Evaluation of the influence of the dispersion-sludge characteristics of the pulp on the beneficiation indicators of technogenic fluorite-containing tailings

Lydia Kienko^{1*} and Olga Voronova¹

¹Mining Institute FEB RAS, 51 Turgenev st., Khabarovsk, 680000, Russia

Abstract. The article provides an assessment of the technological features of mature tailings from the processing of finely disseminated fluorite-containing raw materials of the Yaroslavl Mining Company. The prospects for their secondary processing are considered. It has been established that the waste stored in various sectors of the enterprise's tailings contain from 13 to 23% fluorite, 12-14% calcite. The characteristic is given to the technological features of raw materials. The fluorite grains present in the technogenic tailings are characterized by the presence of thin inclusions and veins of silicate minerals. An obstacle to the selective separation of minerals by the flotation method is the shielding coatings of the surface zone of mineral particles, formed from contact with reagents at the stage of primary ore processing and in the process of interaction with the water-air environment in the tailing dump. The ways of increasing the contrast of the adsorption properties of minerals are proposed. Important factors influencing the process of mineral selection, allowing to influence the quality characteristics of flotation of refractory secondary raw materials is fine grinding of the material in combination with a high degree of dilution of the pulp. The possibility of extracting concentrates with a CaF_2 content of 95.2-95.6% with the recovery of fluorite in them of 57-60.7% is shown. The introduction of inter-cycle regrind of foam products into the operation scheme allows to reduce the content of silicone dioxide in concentrates to 0.98%, which meets the requirements of consumers.

Key words: Technogenic raw materials, shielding coatings, dispersion, selectivity, fluorite, calcite, pulp density.

1 Introduction

Fluorite is practically the only industrial mineral that is a source of fluorine and belongs to economically and strategically important minerals. Fluorine compounds are widely used in the aluminum industry, steel production, various branches of the chemical industry, in the glass, ceramic industry, etc. In Primorye, there is one of the largest ore regions in terms of fluorite reserves - the Voznesenskiy ore region (VOR). The mining of its deposits was carried out by open-pit method for more than 45 years. On the basis of the mined ores, the

* Corresponding author: kienkola@rambler.ru

Yaroslavl Mining and Processing Plant worked for a long time, then (since 2005) the Yaroslavl Mining Company. Despite the fact that VOR ores have been mined out only partially and a significant part of them is prospective reserves, at present there is a serious problem of ore deficit. The inaccessibility of the existing ore reserves is associated with a sharp reduction in stripping operations in the context of economic instability. In addition, the need for mining at low levels implies a significant increase in costs. In the context of a progressive decline in the quality of ores and a corresponding decrease in the economic and technological performance of the company, the use of alternative sources of raw materials, in particular, wastes from the concentration of previously processed ores, may serve as a solution.

During the period of operation preceding the shutdown of the enterprise (from 2009 to 2013), the ores available for mining contained no more than 26-29% CaF_2 . In this case, the content of calcite, which significantly complicates the technological process during flotation concentration, was 20-28% [1].

2 Materials and research methods

The content of fluorite in the tailings stored in the tailings dump of the enterprise according to the results of the tests carried out ranges between 13-23%, calcite - 12-14%. Tailings reserves according to the available data are at least 30 million tons. It should be noted that the content of components in secondary raw materials only partially characterizes its quality. The enrichment technology should be built taking into account the specific state of the mature material that has passed the primary stage of processing. The search for effective ways to process technogenic tailings remains one of the most difficult scientific, technical, economic and environmental problems [2, 3].

The crushed ore mass that has passed the stage of primary beneficiation, treatment with flotation reagents, which has undergone long-term contact with the air and water-salt environment of tailing dumps during storage, significantly differs from natural ore material both in the structural and textural features of the structure of mineral grains and in the characteristics of their surface layer, which is of paramount importance in flotation. In this regard, the development of technologies for the processing of secondary fluorite-containing raw materials involves the solution of a set of tasks for the preparation of the material and, first of all, the inclusion in the scheme of operations that ensure the correction of the surface properties of mineral particles. Of no less importance is the selection of the optimal parameters of the liquid phase of the pulp, which creates conditions for the interaction of finely ground particles with each other, as well as their contact with the reagents used.

One of the main features of the ores of the VOR deposits is the extremely fine mutual intergrowth of mineral components. Even in finely ground raw materials (80-90% of the class -0.044 mm), as shown by numerous results of mineralogical studies [4, 5], the main part of the minerals is presented in the form of aggregate intergrowths. During the primary processing, a large proportion of fluorite grains, which was in a relatively free form (apart from the finest inclusions of silicate minerals, from which it is almost impossible to remove by conventional mechanical methods), was recovered. The fluorite remaining in the tailings is represented by grains with a rather high concentration of extraneous diluting mineral components.

Analysis of the particle size distribution of the tailings samples taken for research using a laser particle measuring device ANALIZETTE 22 of the German company FRITSCH showed that in the initial form the content of fine grains less than 0.044 mm in size is significantly less (51% versus 70-80%) than in the discharged processing plant waste from ore processing. Obviously, this is due to the processes of natural segregation taking place in the tailing dump. The need to increase the fineness of the grinding of the studied raw

material in connection with the concentration of mineral aggregates in the discharged tailings is beyond doubt. In addition, hydrophobic coatings on mineral particles remaining after primary processing, in particular, compounds formed by the interaction of the mineral cation with the carboxyl anions of the collectors used and other surfactants, have high strength and remain for a long time. In addition to this, film formations formed during the long stay of the material in the tailing dump can shield the crystal lattice from contact with the water-salt environment of the flotation pulp and newly added collectors. The real, predicted interaction of mineral particles with reagents can be carried out only in the zone of formation of fresh surfaces. Thus, regrinding mature tailings is a multi-faceted factor. The studies were carried out on the material of a sample of technogenic tailings with a content of CaF_2 - 19.0%, CaCO_3 - 12.9%, SiO_2 - 33.98%. Table 1 shows the results of a series of experiments with variable grinding time of the starting material. The presented data reflect the indicators of fluorite concentration according to the scheme with 7-8-fold re-cleaning of foam products of the main flotation.

Table 1. Results of flotation of fluorite from technogenic tailings in various grinding modes

Experiment	Product	Content, %			Recovery CaF_2 , %	Grinding parameters
		CaF_2	CaCO_3	SiO_2		
1	8 th re-cleaning concentrate	93.26	0.85	2.18	55.32	Time – 35 min. Class +44 μm – 8.3 %
	7 th re-cleaning concentrate	92.59	1.15		57.89	
	Flotation feed	18.92	13.08		100	
2	8 th re-cleaning concentrate	94.7	0.75	1.65	59.97	Time – 40 min. Class +44 μm – 6.4 %
	7 th re-cleaning concentrate	94.04	1.12		63.45	
	Flotation feed	19.02	13.04		100	
3	8 th re-cleaning concentrate	95.22	0.59	1.51	57.61	Time – 45 min. Class +44 μm – 5.59 %
	7 th re-cleaning concentrate	94.77	0.71		61.08	
	Flotation feed	18.83	13.19		100	
4	8 th re-cleaning concentrate	94.67	0.59	1,61	60.24	Time – 50 min. Class +44 μm – 3.97 %
	7 th re-cleaning concentrate	94.12	0.88		63.09	
	Flotation feed	18.9	13.04		100	
5	8 th re-cleaning concentrate	94.2	0.95	1,53	57.50	Time – 55 min. Class +44 μm – 3.1 %
	7 th re-cleaning concentrate	93.38	1.23		60.81	
	Flotation feed	19.08	12.96		100	
6	8 th re-cleaning concentrate	94.76	0.56	1,42	55.02	Time – 60 min. Class +44 μm – 2.55 %
	7 th re-cleaning concentrate	94.48	0.71		57.44	
	Flotation feed	19.01	12.9		100	

A concentrate with a CaF_2 content over 95% was obtained with a grinding time of 45 minutes. An increase in the duration of grinding does not lead to an increase in processing parameters: the content of fluorite in the concentrate even drops somewhat; at the same

time, it is not possible to achieve a decrease in the content of a strictly limited harmful impurity - silicon dioxide to the required (less than 1%) value.

Strict requirements for concentrates for SiO_2 content are dictated by the fact that the presence of this impurity leads to a significant decrease in the efficiency of the subsequent chemical processing. At the same time, as studies show using a JEOL scanning electron microscope equipped with a JCM-6000 PLUS energy dispersive analyzer (Fig. 1), complete purification of the concentrate from silicate minerals without special influences that reveal the crystal structure of the ore-mineral particle is practically impossible. Even fluorite grains 10-20 microns in size contain streaks and ingrowths of silicate minerals. Reducing the SiO_2 content to 1% and below, in accordance with the current requirements for high-grade concentrates of the FF-95 brand, is an extremely difficult task.

Fig. 1. Picture of fluorite concentrate

One of the most important conditions for selective flotation of especially finely ground materials, as evidenced by data from various sources, including our earlier studies [6-8], is the choice of density characteristics of flotation slurries. So, when studying the possibility of processing low-grade high-carbonate ores with a carbonate module (the ratio of fluorite and calcite content) below 1, classified by the enterprise as off-balance, the selectivity of the process was achieved due to the beneficiation of the finest, slime-like part of the crushed ore as a separate product. Its flotation was carried out in the mode of low densities with an increase in the time of the material in the cell of the flotation machine by 1.3-2 times. At the same time, it was possible to achieve a significant increase in processing parameters, [9] to obtain concentrates with a CaF_2 content of up to 96.2% with the extraction of fluorite in them over 60%.

A high degree of slurry dilution is a tool that reduces the number of mineral particles per unit volume and, accordingly, increases the distance between them. In conditions of very fine grinding, with the corresponding presence of a large volume of sludge in the crushed mass, the parameters of pulp density traditionally used in the practice of flotation concentration cannot be taken as a basis.

3 Results and discussion

Studies of the effect of the degree of dilution of the product at the stage of main flotation, reflecting the water-dispersed characteristics of the pulp, were carried out on the material crushed to a content of more than 95% of the size class less than 44 microns. The pulp density varied from 14 to 18% solids. Fig. 2 graphically presents data on the quality of concentrates and the extraction of fluorite in them with a variable number of re-cleaning operations.

Fig. 2. Dependence of processing parameters on the degree of pulp dilution:
1 - 4 re-cleanings, 2 - 5 re-cleanings, 3 - 6 re-cleanings, 4 - 7 re-cleanings, 5 - 8 re-cleanings

The influence of density, as the obtained data show, is quite significant: the content of CaF₂ in concentrates of the sixth, seventh, eighth re-cleanings moderately decreases with an increase in the flotation density. In this case, the extraction of fluorite into concentrates noticeably increases with an increase in density from 14 to 16%, changes little in the range from 16 to 18%, and then slowly decreases. According to the totality of indicators, the optimal pulp density is 16% of the mineral phase. It is important to note that flotation at a density of 14% allows you to obtain a concentrate containing over 95% CaF₂ after five re-cleanings. Analysis of concentrates containing 95.54-96.12% CaF₂ for silicon dioxide found that the SiO₂ content is 1.37-1.12%, which is slightly higher than the current standards limiting the SiO₂ content to 1%.

The possibility of upgrading concentrates to the required standards for the content of silicon dioxide increases, as studies have shown, with the introduction of the regrinding operation of the foam product in the upgrading-recleaning cycle, between the third and fourth re-cleanings. The use of such an additional operation made it possible to reduce the

SiO₂ content in concentrates by 0.14-0.4%. As a result, a fluorite concentrate was obtained, with a CaF₂ content of 95.26%, SiO₂ - 0.98% with a fluorite recovery of 58.5%.

4 Conclusion

1. It has been established that the waste from the processing of fluorite ores of the Yaroslavl Mining Company, stored in the tailing dump of the enterprise, contains 13-23% fluorite. Fine grinding of the material to a content of a class of -0.044 mm at least 94-96% is a prerequisite for the flotation extraction of fluorite from technogenic tailings.
2. The choice of the optimal dilution of the pulp in the primary operations of the technological scheme makes it possible to successfully carry out the selection of minerals in the conditions of finely dispersed pulps. With a solid mass fraction of 16-18%, it is possible to obtain fluorite concentrates with a content of more than 95% CaF₂ with the extraction of fluorite more than 60%.
3. Obtaining concentrates, conditioned by the content of silicon dioxide, is a difficult problem to solve due to the presence of the finest silicate ingrowths in fluorite particles. The inclusion of the intercycle regrinding of the foam product into the enrichment scheme allows the SiO₂ content to be reduced to 0.98%.

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