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Natural oleophilicity/hydrophobicity of sulphide minerals, II. Pyrite*

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ABSTRACT

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Oleophilicity/hydrophobicity of pyrite has been investigated by using two-liquid flotation and contact-angle measurements with and without the conditions of controlled electrochemical potential techniques. Unoxidised pyrite was oleophilic in a mineral/oil/water system but hydrophilic in a mineral/vapour/water system. The oleophilicity was Eh–pH dependent. In alkaline and neutral pH conditions it decreased with oxidation due to the formation of $Fe(OH)_2$ and $Fe(OH)_3$. However, in acidic solutions of $pH < 4$, the oleophilicity first increased with oxidation due to the formation of S^0, then decreased as the $Fe(OH)_3$ also formed on the surface.

INTRODUCTION

In the froth flotation technique, minerals are treated with the surface active collectors to make them adhere to the air bubbles. However, it is known that some minerals, such as molybdenite and graphite, can be floated without a collector.

One of the controversial issues of flotation chemistry, since the early days of this technique, has been whether sulphide minerals are naturally floatable (Ravitz and Porter, 1933; Lepetic, 1974; Trahar, 1983). However, one result reported by Wark and Cox (1934a,b) was interesting, in that sulphide minerals, galena, chalcopyrite and pyrite, although gave a 0° contact angle with gas bubbles, were oleophilic and gave contact angles of 55°, 90–90° and $75 \mp 5°$ with benzene drops, respectively.

A mineral/oil/water system differs from a mineral/vapour/water system. The absence of dispersion forces in vapour constrains the maximum contact

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angle to 120° in the later system, while it is 180° in the former system (Lucassen-Reynders and Lucassen, 1984). This means that larger contact angles will be obtained with the former system at the same degree of wettability by water. This could be useful for seeing small changes in the wettability of minerals.

In the first part of this work, it was reported that unoxidised galena was oleophilic (Kocabag et al., 1990). In this paper results with pyrite are reported. The oleophilic/hydrophobic nature of pyrite has been studied by using a two-liquid flotation method with a non-polar oil. Comparative contact-angle measurements were carried out with oil drops and nitrogen bubbles. A steady-state potentiostatic technique was used to control the redox potential of sulphide mineral electrodes and the change of wettability with potential has been determined by measuring the contact angles.

EXPERIMENTAL

High purity pyrite from Spain was used. XRF analyses showed the presence of 0.5–5% As and Cu, 0.05–0.5% Sb and $<0.05\%$ Ca, Ti and Zn as impurities. The mineral obtained as large pieces was broken down with a hammer and then with a laboratory jaw crusher. Appropriate sized pieces were hand-picked to make mineral electrodes and contact-angle measurements. The remainder was kept in plastic containers.

Two-liquid flotation tests, contact-angle measurements and the effect of redox potential on the wettability of pyrite were studied by using the same reagents, high-purity conductivity water, oxygen-free nitrogen, experimental techniques and equipments as described for galena in part I (Kocabag et al., 1990). Trimethyl pentane (iso-octane) was used as the organic phase. To control the pH, buffer electrolytes described in Table I were employed.

For two-liquid flotation tests, the following samples of pyrite were prepared daily by grinding 30 g of mineral in a stainless steel tema mill: (a) wet ground with deoxygenated water; the product was stored in deoxygenated water, un-

TABLE 1

The composition of buffer electrolytes

pH	Composition of electrolyte
1.0	0.1 M $HClO_4$
1.68	0.05 M $KH_3\ (C_2O_4)\ 2H_2O$
4.0	0.05 M $KHC_8O_4H_4$
6.89	0.025 M KH_2PO_4 + 0.025 M $Na_2\ HPO_4$
9.2	0.05 M $Na_3B_4O_7$
11.0	0.025 M $NaHCO_3$ + 0.023 M NaOH

der a nitrogen atmosphere and is referred to as "unoxidised"; (b) the same as (a) but the product was oxidised with 10% H_2O_2 solution; (c) dry ground. The particle size was about 75% $<20\,\mu$m.

RESULTS AND DISCUSSION

Two-liquid flotation

The recovery of pyrite at the oil/water interface is shown as a function of pH in Fig. 1. There is about 90% recovery of unoxidised pyrite between pH 6 and 9. At higher pH values the recovery decreases. The recovery of "unoxidised" pyrite went through a minimum at pH 4. The cause of this minimum was not understood. A similar minimum was obtained by Fuerstenau et al. (1968) between pH 4 and 5.5 in the flotation of pyrite with xanthate collectors. They found that the recovery was dependent on the ratio of ferrous and ferric ion concentrations in the solution and explained the results by invoking the formation of colloidal ferric hydroxide which adsorbed dixanthogen. The Eh–pH diagram of the Fe–S–H_2O system (Fig. 2) shows that oxidation of pyrite yields S^0, Fe^{2+}, $Fe(OH)_2^+$ in the solution, depending on pH, for pH$<$6. Although in the present work the oxygen content of the system was minimised, the depression of the two-liquid flotation of pyrite at pH 4 could be due to the adsorption of these hydroxy species on the surface of pyrite. At pH values <3 the recovery increases again as ferric hydroxide does not form. The

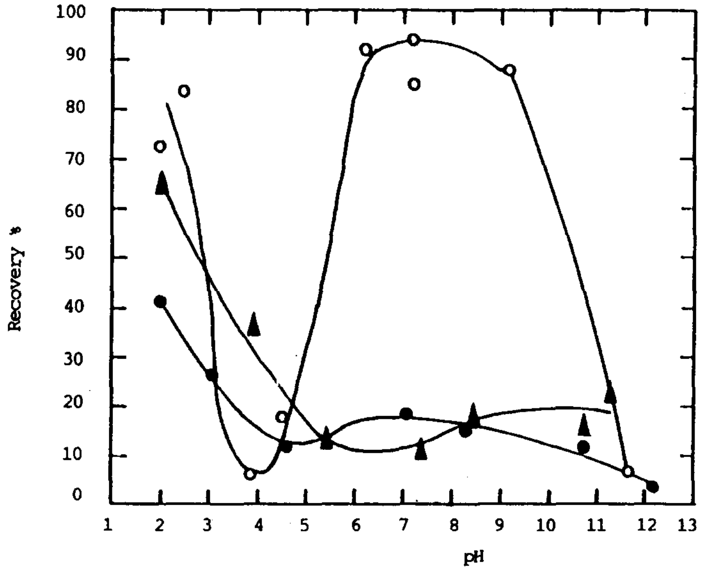

Fig. 1. The recovery, at the oil/water interface, of pyrite samples subject to different pretreatments: ○ = unoxidised; ● = oxidised with H_2O_2; ▲ = dry ground.

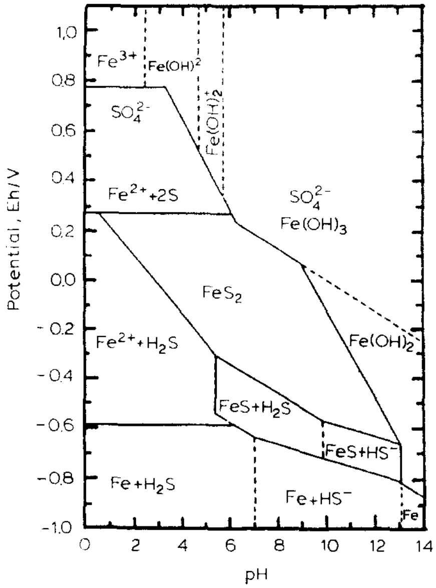

Fig. 2. Eh–pH diagram of the Fe–S–H_2O system at 298 K and 10^{-5} *M* (Kocabag, 1983).

decrease in the recovery of pyrite above 9.5 is due to the formation of $Fe(OH)_2$ on pyrite, as $Fe(OH)_2$ is the thermodynamically favoured oxide species in equilibrium with pyrite.

The recovery of pyrite is substantially decreased by oxidation. In acid media the results with oxidised pyrite are similar to those of oxidised galena reported elsewhere (Kocabag et al., 1990). However, in alkaline solutions there was no increase in recovery as observed with galena. At low pH elemental sulphur or/and dissolution of iron hydroxides from the mineral surfaces could be responsible for the increase in the recovery.

One could suspect that if the mineral particles were coagulated, the coagulates would entrap oil drops and the particles would be carried by the oil drops without actually attaching to them. However, in the pH range 5.5–9.5, where maximum recovery of pyrite was obtained independent of sample preparation, all of the pyrite suspension was reasonably stable (see Fig. 3). The dry-ground pyrite differed from unoxidised and H_2O_2-oxidised pyrite in acid solutions, as its stability decreased with decreasing pH, whereas the stability of unoxidised and oxidised samples increased slightly. The difference might be due to the presence of sulphur on the surface of dry-ground pyrite or to the physical adsorption of oxygen as suggested by Plaksin (1960) and Lepetic (1974). Pyrite surfaces produced by dry grinding were given sufficient time to adsorb atmospheric oxygen. It has been suggested that this would increase surface hydrophobicity by decreasing the hydration of the mineral surface for relatively short exposures to water of this surface. Thus the surface of dry-

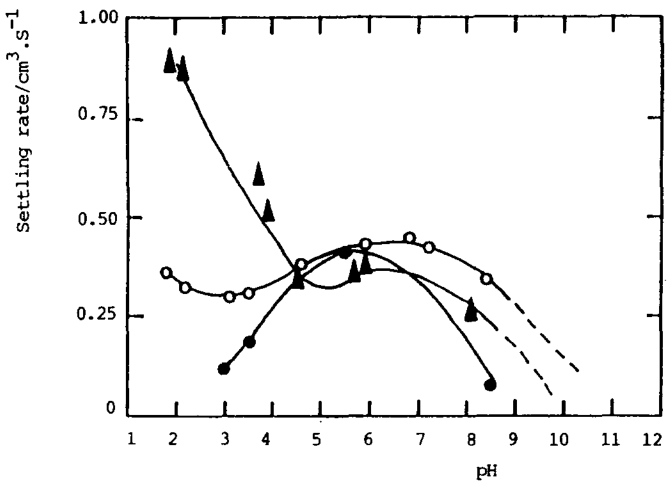

Fig. 3. Settling rate vs pH for pyrite samples subject to different pretreatments: ○ = unoxidised; ● = oxidised with H_2O_2; ▲ = dry ground.

ground pyrite could be less hydrated and therefore more hydrophobic compared to H_2O_2-oxidised samples. This is also indicated by the two-liquid flotation results where higher recoveries were obtained with dry-ground pyrite. The slightly lower stability of pyrite samples around pH 6, could be explained by the zpc of pyrite being about pH 6.5 (Fuerstenau et al., 1968), hence pyrite suspensions would tend to coagulate in this pH region.

The recovery of pyrite at the oil/water interface cannot be explained simply by coagulation and it would appear that pyrite could be oleophilic to a degree dependent on the state of surface oxidation.

Contact angle measurements

The advancing contact angles at pyrite/oil/water interfaces as a function of pH, is shown in Fig. 4. The receding contact angles were about 50% of the advancing contact angles. This hysteresis of contact angles could be due to surface roughness or chemical heterogeneity of the surface (Gaudin and Decker, 1967; Huh and Mason, 1977), which might result from the existence of local cells on the surface of sulphide minerals (Pomianowski and Czarnecki, 1974).

Unoxidised pyrite was highly oleophilic, $\theta_{Ad} = 90°$, under pH conditions where the maximum concentration of similarly treated samples occurred at the oil/water interface. A minimum similar to that seen in the recovery of pyrite (Fig. 1) was also observed around pH 4.5 with contact-angle measurements.

Oxidation of pyrite resulted in a decrease in the contact angle and pyrite

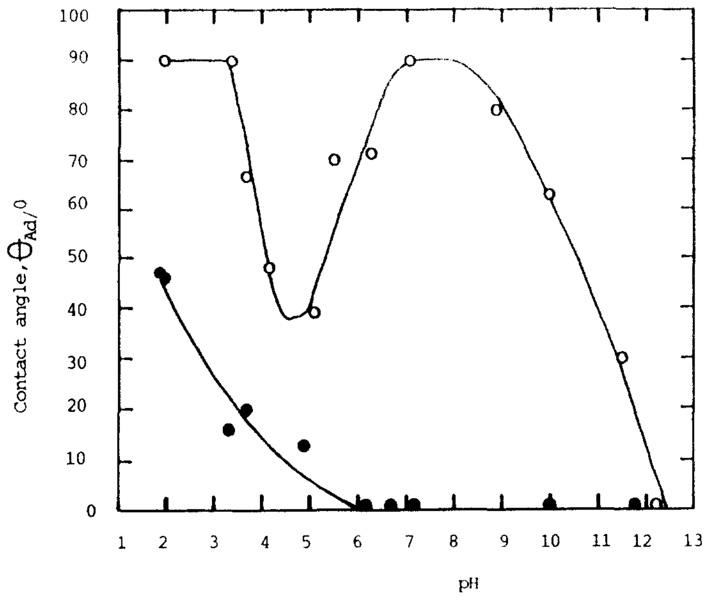

Fig. 4. The contact angle at the pyrite/oil/water interface as a function of pH: ○ = unoxidised; ● = oxidised with H_2O_2.

became oleophobic above pH 6, i.e. the contact angle was zero. The pyrite broken under deoxygenated water at natural pH was also oleophilic. Measurements made with nitrogen bubbles under similar conditions, however, gave zero contact angles, suggesting that the angles measured with the oil drops could not have been caused by contamination from the treatment of minerals.

To further ascertain whether or not the iso-octane used as the oil phase contained surface active impurities which might have been responsible for the measured contact angles, contact-angle measurements were also made on quartz, fluorite and calcite at various pH values. In all cases a zero contact angle was obtained. Crystalline sulphur on the other hand gave 75° and 180° contact angles with nitrogen bubbles and oil drops, respectively.

Therefore, it would appear that under certain redox conditions pyrite is oleophilic, but at the same time hydrophilic with respect to gas bubbles.

The change of wettability with redox potential

When the pyrite electrodes were polished in air with silicon carbide paper and 0.3 μm alumina, neither reduction nor oxidation produced any change in the wettability of pyrite. It remained oleophobic. This could be due to the formation of a $Fe(OH)_3$ surface layer during polishing. The reduction of $Fe(OH)_3$ will form $Fe(OH)_2$ and Fe by (Kocabag, 1983):

$$Fe(OH)_3 + H^+ + e \rightleftharpoons Fe(OH)_2 + H_2O \qquad (1)$$
$$Eh = 0.271 - 0.059\,pH$$

and:

$$Fe(OH)_2 + 2H^+ + 2e^- \rightleftharpoons Fe + 2H_2O \qquad (2)$$
$$Eh = -0.047 - 0.059\,pH$$

so that pyrite remains oleophobic even when cathodically reduced.

The difference between galena, which became oleophilic when oxidised in acid pH values, and pyrite is due to the stability of surface oxidation products formed on the surface, as well as to the less sulphur being formed on the surface of pyrite by the oxidation.

When a pyrite electrode was polished under deoxygenated water with 800 grade silicon carbide paper and with an alumina pad, however, pyrite, like galena, was oleophilic.

The results recorded in Fig. 5 show that the pyrite was oleophilic at open circuit potentials at all pH values. When oxidised at pH 1 and 4 the contact angle first increased, the increase being more at pH 1, and then at higher potentials, however, it decreased and became zero. At higher pH values, the contact angles decreased with anodic oxidation and pyrite became oleophobic. The values of contact angles were dependent on the initial surface. However, once the initial surface was established to the same degree of cleanliness, the contact angles were reproducible within experimental limits.

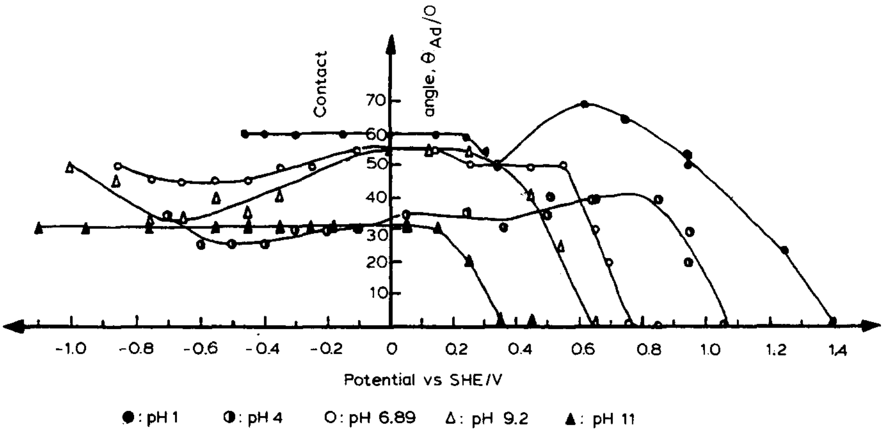

Fig. 5. The change of contact angle with potential of the pyrite/oil/water interface at various pH values.

The increase in contact angle at lower pH values is due to the formation of S^0 on the surface (Hamilton and Woods, 1981; Kocabag, 1983) by:

$$\begin{aligned}&Fe^{2+}+2S+2e\rightleftharpoons Fe\,S_2\\&Eh=0.423+0.0295\log[Fe^{2+}]\end{aligned}\qquad(3)$$

However, with further increase of anodic potential, reactions:

$$\begin{aligned}&Fe^{2+}+2SO_4^{2-}+16\,H^++14e\rightleftharpoons FeS_2+8H_2O\\&Eh=0.367-0.067\,pH-0.008\log[SO_4^{2-}]+0.004\log[Fe^{2+}]\end{aligned}\qquad(4)$$

and:

$$\begin{aligned}&Fe(OH)_3+3H^++e\rightleftharpoons Fe^{2+}+3H_2O\\&Eh=1.056-0.177\,pH-0.059\log[Fe^{2+}]\end{aligned}\qquad(5)$$

became predominant and hence the contact angle decreases and becomes zero.

At higher pH values, the oxidation of pyrite occurs by:

$$\begin{aligned}&Fe(OH)_3+2S+3H^++3e\rightleftharpoons FeS_2+3H_2O\\&Eh=0.64-0.059\,pH\end{aligned}\qquad(6)$$

and/or:

$$\begin{aligned}&Fe(OH)_3+2SO_4^{2-}+19H^++15e\rightleftharpoons FeS_2+11H_2O\\&Eh=0.412-0.0749\,pH+0.0078\log[SO_4^{2-}]\end{aligned}\qquad(7)$$

The formation of very hydrophilic/oleophobic $Fe(OH)_3$, by reaction 6 and 7 on the mineral surface, causes oleophilic pyrite to become oleophobic.

By considering the crystal chemical properties of sulphide minerals, it was suggested that the sulphide minerals should not be wetted strongly by water in the absence of oxygen or other surface reactive compounds. The following characteristics of sulphide minerals were considered to be important (Kocabag et al., 1990): (1) sulphur of sulphide minerals do not form a hydrogen bonding with water; (2) very low solubility of sulphide minerals in water suggests that there is very little interaction between sulphide minerals and water; (3) covalent bonding of sulphide minerals means that when broken their surface charge will be very small.

Therefore it was suggested that under an inert atmosphere sulphide minerals could be oleophilic. However, oleophilicity will be highly dependent on the environment. If oxygen is present, oxidation of the mineral surface can increase the oleophilicity by forming sulphur or it can decrease it by forming metal oxide or sulphoxy compounds on the surface.

Present results show that pyrite is oleophilic when its surface is not oxidised. Oxidation at acidic pH, $pH<4$, increases the oleophilicity by forming sulphur, whereas oxidation at neutral and alkaline solutions (pH 6.89, 9.2

and 11) decreases it due to the formation of $Fe(OH)_2$ and/or $Fe(OH)_3$ on the surface of the mineral.

CONCLUSIONS

(1) When its surface is free of oxidation, pyrite is oleophilic, but it is hydrophilic with respect to a gas bubble.

(2) Formation of sulphur by oxidation at acidic pH <4 will increase oleophilicity.

(3) At neutral and alkaline solutions oleophilicity decreases with oxidation due to the formation of $Fe(OH)_2$ and/or $Fe(OH)_3$ on the surface.

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