

Circular 65

SULFONATE FLOTATION OF BERYL

by Maurice C. Fuerstenau and Roshan B. Bhappu

Reprinted from *TRANSACTIONS OF SME, June 1963; AIME Trans., vol. 226, 1963.*

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

E. J. Workman, President

STATE BUREAU OF MINES AND MINERAL RESOURCES

A. J. Thompson, Director

SULFONATE FLOTATION OF BERYL

by Maurice C. Fuerstenau and Roshan B. Bhappu

The response of beryl to sulfonate flotation was examined. The dependence of flotation recovery on sulfonate concentration, pH, and the absence or presence of various ions is also demonstrated. The response of quartz and feldspar to sulfonate flotation at various values of pH is given to show the conditions necessary for selective separation. Finally, beryl was successfully concentrated from a natural ore using a technique devised from experimental observations on systems of pure minerals.

With the possible exception of quartz, the flotation characteristics of silicate minerals are rather poorly understood. This is due in part to the com-

plexity of the mineral systems themselves and in part to an insufficient amount of flotation data.

The complexity of the systems arises from the wide range of chemical composition that the silicate minerals can assume. This is reflected in the variability of such physical properties as hardness and cleavage.

Although the chemical composition of silicate minerals can vary considerably, a general grouping can be accomplished conveniently on the basis of the assemblage of SiO_4 tetrahedra in all the silicates.^{1,2} That is, it has been shown that six basic groups can be obtained, depending on the arrangement of oxygen sharing between adjacent silicon atoms (or substituted aluminum). When all four oxygen atoms are shared, a framework structure such as quartz or feldspar is obtained. When three oxygens are shared, infinite sheets are obtained as in the micas and clays. When two oxygen atoms of the tetrahedra are shared, infinite chains are obtained, such as those in

M. C. FUERSTENAU is Research Engineer, and R. B. BHAPPU is Metallurgist, New Mexico Bureau of Mines, Socorro, N.M. TP 62B248. Manuscript, Nov. 2, 1962. Discussion of this paper, submitted in duplicate prior to Sept. 1, 1963, will appear in SME Transactions, March 1964, and AIME Transactions, 1964, vol. 229.

the pyroxenes and amphiboles. Finally, when only one oxygen is shared or when no oxygens are shared, structures such as those in hemimorphite and olivine are obtained.

Selective separation of minerals contained in the same general group as well as separations between minerals of different groups have been accomplished by froth flotation; for example, feldspar from quartz in the former instance and mica from quartz in the latter.

However, the mechanism of collection involved is still rather obscure in many cases. In order to obtain a fuller understanding of silicate flotation in general, a research program was initiated to investigate the **flotation** characteristics of selected pure mineral systems from the six general groups of silicate minerals. This publication is a report of the first of the mineral systems examined in some detail, namely, beryl.

The previously reported responses of beryl to froth flotation techniques can probably best be described as indifferent.³⁻⁷ The investigations have centered mainly around fatty acids and alkyl sulfonates as collecting agents in the presence of various modifiers and activators. Problems of recovery as well as selectivity have been encountered in most of the work reported.

Of these two groups of collectors, alkyl sulfonates appeared to be the most promising for good flotation collection of beryl. As such, an alkyl sulfonate containing a relatively long hydrocarbon chain was selected to study the flotation behavior of beryl in various chemical environments. In addition, the flotation response of the principal gangue constituents, quartz, and feldspar, in similar environments was examined to determine the optimum experimental conditions for selective separation.

EXPERIMENTAL MATERIALS AND METHOD

Materials: The beryl used in the experimental work was supplied through the courtesy of Mr. H. R. Van Wagenen, manager of the Harding Mine, Dixon, N.M. When received the samples were hand-picked lumps of pure beryl which analyzed 11.16% BeO.* Both the

*Various analyses, such as BeO of beryl and ferric iron content of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and others, were made by Dr. Dexter Reynolds, analytical chemist, in the Bureau laboratory.

quartz and feldspar (microcline) were hand-picked lumps of pure minerals from the Harding Mine.

Sodium alkyl aryl sulfonate was chosen as collector for the experimental work. The reagent, supplied as a courtesy sample by the Shell Oil Co., has the following physical properties:⁸ physical form, solid, finely ground; sulfonate content (% weight), 95 to 97; molecular weight, 450 to 470; number of carbon atoms in hydrocarbon chain, 25 to 30; melting point ($^{\circ}\text{F}$), 250 to 260; and solubility, soluble in water with gel

Table I. Analysis of Tap Water Used in the Experiments

Substance	Quantity (ppm)
Silica	39
Barium	2
Sodium	55
Potassium	3
Calcium and magnesium	30
Carbonate – bicarbonate	170
Sulfate	33
Chloride	16
Fluoride	<1
Nitrate	1

formation at concentrations higher than 25% by weight sulfonate.

This particular reagent was chosen because of its high active sulfonate content, long chain length and solid form. All other chemicals were of reagent grade quality.

Two types of water were used in the experimental work; namely, conductivity water and tap water. The conductivity water, made by passing distilled water through an ion exchange column, had an average measured conductivity of two micromhos. An analysis of the tap water is found in Table I.

Method: Experiments were conducted at room temperature in a Fagergren flotation cell with the following procedure: 1) 2.6 liters of water were added to the cell and the pH of the system adjusted to a predetermined value, 2) a desired amount of collector pipetted, 3) the pH of the system (termed *initial pH*) measured, 4) 100 g of dry solids (48 x 150 mesh) added, 5) 31 mg methyl isobutyl carbinol added as frother, 6) the system conditioned for 3 min, 7) the pH of the system (termed *flotation pH*) measured, 8) the system floated for 2 min, and 9) the pH of the system (termed *final pH*) was measured.

Slight variations from this procedure occurred when various salts were added to the system. For example, in the case of ferric chloride additions, a given amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the system after the pulp had been conditioning for one minute with the collector. The pulp was then conditioned for two more minutes with the ferric chloride and then floated. **Reproducibility of Experimental Results:** To determine the reproducibility of experimental results, eight experiments were performed under similar conditions with separate samples of unleached beryl in tap water. Applying the standard deviation expression, the reliability of the experimental results is $\pm 8.5\%$.

EXPERIMENTAL RESULTS

Leached Beryl-Conductivity Water: Preliminary experimentation revealed that beryl ground in a mild steel rod mill responded much more readily to flota-

tion than did material ground in a porcelain mill. This obviously made iron suspect, and to determine the response of beryl to sulfonate flotation in the absence of iron, the material was batch-leached with aqua regia for 18 hr. Following this, the material was washed with conductivity water until the liquor was at the pH of the conductivity water and dried. Since some iron was found to be present on the particle surfaces even after this treatment (presumably due to precipitation of ferric hydroxide during the washing step), the leached beryl was releached with concentrated HCl for a period of one week. The releach was conducted with a percolation technique using successive residence times of 24 hr. This material was then washed with conductivity water again until the liquor was at the pH of the water and dried. Following this treatment, the beryl was found to contain 110 ppm iron. It is presumed that this iron is contained within the crystal and not on the surface.

Separate flotation experiments were then conducted with 100-g charges of this material with various amounts of sulfonate in acid media with and without added ferric iron. As shown in Fig. 1, virtually no flotation could be effected at a sulfonate concentration of 2.13×10^{-5} mole per liter. Increasing the collector concentration resulted in an increase in recovery, and finally when a concentration of 1.68×10^{-4} mole per liter was used, a recovery of 70% was achieved.

It can also be noted in the same figure that the addition of a small amount of ferric iron results in two phenomena, dependent on the amount of ferric iron added. When $1.36 \pm 0.02 \times 10^{-5}$ mole per liter Fe^{+++} was added, flotation recovery was actually decreased at most of the sulfonate concentrations used. However, when $2.05 \pm 0.01 \times 10^{-5}$ mole per liter Fe^{+++} was added, flotation recovery was enhanced significantly. Increased additions of ferric iron, i.e., $2.72 \pm 0.01 \times 10^{-5}$ mole per liter, result in increased recoveries at lower sulfonate concentrations. The ferric iron concentrations are reported with some deviation because the experiments were run with reagent additions based on solids content (1b per

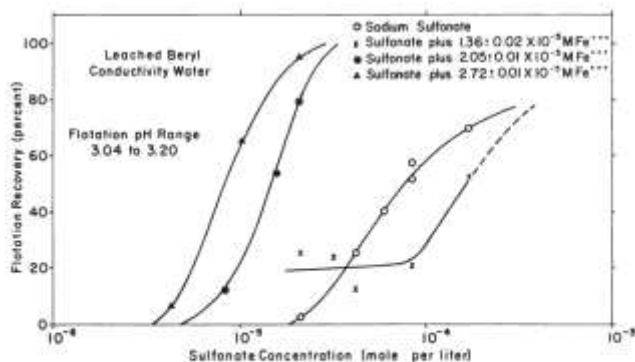


Fig. 1—Relationship between flotation recovery of leached beryl and sulfonate concentration in the absence and presence of added ferric chloride (separate experiments).

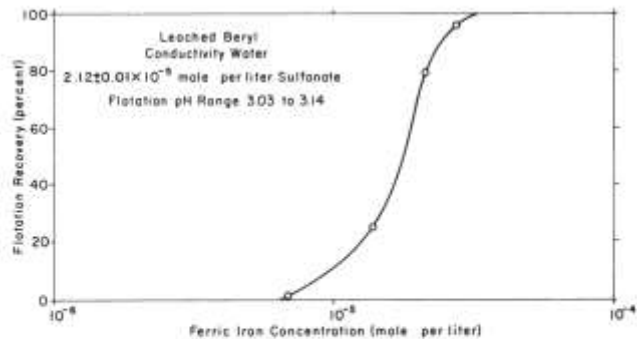


Fig. 2—Relationship between flotation recovery and Fe^{+++} iron concentration at constant sulfonate concentration in conductivity water (separate experiments).

Table II. Recovery of Leached Beryl in Conductivity Water*

Salt	Recovery, %	Flotation pH
No added salts	57.7	3.17
$AlCl_3 \cdot 6H_2O$	3.0	3.18
$CaCl_2 \cdot 2H_2O$	2.1	3.19
$Co(NO_3)_2 \cdot 6H_2O$	14.6	3.18
$CuCl_2 \cdot 2H_2O$	9.4	3.12
$CrCl_3 \cdot 6H_2O$	50.2	3.19
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	19.8	3.22
$FeCl_3 \cdot 6H_2O$	100.0	3.16
$MnCl_2 \cdot 4H_2O$	9.4	3.19
$RuCl_3$	31.5	3.17

*At a sulfonate concentration of 8.46×10^{-5} M (38.1 mg per liter) with various salts present at a concentration of 15.2 mg per liter.

ton). It was decided later that reagent concentrations expressed in terms of molarity were more useful. Slight differences are then present because of the differences in total solution volume.

Since ferric iron is obviously very beneficial in this flotation system, the question arose as to the recovery that could be expected with various amounts of iron added at constant sulfonate concentration. As revealed in Fig. 2, a $FeCl_3 \cdot 6H_2O$ concentration of 2.72×10^{-5} mole per liter Fe^{+++} was required to obtain a recovery of 96% at a sulfonate concentration of $2.12 \pm 0.01 \times 10^{-5}$ mole per liter. Since 2626 cc of solution were used, this corresponds to a concentration of 1.53 mg Fe^{+++} per liter or 1.53 ppm.

Experiments similar to those illustrated in Fig. 2 were also conducted with this sulfonate in purified form. The purification was accomplished by Dr. Dexter Reynolds according to the procedure described in the literature,⁹ in which the neutral oils were removed (amounting to about 4% by weight of the original sample). No significant difference in recoveries was noted between the two products.

Because ferric iron was found to affect flotation recovery so significantly, experiments were conducted with other salts to determine what effect, if any, other cations might have. The experimental procedure was the same as that described for the

FeCl₃ • 6H₂O additions. The results of this series of experiments are listed in Table H.

These results are especially interesting and significant since only one salt (FeCl₃ • 6H₂O) of those examined had a beneficial effect on flotation recovery. With the exception of chromium, which is very similar to ferric iron, all of the other salts actually hindered the flotation process considerably. Even ferrous iron was found to be detrimental. In terms of cation concentration, about 3 ppm Fe⁺⁺⁺ increased the recovery from 58 to 100%, while about 4 ppm Ca⁺⁺ decreased the recovery from 58 to 2%.

The effects of all the cations can probably be explained on the basis of solution phenomena. Reed and Tartar¹⁰ have shown the insolubilities of calcium and magnesium sulfonates as a function of chain length. In view of this, other polyvalent cations would be expected to form insoluble sulfonates, especially with those sulfonates containing very long chain lengths such as were used in this investigation.

Since ferric iron was found to be the only cation that affected flotation results favorably, it is apparent that quantitative information on the amount of free Fe⁺⁺⁺ and sulfonate ions that can be tolerated in solution before precipitation of ferric sulfonate would be extremely useful. An experiment was conducted by titrating ferric chloride into a solution containing 2.2×10^{-5} mole per liter sulfonate at pH 3.0. When 9×10^{-8} mole per liter Fe⁺⁺⁺ (as ferric chloride) was added, the solution became turbid or cloudy. Assuming that three moles of sulfonate are consumed with one mole of Fe⁺⁺⁺ in the precipitation of ferric sulfonate, this would then correspond to a solubility product on the order of 10^{-21} . Another time, using an identical experimental technique, a solubility product on the order of 10^{-20} was determined.

Sulfonate, of course, is not the only ion competing for Fe⁺⁺⁺ ion in solution. Hydroxyl ion is in constant competition with sulfonate for the iron. The effect of hydroxyl ion concentration was examined in a series of experiments in which sulfonate and Fe⁺⁺⁺ ion concentrations were held constant while pH was varied. Fig. 3 reveals that, at a constant sulfonate concentration of 2.12×10^{-5} mole per liter and con-

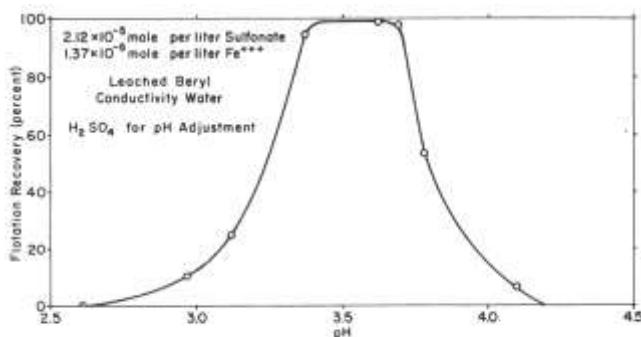


Fig. 3 — Relationship between flotation recovery and pH at constant additions of sulfonate and ferric chloride (separate experiments).

stant Fe⁺⁺⁺ concentration at 1.37×10^{-5} mole per liter, virtually no flotation could be effected below pH 3.0. However, when the pH was increased slightly to 3.37, complete flotation was obtained. Complete flotation was possible in the range from pH 3.37 to 3.70. When the pH was increased to 3.78, recovery was decreased by 50%; and finally, no flotation could be effected at pH 4.10.

Leached Beryl-Tap Water: The experimental results obtained with leached beryl in conductivity water with the addition of various salts suggest that insoluble cation-sulfonates are formed in solution and that the only cation-sulfonate possessing collector properties is ferric sulfonate. The results also showed that the addition of about 4 ppm Ca⁺⁺ reduced the recovery to essentially zero. Since Fe⁺⁺⁺ and Ca⁺⁺ ions exhibited diametrically opposed effects in separate systems, it is apparent that data on their relative competition for the sulfonate in the same system is required from the standpoint of practical application, especially when the Ca⁺⁺ concentration greatly exceeds that of the Fe⁺⁺⁺. In this regard, experiments were conducted with leached beryl in a tap water containing 30 ppm total calcium and magnesium, with and without specific additions of ferric iron at two different concentrations of sulfonate. See Table HI.

As expected, no flotation could be effected without specific additions of ferric iron at both of the sulfonate concentrations used. In the presence of added iron, however, flotation recoveries were enhanced significantly. The iron addition to both systems was about 2 ppm; since the tap water contained 30 ppm total calcium and magnesium, it is apparent that ferric sulfonate is more insoluble than calcium sulfonate and, as such, will form in preference to it.

Table III. Flotation Recovery of Leached Beryl in Tap Water*

Conditions	Recovery, %
2.13×10^{-5} M sulfonate No added iron Flotation pH 2.92	0.4
2.11×10^{-5} M sulfonate 3.39×10^{-5} M Fe ⁺⁺⁺ Flotation pH 2.88	51.6
6.37×10^{-5} M sulfonate No added iron Flotation pH 2.92	2.6
6.31×10^{-5} M sulfonate 3.37×10^{-5} M Fe ⁺⁺⁺ Flotation pH 2.84	81.8

*In the presence and absence of added ferric iron.

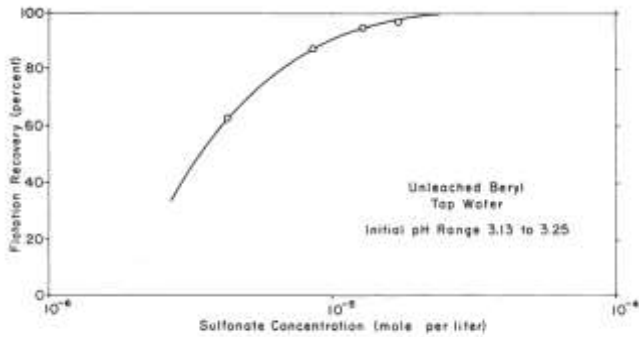


Fig. 4—Relationship between flotation recovery of unleached beryl and sulfonate concentrate in tap water.

Unleached Beryl-Tap Water: With practical application in mind, experiments were conducted with unleached beryl in tap water with various amounts of sulfonate present in acid media. Unleached beryl simply designates material that was wet-ground in a mild steel rod mill, sized to 48 x 150 mesh, and dried.

Fig. 4 reveals that high recoveries were obtained at relatively low concentrations of sulfonate, i.e., a recovery of 95% was achieved at a sulfonate concentration of 1.28×10^{-5} mole per liter. Since leached beryl could not have floated under these same conditions, it is apparent that a considerable amount of iron was imparted to the system during the grinding step.

Effect of pH: Hydrogen ion concentration is known to be one of the most important parameters of a flotation system. Its significance arises from the fact that it not only affects the electrical charge at solid-liquid interfaces but it also determines the extent of hydrolysis of various ions present in flotation systems. To determine the effect of pH, experiments were conducted with leached and unleached beryl in conductivity water and tap water at constant concentrations of sulfonate.

An interesting phenomenon was noted when pulps were conditioned and floated near neutral pH. The pH of the pulp increased rather markedly in weakly acidic systems (conductivity water and tap water) and decreased rather markedly in weakly basic systems (conductivity water only) when air was introduced into the cell. Since the changes were also observed with water alone in the flotation cell, the pH change in weakly acidic media has been ascribed to the evolution of CO_2 from the water, while the fall in pH in weakly basic media has been attributed to the introduction of CO_2 into the water.

The immediate problem created by this phenomenon was that it was difficult to determine accurately the pH at which flotation occurred in weakly acidic and weakly basic media. A chart of flotation recovery of leached beryl at constant sulfonate concentration as a function of pH is shown in Fig. 5. The data points are those values of pH measured after three minutes of conditioning and just prior to flotation. Maximum

recovery was obtained at pH 4.0. At values of pH lower than 4.0, flotation recovery decreased; i.e., a recovery of 74% was obtained at pH 4.0, while a recovery of 32% was obtained at pH 2.5. The decreased recovery at lower values of pH can probably be ascribed to the relatively high concentration of sulfate (actually sulfate-bisulfate) ions from the H_2SO_4 used for pH adjustment. (When HCl was used for pH adjustment, the recoveries were much greater at lower values of pH than those noted when H_2SO_4 was used). For example, at pH 2.5, there is a total sulfate concentration of 3.16×10^{-3} mole per liter. Since a sulfonate concentration of 8.46×10^{-5} mole per liter was used, the total sulfate concentration is 40 times greater than the sulfonate concentration. Furthermore, at pH 2.5, about 75% of the total sulfate is SO_4 , the remaining 25% being HSO_4 . The relatively high concentration of SO_4 , together with its divalency, makes it rather effective in competing with the sulfonate for the beryl surface.

The decrease in recovery at values of pH greater than 4 can probably be attributed to surface phenomena. The data suggest that the surface is positively charged in relatively acid media because good flotation can be effected with an anionic collector. With increasing pH, the surface will tend to become negatively charged, thereby resulting in lower flotation recoveries. As stated earlier, the data points represent the pH at which flotation was commenced. Since the pH was observed to change rather dramatically upon air introduction in weakly acidic and basic systems, the data points are not too meaningful in this region. Furthermore, these sulfonate systems were observed to foam quite badly above about pH 6. Actually, above this pH, the systems appeared to be one continuous column of foam, and it is felt that the recoveries obtained were not due to flotation so much as to physical levitation. Therefore, a dashed line has been drawn in Fig. 5 to suggest a curve of recovery as a function of pH.

From the standpoint of practical application, experiments were conducted with unleached beryl in tap water at constant sulfonate concentration but variable pH to determine the optimum hydrogen ion

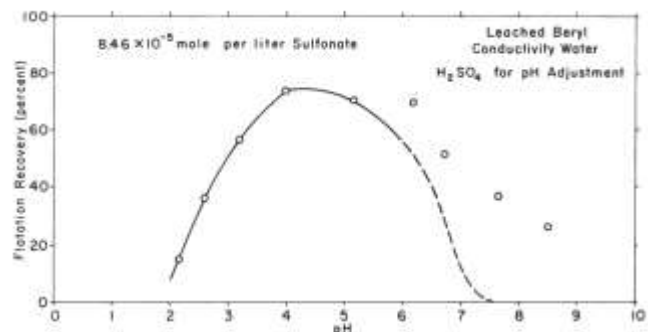


Fig. 5—Relationship between flotation recovery and pH at constant sulfonate concentration in conductivity water (separate experiments).

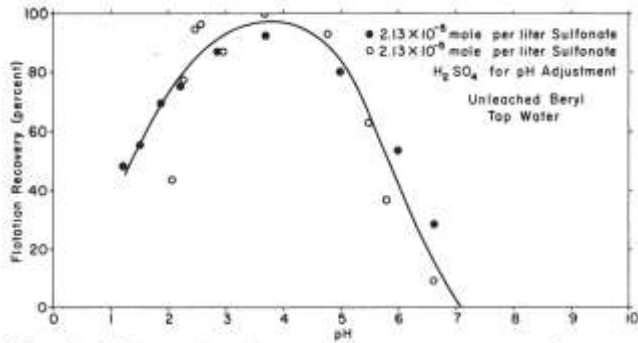


Fig. 6—Relationship between flotation recovery of unleached beryl and pH at constant sulfonate concentration in tap water (separate experiments).

concentration for maximum flotation recovery in the presence of various ionic impurities. Fig. 6 illustrates the results of this series of separate experiments in which flotation recovery is charted as a function of pH at a constant sulfonate concentration of 2.13×10^{-5} mole per liter. The circles and darkened circles represent data that were determined with samples of beryl ground at two different times and also used in the experimentation at two different times. Again, the data points are the values of pH recorded at the commencement of flotation. As shown, complete flotation was effected at pH 3.7; however, there was a fairly broad range of pH in which high recoveries were possible, i.e., from about pH 2.5 to 5.0. At low values of pH (approaching 2.0), recovery dropped rapidly because of the high total sulfate concentration. A similar drop in recovery occurred above pH 5; this was apparently due to electrical phenomena at the surface.

Flotation Response of Principal Gangue Constituents with Sulfonate: The experiments on samples of pure beryl revealed that the optimum hydrogen ion concentration for flotation was between 10^{-4} and 10^{-3} mole per liter and also that the addition of ferric iron was very beneficial. To determine the flotation response of the two principal gangue constituents under these same conditions, experiments similar to those conducted with beryl were run with pure samples of quartz and feldspar. A large number of experiments have been performed with both quartz and feldspar, but for the sake of brevity, only those results that have a direct bearing on the selective separation of beryl are presented here.

Quartz: The first series of separate experiments with systems of pure quartz concerned the determination of flotation recovery as a function of pH. The results are charted in Fig. 7 which shows data for constant sulfonate concentrations of 6.37×10^{-5} and 1.68×10^{-4} mole per liter. (The circles and darkened circles represent data that were determined using samples of quartz ground at two different times). As shown, maximum recovery was obtained in the vicinity of pH 4. Above and below pH 4, the curve of recovery as a function of pH drops very steeply. Above pH 4,

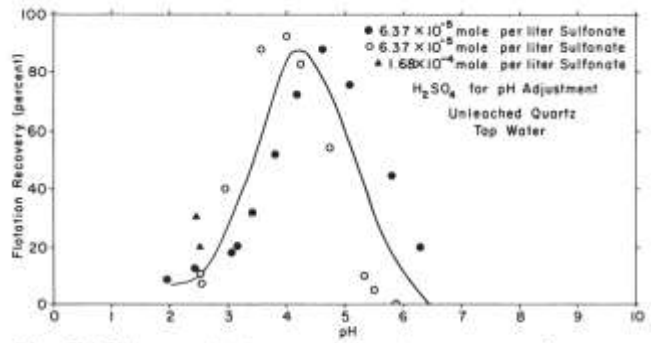


Fig. 7—Relationship between flotation recovery of unleached quartz and pH for two different constant sulfonate concentrations in tap water (separate experiments).

the decrease in recovery may again be directly attributable to electrical phenomena at the surface.

As the pH is lowered below 4, the sulfate ion concentration is also increased, since H_2SO_4 was used for pH adjustment. (It should be mentioned at this point that the tap water used contained 33 mg per liter sulfate). The data reveal the high sensitivity of the quartz surface to sulfate ions; note the steep slope of the curve below pH 4. Finally, when the pH was 2.5, virtually no flotation was effected. However, about 25% of the material can be floated with the relatively high sulfonate concentration of 1.68×10^{-4} mole per liter.

With reference to Fig. 6, beryl still responds well to flotation at pH 2.5; in fact, a recovery of about 90% was obtained at a sulfonate concentration of 2.13×10^{-5} mole per liter. A comparison of the data in these two figures reveals that a good selective separation of beryl from quartz can only be achieved at the relatively low pH of 2.5.

Feldspar: Experiments were also conducted with another principal gangue constituent, feldspar (microcline), to compare its flotation response to that of beryl.

In the first series of separate experiments with microcline, the relationship between flotation recovery and pH was established for unleached feldspar in tap water. Fig. 8 illustrates the results of these experiments; it will be noted that virtually no flotation could be effected at any pH with 6.37×10^{-5}

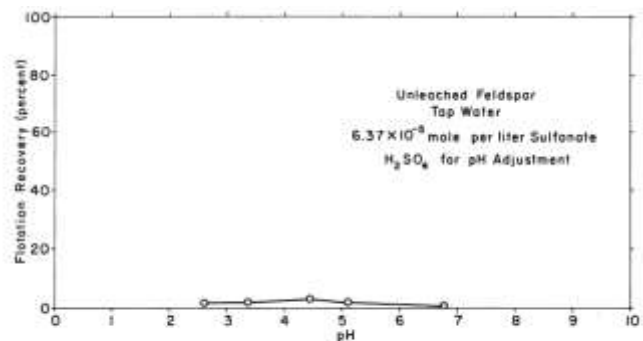


Fig. 8—Relationship between flotation recovery of unleached feldspar and pH at constant sulfonate concentration in tap water (separate experiments).

mole per liter sulfonate. This was somewhat surprising in view of the fact that nearly complete flotation was effected with both beryl and quartz in the vicinity of pH 4 at 6.37×10^{-5} mole per liter sulfonate

However, a comparison of this data obtained in tap water with data from similar experiments in conductivity water shows that the complete depression of the feldspar may be directly attributed to the relatively high sulfate ion concentration in the tap water. This can be seen from the fact that 1) the tap water used in the experimentation contains 33 mg per liter or 3.44×10^{-4} mole per liter sulfate, and 2) recovery of unleased feldspar in conductivity water with a constant sulfonate concentration of 6.37×10^{-5} mole per liter at various values of pH is as follows:

Recovery, %	Flotation pH
68.3	5.72
5.1	3.66

Feldspar floated well in mildly acidic conductivity water at a sulfonate concentration of 6.37×10^{-5} mole per liter. When the pH was lowered with H₂SO₄ to a value of 3.66, however, flotation was well nigh impossible, that is, a recovery of about 5% was obtained.

Even sulfonate concentrations greater than 6.37×10^{-5} mole per liter did not result in good flotation of feldspar in tap water, as shown below.

Sulfonate Concentration, M	Recovery, %	Initial pH
8.46×10^{-5}	2.3	3.29
1.68×10^{-4}	8.4	3.28

The extreme sensitivity of the feldspar surface to sulfate ions can be used to advantage in different ways; one, by working at relatively low values of pH, such as 2.5, a selective separation of beryl from feldspar should be possible, and two, at a slightly higher pH, a selective separation of quartz from feldspar should also be possible.

Experiments performed with separate systems of the pure minerals (beryl, quartz and feldspar) showed

that a good selective separation of beryl from the two principal gangue constituents should be effected at pH ~2.5. As such, experiments were conducted with a natural ore to confirm this observation.

Natural Ore: The ore investigated was from the Harding Mine dump, Dixon, N.M. The ore assayed 0.55% BeO and contained quartz, feldspar, apatite, mica schist and a substantial amount of iron-bearing silicates. The optimum experimental procedure employed in selectively separating beryl from the gangue is as follows:

- 1) A 500-g charge of ore was ground through 48 mesh.
- 2) The charge was then deslimed by decantation at 20g.
- 3) After repulping with tap water, the pH was adjusted to 2.40 with sulfuric acid.
- 4) The pulp was conditioned with 0.73 lb per ton primary tallow amine acetate and two drops (0.12 lb per ton) of methyl isobutyl carbinol for 3 min.
- 5) The mica schist was then removed during 3 min of flotation.
- 6) The pulp was thickened.
- 7) After repulping, the pH was adjusted to 2.60 with sulfuric acid.
- 8) The pulp was stage-conditioned with 0.98 lb per ton sodium alkyl aryl sulfonate and one drop of methyl iso-butyl carbinol for 3 min.
- 9) A beryl concentrate was obtained in 3 min of flotation (the final pH 2.65).
- 10) The rougher beryl concentrate was cleaned and recleaned at pH 2.7 with only an addition of one drop of frother.
- 11) The recleaner concentrate was then dried and passed through a high-intensity magnetic separator to remove apatite and iron-bearing gangue minerals. Typical results obtained from one of several experiments using this technique are listed in Table IV. A recleaner concentrate amounting to a recovery of about 70% of the beryl at a grade of 8.00% BeO was obtained by this procedure. The data also reveal that a relatively large amount of material (127.2 g out of

Table IV. Flotation Products and Their BeO Assays Obtained with a Natural Ore

Product	Weight, G	Weight, %	Percent BeO	BeO Content	Percent Distribution
Recleaner concentrate (non-magnetic)	23.4	4.86	8.00	0.389	67.83
Recleaner concentrate (magnetic)	13.2	2.74	0.290	0.008	1.39
Recleaner tails	30.2	6.28	1.360	0.086	15.00
Cleaner tails	60.4	12.56	0.298	0.037	6.45
Final tails	257.0	53.38	0.016	0.009	1.57
Mica concentrate	74.0	15.40	0.122	0.019	3.32
Slimes	23.0	4.78	0.542	0.026	4.54
Calculated heads	481.2	100.00		0.574	100.10
Heads assay			0.550		

400 g) had to be floated to obtain a good rougher tailing (0.016% BeO). Although experimentation on systems of pure quartz indicated that the flotation response of quartz should be *sluggish* at pH 2.5, a sufficient amount floated from the ore to require two cleanings to raise the grade of the final beryl concentrate.

As anticipated, feldspar did not float at this pH and contaminate the concentrate.

The other principal contaminants of the recleaner concentrate were apatite and iron-bearing silicates. Their response to flotation was such that the only method available for separating them from the beryl was by high-intensity magnetic separation. The iron-bearing silicates will always present problems of concentrate contamination with this technique because of their amenability to sulfonate flotation. Ferric sulfonate has been demonstrated to be relatively insoluble, and as a result, the compound, ferric sulfonate, should be formed at the surface, resulting in good flotation even in the cleaning steps.

DISCUSSION AND SUMMARY OF RESULTS

Experimentation with leached beryl in conductivity water led to some interesting and important observations: 1) at moderate concentrations of sulfonate (e.g., 8.46×10^{-5} mole per liter), leached beryl responds well to sulfonate flotation; 2) the optimum pH for flotation is in the vicinity of 4; and 3) the presence or absence of various cations affects flotation response significantly.

When leached beryl was floated in conductivity water in the absence of added salts, recovery was noted to increase with increasing collector concentration. Extrapolation of data presented by Wark¹¹ suggests that micelles should form with this particular sulfonate (25 to 30 carbon atoms) at about 10^{-6} mole per liter. As the concentration of sulfonate exceeded this value in all of the experiments, micelles must have been present in these systems. Flotation recoveries could increase with increasing collector concentration if the micelles rupture when contacting mineral particles, thereby enabling individual ions to adsorb onto the particle surfaces.

When various salts were added to flotation systems of leached beryl and conductivity water, two phenomena were noted to occur. First, when salts of aluminum, calcium, copper, cobalt, ferrous iron, manganese and ruthenium were added, flotation recoveries were decreased drastically. Secondly, when ferric iron was added to similar systems, flotation was enhanced significantly. The data suggest that these phenomena are due to reactions in solution rather than to reactions at the solid-liquid interface. This suggestion is in agreement with the results obtained by Reed and Tarter who have determined the insolubilities of calcium and magnesium sulfonates as a function of chain length. If calcium and magne

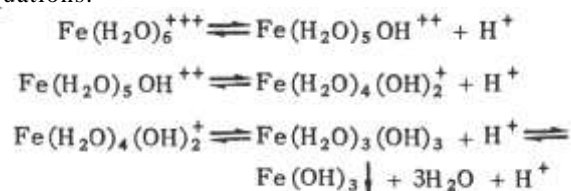
sium form insoluble sulfonates, it is expected that other polyvalent cations will form insoluble sulfonates, especially with those sulfonates containing very long chain lengths as used in this investigation.

Since ferric iron was found to be the only cation of those investigated that affected flotation results favorably, it is apparent that quantitative information concerning the amount of free Fe^{+++} and sulfonate ions that can be tolerated in solution before precipitation of ferric sulfonate would be extremely useful. Titration experiments involving ferric chloride and sulfonate at pH 3.0 showed that an insoluble cloud formed at the following concentrations, 2.2×10^{-5} mole per liter sulfonate and 9×10^{-8} mole per liter Fe^{+++} .

This titration technique is only qualitative at best since the exact point at which the solution became cloudy was somewhat difficult to define. Although the solution assumed a cloudy appearance, a thick precipitate was not formed. In view of this, more accurate determinations were attempted by using a spectrophotometer as a turbidimeter. This technique was also not sensitive enough. Therefore, a *reflectance turbidimeter*, or nephelometer, is presently being set up to enable more accurate determinations of the concentrations of salts and sulfonate at which cloud formation appears.

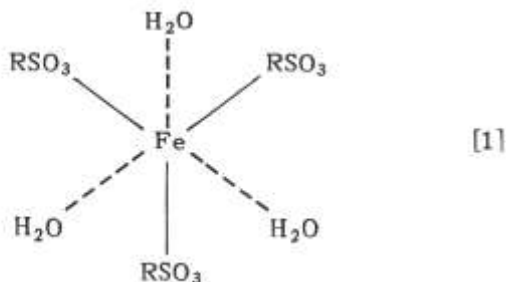
In all of the experiments involving ferric iron additions, the solubility product of ferric sulfonate was exceeded. That is, ferric iron additions on the order of 10^{-5} mole per liter were made to systems containing 10^{-5} mole per liter sulfonate or greater. Furthermore, with reference to Fig. 2, it can be noted that 2.72×10^{-5} mole per liter Fe^{+++} was required for complete flotation with 2.12×10^{-5} mole per liter sulfonate. This means that the solubility product of ferric sulfonate was exceeded by at least two orders of magnitude at the point of complete flotation. This suggests that ferric sulfonate is precipitated immediately in solution and, as such, suggests strongly that *solid ferric sulfonate in some form* is functioning as the collecting agent.

Sulfonate, of course is not the only ion competing for the Fe^{+++} ion. Hydroxyl is in constant and direct competition with the sulfonate. The competition arises because of the hydrolysis of ferric salts in water. When ferric iron hydrolyzes, three hydroxide complexes are involved between the hydrated ferric ion, $\text{Fe}(\text{H}_2\text{O})_6^{+++}$, and the insoluble $\text{Fe}(\text{OH})_3$ precipitate.¹² This may be represented by the following equations:

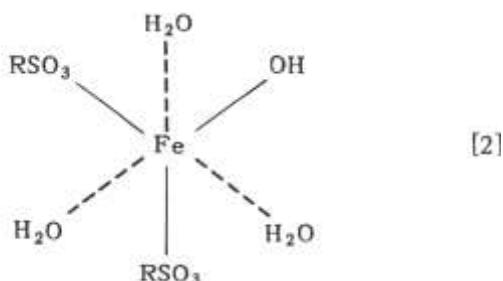


The extent of hydrolysis is determined by both the ferric ion concentration and pH. The configuration of

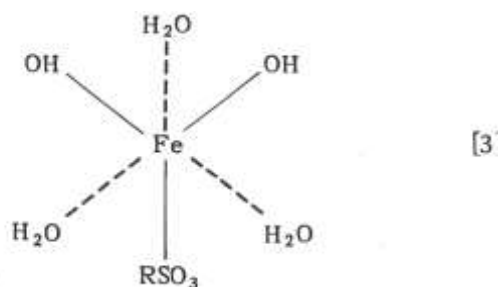
any ferric compound, such as ferric sulfonate, will in turn depend on the extent of hydrolysis of ferric iron. For example, at low concentrations of ferric iron or at low values of pH, ferric iron will probably be present in water predominantly as $\text{Fe}(\text{H}_2\text{O})_6^{+++}$. When sulfonate is present with low concentrations of ferric iron and low values of pH, the compound, $\text{Fe}(\text{RSO}_3)_3$, will probably be formed, provided the solubility product of ferric sulfonate is exceeded. The general configuration of the compound, $\text{Fe}(\text{RSO}_3)_3$, might be as follows:



In water, at higher concentrations of ferric iron or at higher values of pH, ferric iron will probably be present predominantly as the first hydroxide complex, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{++}$. In the presence of sulfonate with higher concentrations of ferric iron or higher values of pH, the compound, ferric sulfonate, will necessarily include the first hydroxide complex. The configuration of this compound, $\text{Fe}(\text{RSO}_3)_2(\text{OH})$, might now be as follows:



At still higher concentrations of ferric ion or at higher values of pH, further hydrolysis of ferric iron is to be expected, and the second hydroxide complex, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{++}$, will probably be the predominate species in water. In the presence of sulfonate, the compound, ferric sulfonate, would then include the second hydrolysis complex. The general configuration of this compound, $\text{Fe}(\text{RSO}_3)(\text{OH})_2$, might be as follows:



Finally, when high concentrations of ferric iron or when relatively high values of pH are involved, the neutral hydroxide complex, $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3$, should predominate in water. Under these conditions, ferric hydroxide should be more insoluble than ferric sulfonate, and as such, will form in preference to it.

With reference to Fig. 1, it can be noted that the addition of ferric iron to flotation systems results in two phenomena, dependent on the amount of iron added. When 1.36×10^{-5} mole per liter Fe^{+++} was added to systems containing various amounts of sulfonate, recoveries were actually decreased from those obtained in the absence of added ferric iron at higher sulfonate concentrations. However, when a somewhat greater amount of ferric iron, i.e. 2.05×10^{-5} mole per liter, was added to systems containing various amounts of sulfonate, higher recoveries were obtained at lower sulfonate concentrations. Increased additions of iron, i.e. 2.72×10^{-5} mole per liter, resulted in complete flotation at even lower sulfonate concentrations.

The former case, in which the additions of ferric iron actually reduced recoveries from those obtained with sulfonate alone, could be explained by the following reasons:

- 1) The solubility product of ferric sulfonate was exceeded at these concentrations of sulfonate and ferric iron.
- 2) If the predominant species of ferric iron in water were $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ at this concentration of iron and at this pH, the compound, ferric sulfonate, formed under these conditions would be $\text{Fe}(\text{RSO}_3)_3$. It is difficult to imagine that a compound *in this form* would possess collector properties, especially when aluminum and calcium sulfonates do not (see Table III). The reduction in recovery observed when 1.36×10^{-5} mole per liter Fe^{+++} was added to systems at higher sulfonate concentrations could then be simply due to the precipitation of ferric sulfonate, $\text{Fe}(\text{RSO}_3)_3$. Since three moles of sulfonate would be consumed with one mole of Fe in the precipitation of ferric sulfonate, the effective concentration of sulfonate in solution would then be reduced, and flotation recoveries would be reduced correspondingly.

The increased floatability observed at higher iron additions, that is 2.05×10^{-5} mole per liter Fe^{+++} , may be explained as follows:

- 1) The solubility product of ferric sulfonate has been exceeded at these concentrations of sulfonate and ferric iron.
- 2) If the predominant species of ferric iron in water were $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{++}$ under these conditions, the compound, ferric sulfonate, should contain this hydroxide complex and would be represented by $\text{Fe}(\text{RSO}_3)_2\text{OH}$. The hydroxyl, or oxygen, contained in this compound would provide a means of bonding to the mineral surface. It is presently thought that this is one of the two forms of ferric sulfonate pos-

sessing collector properties. (The other form will be discussed subsequently).

The interdependence of iron and hydroxyl at constant sulfonate concentration is illustrated in Figs. 1 and 3. For example, as shown in Fig. 1, at 2.12×10^{-5} mole per liter sulfonate and at constant pH, doubling the ferric iron concentration, (i.e., from 1.36 to 2.72×10^{-5} mole per liter) resulted in complete flotation. On the other hand, Fig. 3 demonstrates that, at the same sulfonate concentration of 2.12×10^{-5} mole per liter and at constant ferric iron concentration of 1.37×10^{-5} mole per liter, doubling the hydroxyl ion concentration, i.e., from pH 3.07 to 3.37, again resulted in complete flotation. These results illustrate rather well the direct interdependence of ferric ion and hydroxyl ion in this system.

Fig. 3 also shows that complete flotation can be effected up to pH 3.70. At this pH and with this ferric iron concentration (1.37×10^{-5} mole per liter Fe^{+++}), the ferric iron is probably present predominantly as the first and second hydroxide complexes. Ferric sulfonate would then be present as $\text{Fe}(\text{RSO}_3)_2\text{OH}$ and/or $\text{Fe}(\text{RSO}_3)(\text{OH})_2$. In either case, good flotation would be effected.

However, when the pH is increased from 3.70 to 3.78 at the same sulfonate (2.12×10^{-5} mole per liter) and the same ferric iron (1.37×10^{-5} mole per liter) concentrations, recovery is decreased by 50%. This indicates that the neutral hydroxide complex, $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3$, is probably present in fair concentration at pH 3.78 and, when the pH is raised to 4.1, is probably the predominant species in the system.

With $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3$, all of the residual valences of ferric iron are now satisfied with hydroxyl ions; ferric ion would then be inert to sulfonate ions. In other words, ferric hydroxide is more insoluble than ferric sulfonate at pH 4.1 or above and will form in preference to it.

The utility of the collector, $\text{Fe}(\text{RSO}_3)_2(\text{OH})$ or $\text{Fe}(\text{RSO}_3)(\text{OH})_2$, can be seen from the flotation data determined with leached beryl in a tap water containing 30 ppm total calcium and magnesium. In the absence of iron, no flotation could be effected with the maximum sulfonate concentration used, which was 6.37×10^{-5} mole per liter. As a matter of fact, assuming two moles of sulfonate are consumed with one mole of calcium in the precipitation of one mole of $\text{Ca}(\text{RSO}_3)_2$, 675 mg per liter or 1.5×10^{-3} mole per liter sulfonate would be consumed by 30 mg per liter or 7.5×10^{-4} mole per liter Ca^{++} .

However, when 1.89 mg per liter or 1.89 ppm Fe^{+++} was added to the leached beryl-tap water system at a sulfonate concentration of 6.31×10^{-5} mole per liter, a recovery of 81% was obtained at pH 2.84. It is apparent that the collector, $\text{Fe}(\text{RSO}_3)_2(\text{OH})$ or $\text{Fe}(\text{RSO}_3)(\text{OH})_2$, is more insoluble than calcium sulfonate and will form in preference to it.

The data determined with *unleached beryl in tap*

water show that deliberate additions of ferric iron are unnecessary when the material is wet ground in a mild steel mill. In this case, high recoveries are obtained at relatively low concentrations of sulfonate (95% recovery at 1.28×10^{-5} mole per liter sulfonate) in the absence of added iron. This observation is of considerable importance from the standpoint of practical application.

In the absence of appreciable concentrations of detrimental cations in solution, the formation of cation-sulfonates between a surface ion and sulfonate at the solid-liquid interface probably accounts for good flotation collection under optimum conditions. With beryl, insoluble compounds at the surface would be beryllium and aluminum sulfonates. (Actually, this phenomenon may well be responsible for the ease of sulfonate flotation of hematite).

The important effect that pH has on the experimental results is also apparent from the data. Hydrogen ion concentration assumes such a significant role in flotation for the following reasons: 1) It establishes the electrical charge at the silicate mineral-liquid interface. 2) It may determine the extent of hydrolysis of certain ions in the system (as described). 3) An anion is contributed to the system; if H_2SO_4 is used for pH adjustment, the anion (SO_4) can affect flotation results significantly.

As to the role assumed by sulfate ions, a selective separation of the minerals studied is probably due only to the *sensitivity* of the various surfaces to sulfate ions, since their surfaces would all have become more positively charged with increased hydrogen ion concentration. Unleached quartz responded poorly to sulfonate flotation in a tap water containing 33 mg per liter sulfate in the vicinity of pH 2.5, whereas beryl still responded well under these conditions. On the other hand, microcline did not respond at all to flotation in this tap water at this pH — even high concentrations of sulfonate did not improve recovery.

The important effect of sulfate is further illustrated with unleached microcline in conductivity water. Microcline floated well at pH 5.72 with 6.37×10^{-5} mole per liter sulfonate. However, when the pH was decreased to 3.66 with H_2SO_4 , no flotation could be effected at this same concentration of sulfonate.

Finally, experiments were conducted with a natural ore to confirm some of the observations made with separate systems of pure minerals (beryl, quartz, feldspar). The natural ore contained 0.55% Be() as beryl; quartz, feldspar, mica, apatite, and iron-bearing silicates constituted the gangue. Following the procedure indicated by the results obtained with pure mineral systems, a recovery of about 70% of the beryl was obtained at a grade of 8.00% BeO in the final concentrate. The overall recovery in the rougher stage was about 90%, the 10% losses being in the slimes, mica concentrate, final tailings and magnetic fractions.

ACKNOWLEDGMENTS

The authors wish to thank A. J. Thompson, Director of the Bureau of Mines, and Drs. K. Brower, D. Reynolds and P. Roeder for their interest and for the many discussions held with them on various phases of the experimental work.

The authors also wish to thank Dr. A.M. Gaudin of the Massachusetts Institute of Technology and Dr. D. W. Fuerstenau of the University of California for their critical review of the manuscript.

REFERENCES

¹R. C. Evans: *An Introduction to Crystal Chemistry*, University Press, Cambridge, England, 1952.

²A. M. Gaudin: *Flotation*, McGraw-Hill Book Co. Inc., New York, 1957.

³S. M. Runke: Beneficiation of Beryllium Ores by Froth Flotation, U.S. Patent No. 2666587.

⁴H. L. Gibbs and H. D. Snedden: Beneficiation of Beryllium Ores, U.S. Patent No. 2395475.

⁵F. D. Lamb and L. Banning: Beneficiation of Beryllium Ores, U.S. Patent No. 2385819.

⁶J. S. Kennedy and R. G. O'Meara: Beneficiation of Beryllium Ores, U.S. Patent No. 2414815.

⁷R. S. Dean and P.M. Ambrose: *USBM Bulletin 449*, 1944.

⁸Shell Chemical Company, Industrial Chemicals Division: *Preliminary Data Sheet*, July 1961.

⁹C. M. Gardner, C.H. Hale, E. A. Setzkom and W. C. Woelfel: Determination of Combining Weight of Sulfonate, *Analytical Chemistry*, 1958, vol. 30, p. 1712.

¹⁰R.M. Reed and H. V. Tarter: *J. Am. Chem. Soc.*, 1936, vol. 58.

¹¹K. L. Sutherland and I. W. Wark: *Principles of Flotation*, Australasian Inst. of Mining & Metallurgy, Melbourne, Australia, 1955, p. 243.

¹²L. Pauling: *General Chemistry*, 2nd Ed., W.H. Freeman and Co., San Francisco, 1956, p. 446.

