*Journal of Mining Science, Vol. 46, No. 3, 2010*

**LOWER TEMPERATURE FLOTATION OF CARBONATE-FLUORITE ORES**

**L. A. Kienko, L. A. Samatova, O. V. Voronova, and S. A. Kondrat'ev***

UDC 622.7:553.068.5

The authors provide insight into the problem of selective flotation of fluorite from carbonate-fluorite ores. It is found that oxyhydrate collectors used in combination with sodium fluoride provide rather high level of selectivity in fluoride flotation from poor high-carbonate ores and make it possible to eliminate high-temperature pulp treatment with acceptable reduction in the flotation temperature to 15°C and below.

*Carbonate-fluorite ores, selective flotation, adsorption, low-temperature mode, modifying agent, degree of dispersion*

Selective flotation of fluorite from carbonate-fluorite ores refers to a general problem of flotation separation of calcium-bearing minerals exhibiting close physic-chemical surface properties. The main targets of researches into flotation processes developed to separate minerals containing calcium cations in their crystalline lattice are to establish and to use fine distinctions in crystal-chemical properties of mineral components and to provide conditions for more pronounced contrast between adsorption surface characteristics of mineral particles.

The Yaroslavl Mining Company processes carbonate-fluorite ores from the Russia's largest Voznesensky deposits in the Primorski Krai as basic raw mineral resource. The ores are rather complex and difficult to float. Moreover, they contain calcium-bearing minerals: fluorite and calcite exhibiting close flotation properties and exclusively fine intergrowth of mineral components. Satisfactory exposure of mineral grains can be gained with grinding down to $-0.044$ mm size 85 – 95% in mass with inevitable abundant formation of fine slimes. Selectivity for minerals worsens with reduction in carbonate module, expressed as a ratio of fluorite content in ore to calcite content ($M_k = \alpha_{CaF_2} / \alpha_{CaCO_3}$). Last years the Company faces a tendency of ore grade deterioration as for fluorite content with respective lower carbonate module.

In practice, processes for selective recovery of valuable calcium-bearing minerals generally involve high-temperature pulp treatment with addition of calcium depressors, including such highly toxic compounds as hexafluorosilicate, sodium silicate, lignosulphonates [1 – 3]. The design flowsheet of the Yaroslavl ore-preparation plant (Fig. 1) involves the rougher and control flotation circuits and 6 – 8 rough concentrate recleaning stages, as well as additional flotation of fluorite from intermediate underflow products at a separate circuit. Besides, two-staged high-temperature treatment was provided: the first stage was treatment of the ground ore at 50 – 65°C; in the second stage the froth product of the second recleaning was steamed at 65 – 85°C concurrently with sodium hexafluorosilicate treatment. However, this technology did not guarantee the required performance level. Ores with carbonate module below 2.5 – 3 were rejected

Institute of Mining, Far East Branch, Russian Academy of Sciences, Khabarovsk, Russia. *Institute of Mining, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia. Translated from Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh, No. 3, pp. 97-104, May-June, 2010. Original article submitted March 23, 2010.

1062-7391/10/4603-0317 

as waste products. High costs of the ore-preparation circuit due to high heat and electric energy consumption under rigorous conditions of chronic deficit and ever-growing costs of energy carriers made the grounds for new approaches, comprehensive investigation, and substantiation of mechanisms to control surface properties of mineral particles and to develop new efficient technologies.

Researchers, Institute of Mining, FEB RAS, developed a new process for selective fluorite flotation from finely disseminated carbonate-fluorite ores with no high-temperature pulp treatment. This very important R&D finding was based on the comprehensive studies of physicochemical properties of fluorite and calcite monofractions, the dependence of their flotation activity on a type and consumption of collectors, modifying agents, and medium characteristics [4 – 6]. It was found that sodium fluoride addition to Flotol-7.9 and Asparal-F promotes higher reagent selectivity to fluorite and appreciably improves the flotation efficiency. Recovery of $CaF_2$ into concentrates of the similar grade increases by 4.45 and 3.9 %, respectively. The 7 – 10 % increase in calcite extraction into tailings at head stages also confirms the higher level of selectivity of the process. The combination of tall-oil fatty acids, exhibiting not outstanding selectivity to fluorite, and sodium fluoride, used as collecting agents, allowed that concentrates of the prescribed grade were produced at the satisfactory recovery of $CaF_2$ at temperature mode of the rougher flotation within 23 – 25$^{o}$C without any thermal pulp treatment.

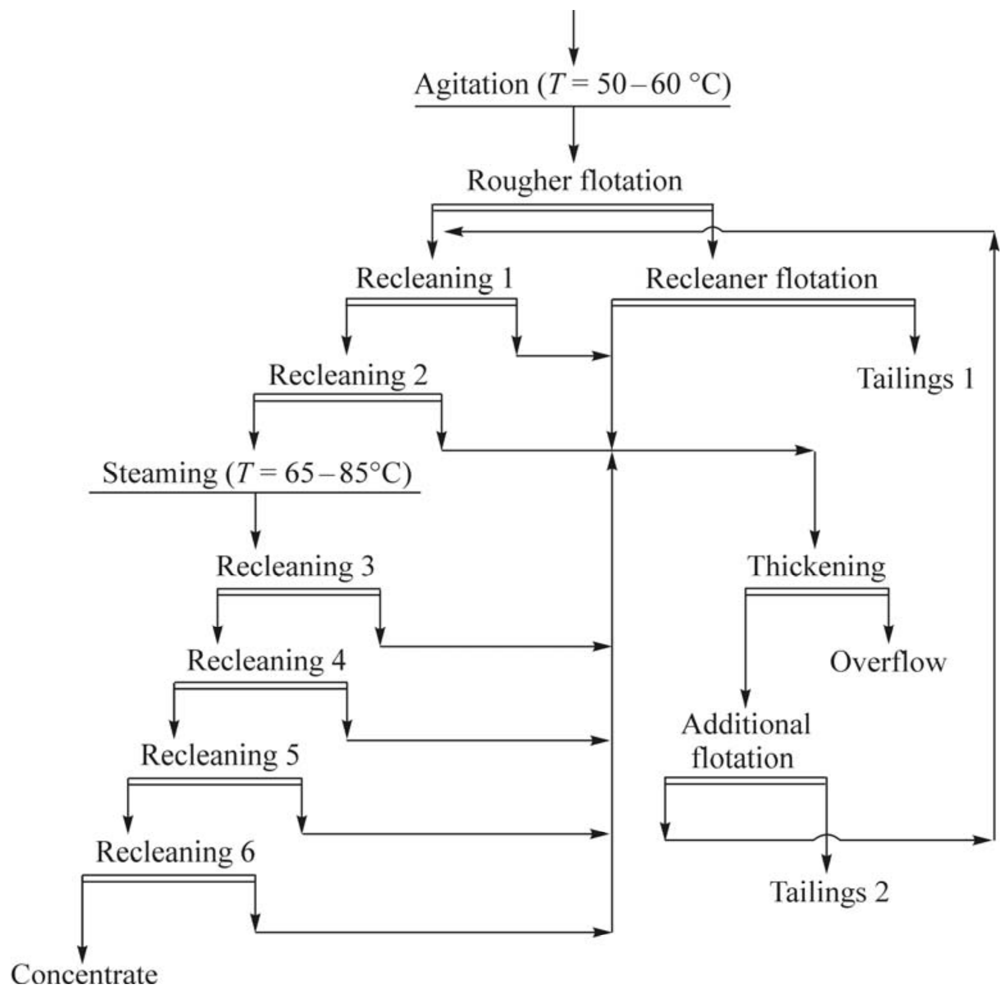


Fig. 1. Flotation circuit with high-temperature pulp treatment

The mechanism for improved selectivity when collectors are used in combination with sodium fluoride, in authors' view, can be explained by formation of fluorine-bearing associates, characterized by higher affinity to fluorite rather than to calcium carbonates. Furthermore, we should take into account that in the vicinity of solid – liquid interface there is an intermediate layer where mineral molecules and their atoms exist in a semi-solved state and exhibit much higher mobility as compared to its internal volume [7, 8]. Fluorite activation can be explained by restructuring of the fluorite surface layer under action of fluorine ion excess, delivered by sodium fluoride. Thereto, the calcite surface is neutralized by $F^-$ anions due to greater force of their interaction with $Ca^{2+}$ cations as compared to $CO_3^{2-}$ anion of the mineral. So it is required much less energy to provide the contact between oxyhydrate collectors and the prepared-in-this-way mineral surface. The process runs efficiently at 25 – 30ºC and even at 20 – 25ºC when the specific reagent combination is used.

The full-scale implementation of the selective carbonate-fluorite ore flotation to recover fluorite without high-temperature pulp treatment at the ore-preparation plant of the Yaroslavl Mining Company made it possible to cut down the thermal energy costs and to work profitably in the times of the economic crisis (Fig. 2).

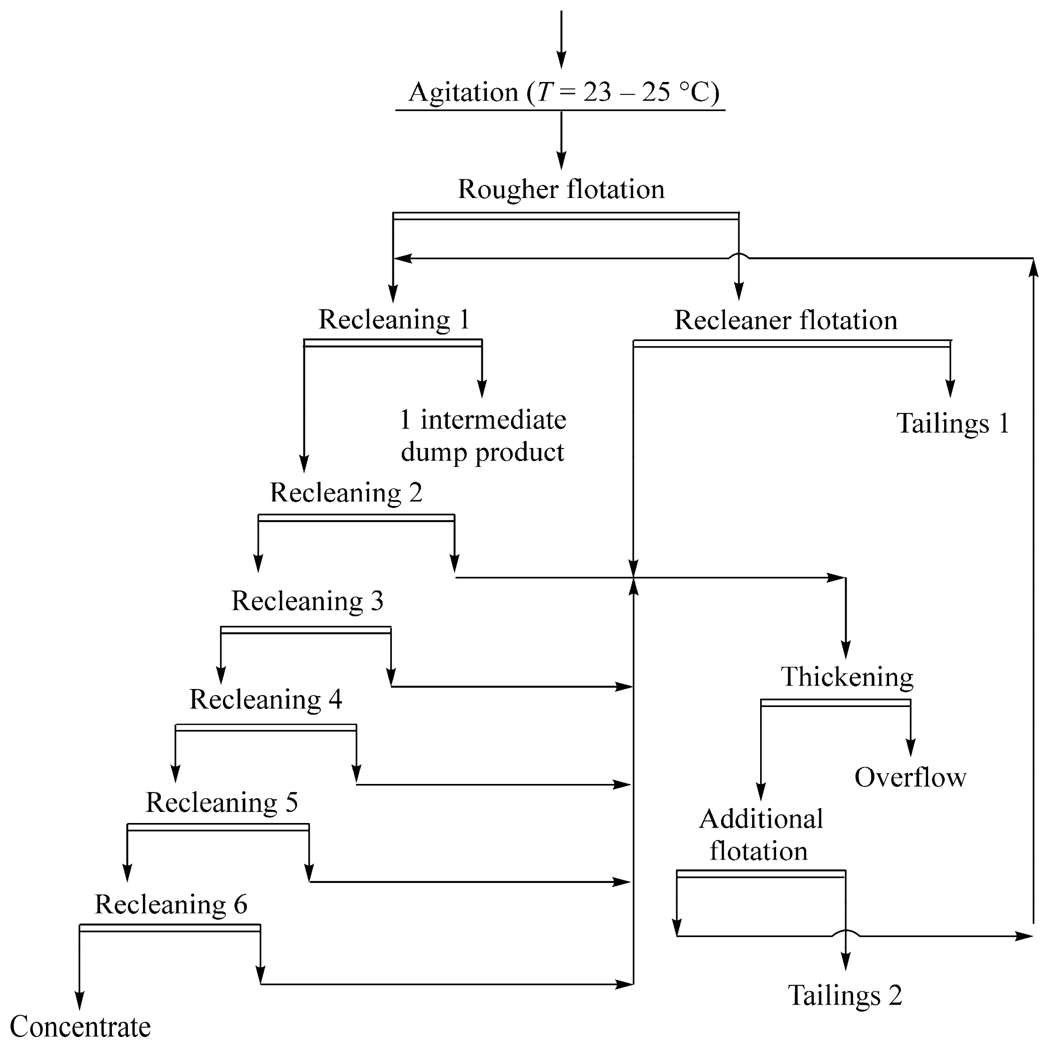


Fig. 2. Updated flotation flowsheet

It is known that the fatty-acid collectors, used to float different mineral ores, work at the temperature mode within at least 20 – 25ºC [1, 7, 8]. As a rule, lower pulp temperature leads to the worse collector dispersion, thereto the degree of fatty-acid dissociation lowers, selectivity of flotation is disturbed and negatively effects technological parameters. Flotation of finely-ground ores with high slime proportion gives a rise to other problems. Moreover, the use of return water with high concentration of different salts, including $Ca^{2+}$ cations, provokes formation of hardly soluble compounds $(RCOO)_2Ca$ from a portion of collector molecules. High concentration of these compounds inevitably suppresses the adsorption activity. Negative factors relating to the use of fatty acids in mineral flotation at lower temperatures can be partially eliminated by employing modifying agents which lower formation of colloidal oxyhydrate compounds and maintain a higher degree of their dispersion. It was established from the experimental data that organic temperature-regulating modificating agents (OTCMA) belonging to oxyethylized compounds are applicable as dispersing additions to fatty-acid collectors and appreciably improve parameters of the fluorite flotation proceeding at temperature below 15ºC. The tests were performed on the present-day ore feed: $CaF_2$ — 30.6 %, $CaCO_3$ — 18.4 % of the Yaroslavl ore-preparation plant.

As the comparative analysis of kinetics for fluorite flotation at 12 and 25ºC with additions to a dispersing collector and without it show that OTCMA normalizes the rougher fluorite flotation at temperature of 12ºC. Experimental data were used to calculate the concentration parameters and flotation characteristics.

Index of selective flotation:

$$I_c = \frac{(\varepsilon_{\mathrm{CaF_2}})_i}{(\varepsilon_{\mathrm{CaCO_3}})_i},$$

where $\varepsilon_{\mathrm{CaF_2}}$, $\varepsilon_{\mathrm{CaCO_3}}$ is recovery into froth product $CaF_2$ and $CaCO_3$, %; $i$ is serial number of flotation in terms of sampling time. Concentration efficiency $E$ is the Hancock criterion:

$$E = \frac{\gamma_i(\beta_i - \alpha)}{\alpha(100 - \alpha)},$$

where $\gamma$ is froth product yield; $\beta_i$ is $CaF_2$ content in froth product; $\alpha$ is $CaF_2$ content in ore.

Curves of time variations in $CaF_2$ content in a froth product of the rougher flotation, concentration factor and selectivity factor are presented in Fig. 3*a* – *c*.

As the experimental data show the dispersing modifier substantially improves flotation parameters. Thus, higher position of curves for flotation with OTCMA additions demonstrates higher values of respective parameters. Temperature, lowered from 25°C to 12ºC, results in a bit lower flotation efficiency [4]. Nevertheless, efficiency remains higher as compared to one in tests with no OTCMA additions.

Comparative results cited in the Table demonstrate the carbonate-fluorite ore flotation, involving 6 recleanings of the rough fluorite concentrate in an open cycle with fresh and return water at lower temperature (10 – 12ºC).

In the first series of tests the employed collectors were fatty acids of tall oil or industrial soap with no addition of dispersing agents. The same collectors in combination with OTCMA were used in the second series. From the experimental data obtained it can be concluded that flotation with no dispersing agent additions fails to produce fluorite concentrates of the required grade (minimum 90 % $CaF_2$ concentrate in our case). The concentrates of 91.56 – 92.75 % $CaF_2$ in grade are produced at flotation with OTCMA additions and this stable result is quite satisfactory for the open-cycle tests on recovery of fluorite as a concentrate. The above reported results are considered as rather high for the grade of study ores: finely disseminated poor-fluorite (26.2 – 30.55 % $CaF_2$), high-carbonate (17.63 – 25.31 % $CaCO_3$) ores.

The reported research work is of the current interest with high potential for commercialization and of particular value for the Yaroslavl Mining Company because of progressing deterioration of mineral ore grade and worse technological parameters in the mineral ore processing circuit. In the period from 2006 to 2009, $CaF_2$ content in ores declined from 35 – 39 to 25 – 30 %. On contrary, $CaCO_3$ content increased from 8 – 10 to 17 – 20 % and higher, thus the specific costs per 1 ton of fluorite concentrate produced escalated substantially. In view of the above, it is reasonable to go on with development of the process with lower flotation temperature as one of ways to surmount the complicated economical situation in winter, in particular.

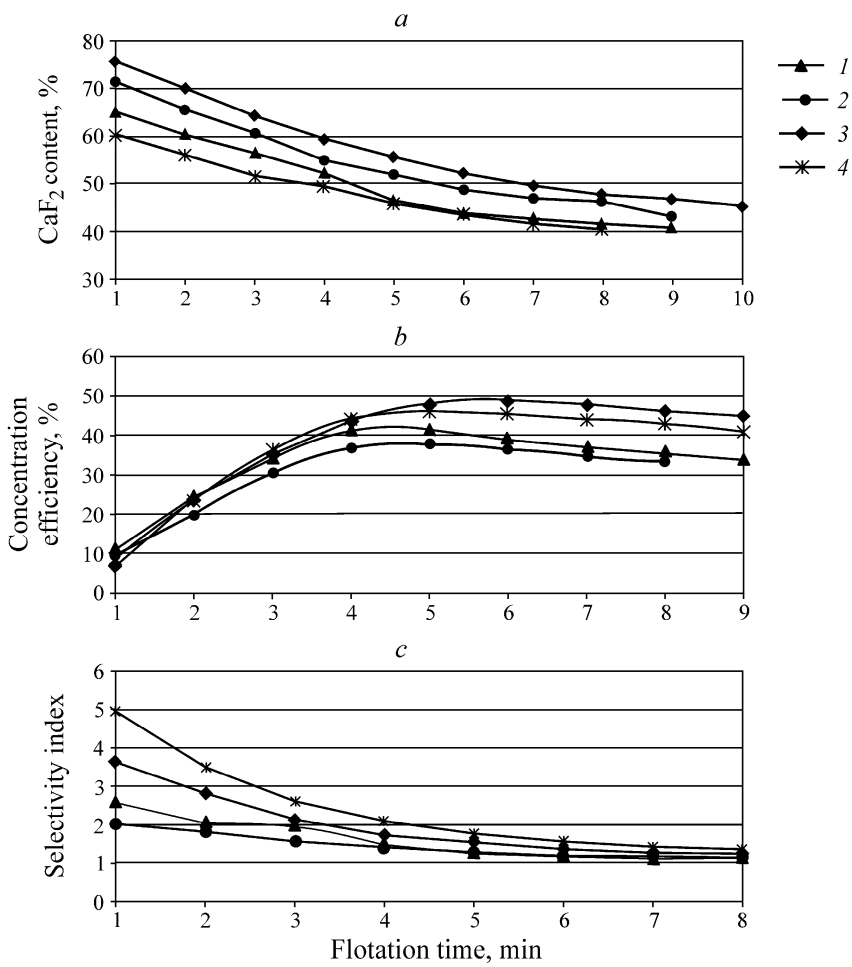


Fig. 3. Influence of temperature and OTCMA doses on the grade of the froth product in rougher fluorite flotation (*a*); dependences of time variations in concentration efficiency on temperature and OTCMA doses (*b*), and selectivity index for separation of fluorite and calcite on temperature of flotation and OTCMA doses (*c*): *1* — $T$ = 25°C, without OTCMA; *2* — $T$ = 12°C, without OTCMA; *3* — $T$ = 25°C, with OTCMA dosage; *4* — 12°C, with OTCMA dosage

TABLE. Flotation of High-Carbonate-Fluorite Ore

| Number | Product | Yield, % | Content, % | | Recovery, % | | Test conditions |
|---|---|---|---|---|---|---|---|
| | | | $CaF_2$ | $CaCO_3$ | $CaF_2$ | $CaCO_3$ | |
| With no OTCMA | | | | | | | |
| 1 | Concentrate | 25.74 | 84.07 | 10.08 | 70.83 | 14.14 | $T_{\text{rough flot.}}$ — 11°C; Collector — fatty-acid of tall oil Flotation with fresh water |
| | End product 1-2 | 24.87 | 12.46 | 23.47 | 10.14 | 31.53 | |
| | End product 3-6 | 15.16 | 26.15 | 44.93 | 12.98 | 37.12 | |
| | Tailings | 34.23 | 5.40 | 9.23 | 6.05 | 17.21 | |
| | Ore | 100.00 | 30.55 | 18.35 | 100.00 | 100.00 | |
| 2 | Concentrate | 18.64 | 88.92 | 5.15 | 61.42 | 5.27 | $T_{\text{rough flot.}}$ — 12°C; Collector — industrial soap; Flotation with return water |
| | End product 1-2 | 30.27 | 12.73 | 30.34 | 14.28 | 50.46 | |
| | End product 3-6 | 13.55 | 32.84 | 37.20 | 16.49 | 27.69 | |
| | Tailings | 37.54 | 5.62 | 8.04 | 7.81 | 16.58 | |
| | Ore | 100.00 | 26.3 | 18.17 | 100.00 | 100.00 | |
| With OTCMA | | | | | | | |
| 1 | Concentrate | 22.2 | 92.50 | 3.12 | 67.82 | 3.92 | $T_{\text{rough flot.}}$ — 11°C; Fatty-acid of tall oil + OTCMA = 5:1; Flotation with fresh water |
| | End product 1-2 | 29.45 | 13.67 | 30.21 | 13.29 | 50.45 | |
| | End product 3-6 | 11.63 | 35.88 | 36.70 | 13.78 | 24.21 | |
| | Tailings | 36.72 | 4.21 | 10.28 | 5.11 | 21.42 | |
| | Ore | 100.00 | 30.28 | 17.63 | 100.00 | 100.00 | |
| 2 | Concentrate | 21.58 | 91.56 | 3.22 | 65.20 | 3.67 | $T_{\text{rough flot.}}$ — 13°C; Industrial soap + OTCMA = 5:1; Flotation with fresh water |
| | End product 1-2 | 27.36 | 13.88 | 30.81 | 12.53 | 44.52 | |
| | End product 3-6 | 12.90 | 34.03 | 32.14 | 14.49 | 21.90 | |
| | Tailings | 38.16 | 6.18 | 14.84 | 7.78 | 29.91 | |
| | Ore | 100.00 | 30.30 | 18.93 | 100.00 | 100.00 | |
| 3 | Concentrate | 19.82 | 92.28 | 1.98 | 67.83 | 2.22 | $T_{\text{rough flot.}}$ — 10 – 12°C; Fatty-acid of tall oil + OTCMA = 3:1; Flotation with return water |
| | End product 1-2 | 24.84 | 10.96 | 29.21 | 10.10 | 41.00 | |
| | End product 3-6 | 12.96 | 31.38 | 40.15 | 15.08 | 29.41 | |
| | Tailings | 42.38 | 4.45 | 11.43 | 6.99 | 27.37 | |
| | Ore | 100.00 | 26.96 | 17.70 | 100.00 | 100.00 | |
| 4 | Concentrate | 18.66 | 92.75 | 2.82 | 65.17 | 2.08 | $T_{\text{rough flot.}}$ — 10 – 12°C; Industrial soap + OTCMA = 3:1; Flotation with return water |
| | End product 1-2 | 22.83 | 8.40 | 34.87 | 7.20 | 31.46 | |
| | End product 3-6 | 22.42 | 23.81 | 50.32 | 20.10 | 44.58 | |
| | Tailings | 36.09 | 5.54 | 15.34 | 7.53 | 21.88 | |
| | Ore | 100.00 | 26.96 | 25.31 | 100.00 | 100.00 | |

## CONCLUSIONS

1. Oxyhydrate collectors in combination with sodium fluoride, used to float poor finely-disseminated carbonate-fluorite ores, provide the acceptable flotation selectivity and make it possible to eliminate the high-temperature pulp preparation cycle. The flotation runs at pulp temperature ranging within $23-25^{o}C$.

2. Negative factors affecting the stability of the process when flotation temperature falls down to $15^{o}C$, can be avoided. The dispersing modifiers depress formation of colloids and activate action of the collector.

3. Comparative analysis of kinetics in flotation of carbonate-fluorite ores shows that fatty-acid collectors, used in combination with dispersing agents, produce the higher-grade froth product, improve selectivity and concentration efficiency at as low as $12^{o}C$ temperature as well.

4. It is found that 91.56 – 92.75 % $CaF_2$ concentrates can be produced from poor high-carbonate ores at the lower-temperature flotation ($12^{o}C$) with fluorite recovery, acceptable for the open-cycle tests.

*The study was conducted with financial support from the Siberian Branch of the Russian Academy of Sciences, Integration Project No. 124.*

## REFERENCES

1. L. A. Barsky, O. V. Kononov, and L. I. Ratmirova, *Selective Flotation of Calcium-Bearing Minerals* [in Russian], Nedra, Moscow (1979).
2. G. M. Adosik, et al., "Russian Federation Patent No. 2192314. Process for flotation of calcite-fluorite ores," *Byul. Izobret.*, No. 31 (2002).
3. A. Day and H. Hartjens, *US Patent No. 3830366*. *Mineral Flotation with Sulfosuccinamate and Depressant*, American Cyanamid Company (1974).
4. L. A. Samatova, L. A. Kienko, O. V. Voronova, and L. N. Plyusnina, "Theoretical foundation for selective flotation of calcium-bearing mineral constituents of the Primorski Krai ores," in: *International Science and Practice Conference proceedings "Integrated Mineral Development Issues"* [in Russian], GIAB (2005).
5. L. A. Kienko, L. A. Samatova, G. Yu. Zuev, et al., "Fluorite flotation from carbonate ores," *Obog. Rud*, No. 4 (2007).
6. L. A. Kienko, L. A. Samatova, G. Yu. Zuev, et al., "Russian Federation Patent No. 2286850. Process for fluorite ore processing," *Byul. Izobret.*, No. 31 (2006).
7. O. S. Bogdanov, *Theory and Process for Ore Flotation* [in Russian], Nedra, Moscow (1990).
8. M. A. Eigeles, *Fundamentals of Nonsulfide Mineral Flotation* [in Russian], Metallurgizdat, Moscow (1964).