# Fluoride activation in oleate flotation of collophanite

**J.D. Miller, M. Misra, A. Yehia, and J.S. Hu**

**Abstract** – *Fluoride activation has been evaluated by Hallimond tube flotation of collophanite in terms of fluoride concentration, conditioning time, pH, and temperature. The results reveal that efficient oleate flotation of collophanite can be achieved by fluoride activation. Experimental results of fluoride adsorption by collophanite suggest that, at low fluoride concentration, a fluoroapatite-type compound may form on the collophanite surface by chemisorption of fluoride ions at calcium sites. At high fluoride concentration, calcium fluoride appears to form at the collophanite surface involving a surface precipitation phenomenon. The formation of* $CaF_2$ *on the surface of fluoride-treated collophanite is further substantiated by the FTIR spectroscopic measurements, which suggest a metathetic exchange with phosphate from the collophanite lattice during the surface precipitation process.*

## Introduction

Collophanite, a cryptocrystalline carbonate apatite, is a major mineral constituent of phosphate rock, an important worldwide commodity for the production of fertilizer. US resources of phosphate rock, which amount to billions of tons, are ample to supply domestic needs for centuries (Stowasser, 1983). A critical part of phosphate rock processing is the separation of the phosphate minerals — mainly collophanite in the US — from sand, clay, and/or calcareous minerals by froth flotation. Of all US mineral commodities concentrated by flotation, phosphate rock has the largest operating plant capacity.

Over the years, considerable effort has been made to improve the strategy for phosphate flotation. Nevertheless, process engineers still rely on a complex flotation technique that traditionally has been used for the beneficiation of phosphate. Conventional flotation practice for siliceous phosphate ores requires desliming, conditioning at 70% to 75% solids, with the addition of oil to complement the fatty acid collector. Furthermore, the fatty acid flotation concentrate often has to be deoiled at low pH and high percent solids and then subjected to cationic flotation to remove entrained siliceous gangue (Lawver, McClintok, and Snow, 1978). One major process inefficiency is that, in many instances, 27% to 30% of the deslimed phosphate rock is discarded as a dilute waste slime (Lawver, Snow, and Clingan, 1979; Jordan et al., 1982). The $P_2O_5$ content of the slime depends on the matrix being processed but usually contains 6% to 17% $P_2O_5$. Some of the earlier discarded slimes from high-grade deposits contain an even higher content of $P_2O_5$. Each year, large quantities of these slimes are discarded, amounting to several million tons of 31% $P_2O_5$ material (Jordan et al., 1982; USBM, 1975).

---

**J.D. Miller**, member SME, **M. Misra**, **A. Yehia**, and **J.S. Hu**, member SME, are with the Department of Metallurgy and Metallurgical Engineering, University of Utah, Salt Lake City, UT. SME preprint 86-378, SME Fall Meeting, St. Louis, MO, September 1986. MMP paper 86-666. Manuscript September 1986. Discussion of this paper must be submitted, in duplicate, prior to Oct. 31, 1987.

For high carbonate ores, several processing strategies have been developed. The techniques generally involve the flotation of dolomite or phosphate minerals from the ore, depending on the reagent used. In one case, dolomite is floated from the phosphate minerals using an anionic collector for calcareous minerals and a depressant for the phosphate minerals (Lawver et al., 1982, 1983; Houot, 1982; Rule et al.; Snow, 1982; Hsieh et al., 1985; Smani et al., 1975). Most of the processes are similar in principle. Reagent demand and the extent of recovery limit the effectiveness of flotation for the separation of calcareous ores, although recent developments suggest that very efficient separations can be made.

From the previous discussion, it can be realized that the flotation processes to recover collophanite either from the siliceous slimes or from calcareous rock need to be improved. During the past 20 years, innovations and improvements have been made in the beneficiation of phosphate ore, but few innovations have considered an activation technique to enhance the flotation response of phosphate minerals such as collophanite.

In this study, fluoride activation in the oleate flotation of collophanite has been evaluated by Hallimond tube flotation experiments in terms of fluoride concentration, conditioning time, pH, and temperature. Using an ion selective electrode, quantitative determination of fluoride uptake was carried out over a wide range of fluoride concentrations and solution pH values. The surface compounds formed during the fluoride activation process were studied using an FTIR spectroscopic technique. Finally, the mechanism of fluoride activation in the oleate flotation of collophanite is discussed.

## Experimental procedure

### *Materials*

Mineral samples of collophanite (Conda, ID), hydroxyapatite (Holly Springs, GA), and chloroapatite (Snarum, Norway) were obtained through Ward's Natural Science Establishment. The materials were dry ground in stages to $-150$ μm ($-100$ mesh) with an alumina mortar and pestle. The size fraction of $150 \times 106$ μm ($100 \times 150$ mesh), separated by wet screening, was used for flotation experiments, and the $-106$-μm ($-150$-mesh) size fraction was used for the fluoride uptake measurements. Oleic acid of 99% and NaF of 99.98% purity were supplied by Alfa Products. IR-grade KBr was obtained from Fisher Scientific Co. Synthetic apatite minerals were prepared by precipitation as described in well established procedures (Soleimani, 1978).

### *Hallimond tube flotation*

Two grams of collophanite ($150 \times 106$ μm, or $100 \times 150$ mesh) were first conditioned either in water or NaF solution at the desired pH for a specific time. An oleate solution was then added to the suspension and reconditioned for another five minutes. The total volume of oleate solution was 150 mL. A flotation time of two minutes was used at a nitrogen flow rate of 45 cc per minute. The pH was measured after each experiment.

### *Fluoride uptake*

Three grams of collophanite (specific surface area = 4.501 $m^2/g$) were added to 25 mL of $2 \times 10^{-1}$ $\underline{M}$ $KNO_3$ solution. After one hour's equilibration, 25 mL of NaF solution of known fluoride ion concentration was then added to bring the total solution volume to 50 mL. The suspension was filtered after conditioning for another three hours, and the equilibrium fluoride ion concentration in the filtrate was determined using a fluoride ion-selective electrode. The fluoride uptake was determined by the difference between the initial concentration of the fluoride and the residual concentration of fluoride in the solution.

### *Solubility*

A 2-g sample of calcium fluoride was conditioned in 50 mL $H_2O$ at pH 6 for 12 hours. The suspension was filtered, and the $Ca^{+2}$ concentration in the filtrate was determined by direct-coupled plasma (DCP) spectroscopy, while the fluoride concentration was measured with a fluoride ion-selective electrode.

### *FTIR spectroscopy*

A 2-g sample of collophanite was conditioned in NaF solution of known concentration at the desired pH for a specific period of time. The suspension was filtered, and the collophanite was dried at 60°C (140°F) under atmospheric conditions.

KBr disks were prepared using the following sequence of steps. First, 300 mg of mixture (sample and KBr) at a desired proportion, typically 1%, was mixed for five minutes in a stainless steel vial on a Wig-L-Bug mixer. Second, a 150-mg portion of the mixture was weighed carefully and transferred to a die. Finally, the die was evacuated for five minutes with no load; then a load of 138 MPa (20,000 psi) was imposed for five minutes. The pressure usually dropped to 124 MPa (18,000 psi) after five minutes, so the pressure was raised to 138 MPa (20,000 psi) for an additional minute. This pressing technique resulted in disks of about 1.2 cm in diameter and 0.12 cm in thickness. The pressed sample served as a window during FTIR experiments.

Infrared spectra were recorded by a Digilab FTS-40 Fourier Transform Infrared Spectrometer at 4 $cm^{-1}$ resolution. A germanium-coated KBr beam splitter and a liquid nitrogen-cooled Hg-Cd-Te detector were used. Each sample was scanned 64 times.

## Results and discussion

### *Hallimond tube flotation*

Fluoride activation in oleate flotation of collophanite was studied by Hallimond tube flotation experiments as a function of fluoride concentration, conditioning time, pH, and temperature. As shown in Fig. 1, it is evident that flotation of collophanite can be achieved at a rather modest oleate addition ($7 \times 10^{-5}$ $\underline{M}$) with fluoride activation. In the absence of sodium fluoride, flotation does not occur at this collector concentration.

The effect of activator concentration as a function of conditioning time is given in Fig. 2. It is apparent that with an NaF addition of $10^{-1}$ $\underline{M}$, complete flotation can be achieved after 15 minutes of conditioning. Although the flotation speed decreases with a decrease in NaF addition, complete flotation with sodium fluoride is still possible even at low NaF addition ($10^{-3}$ $\underline{M}$) if sufficient conditioning time is provided. In the absence of NaF, however, the recoveries of collophanite are always less than 20% even after lengthy conditioning. These results demonstrate the significant effect of fluoride activation.

The recovery of collophanite is presented in Fig. 3 as a function of pH. It is interesting to note that the recovery increases with a decrease in pH, resulting in a recovery of 95% at pH 5. Under similar conditions, it has been found in our laboratory (Yehia, 1986) that without fluoride addition, the flotation of collophanite can only be achieved in a very narrow pH range around pH 9, and the maximum recovery does not exceed 60%. These phenomena indicate that fluoride activation not only enhances the recovery of collophanite but also greatly extends the flotation pH to the acidic region. The same experiments were performed by using NaCl instead of NaF (also shown in Fig. 3). Recoveries less than 25% at all pH values eliminate the possibility that the higher recoveries by fluoride activation result from an increase in ionic strength.

It is well established that fluorite has a greater intrinsic flotation response than other semisoluble salt minerals (Hanna and Somasundaran, 1978; Sorensen, 1973). The foregoing experimental results imply that, under certain circumstances, fluorite may form at the collophanite surface, thus accounting for the improved flotation response. Studies on the effect of temperature on collophanite flotation seem to support this implication. Figure 4 shows that when the mineral was conditioned in NaF solution ($10^{-2}$ M) at the desired temperature for one hour, the fluoridated collophanite is very sensitive to temperature and shows a sharp increase in flotation recovery with an increase of temperature. On the other hand, in the absence of NaF, there is no temperature effect on flotation recovery, even at higher oleate concentration ($7 \times 10^{-5}$ M).

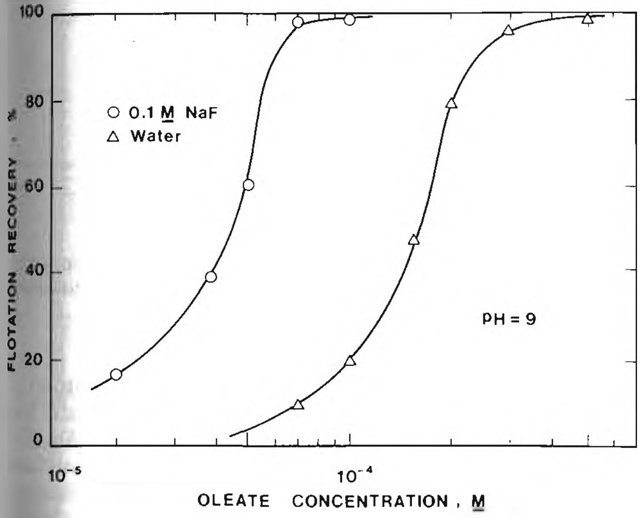

Fig. 1 — Effect of sodium fluoride on the recovery of collophanite. The fluoridation-conditioning time is five minutes.

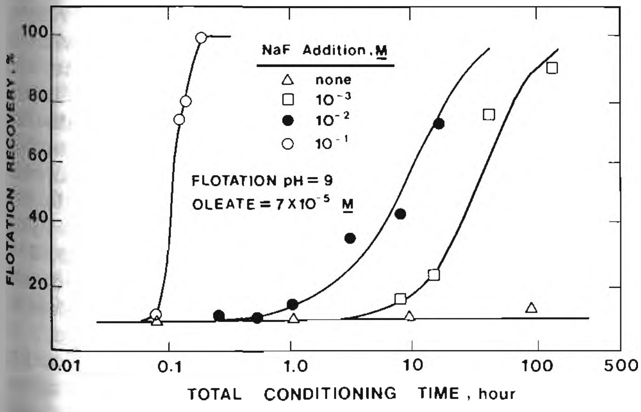

Fig. 2 — Effect of conditioning time on the recovery of collophanite at four fluoride addition levels

It is well known that improved oleate flotation of fluorite can be achieved at elevated temperatures (Richards and Locke, 1925; Cook and Last, 1950; Miller et al., 1984; Miller and Misra, 1985; Hu, Misra, and Miller, 1986, 1986a). Therefore, these flotation results give further evidence for calcium fluoride formation at the surface of collophanite, a phenomenon that has been reported by other investigators for synthetic hydroxyapatite (McCann, 1953; Leach, 1959; Somasundaran and Wang, 1982).

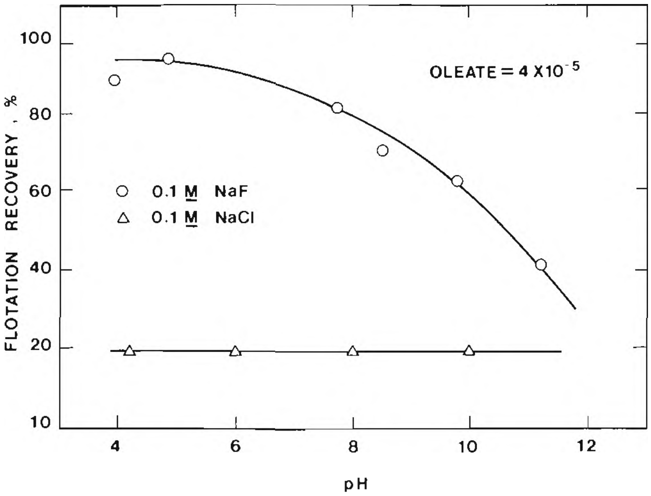

Fig. 3 — Comparison of the effect of sodium fluoride and sodium chloride on the recovery of collophanite at different pH values. The fluoridation-conditioning time is five minutes.

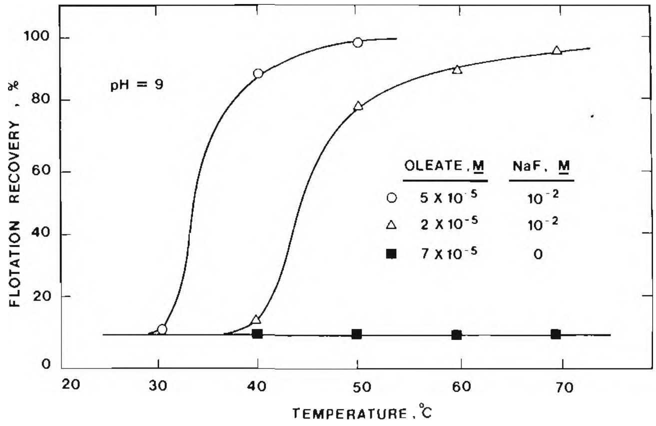

Fig. 4 — Effect of sodium fluoride on the recovery of collophanite measured at various temperatures. The fluoridation-conditioning time is one hour.

In a set of flotation experiments, collophanite was added to NaF solution. In this case (Fig. 5), complete flotation is achieved after 10 minutes of conditioning. However, in another set of experiments, when NaF is added to the collophanite suspension, complete flotation can be attained only after eight hours of conditioning. These results indicate that fluoride adsorbs on the mineral surface when collophanite is added to an NaF solution and that this reaction is rapid. On the other hand, when NaF is added to the collophanite suspension, $F^-$ ion may first react with the aqueous $Ca^{+2}$ ion. Then the precipitated $CaF_2$ slowly readsorbs or redistributes itself on the collophanite surface. In either case, these results show that fluoride addition has a significant effect on activation and flotation of collophanite.

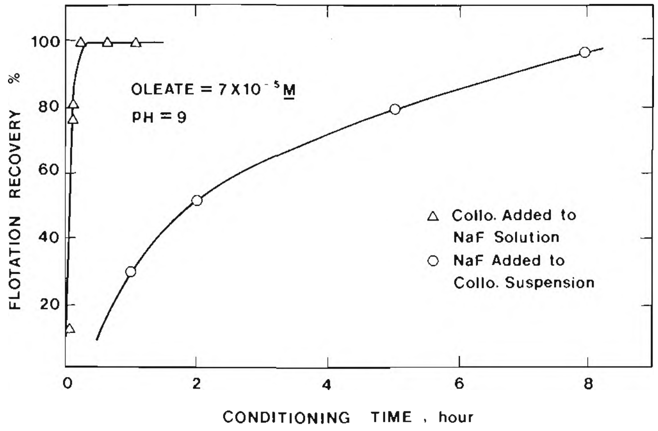

Fig. 5 — Effect of conditioning time on the recovery of collophanite for two flotation procedures

### *Fluoride uptake*

To investigate the mechanism of fluoride activation, fluoride uptake by collophanite was measured by an ion-selective fluoride electrode in terms of fluoride concentration, temperature, pH, and crystal structure. The fluoride uptake in presented in Fig. 6 as a function of residual fluoride concentration measured at three temperatures and pH 6. It is interesting to note that all three isotherms demonstrate two distinct regions and that a critical fluoride concentration, $8 \times 10^{-3}$ M, can be detected that is reported (Lin, Raghavan, and Fuerstenau, 1981; Chander and Fuerstenau, 1982) to correspond to the concentration required to initiate the bulk precipitation of calcium fluoride. When the fluoride concentration is lower than $8 \times 10^{-3}$ M (region I), the uptake of fluoride increases with an increase of temperature, and the extrapolations into region II level off at a plateau equivalent to an uptake of $8.5 \times 10^{-10}$ mole/cm². When the fluoride concentration is higher than $8 \times 10^{-3}$ M (region II), the fluoride uptake still follows the same order, i.e., increasing with an increase of temperature until the fluoride concentration reaches $4 \times 10^{-2}$ M. However, the effect of temperature is weakened. When fluoride concentration is higher than $4 \times 10^{-2}$ M, the lowest adsorption occurs at the highest temperature, 80°C (176°F).

Collophanite crystals belong to the hexagonal system. The hexagonal unit cell is of the type $P6_3|m$ with the dimensions a = b = 9.34 Å and c = 6.88 Å. It has been reported that the [10$\bar{1}$0] plane contributed most of the available surface area of the solid, and an average of 3.3 calcium atoms and two phosphorus atoms share the [10$\bar{1}$0] surface (Smith, Posner, and Quirk, 1972, 1974). Accordingly, the density of calcium on the collophanite surface is found to be $8.5 \times 10^{-10}$ mole/cm², which is identical to the value of fluoride uptake corresponding to the plateau (Fig. 6). Therefore, it can be concluded that, in region I (equilibrium fluoride concentration less than $8 \times 10^{-3}$ M), the adsorbed fluoride ions are localized on the calcium atoms at the 10$\bar{1}$0 surface of collophanite as a result of a surface chemisorption reaction. Using the adsorption density plateau level as a condition for surface saturation ($\Gamma_m$), the adsorption free energy ($\Delta G_{ads}$) can be evaluated from the adsorption density ($\Gamma$) and the corresponding equilibrium concentration (C, in M),

$$\frac{\Gamma}{\Gamma_m - \Gamma} = \frac{C}{55.55} \exp\left(-\Delta G_{ads}/RT\right). \quad (1)$$

Under these circumstances, the adsorption free energies at 20°, 50°, and 80°C (68°, 122°, and 176°F) were found to be −5.3, −6.2, and −7.1 kcal/mole for a fluoride uptake of 0.076 mg/m² (Yehia, 1986). Knowing the adsorption free energies at three different temperatures, the isosteric enthalpy of adsorption ΔH was estimated to be 3.7 kcal/mole by the Clausius-Clapeyron equation,

$$\Delta H = \left| \frac{d\left(\frac{\Delta G_{ads}}{T}\right)}{d\left(\frac{1}{T}\right)} \right|_{\Gamma} . \quad (2)$$

From these considerations, it is evident that an endothermic chemisorption reaction occurs in region I.

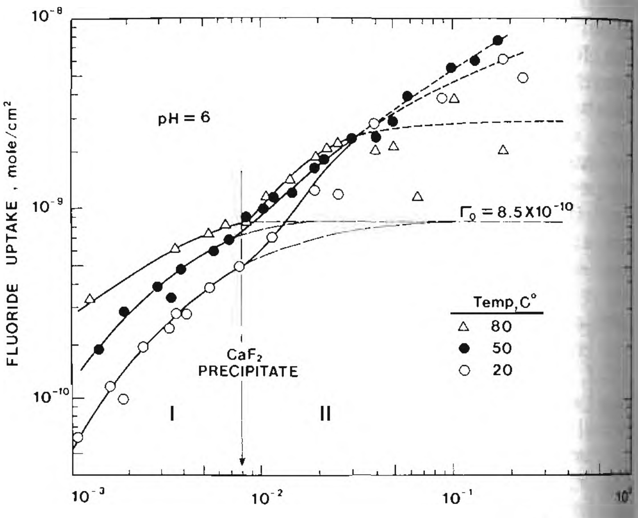

Fig. 6 — Adsorption isotherms of fluoride by collophanite measured at three temperatures. The fluoridation-conditioning time is one hour.

Referring to Fig. 6, the fluoride uptake in region II follows the same order as that of region I until the fluoride concentration reaches $4 \times 10^{-2}$ M. As discussed earlier, it is believed that, in region II, surface precipitation contributes to the adsorption phenomena. From solubility product determinations of calcium fluoride (Table 1), it is found that, as the temperature increases, the solubility of the calcium fluoride increases slightly. These results suggest that the surface precipitation reaction should be exothermic with a slight decrease in adsorption density at higher temperatures. A combination of the heat contribution from the chemisorption reaction, which is endothermic, and the heat contribution from the surface precipitation reaction, which is slightly exothermic, maintains an overall endothermic heat of adsorption for fluoride concentrations less than $4 \times 10^{-2}$ M. When the fluoride concentration is higher than $4 \times 10^{-2}$ M, despite the scatter in data, a decrease of fluoride uptake with temperature is obvious if the results at 20° and 80°C (68° and 176°F) are considered. These results indicate an exothermic heat of adsorption that might be expected from the solubility product measurements.

To probe the essence of the fluoride activation phenomena, fluoride uptakes were measured under the same conditions for three different synthetic apatite minerals: hydroxyapatite (OHA), carbonate apatite (CO3A), and chloroapatite (ClA). As shown

Fig. 7, it is apparent that in region I the fluoride uptakes are in the order OHA > CO3A > ClA. The ionic radii of $OH^-$ and $Cl^-$ ions are reported to be 1.40 Å and 1.80 Å, respectively (Bell, Posner, and Quirk, 1973). The ionic radius of $CO_3^{-3}$ was estimated to be 1.66 Å by the XIRIS computer-aided molecular modeling system. These radii are all larger than the ionic radius of $F^-$ (1.36 Å) and increase in the order of $OH^- < CO_3^= < Cl^-$. It is evident that the closer the anion size to the size of the fluoride ion, the higher the adsorption or exchange with fluoride. Therefore, these phenomena indicate that in region I, the fluoride uptake may involve a surface substitution reaction, with the crystal structure being the controlling factor.

Table 1 — Solubility Products ($K_{sp}$) for Calcium Fluoride at Three Temperatures and pH 6. Fluoride ion concentration measured by a selective electrode; calcium ion concentration measured by DCP.

Fluorite/Water = 2 g/50 mL
Conditioning Time = 12 hrs

| Temperature (°C) | Concentration of $Ca^{++}$ ($\underline{M}$) | Concentration of $F^-$ ($\underline{M}$) | $K_{sp}$ |
|---|---|---|---|
| 20 | $1.26 \times 10^{-4}$ | $2.96 \times 10^{-4}$ | $1.10 \times 10^{-11}$ |
| 50 | $1.22 \times 10^{-4}$ | $3.29 \times 10^{-4}$ | $1.32 \times 10^{-11}$ |
| 80 | $1.26 \times 10^{-4}$ | $3.56 \times 10^{-4}$ | $1.61 \times 10^{-11}$ |

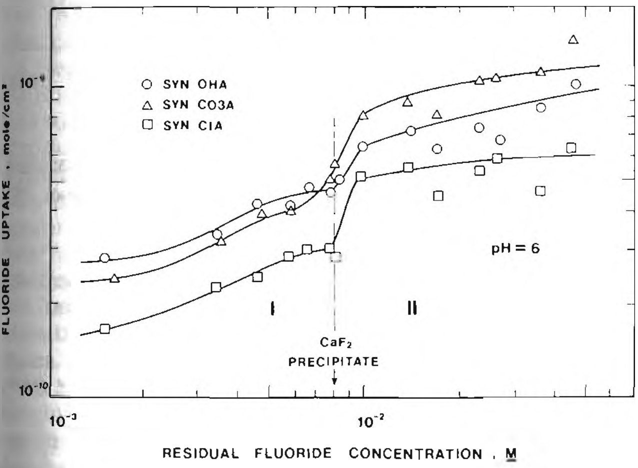

Fig. 7 — Adsorption isotherms of fluoride by three synthetic apatites: hydroxyapatite, carbonate apatite, and chloroapatite. The fluoridation-conditioning time is one hour.

In region II, however, the fluoride uptake demonstrates a different order, i.e., CO3A > OHA > ClA. These results can be explained in terms of the solubilities of various apatites given in Table 2 (Yehia, Misra, and Miller, 1984). The solubilities of these apatites follow the same order as the capacity for fluoride adsorption, CO3A > OHA > ClA. For example, OHA has fluoride adsorption twice as high as ClA, and the solubility is almost twice as great. These results support the hypothesis that when the fluoride concentration is higher than $8 \times 10^{-3}$ $\underline{M}$, the precipitation reaction of $CaF_2$ is predominant, and more fluoride will be taken up if more calcium is available.

Turning attention again to collophanite, the uptake of fluoride ions by collophanite is illustrated in Fig. 8 as a function of pH. Two features are evident. First, for all three fluoride concentrations, the fluoride uptake increases with a decrease of pH value. Second, for a fluoride concentration of $5.6 \times 10^{-2}$ $\underline{M}$ (curve I), the effect of pH is very strong, showing a 10-fold increase in fluoride adsorption when the pH value drops from pH 10 to pH 4. As mentioned before, when the fluoride concentration is higher than $8 \times 10^{-3}$ $\underline{M}$, a surface precipitation reaction occurs. The reactions can be represented by equations (3) and (4):

$$Ca_{10}(PO_4)_6CO_3 + xH^+ = Ca^{++} + yH_2CO_3 + z\,\text{Phosphate} \qquad (3)$$

$$Ca^{++} + 2F^- = CaF_2 \qquad (4)$$

where "phosphate" can be $H_2PO_4^-$, $HPO_4^=$, $CaHPO_4$, or $CaPO_4^-$, depending on pH and calcium concentration. In any case, the equilibria indicate that the $Ca^{++}$ concentration will increase with an increase of $H^+$ concentration. As a result, the precipitation reaction will be promoted at lower pH values.

On the other hand, when the fluoride concentration is less than $8 \times 10^{-3}$ $\underline{M}$ (curves II and III), the effect of pH is relatively weak. At low fluoride concentration, fluoridation is mainly due to the surface chemisorption. Therefore, the reduction in fluoride uptake at high pH values may be caused by electrostatic repulsive forces arising from the negative surface charge (IEPs = pH 4-5) and competition between fluoride and hydroxyl ions as shown below:

$$Ca_{10}(PO_4)_6CO_3 + 2F^- = Ca_{10}(PO_4)_6F_2 + CO_3^= \qquad (5)$$

$$Ca_{10}(PO_4)_6CO_3 + 2OH^- = Ca_{10}(PO_4)_6(OH)_2 + CO_3^= \qquad (6)$$

Table 2 — Concentrations of Calcium Released by a Variety of Synthetic Apatites After One Hour of Conditioning in Water at pH 10 (Yehia, Misra, and Miller, 1984)

Solid/Liquid = 0.5 g/100 mL

| Mineral | Concentration of Calcium, ppm |
|---|---|
| Chloroapatite (ClA) | 0.46 |
| Hydroxyapatite (OHA) | 0.78 |
| Carbonate Apatite ($CO_3A$) | 0.80 |
| Fluoroapatite (FA) | 1.67 |

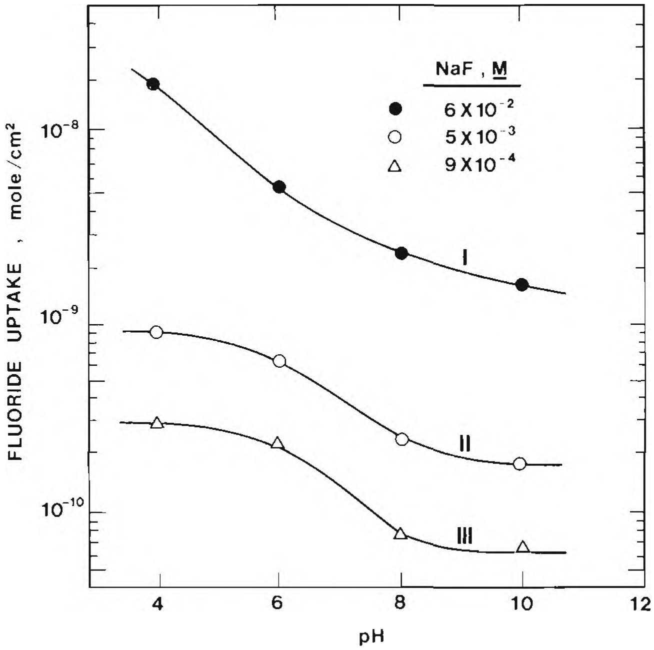

Fig. 8 — Effect of pH value on the uptake of fluoride by collophanite measured at three fluoride addition levels

## *FTIR spectroscopy*

An FTIR spectroscopic technique was used to study the chemical nature of the reaction products from fluoridation. Figure 9 shows the control spectrum of collophanite. Strong infrared absorption between 950 and 1150 $cm^{-1}$ is resolved into two bands at about 1090 $cm^{-1}$ and 1040 $cm^{-1}$, which are assigned to the ionic phosphate vibration and ionic P-O stretching, respectively (Corbridge and Lowe, 1954). The broad band around 3200 and 3600 $cm^{-1}$ is assigned to the symmetric and asymmetric stretching vibrations of water, modified by strong hydrogen bonding. Two pairs of split bands are related to asymmetric-stretching (1430 to 1460 $cm^{-1}$) and planar-bonding (710 to 800 $cm^{-1}$) frequencies of $CO_3^{-2}$ groups in the crystal (Huang and Kerr, 1960; Aaler and Kerr, 1963).

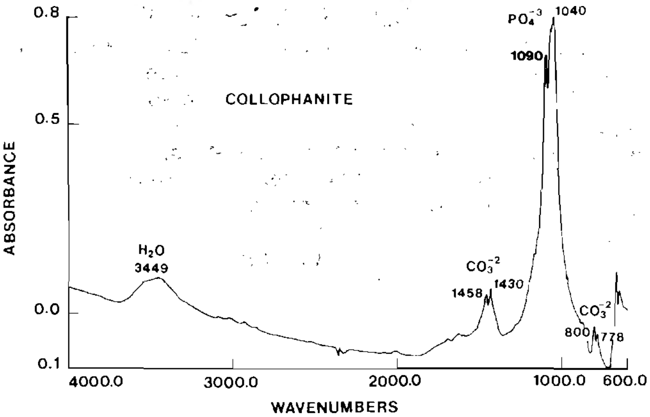

Fig. 9 — FTIR spectrum of collophanite

After baseline correction, the spectrum of collophanite is shown in Fig. 10 between 2000 and 600 $cm^{-1}$. Three measurements related to the phosphate radical, $PO_4^{-3}$, characterize adsorption or surface reaction phenomena:

- $A_{1090}$ — the absorbance at 1090 $cm^{-1}$ measured from the baseline,
- $A_{1040}$ — the absorbance at 1040 $cm^{-1}$ measured from the baseline, and
- Integrated area — the area enclosed by the spectrum and the baseline.

The infrared absorption intensities of phosphate are listed in Table 3 as a function of fluoridation time, fluoride concentration, and pH. It can be seen that the three infrared absorption measurements of phosphate in collophanite all indicate a decrease in phosphate with an increase in fluoridation time, fluoride concentration, and pH.

Table 3 — Reduction of Phosphate Absorbance Intensity Observed for Fluoridated Collophanite at Various pH Values, Fluoride Concentrations, and Fluoridation-Conditioning Times

| 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 | 182.6 |
| 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 | 0.802 | 199.5 |
| 5 | $10^{-1}$ | 13 | 0.560 | 0.452 | 134.9 |

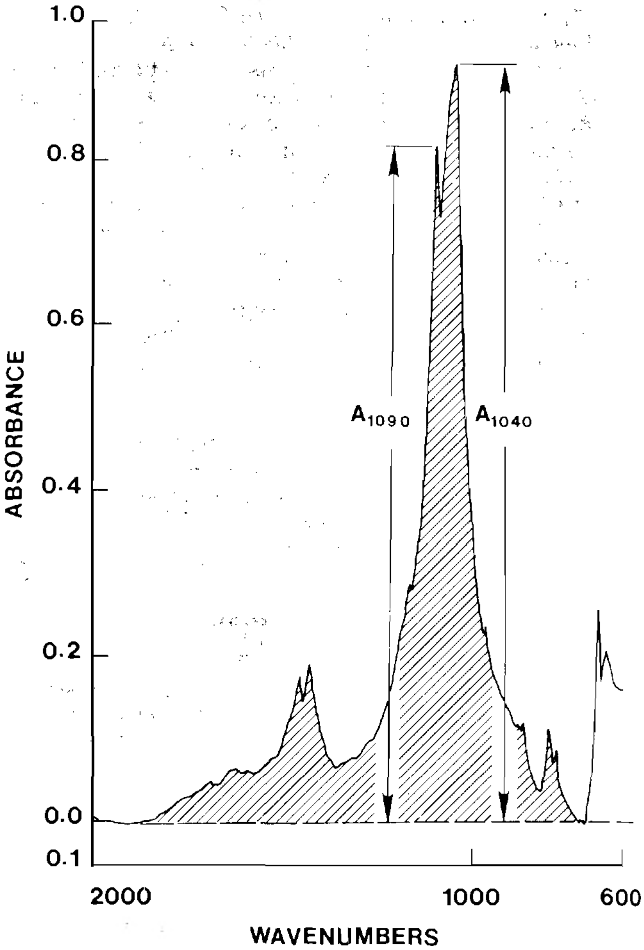

Fig. 10 — Three characteristic features from the baseline-corrected FTIR spectra of collophanite ($A_{1090}$, $A_{1040}$, and integrated area) between 2000 and 600 $cm^{-1}$

Coupling the FTIR spectroscopic measurements with the results from Hallimond tube flotation and fluoride uptake measurements, it can be seen that as more fluoride is taken up by collophanite, more phosphate is released, resulting in formation of $CaF_2$ at the surface. Under these circumstances, a higher recovery of collophanite will be achieved in oleate flotation. Similar phenomena were observed for mineral and synthetic apatites (Table 4). In summary, the results of FTIR spectroscopic measurements indicate that the removal of phosphate from the collophanite surface occurs during fluoridation with the formation of calcium fluoride at the collophanite surface. Such a phenomenon has been reported for synthetic hydroxyapatite by using X-ray photoelectron spectroscopy (XPS) (Chander and Fuerstenau, 1984) and using electron spectroscopy for chemical analysis (ESCA) (Lin, Raghavan, and Fuerstenau, 1981).

## Summary

Fluoride activation for oleate flotation of collophanite has been evaluated by Hallimond tube flotation experiments as a function of fluoride concentration, conditioning time, pH, and temperature. The results reveal that more efficient oleate flotation of collophanite can be achieved by fluoride activation:

- Complete flotation of collophanite can be obtained at a rather modest oleate addition ($7 \times 10^{-5}$ $\underline{M}$) with fluoride activation. In the absence of sodium fluoride, flotation does not occur at this collector concentration.

Table 4 — Reduction of Phosphate Absorbance Intensity Observed After Fluoridation for Various Mineral and Synthetic Apatites at pH 6

Fluoridation-conditioning time = 13 hrs
Fluoride concentration = $10^{-1}$ $\underline{M}$

| Material | Fluoridation | $A_{1040}$ | $A_{1090}$ | Integrated Area |
|---|---|---|---|---|
| SYN OHA | no | 1.343 | 0.988 | 145.5 |
| | yes | 1.555 | 0.896 | 134.8 |
| SYN CO3A | no | 1.438 | 1.624 | 241.4 |
| | yes | 1.352 | 1.391 | 209.6 |
| MIN CIA | no | 1.181 | 1.953 | 279.8 |
| | yes | 0.870 | 0.615 | 170.6 |
| MIN OHA | no | 1.576 | 0.853 | 240.4 |
| | yes | 1.035 | 0.537 | 140.8 |

- Activation and complete flotation with sodium fluoride is possible even at low fluoride concentration if sufficient conditioning time is provided.
- The fact that recovery of collophanite increases with a decrease in pH indicates that fluoride activation not only enhances the recovery of collophanite but also greatly extends the flotation pH to the acidic region.
- After fluoride activation, collophanite flotation is very sensitive to temperature, showing a sharp increase in flotation recovery with an increase in temperature.

To investigate the mechanism of fluoride activation, fluoride adsorption by collophanite was measured by a fluoride ion-selective electrode as a function of fluoride concentration, temperature, pH, and crystal structure. Two regions of adsorption can be identified from the adsorption isotherms.

- Region I — chemisorption. In this region, when the fluoride concentration is lower than $8 \times 10^{-3}$ $\underline{M}$, a fluoroapatite-type compound may form on the surface of collophanite by chemisorption of fluoride at calcium surface sites. The adsorption is endothermic in nature, showing an increase in fluoride adsorption with temperature. The nature of this chemisorption reaction is determined by the ionic radii of the phosphate mineral substrate and surface charge.
- Region II — surface precipitation. In this region, when the fluoride concentration is higher than $8 \times 10^{-3}$ $\underline{M}$, calcium fluoride forms at the surface of collophanite by a surface precipitation process. This adsorption reaction is exothermic in nature, showing a slight decrease in fluoride uptake with an increase in temperature. The formation of $CaF_2$ on the surface of fluoride-treated collophanite is substantiated by the FTIR spectroscopic measurements, which clearly show the removal of phosphate during surface precipitation.

Finally, it has been found that fluoride ion does not activate calcite and dolomite in oleate flotation. On the contrary, in the presence of fluoride, a decrease in the flotation response of these minerals was observed. This intriguing phenomenon is not yet understood. However, it seems that selective flotation of phosphate minerals from calcareous rock can be accomplished by the fluoride activation technique. ■

## Acknowledgment

This research was supported by the Department of Energy, Grant No. DE-FG-02-84ER13181.

## References

Adler, H.H., and Kerr, P.F., 1963, "Infrared Absorption Frequency Trends for Anhydrous Normal Carbonates," *The American Mineralogist*, Vol. 48.

Bell, L.C., Posner, A.M., and Quirk, J.P., 1973, "The Point of Zero Charge of Hydroxapatite and Fluorapatite in Aqueous Solutions," *Journal of Colloid and Interface Science*, Vol. 42, No. 2, p. 250.

Chander, S., and Fuerstenau, D.W., 1982, "Solubility and Interfacial Properties of Hydroxyapatite — A Review," *Proceedings*, Symposium on Adsorption and Surface Chemistry of Hydroxyapatite, p. 29.

Chander, S., and Fuerstenau, D.W., 1984, "An XPS Study of the Fluoride Uptake of Hydroxyapatite," *Colloids and Surfaces*, Vol. 13, pp. 137-144.

Cook, M.A., and Last, A.W., 1950, "Theory of Oleic Acid Collector Action," Bulletin No. 47, Utah Engineering Experiment Station, Utah.

Corbridge, D.E.C., and Lowe, E.J., 1954, "Infrared Spectra of Inorganic Phosphorus Compounds, Part I and II," *Journal of Chem. Soc.*, pp. 493 and 4555.

Hanna, H.S., and Somasundaran, P., 1978, "Flotation of Salt-Type Minerals," *Flotation*, A.M. Gaudin Memorial Volume 1, M.C. Fuerstenau, ed., AIME, p. 197.

Houot, R., 1982, "Beneficiation of Phosphatic Ores through Flotation: Review of Industrial Applications and Potential Development," *International Journal of Mineral Processing*, Vol. 9, p. 353.

Hsieh, S.S., and Lehr, J.R., 1985, "Beneficiation of Dolomitic Idaho Phosphate Rock by the TVA Diphosphonic Acid Depressant Process," *Minerals & Metallurgical Processing*, Vol. 2, No. 1, pp. 10-13.

Hu, J.S., Misra, M., and Miller, J.D., 1986, "Effect of Temperature and Oxygen on the Adsorption of Fluorite," *International Journal of Mineral Processing*, Vol. 18, pp. 57-72.

Hu, J.S., Misra, M., and Miller, J.D., 1986a, "Characterization of Adsorbed Oleate Species at the Fluorite Surface by FTIR," *International Journal of Mineral Processing*, Vol. 18, pp. 73-84.

Huang, C.K., and Kerr, P.F., 1960, "Infrared Study of the Carbonate Minerals," *The American Mineralogist*, Vol. 45, pp. 311-324.

Jordan, G.E., et al., 1982, "Recovery of Phosphate from Florida Phosphate Operation Slimes," RI 8731, US Bureau of Mines.

Lawver, J.E., McClintok, W.O., and Snow, R.E., 1978, "Beneficiation of Phosphate Rock — A State of the Art Review," *Mineral Science Engineering*, Vol. 10, No. 4, October, p. 27.

Lawver, J.E., Snow, R.E., and Clingan, B.J., 1979, "A Computerized System for Using Response Surface Methodology to Evaluate Phosphate Flotation Variables," *Mining Engineering*, August, p. 1230.

Lawver, J.E., et al., 1982, "Beneficiation of Dolomite Florida Phosphate Reserves," 14th International Mineral Processing Congress, Toronto, Canada.

Lawver, J.E., et al., 1983, "Method of Beneficiation of Phosphate Ores Containing Dolomite," US Patent No. 4,372,843, February.

Leach, S.A., 1959, "Reaction of Fluoride with Powdered Enamel and Dentine," *Brit. Dent. S.*, Vol. 106, pp. 133-142.

Lin, J., Raghavan, S., and Fuerstenau, D.W., 1981, "The Adsorption of Fluoride Ion by Hydroxy Apatite from Aqueous Solution," *Colloids and Surfaces*, Vol. 3, p. 357.

McCann, H.G., 1953, "Reaction of Fluoride Ion with Hydroxyapatite," *Journal of Biol. Chem.*, Vol. 201, pp. 274-258.

Miller, J.D., Wadsworth, M.E., Misra, M., and Hu, J.S., 1984, "Flotation Chemistry of the Fluorite/Oleate System," *Principles of Mineral Flotation*, The Wark Symposium, Aust. Institute of Mining & Metallurgy, No. 40, pp. 31-42.

Miller, J.D., and Misra, M., 1985, "The Hydrophobic Character of Semi-Soluble Salt Minerals with Oleate as Collector," *Proceedings, Recent Advances in Mineral Science and Technology*, MINTEK 50.

Newesely, H., 1970, "Factor Controlling Apatite Crystallization with Particular Reference to the Effect of Fluoride with Accompanying Ions," *Advances in Oral Biology*, Vol. 4, P.H. Staple, ed., Academic Press, New York, NY.

Richards, R., and Locke, C.E., 1925, "Progress in Ore Dressing and Coal Washing in 1925," *Mineral Ind.*, Vol. 34, pp. 752-812.

Rule, A.R., et al., "Flotation of Carbonate Minerals from Unaltered Phosphate Ores of the Phosphoria Formation," RI 7864, US Bureau of Mines, p. 18.

Smani, M.S., et al., 1975, "Beneficiation of Sedimentary Moroccan Phosphate Ores," *Trans. SME-AIME*, Vol. 258, p. 168.

Smith, A.N., Posner, A.M., and Quirk, J.P., 1972, "Incongruent Dissolution and Surface Complexes of Hydroxyapatite," *Journal of Physical Chemistry*, Vol. 76, No. 6, pp. 900-904.

Smith, A.N., Posner, A.M., and Quirk, J.P., 1974, "Radioisotope Determination of the Surface Concentration of Calcium and Phosphorus on Hydroxyapatite in Aqueous Solution," *Journal of Colloid and Interface Science*, Vol. 48, No. 3, pp. 442-449.

Snow, R.E., 1982, "Flotation of Phosphate Ores Containing Dolomite," US Patent No. 4,364,824, December.

Soleimani, G.B., 1978, "Phosphate Mineralogy, with Particular Reference to Carbonate Substitution," PhD Thesis, University of Leeds, London.

Somasundaran, P., and Wang, Y.H.C., 1982, "Surface Chemical Characteristics and Adsorption Properties of Apatite," Symposium on Adsorption and Surface Chemistry of Hydroxyapatite.

Sorensen, E., 1973, "On the Adsorption of Some Anionic Collectors on Florida Minerals," *Journal of Colloid and Interface Science*, Vol. 45, No. 3, December, p. 601.

Stowasser, W.F., 1983, *Phosphate, Mineral Commodity Profile*, Vol. 18, US Bureau of Mines, p. 9.

US Bureau of Mines, 1975, "The Florida Phosphate Slime Problem: A Review and a Bibliography," IC 8668, p. 41.

Yehia, A., 1986, "The Surface Physico-Chemical Studies on the Flotation of Apatite Minerals," PhD Thesis, Cairo University.

Yehia, A., Misra, M., and Miller, J.D., 1984, "Flotation Chemistry of Synthetic Apatite Minerals with Oleate as Collector," presented at SME-AIME Annual Meeting, New York, NY, February 1985.