V. VIGDERGAUZ, V. CHANTURIYA, T. NEDOSEKINA [*]

PYRITE SURFACE HYDROPHOBICITY: ELECTROCHEMICAL STUDY

The wetting properties of mineral pyrite FeS_2 induced by xanthates with the different lengths of an alkyl chain have been studied by the measurements of a detachment force of an air bubble and induction time. The study was carried out at different potentials monitored by the electrochemical polarization in borate buffer solution. The outcome of these measurements has been successfully compared with the thermodynamics results and the experimental data obtained for representative cases such as the xanthate sorption and the flotation recovery.

INTRODUCTION

The improvement in hydrodynamic conditions in the modern flotation cells can lead to very high recoveries. At the same time the selectivity of the process relies on controlling the surface forces involved in the bubble-particle interactions. Creating a difference in hydrophobicities between those of wanted and unwanted minerals is the key to the improvement separation results (Yoon 1991). The contact angle at the bubble/mineral/solution interface has been employed for many years as a measure of the hydrophobicity of mineral surfaces and hence conditions for mineral flotation (Sutherland and Wark 1955; Gardner and Woods 1977). However, it is common to find hysteresis of the contact angle (Freundlich 1923). Any experimental measures can not eliminate 30 degree or more of hysteresis on actual surfaces (alkanethiols on gold, for example) (Folkers et al. 1992).

That is why we have been studying the mineral wetting properties by detachment force and induction time measurements as a function of mineral potential. The study was carried out on the mineral electrode and the potential was monitored by means of potentiostat. It provided the possibility to determine activation/passivation potentials and in some approximation the flotation potentials regions.

---

[*] Institute of Complex Exploitation of Mineral Resources, Russian Academy of Sciences, IPKON RAN, 4 Kryukovsky Tupik, 111020 Moscow, Russia Phone: 7-095-360-89-64; Fax: 7-095-360-89-60.

EXPERIMENTAL

Reagents preparation. Potassium xanthates were obtained as a commercial product from the Hehst Company. Fresh stock solutions ($5 \cdot 10^{-3}$ M) in borate buffer (pH 9.2; ionic strength = $5 \cdot 10^{-2}$ M) were prepared daily. Dilutions were made with the borate buffer.

Surface preparation. A 6 mm in diameter disc of pyrite (> 97% from Berezovsk, the Urals) was mounted in fluoroplast holder. The working surface was dry-polished in stages using alumina down to 0.05 μm and rinsed with distilled water or sometimes in ethanol between polishing stages. The surface was repolished immediately before using.

Wetting studies. Electrochemical cell with the three-electrode system was used for measurements. Potential was measured and is reported against a silver-chloride reference electrode which had a potential of +0.22 V against the standard hydrogen electrode. The potential of pyrite electrode was controlled by a PI 50 (Izmeritel, Gomel, Belaruss) potentiostat programmed with a sweep generator. The working electrode consists of the pyrite disc. The wire connects the disc to the external electrical circuit. The reference electrode was connected to the main compartment through a Lugging probe capillary. Under potentiostatic control, the current passed between the FeS$_2$ disc and a platinum counter electrode which is housed in the compartment, separated from the main cell by a sintered glass disc.

A torsion balance and a modified Sven–Nilsson device (Sven–Nilsson 1935) were used for the detachment force and the induction time measurements. Induction time is defined as the minimum time for an air bubble and a mineral attachment with each other. Air bubbles for measurements were deposited on the pyrite surface from a small diameter flat-nosed needle positioned below the holder.

The bubble formation and size were controlled using a combination of plug and needle. The needle was detached from the bubble before measuring of the detachment force or the induction time. A freshly polished sample was used for each new reagent.

RESULTS AND DISCUSSION

Figure 1a shows that ethyl xanthate does not make the surface of pyrite appreciably hydrophobic. A detachment force increased only by 2 dynes with increasing xanthate concentration. For the butyl, amyl, and hexyl xanthates the increase of the detachment force is 5 dynes at the concentrations of 20, 15, and 10 mg/l, respectively. The following increasing of the xanthate concentration increases the detachment force progressively. At 45–50 mg/dm^3 the detachment force reaches a maximum value, that exceeds the initial value by 7.5, 10, and 12.5 dyne for butyl, amyl, and hexyl xanthates, respectively. Without polarisation, under steady-state potential we observe an increase of the

maximum detachment force on the xanthate concentration axis along with the increasing length of the alkyl chain.

In the experiments with butyl xanthate the increase of xanthate concentration up to 15 mg/l causes the decrease of the induction time to a value that does not vary with a further rise of the concentration, Fig. 1b.

The examination of the effect of xanthate concentration on the induction time reveals its decrease at certain concentration (critical value). A further rise of the concentration does not effect the kinetics of adhesion.

Adhesion kinetics is influenced by the carbon chain length and electrochemical potential of the surface. The change of the carbon chain from ethyl to amyl resulted in a decrease of the induction time (Table 1). For hexyl xanthate the adhesion strength is the largest one, and for the formation of the three-phase contact 2.5 sec or more is required (Table 1).
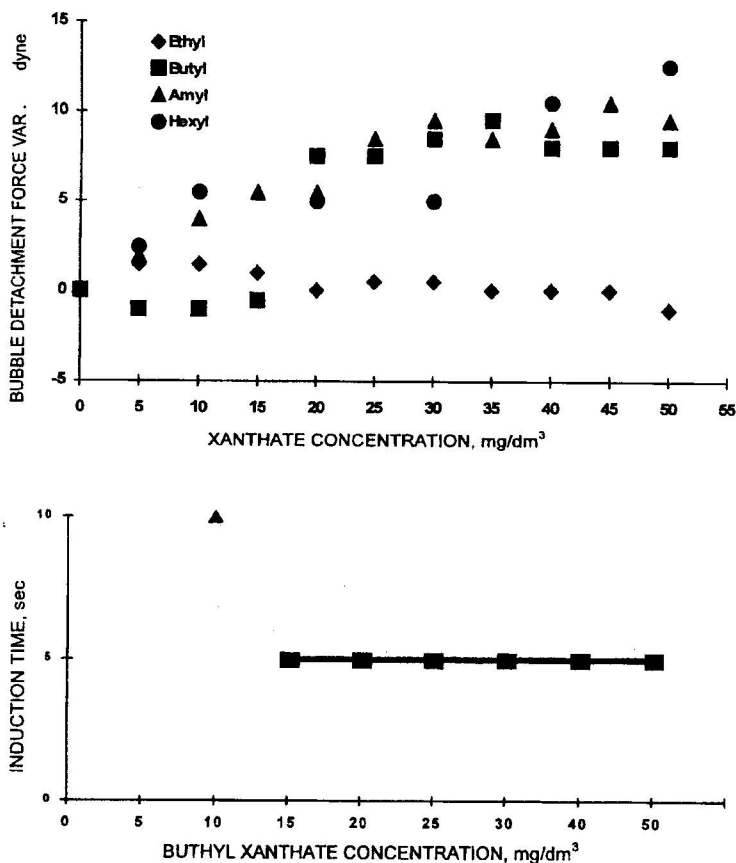

Fig.1. Influence of xanthate concentration on the detachment force variation (a) and induction time (b) in 0,05 M sodium tetraborate solution

In the case of an electrochemical polarization of pyrite and in the presence of long chain xanthates the interval of adhesion potentials is 0.7 V for the induction time 5 sec and below. In the experiments with hexyl xanthate we observed a cathodic shift of adhesion area about 200 mV in comparison with the amyl xanthate experiment. Due to a narrow adhesion interval, butyl xanthate collector is suitable for the electrochemical regulation of selective flotation processes.

Table 1. The influence of the potential of pyrite electrode (V)
and the length of xanthate carbon chain on the induction time (sec).
Xanthate concentration: 50 mg /dm³ in 0,05 M sodium tetraborate solution;
pH = 9.2; reference electrode: Ag / AgCl / KCl (sat.)

Collector	−0.6	−0.5	−0.4	−0.3	−0.2	−0.1	0	0.1	0.2	0.3	0.4	0.5	0.6
Without	no	no	no	no	no	no	no	no	no	no	no	no	no
Ethyl	no	no	no	no	no	no	> 5	5	> 5	no	no	no	no
Butyl	no	no	no	no	no	> 5	5	3.5	3	3	3	> 5	no
Amyl	no	no	no	> 5	3.5	3.5	3	0.5	0.5	2.5	4	> 5	no
Hexyl	no	> 5	5	3.5	3	2	3	2.5	> 5	5	no	no	no

Detachment force/potential polarization curves are similar in shape for all the xanthates studied, (Fig. 2). These curves exhibit two maxima and one minimum. The first, the higher maximum is observed about the potential of 0.2 V. This potential corresponds to the potential of dixanthogen layer formation on the surface. Maximum value of the detachment force changes between 25 and 39 dynes with the increasing length of an alkyl chain of the collector. Minimum and maximum values are observed for ethyl and hexyl xanthates, respectively.
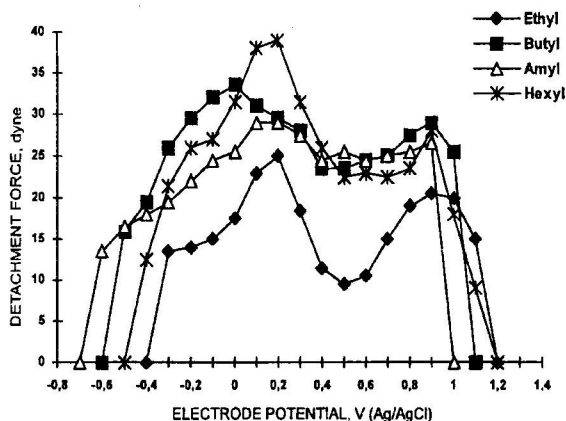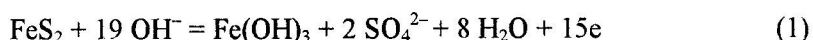

Fig. 2. Dependence of an air bubble detachment force on the potential of pyrite electrode
in 0,05 M sodium tetraborate solution containing 50 mg/dm³ potassium xanthates.
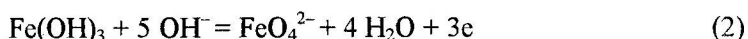Reference electrode, Ag/AgCl/KCl (sat)

The next maximum of the detachment force is observed at about the potential of 0.9 V and its value seems to be slightly dependent on the xanthate chain length. For butyl, amyl, and hexyl xanthates the detachment forces are within the range of 26–28 dynes.

According to Fig. 2, there is a minimum in the the detachment forces. The potential of the minimum is around 0.5 V. The existence of the minima on the curves relating-detachment force, contact angle, 1/induction time, flotation recovery and the potential of electrochemical polarization corresponds to the earlier observations of Trahar (1984) who regulated the redox-potential by sodium dithionate addition. Between the two maxima of pyrite flotation with nitrogene (at –0.25 V and 0.5 V), the minimum recovery at about –0.15 V was observed.

When the potential exceeds 0.16 V the dissolution of pyrite is observed in stages (Radiushkina et al.1986):

$$FeS_2 + 19\ OH^- = Fe(OH)_3 + 2\ SO_4^{2-} + 8\ H_2O + 15e \tag{1}$$

$$E = 0.2 - 0.075\ pH$$

$$Fe(OH)_3 + 5\ OH^- = FeO_4^{2-} + 4\ H_2O + 3e \tag{2}$$

$$E = 1.41 - 0.1\ pH$$

After the first stage the surface of pyrite is covered with hydrophilic iron hydroxide that leads to an increase of wettability.

With the increase of the alkyl chain length the cathodic limit of the potential of adhesion shifts to higher values (Fig. 2). We observed a similar shift for galena and copper sulphides (Chanturiya et al. 1996). Ninety millivolts of cathodic shift was described for the start of the flotation of pyrite for the ethyl to butyl xanthate substitution. This value well corresponds to the finite contact angle.

Only a qualitative correspondence could be observed between the values of potentials in bulk and powder pyrite polarization experiments. Furthermore, it is difficult to compare quantitatively the results for various pyrites because of the essential differences both in the electrochemical behaviour and in floatability (Chmielewski and Nowak 1993). The perspective way to distinguish differences between real flotation involving particle–bubble attachment and mechanical carryover could be achieved using mono-bubble Hallimond tube technique (Drzymała and Lekki 1989).

Electrochemical study of the influence of the pyrite potential on the detachment force and induction time confirms the flotation results. It was found that the cathodic pre-treatment of pulp at the voltage from –0.6 to –0.8 V depressed pyrite, thus making it possible to improve selective flotation in which pyrite remains in the chamber product (Chanturiya and Vigdergauz 1993).

REFERENCES

CHANTURIYA V.A., VIGDERGAUZ V.E. (1993), *Electrochemistry of Sulphides: Theory and Practice of Flotation*, Moscow, Nauka.

CHANTURIYA V.A., VIGDERGAUZ V.E., NEDOSEKINA T.V. (1996), Fiziko-tekhn. Probl. Razr. Polezn. Iskop. 1, 73–80.

CHMIELEWSKI T., NOWAK P. (1992), Fizykochem. Probl. Mineral. 25, 59–67.

DRZYMALA J., LEKKI J. (1989), J. Colloid Interface Sci., 130, 205–210.

FOLKERS J.P., LAIBINIS P.E., WHITESIDES G.M. (1992), J. Adhesion Sci.Technol., 6,1397–1410.

FREUNDLICH H. (1923), *Colloid and Capillary Chemistry*, New York, Dutton.

GARDNER J.R., WOODS R. (1977), Aust. J. Chem., 30, 981–991.

RADIUSHKINA K.A., VIGDERGAUZ V.E., TARASEVICH M.R., CHANTURIYA V.A. (1986), Sov. Elchem., 22, 1394–1398.

RICHARDSON P.E., WALKER G.W. (1985), Trans. XV IMPC, 2, 198–210.

SUTHERLAND K.L., WARK I.W. (1955), *Principles of Flotation*, Melbourne, AIMM.

SVEN-NILSSON I. (1935), Ing. Vetenskaps Akad. Handl., 133,

TRAHAR W.J. (1984), *Principles of Mineral Flotation*, Parkville. 117–135.

WALKER G.W., RICHARDSON P.E. (1983), SME-AIME Annual Meeting, Atlanta

YOON R.-H. (1991), Aufbereitungs-Technik, 32, 474–485.

Vigdergauz V., Chanturiya V., Nedosekina T. (1996), Hydrofobowość powierzchni pirytu. Badania elektrochemiczne, *Fizykochemiczne Problemy Mineralurgii*, 30, 187–192 (w języku angielskim)

Badano zwilżalność pirytu w obecności ksantogenianów o różnej długości łańcucha węglowodorowego, stosując pomiar siły odrywu pęcherzyka powietrza od powierzchniu pirytu oraz pomiar tzw. czasu indukcji. Pomiary prowadzono przy różnych potencjałach regulowanych przez elektrochemiczną polaryzację pirytu umieszczonego w wodnych roztworach buforu boranowego. Uzyskane wyniki zostały z powodzeniem porównane z wielkościami obliczonymi z danych termodynamicznych, z pomiarami sorpcji ksantogenianów oraz z wynikami flotacji.