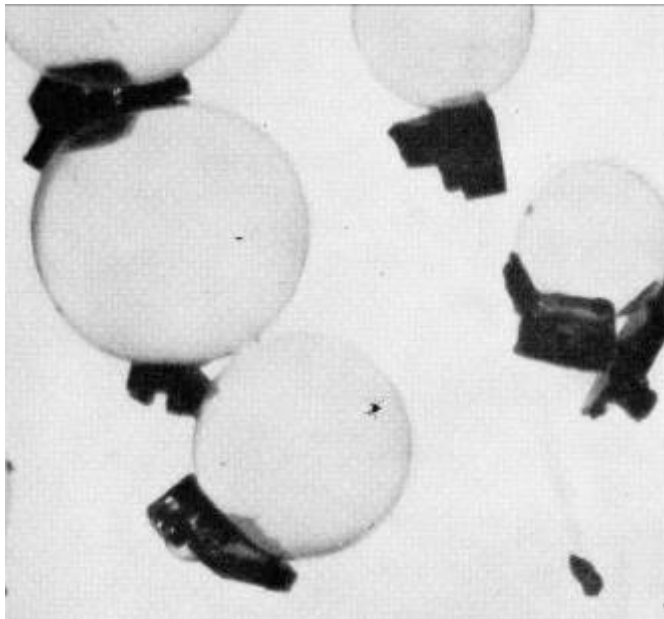


A Century of Developments in the Chemistry of Flotation Processing

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University of California at Berkeley*



**Centenary of Flotation
Symposium**

*Brisbane, Australia
June 2005*

**Types and Amount of Ore Treated by Flotation in the United States
in 1926, 1960 and 1980**
(million tonnes)

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

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)

Reagent Amount	1925	1926	1980
Ore Treated	41,300,000 t	41,600,000 t	440,400,000 t
Frothers	2,200 t	2,900 t	12,500 t
Collectors			
Oils	8,800	2,700	115,200
Chemicals	1,900	1,900	108,900
Modifiers			
Acids	18,200	2,100	35,200
Alkalis	1,700	75,700	413,100
Other	---	---	28,700
Activators	3,200	5,000	3,900
Depressants	800	1,100	33,400
Flocculants	---	---	18,100

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.

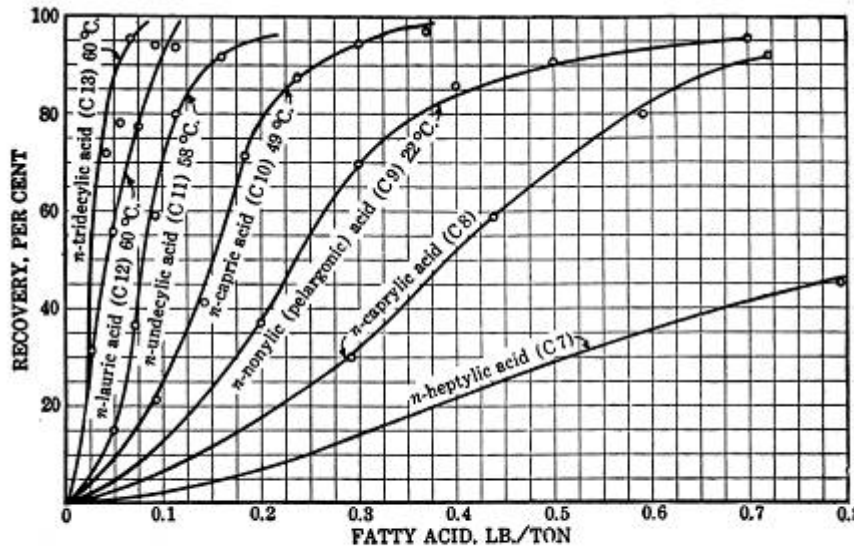
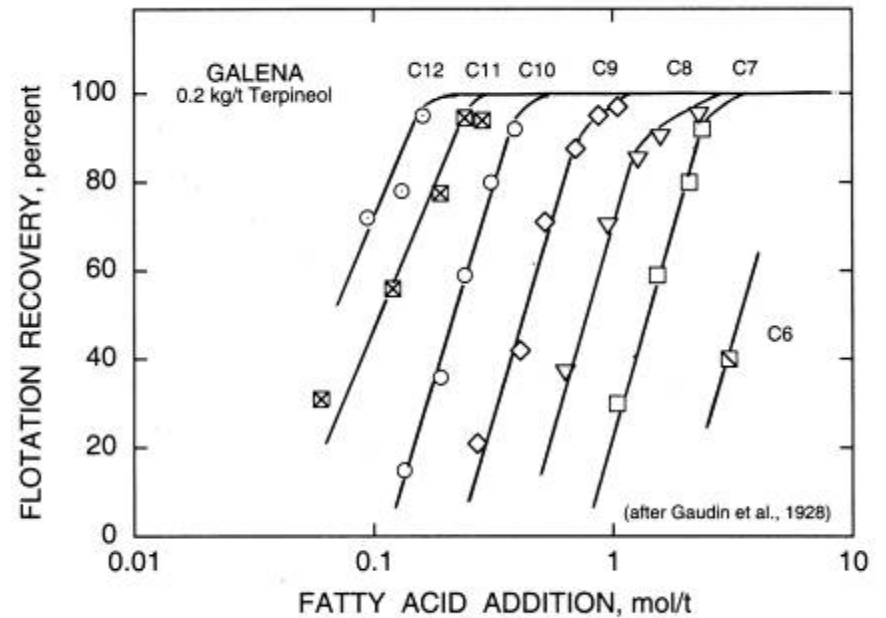


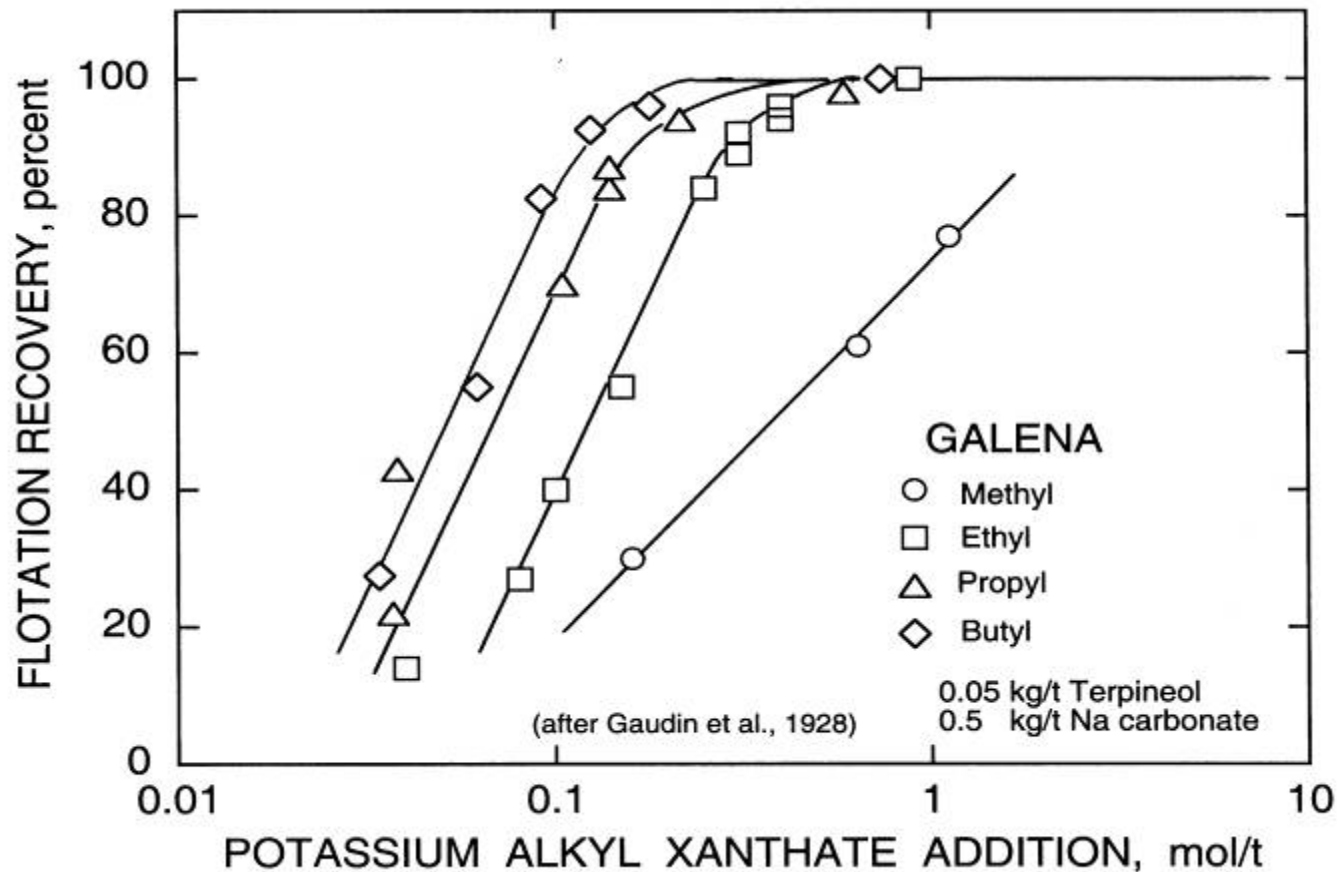
FIG. 51.—Galena.

Flotation of 100/600-mesh particles with saturated fatty acids and terpeneol 0.40 lb. per ton.



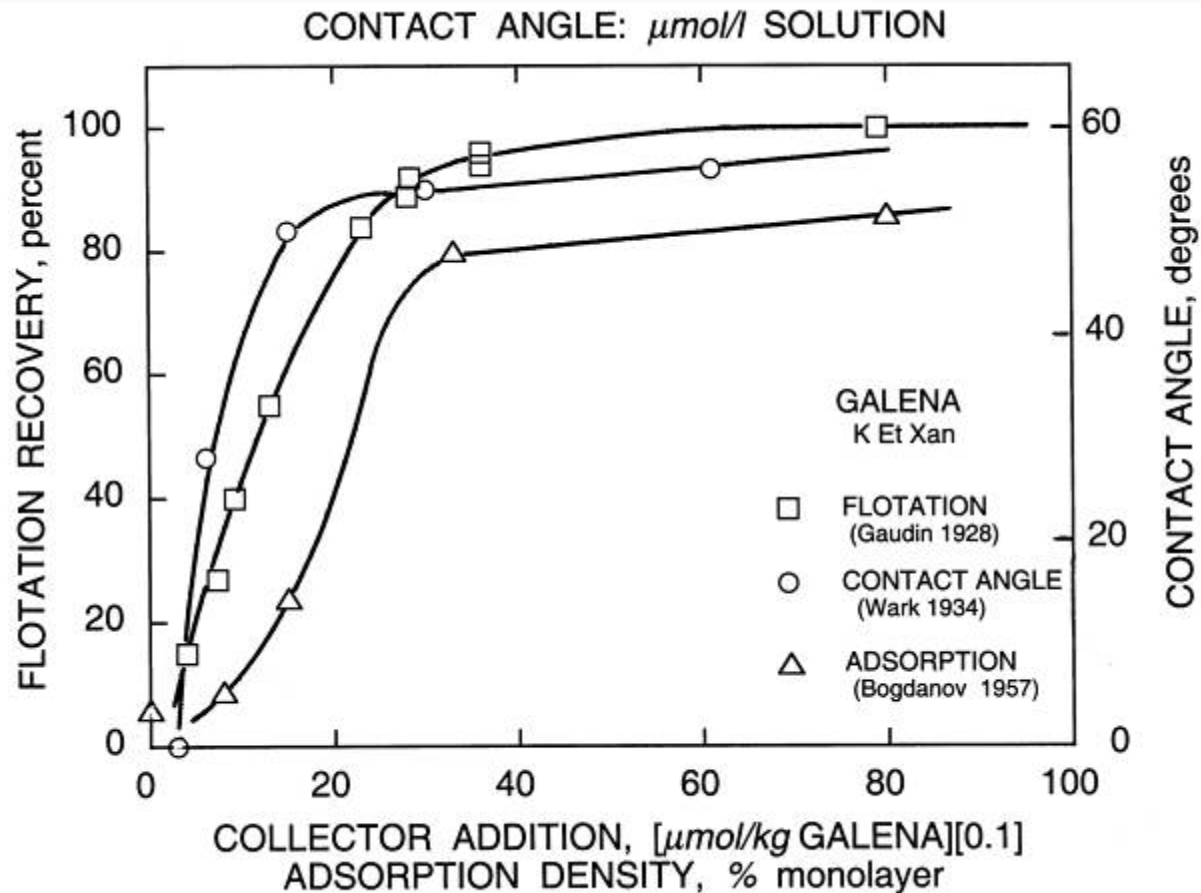
FLOTATION OF GALENA WITH ALKYL XANTHATES

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.



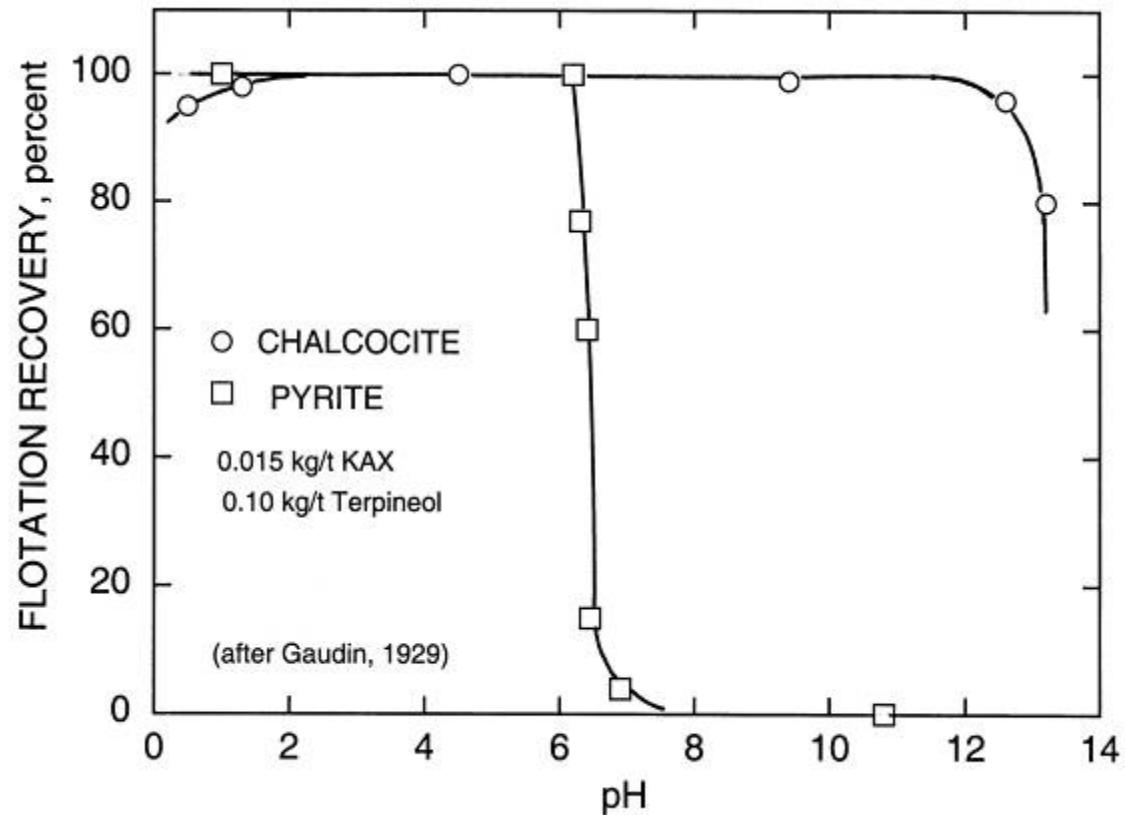
CORRELATION BETWEEN THE RESULTS OF EARLY FLOTATION EXPERIMENTS AND INTERFACIAL MEASUREMENTS FOR THE XANTHATE-GALENA SYSTEM

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



EARLY DELINEATION OF THE ROLE OF pH IN SULFIDE MINERAL FLOTATION

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.

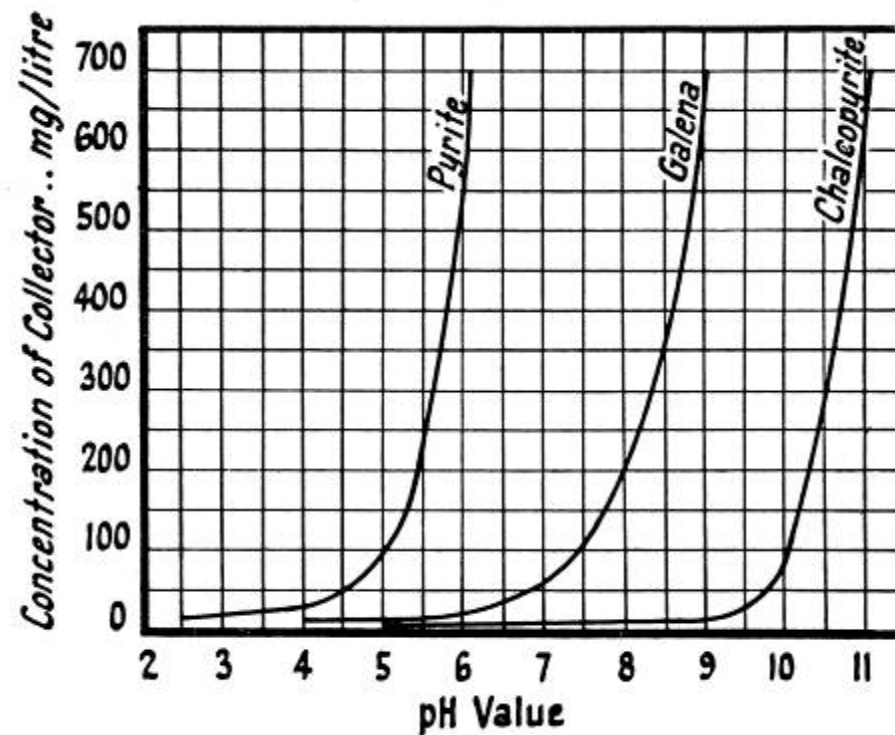


ASSESSMENT OF CONDITIONS FOR FLOTABILITY

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, $[X^-] / [OH^-] = \text{constant}$, interpreted by Gaudin and Wark as ion exchange.



_____ Sir Ian Wark

1983

Alwyn Cox



Professor Nat Arbiter

Sir Ian Wark

DWF

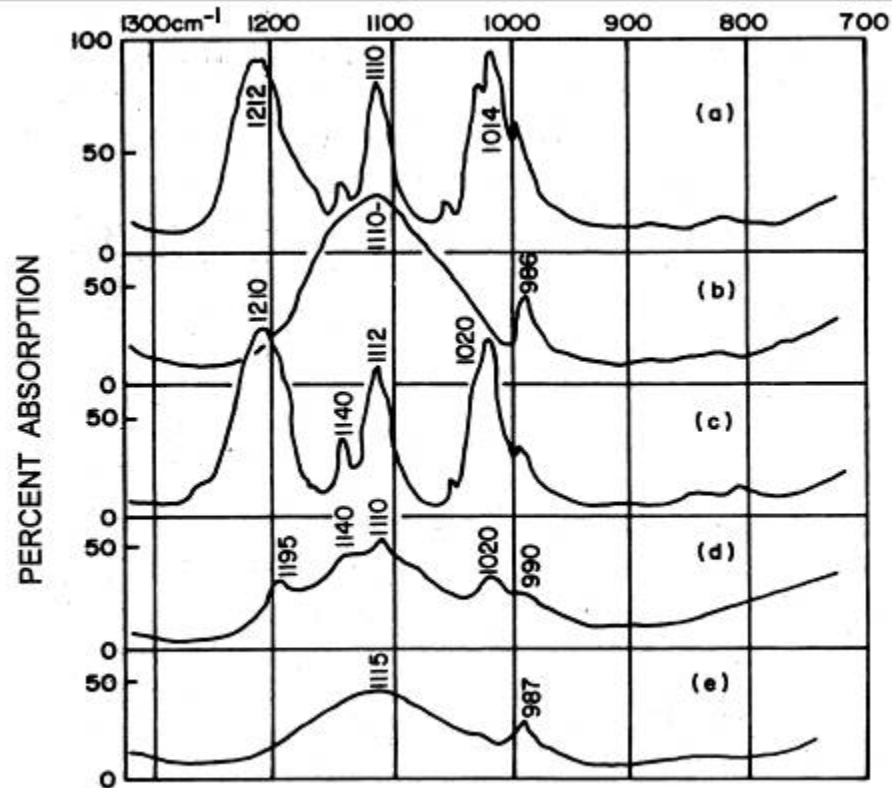
1983



INFRARED SPECTROSCOPY IN FLOTATION CHEMISTRY RESEARCH

(Leja, Little and Poling 1962-63)

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.

Dr. George Poling

1983

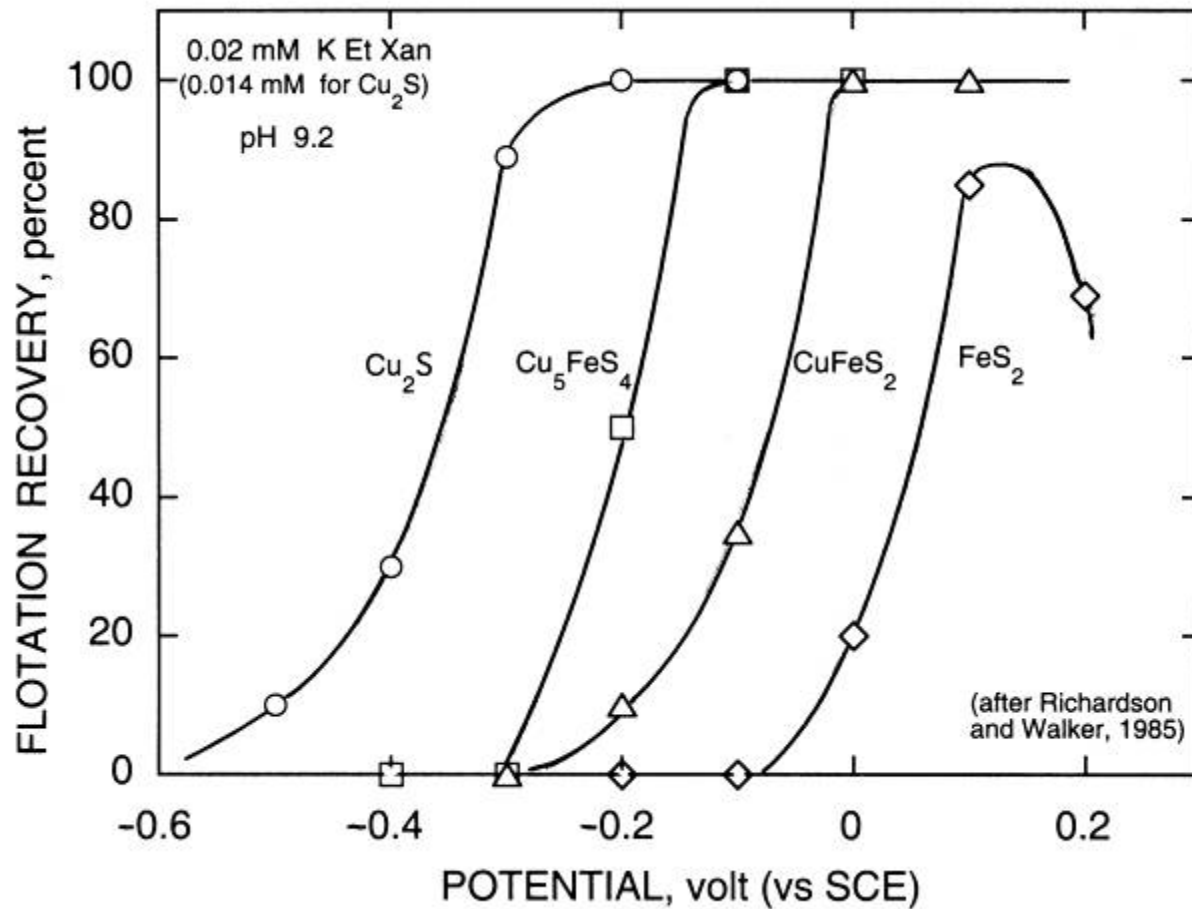
Dr. Ron Woods



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.

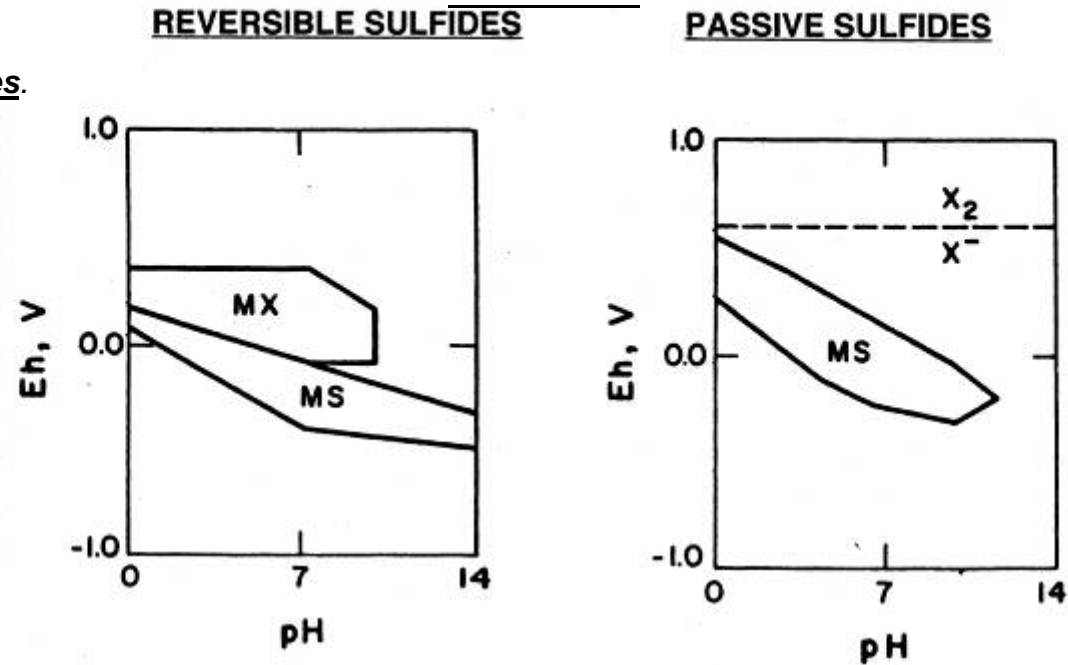


(Chander, 1985)

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.



FLOTATION SPECIES	Metal/collector compound(s) MX, MX_2	Oxidation product of collector, X_2
DEPRESSANT SPECIES	a) Mineral oxid'n product layer MO, $M(OH)_n$, etc. b) Hydrophilic layer of mineral-depressant compound, MD c) Removal of surface MX, MX_2 by oxid'n, red'n or hydrolysis	a) Mineral oxid'n product layer MO, $M(OH)_n$, etc. b) Hydrophilic MD layer c) Removal of surface X_2 by reduction

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.”*

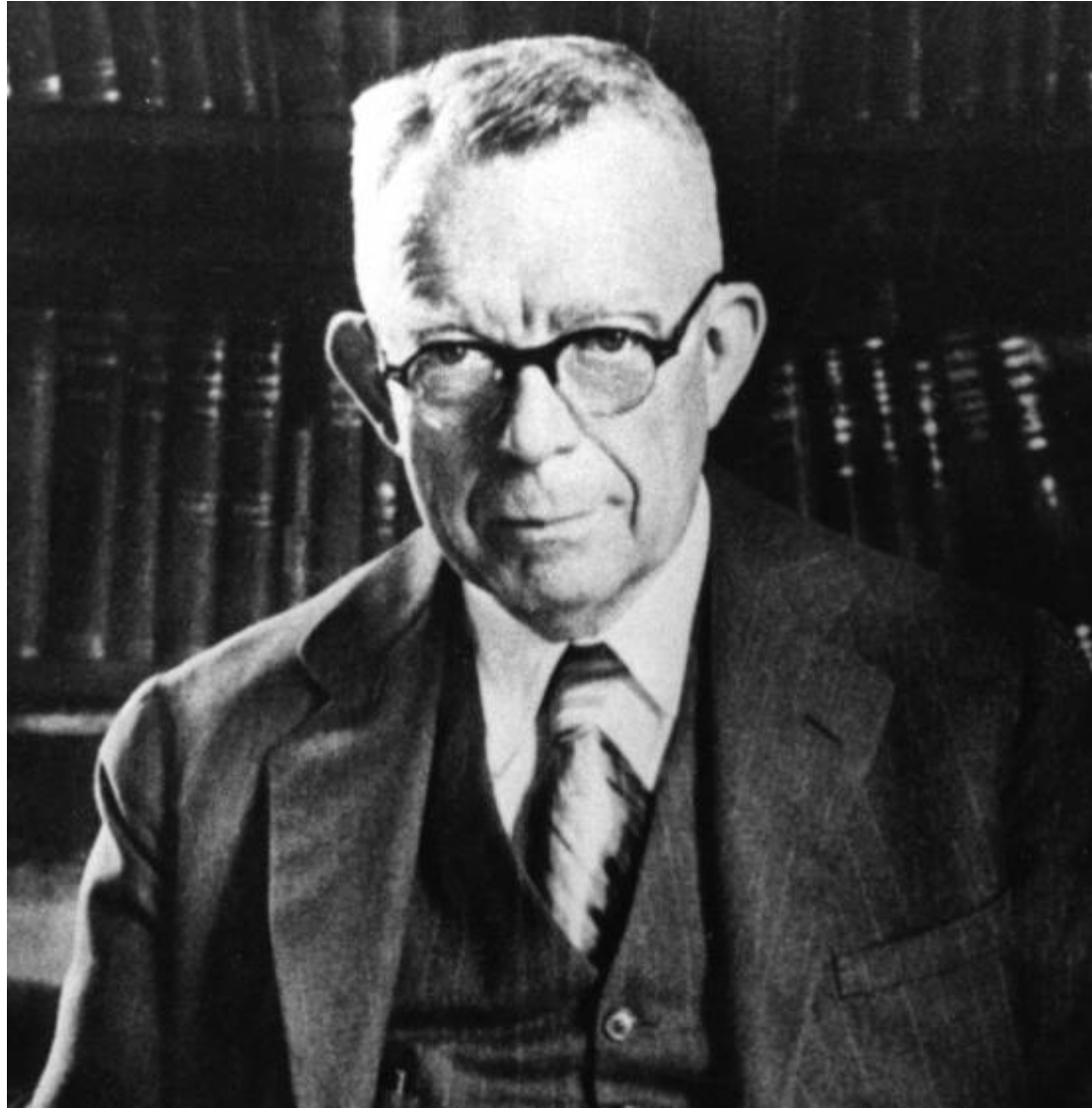
Wark and Cox (1934): *“We find that there is a strong connection between adsorption of xanthate ion and the solubility of the heavy-metal xanthates, but are unable to decide if this is an identity.”*

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.”*

Professor Arthur F. Taggart



WIDELY USED EXPERIMENTAL TECHNIQUES IMPORTANT TO FLOTATION RESEARCH

Miniature flotation cell: (*Gaudin, M.C. Fuerstenau*)

Captive-bubble contact angle: (*Taggart, Wark*)

Modified Hallimond tube: (*Ewers, Fuerstenau*)

Adsorption isotherms: (*Gaudin, deBruyn, Cases, Somasundaran*)

Electrokinetics (zeta potential): (*Sun, Buchanan, Fuerstenau*)

Infrared spectroscopy: (*Wadsworth, Poling, Miller*)

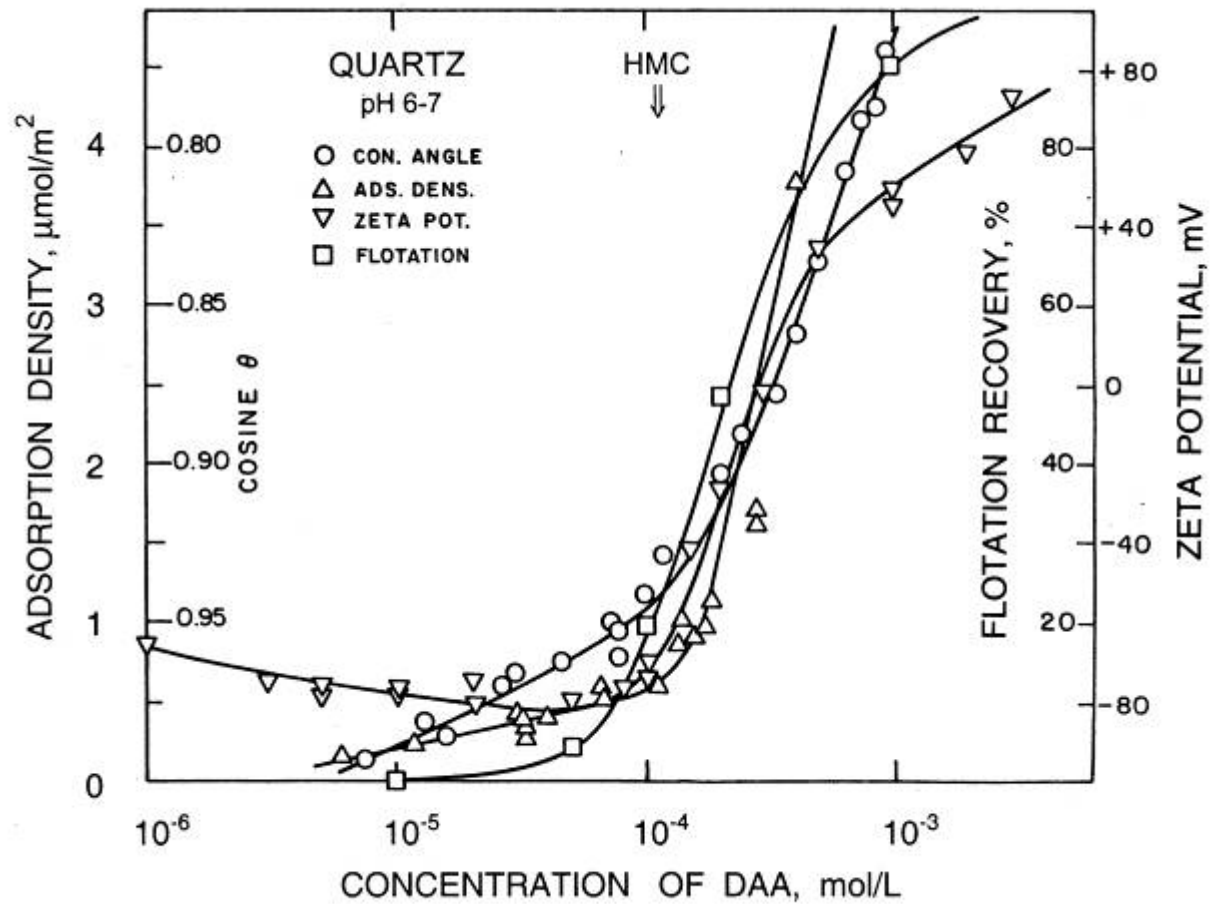
Electrochemical techniques: (*Nixon, Woods, Chander, Richardson*)

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*

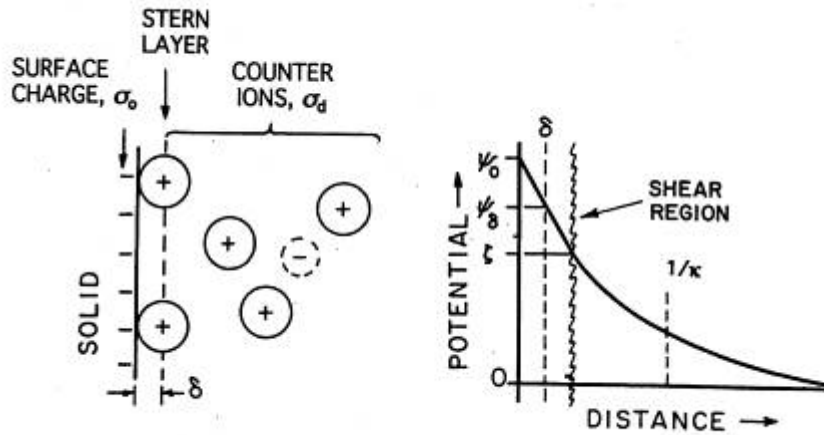
Two phases: *adsorption, zeta potentials*

END OF PROFESSOR OVERBEEK'S YEAR IN THE GROUP AT MIT (1953)

Modi, Charles, Fuerstenau, Overbeek, deBruyn, Stigter, Bergna, Tournesac, Larson



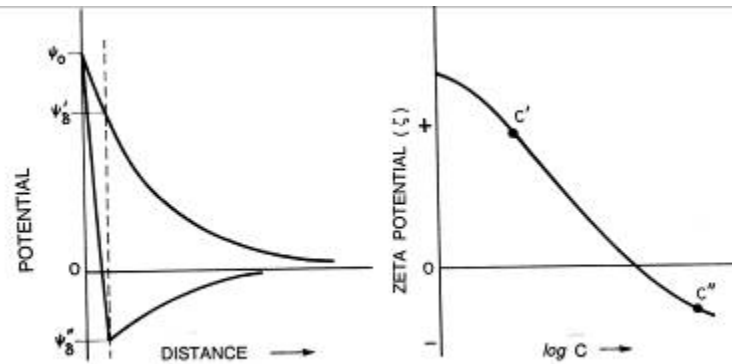
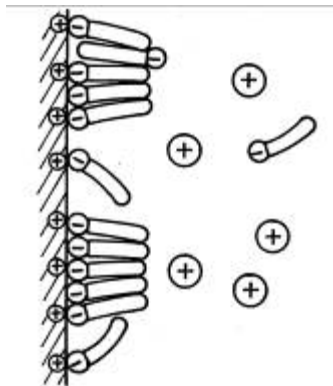
SIMPLIFIED SCHEMATIC OF THE ELECTRICAL DOUBLE LAYER



The point of zero charge (PZC) defines conditions when $\sigma_0 = 0$.

TRIPLE LAYER FROM SUPEREQUIVALENT ADSORPTION

$$[-\sigma_\delta] > [\sigma_0]$$



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***

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

- ***The Stern-Grahame Equation***

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

- ***The standard free energy of adsorption***

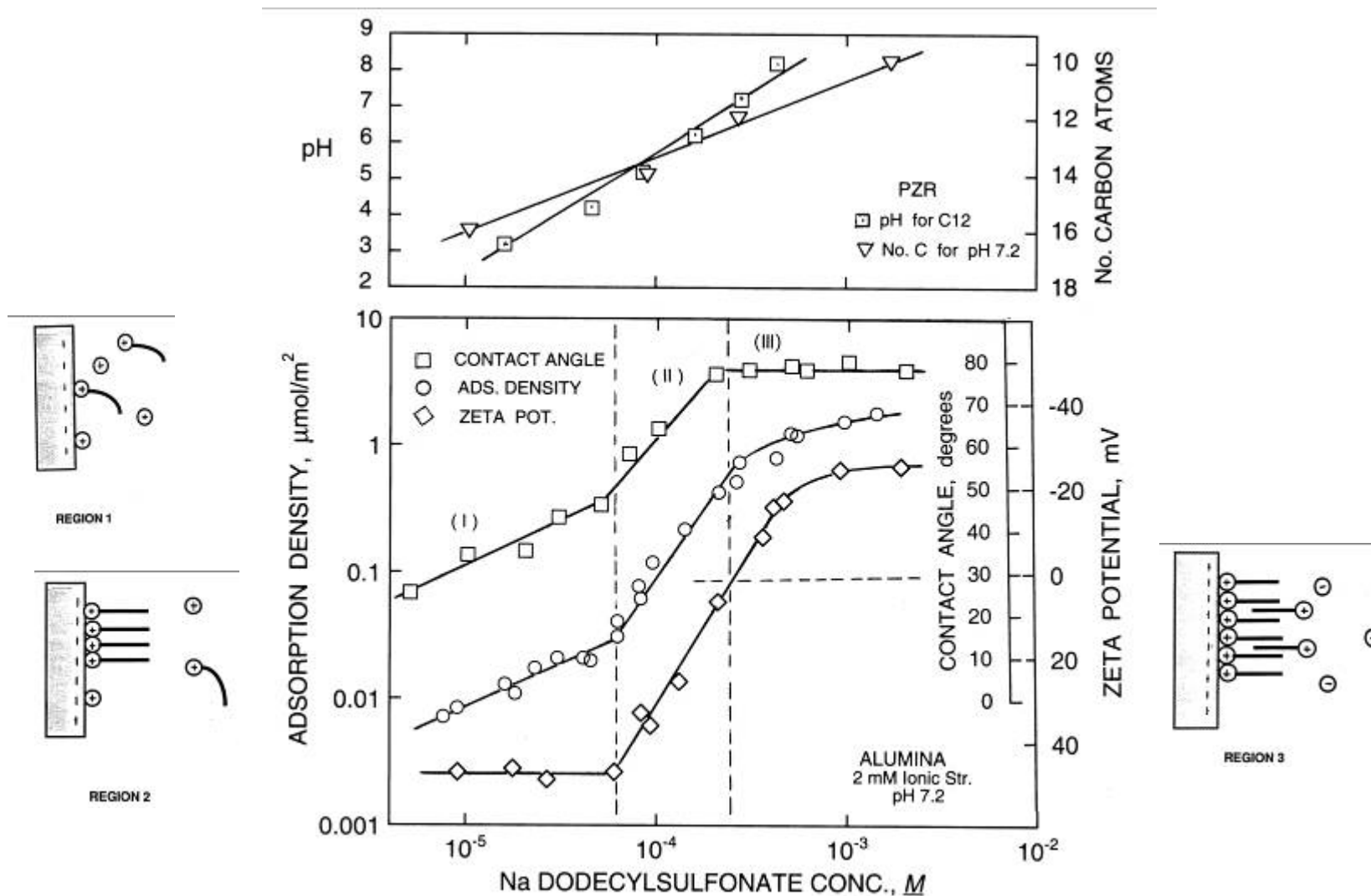
$$\Delta G_{\text{ads}}^{\circ} = zF\psi_{\delta} + \Delta G_{\text{spec}}^{\circ} \quad (\Delta G_{\text{spec}}^{\circ} \text{ is zero with only electrostatic interaction})$$

$$\Delta G_{\text{spec}}^{\circ} = \Delta G_{\text{hpb}}^{\circ} + \Delta G_{\text{chem}}^{\circ} + \Delta G_{\text{H}}^{\circ} + \Delta G_{\text{hpb}^*}^{\circ} + \dots \quad (\text{where these terms represent adsorbed chain association, chemical bonding, hydrogen bonding, hydrophobic bonding with a naturally floatable mineral, respectively})$$

PHYSISORPTION PHENOMENA OF SODIUM DODECYLSULFONATE ON ALUMINA

(after Somasundaran, Wakamatsu and Fuerstenau, 1964 - 1968)

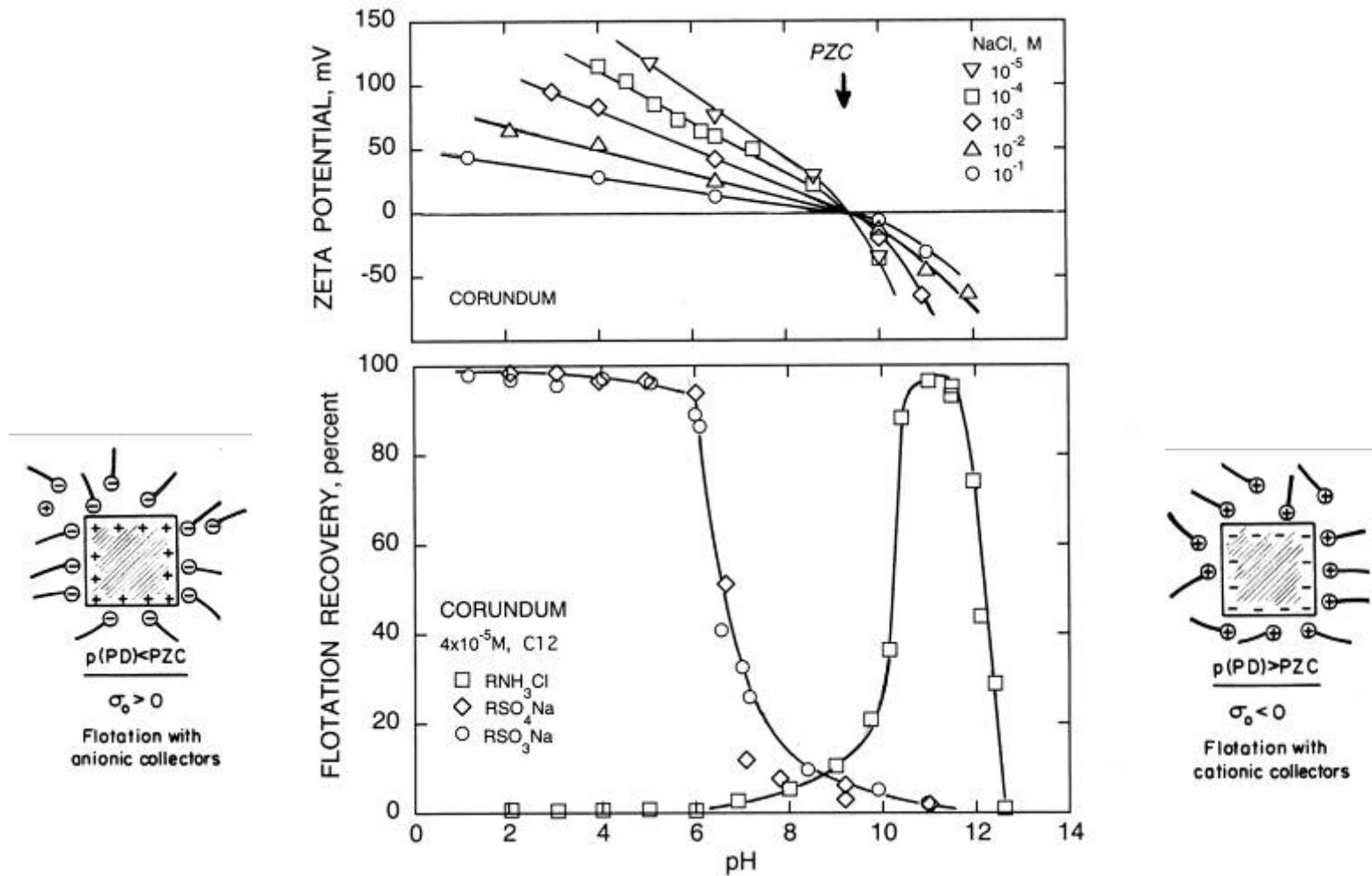
Alkyl chain association (hemimicelle formation) of adsorbed surfactant at the surface controls the shape of the adsorption isotherm, zeta potentials, and contact angles. Both pH and chain length enter into the behavior of these systems.



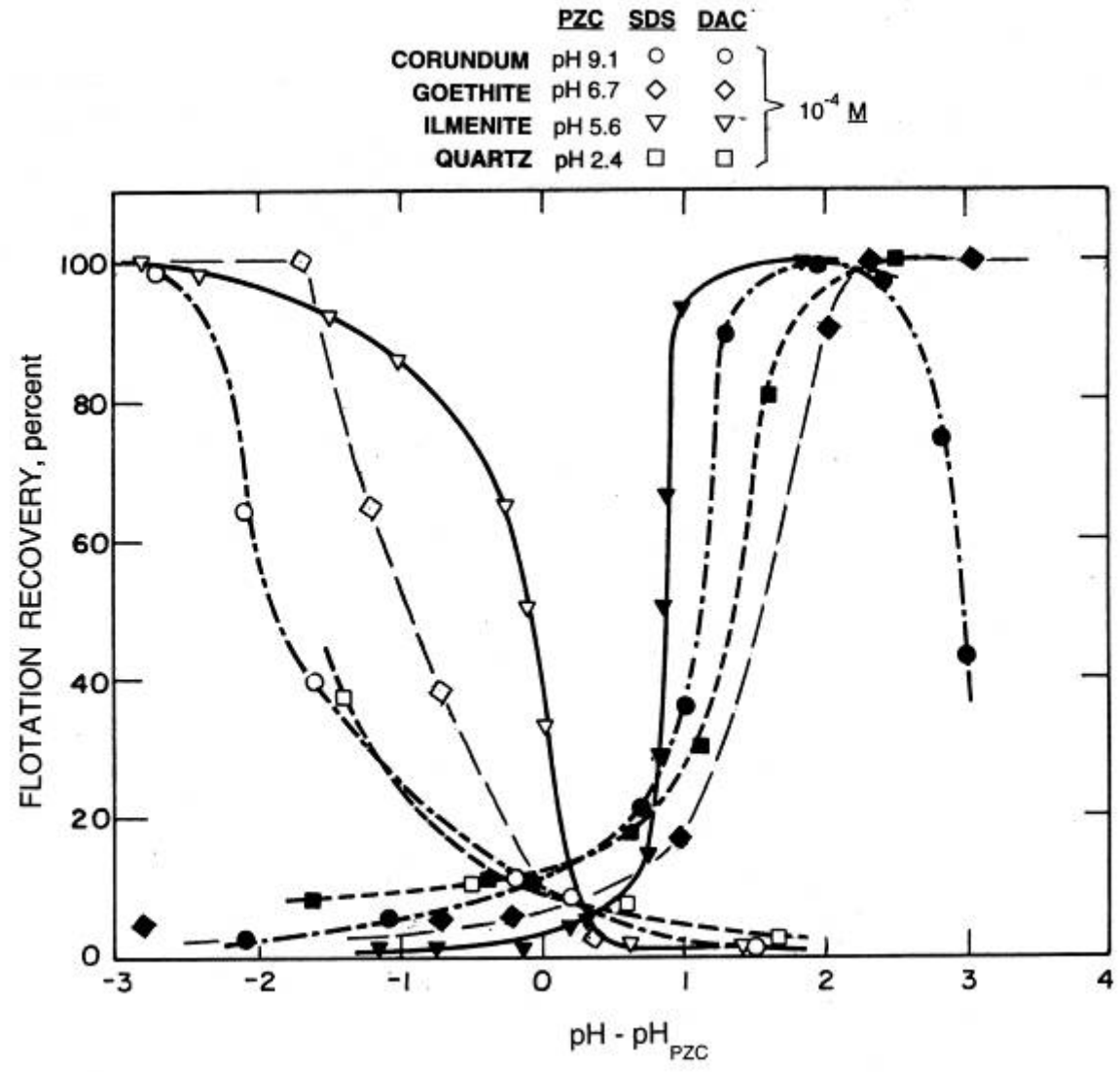
THE ELECTROSTATIC MODEL OF FLOTATION

(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 PHYSISORBING COLLECTORS

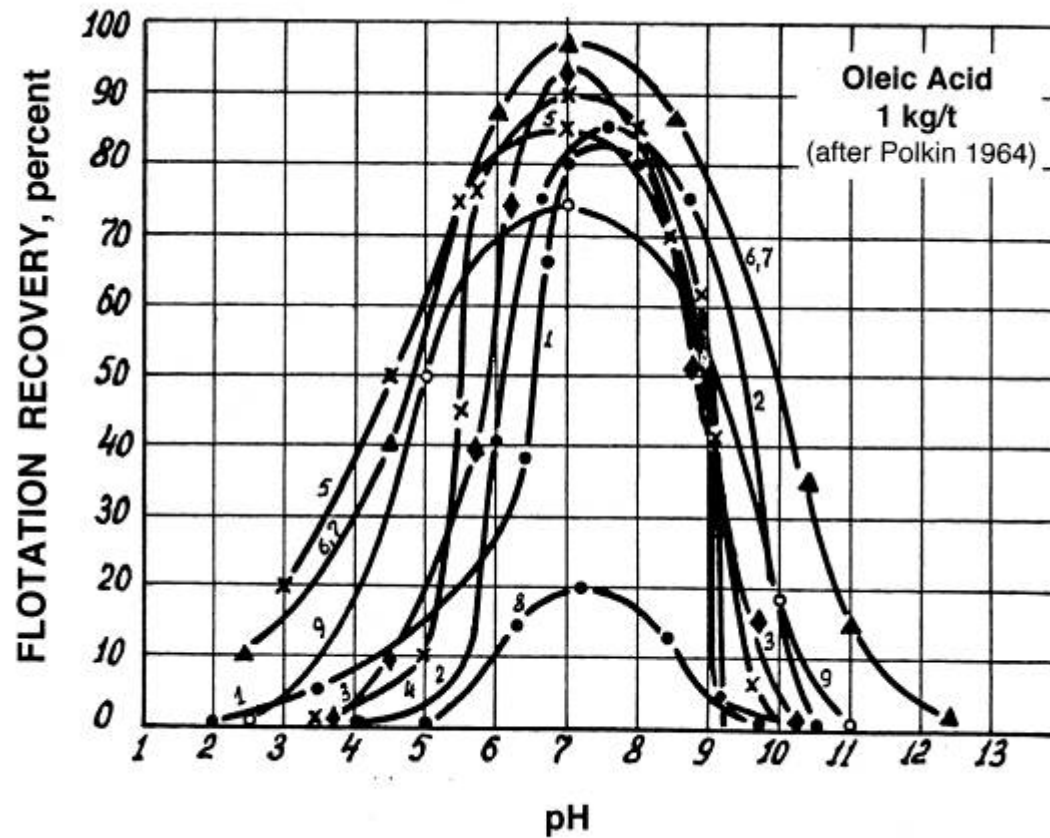


1965



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

Prof. V.I. Klassen

1968

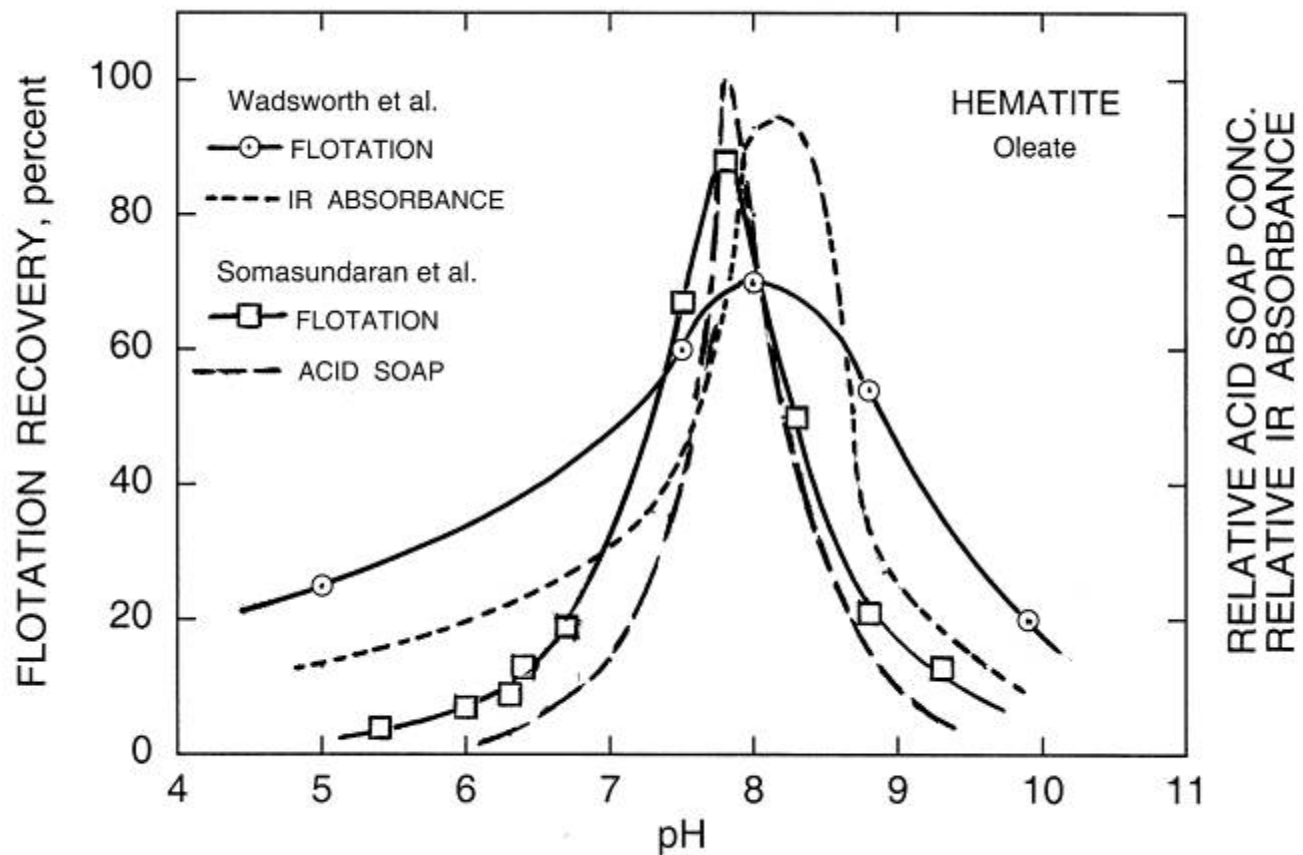
Prof. S.I. Polkin



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.

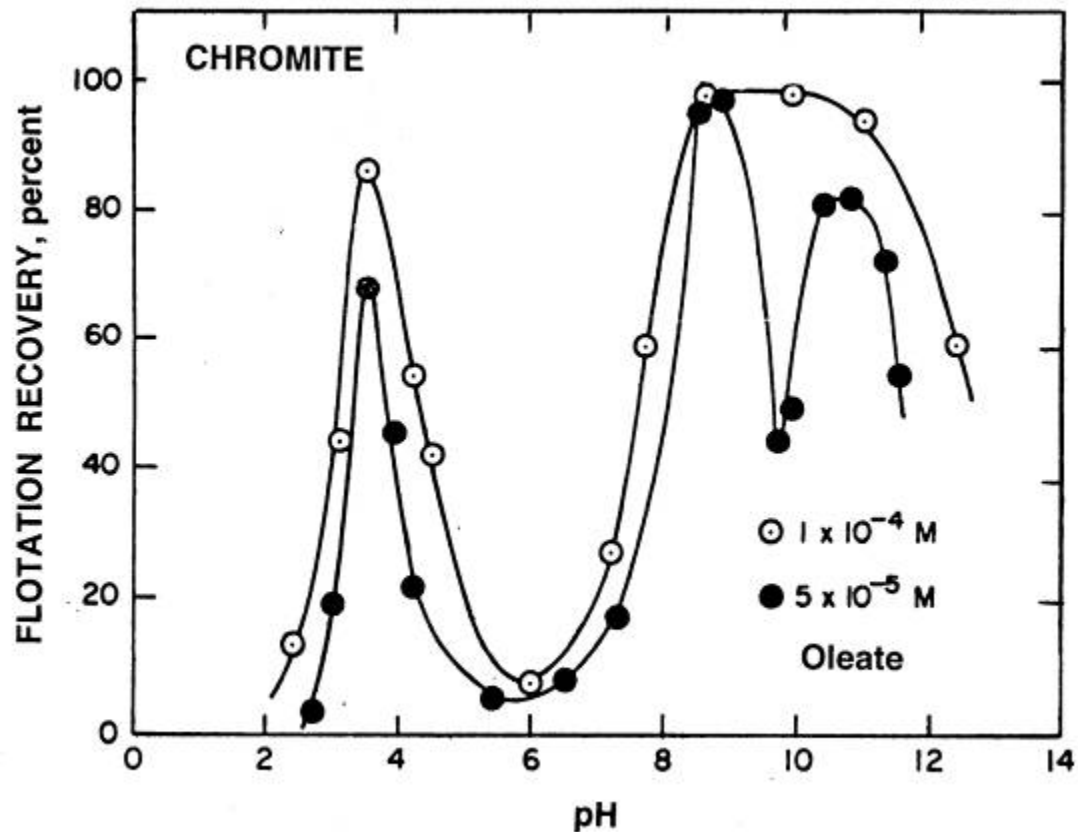
Somasundaran et al. (1980) correlated the flotation peak with acid soap dimer formation. At the peak, the acid soap dimer concentration in solution is 5×10^{-8} M.



THE INFLUENCE OF pH AND OLEATE CONCENTRATION ON CHROMITE FLOTATION

(after Palmer, M.C.Fuerstenau and Aplan, 1975)

This chromite, $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, assayed 42% Cr(III), 8% Al_2O_3 , 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)

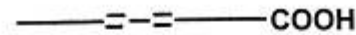
The PZC of this rutile sample occurs at pH 6.7.

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.

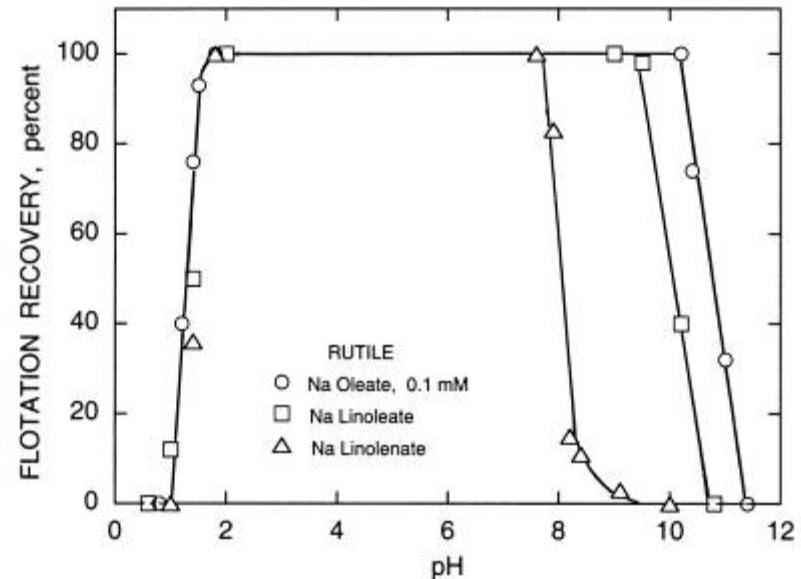
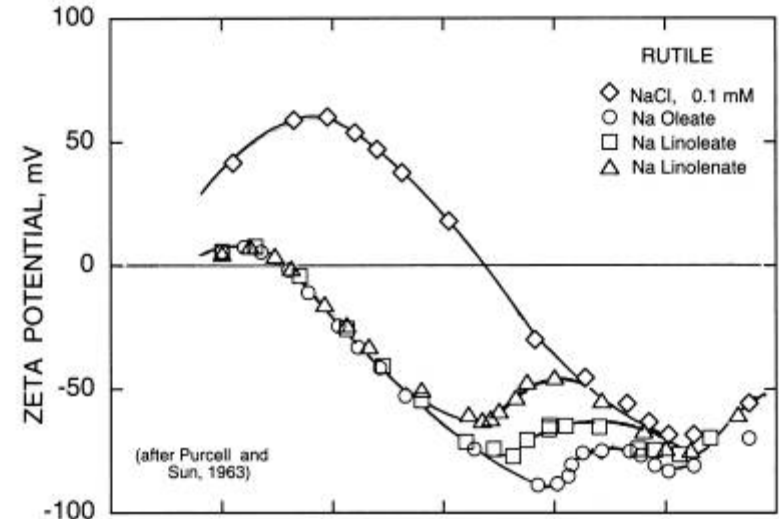
OLEIC ACID [C₁₇H₃₃COOH]



LINOLEIC ACID [C₁₇H₃₁COOH]



LINOLENIC ACID [C₁₇H₂₉COOH]

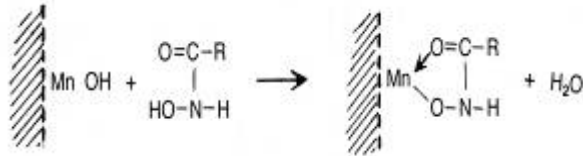


MANGANESE DIOXIDE FLOTATION WITH PHYSISORBING AND CHEMISORBING COLLECTORS

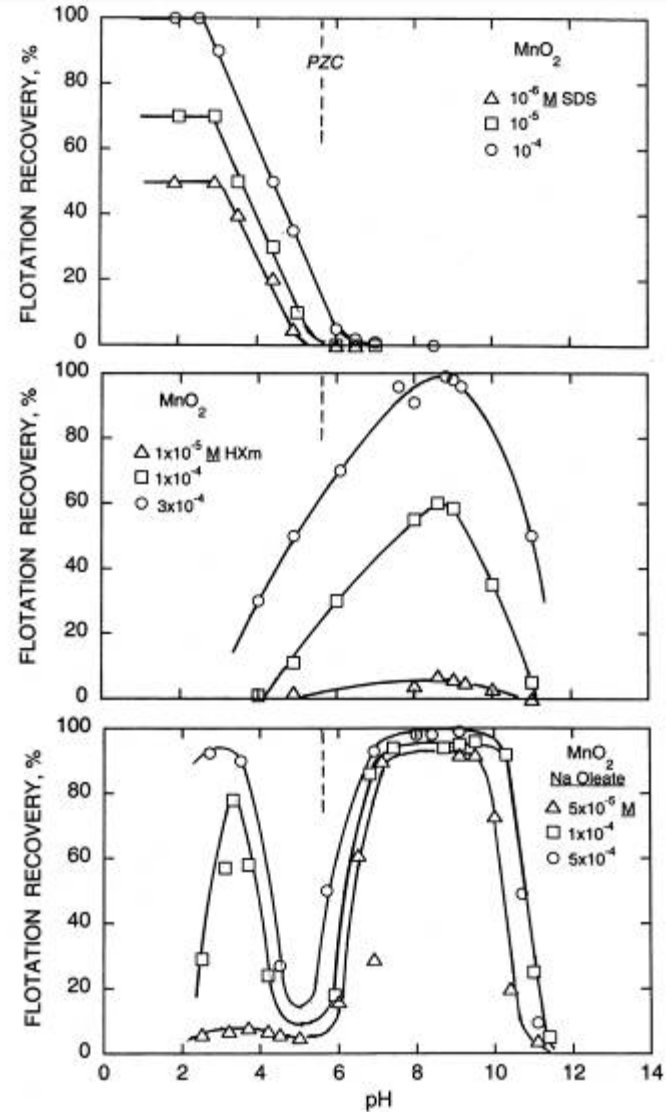
(after Fuerstenau, Natarajan and Shibata, 1983)

The PZC of MnO_2 occurs at pH 5.6. Sodium dodecylsulfonate is a collector that physically adsorbs below the PZC.

K octyl hydroxamate (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).

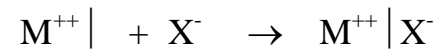
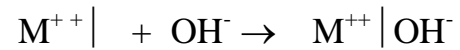


Oleate chemisorbs between pH 6 and 11 (above the PZC). At the PZC, flotation is minimal, but increases again as the pH is lowered, due to the physisorption of oleate anions, but ceases again as molecular oleic acid dominates.

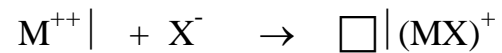
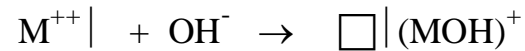


SCHEMATIC ILLUSTRATION OF REAGENT / MINERAL INTERACTIONS

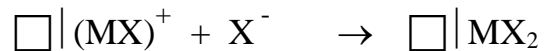
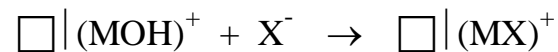
Chemisorption



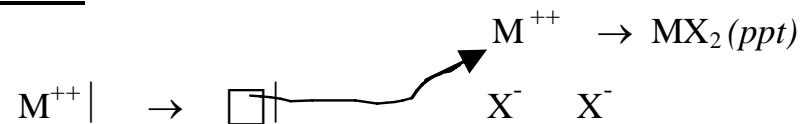
Adsorption with Surface Reaction



Surface Reaction



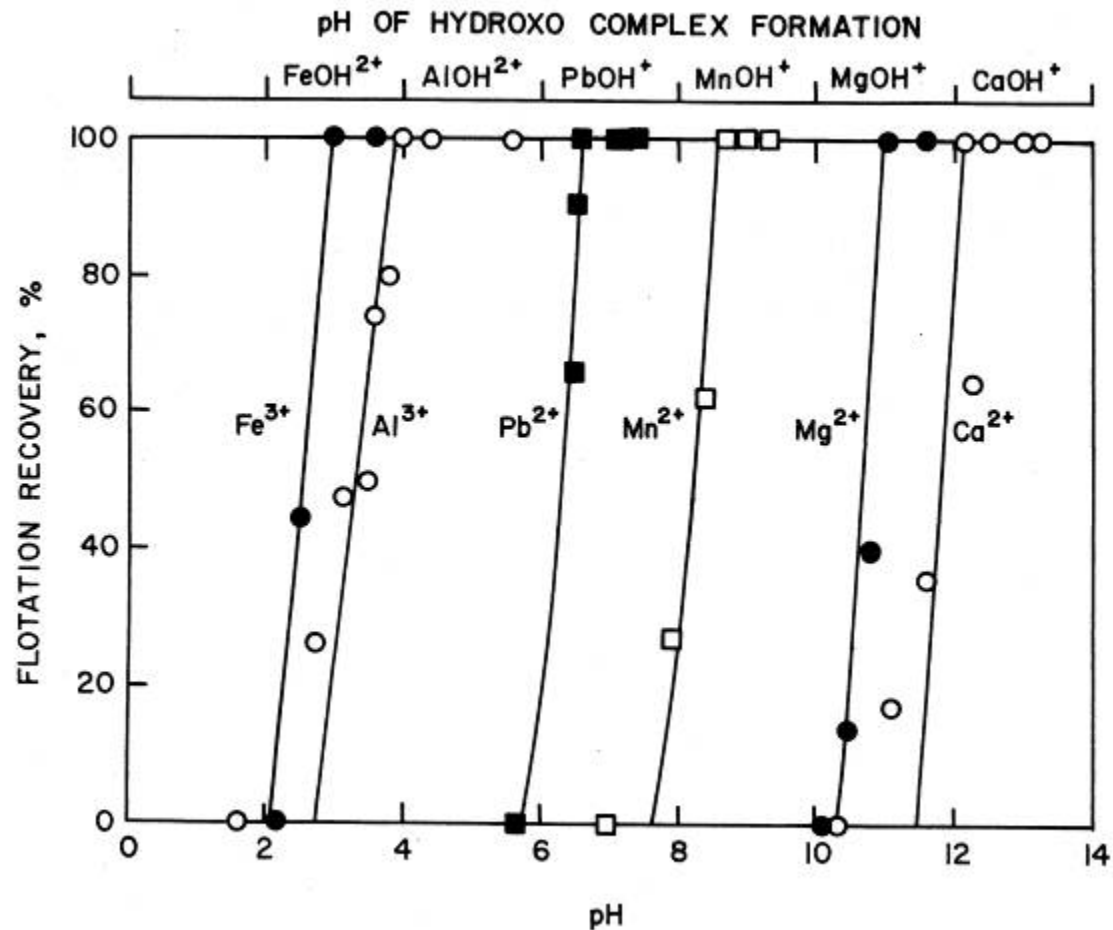
Bulk Precipitation



THE ROLE OF METAL ION HYDROLYSIS IN THE ACTIVATION OF QUARTZ

(after M.C. Fuerstenau and Palmer, 1976)

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).

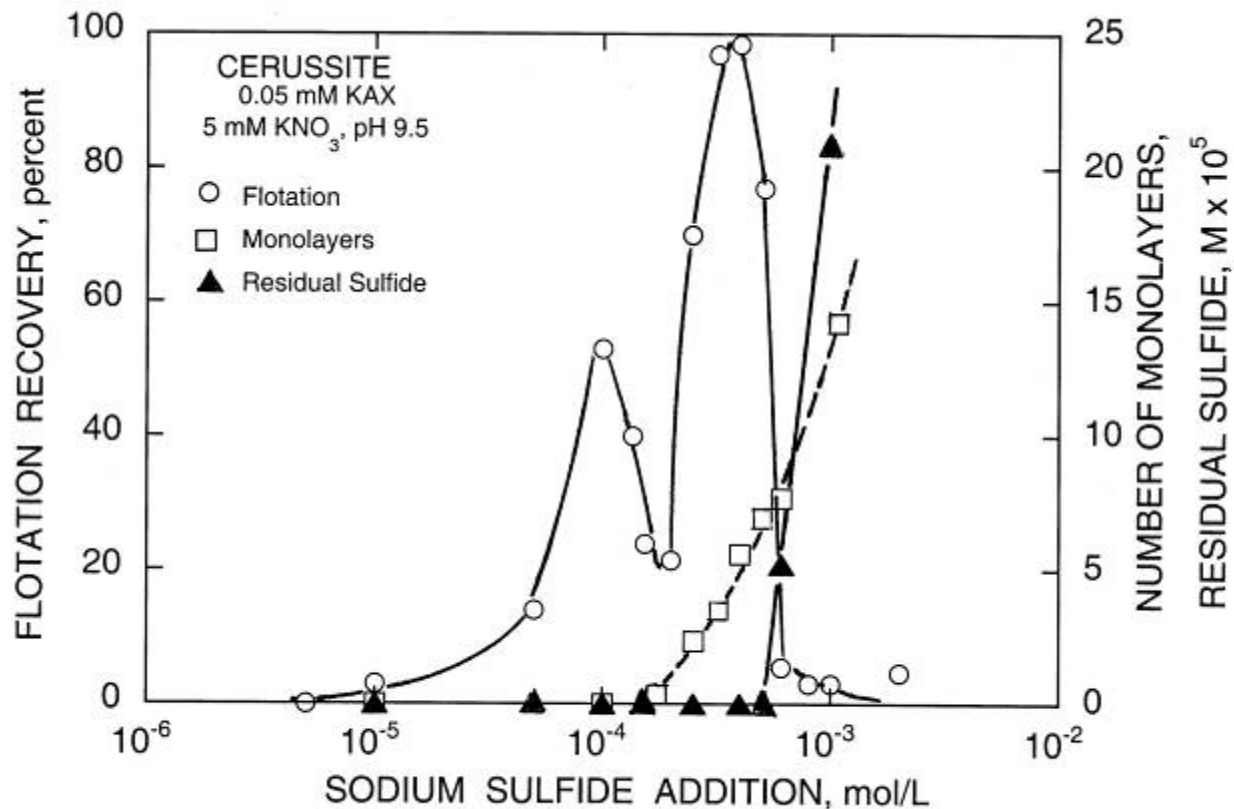


PHENOMENA INVOLVED IN THE SULFIDIZATION AND FLOTATION OF CERUSSITE

(after Herrera-Urbina, Sotillo and Fuerstenau, 1999)

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:

- Initially PbS precipitate coagulates onto the cerussite surface
- Aqueous sulfide concentration reaches that for galena depression
- PbS layers start to build up on cerussite leading to a sharp increase in flotation
- As the PbS film thickens, diffusion slows down the exchange reaction, increasing sulfide in solution
- Increasing aqueous sulfide again depresses flotation
- Here, 15 monolayers of PbS rapidly built up because of the porosity of the growing film

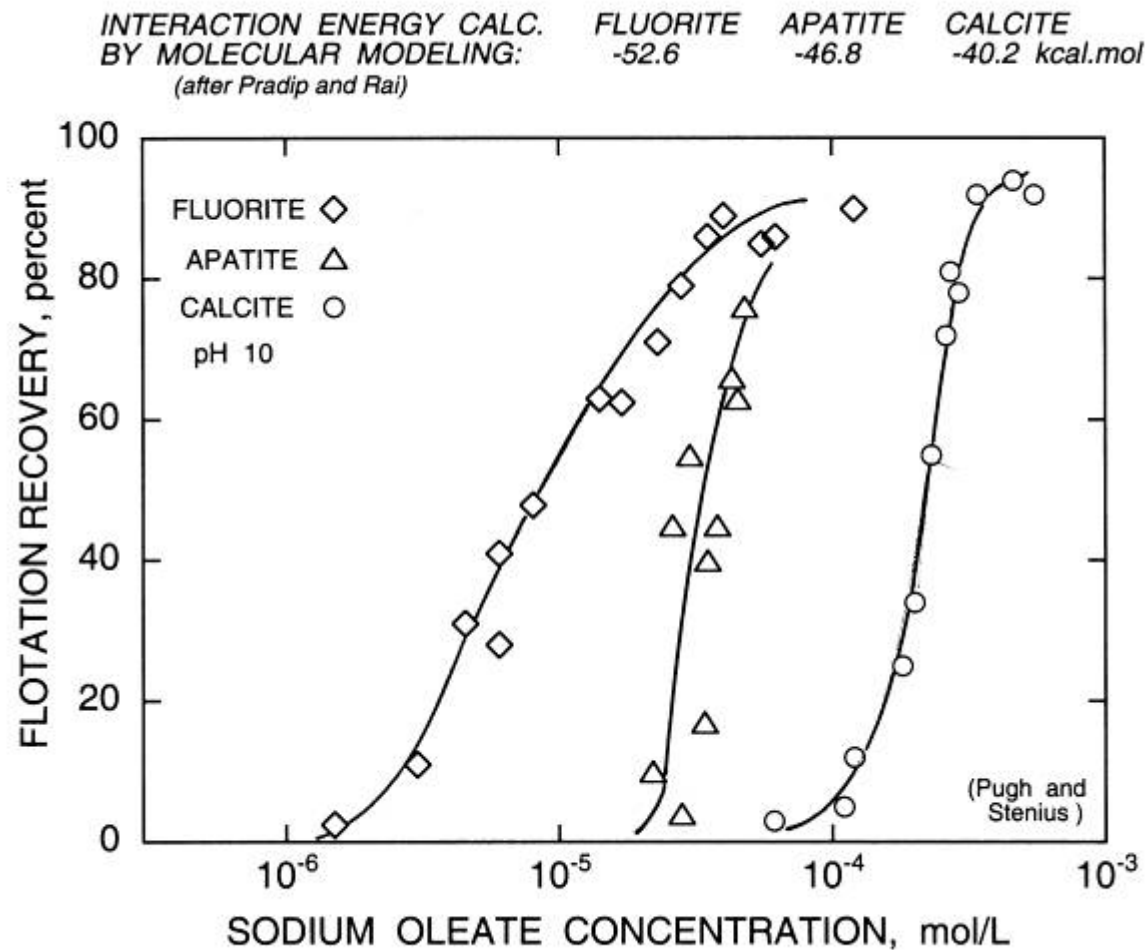


THE FLOTATION OF APATITE, CALCITE AND FLUORITE WITH OLEATE COLLECTOR

(after Pugh and Stenius, 1985)

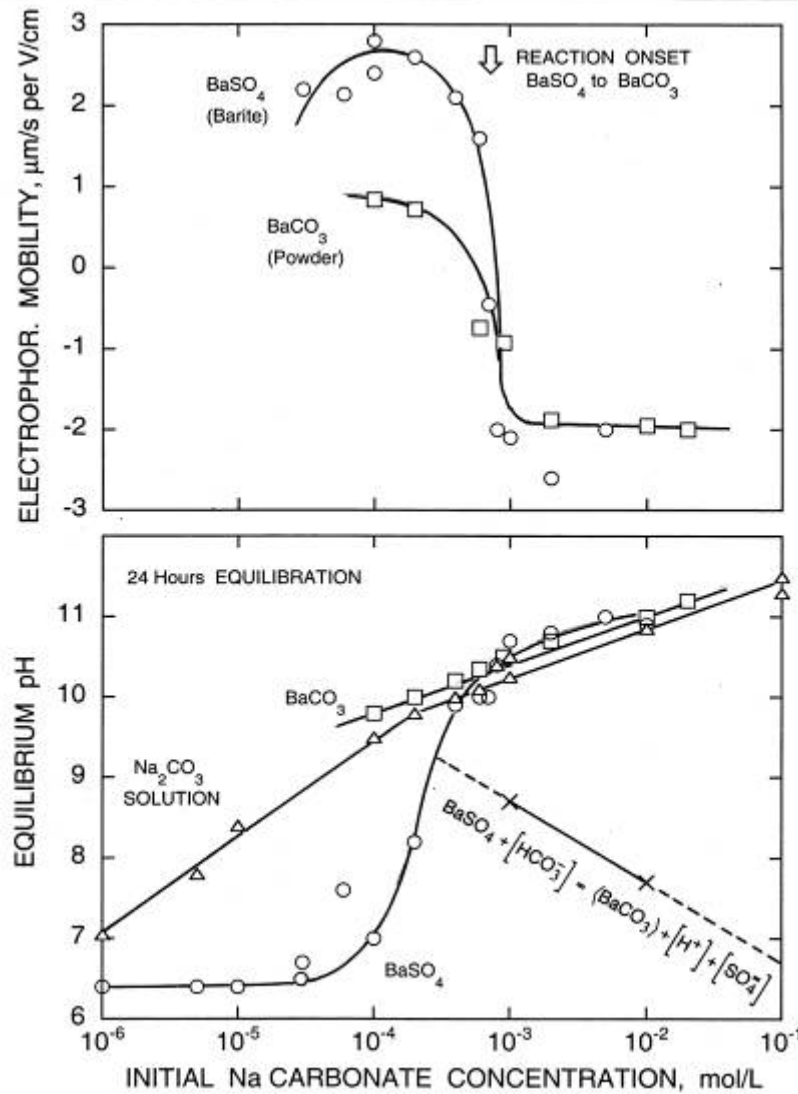
Various researchers have found the order of flotability of calcium salt minerals with oleate to be:

FLUORITE > FLUORAPATITE > CALCITE



SURFACE TRANSFORMATION OF BARIUM SULFATE TO BARIUM CARBONATE UPON THE ADDITION OF SODIUM CARBONATE

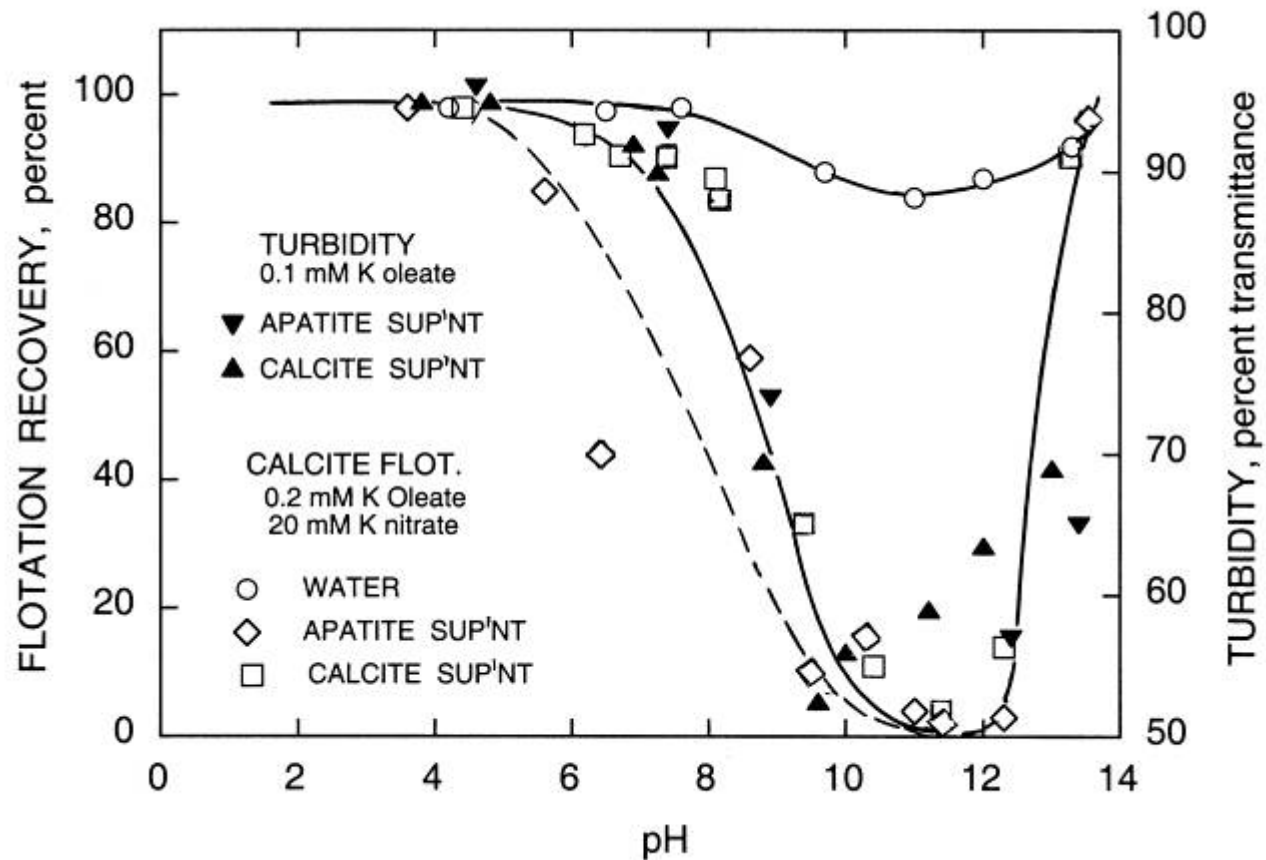
(after Pradip and Fuerstenau, 1991)



THE ROLE OF DISSOLVED MINERAL SPECIES IN CALCITE-APATITE FLOTATION

(after Ananthapadmanabhan and Somasundaran, 1984)

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**.

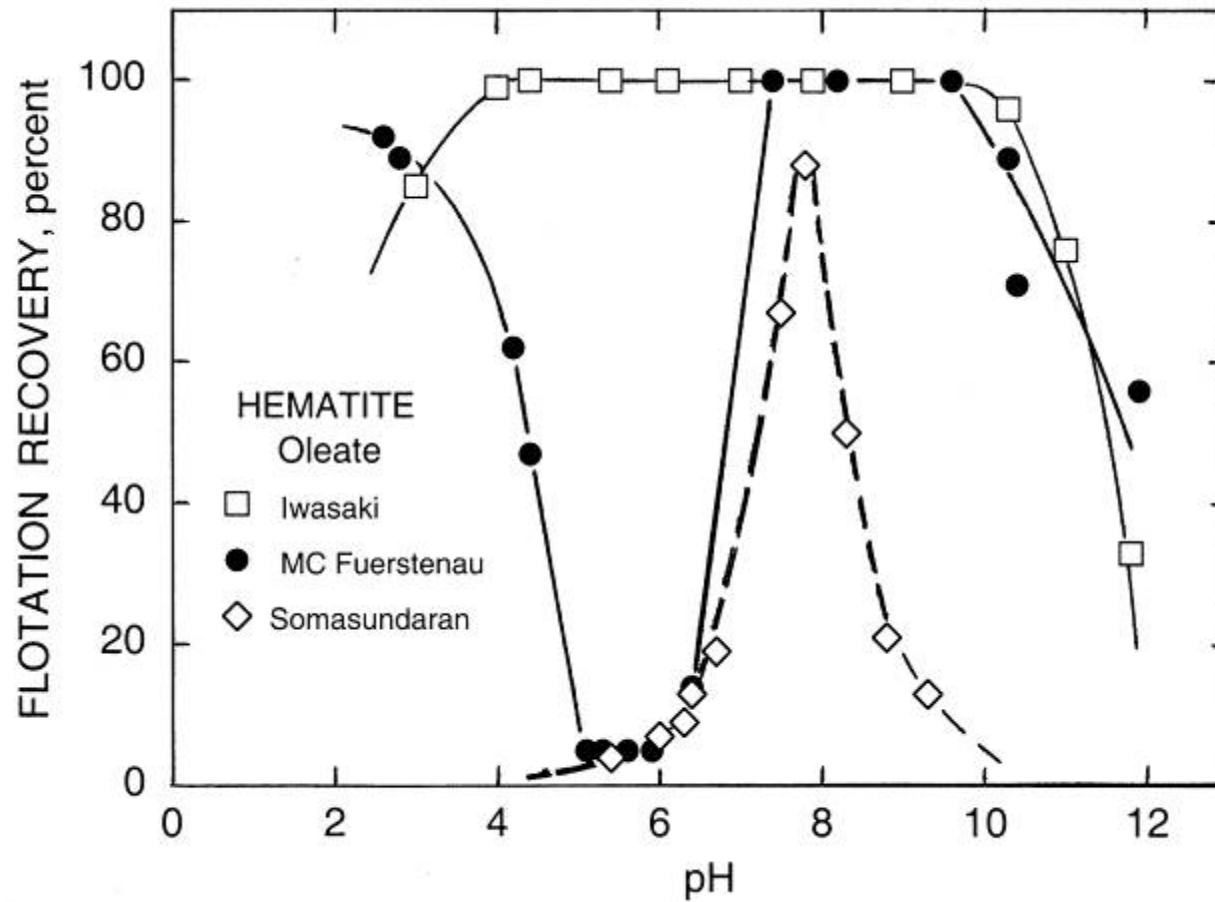
March 1974



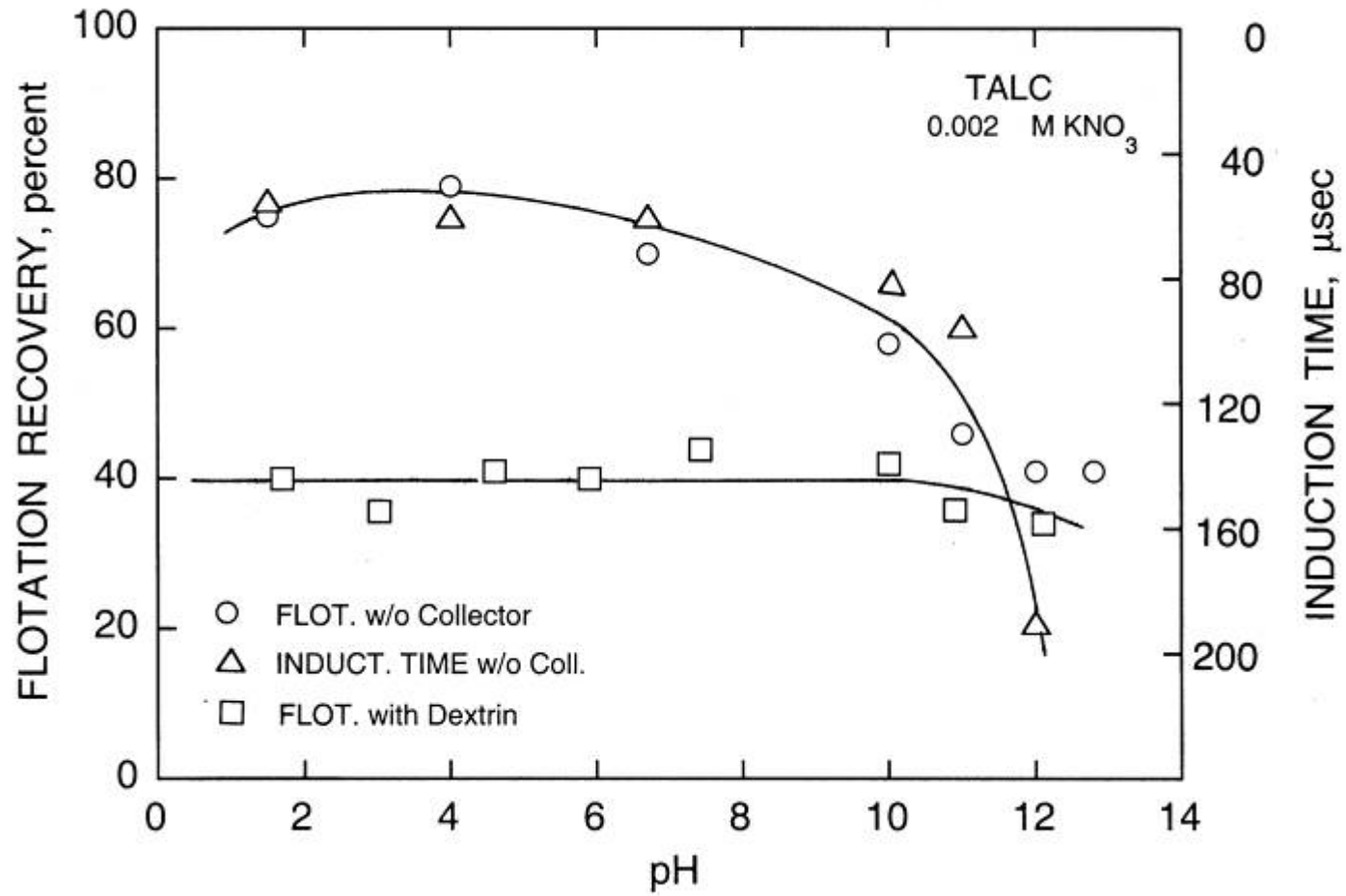
DEPENDENCE OF FLOTATION OBSERVATIONS ON EXPERIMENTAL TECHNIQUE

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

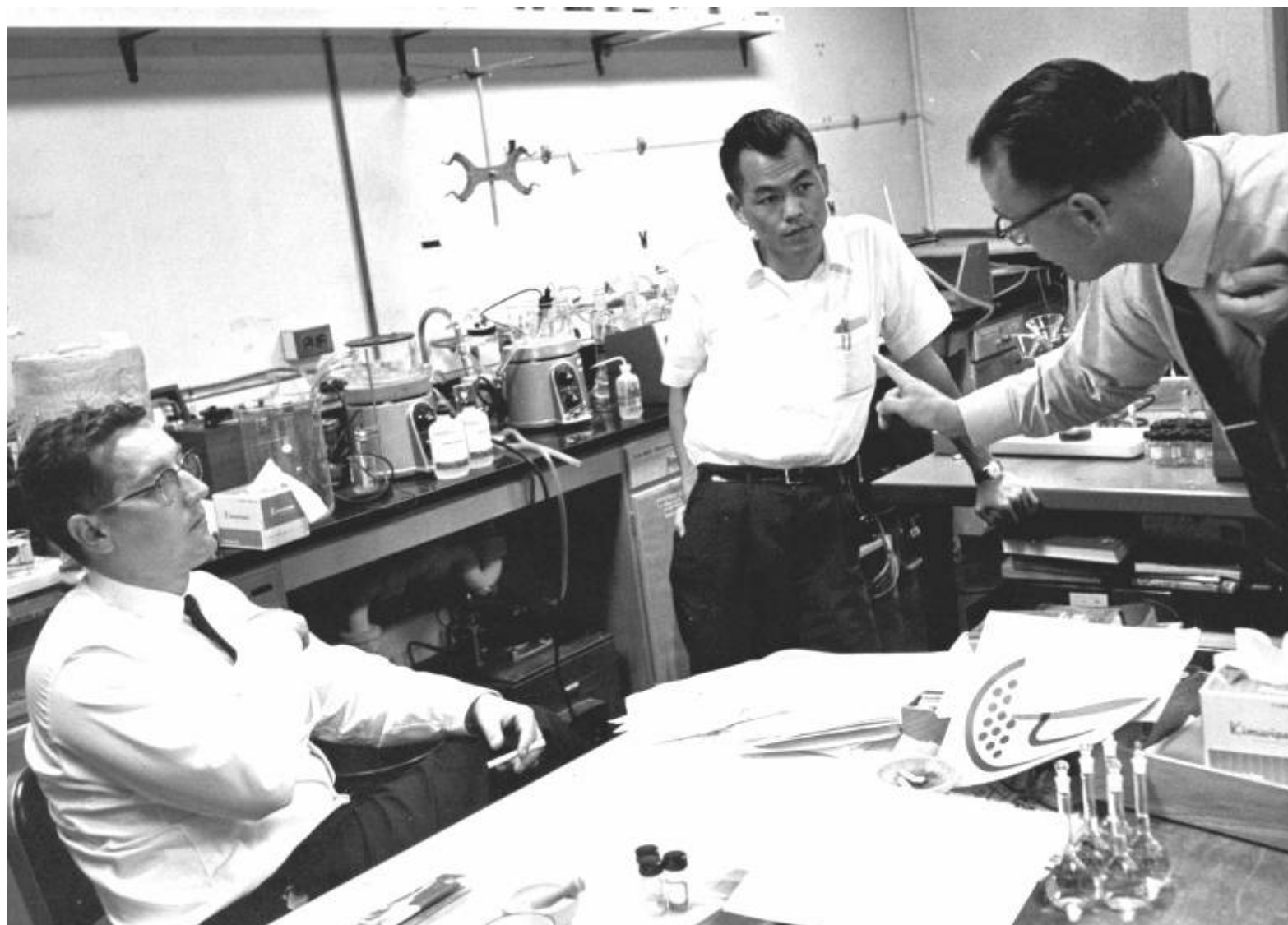
Somasundaran **10 seconds**, *M.C. Fuerstenau* **45 seconds**, *Iwasaki* **300 seconds** (5 min)



THE ROLE OF pH AND ADDED DEXTRIN ON THE FLOTATION OF TALC







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)

