

A.A. ABRAMOV\*, D.V. MAGAZANIK\*

## **REGULARITIES OF HYDROPHOBISATION AND FLOTATION OF FLUORITE\*\***

As a result of thermodynamic analysis of fluorite–sodium oleate–water system, flotation and adsorption tests at various pH values and sodium oleate concentrations, it has been established that regularities of fluorite flotation cannot be explained by the oleate of alkali-earth metals formation on its surface. The hypothesis, connecting optimal conditions for mineral flotation with zero charge of its surface, allowed to explain the regularity of mineral flotation observed and elaborate a quantitative physicochemical model of fluorite flotation suitable for improving industrial processes and application of automatic control systems at the plants.

### **INTRODUCTION**

Fluorite is an important raw material for metallurgical and chemical industries. The flotation with oxihydrilic collectors (sodium oleate etc.) is the main process of fluorite recovering from ores, and a considerable amount of study has been devoted to the physicochemical aspects of its flotation (Hanna and Somasundaran, 1976; Finkelstein, 1989; Rao and Forssberg, 1992 and others) to understand the reasons of mineral surface hydrophobisation, establish the regularities of its flotation and improve the industrial processes of this mineral flotation.

Results of physicochemical investigations of systems including fluorite show that on mineral surface contacted with sodium oleate there will be such adsorbed products as chemisorbed oleate, physisorbed ‘surface’ and ‘precipitated’ calcium oleates, ions and molecules of oleic acid and sometimes sodium oleate (Finkelstein, 1989; Mielczarski et al.1993; Drzymala and Lekki, 1992). Their ratio on the surface depends on the state of a mineral and on the state and concentration of collector in the solution (Finkelstein, 1989; Abramov, 1994).

---

\* Moscow State Mining University, Leninski Prospect 6, Moscow 17049.

\*\*The Editor and Editorial Board approves publication of this work regardless of disputable key assumptions in the paper regarding the reactions that determine the potentials and hydrophobicity of fluorite which are of paramount importance to the paper.

Accumulated knowledge on the chemistry and physicochemistry of fluorite with fatty acid collectors and modifiers is extensive, but at present time it is far from being at the level at which it can be used to predict or control performance in a practical system. There is no agreed views of the chemistry of reactions that occur at the surface of this mineral under flotation conditions or of the significance of these reactions and forms of collector sorption products forming on the mineral surface for the flotation process and its selectivity (Filkelstein, 1989; Abramov, 1994).

Cleaning up the reasons of fluorite hydrophobisation and regularities of its flotation in the presence of fatty acid collectors is the main aim of this investigation.

## MATERIAL AND METHODS

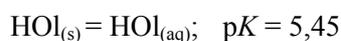
Flotation studies were carried out by using modernised Hallimond tube with 0.1-liter Pyrex glass sell (Melik-Gaikazyan et al.1990). Mineral (without secondary phase impurities) after grinding them in a ceramic ball mill was screened to receive  $-100 + 325$  mesh material for flotation (one gram in each test). Reagents utilised included NaOH, H<sub>2</sub>SO<sub>4</sub> and sodium oleate.

Physicochemical environment in the presence of sodium oleate and mineral was estimated on the basis of solution chemical equilibria.

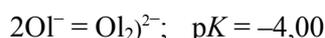
Modeling of processes with the application of thermodynamic analysis included modeling of reagent state in solution, mineral surface state in solution and the whole system state under the same condition.

Modeling sodium oleate state in solution was made on the basis of reactions taking into account undissociated oleic acid (HOI), oleate ion (OI<sup>-</sup>), oleate dimer (OI<sub>2</sub><sup>2-</sup>) and the acid soap (HOI<sub>2</sub><sup>-</sup>):

Bogdanov et al., 1980:



Somasundaran, Ananthapadmanabhan, 1979, 1984:



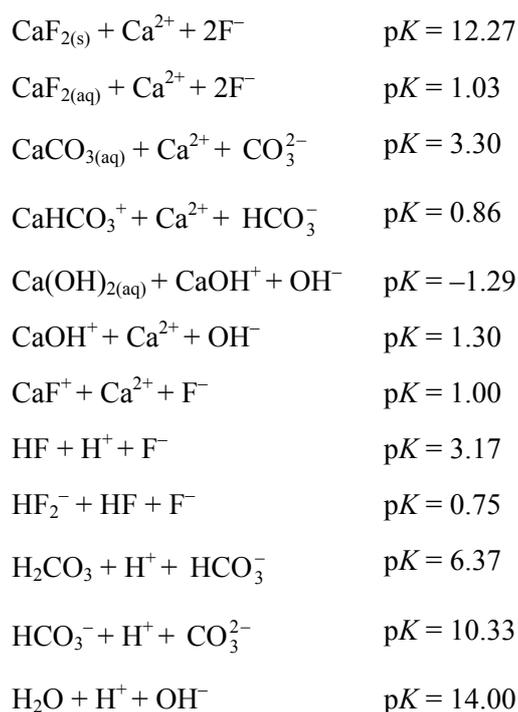
Somasundaran, Ananthapadmanabhan, 1979, 1984:



Somasundaran, Ananthapadmanabhan, 1979, 1984



Modeling of mineral state in close and open systems was made on the basis of reactions shown below for all known possible ions and molecules which can take part in the reactions:



Besides these reactions, balance equations and electroneutrality equations were used while carrying calculations out according to the methodology of thermodynamic analysis elaborated for the flotation system by Melik-Gaikazyan et al., 1990 and Abramov, 1978.

## RESULTS

The distribution of oleate species as a function of pH value is shown in Fig. 1. The total sodium oleate concentrations (from  $10^{-5}\text{M}$  to  $3 \cdot 10^{-4}\text{M}$ ) cover practically complete range of possible collector concentrations in industrial pulps.

Thermodynamic analysis of mineral-pure water system (close system) allowed to determine the pH value of minimum fluorite solubility. It turned out to be equal to 7.0. Since the state of a mineral under these conditions is defined by the minimum of its surface energy, the calculated pH value of minimum solubility of mineral may be considered as pH value of zero charge of its surface. The pH value received is confirmed by results of zeta potentials measuring carried out with fluorite (Le Bell and Lindstrom, 1982) in pure water (close systems).

When the mineral suspension is open to the atmosphere, the pH value of isoionic equilibrium is settled which is not equivalent to the pH value of minimum solubility of mineral (in close system) (Lopez-Valdivieso, 1988) and zero charge of its surface. The

effect of atmospheric  $\text{CO}_2$  involves the formation of soluble carbonate complexes, carbonate and bicarbonate ions which shift the pH value of isoionic equilibrium of fluorite suspension in an open system from 7.0 to 5.9. Zero point of zeta potential in this conditions disagree with the zero point of charge of the mineral surface. Its pH value will be changed considerably depending on conditions of testing and experience of investigator. Published results of investigations (Finkelstein, 1989) indicate that the pH value of zero point of zeta potential is changed for fluorite from 4.2 up to 11.3.

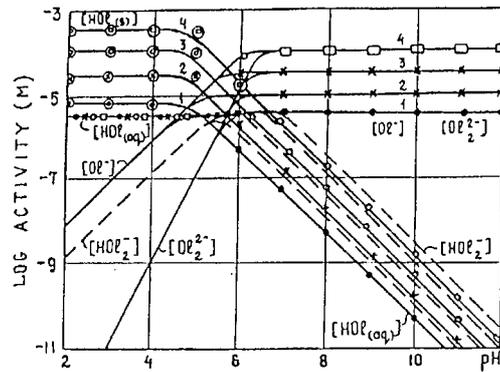


Fig. 1. Distribution of oleate species as a function of pH; total oleate concentration (mol/l):  $1 \cdot 10^{-5}$  (1);  $3 \cdot 10^{-5}$  (2);  $1 \cdot 10^{-4}$  (3);  $3 \cdot 10^{-4}$  (4)

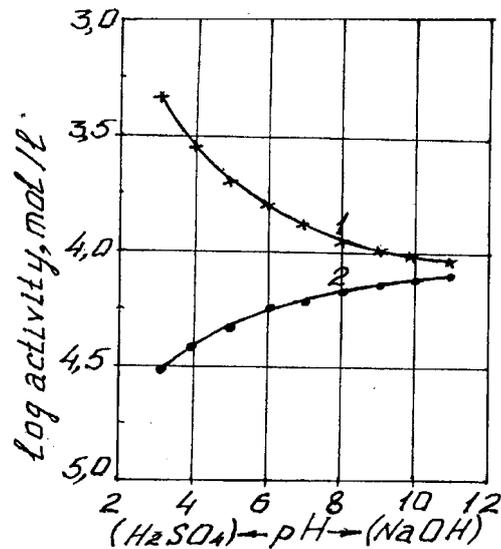


Fig. 2. Distribution of main species in fluorite-water system as the function of pH: 1 -  $\text{Ca}^{2+}$ ; 2 -  $\text{F}^-$

The distribution of main (potential-determining) cations and anions in the presence of fluorite in solution opened to the atmosphere and at usual for flotation systems total concentration of carbon-containing species  $10^{-5}$  M (Abramov, 1994; Garrels and Christ, 1965) is shown in Fig. 2.

Calculated values of  $\text{Ca}^{2+}$  ions (Fig. 2) and oleate ions (Fig. 1) concentrations in solution were used to evaluate the possibility of calcium oleate ( $\text{CaOl}_2$ ) formation in the presence of the mineral at various pH values and sodium oleate concentration in solution required for complete recovery of mineral in flotation. Results of such calculations are shown in Fig. 3. Their comparison with the flotation results received (Fig. 3) shows that wide spread point of view connecting the optimal conditions of salt-like minerals flotation with oleates of alkali-earth metals formation on their surface (Finkelstein, 1989 and others) cannot be accepted.

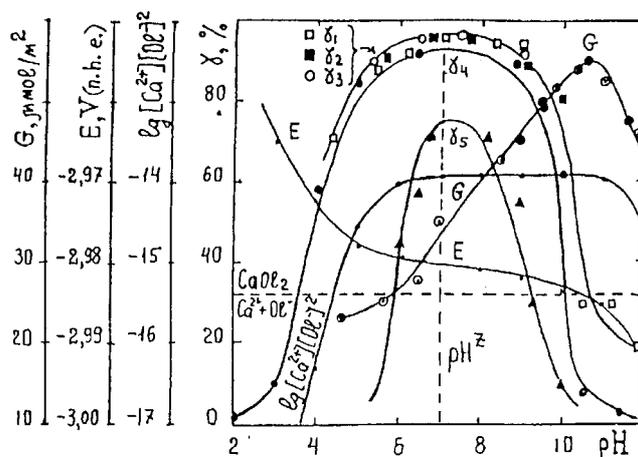


Fig. 3. Effect of pH on fluorite surface potential E value in the absence of collector, floatability of fluorite  $\gamma_1$  after Marinakis and Shergold (1985) at  $[\text{NaOl}]_{\text{initial}} - 1 \cdot 10^{-6}$  M, fluorite from Kazakhstan  $\gamma_2$  and Far East  $\gamma_3$  at  $[\text{NaOl}]_{\text{equil.}} - 1 \cdot 10^{-5}$  M, fluorapatite  $\gamma_4$  and  $\gamma_5$  after Pugh and Stenius (1985) at  $[\text{NaOl}]_{\text{initial}} - 2 \cdot 10^{-3}$  M and  $3,6 \cdot 10^{-6}$  M, value of  $\log[\text{Ca}^{2+}][\text{Ol}^-]^2$  at  $[\text{NaOl}]_{\text{equil.}} - 1 \cdot 10^{-5}$  M and collector sorption density G after Marinakis and Shergold (1985) at  $[\text{NaOl}]_{\text{initial}} - 5 \cdot 10^{-5}$  M

Starting with  $\text{pH} > 4.5$  flotation of fluorite takes place upon calcium oleate  $\text{CaOl}_2$  formation (Fig. 3). But practically under the same conditions of  $\text{CaOl}_2$  formation (at solubility product of  $[\text{Ca}^{2+}][\text{Ol}^-]^2 = -15.4$  (Bogdanov et al.)) we can observe complete flotation of mineral ( $\text{pH} 7.0$ ) and complete depression of its flotation ( $\text{pH} 10.5$ ) despite the maximum oleate adsorption density in the last case (Fig. 3, curve G).

At the same time a remarkable and wonderful coincidence of pH values of maximum mineral floatability and pH value of its minimum solubility ( $\text{pH}^z$ ), corresponding to zero charge of its surface, is observed (Fig. 3, curves  $\gamma$  and  $\text{pH}^z$ ).

## DISCUSSION

There are two indispensable conditions required for effective mineral flotation (Abramov, 1978, 1994) :

- Sufficient hydrophobicity of the mineral surface securing the thermodynamic possibility of mineral particles attachment to the bubbles.
- The presence of physically sorbed collector species, non-polar or non-ionogenic hetero-polar compounds in the adsorption layer on mineral surface to decrease the 'induction time' during the particle attachment to the bubble, to increase the 'floatability index' value of the mineral and multiple strengthening of the particle-bubble contact under the action of tearing forces in flotation (Abramov, 1994).

Results of physicochemical investigations (Mielczarski et al., 1993) show that poorly organised three-dimensional structure of calcium oleate on the apatite surface does not produce high hydrophobicity. As a result, there is an absence of a dependence between floatability of minerals and calcium oleate formation. This is also shown in Fig. 3.

The reasons for a low hydrophobisation ability of calcium oleate in salt-like minerals flotation may be as follows:

- Inadequate coverage density because of discrepancy of crystal lattice size of mineral and oleate of alkali-earth metals resulting in friable structure of oleates forming on the mineral surface (Finkelstein, 1989; Abramov, 1978) incapable to ensure hydrophobicity.
- Hydration of central cations into friable structure of precipitate of calcium oleate on the surface (Finkelstein, 1989).
- Insufficient strength of calcium oleates adhesion to the chemisorbed oleate layer which can result in their tearing off the mineral surface by the bubbles without particle flotation (phenomenon of depression by hydrophobic slimes (Abramov, 1994)).

Suitable hydrophobicity of surface is provided with two-dimensional monolayer of chemisorbed ions and physisorbed molecules of collector assembled on the mineral surface into well-organised closely packed patches with hydrocarbon chains directed towards the solution (Mielczarski et al., 1993).

Two main reasons can be responsible for the most effective flotation of fluorite (Fig. 3) at its zero point charge pH value. The first one is ensuring the maximum hydrophobicity of mineral surface owing to both zero charge of the surface (that is its unpolar state) and chemisorbed collector with hydrocarbon chains directed towards solution. It must be taken into account that since the effective area of a calcium ion on the (100) crystal faces of calcium fluoride is  $11.7 \cdot 10^{-20} \text{ m}^2$  and molecular coverage area for oleate molecule (in liquid-crystal state) in chemisorbed layer is  $33 \text{ \AA}^2$  (Finkelstein, 1989; Rao and Forssberg, 1992), only one surface calcium ion out of every three will be occupied by oleate when the chemisorbed layer is complete. This means that any moving off zero point of charge will increase the polarisation of

unoccupied cations and hydrophilisation of these places on the surface decreasing its total hydrophobisation degree.

It should be noted that the replacement of surface anion group by oleate ion while chemisorption cannot be the reason for moving zero point charge as well as a change in the total charge of Stern layer and electrokinetic potential value up to the point when oleate ions became potential-determining ones. For instance, the results of investigations on calcite and apatite (Rao and Forssberg, 1992) show that after initial increase in negative potential by 10 mV (caused by increase in the thickness of electrical double layer because of long oleate hydrocarbon chain) is fairly constant up to monolayer formation.

The second reason is the creation of optimal conditions for physical adsorption of collector ions and molecule species on the mineral surface at zero point charge which plays a special role in kinetic of attachment of particles to bubbles and preservation of particle-bubble complex in flotation (Abramov, 1994).

The zero charge of surface must promote the physisorption of both collector species and calcium oleates on it. The maximum adsorption of oleate on the surface of fluorite was observed at around mid pH region (Pugh, 1986). The less is the oleate sorption density, the closer the observed pH values of adsorption maximum are to the pH values of zero point charge of minerals. There is rather a tight correlation between floatability and adsorption density of the collector only within the limits of its chemisorption on the mineral surface. Beyond these limits no such correlation is observed.

Location of the maximum mineral floatability at pH value of zero point charge of the mineral surface allow to elaborate a physicochemical model of optimal conditions for its flotation.

The potential value of a mineral in the absence of oleate ( $E_m$ ) will be determined on the basis of the reaction (a):



by concentration of  $\text{F}^-$  ions and can be calculated in accordance with the equation (1):

$$E_m = E_m^0 - 0.059 \log[\text{F}^-] \quad (1)$$

using  $[\text{F}^-]$  values shown in Fig. 2. Calculated values of  $E_m$  at various pH values of solution for minerals studied are shown in Fig. 3 (curve E).

In the presence of sodium oleate in solution,  $\text{Ol}^-$  ions will be chemisorbed on the mineral surface converting it into surface  $\text{CaF}_2\text{]-Ol}$ . Oleate ions become potential-determining in this case.

The potential value of mineral surface in the presence of oleate ( $E_0$ ) can be calculated on the basis of the reaction (b) in accordance with the equation (2):



$$E_0 = E_o^0 - 0.059 \log [\text{OI}^-] \quad (2)$$

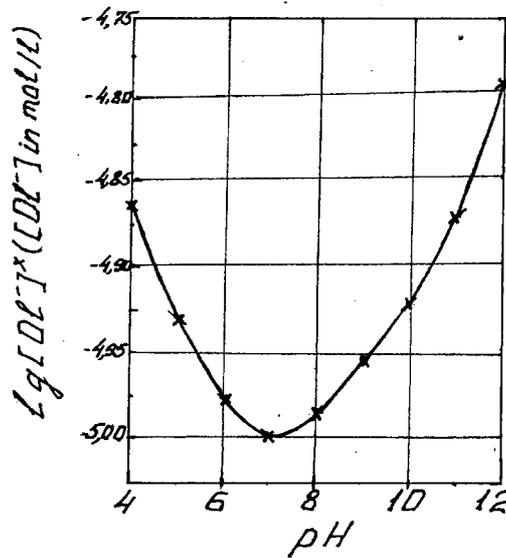


Fig. 4. Relationships between values of pH and required oleate ions concentration  $[\text{OI}^-]^x$  in fluorite flotation

Oleate ions will compete with  $\text{F}^-$  ions on the mineral surface. Ratio of these ions under the optimal conditions of mineral flotation, that is at the zero charge potential of mineral surface ( $E_m^z$  and  $E_o^z$ ) can be determined on the basis of the equality:  $E_m^z = E_o^z$ . Equations (1) and (2) in this case will take the forms for  $E_m^z$  and  $E_o^z$ :

$$E_m^z = E_m^0 - 0.059 \log [\text{F}^-]_m^z \quad (3)$$

$$E_o^z = E_o^0 - 0.059 \log [\text{OI}^-]_m^z \quad (4)$$

and the expression for oleate ions concentration required in mineral flotation under this condition ( $[\text{OI}^-]_m^z$ ) is:

$$\log [\text{OI}^-]_m^z = \frac{E_o^0 - E_m^0}{0.059} + \log [\text{F}^-]_m^z \quad (5)$$

and for other conditions ( $E_m^x$  and  $E_o^x$ ):

$$\log [\text{OI}^-]_m^x = \frac{(E_o^0 - E_m^0)}{0.059} + \log [\text{F}^-]_m^x \quad (6)$$

Simultaneous addition and subtraction of the  $\log [F^-]_m^x$  term to the right part of equation (6) permits to transform it as follows:

$$\log [OI^-]_m^x = \left[ \frac{E_o^0 - E_m^0}{0.059} + \log [F^-]_m^z \right] + \left[ \log [F^-]_m^x - \log [F^-]_m^z \right] \quad (7)$$

$$\log [OI^-]_m^x = \log [OI^-]_m^z + \left| \log \frac{[F^-]_m^x}{[F^-]_m^z} \right|$$

or in a general form :

$$\log [OI^-]_m^x = \log [OI^-]_m^z + \left| \frac{E_m^x - E_m^z}{0.059} \right| \quad (8)$$

Absolute value of the second term in equations (7) and (8) is caused by a different sign of surface potential relatively to zero charge potential of mineral.

Calculated  $\log [OI^-]_m^x$  values for a complete flotation are shown in Fig. 4 and illustrate changing zero charge pH values of minerals. A reliability of  $\log [OI^-]_m^x$  values calculated from equation (7) has been proven experimentally (Fig. 5).

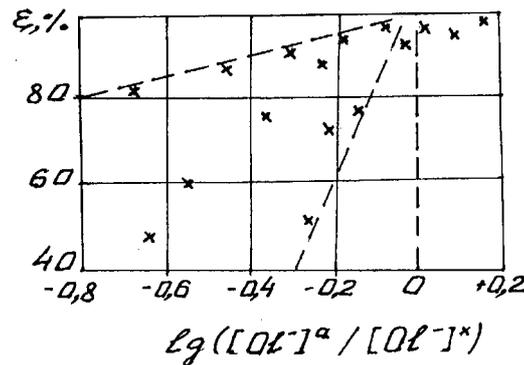


Fig. 5. Effect of ratio of available  $[OI^-]^a$  and required  $[OI^-]^x$  oleate ions concentrations on fluorite flotation

A complete flotation of the minerals under investigation is reached at various pH values when available  $[OI^-]^a$  and required  $[OI^-]^x$  are equal:  $\log([OI^-]^a/[OI^-]^x) = 0$ . Consequently, equation (7) or general equation (8) represent the quantitative physicochemical model of fluorite flotation. Availability of the model makes it possible to elaborate a reliable automatic control system for flotation process of fluorite at plants to gain maximum indexes for concentration, reductions in reagents consumption, cost of flotation, and environment pollution.

The hypothesis presented considering zero charge potential of mineral surface in the presence of a collector as an optimal condition for fluorite flotation is true for other salt-type minerals. For example, it allowed to explain the optimal conditions of selective flotation of carbonates and phosphate minerals (fluorapatite, hydroxiapatite, carbonatoapatite) on an industrial scale (Abramov et al.1993).

## Conclusion

As a result of thermodynamic analysis of fluorite–sodium oleate–water system, flotation and sorption tests at various pH values and sodium oleate concentrations, it has been established:

- The regularities of fluorite flotation cannot be explained by the calcium oleate formation on its surface. Under conditions of its formation the floatability of mineral can be changed from excellent flotation to complete depression despite the maximum oleate sorption density in the latter case;
- The optimal conditions for mineral flotation are observed at pH value corresponding to zero charge of the mineral surface which can be calculated by the use of thermodynamic analysis of mineral-pure water system. The pH value calculated cannot coincide with the zero value of the electrokinetic potential measured. Maximum floatability of the mineral at zero charge pH values is due to the optimal conditions for physical sorption of collector species on the mineral surface hydrophobized by chemisorbed collector in this case and creation of adsorption layer required composition on the mineral to be floated;
- The regularities of collector concentration change necessary for a complete mineral flotation at different pH values are dependent on the regularities of change in the ratio of potential-determining mineral ions and collector ions concentration in the liquid phase of pulp which is necessary to maintain at quite definite value to secure the potential of zero charge on the mineral surface;
- The quantitative physicochemical model of fluorite flotation elaborated may be used in automatic control system to regulate the process of their flotation at plants.

## REFERENCES

- ABRAMOV A.A., 1978, *Theoretical base of optimisation of sulphide ores selective flotation*, Moscow, Nedra, 399.
- ABRAMOV A.A., ABRAMOV AL. AL., ONAL G., ATAKA S., CELIK MC., 1993, *Mechanism of reverse flotation of calcareous phosphate ores* [in:] H. El-Shall, B.M. Moudgil, R. Wiegel (Ed.), *Beneficiation of phosphate. Theory and practice*, Littleton, Colorado, 281–288.
- ABRAMOV A.A., 1994, *Flotation methods of mineral processing*, 2nd Edition, Moscow, Nedra, 383.
- BOGDANOV O.S., PODNEK A.K., JANIS N.A., MAXIMOV I.I., 1980, *Theory and technology of ores flotation*, Moscow, Nedra, 431.
- DRZYMALA J., LEKKI J., 1992, *A contribution to understanding oleate flotation of minerals* [in:] Proc. 4th Int. Miner. Proc. Symp., Turkey, Antalia, 1, 213–224.

- FINKELSTEIN N.P., 1989, *Review of interactions in flotation of sparingly soluble calcium minerals with anionic collectors*, Trans. JMM, Sec. C, 98, 157–177.
- GARRELS R.M., CHRIST S.L., 1965, *Solutions, minerals and equilibria*, San Francisco, Freeman Cooper, 450.
- HANNA H.S., SOMASUNDARAN P., 1976, *Flotation of salt-type minerals* [in:] M.C. Fuerstenau (Ed.), *Flotation*, A.M. Gaudin Memorial Volume, New York, AIME, 1, 197–272.
- LE BELL J.C., LINDSTROM L., 1982, *Electrophoretic characterization of some calcium minerals*, Finn. Chem. Lett., 134–138.
- LOPEZ-VALDIVIESO A., 1988, *Technical note. Isoionic point and minimum solubility of carbonate minerals*, Minerals Eng., 1, 1, 85–87.
- MARINAKIS K.I., SHERGOLD H.L., 1985, *The mechanism of fatty acid adsorption in the presence of fluorite, calcite and baryte*, Int. Min. Process., 14, 161–176.
- MELIK-GAIKAZYAN V.I., ABRAMOV A.A., RUBINSTEIN U.B., AVDOHIN V.M., SOLOGENKIN P.M., 1990, *Investigation methods of the flotation process*, Moscow, Nedra, 301.
- MIELCZARSKI J.A., CASES J.M., BOUQUET E., BARRES O., DELON J.F., 1993, *Nature and structure of adsorption layer on apatite contacted with oleate solution. 1. Adsorption and Fourier transform infrared reflection studies*, Langmuir, 9, 2370–2382.
- PUGH R.J., 1986, *The role of the solution chemistry of dodecylamine and oleic acid collectors in the flotation of fluorite*, Coll. & Surf., 18, 19–41.
- PUGH R.J., STENIUS P., 1985, *Solution chemistry studies and flotation behaviour of apatite, calcite and fluorite minerals with sodium oleate collector*, Int. Miner. Process., 15, 193–218.
- RAO K.H., FORSSBERG K.S.E., 1992, *Interactions of anionic collectors in flotation of semi-soluble salt minerals* [in:] P. Mavros, K.A. Matis (Ed.), *Innovations in flotation technology*, Netherlands, Kluwer Academic Publishers, 331–356.
- SOMASUNDARAN P., ANANTHAPADMANABHAN K.P., 1979, *Solution chemistry of surfactants and the role of it in adsorption and froth flotation in mineral /water system* [in:] K.L. Mittal (Ed.), *Surface chemistry and surfactants*, New York, Meusen Press, 2, 777–800.
- SOMASUNDARAN P., ANANTHAPADMANABHAN K.P., 1984, *Dimerization of oleate in aqueous solutions*, J. Colloid Interface Sci., 99, 128–135.

**Abramov A.A., Magazanik D.V.**, Prawid<sup>3</sup>owoœci dotycz<sup>1</sup>ce hydrofobizacji i flotacji fluorytu. *Fizykochemiczne Problemy Mineralurgii*, 32, 183–193 (w jêz. angielskim)

W wyniku analizy termodynamicznej układu fluryt–oleinian sodu–woda oraz testów flotacyjnych i adsorpcji przy różnych wartościach pH i stężenia oleinianu sodu ustalono, że flotacji fluorytu nie może być wyjaśnione poprzez tworzenie się oleinianów ziem alkalicznych na jego powierzchni. W pracy przedstawiono hipotezę łączącą optymalne warunki flotacji z punktem zerowego ładunku. Hipoteza ta pozwoliła na wyjaśnienie prawideł flotacji fluorytu i wypracowanie ilościowego fizykochemicznego modelu flotacji tego minerału. Zaprezentowana hipoteza pozwala również na poprawę przemysłowego procesu flotacji i zastosowanie systemów automatycznej kontroli w zakładach przerobczych.