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PRODUCTION OF GRAINED FREE-FLOWING POTASH FERTILIZERS (KCL-STANDARD) FROM FINELY-DISSEMINATED SYLVITE ORES[1]

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SUMMARY

Efficiency of potash fertilizer application greatly depends upon the absence of caking and dust during transportation, storage and application.

Unlike the potash deposits of USA and Canada, featuring coarse (up to 5 mm) dissemination of sylvite (KCl), the potash ore deposits in Europe (Germany, Spain, France, Russia and Bielorussia) feature finer dissemination of sylvite, not exceeding 1.5-2 mm. This provides high content of fine grained fractions (under 0.2 mm) in the flotation concentrate of potash ores (up to 30-35%), thus making economically unprofitable the processing of fine-grained KCl fractions by means of dissolution-crystallization process widely used in the USA and Canada. The studies performed had established that as the content of water-insoluble clayish carbonate ore impurities grows, the amount of fine grain fractions suppress the growth of KCl and NaCl in fine ore fractions, decreasing even more the quality of the product.

RESUME

L'efficacité des engrais potassiques dépend beaucoup de l'absence de prise en masse et de poussière pendant le transport, le stockage et l'application.

Contrairement aux gisements des USA et du Canada, caractérisés par la dissémination d'une texture grossière (jusqu'à 5 mm) du minerai de sylvite (KCl), les gisements de potasse d'Europe (Allemagne, Espagne, France, Russie et Biélorussie) ont une dissémination plus fine du sylvite ne dépassant pas 1,5-2 mm. Ceci assure une teneur élevée en fractions fines (jusqu'à 0,2 mm) dans le concentré de flottation de minerai de potasse (jusqu'à 30-35 %) rendant non économique le traitement des fractions fines de KCl par un procédé de dissolution-cristallisation largement utilisé aux USA et au Canada. Les études effectuées ont montré que, lorsque la teneur en impuretés argilo-calcaires insolubles dans l'eau du minerai augmente, la quantité de fines produites formées diminue la quantité de KCl et NaCl combinés, ce qui réduit encore la qualité du produit.

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INTRODUCTION

Designing of flowsheets for potash ore concentration is determined first of all, by size of sylvite dissemination and by the content of clayey-carbonate admixtures in the ore. Coarse-disseminated potash ores of Canada and USA are mainly processed in circuits of separate concentration for ore fractions of +1 mm and -1 mm sizes after breaking the sylvite aggregates and grinding down to size of 3.5-5 mm. The concentrate produced undergoes hydroclassification or pneumoclassification and the fine fraction is granulated or processed into products with high content of KCl (98% and more) by solution-and-crystallization method [1].

Potash ores from European deposits feature more fine dissemination and the sylvite flotation feed needs to be ground down to size under 1.2-1.5 mm, resulting, even when using well-developed circuits for ore classification, in forming great quantity of fine-grained fractions with size under 0.25-0.1 mm. It causes greater consumption of reagents, increases expenses for classification of flotation concentrate and processing of fine-grained KCl fractions.

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1 *Production d'engrais potassiques granulés fluides (KCl) standard à partir de minerais de sylvinite à faible granulométrie*

When designing the process and reagent conditions for sylvite flotation the basis used is the data about degree of liberation for aggregates of sylvite and halite. These data being are obtained as a result of fractional analysis in heavy organic liquids. If data obtained about a relatively high degree of sylvite aggregates liberation in the ore sample ground to same specified size, further fractional analysis of smaller ore fractions is not often made because of presumption that in these ore fractions from the sample the liberation of aggregates cannot worsen. One needs to recognize that to some extent it is related to the fact that lessening in size of saline minerals under separation (less than 0.25 mm) considerably enhances the difficulty of fractional analysis.

For a number of years at WNIIG studies have been made as to the structure of saline minerals aggregates in the products of concentration of potash ores from Starobin (Belarus Republic) and Upper Kama (Russia) deposits. It was found that while grinding fine-disseminated potash ores there was formed a greater quantity of fine-grained particles with mixed composition. On the basis of results obtained the directions have been specified for improving the technology of flotational concentration for potash ores of this type, the reagent conditions were suggested to control the liberation of sylvite aggregates in the process of ore grinding, and a new flowsheet has been developed for production of grained potash flotational concentrate.

EXPERIMENTATION

Study of the aggregate structure

Study of the aggregate structure was made through a method of fractional analysis in heavy organic liquids with separation density of 2.0-2.20 g/cm^3. For the study were taken samples of feed and tails from sylvite flotation obtained at potash operations during concentration of potash ore with different contents (Table 1) of water-insoluble clayey-carbonate admixtures, i.e. insoluble residue (I.R.).

Table 1 - Composition of potash ore concentrating which the samples were taken for fractional analysis

Sample№	Ore Deposit	Chemical Composition		
		KCL	NaCl	I.R.
1	Upper Kama	24.1	74.4	1.5
2	Starobin	22.7	71.7	5.5
3	Starobin	32.3	58.9	8.9

Fractional analysis of potash ores is related with a number of complications, as compared to fractional analysis of water-insoluble minerals. When preparing for the analysis it is necessary to provide conditions when the solid phase will not be contaminated with salts being present in the impregnating salt solution. Some investigators wash precipitate with alcohol during the process of sample filtration, but it is inadmissible, as alcohol salts-out KCl from saline solution. The preparation of samples for fractional analysis was made according to the technique especially designed by us for purpose. It eliminates penetration of salts into solid phase of the sample under study.

Results of the study in aggregate structure of sylvite and halite have shown a number of peculiar features in crushing saline minerals. Not-withstanding the fact that liberation of aggregates of sylvite and halite mainly occurs at 0.8-1.5 mm size, the study performed had shown that flotation feed may contain a considerable quantity of sylvite in the form of aggregates with 45-60% of KCl contents (middling product fraction) or in the form of small inclusions into halite grains (halite fraction).

Analysis of KCl distribution in different size classes in sylvite floatation feed has shown (Figure 1) that the smaller the size the more becomes the quantity of KCl present in the middlings and halite fractions, and at size of salt grains under 0.25 mm over 50% of sylvite are represented by mineral aggregates.

The data obtained show that grinding of sylvite and halite grains may, to a considerable extent, take place not on the surface boundary of sylvite and halite grains. One should take into account that when potash deposits were formed crystallization of saline layers was accompanied by forming the interlayers of water-insoluble admixtures of higher strength as compared to strength of sylvite and halite crystals. In consequence of that, more energetically-favorable conditions are established for cleaving the agglomerates of saline particles not along the boundary of sylvite and halite grains but along salt crystals with forming mixed grains of sylvite and halite (the middlings fraction) and halite grains with small inclusions of sylvite named by us “fragments” [2]. Corroboration of this are the data about increasing the quantity of fine-grained mixed grains of sylvite and halite as the content of water-insoluble clayey admixtures in the ore grows (Figure 1, Table 2).

Table 2 - Fractional analysis of sylvite flotation feed when concentrating potash ores with different content of water-insoluble admixtures

Content of I.R. in ore, %	**KCL recovery,%**		
	Fractions		
	Sylvite d < 2.04 g/cm^3	Middlings d = 2.04-2.15 g/cm^3	Halitic d >2.15 g/cm^3
	Sylvite floatation feed		
1.5	64.1	27.7	8.2
5.5	56.5	30.9	12.6
8.9	52.9	32.2	14.9
	Floatation tails		
1.5	21.1	69.5	9.4
5.5	46.8	42.0	11.2
8.9	35.1	26.2	38.7

Aggregates of sylvite and its “fragments” on halite are ill-floatated and, as has shown the analysis for distribution of KCl in tails of floatation, the aggregates and “fragments” account for the major quantity of KCl lost in floatation tails (Table 2). KCl losses in the form of halite fraction occur mainly in fine fractions of flotation tails, KCl losses in the form of sylvite and aggregates (middling fraction) occur in coarse fraction of flotation tails.

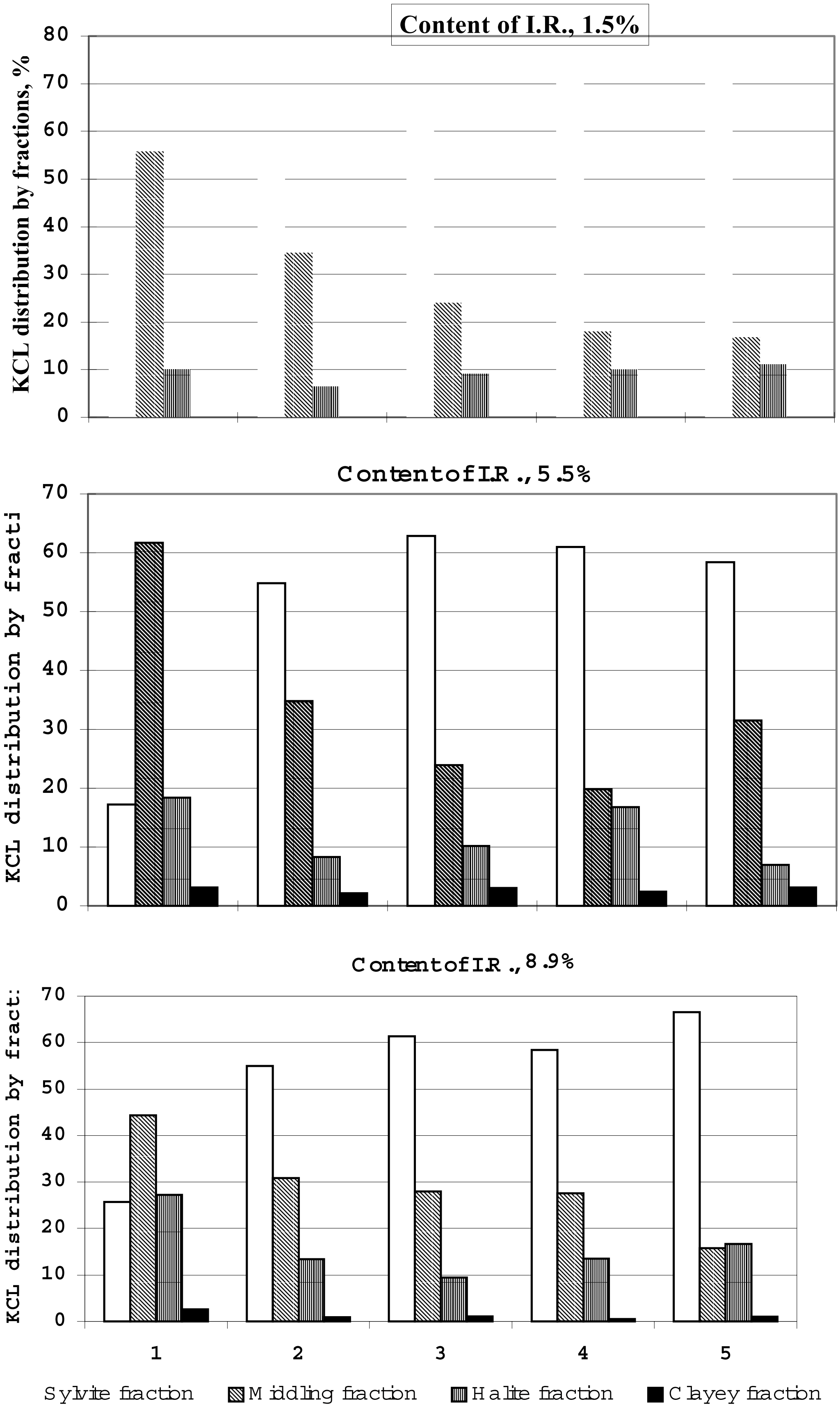
Investigations performed have enabled us to specify the trends for improving the technology in flotational concentration of fine disseminated potash ores:

1. Controlling the conditions of ore grinding in order to increase the degree of sylvite aggregates liberation, diminish forming of sylvite “fragments” on halite grains and to diminish KCL loss in fine fractions of flotation tails.

2 Diminishing of KCl loss in coarse fractions of floatation tails by means of increasing the degree of aggregates’ liberation in the process of ore grinding, classifying and regrinding of coarse fraction of flotation tails.

3 Carrying out of separate flotation for coarse (+0.2 mm) and fine-grained fractions with reagents’ consumption being optimal for every fraction and isolation of major quantity of fine-grained KCl in the flotation circuit.

Figure 1 - KCl distribution by mineral fractions of potash ore flotational feed



Size fraction:

1 -0.1mm, 2 -0.25+0.1mm, 3 -0.5+0.25mm, 4-0.8+0.5mm, 5-1.0+0.8mm

Increase in degree of aggregates' liberation during ore grinding

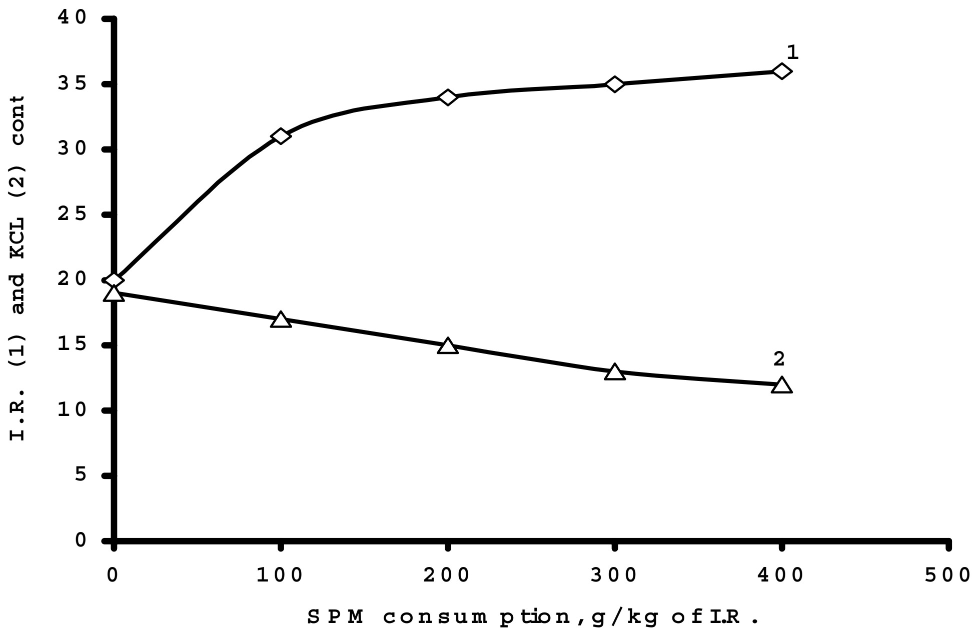
On the basis of results from the fractional analysis made, it was presumed that forming of fine-grained mixed grains of sylvite and halite - when grinding ore - could have been diminished provided the dispersing action would be rendered onto clayey-saline interlayers between crystals of sylvite and halite. Decrease in strength of clayey-saline intercalations has to increase the probability of crushing salt grains' agglomerates on the cleavage surface and surface boundary of sylvite and halite grains.

To this end we had studied the dispersing action of organic and non-organic modifying reagents onto clayey slimes. Organic modifiers (lignosulfonates or LS) show strong dispersing effect on the clayey slimes [3], but the maximum effect is observed with a consumption rate provoking enhanced foam-forming and reduction in sylvite flotability due to interaction of cationic collector (aliphatic amines) and residual LS concentration in liquid phase.

Our study has shown that of considerable interest in this respect are inorganic dispersing reagents without foam-forming properties. It has been established that salts of polyvalent metals - already at low concentrations in saline solutions, as distinct from well-known coagulating action in water-render strong dispersing effect [4, 5]. The obtained effect may be explained through recharging of surface of clayey slimes having minimal surface charge in saturated solution of electrolytes [3].

Dispersing effect from salts of polyvalent metals (SPM) increases efficiency in preliminary desliming of potash ores, thus increasing selectivity in isolation of water-insoluble impurities into the slime product and reducing KCl loss in slimes (Figure 2).

**Figure 2 - Effect of polyvalent metals salts on potash ore desliming.
Content in slime product: 1-I.R. content, 2- KCl content**



Efficiency of modifiers may be augmented through their bringing into the mill for ore grinding. In this case the maximum effect is reached as a result of mechanical-chemical dispersing of slimes. Experiments in potash ore grinding have shown that adding SPM into grinding intensifies slime dispersing and increases the output of material finished in size (Table 3) which simultaneously takes place while intensifying slime dispersing.

Table 3 - Results of laboratory tests in potash ore grinding with SPM adding:
Time of grinding - 10 min.
Initial ore size - 10 + 5 mm
Chemical analysis of initial ore - KCl -27.85%, NaCL - 65.02%, I.R. - 7.13%
Size of ground ore -1 + 0 mm

Tests were made in closed circuit, by liquid phase

SPM consumption g/t ore	**Circuit**	**Ground ore**					**Increase of index, % relative**	
		Output, %	Content, %		Recovery, %		Output, %	Recovery of I.R., %
			KCl	I.R.	KCl	I.R.		
0	1	20.3	33.0	19.0	24.0	54.1	-	-
100	1	25.3	34.9	19.0	31.7	67.4	+ 24.6	+ 24.6
100	2	26.9	34.4	19.7	33.2	74.2	+ 32.5	+ 37.2
100	3	27.3	35.0	20.8	34.3	79.4	+ 34.5	+ 46.8

Test in pilot plant of 5 t/hr ore capacity have confirmed the possibility to augment the degree of liberation in sylvite aggregates. Bringing of SPM into a rodmill has increased the sylvite quantity in free form in fine fractions (Table 4).

Simultaneously there was noted improvement in ore desliming, insoluble residue content in slime product was increased and KCl loss was decreased. Combined use of organic and inorganic dispersing reagents augments their efficiency at lower reagent consumption.

Table 4 - Grinding and desliming of potash ore in presence of modifying reagents (Starobin deposit)

Performances		**Consumption of modifiers, d/t ore**			
		Without reagents	SPM - 50	LS - 40	SPM - 30 LS - 15
Ore after grinding is the desliming feed					
Recovery of KCl into sylvite fraction of 0.25 mm size		40.0	51.0	40.8	58.0
Slime product					
Content, %	KCl	32.7	28.5	31.4	27.0
	I.R.	47.1	52.1	49.5	54.1
Recovery, %	KCl	6.5	3.8	5.0	3.6
	I.R.	49.7	49.0	45.7	49.4

Negative effect of SPM residual concentration has not been observed, and it was shown that use of SPM improves the performances of sylvite flotation (Table 5)

Table 5 - Potash ore flotation (Zielitz deposit Germany using salts of polyvalent metals (spm) as slime depressor

Reagent consumption, g/t ore		**Concentrate**			**Floatation tails**
SPM	Amine	Content, %		Recovery, %	Content, %
		K_2O	I.R.	K_2O	K_2O
-	60	45.0	0.7	80.0	3.7
-	80	44.3	0.6	84.3	2.8
10	60	48.8	0.1	84.5	2.6
25	60	47.5	0.3	91.4	1.5

Separate flotation

The current technology for flotating sylvite from polydisperse suspension of -1.5 (1.2) mm size provides for treatment by the collector of coarse sylvite grains in presence of its fine-grained fractions (under 0.2-0.3 mm). Considering the ability of sylvite fractions (size under 0.25 mm) to make sorption of significantly greater quantity of amine than it is needed for their flotation, it is necessary to maintain the collector consumption flotation at higher level than it is needed to provide flotation of each from these sylvite fractions. When clayey slimes are present in flotation feed, such a technology of KCl treatment with collector results in even greater consumption of reagents.

Flotational concentrate contains up to 35-40% of fractions under 0.25 mm and its classification is inefficient.

Separate flotation circuit takes account of differences in the structure of sylvite and halite aggregates in coarse and fine-grained fractions in sylvite floatation feed and allows to flotate under reagent conditions that are optimal for every size fraction of KCl, to isolate already at the beginning of the production process the major quantity of fine-grained KCl and obtain after floatation the main quantity of floatation concentrate with minimum content of fine-grained fractions. Checking classification of such concentrate is done at high efficiency and less cost.

Fine-grained concentrate flotated under lower consumption of the collector than in case of combined floatation will contain lower amount of amine, thus facilitating its further processing.

Laboratory tests were made with samples taken at the flotation plant of the Belaruskali Production Group; the samples are fine-grained and coarse fractions of sylvite flotation feed (Table 6).

Table 6 - Characterization of samples from sylvite flotation feed

Size classes mm	**Fine-grained fraction**		**Coarse fraction**	
	Output, %			
	specific	total	specific	total
+ 1.1	-	-	4.7	4.7
- 1.1.0+1,0	-	-	16.3	21.0
- 1,0+ 0,8	-	-	10.1	31.1
- 0.8+0,5	-	-	26.2	57.3
- 0.5+ 0.25	4.6	4.6	26.1	83.4
- 0.25+0.1	21.8	26.4	11.9	95.3
- 0.10	73.6	100.0	4.7	100.0
Total	100.0	-	100.0	-
Average size, micrometer	92		607	
Content, % KCl	29.9		27.6	
Content, % I.R.	3.8		1.8	

Flotation of KCl from fine-grained fraction features some peculiarities. Under equal density of suspension one volume of flotation feed contains 160-200 times more of saline particles than in combined flotation circuit. In view of that, to provide efficient sorption of the collector, one needs to enhance the time of contacting and treatment of KCl with collector in suspension having over 30-35% of solids content at elevated intensity of agitation (Table 7).

Table 7 - Effect of conditions of contacting with collector on performances of fine-grained sylvite flotation

Consumption of amine - 40 g/t

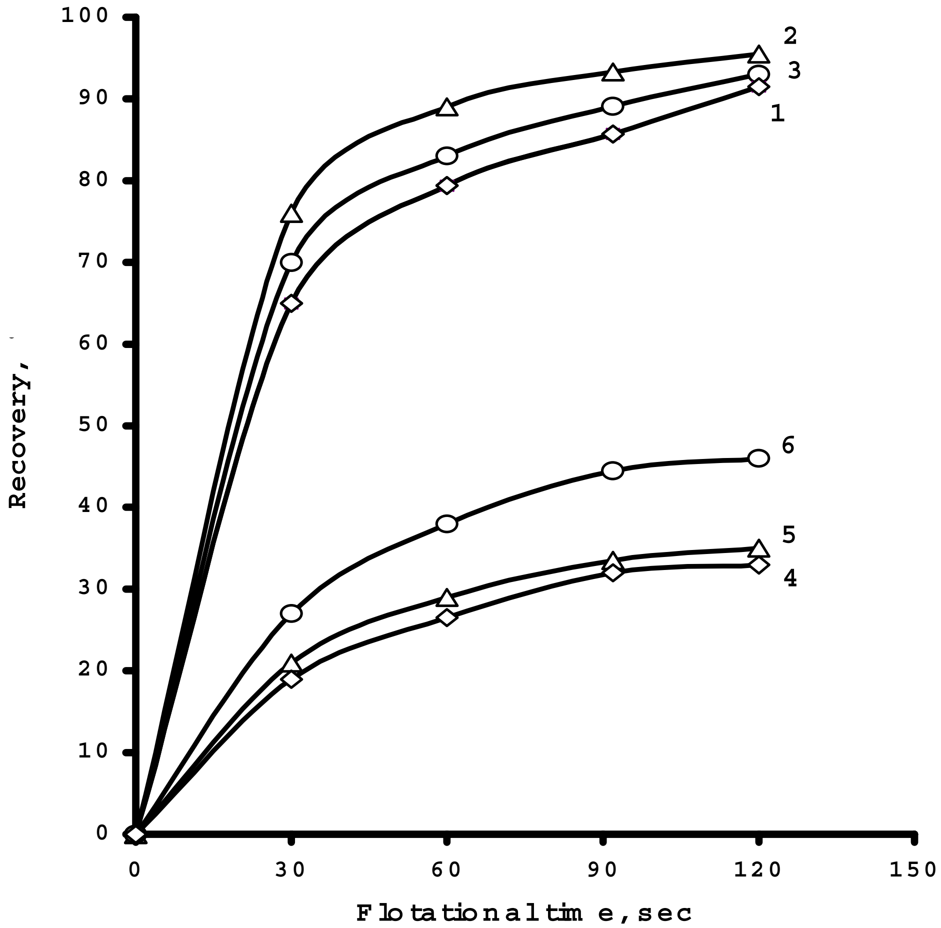
Conditions of contacting			Concentrate				Floatation tails	
Solid content, %	Duration, min	Agitation intensity	Content, %		Recovery, %		Content, %	
			KCl	I.R.	KCl	I.R.	KCl	I.R.
Effect of suspension density when contacting with the collector								
40	0.5	Normal	68.0	2.25	92.0	23.0	3.7	4.70
33.3	0.5	Normal	68.2	1.87	90.6	19.0	4.4	4.92
28.6	0.5	Normal	68.6	1.80	89.2	16.4	5.0	5.55
Effect of contacting duration with the collector								
40	0.5	Normal	68.0	2.25	92.0	23.0	3.7	4.70
40	1.0	Normal	62.6	2.08	94.8	25.5	3.0	5.29
40	1.5	Normal	64.6	1.92	95.2	23.2	2.6	5.07
Effect of contacting intensity with the collector								
40	1.0	Normal	62.6	2.08	94.8	25.5	3.0	5.29
40	1.0	2 times as much	67.7	1.81	95.6	21.5	2.5	5.44
40	1.0	3 times as much	67.6	1.80	96.9	21.7	1.8	5.50

Further treatment of KCl by activator had increased the rate of flotation (Figure 3). The tests performed had shown the need to take account of the quantity and composition of water-insoluble impurities present in floatation feed, when choosing the activator. Depending on the activator type, along with activating the fine-grained sylvite flotation, may occur an increase in I.R. content in the concentrate.

Figure 3 - Kinetics of KCl flotation from fine-grained sylvite flotational feed

1,4 - without the Activator: 2,5 - Activator-1; 3,6 - Activator-2

1 - 3 - KCl recovery; 4 - 6 - I.R. recovery



Flotation of KCl coarse fraction is facilitated due to a minimum content of fine-grained halite and middlings fractions in the floatation feed, but one needs to provide conditions for fixing coarse sylvite grains on air bubbles. To improve the sylvite flotability it was suggested to use the separate supply of amine and emulsion of extender oil. Production of emulsion was made by means of chemical self-emulsifying [6], which enabled to produce a fine-dispersed stable emulsion and enhance the KCl recovery into the concentrate (Table 8).

Table 8 - Effect of the collector composition on sylvite floatation performances

Reagent consumption, g/t ore			Concentrate			Tails	
Amine	extender oils	Foamer	Content, %		Recovery, %	Content, %	
			KCl	I.R.	KCl	KCl	I.R.
Separate supply: amine as a water solution, extender oil and foamer, both - as emulsion							
50	15	20	87.4	1.12	94.6	1.92	1.77
60	15	20	85.4	1.14	95.5	1.80	2.00
Combined supply of reagents							
50	15	20	86.5	1.21	92.5	2.94	1.78
60	15	20	83.8	1.20	94.4	2.00	2.03

Important provision for successful flotation of sylvite coarse fractions is treatment of flotation feed in dense suspension (solids content not under 35-40%) with the collector. Under commercial conditions it is often difficult to carry out the installation in series of conditioning tanks for treating the flotation feed with depressor and collector under required duration. We have established that using as depressors non ion ionic or low-ionic polymers and oligomers enables us to perform simultaneous treatment of flotation feed with depressor and collector.

Table 9 shows the results of comparative tests in rougher flotation of KCl according to combined and separate flotation circuits, where one sees that separate flotation enables lower total amine consumption and KCl loss in floatation tails.

Table 9 - Performances of laboratory tests in combined and separate flotation of sylvite

Reagent consumption, g/t flotation feed			Concentrate				Tails	
Depressor	Flotigam S	Activator	Content, %		Recovery, %		Content, %	
			KCl	I.R.	KCl	I.R.	KCl	I.R.
Separate flotation								
Concentrate of KCl rougher flotation from fine-grained fraction of sylvite flotation feed (- 0.25 mm)								
400	50	4	67.6	1.80	96.5	20.2	1.8	5.30
Concentrate of KCl rougher flotation from coarse-grained fraction of sylvite flotation feed (+ 0.25 mm)								
400	50	-	85.4	1.14	95.5	19.5	1.8	2.10
Combined concentrate of rough flotation								
400	50	0.5	80.8	1.31	95.65	19.8	1.8	3.37
Combined flotation								
400	50	-	79.6	1.45	92.6	21.5	3.1	2.56
400	60	-	79.8	1.40	95.4	21.3	1.9	2.60

PILOT PLANT TESTS

Separate flotation tests were carried out at the flotation plant of Belaruskali Production Group according to the circuit providing for supply into one section of fine-grained flotation feed fraction from the rest process sections of the plant.

Ore desliming circuit at Belaruskali refineries and producing two fractions of sylvite flotation feed having size of + 0.15 mm (hydrocyclones underflow from ore desliming) and - 0.15 mm (cell product from slime flotation) make favorable conditions for commercial implementation of the suggested technology.

The tests had shown possibility to produce in the circuit of fine-grained flotation of tails having KCl content equal to 1.2-2.0%, with amine consumption of 3.3-3.7 g/t and activator of 0.3-0.35 g/t of ore. KCl floatation from coarse fraction was made by means of separate supply into the process of amine and paraffin emulsion and foaming agent. Flotation tails had been produced with KCl content of 2% at the consumption's: amine-36-37 g/t, paraffin-9-10 g/t, foaming agent - 15-20 g/t of ore. As compared to the combined floatation circuit here is shown the possibility to reduce the amine consumption and KCL loss in flotational tails.

Concentrate from combined flotation, according to the current circuit, contains fractions of - 0.25mm size as 35-40%, contents of these fraction in coarse concentrate produced by separate flotation circuit did not exceed 15%, thus providing a high efficiency of classification. Fine-grained concentrate contained 1.5-2 times less of amine than fine-grained fraction in the concentrate of combined flotation.

Use of the separate flotation circuit in enhancing the selectivity of potash ore grinding in presence of dispersing reagents will improve performances of processing finely disseminated potash ores and reduce the cost of crystal grain fertilizers production.

CONCLUSION

Specific features have been shown in crushing of aggregates of saline minerals, namely sylvite and halite, and process conditions have been developed to improve the efficiency in concentration of finely disseminated potash ores and to lower expenses for production of crystal grain fertilizers.

The suggested technology involves ore grinding in presence of dispersing reagents and separate flotation of KCl out of coarse and fine grain fractions of sylvite flotation feed, along with isolation of major quantity of KCl fine fractions in the flotation circuit.

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