A Century of Developments in the Chemistry of Flotation Processing

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### Types and Amount of Ore Treated by Flotation in the United States in 1926, 1960 and 1980

(million tonnes)

<table>
<thead>
<tr>
<th>Type of Ore</th>
<th>Ore Treated (Mt)</th>
<th>Conc. Produced (Mt)</th>
<th>Ore Treated (Mt)</th>
<th>Conc. Produced (Mt)</th>
<th>Ore Treated (Mt)</th>
<th>Conc. Produced (Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1926-</td>
<td></td>
<td>-1960-</td>
<td></td>
<td>-1980-</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>39.3</td>
<td>2.2</td>
<td>133.4</td>
<td>4.8</td>
<td>211.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Lead-Zinc</td>
<td>5.6</td>
<td>0.8</td>
<td>7.4</td>
<td>0.5</td>
<td>11.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Iron</td>
<td>1.4</td>
<td>0.5</td>
<td>1.4</td>
<td>0.5</td>
<td>37.9</td>
<td>21.5</td>
</tr>
<tr>
<td>Phosphate</td>
<td>19.0</td>
<td>6.4</td>
<td>108.7</td>
<td>26.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potash</td>
<td>10.9</td>
<td>2.8</td>
<td>12.9</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>3.7</td>
<td>2.5</td>
<td>11.7</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicate Minerals</td>
<td>1.7</td>
<td>1.1</td>
<td>11.6</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>46.2</strong></td>
<td><strong>2.8</strong></td>
<td><strong>179.9</strong></td>
<td><strong>19.5</strong></td>
<td><strong>404.3</strong></td>
<td><strong>71.9</strong></td>
</tr>
</tbody>
</table>

This table provides an indication of the minerals emphasized in flotation chemistry research:

- **Sulfide minerals**: 1915 - 1945
- **Nonmetallic minerals, oxides**: 1945 - 1975
- **Sparingly soluble salt minerals**: 1975 - 2000
- **Sulfide minerals (new analytical instrumentation)**: 1975 - 2000
- **Coal**: 1980 - 1995
### Reagents Used for Flotation in the United States in 1925, 1926 and 1980
*(in tonnes)*

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount</th>
<th>1925</th>
<th>1926</th>
<th>1980</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore Treated</td>
<td></td>
<td>41,300,000 t</td>
<td>41,600,000 t</td>
<td>440,400,000 t</td>
</tr>
<tr>
<td>Frothers</td>
<td>2,200 t</td>
<td></td>
<td></td>
<td>12,500 t</td>
</tr>
<tr>
<td>Collectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oils</td>
<td>8,800</td>
<td>2,700</td>
<td>115,200</td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td>1,900</td>
<td>1,900</td>
<td>108,900</td>
<td></td>
</tr>
<tr>
<td>Modifiers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acids</td>
<td>18,200</td>
<td>2,100</td>
<td>35,200</td>
<td></td>
</tr>
<tr>
<td>Alkalis</td>
<td>1,700</td>
<td>75,700</td>
<td>413,100</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>---</td>
<td>---</td>
<td>28,700</td>
<td></td>
</tr>
<tr>
<td>Activators</td>
<td>3,200</td>
<td>5,000</td>
<td>3,900</td>
<td></td>
</tr>
<tr>
<td>Depressants</td>
<td>800</td>
<td>1,100</td>
<td>33,400</td>
<td></td>
</tr>
<tr>
<td>Flocculants</td>
<td>---</td>
<td>---</td>
<td>18,100</td>
<td></td>
</tr>
</tbody>
</table>
ANTOINE M. GAUDIN  (1900 - 1974)

THE FATHER OF SYSTEMATIC, FUNDAMENTAL  FLOTATION RESEARCH

Although numerous other people (Coghill, Fahrenwald, Langmuir, Norris, Ralston, Sulman, Taggart, et al.) had conducted sporadic experiments to try to ascertain why minerals float using a number of flotation techniques, including contact angle measurements, it was Gaudin and his colleagues at the University of Utah/U.S. Bureau of Mines who systematically investigated the function of reagents on the flotation behavior of pure minerals, during the period, 1926 -1929.

A.M. Gaudin in 1935 at the Montana School of Mines
ILLUSTRATION OF THE QUALITY OF THE SYSTEMATIC FLOTATION RESEARCH BY GAUDIN et al. AT THE UNIVERSITY OF UTAH 1926-29

Using a 50-gram miniature flotation cell devised by Gates and Jacobson in the Bureau of Mines at the University of Utah, Gaudin and his colleagues conducted systematic flotation experiments on 100 x 600 mesh high-purity mineral samples with high-purity reagents and distilled water.
In 1928, Gaudin et al. published their results on the flotation of galena (100x600 mesh) with alkyl xanthates of different hydrocarbon chain lengths, ranging from methyl to butyl. With reagent addition expressed in mol/t, 80 percent recovery is achieved with 1 mol/t methyl xanthate and 0.2 mol/t ethyl xanthate, showing the high chemical affinity for xanthate in exchange adsorption with surface oxidation ions on the galena surface.
CORRELATION BETWEEN THE RESULTS OF EARLY FLOTATION EXPERIMENTS AND INTERFACIAL MEASUREMENTS FOR THE XANTHATE-GALENA SYSTEM

Gaudin (1928): pure mineral flotation as a function of collector addition
Wark and Cox (1934): contact angle measurements
Bogdanov et al. (1957): flotation versus adsorption density
In the 1929, Gaudin published the first systematic results on the effect of pH on the flotation of minerals, including the possibility of separating pyrite and chalcocite by pH control.
ASSESSMENT OF CONDITIONS FOR FLOTABILITY

WARK AND COX (1934)

Wark and Cox selected the measurement of contact angles under closely controlled conditions to be their method for determining the limits of flotability. Below is one of their classic plots that gives the critical pH value for the limit of flotation of pyrite, galena and chalcopyrite as a function of the concentration of Na diethyldithiophosphate as collector.

Along these curves, [X⁻] / [OH⁻] = constant, interpreted by Gaudin and Wark as ion exchange.
Sir Ian Wark 1983 Alwyn Cox
The work of Wadsworth and Peck led to infrared spectroscopy becoming a widely used tool to study chemisorption of flotation collectors. The investigation of Leja, Little and Poling on the adsorption of ethyl xanthate on lead sulfide is classic.

(a) Bulk lead ethyl xanthate, solid as Nujol mull, (b) freshly evaporated PbS film after atmospheric oxidation, (c) above treated in aqueous solution of ethyl xanthate, (d) above after prolonged washing in ether, (e) above washing in pyridine.
RELATIONSHIP BETWEEN CONDITIONING POTENTIAL AND FLOTABILITY OF SULFIDES

(Richardson and Walker, 1985)

Richardson and Walker showed that the flotation of *chalcocite*, *bornite*, *chalcopyrite* and *pyrite* with potassium ethyl xanthate is controlled by the conditioning potential, similar to earlier findings by Heyes and Trahar. The active surface entities for chalcocite and bornite were found to be metal xanthates, dixanthogen for pyrite, and metal xanthate for initial flotation of chalcopyrite and dixanthogen for full flotation.

![Graph showing the relationship between potential and flotation recovery](image)
Chander and Fuerstenau differentiated between reversible and passive sulfides.

The rest potential of reversible sulfides follows Nernstian behavior with its response predicted by thermodynamics.

That of passive sulfides follows non-Nernstian behavior and is determined by reaction kinetics.

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**Table:**

<table>
<thead>
<tr>
<th>FLOTATION SPECIES</th>
<th>Metal/collector compound(s)</th>
<th>Oxidation product of collector, X₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>REVERSIBLE SULFIDES</td>
<td>MX, MX₂</td>
<td></td>
</tr>
<tr>
<td>PASSIVE SULFIDES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEPRESSANT SPECIES</td>
<td>a) Mineral oxid’n product layer MO, M(OH)_n, etc.</td>
<td>a) Mineral oxid’n product layer MO, M(OH)_n, etc.</td>
</tr>
<tr>
<td></td>
<td>b) Hydrophilic layer of mineral-depressant compound, MD</td>
<td>b) Hydrophilic MD layer</td>
</tr>
<tr>
<td></td>
<td>c) Removal of surface MX, MX₂ by oxid’n, red’n or hydrolysis</td>
<td>c) Removal of surface X₂ by reduction</td>
</tr>
</tbody>
</table>
SPIRITED DEBATE OVER THE MECHANISM OF SULFIDE MINERAL FLOTATION

Gaudin (1927): “The mechanism by which xanthates float sulfides other than galena may involve a adsorption of xanthate without further reaction.”

Taggart (1930): “All dissolved reagents which, in flotation pulps, either by action on the to-be-floated or not-to-be-floated particles affect their floatability, by function of the reason of chemical reactions of well-recognized types between the reagent and the particle affected.”

Wark and Cox (1934): “We find that there is a strong connection between adsorption of xanthate ion and the solubility of the heavy-metal xanthates, but are unable to decide if this is an identity.”

Cook and Nixon (1950): “Assuming a complete or nearly complete monolayer of ‘ions’ on the mineral particles, one would obtain a bulk concentrate with so much charge that it would explode with greater violence than an equal weight of nitroglycerine.”

Nixon (1957): “Prominent theories could be reconciled by the electrochemical approach.”

Woods (1984): “Electrochemical investigations of the interaction of thiol collectors with sulfide mineral have demonstrated that each of the three anodic processes - chemisorption, reaction to form a metal collector compound, and the formation of a dithiolate -- play a role in creating hydrophobic surfaces.”
Initially most flotation surface chemistry research was conducted using a single experimental technique. Major progress was made after the use of a combination of experimental methods became standard, together with the physical chemistry involved.

- Flotation, adsorption, zeta potentials, contact angles
- Flotation, zeta potentials
- Flotation, infrared spectroscopy, zeta potentials
- Electrochemical polarization, flotation, adsorption, contact angles
- Adsorption, contact angles, induction times, flotation
CORRELATION BETWEEN FLOTATION RESPONSE, CONTACT ANGLES, ZETA POTENTIALS AND ADSORPTION DENSITY

(after Fuerstenau, Healy and Somasundaran, 1964)

Three phase systems: flotation, contact angles

Two phases: adsorption, zeta potentials
END OF PROFESSOR OVERBEEK’S YEAR IN THE GROUP AT MIT (1953)

Modi, Charles, Fuerstenau, Overbeek, deBruyn, Stigter, Bergna,Tournesac, Larson
The point of zero charge (PZC) defines conditions when $\sigma_0 = 0$. 

SIMPLIFIED SCHEMATIC OF THE ELECTRICAL DOUBLE LAYER

TRIPLE LAYER FROM SUPREEQUIVALENT ADSORPTION

$[-\sigma_0] > [\sigma_0]$
SPECIFIC ADSORPTION IN THE STERN LAYER

The adsorption density in the Stern layer of specifically adsorbed ions can be related to their bulk concentration by several related approaches.

- **The Stern-Langmuir Equation**

\[
\frac{\theta}{1-\theta} = \frac{C}{55.5} \exp \left[-\frac{\Delta G_{ads}^o}{RT}\right]
\]

- **The Stern-Grahame Equation**

\[
\Gamma_{\delta} = 2rC \exp \left[-\Delta G_{ads}^o/RT\right]
\]

- **The standard free energy of adsorption**

\[
\Delta G_{ads}^o = zF\psi_{\delta} + \Delta G_{spec}^o \quad (\Delta G_{spec}^o \text{ is zero with only electrostatic interaction})
\]

\[
\Delta G_{spec}^o = \Delta G_{hpb}^o + \Delta G_{chem}^o + \Delta G_{H}^o + \Delta G_{hpb^*}^o + \ldots \quad (\text{where these terms represent adsorbed chain association, chemical bonding, hydrogen bonding, hydrophobic bonding with a naturally flotable mineral, respectively})
\]
PHYSISORPTION PHENOMENA OF SODIUM DODECYLSULFONATE ON ALUMINA
(after Somasundaran, Wakamatsu and Fuerstenau, 1964 - 1968)

Alkyl chain association (hemimicelle formation) of adsorbed surfactant at the surface controls the shape of the adsorption isotherm, zeta potentials, and contact angles. Both pH and chain length enter into the behavior of these systems.
THE ELECTROSTATIC MODEL OF FLOTATION
(after Fuerstenau and Modi, 1956)

During the years, 1954-1956, the concepts underlying the electrostatic model of flotation were conceived and tested experimentally, namely that physisorbed collectors function as counter ions in the electrical double layer. Thus, flotation should respond to anionic collectors below the PZC and to cationic collectors above the PZC.
ROLE OF THE PZC IN OXIDE MINERAL FLOTATION WITH PHYSOSORBING COLLECTORS
THE UNIVERSALITY OF THE EFFECT OF pH ON FLOTATION WITH OLEIC ACID
(after Polkin and Najfonow, 1964)

Minerals floated: (1) columbite, (2) zircon, (3) tantalite, (4) ilmenite, (5) rutile
(6) garnet, (7) tourmaline, (8) albite, (9) perovskite
SPECIFIC ADSORPTION OF OLEATE ON HEMATITE AS A FUNCTION OF pH

Wadsworth et al. (1966) showed the formation of ferric carboxylate bonds at the hematite surface, and correlated flotation and the IR absorbance. Somasundaran et al. (1980) correlated the flotation peak with acid soap dimer formation. At the peak, the acid soap dimer concentration in solution is $5 \times 10^{-8}$ M.
This chromite, FeO·Cr₂O₃, assayed 42% Cr(III), 8% Al₂O₃, 4% Fe(III), 7% Fe (II), and 8% Mg(II), with a PZC at about pH 7. Flotation response at high pH match the hydrolysis peaks of FeOH and MgOH, respectively. Due to octahedral coordination, Cr and Al appear not to participate in the surface hydrolysis reactions. Flotation at low pH most likely results from physisorption.
THE ROLE OF DOUBLE BONDS IN THE ALKYL CHAIN IN FLOTATION COLLECTION

(after Purcell and Sun, 1963)

The PZC of this rutile sample occurs at pH 6.7.

Chemisorption of the soaps causes a marked change in the zeta potential of rutile, depending on double bonds in the alkyl chain, with the curves for the various soaps joining that for NaCl at pHs where electrical repulsion inhibits adsorption and flotation.

OLEIC ACID \[ \text{C}_{17}\text{H}_{33}\text{COOH} \]

\[\text{COOH}\]

LINOLEIC ACID \[ \text{C}_{17}\text{H}_{31}\text{COOH} \]

\[\text{COOH}\]

LINOLENIC ACID \[ \text{C}_{17}\text{H}_{29}\text{COOH} \]

\[\text{COOH}\]
MANGANESE DIOXIDE FLOTATION WITH PHYSISORBING AND CHEMISORBING COLLECTORS
(after Fuerstenau, Natarajan and Shibata, 1983)

The PZC of MnO₂ occurs at pH 5.6. Sodium dodecylsulfonate is a collector that physically adsorbs below the PZC.

K octyl hydroxamate ($\text{pK}_a$ of about 9) is a chelating agent that chemisorbs. Flotation is maximal where hydroxamic acid molecules and hydroxamate anions are about equal (pH 9).

Oleate chemisorbs between pH 6 and 11 (above the PZC). At the PZC, flotation is minimal, but increases again as the pH is lowered, due to the physisorption of oleate anions, but ceases again as molecular oleic acid dominates.
SCHEMATIC ILLUSTRATION OF REAGENT / MINERAL INTERACTIONS

**Chemisorption**

\[ M^{++} + OH^- \rightarrow M^{++}OH^- \]
\[ M^{++} + X^- \rightarrow M^{++}X^- \]

**Adsorption with Surface Reaction**

\[ M^{++} + OH^- \rightarrow (MOH)^+ \]
\[ M^{++} + X^- \rightarrow (MX)^+ \]

**Surface Reaction**

\[ (MOH)^+ + OH^- \rightarrow M(OH)_2 \]
\[ (MOH)^+ + X^- \rightarrow (MX)^+ \]
\[ (MX)^+ + X^- \rightarrow MX_2 \]

**Bulk Precipitation**

\[ M^{++} \rightarrow MX_2 \text{(ppt)} \]
In 1928 Gaudin first showed that quartz could be activated with ferric chloride in a fairly narrow pH region for oleate flotation. Fuerstenau and Palmer studied the flotation of quartz with 0.1 mM sulfonate collector and 0.1 mM activator and related flotation response to activator hydrolysis. This figure only presents the onset of flotation, but flotation ceases by pH 3.8 in the case of Fe(III).
Urbina et al. studied the flotation of cerussite (lead carbonate) with K amyl xanthate as a function of the addition of sodium sulfide and observed the following sequentially:

1. Initially PbS precipitate coagulates onto the cerussite surface
2. Aqueous sulfide concentration reaches that for galena depression
3. PbS layers start to build up on cerussite leading to a sharp increase in flotation
4. As the PbS film thickens, diffusion slows down the exchange reaction, increasing sulfide in solution
5. Increasing aqueous sulfide again depresses flotation
6. Here, 15 monolayers of PbS rapidly built up because of the porosity of the growing film
Various researchers have found the order of flatability of calcium salt minerals with oleate to be:

\[
\text{FLUORITE} \succ \text{FLUORAPATITE} \succ \text{CALCITE}
\]
SURFACE TRANSFORMATION OF BARIUM SULFATE TO BARIUM CARBONATE UPON THE ADDITION OF SODIUM CARBONATE

(after Pradip and Fuerstenau, 1991)
Bulk precipitation of calcium oleate occurs because of dissolved calcium ions in the apatite and calcite supernatants. Calcite depression is governed by bulk collector precipitation.
SUMMARY AND PROGNOSIS

During the past 80 years, investigations with pure single minerals have slowly delineated the basic principles involved in how various chemicals function as flotation reagents for sulfide, oxide, silicate, and salt minerals. Yet processing ores that are mixtures of minerals is far more complex than studying the behavior of pure single mineral systems. This is further complicated because ores of the future will be characterized by decreasing grade, decreasing grain size, more highly active surfaces produced by finer grinding, and increasing complexity.

Because of this, there is an ongoing need for more selective and effective flotation reagents and reagent schemes, possibly designing reagents which adsorb rather than react with a mineral in order to reduce reagent consumption.

Hypothetically there should be a systematic way to plan the flotation processing of an ore by establishing the surface chemistry of all the constituent minerals along with their response to the reagents relevant to the process, then determining likely interferences between the various species, and finally planning the best conditions for securing a large difference in hydrophobicity between the reagent-treated minerals. This should be the broad aim of flotation chemistry researchers in the SECOND CENTURY OF FLOTATION.
DEPENDENCE OF FLOTATION OBSERVATIONS ON EXPERIMENTAL TECHNIQUE

Using different flotation times for conducting experiments with a modified Hallimond tube can mask results and lead to different conclusions:

Somasundaran 10 seconds, M.C. Fuerstenau 45 seconds, Iwasaki 300 seconds (5 min)
THE ROLE OF pH AND ADDED DEXTRIN ON THE FLOTATION OF TALC

![Graph showing the relationship between pH and flotation recovery and induction time with and without collector. The graph includes data points and lines indicating the effects of pH on flotation recovery and induction time for talc with and without dextrin.]
THE INFLUENCE OF HYDROCARBON CHAIN LENGTH ON HEMATITE FLOTATION AS A FUNCTION OF pH WITH ALKYL SULFATES AND AMINES AS COLLECTORS

(after Iwasaki, Cooke and Choi)