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INTRODUCTION

Froth flotation is the most common mineral-processing method for the separation and recovery of mineral resources. Flotation of nonsulfide minerals alone accounted for approximately 700,000 tons per day of material processed by this technology.(1) An important overriding concern in all flotation plants is the huge energy consumption involved in this unit operation. In fact, it has been estimated that froth flotation in the U.S. accounts for 0.3 quads per annum.(2) Flotation of desired minerals from unwanted gangue minerals is accomplished by surface chemistry control of the mineral particle suspension. The floated minerals are most often rendered hydrophobic by adsorption of surfactants, called collectors, from the aqueous phase in self-assembling monolayers. Fatty acids composed primarily of oleic and linoleic acids are often used as collectors in nonsulfide flotation systems. The corresponding adsorption reactions have some very unique features which are little understood. At elevated temperatures and/or high oxygen activity, certain nonsulfide minerals such as fluorite, CaF_2, and the rare-earth fluocarbonate bastnaesite exhibit enhanced hydrophobicity and hence an improved flotation response. This effect is shown in Table 1 for contact angle and bubble attachment time measurements on fluorite at ambient conditions and at elevated temperatures and high oxygen potential.

Table 1. *Effect of Temperature and Oxygen on Bubble Attachment Time Measurements at a Fluorite Surface.*

Gas Phase	Temperature, °C	Attachment Time, milliseconds (ms)	Contact Angle, degrees
Air	22	260-270	70-73
Air	60	20-22	90-95
Oxygen	22	20-25	90-92

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An important group of minerals among nonsulfides are those which contain rare-earth elements such as lanthanum, europium, yttrium, and cesium. Rare-earth minerals are both strategically and economically vital. The use of rare earths in magnets and the new high T_c superconductors along with their use in the nuclear power industry and many other less exotic industries assure a continued demand for years to come. Within the past year many conferences on rare earths have been held including Rare Earths in Alaska, 9th International Workshop on Rare-Earth Magnets and Their Applications, 18th Rare-Earth Research Conference and the TMS-AIME Rare-Earth Symposium. Also, the Institute for Physical Research and Technology at Iowa State University publishes a quarterly Rare-Earth Information Center Newsletter. These conferences and related activities demonstrate the need for development of U.S. rare-earth mineral deposits. Currently, the U.S. is self-sufficient in rare-earth production due to the deposit at Mountain Pass, California.(3) As the demand for rare earths increases and the Mountain Pass deposit becomes played out, new methods for efficient rare-earth mineral recovery will become necessary.

Another group of nonsulfide minerals are the phosphate rock minerals such as fluorapatite and collophanite. Phosphate minerals account for the greatest tonnage of nonsulfide flotation capacity in the United States. Present flotation technology results in the discarding of up to thirty percent of mined phosphate rock. These semisoluble salt minerals are most often used as fertilizers and are of critical importance to the agricultural industry. In summary, nonsulfide mineral recovery and concentration is fundamental to a wide-ranging number of critical industries in the United States.

Flotation has in the past often been treated more as an art than a science. With advanced analytical methods and Fourier transform infrared (FTIR) spectroscopy in particular, fundamental aspects of flotation can be elucidated, and improvements in both mineral recovery and energy efficiency will be realized.

This report summarizes the last thirty-month period of Grant No. DE-FG-02-84ER13181. Research has focussed on the mineral/collector systems mentioned above as well as other systems of academic interest. Our research laboratories at the University of Utah were visited on two occasions by officials from the Division of Chemical Sciences, Department of Energy. In August of 1985, Dr. Roland Hirsch, Project Officer, visited our laboratories and reviewed the status of the research program. Later, in March of 1987, Dr. F. Dee Stevenson, Chief of the Processes and Techniques Branch, visited us for a similar review. As a result of this research, fundamental in-situ spectroscopic measurements of collector adsorption in nonsulfide flotation systems have been made and significant breakthroughs in this area have been accomplished. Similarly, thermochemical data for these systems are limited. Heats of oleate adsorption and heats of reaction between chemisorbed oleate monomers at the fluorite surface have been measured and have been invaluable in understanding the mechanisms involved in the surface chemistry of nonsulfide flotation systems. Surface modification techniques to promote the improved hydrophobicity mentioned previously using both inorganic modifiers and electrochemical control have also been developed.

PROGRAM OBJECTIVES

The primary objective of this research is to improve the flotation efficiency of nonsulfide mineral systems by establishing the fundamental features of collector adsorption reactions and developing appropriate chemical control strategies. In-situ real-time spectroscopic measurements, microcalorimetry, and surface modification have been used to accomplish this goal. Using these techniques, measurements have been completed to establish important fundamental information on nonsulfide flotation systems. In this regard, an innovative in-situ FTIR spectroscopy procedure which can detect adsorption from very dilute collectors solutions ($\sim 5 \times 10^{-7}$ M) is being developed to simultaneously study collector adsorption kinetics, equilibrium collector adsorption density, and collector orientation in-situ. Few researchers have taken this approach, and none have applied this method to the analysis of flotation phenomena.

FLUORITE/OLEATE SYSTEM

In-Situ FTIR Spectroscopy

In the first twelve months of this research, a Digilab FTS-40 FTIR spectrometer was purchased (partially funded by Grant No. DE-FG-02-84ER13181) and installed. Although the purchase and installation were time-consuming, use of the resulting FTS-40 system has been fruitful, in that important and exciting results have been obtained.

Initially, in-situ measurements were attempted using more traditional methods such as pressing a partially dewatered mineral particle/surfactant paste against an inert germanium internal reflection element (IRE). Sampling of the paste occurs during internal reflection as an infrared evanescent wave actually passes a few microns from the IRE into the sample and back to the IRE. Multiple internal reflections allow weak signals from adsorbed collector species to be magnified. The cell designed for this purpose is similar to the one described by Leppinen.(4) Unfortunately, this apparatus yielded only semiqualitative results. It was also found that the germanium IRE was easily contaminated by surfactant from solution and interfered with the interpretation of experimental results.

The contamination of the germanium element led to a novel approach in making quantitative in-situ real-time FTIR measurements. Put succinctly, an ambitious program was undertaken to fabricate internal reflection elements from single crystals of a particular mineral of interest and monitor adsorption onto the IRE. Such a design allows one to study adsorption kinetics, determine the equilibrium collector adsorption density, and to describe collector orientation in-situ. This procedure makes use of a flow-through variable angle internal reflection prism cell as shown in Figure 1.

Figure 2 shows the kinetics of adsorption of oleate on a fluorite IRE for an oleate concentration of 3.4×10^{-5} M. The peaks in the infrared region 3050 to 2800 cm^{-1} are due to the aliphatic portion of the oleate molecule. To obtain this data, deuterium oxide, D_2O, was used in place of H_2O to remove the strong absorbance (circa 2.0 absorbance units) in this region from OH stretching vibrations. The possible difference in surface chemistry in changing solvents to aid in spectroscopic investigations was also considered. Table 2 presents a comparison of bubble attachment times for the CaF_2/oleate system in H_2O and D_2O. No significant difference in hydrophobicity was found. This is not surprising when one considers that the physical properties of the two solvents are almost identical.

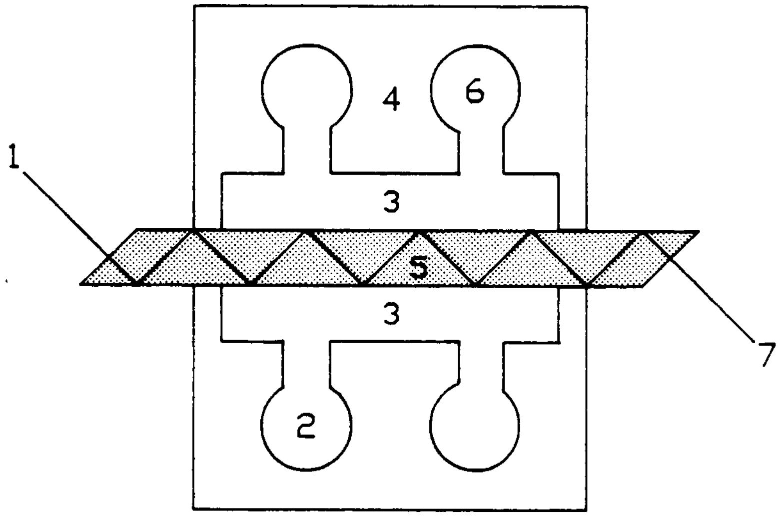

Figure 1. Schematic drawing of a flowthrough internal reflection cell.

1. Incident IR Beam.	4. Teflon Outer Body.	6. Exit Port.
2. Inlet Port.	5. IRE.	7. IR Beam to Detector.
3. Liquid Compartment.		

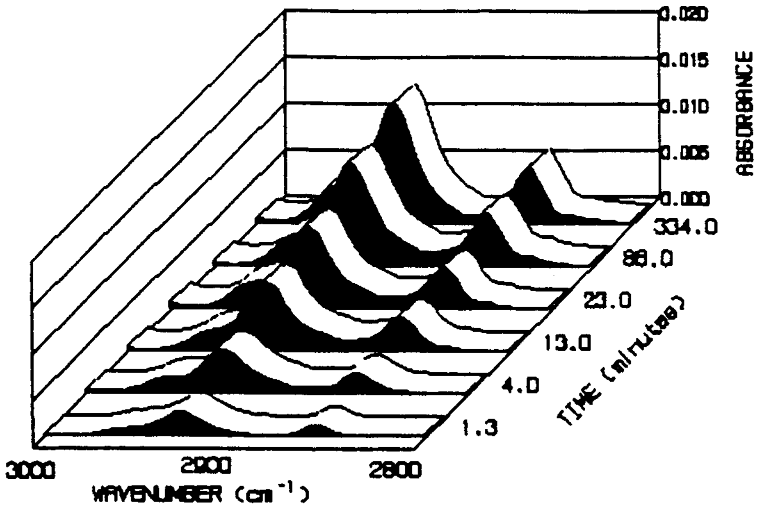

Figure 2. The kinetics of oleate adsorption at a fluorite surface as revealed by in-situ FTIR internal reflection spectroscopy.

Table 2. Bubble Attachment Times for Fluorite Particles with Adsorbed Oleate in H_2O and D_2O at Two Different Temperatures.

Solvent	Attachment Time (ms)	
	24°C	64°C
H_2O	1.73	1.15
D_2O	1.89	1.11

As is evident from Figure 2, the equilibrium surface state is achieved after several hours. The relatively slow adsorption kinetics suggest that the adsorption reaction is limited by the chemisorption and surface precipitation reactions to form calcium oleate, $Ca(Ol)_2$, a surface species which had been established from previous work.

The previous research grant period (No. DE-FG-02-84ER13181, March 1984-March 1986) used a radiotracer technique to determine the adsorption density of oleate on powdered fluorite for two different temperatures. See Figure 3.

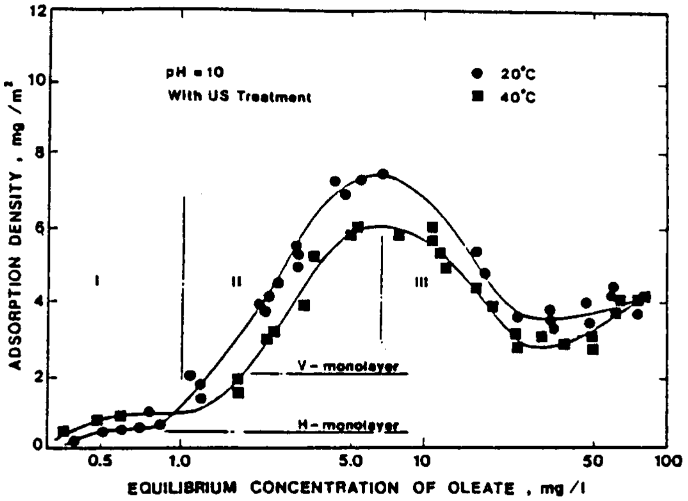

Figure 3. Adsorption density of oleate by fluorite at two different temperatures.(5)

It was found that, at lower concentrations (Region 1), oleate chemisorbs endothermically. However, at higher concentrations (Region 2), surface precipitation of calcium oleate occurs. These findings are being tested using the in-situ internal reflection technique referred to earlier. A theory has been developed(6) which allows direct measurement of adsorption density from fundamental considerations. Equation (1) allows calculation of adsorption density of a surfactant at the surface of an IRE:

$$\Gamma = \left[\frac{A}{(\ell/t)\cot\theta} - \varepsilon C_b d_e\right]/1000\ \varepsilon \left(\frac{2d_e}{d_p}\right) \tag{1}$$

where Γ = adsorption density (mol/cm^2)

A = integrated absorbance (cm^{-1})

ℓ = length of IRE (cm)

t = thickness of IRE (cm)

θ = incident angle of light (degrees)

ε = molar absorptivity (ℓ/(cm^2·mol))

C_b = concentration of surfactant in bulk (mol/ℓ)

d_e = effect depth (cm)

d_p = depth of penetration (cm)

All of the above quantities except d_p and d_e can be determined experimentally. The d_p and d_e terms are a complex function of the optics of the system and can be readily calculated.(7)

Using Equation (1), the adsorption density of oleate on a fluorite IRE was determined for five equilibrium concentrations. These adsorption densities are compared in Table 3 to those found by other researchers using more traditional methods. The agreement is outstanding when one considers the fundamental basis from which Equation (1) was derived.

Table 3. Adsorption Density of Oleate by Fluorite as Calculated from Internal Reflection Theory and Compared to Previous Work.

Equilibrium Concentration (M)	Adsorption Density ($mole/cm^2 x 10^{10}$)		
	In-Situ FTIR	Radiotracer(5)	UV-VIS(8)
$5.3x10^{-7}$	0.83	0.31	-
$2.1x10^{-6}$	3.0	1.76	-
$4.3x10^{-5}$	7.5	27.0	6.1
$9.0x10^{-5}$	19.5	13.1	9.1
$1.7x10^{-4}$	46.5	13.5	13.1

Also of interest is the form of the adsorbed oleate species at the fluorite surface. Various researchers have found from ex-situ measurements that oleate forms a $Ca(Ol)_2$ salt upon adsorption. Figure 4 shows the infrared spectrum of adsorbed oleate on fluorite between 1600 and 1400 cm^{-1}. The peaks at 1572, 1535, 1467, 1433, and 1421 wavenumbers correspond to the carboxylate functionality $Ca(Ol)_2$ of the complex referred to earlier. It was found that true equilibrium is not reached for periods less than 24 hours, most probably due to the slow formation of $Ca(Ol)_2$ species. Thus these in-situ measurements elucidate some of the complexities of the CaF_2/oleate system.

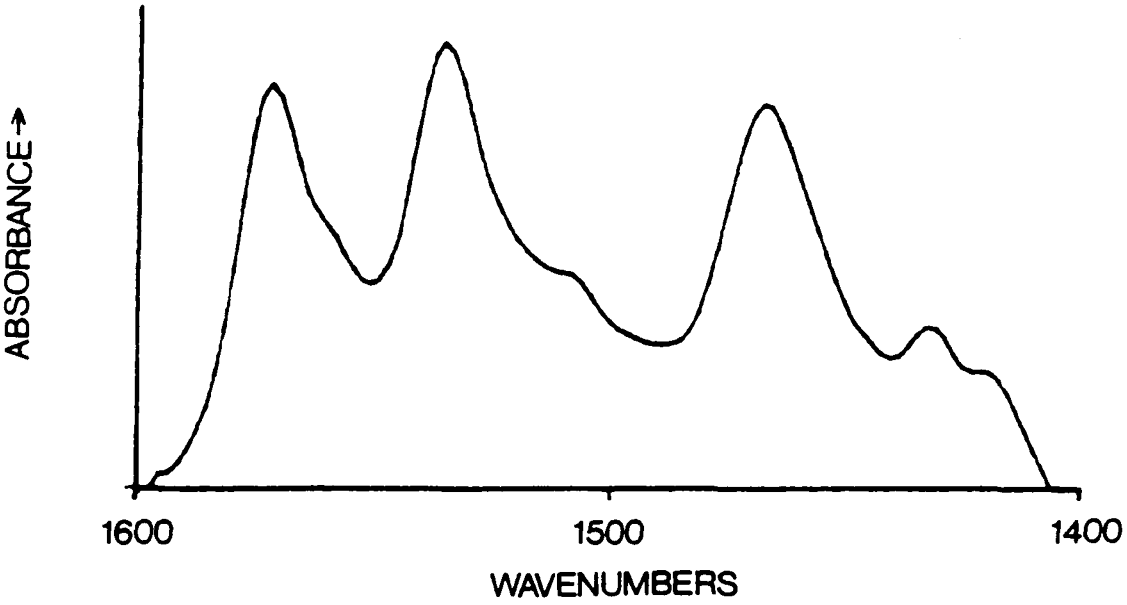

Figure 4. In-situ FTIR spectrum of oleate adsorbed at fluorite IRE.

Thermochemistry

From the previous research results presented in Figure 3, the adsorption free energy (ΔG_{ads}) of oleate at the fluorite/water interface can be evaluated using the adsorption density plateau level as a condition for surface saturation (Γ_m), according to the following equation:

$$\frac{\Gamma}{\Gamma_m - \Gamma} = \frac{C}{55.55} \exp(-\Delta G_{ads}/RT) \qquad (2)$$

where Γ is the adsorption density, C is the corresponding equilibrium concentration, T is absolute temperature, and R is the gas constant.

Knowing the adsorption free energies at two different temperatures, the isosteric heats of adsorption (ΔH) for oleate at the fluorite/water interface were estimated from the Clausius-Clapeyron equation for different oleate concentrations:

$$\frac{\Delta H}{R} = \frac{\Delta\left(\frac{\Delta G_{ads}}{T}\right)}{\Delta\left(\frac{1}{T}\right)} \qquad (3)$$

The estimated heat was 2.77 kcal/mole at lower oleate concentrations (Region 1) and -6.60 kcal/mole at higher oleate concentrations (Region 2). See Figure 3. This analysis indicates that the chemisorption of oleate at lower concentrations is endothermic, and that the surface precipitation of oleate at higher concentrations is exothermic. Direct microcalorimetric measurements were made to further substantiate this analysis.

The thermochemical measurements were accomplished with a microcalorimeter, Model 850 manufactured by TRONAC, Inc., Orem, Utah. Isoperibolic measurements which record the temperature change inside the reactor were used to determine the heat of adsorption of oleate monomers. After completing microcalorimetric measurements, the fluorite particles were immediately separated from the suspension for FTIR adsorption density measurements. It has been found that the FTIR absorbance band of 2927 cm^{-1} is linearly proportional to the weight percentage of calcium oleate. Such a linear relationship was used to determine the adsorption density of oleate at the fluorite surface.

By combining the experimental results of microcalorimetric measurements and FTIR adsorption density measurements, a relationship between the heat of adsorption and surface coverage was established. The measured heats of adsorption of oleate at the fluorite/water interface for chemisorption and surface precipitation are presented and compared to the isosteric heats of adsorption in Table 4. The microcalorimetric results included in this table confirm that the oleate chemisorption reaction is endothermic while the oleate surface precipitation reaction is exothermic. Also note that the heats of adsorption measured by microcalorimetry are in close agreement with the isosteric heats of adsorption calculated from adsorption isotherm data. These consistent heats of adsorption obtained from two different approaches substantiate our understanding about the complex adsorption reactions involved in the fluorite/oleate flotation system.

Furthermore, from the microcalorimetric and FTIR results, the packing area of oleate at the fluorite surface has been calculated to be 34.2 Å^2, which is consistent with the molecular area of oleate in the liquid crystal state (35 Å^2) determined by Cases et al.(9)

Table 4. Comparison of the Measured Heat of Adsorption of Oleate at the Fluorite/Water Interface with Isosteric Heats of Adsorption for Different Levels of Surface Coverage.

	Heats of Adsorption, kcal/mole of oleate	
	Measured by Microcalorimetry	Calculated from Adsorption Isotherm Data
Chemisorption (monolayer coverage)	2.36	2.77
Surface Precipitation (above monolayer coverage)	-5.31*	-6.60

*at oleate surface coverage $\theta = 1.59$

Microcalorimetric experiments were also undertaken to determine the heats of interaction of adsorbed oleate monomers. These results seem to show that these reactions are not greatly exothermic or endothermic, and the heat produced is less than the detection limits of the equipment.

Research in Progress -- Orientation

Are collector molecules horizontally oriented with their carbon chain backbone parallel to the mineral surface, or is this backbone vertically oriented, perpendicular to the surface? This question is of fundamental importance in flotation, flocculation, and other areas of surface chemistry. With the aid of a single-diamond Brewster's Angle polarizer, in-situ FTIR spectroscopic analysis of orientation of oleate monomers at the surface of the fluorite IRE is under study.

The Brewster's Angle polarizer allows infrared light to be resolved into parallel (ll) or perpendicularly (⊥) polarized components. Parallel polarized light has electric field components in the x and z spatial directions. Perpendicularly polarized light has an electric field component in the y direction. The electric fields in these three spatial directions across a thin film of adsorbed collector on an IRE are easily calculated and equations for this purpose are given below:

$$E_y = \frac{2 \cos \theta}{[1 - n_{31}^2]^{1/2}} \tag{4}$$

$$E_x = \frac{2 (\cos \theta) [\sin^2 \theta \; n_{31}^2]^{1/2}}{(1 - n_{31}^2)^{1/2}[(1 + n_{31}^2) \sin^2 \theta - n_{31}^2]^{1/2}} \tag{5}$$

$$E_z = \frac{2(\cos \theta \sin \theta) \, n_{32}^2}{(1 - n_{31}^2)^{1/2} [(1 + n_{31}^2) \sin^2 \theta - n_{31}^2]^{1/2}} \tag{6}$$

where θ = incident angle of light (degrees)

n_{31} = refractive index of solvent/refractive index of IRE

n_{32} = refractive index of film/refractive index of IRE

Haller and Rice(10) used these equations to find the orientation of a stearic acid monolayer deposited on sapphire, Al_2O_3. They showed that if the hydrocarbon chains are normal to the IRE, the E_z component will not interact with the $-CH_2$ stretching vibrations, since these vibrations would not have a component in the z direction. Also, since infrared absorbance, A, is proportional to the square of the electric field, two limiting cases can be found. One is for completely random hydrocarbon chain orientation and the other is for perfect vertical orientation (i.e., normal to the IRE):

random orientation $$\frac{A_\perp}{A_\parallel} = \frac{E_y^2}{E_x^2 + E_z^2} \qquad (7)$$

perfect vertical orientation $$\frac{A_\perp}{A_\parallel} = \frac{E_y^2}{E_x^2} \qquad (8)$$

Equations (7) and (8) are significant in that they give the criterion to quantitatively determine the orientation of adsorbed collectors on IRE substrates.

Research in Progress -- Double-Bond Reactivity

Of primary importance in this research program is the increased hydrophobicity exhibited by fluorite and other nonsulfide minerals with oleate as collector at higher temperatures and/or oxygen potentials. The increase in hydrophobicity is demonstrated by a decrease in attachment time and an increase in contact angle with high temperature or high oxygen potential. See Table 1. As shown in Figure 3, the adsorption density of oleate is not greatly influenced by high temperatures, and therefore increased loading of oleate is not the reason for the increased hydrophobicity. Previous work has shown for ex-situ spectroscopic methods that the double bond of the adsorbed oleate monomer ruptures and that polymerization occurs. One means of quantifying this reaction is to plot the ratio of the absorbance of the asymmetric $-CH_2$ stretch peak (2925 cm^{-1}) to that of the -CH stretch peak (3005 cm^{-1}) adjacent to the C=C double bond. As shown in Figure 5, for ex-situ transmission measurements, this ratio does indeed decrease with an increase in temperature, indicating polymerization of oleate monomers. Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements were performed to substantiate earlier transmission findings. Shown in Figure 5 is the Kubelka-Munk functions for the ratio $=CH/-CH_2$ of adsorbed oleate on fluorite powder as found by the ex-situ DRIFT technique.

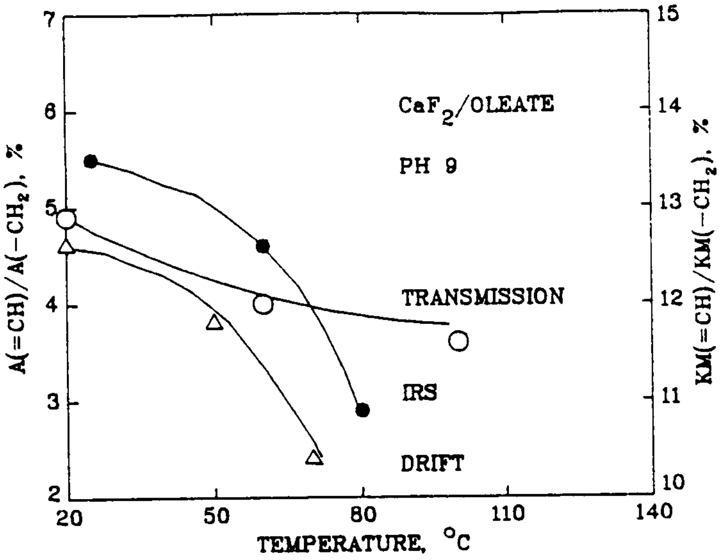

Figure 5. Comparison of the decrease in the relative double-bond intensity with increase in temperature, using transmission (9.9×10^{-5} M oleate), DRIFT (1×10^{-4} M oleate), and IRS (4.4×10^{-5} M oleate).

To provide further evidence and to establish the relevancy of the prior ex-situ measurements, it was critical that in-situ measurements be developed to investigate the double-bond reactivity of adsorbed oleate. Also shown in Figure 5 are preliminary in-situ results that support earlier transmission and DRIFT experiments. However, unlike the earlier ex-situ measurements, the in-situ measurements indicate that the decrease in the ratio A-CH$_2$/A=CH is reversible. In other words, the apparent polymerization of oleate monomers seems to reverse itself upon temperature cycling. Such behavior is very interesting and is presently being investigated further.

The ultimate intent of the research program is to prompt double-bond reactivity of unsaturated collectors such as oleate by the use of catalysts or inorganic compounds. Several compounds will be used in these in-situ spectroscopic measurements. The most promising results from these studies will then be further investigated in batch flotation systems involving semisoluble minerals. These results along with previous spectroscopic results already discussed will be presented at the 1989 AIME meeting in the paper entitled "In-

Situ Internal Reflection Analysis of the Polymerization of Adsorbed Oleate Monomers at a Fluorite Surface."

In summary, current research involves this extremely sensitive internal reflection FTIR spectroscopic technique, which yields in-situ quantitative surface chemistry detail of the adsorption density, kinetics, and orientation at surfactant concentrations never before attained by other analytical methods.

OTHER NONSULFIDE SYSTEMS

Electrochemistry of Lanthanum Fluoride/Oleate

Previously, it had been shown that the hydrophobic character of fluorite with adsorbed oleate could be significantly enhanced by increasing the temperature and/or oxygen potential. This increase in hydrophobicity has been attributed to reaction between adjacent double bonds of the chemisorbed calcium oleate monomer. Lanthanum fluoride exhibits a hexagonal crystal structure with planes of fluoride ions separated by LaF_2^+ planes. Both of these planes are oriented perpendicular to the c-axis. Since the fluoride ion planes are located at the terminus of the unit cell, it is expected that the surface of the lanthanum fluoride electrode will be composed of fluoride ions similar to the surface of fluorite.

Experiments were conducted to determine the effects of increasing the temperature or applying a potential bias on the hydrophobic character of lanthanum fluoride electrodes in aqueous sodium oleate solutions. For 1×10^{-5} M sodium oleate solutions, increasing the temperature or applying an anodic potential bias for thirty minutes led to a significant increase in the contact angle of the lanthanum fluoride electrode surface. Applying a cathodic bias did not increase the contact angle. These results are shown in Table 5.

Table 5. Effect of Potential Bias on the Contact Angle at a Lanthanum Fluoride Electrode Surface in 1×10^{-5} M Sodium Oleate Solution at pH 9.4, Reaction Time 30 Minutes.

Potential Bias (mV)	Contact Angles (degrees)	Charge Passed (coul/cm^2)
(rest potential)	62	--
100 cathodic	63	5.77×10^{-6}
80 anodic	85	2.73×10^{-6}
150 anodic	80	3.18×10^{-6}
180 anodic	81	1.71×10^{-5}
300 anodic	86	2.46×10^{-5}

Anodic potential biases applied for less than thirty minutes exhibited an interesting pattern of behavior. The contact angle increased with the amount of time the bias was applied until approximately 3×10^{-6} coul/cm^2 of charge were passed. After this amount of charge was passed, no further increase in the contact angle was observed. Table 6 shows this data, and these findings suggest that the reaction of adsorbed olefinic monomers can be stimulated by the application of oxidizing electrochemical biases and by increasing the temperature. The details of this work have been reported in "The Effect of Potential Bias on the Hydrophobic Character of Lanthanum Fluoride Electrodes in Oleate

Table 6. Effect of Anodic Polarization Time on the Contact Angle at a Lanthanum Fluoride Electrode Surface in 1×10^{-5} M Sodium Oleate Solution at pH 9.4, Anodic Potential Bias 120-150 mV.

Time (sec)	Charge Passed (coul/cm^2)	Contact Angle (degrees)
0	--	62
75	1.61×10^{-6}	73
300	2.95×10^{-6}	81
1800	3.18×10^{-6}	80

Solutions" which is to be published in The Proceedings of an International Symposium on Electrochemistry in Minerals and Metals Processing II, the Electrochemical Society, Pennington, New Jersey, 1988.

Calcium Phosphate Minerals/Oleate

During this grant period, the oleate flotation properties of the calcium phosphate minerals collophanite, fluorapatite, chlorapatite, and hydroxyapatite were investigated. Figure 6 shows the flotation response of some of the calcium phosphate minerals as a function of oleate concentration. Fluorapatite is the most readily floated calcium phosphate mineral, while chlorapatite and collophanite are the most difficult to float. In this regard, collophanite was selected for study in greater detail.

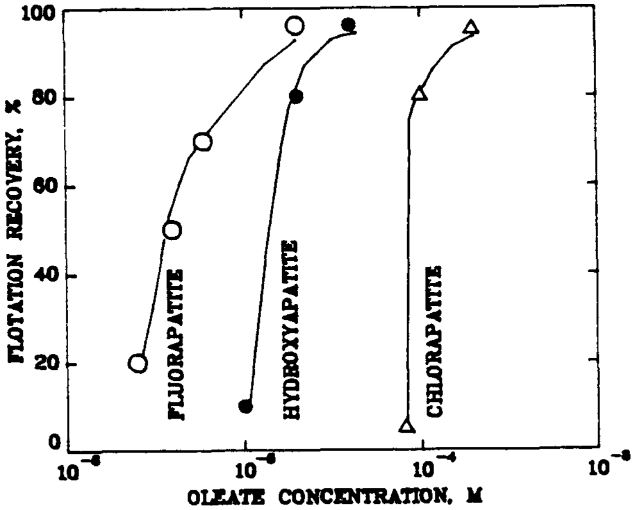

Figure 6. Flotation of natural apatites as a function of oleate concentration at pH 9.0.

Fluoridation of many apatite minerals has been studied extensively and is well documented in the literature.(11,12) However, such a reaction has not been studied for collophanite. It was found that complete flotation of collophanite could be obtained at a moderate oleate concentration (7×10^{-5} M) with sodium fluoride addition as low as 1×10^{-3} M, if the conditioning time was approximately 200 hours. Increasing the sodium fluoride concentration to $1\text{x}10^{-2}$ M decreased the conditioning time necessary for complete flotation to approximately 20 hours. Further increase in the sodium fluoride concentration to $1\text{x}10^{-1}$ M yielded a conditioning time necessary for complete flotation of only fifteen minutes. In the absence of sodium fluoride, flotation of collophanite did not occur with $7\text{x}10^{-5}$ M sodium oleate. Figure 7 contains these results.

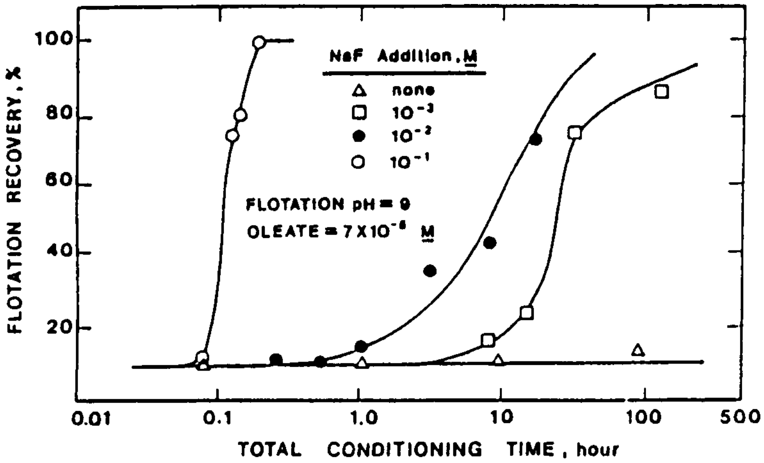

Figure 7. Effect of NaF concentration on collophanite flotation as a function of conditioning time.

Increasing the temperature of the aqueous collophanite/oleate mixture exhibited different behavior in the presence and absence of sodium fluoride. In the absence of sodium fluoride, increasing the temperature of the system only slightly increased the collophanite flotation recovery, while, with sodium fluoride present, an increase in temperature significantly enhanced the flotation recovery of collophanite to such an extent that complete recovery of collophanite was achieved. These results are shown in Figure 8. The beneficial effects of fluoridation appear to stem from substitution of lattice anions by fluoride ions.

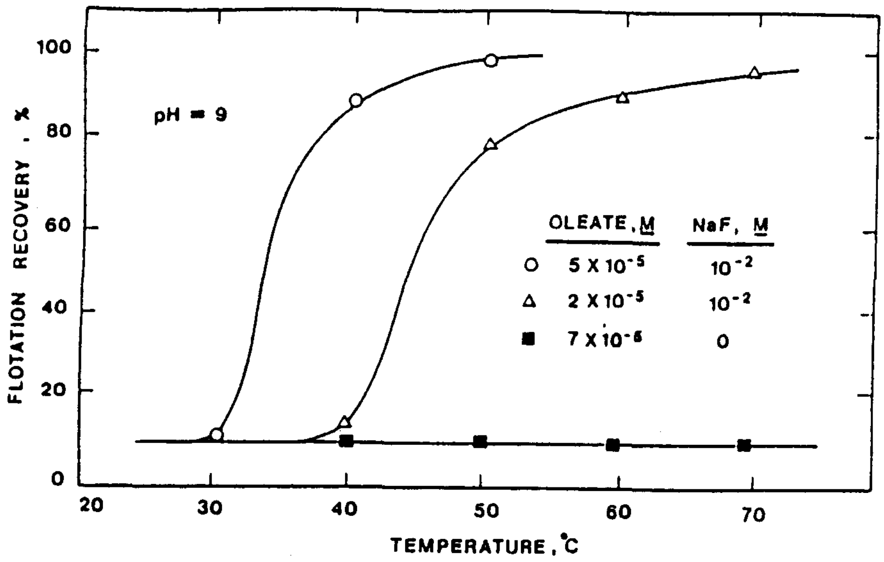

Figure 8. Fluoridation effect on collophanite flotation as a function of temperature.

At low fluoride ion concentrations, this substitution is a fluoride ion replacing the nonphosphate lattice anion, i.e., hydroxyl ions in hydroxyapatite or chloride ions in chlorapatite. For these fluoride levels, the degree of substitution is primarily determined by the relative difference in the ionic radii. Thus the hydroxyapatite lattice will accept more fluoride substitution than the chlorapatite lattice since the radius of the fluoride ion is much closer in size to the radius of the hydroxyl ion than it is to the radius of the chloride ion.

At higher fluoride ion concentrations, the substitution reaction that occurs is the substitution of fluoride ions for lattice phosphate ions. This substitution reaction leads to the formation of fluorite at the apatite surface. In this region, the ability to form fluorite at the surface seems to be governed by the solubility of the apatite form. Thus carbonate apatite will adsorb more fluoride ions than hydroxyapatite which adsorbs more fluoride ions than chlorapatite. This point of CaF_2 precipitation occurs at a fluoride addition of $8x10^{-3}$ M for collophanite and probably accounts for the temperature sensitivity of collophanite flotation with 1×10^{-2} M sodium fluoride. See Figure 8. If the mineral surface is given sufficient time to form fluorite, the flotation characteristics of collophanite become similar to those of fluorite.

FTIR spectroscopy was used to examine the surface of collophanite following treatment with fluoride ions. Figure 9 shows a baseline corrected spectrum of collophanite between 2000 and 600 cm^{-1}. In this region, collophanite displays two major phosphate peaks at 1040 and 1090 cm^{-1} and carbonate peaks at 778, 800, 1430, and 1458 cm^{-1}. Since the area under a peak is related to the concentration of that species, the loss of phosphate by the surface during fluoridation was followed by integrating the area under the phosphate peaks at 1040 and 1090 cm^{-1}. Table 7 shows the effect of various fluoride conditioning techniques on this integrated area.

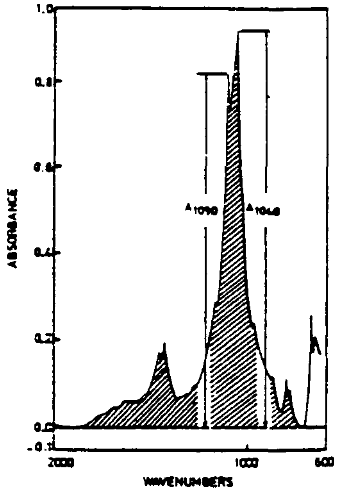

Figure 9. FTIR transmission spectrum of collophanite in the region 2000-600 cm^{-1} after baseline correction.

Table 7. Reduction of Phosphate Absorbance Intensity Observed for Fluoridated Collophanite at Various pH Values, Fluoride Concentrations (Conc.), and Fluoridation-Conditioning Times (Time).

Conditions					
pH	Conc. (M)	Time (hr)	A_{1040}	A_{1090}	Integrated Area
Blank			1.271	1.127	237.8
6	10^{-3}	1	0.875	0.971	216.2
6	10^{-3}	10	0.780	0.889	200.8
6	10^{-3}	16	0.715	0.799	132.6
6	10^{-3}	1	0.875	0.971	216.2
6	10^{-2}	1	0.752	0.862	194.5
6	10^{-1}	1	0.769	0.805	193.6
9	10^{-1}	13	1.045	0.801	199.5
5	10^{-1}	13	0.560	0.452	134.9

As can be seen, all treatments lead to a decrease in the amount of phosphate in the collophanite. One interesting effect observed is that decreasing the solution pH during mixing increases the ability of the collophanite to adsorb fluoride and release phosphate. Flotation experiments also exhibit this trend, as Figure 10 shows. With 4×10^{-5} M sodium oleate, 1×10^{-1} M sodium fluoride, and 1×10^{-1} M sodium chloride, decreasing the pH increased the recovery of collophanite from 42.5% at pH 11.2 to 100% at pH 4.85.

Since fluoride additions depress the oleate flotation of calcite and dolomite, it appears possible to selectively float phosphate minerals from calcareous ores by the use of fluoridation techniques. Details of this work are given in "Fluoride Activation in Oleate Flotation of Collophanite," published in the August 1987 issue of Minerals and Metallurgical Processing.

Rare-Earth Phosphate Minerals/Oleate

In these experiments, the hydrophobic character of the rare-earth phosphate minerals monazite (Ce,La,Nd(PO_4)) and xenotime (YPO_4) was studied

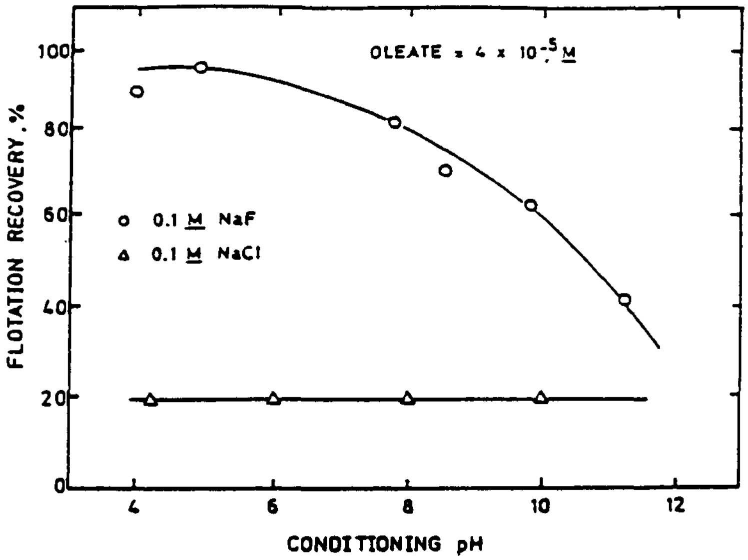

Figure 10. Effect of fluoridation pH and ionic strength on collophanite flotation.

through bubble attachment time measurements. The bubble attachment times were measured with an induction timer apparatus designed by Virginia Coal and Mineral Services, Blacksburg, Virginia. Figure 11 shows a typical plot of percent attachment versus contact time. The percent attachment is determined by recording the number of times in ten trials at each contact time that at least

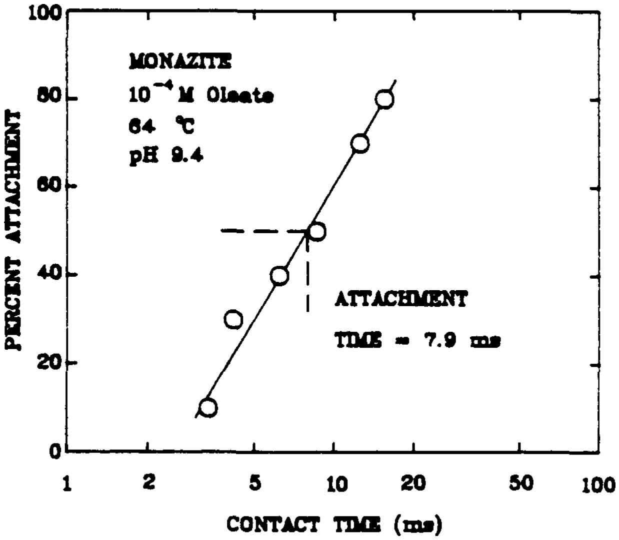

Figure 11. Percentage of bubble attachments at a given contact time for monazite in 1×10^{-4} M oleate, conditioned at 64°C for forty minutes.

one mineral particle attached to the air bubble. The bubble attachment time for a particular set of conditions is defined from the contact time at which the least square line which best fits the data has a fifty percent attachment value.

For comparative purposes, initial experiments were conducted to determine the relative hydrophobicities of the rare-earth phosphates, monazite and xenotime, and the calcium phosphates, fluorapatite and collophanite. As Table 8 shows, fluorapatite has a considerably smaller attachment time than any of the other minerals studied and thus has the most hydrophobic surface in 1×10^{-5} M oleate solutions. Xenotime was the next most hydrophobic, followed by monazite and collophanite, respectively.

Table 8. Bubble Attachment Times for Selected Phosphate Minerals in 1×10^{-5} M Oleate Solutions.

Mineral	Attachment Time (ms)
Fluoroapatite, $Ca_5F(PO_4)_3$	4.9
Xenotime, YPO_4	13.9
Monazite, $(Ce,La,Nd)PO_4$	18.9
Collophanite, $Ca_5HCO_3(PO_4)_3$	26.2

For monazite and xenotime bubble attachment time measurements, the first variable studied was oleate concentration. Raising the oleate concentration from 1×10^{-6} M to 1×10^{-5} M resulted in a slight decrease in the bubble attachment time for both monazite and xenotime. A further increase in the oleate concentration to 1×10^{-4} M resulted in a significant decrease in both of the rare-earth phosphate's attachment times as compared to their attachment times in 1×10^{-5} M oleate solutions. These results are shown in Table 9. This table also shows the effect of increasing the solution temperature on the bubble attachment times. Raising the temperature to 64°C causes a slight decrease in the attachment time of both monazite and xenotime at all oleate concentrations studied. This effect, however, is small and probably due to the increase in temperature rather than to oleate reaction. Increasing the temperature past 64°C did not significantly affect the bubble attachment time of either monazite or xenotime. These results seem to indicate that monazite and xenotime adsorb oleate from solution in a manner similar to fluorapatite, although exact details were not determined.

Table 9. The Effect of Oleate Concentration and Temperature on the Bubble Attachment Times for Rare-Earth Phosphate Minerals.

	Attachment Time (ms)			
	Xenotime		Monazite	
Oleate Concentration (M)	24°C	64°C	24°C	64°C
1×10^{-6}	15.9	14.0	22.3	21.2
1×10^{-5}	13.9	10.7	18.9	16.0
1×10^{-4}	3.4	1.5	11.2	7.9

Experiments were also conducted to determine the effects of sodium fluoride addition on the bubble attachment times for monazite and xenotime. Figure 12 shows the effect of sodium fluoride addition on the room temperature attachment times of the rare-earth phosphate minerals monazite and xenotime in 1×10^{-5} M oleate solutions at pH 9.4. As a general rule, the addition of sodium fluoride decreases the attachment time. However, this decrease is much greater at 1×10^{-1} M sodium fluoride than at any other fluoride level. This is most likely due to precipitation of rare-earth fluorides at the mineral surface similar to the surface fluoride precipitation discussed earlier for collophanite.

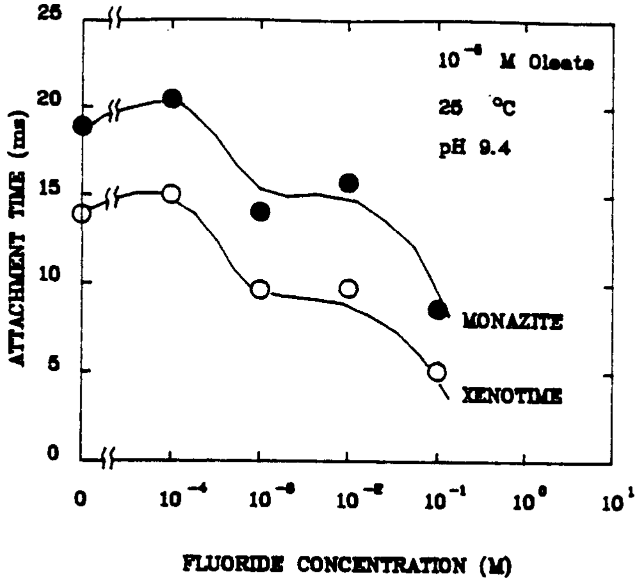

Figure 12. The effect of sodium fluoride addition on the bubble attachment times for xenotime and monazite in 1×10^{-5} M oleate solution.

Increasing the temperature of the solution when sodium fluoride was added at concentrations less than the presumed rare-earth fluoride precipitation point resulted in an increase in the attachment time of xenotime. However, when the fluoride concentration is high enough to cause surface precipitation, raising the solution temperature substantially decreases the bubble attachment time in 1×10^{-5} M oleate solution. Table 10 shows these results, which are again similar to the collophanite/oleate system.

Table 10. The Effect of Temperature on the Bubble Attachment Time for Xenotime at Different Fluoride Ion Concentrations with 1×10^{-5} M Oleate.

Fluoride Concentration (M)	Attachment Time (ms)	
	24°C	64°C
0	13.9	10.7
1×10^{-4}	15.4	20.5
1×10^{-2}	9.5	14.6
1×10^{-1}	5.3	2.5

Details of this work are given in "Bubble Attachment Time Measurements for Selected Rare-Earth Phosphates Minerals in Oleate Solutions," to be published in The Proceedings of the 1989 TMS/AIME Annual Meeting Symposium on Rare Earths, TMS/AIME, Las Vegas, Nevada, February 1989.

Alumina/Sodium Dodecyl Sulfate

To examine the efficacy of the in-situ infrared measurements demonstrated in the fluorite/oleate system, another model system, sapphire/sodium dodecyl sulfate (SDS), was chosen for investigation. As was the case for the fluorite/oleate system, D_2O was used as the solvent. A sapphire (Al_2O_3) single crystal was used as the IRE and SDS adsorption monitored in real-time. Table 11 shows the adsorption density measurements found at pH 7.5 and various SDS equilibrium concentrations using Equation (1). These results are quite interesting and agree reasonably well with measurements made by solution depletion experiments with powdered alumina of high specific surface area.(13)

Table 11. Adsorption Density of SDS by Al_2O_3 as Calculated from Internal Reflection Theory.

Equilibrium Concentration (M)	Adsorption Density (mol/cm^2)
4.8×10^{-5}	1.54×10^{-10}
1.18×10^{-3}	4.37×10^{-10}
3.85×10^{-3}	5.25×10^{-10}

Along with adsorption measurements, the orientation of SDS on Al_2O_3 was examined. Using parallel and perpendicular polarized light and the corresponding absorbance peak height ratios, one can deduce the orientation of adsorbed species as described earlier. See pp. 12-13. Table 12 lists these theoretical ratios based on the asymmetric $-CH_2$ peak at 2920 cm^{-1} as expected for SDS adsorbed with the hydrocarbon chain normal to the surface and as expected for random orientation. These values are 4.85 and 0.82, respectively. Also listed are the experimental values found at two equilibrium concentrations of SDS. At both values it appears that SDS is adsorbed in a nonordered fashion, although some ordering may be indicated by the slightly higher ratio of 1.42 at 1.0×10^{-3} M SDS. These results are exciting and provide insight into the fundamental processes involved in flotation and other surface chemistry-dominated processes. This work is detailed in "Quantitative In-Situ Analysis of Collector Adsorption Reactions by Internal Reflection FTIR Spectroscopy," to be published in Challenges in Mineral Processing, the Proceedings of the SME Topical Congress to be held at Berkeley, California, December 1988.

Table 12. Orientation of SDS on Al_2O_3 as Established by Absorbance Ratios According to Internal Reflection Theory. See Equations (7) and (8) on p. 13.

Vertical Orientation, $A_\perp/A_\parallel = 4.85$
Random Orientation, $A_\perp/A_\parallel = 0.82$

Equilibrium Concentration (M)	$A_\perp/A_\parallel$
2.0×10^{-6}	0.95
1.0×10^{-3}	1.42

Research in Progress

Current research in progress in this area includes in-situ FTIR spectroscopy measurements with a natural fluorapatite crystal as the internal reflection element. This represents a new dimension in flotation research and FTIR spectroscopy, since natural minerals have never before been used as internal reflection elements to study collector adsorption phenomena and interactions.

Another new dimension in flotation research is the advent of electrochemical techniques. It has already been shown that anodic potential biases induce a significant increase in the hydrophobicity of lanthanum fluoride electrodes in oleate solutions. Electrochemical potential control is acknowledged to be responsible for selective flotation of sulfide minerals. However, collector behavior under electrochemical control in nonsulfide systems has received little attention due to lack of good experimental methods. The advent of FTIR spectroscopy will allow the use of new spectroelectrochemical techniques for the study of surfaces. In-situ internal reflection spectroelectrochemistry is currently being used to study collector adsorption phenomena in the presence of an electric field. Internal reflection elements chosen for these experiments include germanium and titanium dioxide. Previous work in infrared spectroelectrochemistry has mainly focussed on single-bounce external reflection methods or on metal-coated internal reflection elements. Some research has been done using the internal reflection element as the working electrode, but these investigations have not examined surfactants used in flotation research.

FUTURE RESEARCH ACTIVITIES -- PROPOSAL RENEWAL

Excellent progress has been made in analyzing several nonsulfide/collector systems. The important features investigated include collector adsorption phenomena, most particularly orientation and kinetics. For many years, mineral collectors have been believed to adsorb at surfaces in an orientation normal to the mineral surface. The evidence for this behavior is mainly indirect, due to a lack of experimental techniques sophisticated enough to directly probe the mineral/collector interface. Research performed at the University of Utah during the period of this grant has shown that internal reflection FTIR spectroscopy is capable of non-intrusive, real-time quantitative examination of all aspects of mineral/collector adsorption phenomena. This technique has only recently been developed to a significant level of confidence, but important discoveries have already begun. Preliminary results for the model system alumina/SDS indicate that vertical orientation of adsorbed collector species is not particularly significant. A systematic study of the effect of process variables on adsorbed collector molecules is to be undertaken. This study will include the effects of temperature, oxygen potential, catalysts, and prior reagent addition on the kinetics and orientation of adsorbed collector monomers. Also, further investigations into natural mineral systems using internal reflection techniques will be engendered. These investigations will center on the near-IR region (12,500-4000 cm^{-1}) since many nonsulfide minerals do not absorb these wavelengths of light.

Another area of research which deserves further study and will be pursued is the effect of electrochemical treatment on nonsulfide mineral/collector systems. The electrochemical aspects of sulfide mineral flotation have been known for years; however, electrochemical phenomena in nonsulfide mineral flotation have not been extensively studied. It has already been shown that the application of an anodic potential bias to a doped lanthanum fluoride single-crystal electrode significantly enhances the hydrophobicities of these electrodes in oleate solutions.

The processes responsible for this increase in hydrophobic character need to be investigated. Studies are to be undertaken using the previously discussed internal reflection techniques in conjunction with electrochemical analysis to examine the behavior of adsorbed collector molecules. The internal reflection methods developed will be used to probe the adsorbed collector molecule's orientation, adsorption and interaction, before, during, and after electrochemical control is initiated. Aside from the ionic conductor lanthanum fluoride, these spectroelectrochemical experiments will be extended to semiconducting single-crystal internal reflecting elements such as TiO_2, MgO, and Ge. Especially significant among these semiconducting IREs is TiO_2, because of its strategic importance.

Internal reflection spectroelectrochemistry has been used for a very few systems. For nonsulfide mineral flotation systems it is ideal, in that the tradeoffs necessary for internal reflection spectroelectrochemistry are not critical, and excellent results should be obtainable.

A detailed study of the effect of isomerism, degree of unsaturation, hydrocarbon chain length, and polar head group of unsaturated collectors has never been performed. For instance, does elaidic acid, the cis-isomer of oleic acid, exhibit the same polymerization phenomena as oleic acid? Unsaturated collectors almost exclusively use carboxylate head groups. An interesting possibility is the use of unsaturated phosphonic acids as collectors in phosphate mineral systems.

Previous work done under the auspices of this grant has shown that it is possible to significantly enhance the flotation characteristics of collophanite and the hydrophobic character of lanthanum fluoride, monazite, and xenotime surfaces in oleate solutions. Also, application of in-situ FTIR techniques to flotation chemistry investigations has exhibited great promise for elucidating the features of collector adsorption and interaction which are of critical importance in the flotation process. In view of the significance of these findings, a renewal proposal has been submitted to the Office of Basic Energy Science, DOE, to extend this research program an additional three years.

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APPENDIX

Presentations and Publications

As a result of the research progress during this grant period, the following presentations and papers have been accomplished:

"In-Situ FTIR Spectroscopy Measurements of Adsorbed Oleate Species at the Fluorite Surface by DRIFT and ATR Techniques," Kellar, J. J., Hu, J. S., and Miller, J. D., presented at the SME/AIME Annual Meeting, Denver, Colorado, March 1986.

"Fluorite Activation in Oleate Flotation of Collophanite," Miller, J. D., Misra, M., Yehia, A., and Hu, J. S., Minerals and Metallurgical Processing, SME/AIME, pp. 133-139, August 1987.

"The Significance of Electrochemistry in the Analysis of Mineral Processing Phenomena," Miller, J. D., by invitation of the RACI, in: Electrochemistry: Current and Potential Applications, Proceedings of the Seventh Australian Electrochemistry Conference, eds. T. Tran and M. Skyllas-Kazacos, Royal Australian Chemical Institute, University of New South Wales, Sydney, February 1988.

"The Effect of Potential Bias on the Hydrophobic Character of Lanthanum Fluoride Electrodes in Oleate Solutions," Cross, W. M., Wan, R., and Miller, J. D. in: Electrochemistry in Minerals and Metals Processing II, Proceedings of the 173rd Electrochemical Society Meeting, eds. P. Richardson and R. Woods, Pennington, New Jersey, 1988.

"Comparison of FTIR Techniques for the Analysis of Surfaces in Mineral Flotation Systems," Kellar, J. J. and Miller, J. D., presented at the 62nd Colloid and Surface Science Symposium, Pennsylvania State University, June 1988.

"Quantitative In-Situ Analysis of Collector Adsorption Reactions by Internal Reflection FTIR Spectroscopy," Miller, J. D. and Kellar, J. J., by invitation and to be published in: Challenges in Mineral Processing, SME/AIME Topical Conference, Berkeley, California, December 1988.

"Thermochemistry of Oleate Adsorption at Fluorite/Water Interface," Hu, J. S., Jin, R., and Miller, J. D. to be published in Colloids and Surfaces, 1988.

"Bubble Attachment Time Measurements for Selected Rare-Earth Phosphate Minerals in Oleate Solutions," Cross, W. M. and Miller, J. D., by invitation, and to be published in: Rare Earths, Proceedings of a Symposium on Rare Earths, 1989 TMS/AIME Annual Meeting, Las Vegas, Nevada, February 1989.

"In-Situ Internal Reflection Study of the Polymerization of Adsorbed Oleate Monomers at a Fluorite Surface," Kellar, J. J. and Miller, J. D. 1989 Annual SME/AIME Meeting, Las Vegas, Nevada, February 1989.