobility of the alkali metal ion which acts at the bond between the individual mica sheets, enables replacement to take place by means of ion exchange, thus facilitating this activation.

The increase in the chlorite type of sheet silicate of the aluminium-to-silicon ratio within the silicate sheets, creates sufficient ionic charge to accommodate more than the coordination type of linkage found between mica sheets. In this group of minerals the linkage mechanism is via a further 'brucite type' layer in which one third of the magnesium ions has been replaced by trivalent aluminium ions to give a positively charged $[Mg_2Al(OH)_6]^+$ layer. Cleavage of these minerals clearly involves breaking the bonds between the silicate layers and the brucite layers, thus leaving alternately charged patches on the new surfaces so created. With such favourable conditions, both anionic and cationic collectors will be readily adsorbed, and will result in the large flotation areas found within the chlorite group.

FRAMEWORK SILICATES

A full description of the flotation properties of each framework silicate studied is given in Chapter 7. The flotation properties of the framework silicates with both anionic and cationic collectors show very consistent properties. With the anionic collector no flotation at all was found with any mineral in this group that was tested. Flotation with cationic collectors of all the minerals in this group was found to vary between good and excellent over a wide range of pH values. The effect of the fluoride ion on minerals in this group was one of mild activation.

The floatability of a group of silicate minerals was studied as long ago as 1934 by Patek[6]. He determined the contact angle between various silicate minerals and a solution containing 500 mg/l sodium oleate together with 200 mg/l terpineol and also placed these minerals in an order of relative floatability. In Table 1.5.1 the minerals he studied have been listed in order of the magnitude of the contact angles at their solid/solution interface. The classification of silicate structural group has been added together with the oxygen/silicon ratio found in these classes, and finally Patek's order of floatability. It will be seen that, with the exception of the three minerals marked with an asterisk, there is a startling relationship between the order of the contact angles and the oxygen/silicon ratio. This ratio is one measure of the degree of complexity of the silicate mineral structure. It is now generally accepted that contact angle is not necessarily an accurate measure of hydrophobicity and that factors such as surface roughness and impurities, and advancing and receding angle measurement can have a considerable effect on its value. However, if the minerals were to be classified according to the degree of complexity of their silicate structures then it will be seen that all the orthosilicates have a high order of flotation, whereas all the framework silicates floated badly. The number tested from other classes is too small to put them in any particular order, but their floatability obviously lies between that of the ortho- and the framework-silicates.

From the results presented in this section it may be concluded that there is a direct relationship between the flotation properties of silicate minerals and their structures.

The relationship that exists with the sheet silicate class depends on the mode of attachment of one sheet to the next. As this becomes more ionic in character, the adsorption of oppositely charged surface active agents is increased together with the consequent flotation.

By considering the flotation results reported for the orthosilicates, pyroxenes, amphiboles and framework silicates, it will be seen that only the orthosilicates float well with anionic collectors. Pyroxenes float with this collector in some cases but there is no flotation of amphiboles or framework silicates. The flotation properties of silicates with cationic collectors are reversed with orthosilicates and pyroxenes having smaller areas of flotation than the amphiboles and framework silicates. Sensitivity of the flotation areas to pH change when using a cationic collector, decreases as the structure becomes more complex. Almost all the orthosilicates and pyroxenes studied have a common alkaline limit to their flotation areas, a fact which has been discussed elsewhere[4].

Table 1.5.1 – Relative Floatability of some Silicate Minerals
(After Patek)

	Contact Angle°	Structure	Group	O:Si Ratio	Anionic Flotation Order
Zircon	56	Ortho-	SiO_4	4	1
Almandite	54	Ortho-	SiO_4	4	3
Epidote	53	Ortho-	Si_2O_7 SiO_4	3.75*	7
Titanite	52	Ortho-	SiO_4	4	9
Cyanite	51	Ortho-	SiO_4	4	6
Topaz	50	Ortho-	SiO_4	4	4
Olivine	50	Ortho-	SiO_4	4	5
Rhodonite	49	Pyroxene	Si_2O_6	3	10
Augite	48	Pyroxene	Si_2O_6	3	11
Anorthite	48	Framework–	SiO_2	2*	12
Tourmaline	47	Ring-	Si_6O_{18}	3	2
Spodumene	45	Pyroxene	Si_2O_6	3	13
Tremolite	43	Amphibole	Si_8O_{22}	2.75	8
Labradorite	43	Framework–	SiO_2	2*	15
Biotite	34	Sheet-	Si_4O_{11}	2.75	14
Muscovite	31	Sheet-	Si_4O_{11}	2.75	16
Albite	30	Framework–	SiO_2	2	18
Nephelite	23	Framework–	SiO_2	2	17
Quartz	21	Framework–	SiO_2	2	20
Orthoclase	20	Framework–	SiO_2	2	19

The effect of the fluoride modifier on the flotation properties may also be related to the silicate structure. When used in anionic flotation systems this modifier acts as a depressant and in cationic systems as an activator. The reasons for this again are discussed elsewhere[7]. However, the effect is seen to be most marked with the orthosilicates, decreasing with the pyroxenes and amphiboles and with a variable influence on the network silicates. The broad results are summarized in Table 1.5.2.

Table 1.5.2 – Relationship Between Silicate Structure and Flotation Properties With and Without Fluoride Modifier

Conditions	Silicate Class			
	Ortho-	Pyroxene	Amphibole	Framework-
Anionic collector no Fluoride	Good	Poor	Nil	Nil
Cationic collector no fluoride	Mediocre (sensitive to pH change)		Good (not sensitive to pH change)	Very good
Anionic collector with fluoride	Poor (depression)	Very poor (depression)	Nil	Nil
Cationic collector with Fluoride	Mediocre (activation)	(little effect)	Good (slight activation)	Very good

The reasons for the relationships that have been shown to exist between flotation properties and silicate structure can best be understood by considering the two end members of the structural classification – the ortho- and framework-silicates. Pronounced differences will be expected in the types of surface formed when these minerals are ground. Breakage of crystals in the orthosilicate group will be expected to present surfaces in which cations (Al^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+} etc) predominate as high-energy sites and at which collectors of the opposite charge (anionic) may adsorb. Breakage of $[SiO_4]^4$ tetrahedra and hence the silicon/oxygen bond will be small with these minerals. In the framework structures there is no way of cleaving the minerak particles without breaking silicon/oxygen or aluminium/oxygen bonds. This will give rise to active sites of the type $\succ$SiOH and $\succ$SiO$^-$ which will permit ready adsorption of the cationic amine collectors. The state of the charge on the mineral surface is reflected in the value obtained for the zero point of charge (z.p.c.). The more positive sites present on the surface lead to a higher value of this parameter with respect to pH when the potential-determining species are hydrogen and hydroxyl. The above argument, that fracture of orthosilicates leads to predominately positively-charged surfaces and that of network silicates to predominately negatively-charged surfaces, is strengthened by the values of z.p.c. found for these silicate groupings. The values determined for the orthosilicates commonly lie between pH 5.0 and 6.0, whereas those for the framework silicates occur at very acid pH values between 1.0 and 2.0.

It will be appreciated that when the pyroxene and amphibole silicates are ground, (these have progressively more complex structures than the orthosilicates), then an increasing number of silicon/oxygen bonds must be broken. This in turn will lead to a progressively more negative surface which is reflected in the increasing tendency to float with cationic rather than anionic surface-active agents. Unfortunately there is insufficient data available to forecast the z.p.c. ranges of these mineral species without ambiguity, but the values that are known for two crystalline pyroxenes lie between pH 3.0 and 4.0 and it is a reasonable assumption that values for amphibole minerals would lie between pH 2.0 and 3.0.

1.6 INTERPRETATION OF FLOTATION DIAGRAMS

The vacuum flotation method used for the determination of the areas of flotation of the minerals given in this book is described in Chapter 2. It is appropriate, however, to discuss in this introductory chapter some of the limitations of this method and the interpretation of the results obtained.

It will be readily appreciated that no fixed point can exist before which no flotation is possible and after which 100 per cent recoveries may be obtained. It is all a question of degree. For example, as the necessary pH conditions are approached for good flotation at any particular collector concentration, so flotation will increase up to a maximum, which may or may not be 100 per cent. Further increases in pH will eventually lead to conditions where flotation of the mineral begins to deteriorate until, again, conditions for non-flotation or poor flotation are reached. Keeping the pH constant and varying the collector concentration will produce a similar pattern of results where flotation recovery will be low at first, increasing to a maximum and remaining there over a considerable range of collector concentration. The situation where flotation stops at high collector concentrations (this can be observed both with vacuum flotation and with Hallimond tube flotation tests) is due to the adsorption of a second layer of collector molecules with reversed orientation which causes the previously hydrophobic layer to become hydrophilic. This phenomenon is not observed under plant conditions as there is always sufficient surface area available on the gangue minerals present to adsorb the excess collector, causing non-selective flotation to occur.

The flotation areas shown in the diagrams within this book, therefore, are an indication of the conditions under which good flotation recoveries may be expected with that particular mineral. Superimposition of two diagrams * will indicate whether separation may be possible. Obviously if there are large areas between the two which do not coincide, then the conditions within these areas should be exploited. The extent of the separation between any two diagrams must not be taken as conclusive evidence that practical separation of the two mineral species either will or will not be possible. For example, the cationic flotation areas of quartz and feldspar-albite coincide very closely over a considerable range of conditions but the addition of fluoride modifier depresses quartz flotation slightly whilst activating that of albite to a similar degree. The separations between the acid edge of the flotation areas is then about 1½ pH units, which is sufficient in this case for a satisfactory separation of the two minerals. On the other hand there is considerable overlap found when the beryl and spodumene anionic flotation areas are superimposed and it would be expected from this that good separations would be possible at low collector concentrations. However, better separations were obtained by Moir et al[8] in the presence of the fluoride modifier which, it will be seen, decreases the area of overlap of the flotation diagrams. Even absolute coincidence of two flotation diagrams does not automatically rule out the possibility of separating the two minerals as one of them might preferentially adsorb the collector, especially at low concentrations.

When attempting a flotation separation of silicate minerals it is intended that this book should be a guide to the correct lines of investigation to be followed. The flotation areas given in the diagrams should only be used in conjunction with all the available information given in the text. A complete analysis of not only the ore to be treated but also the water to be used in this treatment should be made. As well as this, other possible sources of multivalent ions that may arise during processing should be investigated because of the very considerable effect that they can have on flotation properties of silicate minerals particularly when anionic collectors are being used.

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* A set of flotation diagrams printed on transparent film, suitably arranged for easy superimposition of any two diagrams may be obtained from Warren Spring Laboratory (price on application)

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Chapter 2

EXPERIMENTAL METHODS

Contents:

2.1 MINERAL PREPARATION

The preparation of mineral samples for flotation testwork may be conveniently divided into a number of stages: selection of sample, crushing and grinding, sizing, and cleaning.

SELECTION OF SAMPLE

Every endeavour should be made to obtain the purest possible sample of the mineral to be studied. If a problem arising within a particular ore body is to be investigated where the mineral under study is only present in a finely divided, widely disseminated state, then an attempt should be made to isolate at least a small sample for preliminary flotation testwork. The results of this work may then be compared with the results obtained with samples from other ore bodies which contain the mineral in a more readily available form. If the two samples are found to yield similar results then the more readily available mineral may be used. If this is not the case then the first sample must be concentrated in some manner to yield a sufficient quantity of the desired size range to enable testwork to be carried out. (The author recommends, in this case, the careful calculation of the total weight required for the planned experimental programme making due allowance for losses that will occur during crushing and grinding to the required size. This figure should then be doubled as it is inevitable that further experimental work will suggest itself after the preliminary results become available.) Methods of concentrating a sample may include hand picking – with or without optical aids – wet or dry magnetic separation, and various methods of gravity separation using density gradient techniques may be employed. If the latter method has to be used, then separations should be carried out at the maximum possible particle size even if this results in discarding a major portion of the required mineral as composites. Special care must then be exercised in removing any heavy liquid from the mineral surfaces as traces of this adsorbed at the solid/liquid interface may be sufficient to activate flotation at a later stage. On no account should the particle size range of a sample prepared in this manner overlap that range to be used in subsequent flotation testwork. This ensures that the further wet grinding that will be necessary will produce fresh surfaces on each particle. Any mineral sample that has been treated with organic heavy liquids during the early stages of preparation should be tested for possible flotation over the whole pH range in the absence of any collector addition. This is to ensure that there are no traces of contamination present that may lead to spurious results.

CRUSHING AND GRINDING

If the hand-picked samples of the pure mineral are available in large pieces these will require some preliminary crushing. This may be carried out using a laboratory-size jaw crusher or one of the new grooved roller crushers that are now available. A convenient feed size for grinding is 1680 μm (10 mesh BSS).

In order to ensure that all the sample to be used for the flotation testwork has some surface that has been ground under water, the fine material produced during any preliminary dry crushing operation should be discarded. For example, if the final size range used for testwork is to be between 105 μm and 150 μm (the range used at Warren Spring Laboratory) then any material that is finer than 150 μm is discarded at this preliminary stage.

The choice of mill to be used for the final wet grinding should be made having due regard to the possibility of contaminating the mineral surfaces during the comminution operation. A ceramic pot-mill with a charge of ceramic balls may be used, but the rate of grinding may be slow with this type of mill when treating some species of hard mineral. A good alternative is a stainless steel mill with grinding media of the same metal, either balls or rods. All the mineral samples prepared for the testwork reported in this book were wet ground in a 30 cm by 15 cm stainless steel mill with a charge of ten 2.5 cm diameter stainless steel rods. Deionized water was used throughout this stage of preparation. If only a limited quantity of the mineral to be investigated is available, then it is advisable to grind for a short time only, and then to remove the undersize by wet screening (again in deionized water) before returning the oversize for regrinding.

SIZING

After wet grinding has commenced, all samples should be kept under deionized water throughout the further stages of preparation. The size range to be used in the testwork must lie within that range which is most suitable for flotation, i.e. between 20 and 200 μm. To determine small differences in flotation properties between two minerals, it is advisable to work in a narrower size range than this. The range used for most of the vacuum flotation testwork carried out in the author's laboratory is between 100 and 150 μm unless there is only a small quantity of the mineral available, in which case the lower size limit is extended to 75 μm. The larger size range is normally used when carrying out modified Hallimond tube tests. Any material less than 20 μm produced in the wet grinding process is removed either by beaker decantation methods using Stoke's settling times, or by the use of a small hydrocyclone, and then discarded. Material greater than 20 μm up to the minimum size chosen for the flotation testwork may be used for reagent adsorption determinations, solubility experiments, or, after further hand grinding in an agate mortar, for microelectrophoresis measurements to determine zeta potential.

CLEANING

Many authors advocate acid treatment of mineral surfaces before flotation testwork is carried out. Methods that have been described in the literature range from washing in cold 10 per cent hydrochloric acid up to soxhlet extraction with boiling concentrated acids. The 'minerals' so treated are then washed continually with water until all chloride ions have been removed. Tests carried out by the author at Warren Spring Laboratory have shown that even a mild acid treatment is sufficient to change the surface properties of the mineral to such an extent that its flotation response bears no relationship to that of the original mineral. Other work has shown that this is almost certainly due to the differential solubility of surface cations in the acid. Whilst it is fully appreciated that contamination of the mineral surfaces may lead to apparently spurious flotation behaviour (see, for example, the anionic flotation areas obtained with mica samples), it is the author's considered opinion that this is preferable to the completely misleading flotation properties that result from acid treatment.

Primary crushing and wet grinding frequently introduce a quantity of iron contamination into the sized mineral sample. This, in most cases, may be conveniently removed using a wet magnetic separator. The Davis tube laboratory separator has been found to be particularly useful for this task as the ability to vary the field continuously over a considerable range of intensities enables iron contamination to be removed even in the presence of a weakly magnetically-susceptible mineral. If used at low intensities the mineral pulp will have to be passed through the separator a number of times whilst removing the magnetic fraction between each treatment. The growth of rust spots after storage of the freshly prepared mineral for a number of days under water will indicate whether this stage of the preparation has been successful or not. If these spots are in evidence then further passes through the magnetic separator will be necessary before proceeding to subject the sample to prolonged washing as described below.

So far all the wet operations will have been carried out with deionized water. Although it may be assumed that no contamination of the mineral surface by extraneous cations has taken place, the possibility of organic contamination arising from the very slight solubility of the ion exchange resin beads must not be discounted. The sized samples are therefore washed repeatedly with freshly distilled, deionized water over a period of not less than one week. Not only do frequent changes of the water remove any organic contamination but they also have the effect of removing particles of very fine material that may adhere to the mineral surface and thus escape removal during the sizing process.

The sample that is now ready for flotation testwork is stored under water in a glass jar, preferably one with an air-tight lid. It is advisable to change the water over the mineral surface at regular intervals during the testwork. If it is known that the sample will be required for further experiments at a later date then a wash with at least three changes of water should be carried out at approximately monthly intervals. This is to prevent algal growth that has been found to occur even after the highest purity deionized and distilled water has been used.

2.2 VACUUM FLOTATION

All the flotation diagrams shown in this book have been produced using the vacuum flotation technique that was originally described by Schuhmann and Prakash[1]. In this test the dissolved air which 'boils' out of an aqueous solution is used as the source of bubbles upon which the hydrophobic mineral may collect. The test is mainly qualitative with no products being collected, and the diagrams produced indicate the area within which a particular mineral will float with respect to pH conditions at various collector concentrations. Each area has been determined by carrying out a number of separate tests over a range of pH values, each test being made on a fresh sample of mineral. As the pH is increased at a fixed collector concentration, a point is reached where the mineral starts to float. From this point the mineral will continue to float until the pH has been increased to a sufficiently high value for flotation to be no longer possible. Hence, at each collector concentration investigated, two pH values may be determined, a lower value below which flotation does not occur and a higher value above which flotation is again not possible. By repeating this process over a range of collector concentrations, a series of points is obtained which may be joined to form the final flotation diagram.

The flotation tubes used are 10 cm by 2.5 cm diameter glass sample tubes with a capacity of approximately 40 cc, fitted with polyethylene caps. A water vacuum pump is connected to a manifold to which the glass sample tubes can be attached via a silicone rubber tube and bung. A mercury manometer is also connected to serve as a check on the vacuum obtained, the absolute value of this being less important than consistency. When carrying out comparisons between two sets of conditions, this consistency can be critical. Before use, all glassware must be cleaned with chromic acid and well rinsed with water which has been distilled, passed through a mixed-bed deionizer and then redistilled. The polyethylene caps may be cleaned by gently warming in a 10 per cent solution of sodium carbonate for a period of 30 minutes and then rinsing well with distilled water before letting them drain dry. Great care should be exercised with the clean apparatus as even slight contamination caused, for example, from handling the inner surfaces of the tube may be sufficient to cause some minerals to float. Continuation of the flotation diagram down to low concentrations of collector, where no flotation is observed over the whole pH range, is a good indication that the correct degree of cleanliness has been achieved.

For the determination of the flotation conditions of each mineral a series of solutions of the collector is prepared, each at a constant concentration and covering a range of pH values from 3.0 to 11.0. Approximately 20 cc of each of these solutions is then transferred into a number of flotation tubes and subsequently 25 mg of the wet mineral is added using a glass spoon. Great care must be taken to ensure that this spoon does not become contaminated with collector solution. The tubes are immediately sealed with polyethylene caps and the mineral is conditioned for a 10-minute period by gently shaking each tube at approximately 2-minute intervals. At the end of this conditioning each tube is placed in turn on the vacuum system, and one of three distinct effects is observed. Either no flotation occurs and any bubbles arising tend to nucleate on the tube walls in preference to the mineral surfaces, or when the vacuum is applied the mineral under test flocculates together with small air bubbles and rises as bulky flocs. These two clear-cut effects are recorded as no-float and float respectively. Between these two clear-cut conditions a region of partial flotation, sometimes over a wide pH range, may be observed. In this region bubbles nucleate on the mineral surface and carry a varying number of particles with them to just below the liquid/air interface where either the particles disengage or the bubbles burst. It is normal to designate the region as 'half flotation' (the equivalent to the 'cling' area in bubble pick-up testwork) but for simplicity in the presentation of results this area is not recorded in this publication. It is helpful to plot the points of flotation and partial flotation on log/linear graph paper as the experimental work is in progress. In this way changes in the outline of the flotation diagram (called the flotation edge) with collecter concentration may be observed and the total number of tests at each concentration may be reduced to about eight, four under the acid flotation edge and four under the alkaline edge. Finally the flotation area is plotted by tracing a smooth curve between the outer limits of good flotation and the inner limits of partial flotation.

2.3 REFERENCES

1 Schuhmann, R. Jr. and Prakash, B.
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