УДК 622.7

Working Out
of Resource-Saving Technology
# of Enrichment of Phosphate-Raremetall Ores

Vera I. Bragina,
Natalia I. Konnova and Julia V. Sushkina*

Siberian Federal University,
79 Svobodny, Krasnoyarsk, 660041 Russia [1]

Possibility of complex use of phosphate-raremetall ores of the Tatar deposit is proved.
Results of researches of crystal-chemical features of the minerals which are a part of rejects of electric separation of ore-dressing plant of the Tatar deposit ores on which basis perspective reagents are chosen are stated.
Law of action of the chosen reagents on minerals of electric separation rejects is established.
On the reagents which have given the best indicators of flotation on monofractions, researches on rejects of factory with use of the multilevel factorial plan $3^3/9$ are conducted. It is received an apatite concentrate with the maintenance of P_2O_5 39,9 % at extraction of 98,5 %.

Keywords: rejects, flotation, the collector, a depressor, a regulator pH, apatite, quartz, a calcite, hydrogoethite, the maintenance, extraction.

Introduction

The riches of the soil of Siberia have a defining role of the future prosperity of Russia and its destiny. The center of the mining industry which scales should increase intensively is displaced to Siberia. Therefore especially sharply there is a question of working out of resource-saving technology and complex use of mineral resources.

The decision of this problem will allow to receive a number of valuable products for various branches of a national economy, and also to reduce pollution of areas adjoining to a deposit by a waste of the mining enterprises. Besides, use of technological schemes of complex processing of mineral raw materials promotes increase of economic indicators of manufacture.

The purpose of the given work is extraction of apatite from rejects of electric separation of factory of phosphate-raremetall ores enrichment.

The main source of reception of apatite is apatite and phosphorite ores. Phosphorus and its connections which are widely applied in various branches of a national economy and, especially, in the chemical industry are received from apatite.

---

* Corresponding author E-mail address: yulka-yulenka@mail.ru
[1] © Siberian Federal University. All rights reserved

However the basic volume of extracted apatite and phosphorite ores is used for reception of mineral fertilizers – the main source of increase of efficiency of agriculture and especially in Eastern Siberia, where the phosphorus maintenance in soil is almost on zero.

The general stocks of apatite and phosphorite ores of Russia for 2003, estimated as prepared for working out, were 480,2 million т P_2O_5, and requirements of Russia – 716 million т P_2O_5 [1].

In 2010-2015 the requirement for stocks of apatite and phosphorite ores will exceed their presence, and in 2030 they can be completely fulfilled. Therefore the great value is the complex ores containing apatite, for example, such are phosphate-niobium ores of the Tatar deposit [1].

Phosphate-rareometall ores possess a number of features. First, their mineral structure is more diverse, than nonferrous and ferrous metals ores. Secondly, the structure and textural features of these ores are very difficult. Thirdly, physical and physical and chemical properties of the minerals entering into their structure, are close among themselves. All it complicates technology of processing of these ores and often demands nonconventional methods of enrichment, and at flotation – applications special reagents besides usual [2, 3, 4].

The basic method of enrichment for allocation of a raremetall concentrate is gravitational (a jigging, tables, spiral separators, sluices), allowing to receive the draft low-grade concentrate then subjected operational development [2, 3].

Apatite allocation, basically, carry out by flotation [4, 5, 6, 7, 8].

Low cost of apatite concentrate demands application of cheap reagents. Therefore substitutes of fat acids or soaps are most widely used: sulphatic soap, таловое oil, a mix of fat acids, peat pitch and other reagents often in a mix with nonpolar collectors. Apatite can be floated also by amines [8].

Materials and methods of researches

Rejects of electric separation of ore-dressing plant contain 65 % of apatite, 15 % of quartz, 10 % of a calcite and 10 % hydrogoethite.

Influence of interposition of ions in a lattice on superficial properties of a mineral and specificity of interaction of superficial ions with water and reagents was investigated by consideration of structures of minerals.

For fuller studying of crystalchemical features of apatite, a calcite, hydrogoethite and quartz their infrared (IRS) and electronic-paramagnetic (EPS) spectra are removed.

Spectra IRS was removed on dual-beam spectrometer IRS-14. A prism from chloride sodium, calibrated on semistyrene spectra of indene and ammonia steams is applied in the device. Fine-grained minerals was plunged into vaseline oil or were pressed in bromic potassium for removal of spectra.

Spectra EPS was removed on radio spectrometer RE 1301 in usual conditions.

An apatite

The apatite group is presented by connections of type $A_5[XO_4]_3Z$ in which Sa^{2+}, Pb^{2+} play role of cations, and in the form of isomorphic impurity, sometimes TR^{3+}, y^{3+}, Mn^{2+} and Sr^{2+}, and F^{1-}, Cl^{1-}, OH^{2-} and CO_3^{2-} participate as additional anions.

Feature of this group is that complex anion PO_4^{3-} can be partially replaced by weaker anion SiO_4^{4-} but in a combination with stronger anion SO_4^{2-}.
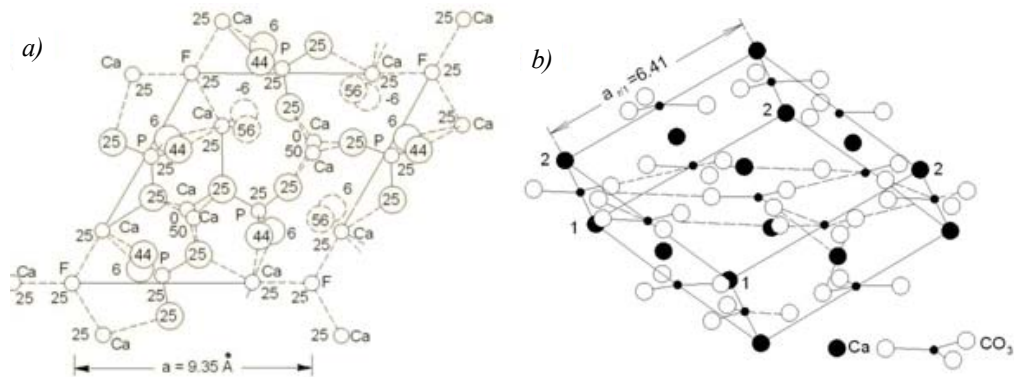
Fig. 1. A structure of an elementary cell of fluorapatite in a projection on 00010 (a) and an arrangement of ions in a cell of welding rhombohedron (1010) (b)

Studied apatite, according to mineralogical and chemical analyses, is presented by fluorapatite – Ca(PO4)$_3$F and practically doesn't contain impurity.

Fluorapatite crystallizes in hexagonal system, has a dypyramidal kind of symmetry with elements of symmetry Z_6PC.

The elementary cell in a projection to a plane (0001) looks like a rhombus (Fig. 1) on which tops ions of F^{1-} settle down sitting on sextuple screw axes in the center of hexane.

Calcium ions occupy double position. One of them settle down on long diagonals of rhombuses (on distance of one third of tops) on threefold rotary axes and form continuous chains (column) in parallel an axis C. In these columns each ion of Ca is connected with nine oxygen ions (with three below, three above and three approximately at level of the ion of calcium). With each other these columns are connected with the help of tetrahedral groups of RO_4 and, as a whole, form as though hollow inside the cylinder in which fluorine ions settle down on a channel axis. On walls of the same channels other ions of calcium and thus in such a manner that 3 ions of calcium are connected with each ion of fluorine at its level sit. As at the next levels of position of ions of calcium round a fluorine ion are turned on 180 ° as a whole not only these channels, but also all structure has hexagonal shape.

As communications in a crystal lattice fluorapatite concerns to heterodecmic connection with two types of communications: covalent and ionic: communications P – O almost covalent, and communications Ca – F – ionic. The infra-red spectrum of apatite has been removed for fuller and detailed studying of structure, and also mineral structure.

Position of strips of absorption of apatite completely (Fig. 2) coincides with the literary data. Thus absorption of 1650 and 1630 sm-1 is caused by deformation fluctuation H – O – H. Strips 1450, 1420, 1380 characterize fluctuations of hydroxyls, the strip 1110 – 964 – communication P – O. By mechanical destruction of a crystal lattice of fluorapatite rupture of communications will occur not in the area of P – O, and on lines of Ca – O and Ca – F, i.e. in any directions, the same features of a crystal lattice of fluorapatite practical is became clear by absence of cleavage at this mineral.

At rupture of lines of Ca – O and Ca – F the rupture surface should have alternate positive and negative potential, is possible with small prevalence of the last at the expense of shielding of ions of calcium by larger ions of fluorine and oxygen.
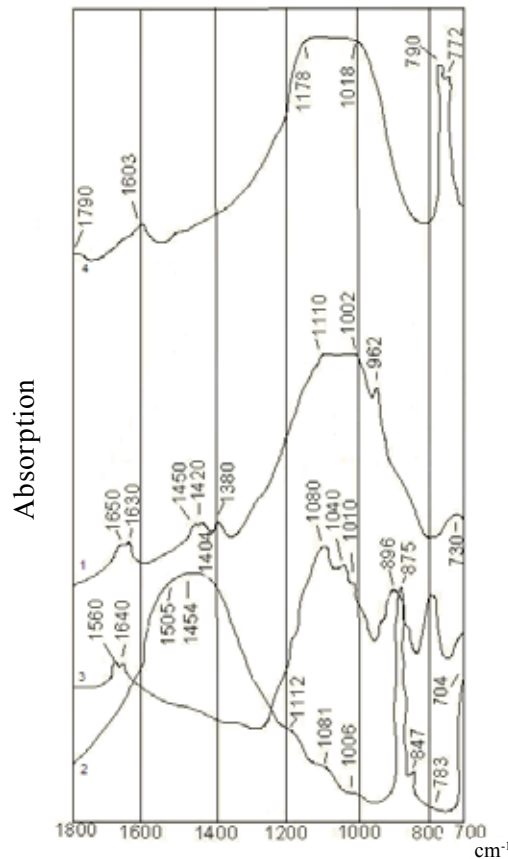
Fig.2. The infrared spectra of the absorption of the minerals: 1 – apatite, 2 – calcite, 3 – hydrogoethite, 4 – quartz

Destruction of a crystal lattice by a mechanical way leads to occurrence of neoradicals of superficial atoms which gather for the separate sites possessing in certain potential (potential holes). Redistribution ofcrystal ions is facilitated by presence of the broken layer of a surface and involves chemisorption of gases and steams that creates chemically active centers presented in most cases by hydroxyls of those atoms which enter into a mineral lattice. The further adsorption of flotation reagents leads to chemical reaction between hydroxyls of superficial atoms and difil substances. At a crystal lattice of apatite there are the atoms forming acid and basic hydrooxides on a surface.

Spectrum EPS of apatite consists of three lines with g-factors: $g_1=2,053\pm0,001$; $g_2=2,006\pm0,001$; $g_3=1,995\pm0,001$ (Fig. 3).

By method of EPS possibility of formation of radical CO_3^- has been shown at replacement $(PO_4)^{3-}$ in apatite structure on CO_3^{2-}.

Formation of radical CO_3^- is accompanied by simultaneous replacement F^- on O^{2-}.

Formation of radical CO_3^{3-} from CO_3^{2-} is accompanied by simultaneous occurrence of the hole center $- O^- - F^-$ ($g_{II}=2,000$; $g_I=2,052$).

Comparison of the received experimental values of g-factors with g-factors for radicals CO_3^{3-}, CO_3^-, $F^- - O^- - F^-$ allows to identify the paramagnetic centers observed in apatite (PC): CO_3^{3-} – the electronic center; CO_3^- – the hole center; $F^- - O^- - F^-$ – the hole center.
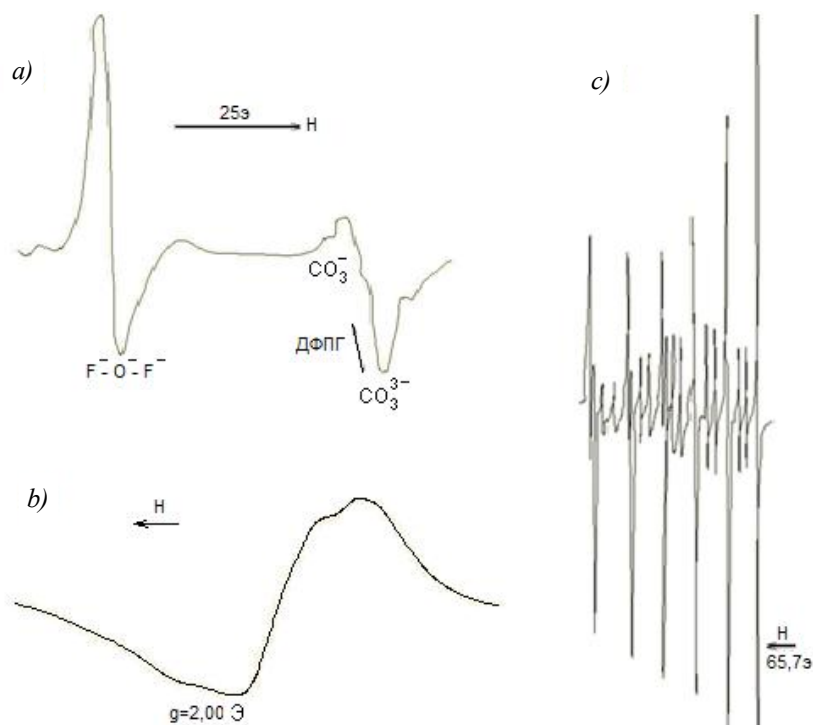
Fig. 3. Spectra EPS of apatite (a), hydrogoethite (b) and a calcite (c)

Besides, in investigated apatite spectrum EPS with width of a line 1000 – 1500 э and g=2,12–2,21 which can be caused trivalent ions of iron is observed.

On the basis of the above-stated, apatite should be floated by anion and cationic collectors, is thus more effective by cationic.

Calcite

The chemical compound of a studied calcite is close to described in the literature. The infra-red spectrum (Fig. 2) contains 4 basic strips of absorption (1454, 1081, 875, 704), characteristic for normal carbonates.

Basis of structure of a calcite is face-centered the rhombohedral cell representing deformed compression along an axis of symmetry of the third order a cubic elementary cell. Cube distortion is caused by presence at structure of the large flat groups CO_3 consisting of carbon atom in the center and three located round it and in tops of an equipotential triangle of atoms of oxygen.

The elementary cell has sharply extended form with a rhombohedral corner 46°07 ' whereas welding rhombohedron possesses a corner between sides of rhombohedron 101°55 '. Calcium ions lie in corners and in the cell center, and flat complex anions CO_3^{2-} settle down on the central threefold axis in return orientation to each other (Fig. 1b).

As communications in a crystal lattice the calcite is heterodesmic connection. In calcite structure there are 2 types of communication: C – O – almost purely covalent, and Ca – O – more ionic which make 62 % of all communications.

Forces of covalent communication between carbon and oxygen in groups SO3 make 4⁄3 (a charge of Ca=4, coordination number 3) whereas forces of communications between Ca and O are equal only 1⁄3 (a charge of Ca=2, coordination number 6). Hence, oxygen in a calcite is much more strongly connected with carbon, than with calcium; rupture at mechanical influence will occur in the area of Ca – O, along planes of perfect cleavage on rhombohedron.

Anions of CO_3 are located in an extreme external layer; access to calcium cations is a little complicated, than to anions (Fig. 1b). Electrostatic charges on a surface are distributed in regular intervals. The size of noncompensated superficial charges is insignificant (identical to all cations and anions) and makes +1⁄3 and-1⁄3.

The widespread impurity meeting in a calcite, is bivalent manganese.

In an investigated calcite observable spectrum EPS (Fig. 3 see) is caused by ions Mn^{2+}, isomorphically replacing Ca^{2+}. G-factors and constants of superthin influence of manganese ions are g=2,0030±0,0005; a=95±1 э.

Besides described spectra Mn^{2+} spectrum EPS with width of a line more than 1000 э and g=2,12 which can be carried to iron (III) is observed also.

Hydrogoethite (limonite) $H \cdot FeO_2$.

The crystal structure [9] is characterized by dense hexagonal packing of ions O^{2-}, and ions Fe^{3+} take place in octahedral emptiness, i.e. between six ions of O. Each ion of oxygen is connected with three ions of Fe. Hence, hydrogoethite should badly be floatable as anion, and cation collectors.

The basic paramagnetic ions in hydrogoethite are Fe^{3+}.

The spectrum of an electronic paramagnetic resonance of hydrogoethite represents very wide single line (Fig. 3 see) which g-factor is equal 2,003.

Quartz SiO_2

Studied quartz actually had no impurity. It contained 98 % of dioxide of silicon and 0,05 % of a five-oxide of phosphorus. The crystal structure of quartz is characterized by that ion Si^{4+} always is in the fourth environment of ions O^{2-} located on tops of a tetrahedron. Each top of such tetrahedron simultaneously serves as top for other adjacent tetrahedron (Fig. 4). Thus, the crystal lattice of quartz consists as though of skeletons of the tetrahedrons linked with each other, and coupling occurs through tops of tetrahedrons. Quartz is characterized by very dense packing of tetrahedrons that causes high hardness of quartz and absence cleavage (bad cleavage on (1010), in three directions). Therefore at mechanical crushing the mineral will break up in any directions, and rupture of communications occurs in the area of Si – O. Thus siloxane groups $Si – O – Si^1$ and ions SiO^- and Si^+ are bared on a surface of quartz crystals. In water ions SiO^- and Si^+ are hydrolyzed and form silanol groups of SiOH (Fig. 4). Interaction of dissociated silanol groups with water in 6 times exceeds the general interaction of a surface of quartz with water. Approximately it is possible to consider that 50 % of a surface of split of quartz are occupied by siloxane groups and 50 % – silonol one. Thus only about 50 % it is occupied the dissociated silanol groups defining the general weak water repellency of all surface of quartz. This data specifies that quartz should be floated by basically the cation collector.

On the basis of the received data reagents anion and cation type are chosen: FATO, FLON-8, Armac T, Duomeen T, FLON-1.
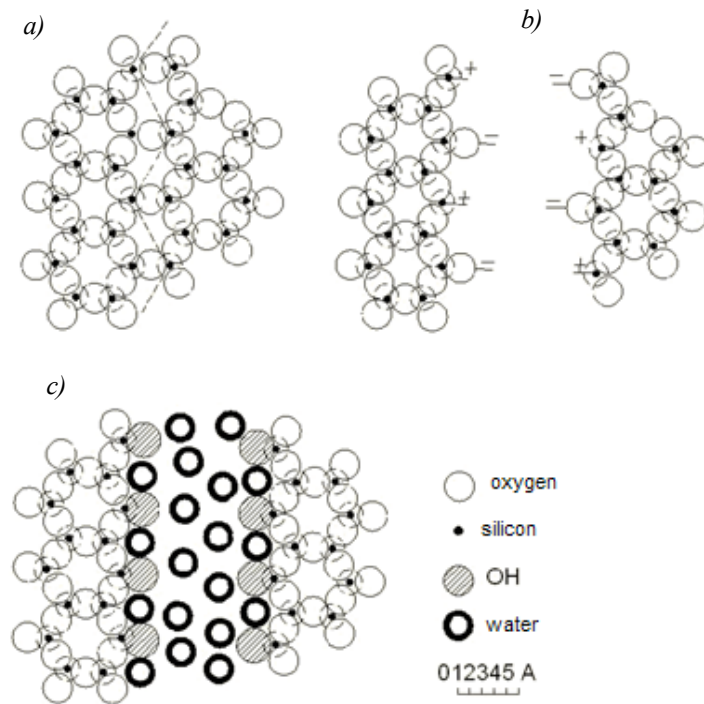
Fig. 4. A crystal structure of quartz: a – quartz structure; b – a split surface in air; c – a surface of split of quartz in water

Working out of a mode of flotation

FATO are fat acids of tal oils which are a product of vacuum rectification crude tal oils.

The fraction of fat acids turns out after branch of fractions of a tal pitch, tal rosin and distilled tal oils, and also fractions nonsaponifying substances.

FATO possesses high collective ability in relation to apatite already at low expenses (Fig. 5), a little smaller – to a calcite, it is considerable smaller to hydrogoethite and especially to quartz. The greatest difference in extraction of apatite and dead rock minerals (50 %) is reached at the expense 0,5 kg/t.

FLON-8 – the cation collector. It is domestic analog of the foreign reactant synthesized on the basis of synthetic diamines, neutralized by organic acids. Chemically it is a diacetate of alkylpropylenediamine $[R_1 - NH_2 - CH_2 - CH_2 - CH_2 - NH_3]_2 R_2 COO$. It gives good foam which badly collapses.

At expense of FLON-8 0,25kg/t selectivity of division of apatite from dead rock minerals is 30 %. The increase in the expense from 0,5 to 2 kg/t leads to that apatite, quartz, a calcite are practically identical floated, i.e. only hydrogoethite can be separated from apatite and that partially (Fig. 5).

Armac T – $[R_1 - NH_2-]CH_3COO$, where R_1 – the rest of fat acids of таллового oils.

At increase in the expense from 0,1 to 0,6 kg/t (fig.6) flotation passes not selectively. A difference in extraction of apatite and quartz no more than 10 %, and apatite and a calcite (since 0,3 kg/t) – 20 %. Thus, Armac T is even less selective, than FLON-8.

Duomeen T – alkyl of diamines with the general formula $R - NH - (CH_2)_3 - NH_2$, where R – alkyl with a direct chain, basically $C_{16} - C_{18}$.
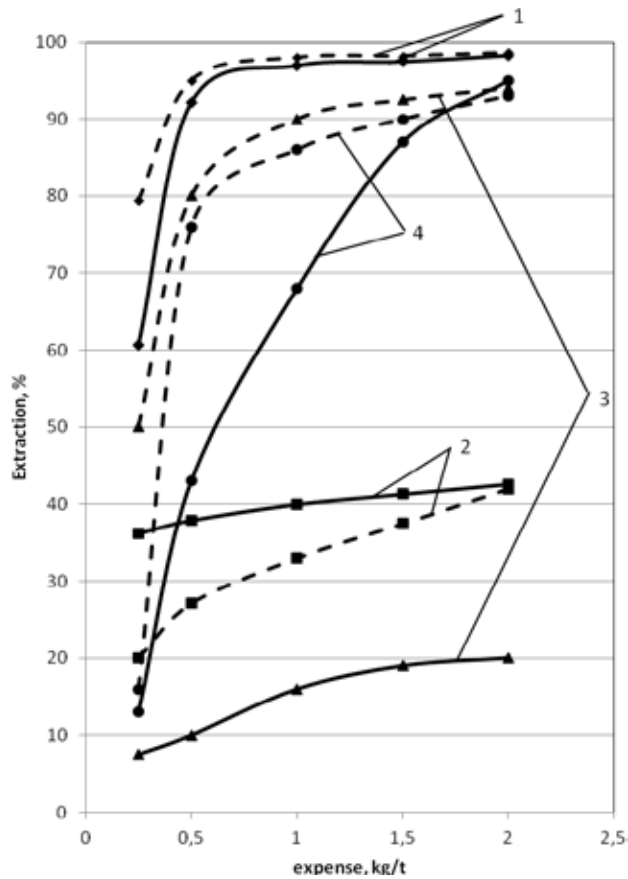
Fig. 5. Influence FATO (continuous lines) and FLON-8 (dashed lines) on flotation of minerals: 1 – apatite; 2 – hydrogoethite; 3 – quartz; 4 – a calcite

At increase in expense Duomeen T about 0,1 kg/t to 0,6 kg/t (Fig. 6) apatite extraction practically doesn't change and there is at level of 97-99 %, but a quartz extraction is also high (75–90 %). The greatest difference in extraction of apatite and minerals of dead rock is 10 %. Hence, this reagent also isn't selective.

FLON-1 is an acetate of primary amines with R=14.

FLON-1 just as FLON-8, Armac T and Duomeen T igood floate apatite, a calcite and quartz (Fig. 7), without allowing to divide them.

Thus, the most selective collector for branch of apatite from a calcite, hydrogoethite and quartz are FATO and to a lesser degree – FLON-8.

In this connection, FATO and FLON-8 have been chosen by the collector at researches on reception of conditioned concentrates from rejects of electric separation of factory by a method of statistical planning of experiment.

Optimum values of expenses of reagents are defined: soda – 5kg/t, alkali silicate – 4 kg/t, FATO – 0,5 kg/t, FLON-8 – 0,15 kg/t.

It is received conditioned apatite concentrate with maintenance of P_2O_5 38,4% and extraction of 95,7%.
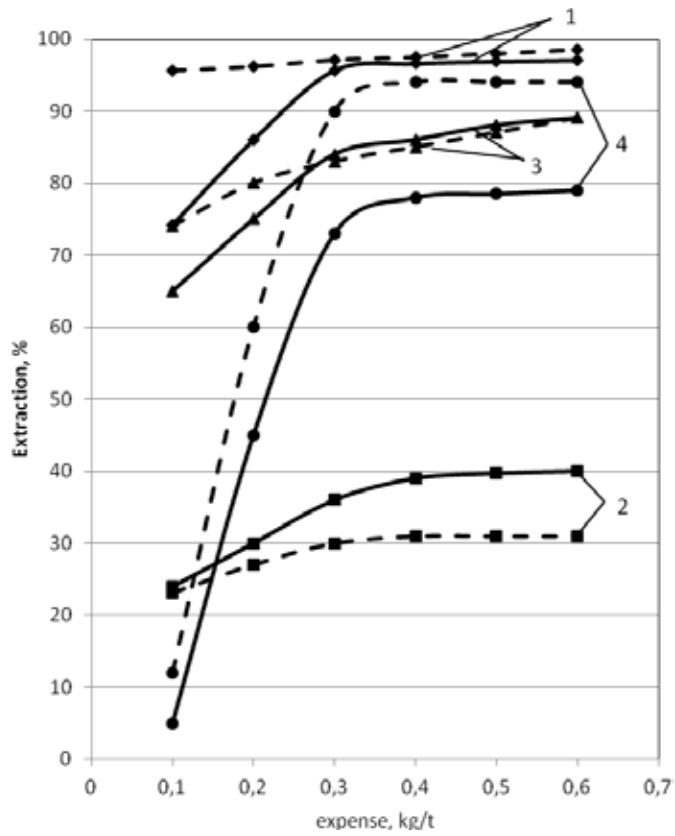
Fig. 6. Influence of Armac T (continuous lines) and Duomeen T (dashed lines) on flotation of minerals: 1 – apatite; 2 – hydrogoethite; 3 – quartz; 4 – a calcite
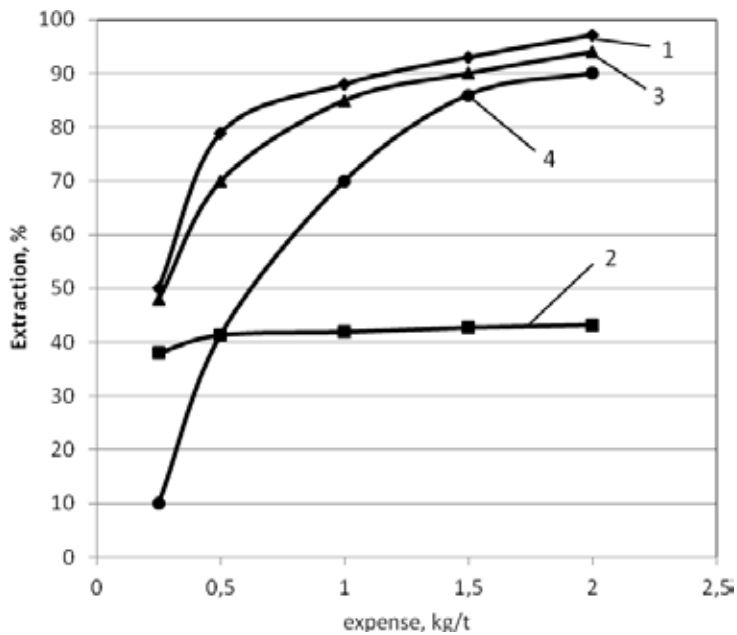

Fig. 7. Influence of FLON-1 on flotation of minerals: 1 – apatite; 2 – hydrogoethite; 3 – quartz; 4 – a calcite

Conclusions

1. Influence of interposition of ions in a mineral lattice on its superficial properties and interaction with water and reagents is shown.

2. Laws of action of anion and cation reagents on minerals floatability are established.

3. The technology of extraction of apatite from rejects of electric separation of factory phosphate – niobium ores of the Tatar deposit, allowing to receive an apatite concentrate with maintenance P_2O_5 of 39,9% at extraction 98,5 is developed.

4. The suggested technology provides possibility to organize complex enrichment of phosphate-raremetall ore of the Tatar deposit with reception of commodity products: niobium and apatite concentrates.

5. The established laws and flotation modes can be used for working out of technologies of enrichment of apatite, phosphorite and complex apatity-nepheline and other ores.

References

[1] About a condition of a mineral-raw-material base of the Russian Federation 2003. URL: http://www.mineral.ru/Chapters/Production/Issues/35/IssueFiles.html

[2] *Bragina V. I, Bragin V. I.* Enrichment of phosphate-raremetall ores. Krasnoyarsk: SANM&G, 2002.

[3] *Bragina V. I, Bragin V. I.* Enrichment and complex use phosphate and phosphate-raremetall ores of Eastern Siberia. Krasnoyarsk: SANF&G, 1996.401c.

[4] *Abramov A.A.* Processing, enrichment and complex use of firm minerals. T.2. M: Publishing house Mosk.st.min.un, 2004.508p.

[5] *Abramov A.A., Magazanik D.V.* Theoretical substantiation of optimum values of concentration of the collector and pH pulps at flotation of not sulphidic minerals // Phisic-tehn. problems devel. minerals. 2006 №2. Page 89-99.

[6] *Bragina V. I, Kisljakov V. E.* Phosphate ores of Krasnoyarsk region. The Minera-raw-material base, technologies of enrichment. Krasnoyarsk: SANF&G, 2006. 387 p.

[7] *Abramov A.A.* Flotation enrichment methods. M.:MSTU, 2008.707 p.

[8] *Shokhin V. N, Shuvakova N.K., Treushchenko N.A.* Flotation enrichment of phosphate ores. M: Nedra, 1991.

[9] *Betehtin A.G.* The course of mineralogy. M: the Book house "University", 2010. 736 p.

[10] *Godovikov A.A.* Mineralogy. M: Nedra, 1983. 647 p.

Разработка ресурсосберегающей технологии обогащения фосфатно-редкометалльных руд

В.И. Брагина,
Н.И. Коннова, Ю.В. Сушкина

Сибирский федеральный университет,
Россия 660041, Красноярск, пр.Свободный, 79

Доказывается возможность комплексного использования фосфатно-редкометалльных руд Татарского месторождения.

Изложены результаты исследований кристаллохимических особенностей минералов, входящих в состав хвостов электрической сепарации обогатительной фабрики руд Татарского месторождения, на основе которых выбраны перспективные реагенты.

Установлена закономерность действия выбранных реагентов на минералы хвостов электрической сепарации.

На реагентах, давших лучшие показатели флотации на монофракциях, проведены исследования на хвостах фабрики с использованием многоуровневого факторного плана $3^3/9$. Получен апатитовый концентрат с содержанием 39,9% P_2O_5 при извлечении 98,5%.

Ключевые слова: хвосты, флотация, собиратель, депрессор, регулятор pH, апатит, кварц, кальцит, гидрогетит, содержание, извлечение.