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# Electrokinetic phenomena in interfaces and valorisation of high-silica bauxites

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*Yugoslavia possesses a great number of deposits of karst type lowgrade bauxite ores with high $SiO_2$ content. Currently, the deposits are not exploited due to the unsolved problem of their concentration for further processing. For that reason, in the Institute of Mines and the Faculty of Mining and Geology, Belgrade, intense studies are being carried out on the possibility of their concentration by various mineral dressing methods.*

*This work deals with the effect of electrokinetic potential changes in the interface mineral —solution on the floatability of individual minerals comprising the mentioned bauxite ores. The investigations are concerned with boehmite and kaolinite, having in view that kaolinite is the principal $SiO_2$ carrier in above bauxites.*

*The work presents changes in zeta potential as a function of solution pH value, as well as in dependence of the presence of individual modifying agents and collectors commonly used in bauxite flotation.*

*The work also presents the results obtained by pure boehmite and kaolinite flotation in a modified Hallimond tube.*

*The final section of the paper discusses the happenings in the interface mineral—solution in the process of boehmite and kaolinite flotation and indicates the correlation between their floatability and electrokinetic potential.*

## 1. INTRODUCTION

Literature does not provide more detailed information on aluminum minerals properties, nor on investigations in the area of concentration of ores containing such minerals. Therefore, today it is not possible to select in advance with certainty a particular concentration method for any one bauxite. However, in recent years the knowledge in this field was considerably increased. Much work has been devoted to the study of aluminum minerals surface properties, particularly of corundum. It was found that natural and artificial corundum, as well as bauxite, may undergo surface changes from hydrophobic to hydrophilic in neutral solutions in dependence of the rate of calcining [1]. Z. Bilo studied the adsorption of α—naphthylamine on $Al_2O_3$ [2]. Taggart and Arbiter [3] found that during oxides flotation, such as $Al_2O_3$, $Fe_2O_3$ and $Fe_3O_4$, they are separated by fatty soaps in the form of slight amounts of ions that react with alkaline metallic soaps and coat the minerals with soapy films.

Evidence also exists on the floatability of corundum by oleic acid [4], [5], hexadecyltrimethylammonium bromide [6] and fatty soaps [7], as well as on the effect of technical sodium silicate on the adsorption of sodium oleate on corundum crystals [4], [5], In the flotation process, oleic acid adsorbs on the active surface of $Al_2O_3$ to a larger extent from slightly acid and neutral solutions, and long chain hydrocarbon ions from highly alcaline ones [8].

It was found that the adsorption of organic collectors on corundum surfaces develops in two stages. The first stage develops very quickly, resulting in the adsorption of the practically maximum possible amount of the collector. There is nearly no-change in the amount of collector on the mineral surface during the second stage. This adsorption sequence of collector organic ions is characteristic for the group of mineral where the surface and collector adsorbed ions are oppositely charged; for instance, with the adsorption of sodium lauryl sulphate ($C_{12}H_{25}OSO_2ONa$) on corundum from diluted solutions. Here zeta potential in water has a positive sign before the beginning of adsorption [9].

The magnitude and sign of zeta potential determine the form of collector adsorbed ion at a given solution pH value. Here an electric double layer in the interface mineral solution has a significant influence on collector ion adsorption on the mineral surface [10]. According to the opinion of B. Dobijaš [11], D. W. Fuerstenau [12], D. Salatić [13] and N. A. Volkova [14], the adsorption of collector ions on mineral surfaces is a function of electrokinetic (zeta) potential.

In this work, the authors also studied the effect of electrokinetic potential changes in the interface mineral—solution on the floatability. However, the investigations were carried out on boehmite and kaolinite, considering that this will contribute to the valorisation of Yugoslav high-silica bauxites, in which boehmite and kaolinite are the major represented minerals.

The work indicates changes in zeta potential as a function of pH, as well as a function of the presence, in the solution, of some modifying agents and collectors commonly used in bauxite flotation.

The work also presents the results obtained by pure boehmite and kaolinite flotation in a modified Hallimond tube.

The final section of the paper discusses the happenings in the interface mineral - solution in the process of boehmite and kaolinite flotation and indicates the correlation between their floatability and electrokinetic potential.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Raw material

For this research, more pure ore samples were selected in the field, in which boehmite or kaolinite were primarly represented. From the samples, after crushing, by handpicking under a binocular microscope relatively clean boehmite and kaolinite were separated.

The separated pure minerals were further classified in order to separate the size fraction — 200 + 325 mesh (— 0.074 + 0.044 mm) for use in the Hallimond tube flotation tests, while the remaining amount of each mineral was ground to a microne size (100% — 0.005 mm) to be used in zeta potential measurement tests.

Chemical analysis results:

| Mineral | $Al_2O_3$% | $SiO_2$% | $Fe_2O_3$% | Residue | $H_2O$% |
|---|---|---|---|---|---|
| Boehmite | 81.72 | 2.16 | 0.18 | 1.54 | 14.40 |
| Kaolinite | 38.83 | 44.38 | 0.45 | 2.60 | 13.74 |

The chemical analysis results indicate that the separeted minerals may be considered sufficiently pure to be successfuly used in a research work of this kind.

### 2.2. Reagents

The effect of two modifying agents and two collectors on changes in electrokinetic potential and flotation recoveries of boehmite and kaolinite was studied. The modifying agents were sodium hexametaphosphate ($Na_2[Na_4(PO_3)_6]$) and sodium silicate ($Na_2SiO_3$), while the collectors were sodium oleate ($C_{17}H_{33}COONa$) and dodecylaminacetate ($C_{12}H_{25}NH_3COOCH_3$).

The concentration of modifying agents in presented results was $1 \times 10^{-3}$ M/l, and of the collectors 50 mg/l.

The solutions pH values were adjusted by hydrochloric acid (HCl) and sodium hydroxide (NaOH).

### 2.3. Apparatus

a) *Zetameter*

The Zetameter (Manufactured by Zeta-Meter Inc., New York) was used for measuring the electrophoretic mobility of mineral particles of colloid size in the solutions, which enables direct observation of particle motion under the influence of electrophoresis. Particle observations were made by binocular microscope in the usual way.

The zeta-potential was calculed by the simplified Helmholtz-Smoluchowski equation adapted for this zeta-meter:

$$\zeta = \frac{113000 \times \eta \times \nu}{\varepsilon}$$

where

$\zeta$ — zeta potential, mV;

$\eta$ — viscosity at a given temperature, P;

$\nu$ — electrophoretic mobility, $\mu$m/s/V/cm;

$\varepsilon$ — dielectric constant at a given temperature.

The values obtained correspond to solution temperature of 22.5 °C, so corrections were made according to solution actual temperature.

b) *Hallimond tube*

In recent years many research works in the field of flotation include the application of a pneumatic cell for frothless flotation. The first type of this cell was described by A. F. Hallimond, and it has been modified on many occasions [15], [16]. One of the latest modifications was made by J. M. Cases [17] in which our flotation tests were carried out. Probable error in recovery for one test, calculated from twelve tests carried out under identical conditions, was only $\pm$ 0.218 per cent.

## 3. RESULTS

### 3.1. Tests without addition of modifiers

Before starting the experimental work the electrokinetic (zeta) potential of boehmite and kaolinite was measured in distilled water, the pH of which was 5.6 prior to the introduction of mineral particles. The zeta potential of boehmite was + 15.5 mV, and that of kaolinite — 23.8 mV. The zeta potential was then determined over a pH range 3 — 11. Variation of pH brings about a considerable change in the zeta potential of both minerals, as shown in Figure 1, curves 1.

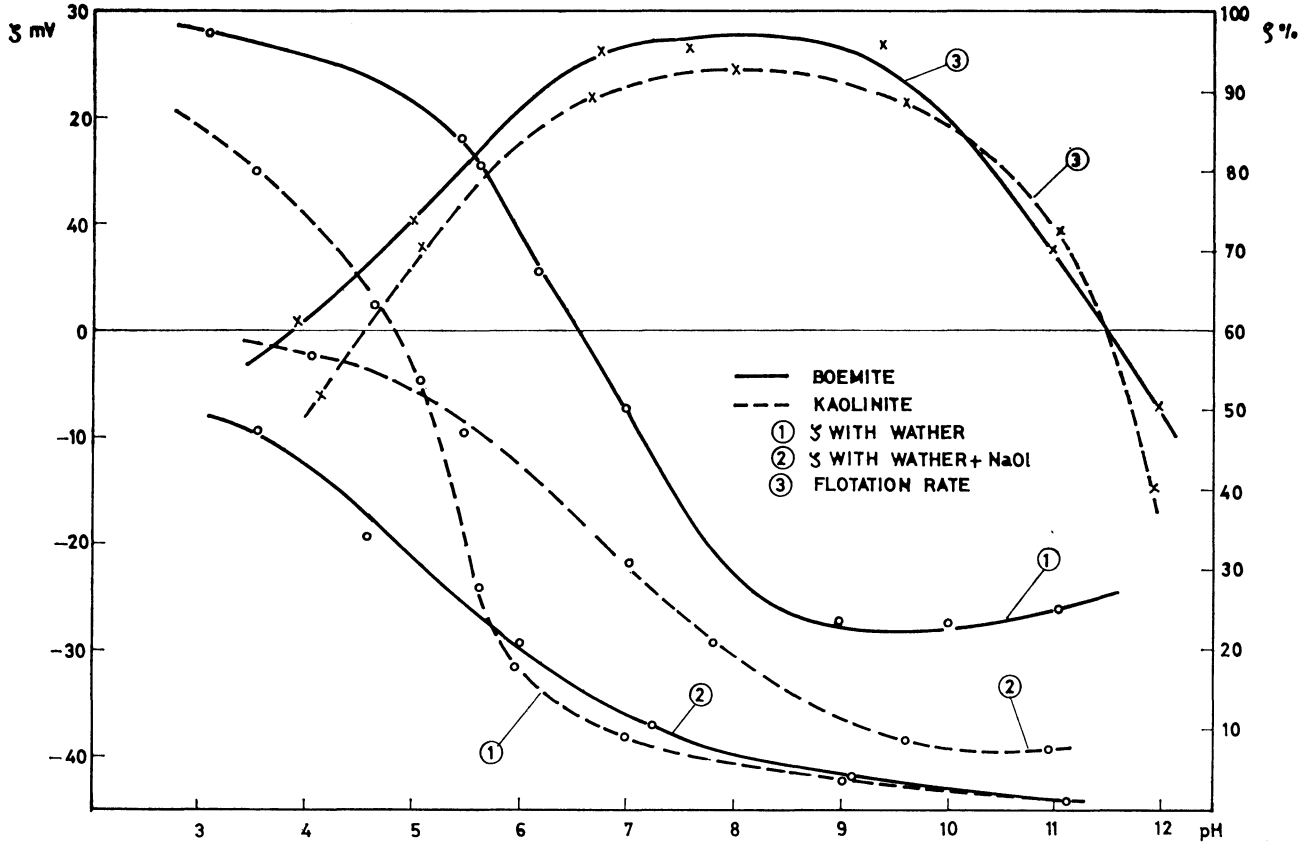


Fig. 1. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with sodium oleate

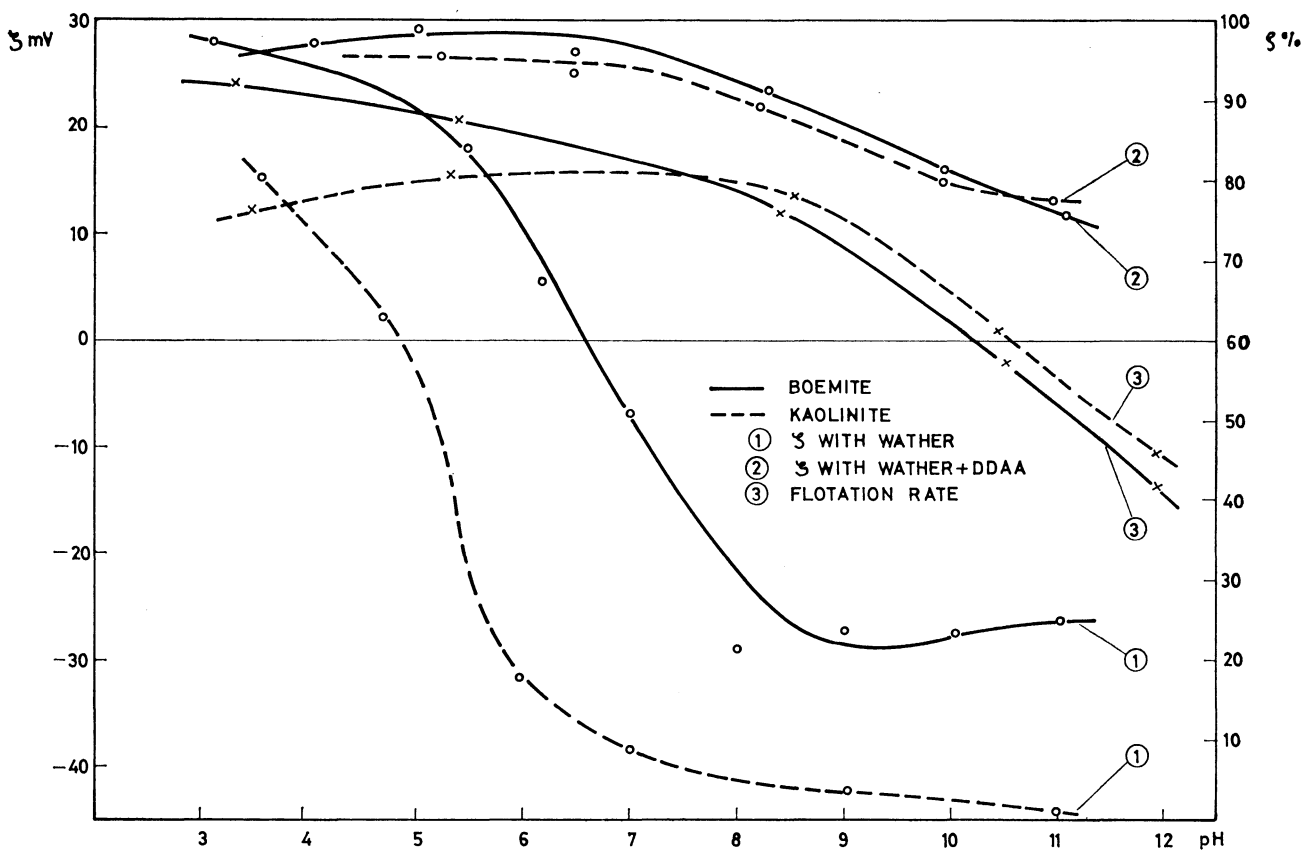


Fig. 2. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with dodecyl amine acetate

Boehmite shows an increasingly positive zeta potential with increase in $H^+$ ion concentration, while the values become negative in alkaline medium. The point of zero charge occurs at pH = 6.6.

Variations in the zeta potential with solution pH were also considerable for kaolinite. Here also an increase of negative zeta potential takes place with increase in $OH^-$ ion concentration. However, with the increase in $H^+$ ion concentration the values decrease reaching the point of zero charge at pH = 4.8, when the sign is changed and positive potential values grow with the increase of solution acidity (Fig. 1, curves 1).

After adding sodium oleate, the zeta potential curves of both minerals (Fig. 1, curves 2) become displaced differently for each mineral. In acid medium both minerals changed the potential sign, having a negative value over the whole pH range, being increased with increase in $OH^-$ ion concentration.

After the completion of zeta potential measurements, the boehmite and kaolinite were placed in the Hallimond tube and tested for floatability. By adding sodium oleate approximately the same attachment of boehmite and kaolinite to bubbles was achived. Both minerals have a specifically outstanding floatability within the pH range 6-10, where recoveries more then of 85 per cent were achieved (Fig. 1, curves 3).

Zeta potential measurements in dodecylaminacetate solution as a function of pH value indicate that both minerals have a positive charge throughout the pH range (Fig. 2, curves 2). The values are approximately identical.

Flotation recoveries in the Hallimond tube do not differ significantly. They are higher in acid than in alkaline media (Fig. 2, curves 3).

### 3.2. Tests in the presence of phosphate ions

The following experiments include measurements of the zeta potential of boehmite and kaolinite in the presence of phosphate ions ($P_2O_5^{2-}$) from sodium hexamethaphosphate solution. The results are presented in Figure 3, curves 1. The zeta potential is negative for both minerals, with increasingly negative values with increase in pH.

Addition of oleate ions ($01^-$) from sodium oleate solution increases the negative zeta potential value of boehmite, and slightly reduces that of kaolinite (Fig. 3, curves 2).

Flotation tests indicate that boehmite floats excellently in alkaline medium, and to a lesser extent in an acid one. However, kaolinite practically does not float, having in view the fact that the highest recovery achieved was below 15 per cent. A particularly good selectivity was achieved in alkaline medium above pH = 8 (Fig. 3, curves 3).

Dodecylaminacetate in presence of phosphate ions only slightly reduces the surface negative charge, both of boehmite and kaolinite (Fig. 4, curves 2).

Flotation recoveries are very low for both minerals over the whole pH range, which gradually fall with increase in solution alkality (Fig. 4, curves 3).

### 3.3. Tests in the presence of silicate ions

The zeta potential of boehmite and kaolinite in the presence of silicate ions ($HSiO_3^-$ and $SiO_3^{2-}$) is presented in Figure 5, curves 1. The curves indicate that in an acid medium boehmite has a positive potential, passing through the point of zero charge at pH = 7.0, followed by increasing negative values with increase in $OH^-$ ion concentration. Kaolinite has a negative charge within the entire pH range, which constantly increases with the decrease in $H^+$ ion concentration.

Addition of sodium oleate to sodium silicate solution reduces the positive and negative zeta potential values of boehmite, while the point of zero charge remains nearly in the same position (Fig. 5, curve 2). The Figure also indicates that the negative values of kaolinite potential also decrease with increase in pH of the solution.

Hallimond tube tests, the results of which are presented in Figure 5, curves 3, indicate that boehmite floats very well within the pH range 6.5 — 11.0, while the recoveries exhibit a sharp drop below and above these pH values. On the other hand, kaolinite flotation

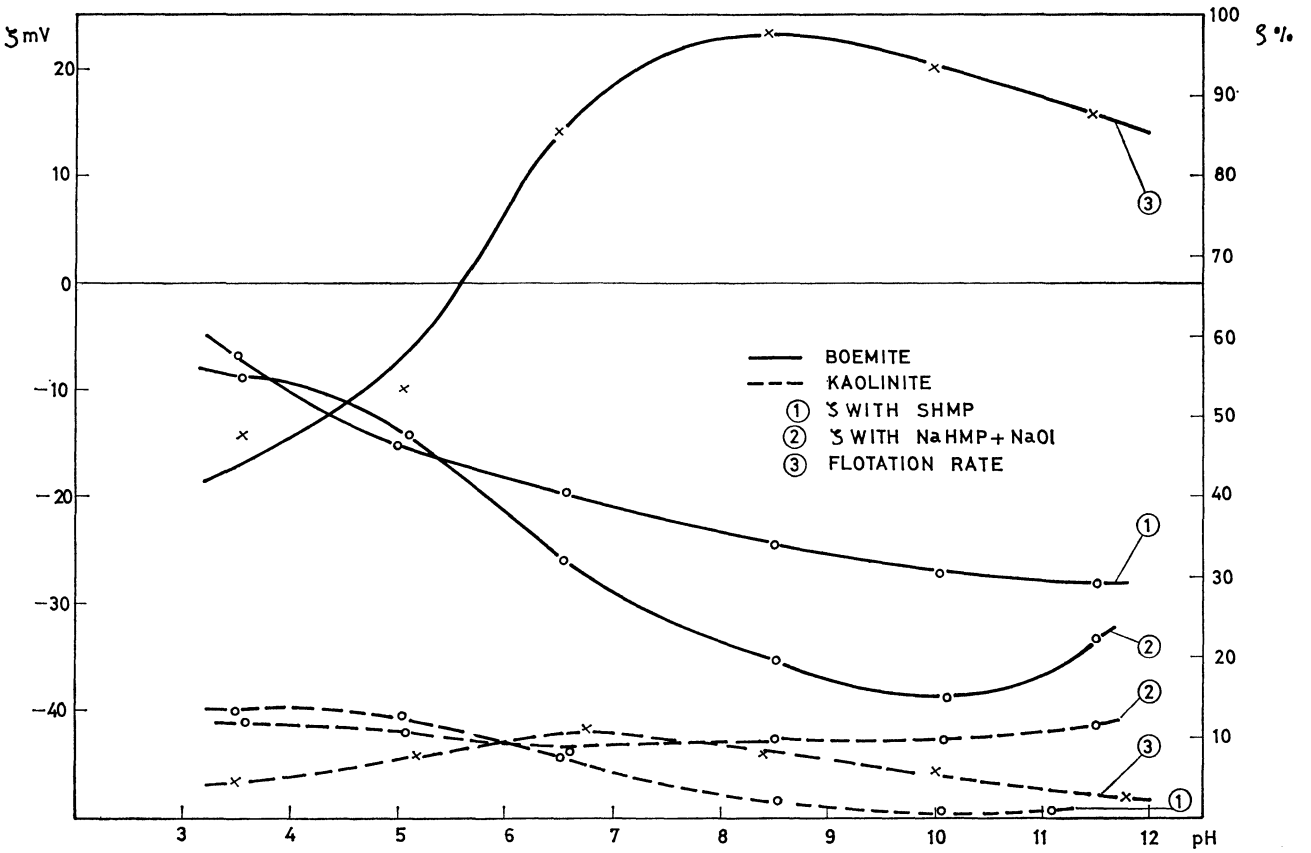


Fig. 3. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with sodium olate and sodium hexameta phosphate

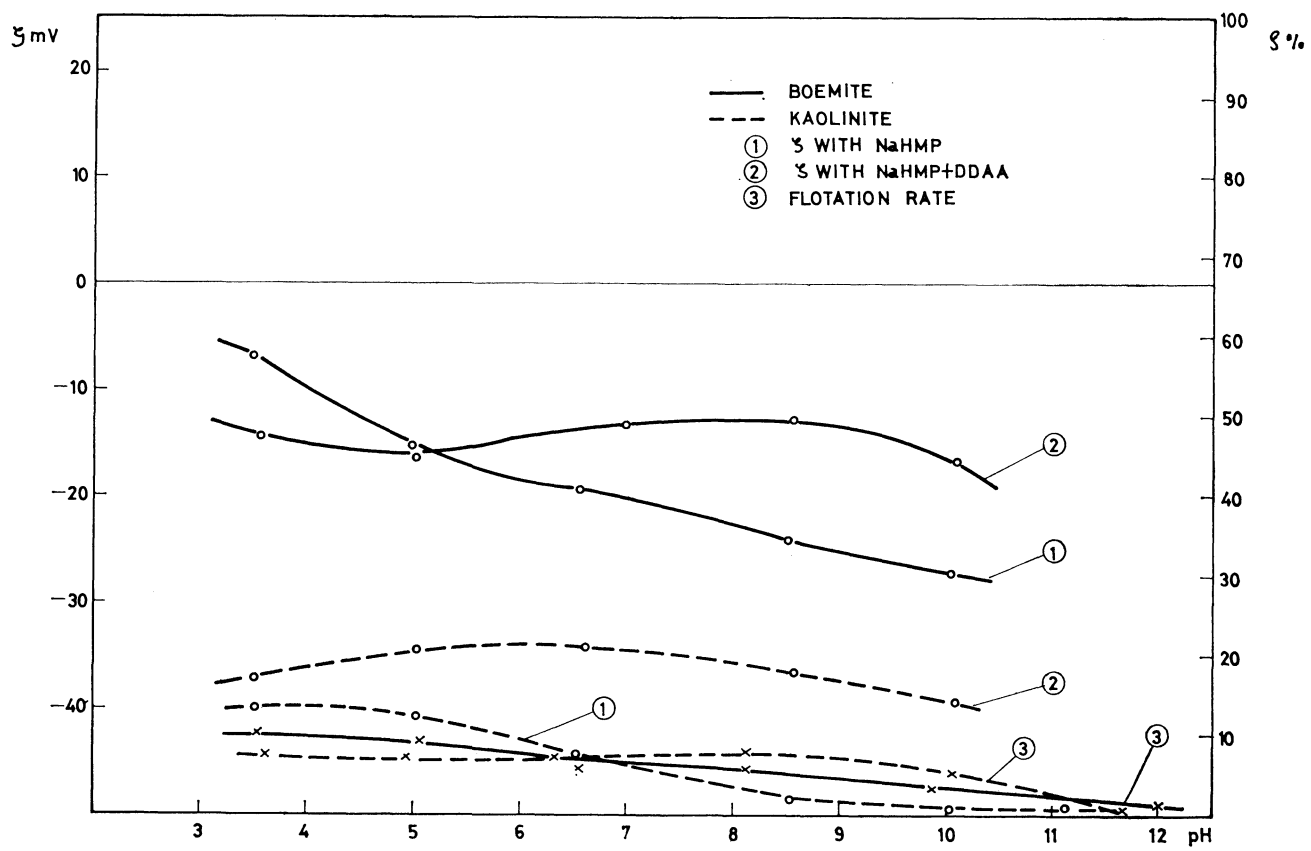


Fig. 4. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with dodecyl amine acetate and sodium hexameta phosphate

yealds higher recoveries in an acid medium. This also brings about a selectivity in boehmite and kaolinite flotation, although it is less marked in regard with the use of sodium hexamethaphosphate as the modifier.

Dodecylaminacetate in the presence of silicate ions changes boehmite surface into a negative one, having a maximum negative value (23.5 mV) at pH = 8.0 (Fig. 6, curve 2).

Boehmite recoveries in the Hallimond tube range between 45 and 60 per cent, and those of kaolinite between 22 and 40 per cent (Fig. 6, curves 3). The results indicate that the desired selectivity in the flotation process is not achieved.

## 4. DISCUSSION

The structure of boehmite and kaolinite crystal lattice in not tipically ionic, so on the base of sign and zeta potential magnitude changes in the interface mineral—solution, it is not possible to demonstrate with certainty the reactions taking place on their surfaces, i.e. in the interfaces mineral—solution.

It is certain that changes in $H^+$ and $OH^-$ ion concentrations result in the change of the sign and zeta potential values of both minerals, indicating that the $H^+$ and $OH^-$ ions are the potential determining ones both for boehmite and kaolinite.

Oleate ions from sodium oleate solution adsorb on the surfaces of both minerals, changing their charge (Fig. 1, curves 2).

This is also proved by the flotation recovery of both minerals in the Hallimond tube (Fig. 1, curves 3).

The amine ions ($RNH_3^+$) from the dodecylaminacetate also adsorb on both mineral surfaces on the inside part of the electrical double layer, bringing about a change of sign and zeta potential values (Fig. 2, curves 2).

Flotation recovery curves 3 on Figure 2 prove this clearly, owing to the fact that considerable recoveries have been achieved in boehmite and kaolinite flotation.

Phosphate ions ($P_2O_5^{2-}$) from sodium hexamethaphosphate solution particularly strongly adsorb on kaolinite surfaces, although their adsorption is observable on boehmite surfaces too (Fig. 3, curves 1). However, curves 3 on the same Figure, representing the flotation recoveries, indicate that the connection of adsorbed phosphate ions on boehmite and kaolinite surfaces is not of the same type. In the first case, oleate anions displace anions from boehmite surface, enabling boehmite to float. Kaolinite flotation recoveries are slight, indicating that hemisorption of phosphate anions occured on kaolinite surface. The correctness of this assumption was confirmed by investigations on sodium hexamethaphosphate adsorption on kaolinite carried out by V. V. Iščenko and coworkers [18].

In regard with $RNH_3^+$ ions from dodecylaminacetate solution, it may be concluded that they were not capable to displace phosphate ions from the surface of kaolinite, as well as boehmite. This is proved by very low flotation recoveries, particularly for kaolinite.

Silicate ions ($HSiO_3^-$ and $SiO_3^{2-}$) from sodium silicate solution have a differing action in flotation by anionic and cationic collectors, both with kaolinite and boehmite. Since undissociated silica acid prevails in sodium silicate solutions up to pH = 9, followed by $HSiO_3^-$ ions to pH = 13, above which $SiO_3^{2-}$ ions prevail, it appears that depression is brought about by $HSiO_3^-$ and $SiO_3^{2-}$ ions, followed by molecular and colloidal-dispersing silica acid. The very mechanism of silicate adsorption on mineral surfaces has not been explaned [19]. The only conclusion made with certainty was that sodium silicate depresses mineral surfaces, and that it may activate some of them at very low concentrations.

Therefore, we may alsc conclude that the presence of sodium silicate in sodium oleate solutions has lead to a more noticeable kaolinite depression, having no influence on boehmite floatability. On the other hand, in the flotation process with dodecylaminacetate,

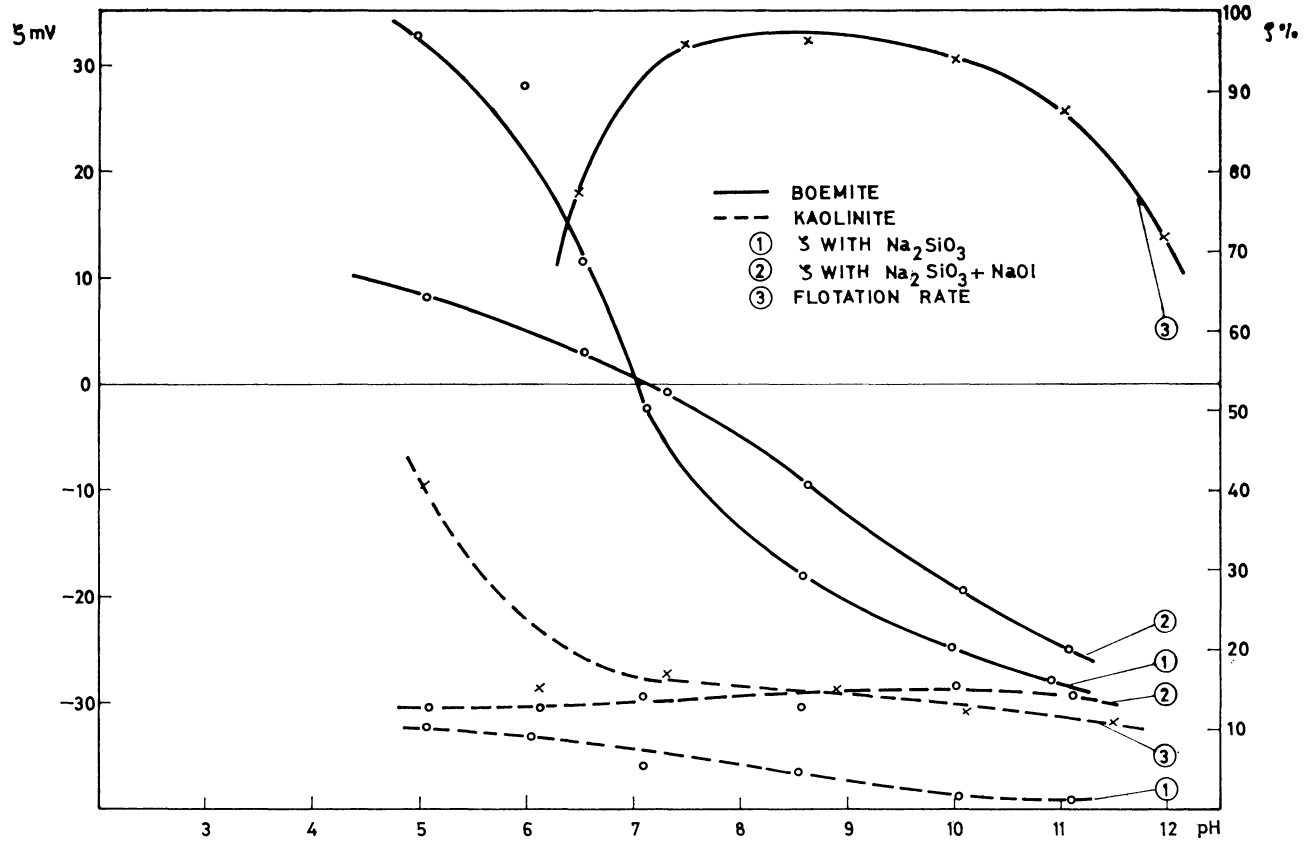


Fig. 5. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with sodium oleate and sodium silicate

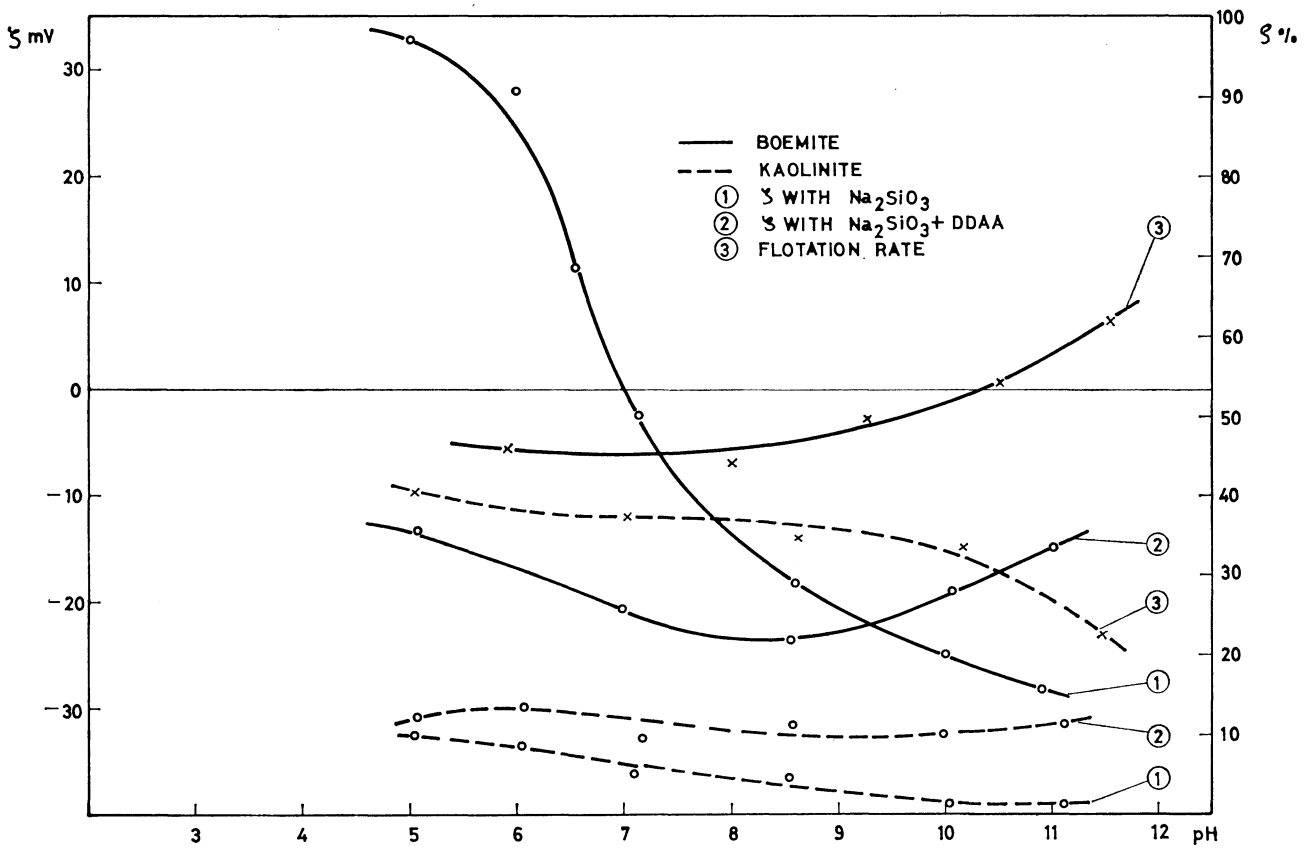


Fig. 6. — Correlation of zeta-potential and flotation rate of boemite and kaolinite with dodecyl amine acetate and sodium silicate

sodium silicate depressed boehmite to a significant extent, while the effect is less depressing on kaolinite in regard with the use of sodium oleate.

It is of interest to note that boehmite flotation recovery increases in basic medium. We assume that this leads to the development of the complex metal—amine, this being in agreement with Taggart's assumption [20].

Finally, the authors wish to indicate that research work on this problem has been extended by investigations on the effects of other modifiers and collectors in order to determine the conditions for selective flotation of boehmite from boehmite-kaolinitic bauxites with high $SiO_2$ contents, which are highly widespread in Yugoslavia.

## REFERENCES


[1] BERL. (E.) und PFANNMÜLLER (W.), 1924. — Kolloid-Z, Bd 35, p. 106-109.

[2] BYLO (Z.), 1957. — Archiwum Hutnictwa, Kraków, t. 2, Zeszyt 3, p. 243-267.

[3] TAGGART (A. F.) and ARBITER (N.), 1943. — Am. Inst. Mining Met. Engrs., *Tech. Pub.*, n° 1585, p. 6.

[4] Flotacija silikatov i okislov. Trudi VIMS MG SSSR Gosgeoltehizdat 1961, vip. 6.

[5] EIGELES (M. A.), 1964. — Osnovi flotacii nesulfidnih mineralov. Izd-vo « Nedra «.

[6] ROGERS (S.) a.o., 1946. — Am Inst. Mining Met. Engrs. Mining Technology, July *Techn. Pub.* 2020.

[7] SUTHERLAND (K. L.), WARK (I. W.), 1954. — Principles of flotation. Melbourne.

[8] DESHPANDE (P. K.) and BHAT (G. N. J.), 1955. — Indian Inst. Sci., v. 37 A, p. 141-146.

[9] DOBIÁŠ (B. Z.), 1966. — Erzbergbau und Metallhüttenwesen, Bd 19, H. I., p. 27-31.

[10] DOBIÁŠ (B.) i dr, 1959. — Collection Czechoslov. Chem Commun., 24, p. 3668-3677. t.

[11] DOBIÁŠ (B.) i dr, 1966. — Collection Czechoslov. Chem Commun., t. 31, n° 1, p. 166-176.

[12] VIII Meždunarodnij kongress po obogoščeniju poleznih iskopaemih, t. II. L. Izd-e Instituta « Mehanobr», 1969 p. 502-504.

[13] SALATIĆ (D. V.), 1967. — Flotability of monazite and zirkon related to electrochemical changes on their surfaces. *Min. process. and Extr. Mettal*, vol. 76.

[14] Tetrja naućno-tehničeskaja konferencija UPI im S.M. Kirova. Tezisi dokladov. Sekcija metallurgičeskogo Fakulteta UPI. Izd-e Uralskogo politehn in-ta im S.M. Kirova. Sverdlovsk, 1970 vip. 1 p. 32.

[15] SUTHERLAND (K. L.) and WARK (I. W.), 1955. — Principles of flotation (Melbourne: Australasian Institute of Mining and Metallurgy), 489 p.

[16] FUERSTENAU (D. W.) et all., 1957. — How to use this modified Hallimond tube for better flotation testing. *Eng. Min J.*, 158, march, 93 p.

[17] Cases, Les phénomènes physicochimiques à l'interface. Application au procédé de la flottation. Thèse Doct. de sciences, Nancy 1967.

[18] IŠĆENKO (V. V.) et all., 1972. — Dejstvie geksameta fosfata i oleinovokislogo natrija na mineraly boksitov. *Cvetnajo metalurgija*, n° 5, p. 8-11.

[19] EIGELES (M. A.). — Osnovi flotacii nesulfidnijih mineralov (Moskva, « Nedra», 1964), p. 283-287.

[20] TAGGART (A. F.) et all.

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