Metal Ion Hydrolysis and Surface Charge in Beryl Flotation*

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SYNOPSIS
The zero point of charge of beryl was determined to be pH 3 to 3. Flotation results below this pH value with a high molecular weight sulphonate through physical adsorption of negatively charged collector ions, whereas virtually no flotation is possible above pH 3 to 3 in the absence of activating metal salts. In the presence of metal salts flotation occurs only in the pH region in which some portion of the metal ion has hydrolysed to its first hydroxide complex. Complete flotation appears to result under conditions in which a metal-hydroxy-sulphonate has precipitated.

RESULTS OF A STUDY of the flotation of high-purity beryl with a high molecular weight sulphonate as collector, special precautions being taken to avoid activation from metallic ions, are presented. Earlier work showed that beryl could be floated in a laboratory Fagergren flotation cell with a sulphonate collector in acidic solution. Subsequent research on the flotation of quartz with a sulphonate collector showed that quartz also floats under similar conditions, and only by conducting the experiments in an all-glass cell without metal components was it possible to inhibit accidental activation of quartz with the sulphonate collector. Experiments were therefore also conducted with beryl in the glass cell. This exploratory research showed that clean beryl responds to flotation only in a narrow region of pH rather than the broad region reported earlier.

Recent work by Moir and co-workers has also shown that flotation of acid-leached beryl is possible with anionic collectors below pH 3 to 4. Nutt, Bromley and Kemp found that beryl which had been ground in a stainless steel mill responded to flotation with a sulphonate collector over a wide pH range, in contrast to the limited flotation obtained with acid-treated material.

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etc. See list of references at the end of the paper.
The present paper sets out the conditions under which pure beryl responds to flotation with a high molecular weight sulphonate in the absence and presence of various metal salts as activators. Surface-charge data were obtained on beryl to explain the flotation in the absence of activators.

EXPERIMENTAL MATERIALS AND METHODS

Crystals of New Mexico beryl were crushed and the $-48 + 150$, $-48 + 65$ and $-20 + 28$ Tyler mesh fractions were acid-cleaned with concentrated HCl at room temperature with a percolation technique until no iron could be detected in the leach liquor and rinsed with conductivity water. Sodium alkyl aryl sulphonate was used as the collector, the reagent having the following physical properties: sulphonate content (per cent weight) 95 to 97; molecular weight 450 to 470; and total carbon atom content 25 to 27. The approximate composition is 50 per cent benzyl and 50 per cent naphthyl sulphonate with side chains.

Streaming potentials were measured by means of the procedure and apparatus described in detail in an earlier publication. For the measurements $-48 + 65$ and $-20 + 28$ mesh beryl were used in the streaming plug. In the flotation experiments 5-g charges of $-48 + 150$ mesh beryl were conditioned for three min with 110 cc solution containing the reagents, together with $2 \times 10^{-3}$ mole/l reagent grade n-amyl alcohol as the frother. Flotation was carried out with a fixed volume of nitrogen gas in each experiment. Details of the small-scale flotation cell and the flotation procedure have been described in previous papers.

EXPERIMENTAL RESULTS

By means of streaming-potential experiments the zeta-potential of beryl was determined at $10^{-4}$, $10^{-3}$ and $10^{-2}$ molar NaCl as a function of pH, using HCl for pH adjustment. As shown in Fig. 1, at pH 3.3 the zeta-potential of beryl becomes positive, independent of the concentration of NaCl. These experiments indicate that H$^+$ and OH$^-$ ions are potential-determining for beryl and that the zero point of charge (zpc) of beryl occurs at pH 3.3. Flotation experiments were conducted with conductivity water at two constant sulphonate concentrations, $5 \times 10^{-4}$ and $1 \times 10^{-3}$ mole/l (assuming 450 as molecular weight) at various pH values; the results are plotted in Figs. 2 and 3.

When HCl is used for pH adjustment (Fig. 2) a maximum recovery of about 50 per cent is obtained from pH 0.7 to 1.5 with $1 \times 10^{-3}$ mole/l sulphonate. An increase in pH to 3.0 results in a recovery of about 10 per cent, virtually no flotation occurring above the pH 3 value. At a sulphonate concentration of $5 \times 10^{-3}$ mole/l the maximum recovery of about 30 per cent occurs at pH 1.0. Flotation recovery decreases as the pH is increased above this value, with essentially no flotation taking place above pH 3.0.

*This quantity of frother has been found to be the optimum for the experimental cell and technique described in reference 3. Data similar to those described in the present paper have been obtained with a Hallimond cell in the absence of frother.
Fig. 1.—Zeta-potential of beryl as a function of pH for different concentrations of NaCl.

Fig. 2.—Relationship between flotation recovery of beryl and pH at two constant concentrations of sulphonate using HCl for pH adjustment (separate experiments).
Fig. 3.—Relationship between flotation recovery of beryl and pH at two constant sulphonate concentrations using H₂SO₄ for pH adjustment (separate experiments).

Fig. 4.—Zeta-potential of beryl as a function of pH in water and in 2 × 10⁻⁵ mole/l sulphonate solution.
Fig. 5.—Relationship between flotation recovery of beryl and pH with additions of $1.8 \times 10^{-4}$ molar ferric and lead salts and $5.5 \times 10^{-6}$ molar sulphonate (separate experiments).

Fig. 6.—Relationship between flotation recovery of beryl and pH with additions of $1.8 \times 10^{-4}$ molar $\text{Cd}^{2+}$, $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ salts and $5.5 \times 10^{-6}$ molar sulphonate (separate experiments).
Fig. 3 shows data determined with the same two sulphonate concentrations, but with H₂SO₄ being used for pH adjustment. In this case the maximum recovery of about 25 per cent is obtained at pH 2 when both 5 × 10⁻⁴ and 1 × 10⁻³ mole/l sulphonate are used. Recovery drops off rapidly above and below this pH for both additions of sulphonate, and especially when 5 × 10⁻⁴ mole/l sulphonate is present. Very little flotation occurs above pH 3—similar to conditions in the presence of HCl. Zeta-potential of beryl was determined in the absence and presence of the sulphonate, the results being shown in Fig. 4. It can be seen that the presence of sulphonate causes considerable change in the zeta-potential of beryl as the pH of the solution is lowered towards the zero point of charge of beryl.

Conditions for activation of beryl with five different metal salts (Fe⁺³, Pb⁺², Cd⁺², Mg⁺² and Ca⁺²) were then examined. In this series of experiments the collector was held constant at 5.5 × 10⁻⁵ molar and the activator was held constant at 1.8 × 10⁻⁴ molar. Flotation recovery was then determined as a function of pH. Fig. 5 presents flotation data for activation with ferric iron and lead; in the presence of ferric chloride under these conditions flotation occurs only between pH 2.1 and 3.7—flotation being complete between pH 2.4 and 3.1. This figure shows that iron maintains its effectiveness as an activator over an exceedingly narrow pH range.

When 1.8 × 10⁻⁴ mole/l Pb⁺² is added in the presence of 5.5 × 10⁻⁵ mole of sulphonate, beryl flotation occurs between pH 4.7 and 12.0, complete flotation occurring between pH 6.0 and 11.5. As shown in Fig. 6, when cadmium chloride was used as an activator under the same conditions, flotation of beryl occurs between pH 7.3 and 9.1. Complete flotation, however, was not obtained at any value of pH. Fig. 6 also shows the flotation response of beryl in the presence of 1.8 × 10⁻⁴ molar magnesium chloride and 5.5 × 10⁻⁵ molar sulphonate added to the system. Complete flotation can be obtained between pH 10.6 and 10.9, with no flotation at pH values less than 10.0 and greater than 11.5.

Similar experiments in the presence of calcium chloride as activator showed that beryl does not respond to flotation below pH 10.2. Complete flotation occurred between pH 11.2 and 13.2. Although experiments were not carried out at pH values greater than 13.2, flotation will probably occur up to pH 13.5 or so, as was found for quartz.

DISCUSSION OF RESULTS
The data contained in Figs. 1, 2, 3 and 4 illustrate flotation by physical adsorption without activation. The zero point of charge of beryl was determined to be pH 3.3, which compares with the data of Moir and Collins⁵ and Moir et al.¹¹ Below pH 3.3 the surface of beryl will be positively charged due to H⁺ adsorption and negatively charged above this pH, which means that anionic sulphonate ions should adsorb physically on beryl only in the pH range where the surface of beryl is positively charged. The data obtained in the absence of metal ions indicate that such is the case and that flotation is possible only below pH 3 to 4. Since flotation did not occur above this pH range it can be concluded that
sulphonate is not chemisorbed on the surface. Similar results have been reported by Moir and Stevens.12

The competition of the various anionic species for the surface is also reflected in the flotation data, the maximum recovery of about 50 per cent being obtained at pH 1.5 with 1 x 10^{-3} mole/l sulphonate using HCl for pH adjustment. Under these conditions there is approximately thirty times more Cl^- than sulphonate in the system. When 5 x 10^{-2} mole/l sulphonate is involved at the same pH, there will be about six hundred times more Cl^- than sulphonate; under these conditions a recovery of only about 25 per cent was obtained.

This phenomenon is even more evident in the systems to which H_2SO_4 was added; there the divalent sulphate which will be more effective in competing with the sulphonate for the surface will be present. As the second acid constant of sulphuric acid is reported4 to be 2 x 10^{-2}, the activities of sulphate and bisulphate will be equal at about pH 2. At values of pH below 2 the activity of HSO_4^- will necessarily be greater than that of SO_4^{2-}, but SO_4^{2-} will be present in substantial amounts. Fig. 3 shows that maximum flotation recoveries were reduced at both of the sulphonate concentrations used, as compared with recoveries obtained when HCl was added for pH adjustment. Greater competition by divalent sulphate ions is also manifested by the rapid recovery drop below pH 2 in the systems containing H_2SO_4.

A second mechanism of collection is involved when metal ions are added to the system. The basic phenomena responsible for flotation under these conditions of activation appear to be twofold: (1) metal ion hydrolysis and (2) precipitation of metal sulphonate. The role of metal ion hydrolysis is demonstrated by the fact that various metal ions act as an activator in a pH region in which some first hydroxide complex of the metal ion has been formed. (Note that Fe^{+++} iron functions as an activator at low values of pH, i.e. 2.5; Pb^{++} starts at about pH 5; and Ca^{++} at about pH 11.)

Correlation of metal ion species with flotation data shows that the first hydroxide complex of the various metal ions is the species responsible for flotation, as is illustrated by Table I, which contains the various species of Fe^{+++} iron as a function of pH for a nominal addition of 1 x 10^{-4} mole/l Fe^{+++}. The following four equations7 and an iron balance were used in the calculations. The waters of co-ordination have been omitted for reasons of clarity, and concentrations rather than activities have been used.

\[
\begin{align*}
    \text{Fe}^{+++} + H_2O & \rightleftharpoons \text{Fe(OH)}^{+++} + H^+; \\
    \text{Fe(OH)}^{+++} + H_2O & \rightleftharpoons \text{Fe(OH)}_2^{+++} + H^+; \\
    2\text{Fe}^{+++} + 2H_2O & \rightleftharpoons \text{Fe}_2\text{(OH)}_3^{+++} + 2H^+; \\
    \text{Fe(OH)}_3^{+++} + 3H^+ & \rightleftharpoons \text{Fe}^{+++} + 3H_2O; \\
\end{align*}
\]

(K = 8.92 x 10^{-4})

(K = 5.50 x 10^{-4})

(K = 1.23 x 10^{-4})

(K = 9.13 x 10^9)

(K = 9.13 x 10^9)

(K = 9.13 x 10^9)

These calculations show that the only species of ferric iron that remain reasonably constant in the region of pH in which flotation is possible
(pH 2.2 to 3.4) are the first and second hydroxide complexes. The concentration of Fe(OH)++, however, is approximately ten times greater than Fe(OH)$_{t^+}$. The polymerized complex, Fe$_2$(OH)$_{t^+}$, has little or no effect under these conditions; Fe+++ ion could not be functioning as the activator in these systems since flotation does not result at pH 2, where it is the most abundant iron species, but does occur at pH 3.2, where it will be present in small amounts.

These calculations also show that ferric hydroxide will start to precipitate at about pH 2.8 and is the most abundant iron species at pH 3. Precipitation of ferric hydroxide was in fact observed at pH 3 and large amounts of coagulated ferric hydroxide were observed at pH 3.5. As no flotation was possible at pH 3.8 and above, it seems likely that depression can be attributed to the formation and stability of ferric hydroxide.

The premise that the first hydroxide complex of the various metal ions is responsible for activation is further corroborated by the data obtained with Pb++ ion. Calculations similar to those made for Fe+++ ion can be made by means of the following equations:

\[
Pb^{++} + H_2O \rightleftharpoons Pb(OH)^+ + H^+; \quad (K = 6.67 \times 10^{-7})
\]
\[
Pb(OH)^+ + H_2O \rightleftharpoons Pb(OH)_2(aq) + H^+; \quad (K = 1.26 \times 10^{-11})
\]
\[
Pb(OH)_2(aq) \rightleftharpoons HPbO_2^- + H^+; \quad (K = 1.2 \times 10^{-11})
\]

When the systems are saturated with respect to lead hydroxide, the following additional equilibria will be present:

\[
Pb(OH)_2(\alpha_s) \rightleftharpoons Pb(OH)_2(aq); \quad (K = 3.65 \times 10^{-4})
\]
\[
Pb(OH)_2(\alpha_s) \rightleftharpoons Pb^{++} + 2OH^-; \quad (K = 4.2 \times 10^{-15})
\]
\[
Pb(OH)_2(\alpha_s) + OH^- \rightleftharpoons HPbO_2^- + H_2O; \quad (K = 4.3 \times 10^{-14})
\]

The equilibrium between Pb(OH)$_2(\alpha_s)$ and Pb(OH)$_2(aq)$ establishes the conditions for saturation—when the activity of Pb(OH)$_2(aq)$ equals or exceeds $3.65 \times 10^{-4}$ saturation will result.

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe$^{+++}$</th>
<th>Fe(OH)$^{++}$</th>
<th>Fe(OH)$_{t^+}$</th>
<th>Fe$<em>2$(OH)$</em>{t^+}$</th>
<th>Fe(OH)$_{t(aq)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>$9.2 \times 10^{-5}$</td>
<td>$8.0 \times 10^{-5}$</td>
<td>$4.4 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>0</td>
</tr>
<tr>
<td>2.2</td>
<td>$8.8 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-10}$</td>
<td>0</td>
</tr>
<tr>
<td>2.4</td>
<td>$8.2 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$2.1 \times 10^{-10}$</td>
<td>0</td>
</tr>
<tr>
<td>2.6</td>
<td>$7.4 \times 10^{-5}$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>$5.7 \times 10^{-6}$</td>
<td>$2.7 \times 10^{-10}$</td>
<td>0</td>
</tr>
<tr>
<td>2.8</td>
<td>$3.6 \times 10^{-5}$</td>
<td>$2.0 \times 10^{-5}$</td>
<td>$6.95 \times 10^{-6}$</td>
<td>$8.20 \times 10^{-11}$</td>
<td>$3.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.0</td>
<td>$9.1 \times 10^{-6}$</td>
<td>$8.1 \times 10^{-6}$</td>
<td>$4.46 \times 10^{-6}$</td>
<td>$1.02 \times 10^{-11}$</td>
<td>$7.83 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.2</td>
<td>$2.3 \times 10^{-6}$</td>
<td>$3.2 \times 10^{-6}$</td>
<td>$2.79 \times 10^{-6}$</td>
<td>$1.03 \times 10^{-12}$</td>
<td>$9.17 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.4</td>
<td>$5.8 \times 10^{-7}$</td>
<td>$1.3 \times 10^{-6}$</td>
<td>$1.80 \times 10^{-6}$</td>
<td>$1.04 \times 10^{-12}$</td>
<td>$9.63 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.6</td>
<td>$1.4 \times 10^{-7}$</td>
<td>$5.0 \times 10^{-7}$</td>
<td>$1.09 \times 10^{-6}$</td>
<td>$9.60 \times 10^{-12}$</td>
<td>$9.82 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
The equilibrium between Pb(OH)$_2$(s) and HPbO$_4^-$ represents the amphoteric nature of lead hydroxide, i.e. its dissolution in strongly basic media to form the complex ion, plumbite, and water.

From the above published equilibria, lead hydroxide will not precipitate at any pH with an addition of $1 \times 10^{-4}$ mole/l Pb$^{++}$ to water. The concentrations and species of lead that will be present at various values of pH for this addition of Pb$^{++}$ are listed in Table II.

**TABLE II.—Concentration of various species of Pb$^{++}$ as a function of pH for an addition of $1 \times 10^{-4}$ mole/l Pb$^{++}$ to water**

<table>
<thead>
<tr>
<th>pH</th>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Pb$^{++}$</td>
<td>$6 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>Pb(OH)$^+$</td>
<td>$6 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>Pb(OH)$_{ultr}$</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>7</td>
<td>Pb$^{++}$</td>
<td>$4 \times 10^{-2}$</td>
</tr>
<tr>
<td>8</td>
<td>Pb(OH)$_{ultr}$</td>
<td>$8 \times 10^{-1}$</td>
</tr>
<tr>
<td>9</td>
<td>Pb(OH)$_{ultr}$</td>
<td>$8 \times 10^{-1}$</td>
</tr>
<tr>
<td>10</td>
<td>Pb$^{++}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>11</td>
<td>Pb(OH)$_{ultr}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>12</td>
<td>Pb(OH)$_{ultr}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>13</td>
<td>Pb$^{++}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

These calculations also show that the only species of lead that remains reasonably constant in the pH range (5 to 12) in which flotation is possible is the first hydroxide complex, Pb(OH)$^+$. The neutral hydroxide complex and plumbite have little or no effect at pH 5 and 6, but are present in significant amounts at pH 10 to 11. At pH 12 almost all of the added lead will be present as plumbite and, by the same token, almost all of the added lead will be present as the first hydroxide complex at pH 9. Similarly to Fe$^{+++}$ ion, Pb$^{++}$ ion could not be functioning as the activator in these systems since flotation does not result at pH 4, where it is the most abundant species of lead, but does occur at pH 11, where it is vanishingly small.

Other polyvalent metal ions also function as activators when a certain portion of the added metal ion has hydrolysed to its first hydroxide complex. Flotation data obtained with Fe$^{+++}$, Pb$^{++}$, Cd$^{++}$, Mg$^{++}$ and Ca$^{++}$ show that flotation results when the ratio of first hydroxide complex to metal ion lies between $10^{-3}$ and $10^{-1}$. This ratio was determined from the hydrolysis schemes given previously for Fe$^{+++}$ and Pb$^{++}$ ions and the following equations:

\[
\begin{align*}
\text{Cd}^{++} + \text{H}_2\text{O} & \Rightarrow \text{Cd(OH)}^+ + \text{H}^+; \\
\text{Mg}^{++} + \text{H}_2\text{O} & \Leftrightarrow \text{Mg(OH)}^+ + \text{H}^+; \\
\text{Ca}^{++} + \text{H}_2\text{O} & \Rightarrow \text{Ca(OH)}^+ + \text{H}^+;
\end{align*}
\]

\[
\begin{align*}
(K = 1.45 \times 10^{-10}) \quad & (K = 3.81 \times 10^{-13}) \\
(K = 3.24 \times 10^{-13}) \quad & (K = 3.24 \times 10^{-13})
\end{align*}
\]
In all the experiments a colloidal dispersed precipitate of the metal sulphonate was noted to be present, both in the regions of flotation and non-flotation. In the case of \( \text{Pb}((R\text{SO}_3)_2) \) a solubility product of \( 9 \times 10^{-19} \) was determined by the Tyndall Effect. This value was determined with the assumption that two moles of sulphonate are consumed with one mole of lead in the precipitation of lead sulphonate.

Since a hydroxyl group in the metal sulphonate is apparently necessary for flotation, and since flotation occurs only in the presence of a precipitate, the form of the collector appears to be a precipitated metal-hydroxy-sulphonate, for example, \( \text{Mg(OH)}_x(R\text{SO}_3)_y \), where \( x \) and \( y \) may have a value other than one. As suggested previously, \(^1\) collection might occur through bonding of this compound to the surface through hydrogen bonding. An alternative mechanism might be that the activating ion is the metal-hydroxy cation that adsorbs on surface sites. Adsorption of sulphonate ions then occurs only on these activated sites when the solution is saturated with sulphonate, i.e. when the precipitate forms. For flotation under these conditions the overwhelming controlling factor appears to be conditions in which the activating cation has hydrolysed to its first hydroxide complex, rather than the charge of the mineral surface.

Comparison of these flotation data with those previously reported for quartz\(^4\) shows a close similarity in flotation response between the two minerals in the presence of added metal ions. The flotation mechanism suggested could well be responsible for the loss of selectivity in natural ore systems.

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