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THE ROLE OF HYDROLYSIS IN SULFONATE FLOTATION OF QUARTZ

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Experiments revealed that quartz could not be floated in conductivity water at any pH with a long-chained sulfonate as collector. Various cations, Fe^{+++}, Al^{+++}, Pb^{++}, Mn^{++}, Mg^{++}, Ca^{++}, *are shown to function as activators when the pH is such that the cation hydrolyzes. As the solubility product of the various cation-sulfonates was exceeded at the concentrations involved, precipitated cation-hydroxy-sulfonates, e.g.* $Fe(RSO_3)_2OH$ *must be functioning as the collector in these systems.*

A number of interesting and important phenomena were revealed during a study of the response of beryl to sulfonate flotation.[1] Perhaps the most important observation is the effect of various cations on flotation response. Experiments showed that in the vicinity of pH 3.0, about three ppm Fe^{+++} increased recovery of leached beryl from about 60 pct to 100 pct, whereas about four ppm Ca^{++} reduced the recovery from 60 pct to 2 pct. With the exception of ferric iron, all of the other cations investigated reduced flotation recoveries drastically at this pH.

As postulated in the paper *Sulfonate Flotation of Beryl,*[1] even with low concentrations of polyvalent cations and sulfonate (on the order of one ppm), cation-sulfonates are precipitated immediately in solution. That is, blueish-white clouds were noted to form after given additions of salts to known solutions of sulfonate. Furthermore, it was also shown that one-hundred-fold more ferric iron than necessary to form the precipitated cloud had to be added to effect complete flotation. In other words, some form of *solid* ferric sulfonate was found to function as the collector in these systems. The form of the compound was suggested to be $Fe(RCO_3)_2OH$ and that bonding to the surface occurs through the hydrogen of the hydroxyl. As the form of this compound was shown to be dependent on the extent of hydrolysis of ferric iron, it is to be expected that ferric iron will be unique in some pH region. Further, if the presence of hydroxyl in the neutral precipitated compound is of primary importance, then other cations should function similarly but at different values of pH, since they will hydrolyze at different concentrations of hydroxyl ion. To determine whether the premise of hydrolysis is correct, the study was extended to quartz systems in the presence of various cations at various values of pH.

EXPERIMENTAL MATERIALS AND METHOD

Sodium alkyl aryl sulfonate was chosen as the collector for the experimental work. The reagent, supplied as a courtesy sample by the Shell Chemical Co., has the following physical properties:[2]

Physical form	Solid – Finely ground
Sulfonate content, pct wt	95 to 97
Molecular Weight	450 to 470
Number of carbon atoms in hydrocarbon chain	25 to 30
Melting Point, °F	250 to 260
Solubility	Soluble in water with gel formation at concentrations higher than 25 pct by weight sulfonate

This particular reagent was chosen because of its high active sulfonate content, long-chain length, and solid form. With the exception of the frother and sulfonate, all other chemicals were of reagent grade quality.

Conductivity water was used in the experimental work. This water, made by passing distilled water through an ion exchange column, had an average measured conductivity of one micromho.

Experiments were conducted at room temperature in a small glass flotation cell with the following procedure:

1) A predetermined amount of water and salt solution (e.g. $CaCl_2 \cdot 2H_2O$) were combined and the pH adjusted to a given value.

2) A given amount of sulfonate was added so that final solution volume was 130 cc.

3) One drop of Dow 250 frother was added.

4) Five g of quartz were added and the system conditioned for five minutes.

5) The pH of the system was measured (termed *flotation pH*).

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6) Thirty cc of purified nitrogen were passed through the cell at an average flow of 120 cc per min.

7) The pH of the system was measured (termed *final pH*).

The small glass flotation cell was made by removing the stem of a 150 cc Buchner funnel (fritted glass filter) with a torch. Another small stem was placed beneath, parallel, and close to the glass filter for nitrogen introduction. Also, a lip was bent at the top of the cell to collect the froth. Agitation was accomplished with a magnetic stirrer.

A constant flotation parameter of 30 cc of N_2 was used, this volume of gas being passed through the cell at constant pressure.

A total solution volume of 130 cc was used in the experiments involving calcium, manganous, and lead chlorides, while 145 cc volume was used with all of the other salts. This occurred because two flotation cells were used, and the lips were not at the same depth.

EXPERIMENTAL RESULTS

Since ferric iron was found to function as an extraordinary activator for beryl, it was expected that it would also affect quartz in a similar manner. To determine the response of quartz to sulfonate flotation in the absence of iron, the quartz was batch-leached with aqua regia for 18 hrs. Following this, the material was washed with conductivity water until the liquor was at the pH of the conductivity water and dried. As some iron was found to be present on the particle surfaces even after this treatment (presumably due to the precipitation of ferric hydroxide during the washing step), the leached quartz was releached with concentrated HCl until no color could be detected in the leach liquor. The releach was conducted with a percolation technique using successive residence times of 24 hrs. This material was then washed with conductivity water again until the liquor was at the pH of the water and dried.

Separate experiments were then conducted with five-g charges of this material at constant sulfonate concentration (6.93×10^{-5} mole per liter, assuming 450 as the molecular weight of the sulfonate) at various values of pH. No flotation could be effected at any pH under these conditions.

As mentioned previously, earlier work with beryl revealed the extraordinary value that ferric iron has as an activator. To determine whether this phenomenon is unique to the beryl surface or due to reactions in solution, similar experiments were conducted with quartz. As revealed in Fig. 1, no flotation could be effected at pH 2.19 at a constant sulfonate concentration of 5.52×10^{-5} mole per liter and constant Fe^{+++} concentration of 1.83×10^{-4} mole per liter. A slight increase in flotation pH (i.e. 2.27) resulted in a recovery of 73 pct, while complete flotation was effected at pH 2.42. Complete flotation was possible in the range from pH 2.42 to pH 3.15. When the pH was increased to 3.42, recovery was decreased by about 65 pct; and finally, no flotation could be obtained at pH 3.70.

In the case of beryl, it was postulated that complete flotation was due to the formation of hydroxide complexes of ferric iron with subsequent precipitation of ferric hydroxy sulfonate.[1] If this model is correct, then other cations should function similarly but in different pH regions. That this is indeed the case can be seen from data determined with additions of aluminum chloride, lead chloride, manganous chloride, magnesium chloride, and calcium chloride (Figs. 2-6).

As revealed in Fig. 2, at constant concentrations of sulfonate and aluminum, no flotation could be effected at pH 3.97 and below. Increasing the pH to 4.42 resulted in essentially complete flotation. A maximum recovery of about 87 pct was achieved in the range from pH 4.42 to pH 7.0. Increasing the pH to 7.52 resulted in a flotation recovery of about 10 pct; and finally, no flotation could be obtained at pH 7.80 or above.

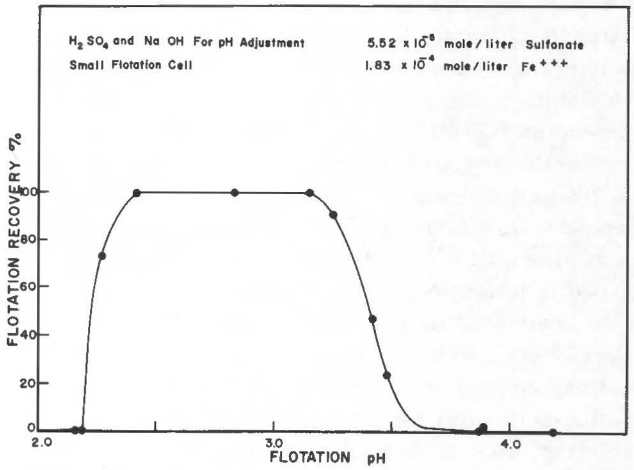


Fig. 1 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and ferric chloride. (Separate experiments.)

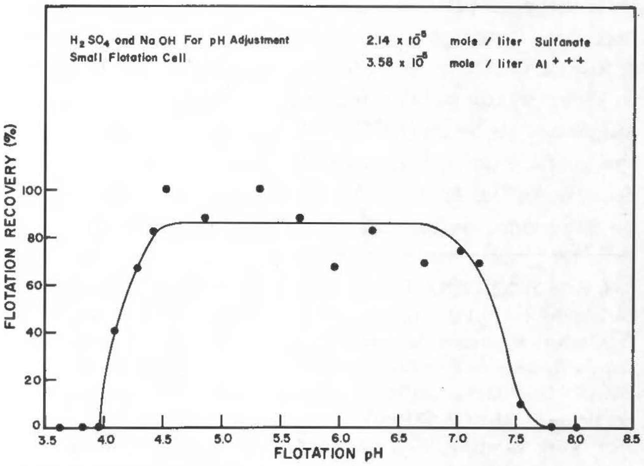


Fig. 2 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and aluminum chloride. (Separate experiments.)

Fig. 3 shows the flotation response of quartz in the presence of 5.44×10^{-5} mole per liter sulfonate and 1.71×10^{-4} mole per liter Pb^{++}. No flotation was obtained at pH 6.09 or below, while complete flotation was effected at pH 6.58. Complete flotation was possible between pH 6.58 and pH 11.72. Flotation was noted to cease at pH 12.1 and above.

When quartz was floated in the presence of 6.29×10^{-5} mole per liter sulfonate and 1.94×10^{-4} mole per liter Mn^{++}, no flotation could be effected at pH 7.9 or below. Complete flotation was achieved at pH 8.25 and was obtained throughout the region of pH 8.25 to pH 8.55. Complete depression resulted at pH 8.90 and above. See Fig. 4.

Considerable scatter in the data can be noted at higher values of pH. Reasons for this are discussed in the section on Discussion and Summary of Results.

Fig. 5 reveals data determined in the presence of 6.56×10^{-5} mole per liter sulfonate and 1.73×10^{-4} mole per liter Mg^{++}. As shown, virtually no flotation could be obtained at pH 10.35 or below. Increasing the pH to 10.75 resulted in complete flotation. Complete flotation was effected from pH 10.75 to pH 11.52. When the pH was 11.62 and above, complete depression of the quartz occurred.

Calcium functions similarly to the other cations but at a higher pH. That is, virtually no flotation was effected at pH 10.90 or below at constant concentrations of sulfonate and Ca^{++}. Increasing the pH to 11.10, however, resulted in complete flotation. Complete flotation was possible in the range of pH 11.1 to pH 13.0. Above pH 13.0 recovery was noted to decrease. (See Fig. 6).

DISCUSSION AND SUMMARY OF RESULTS

The experimental results revealed that cation-sulfonates were precipitated with all of the cations examined at the concentrations used. That is, blueish-white colloidally-dispersed clouds were noted to be present in all of the solutions after the various salts and sulfonate were combined. In other words, some form of these precipitates must be functioning as the collector in these systems.

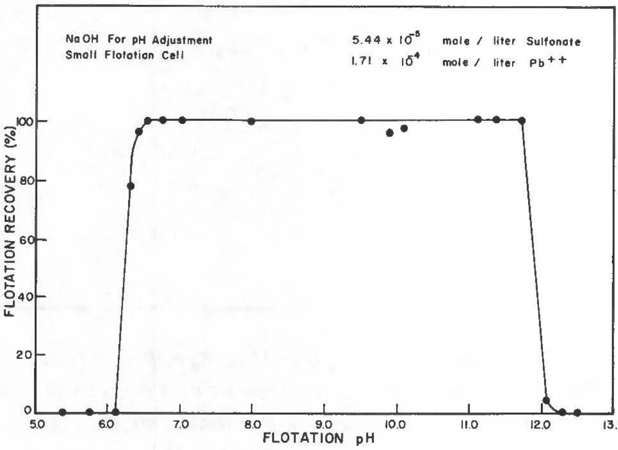


Fig. 3 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and lead chloride. (Separate experiments.)

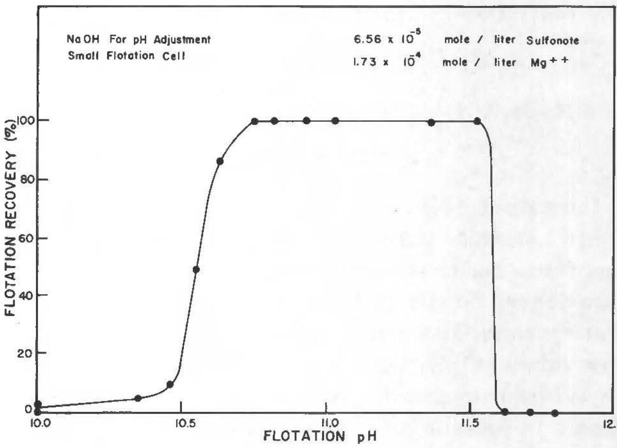


Fig. 5 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and magnesium chloride. (Separate experiments.)

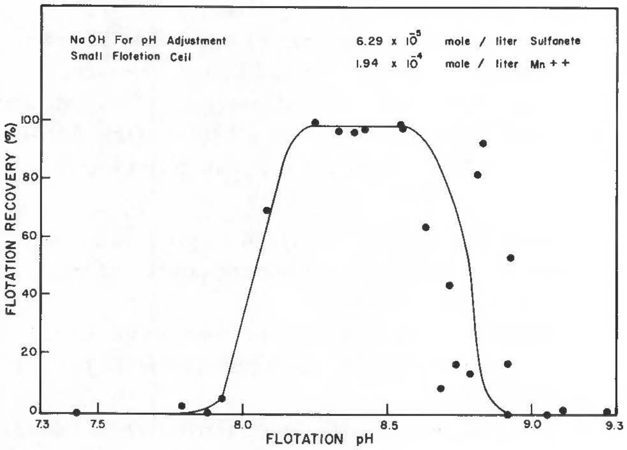


Fig. 4 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and manganous chloride. (Separate experiments.)

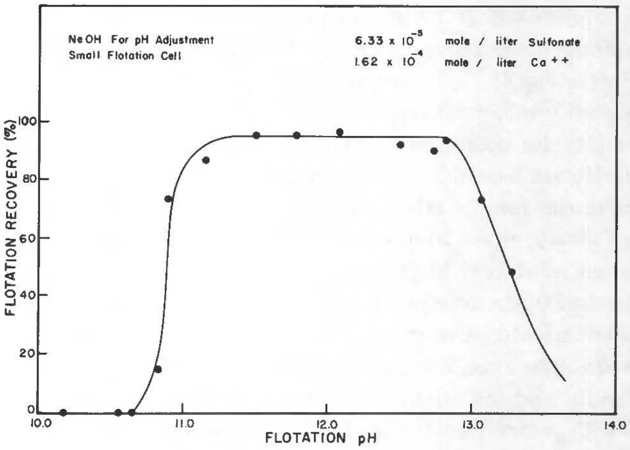


Fig. 6 – Relationship between flotation recovery and pH at constant concentrations of sulfonate and calcium chloride. (Separate experiments.)

In addition, the experimental results showed that trivalent ions activate quartz at relatively low values of pH, while calcium functions as an activator at the highest pH. Actually, when the order of activation, i.e. Fe^{+++}, Al^{+++}, Pb^{++}, etc., is compared with the solubility products of the hydroxides of these cations, it is strongly suggested that their role as activators if intimately related to their hydrolysis. (See Table I.)

Further comparison with precipitation pH values for hydrous oxides and hydroxides of various metal ions[4] supplies very strong support for this premise. (See Table II.)

This table shows, for example, that Fe^{+++} iron starts to hydrolyze at pH 2, Al^{+++} at pH 4, Mn^{++} between pH 8 and pH 9, etc.

The results become quite meaningful when the hydrolysis schemes of the various cations are examined. For example, in the case of ferric iron, three hydroxide complexes are involved between the hydrated ferric ion, $Fe(H_2O)_6^{+++}$, and the insoluble $Fe(OH)_3$ precipitate.[3] This may be represented by the following equations

$$Fe(H_2O)_6^{+++} \rightleftharpoons Fe(H_2O)_5OH^{++} + H^+$$

$$Fe(H_2O)_5OH^{++} \rightleftharpoons Fe(H_2O)_4(OH)_2^{+} + H^+$$

$$Fe(H_2O)_4(OH)_2^{+} \rightleftharpoons Fe(H_2O)_3(OH)_3 + H^+$$

$$\rightleftharpoons Fe(OH)_3 \downarrow \quad + 3H_2O + H^+.$$

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 ion or at low values of pH, ferric iron will probably be present in water predominantly as $Fe(H_2O)_6^{+++}$. When sulfonate is present with low concentrations of ferric iron and low values of pH, the compound, $Fe(RSO_3)_3$, will probably be formed, provided, of course, that the solubility product of ferric sulfonate is exceeded.

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, $Fe(H_2O)_5OH^{++}$. 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 and would have the form, $Fe(RSO_3)_2OH$.

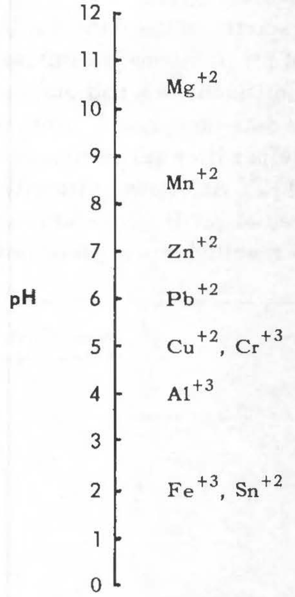
Finally, when high concentrations of ferric iron or when relatively high values of pH are involved, the neutral hydroxide complex, $Fe(H_2O)_3(OH)_3$, should predominate in water. Under these conditions, ferric hydroxide should be more insoluble than ferric sulfonate and, as such, will form in preference to it.

With reference to Fig. 1, at a sulfonate concentration of 5.52×10^{-5} mole per liter and at a constant ferric iron concentration of 1.83×10^{-4} mole per liter, no flotation could be effected below about pH 2.19.

Table I.

Hydroxide	$K_{SP}(3)$	Lowest pH for Complete Flotation
$Fe(OH)_3$	1×10^{-38}	2.42
$Al(OH)_3$	1×10^{-33}	4.42
$Pb(OH)_2$	1×10^{-16}	6.58
$Mn(OH)_2$	1×10^{-14}	8.25
$Mg(OH)_2$	6×10^{-12}	10.75
$Ca(OH)_2$	8×10^{-6}	11.10

Table II. Precipitation pH Values for Hydrous Oxides and Hydroxides of Various Metal Ions.



At pH 2.42, however, complete flotation was effected. As shown, complete flotation was effected up to pH 3.15. Finally, flotation was not possible at pH 3.7 under these conditions. The data can perhaps be explained as follows:

1) At these concentrations of sulfonate and ferric iron, the solubility product of ferric sulfonate has been exceeded.

2) If the predominant species of ferric iron in water were $Fe(H_2O)_6^{+++}$ at pH 2.19 and below, the compound, ferric sulfonate, formed under these conditions would be $Fe(RSO_3)_3$. It is difficult to imagine that a compound *in this form* would possess collector properties.

The complete flotation observed at pH 2.42 at this same ferric iron and same sulfonate concentration may be explained as follows:

1) At these concentrations of sulfonate and ferric iron, the solubility product of ferric sulfonate has been exceeded.

2) If the predominant species of ferric iron in water were $Fe(H_2O)_5OH^{++}$ under these conditions, the compound, ferric sulfonate, should contain this hydroxide complex and would be represented by

$Fe(RSO_3)_2OH$. The hydrogen of this hydroxyl 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 possessing collector properties. The other form is thought to include the second hydroxide complex of ferric iron and have the form, $Fe(RSO_3)(OH)_2$.

When the pH is increased from 3.15 to 3.42 at the same sulfonate and ferric iron concentrations, recovery is decreased by about 65 pct. This indicates that the neutral hydroxide complex, $Fe(H_2O)_3(OH)_3$, is probably present in fair concentration at pH 3.42 and, when the pH is raised to 3.70, is probably the predominate species in the system.

With $Fe(H_2O)_3(OH)_3$, all of the 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 3.7 or above and will form in preference to it.

The same reasoning may be applied when quartz is floated in the presence of other metal ions. First, the hydrolysis schemes of the various metal ions may be represented by the following equations:

$$\begin{aligned}
Al(H_2O)_6^{+++} &\rightleftharpoons Al(H_2O)_5OH^{++} && + H^+\\
Al(H_2O)_5OH^{++} &\rightleftharpoons Al(H_2O)_4(OH)_2^{+} && + H^+\\
Al(H_2O)_4(OH)_2^{+} &\rightleftharpoons Al(H_2O)_3(OH)_3 && + H^+\\
&\rightleftharpoons Al(OH)_3\downarrow + 3H_2O && + H^+
\end{aligned}$$

$$\begin{aligned}
Pb(H_2O)_m^{++} &\rightleftharpoons Pb(H_2O)_{m-1}OH^{+} && + H^+\\
Pb(H_2O)_{m-1}OH^{+} &\rightleftharpoons Pb(H_2O)_{m-2}(OH)_2 && + H^+\\
&\rightleftharpoons Pb(OH)_2\downarrow + (m-2)H_2O && + H^+
\end{aligned}$$

$$\begin{aligned}
Mn(H_2O)_n^{++} &\rightleftharpoons Mn(H_2O)_{n-1}OH^{+} && + H^+\\
Mn(H_2O)_{n-1}OH^{+} &\rightleftharpoons Mn(H_2O)_{n-2}(OH)_2 && + H^+\\
&\rightleftharpoons Mn(OH)_2\downarrow + (n-2)H_2O && + H^+
\end{aligned}$$

$$\begin{aligned}
Mg(H_2O)_6^{++} &\rightleftharpoons Mg(H_2O)_5OH^{+} && + H^+\\
Mg(H_2O)_5OH^{+} &\rightleftharpoons Mg(H_2O)_4(OH)_2 && + H^+\\
&\rightleftharpoons Mg(OH)_2\downarrow + 4H_2O && + H^+
\end{aligned}$$

$$\begin{aligned}
Ca(H_2O)_8^{++} &\rightleftharpoons Ca(H_2O)_7OH^{+} && + H^+\\
Ca(H_2O)_7OH^{+} &\rightleftharpoons Ca(H_2O)_6(OH)_2 && + H^+\\
&\rightleftharpoons Ca(OH)_2\downarrow + 6H_2O && + H^+.
\end{aligned}$$

The hydrolysis schemes of Fe^{+++} and Al^{+++} were found in the literature. The schemes for the other metal ions were not located and are simply patterned after iron and aluminum. Furthermore, the coordination number of hydrated Pb^{++} and Mn^{++} were not located and are designated as *m* and *n*, respectively.

With all of the cations investigated, flotation was possible only in the pH region in which the cation hydrolyzes. Similarly to the case of Fe^{+++} iron, it is suggested that various cation-hydroxy-sulfonates are functioning as the collector in all of these systems. Depression at higher values of pH is attributed to the formation of cation hydroxide in preference to cation-hydroxy-sulfonate. The various values of pH at which cation sulfonate, cation-hydroxy-sulfonate, or cation hydroxide is formed for the ions investigated at the concentrations used are listed in Table III.

Comparison of the data determined with nearly equivalent amounts of Pb^{++} and Mg^{++} at nearly the same sulfonate concentrations shows that Pb^{++} still functions as an activator at a somewhat higher pH than does Mg^{++}. This is somewhat surprising in view of the relative solubilities of their hydroxides. However, all of these systems are exceedingly concentration dependent, that is the pH range in which complete flotation is possible, and for that matter, whether any flotation can be achieved depends on the relative concentrations of sulfonate and *each* cation. There is a constant competition within the system to form cation sulfonate, cation hydroxy sulfonate, and cation hydroxide.

In the case of Mn^{++} additions, an appreciable amount of scatter in the data can be noted at higher values of pH, notably from 8.6 to 8.9, in Fig. 4. Physically, there were appreciable differences in appearance in these systems. That is, some of the systems were light-colored whereas others were brown and murky. When the systems were light in color, flotation was effected; when the systems were murky and brown, flotation response was poor. The brown and murky appearance can undoubtedly be attributed to manganese hydroxide formation. The line between manganese hydroxide and manganese-hydroxy-sulfonate formation is apparently very thin in this system.

The data determined by the authors is similar to that presented by Kraeber and Boppel[5] and by Gutzeit.[6] Their interpretation of the data, however, was simply on the basis of cation abstraction by the quartz. In view of the fact that insoluble compounds (cation sulfonates) were noted to be present both in the regions of flotation and non-flotation, their model

Table III.

Cation	Highest Value of pH Below which Cation-Sulfonate Predominates	pH Range in which Cation-Hydroxy-Sulfonate Predominates	pH at which Cation Hydroxide forms in Preference to Cation-Hydroxy-Sulfonate
Fe^{+++}	2.2	2.4 to 3.2	3.7
Al^{+++}	4.0	4.3 to 7.0	7.5
Pb^{++}	6.1	6.3 to 11.7	12.0
Mn^{++}	7.9	8.2 to 8.7	8.9
Mg^{++}	10.5	10.7 to 11.5	11.7
Ca^{++}	10.8	10.9 to 13.0	13.3

does not appear to be correct. Rather, it would seem that the prime criterion for activation is the presence of a hydroxyl in a neutral precipitated compound. The hydrogen atom of the hydroxyl would provide a means of bonding between the oxygen of the precipitated compound and an oxygen atom of the surface.

In addition, the data would appear to de-emphasize the importance of surface charge in this system. All that is necessary apparently is a concentration of hydroxyl sufficient to hydrolyze the cation used for activation.

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