Synthesis of sodium polysulphide for copper ore processing

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Sodium polysulphide consists of yellow-brown, yellow-green crystals. Its chemical formulas are Na_2S_2, Na_2S_3, Na_2S_4. Currently there are several known methods for the production of sodium sulfide: chemical reduction of sodium sulphate by solid carbonaceous material; reduction of sodium sulfate by gaseous reductant; absorption of hydrogen sulphide with sodium hydroxide; electrolytic (amalgam) method; exchange decomposition of barium sulfide with sulfate, carbonate and sodium hydroxide. In addition to the known methods for the preparation of sodium polysulphide, there are electrochemical methods for the preparation of polysulphides that have been discovered in a long time and have received potentities: an electrochemical method for producing sodium polysulphide, an electrochemical method for producing alkali metal polysulphides.
We examined the main standard methods for the preparation of sodium polysulphide, using mechanochemical activation.
The mineralogical composition of the ore was analyzed, which allows us to conclude that it is possible to use mechanochemical sulphiding. Synthesis of the sulfidizer was carried out using elemental sulfur, caustic soda and sulphonic acid, in a planetary centrifugal mill mark "Pulverizette 6 classic line". Several modifications of sodium polysulphide have been developed, differing in the ratios of the reacting substances that have been tested in the flotation enrichment of the Irtysh deposit. During the testing of various modifications of polysulphides, the best result was revealed which showed an increased copper recovery into the concentrate by 8.98%. To determine the significance of the influence of polysulphide constituents and their consumption on flotation, as well as on the selectivity index, graphical data were presented on the dependence of the change in copper, zinc and selectivity on the ratio of the content in polysulfide: sulfur and caustic sodium, sulfur and sulfonic acid, sodium and sulfonic acid. Based on the data on the approbation of sodium polysulfide in flotation experiments, as well as graphical data, a correlation analysis was performed that showed the best ratio of polysulphide components that would allow higher copper recovery and higher selectivity.

Key words: sulphidation, mechanochemical activation, planetary centrifugal mill, polysulphide, flotation, copper ore, concentrate.

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Introduction

Sodium polysulphide consists of yellow-brown, yellow-green crystals. Its chemical formulas are Na_2S_2, Na_2S_3, Na_2S_4. It is used in various processes, such as sulphidation of steel and cast iron products, the synthesis of polysulfide rubbers, the production of sulfur dyes, the reagent in the flotation separation of mixtures, as well as the sodium-based polysulfide batteries [1].

Currently there are several known methods for the production of sodium sulfide in the world: chemical reduction of sodium sulphate by solid carbonaceous material; reduction of sodium sulfate by gaseous reductant; absorption of hydrogen sulphide with sodium hydroxide; electrolytic (amalgam) method; exchange decomposition of barium sulfide with sulfate, carbonate and sodium hydroxide. In industry, the production of sodium sulfide has been produced in the hearth furnace, rotating drum and in shaft furnaces in a continuous mode. A method of thermal reduction of sodium sulfate by solid carbonaceous materials had been applied in all these furnaces. The side reactions associated with the oxidation and carbonization of sodium sulfide occur along with the main reactions in the process of reduction of sodium sulfate. Side reactions lead to increased consumption of raw materials and contamination by ballast salt product.

In addition to the known methods for the preparation of sodium polysulphide, electrochemical methods are used for the preparation of polysulphides that have been discovered in a long time and have received potentities: an electrochemical method for producing sodium polysulphide, an electrochemical method for producing alkali metal polysulphides [2, 3]

Mechanosynthesis can be used to fabricate a wide spectrum of materials [4]. It is possible to synthesize chemical products by using only mechanical action. The mechanisms of mechanochemical transformations are often complex and different from usual thermal or photochemical mechanisms [5]. Mechanochemistry is radically different from the traditional way of dissolving, heating and stirring chemicals in a solution. Because it eliminates the need for many solvents, mechanochemistry could help to make many industrial chemical processes more environmentally friendly [6].

The article considers a new method for sodium polysulfide production using the mechanochemical activation. The advantages of this method are availability and cheapness of components for sulphidizer, efficient and easy to use components and technological equipment.

Copper oxidized ore deposits at the Irtysh river were the object of our research. The share of the Irtysh ore deposits accounts for 30% out of total volume, while 70% is nonmetallic part: quartz-sericite, quartz-chlorite-sericite and quartz-chlorite schist rocks. Mineralogical and chemical composition of the ore have been determined as the result of the analysis. Mineralization is represented (in descending order) by the following minerals: pyrite, sphalerite, chalcopyrite, faded ore, galenite. In individual cases, traced of pyrrhotite, arsenopyrite, chalcocite, covellite.

According to mineralogical analysis it is evident that the current Irtysh mine ore consists of quartz-sericite-chlorite schists with a relatively low content of ore minerals contained in the original ore (0.9% of copper, 0.34% of lead, 1.9% of zinc). Mainly, the size of the ingrained minerals is the following:

– chalcopyrite from 4 to 56 microns;
– sphalerite from 8 to 40 microns;
– galenite from 4 to 24 microns.

Galenite is the most finely disseminated and least common ore mineral.

The mineralogical ore analysis suggests the possibility of using the mechanochemical sulfidation.

Experimental part

One of the first stages of the study was the ore preparation to neutralize the negative characteristics of the material composition: as a rule, this is achieved through a variety of processing methods, such as separation of ore to the processing varieties, washing, special grinding conditions [7]. To the grinding process, it is necessary to give a lot of attention, since during shredding, there is a sludge formation, which has a negative effect for further metallurgical processing. For example, the effect of ore nano-fraction worsens the process of froth flotation, this is due to the fact that the nano-particles are very poorly separated, moreover, they prevent the flotation of a larger particle size [8].

The next stage of the research (flotation experiments) was to determine the effect of mechanochemical sulphidation and sulphidizer on ore floatability.

Fig. 1. Planetary mill “Pulverisette 6 classic line”

Synthesis of sulphidizer has been performed in a planetary mill brand “Pulverisette 6 classic line” (Fig. 1). The operating principle of the mill is the following: grinding jars are rotated around their own axes while moving in a circular path around the central axis. As a result, the grinding balls and the loaded material are experiencing the force with changing direction and magnitude. Due to the geometry and transmission ratio the optimal movement of the grinding balls is achieved. Grinding balls are captured by the inner wall of the grinding bowl, and under certain conditions can be torn away. After crossing the grinding bowl the loaded material and grinding balls hit the opposite wall. As a result, the impact energy developed in a planetary mill is many times greater than the impact energy in conventional ball mills. The Burgio model is often chosen when analyzing the principle of the planetary mill, because it describes the energy supplied by the planetary mill using only analytic expressions without any numerical calculations [9]. This ensures high efficiency of the synthesis of polysulfide.

All flotation experiments were carried out in an open cycle under comparable conditions, according to reagent regime used in the flotation of the ore enrichment. However, interpretation of the behavior of reagents in flotation is complicated by the existence of secondary effects, which can override the desired effects that enable effective separation, in addition to a predominant role of a flotation reagent, and the incomplete liberation of the mineral particles. Moreover, accumulation of dissolved ions due to the water recycle and reuse practice in processing circuits, which alters the chemical environment in the pulp and impacts the overall performance of the process, is added to this complexity. Therefore, it is often challenging to precisely assess individual contributions of the reagents to the overall performance, and hence the need for a holistic approach in evaluating the behaviour of reagents in flotation [10]. Additional experiments were conducted in order to obtain the optimal reagent regime for Irtysh deposits ore flotation. In the process of the experiments the amount supplied to the flotation, polysulfide grinding and its composition have been varied.

Ore crushing was carried out by the regime of basic experiment with the use of sodium sulfide instead of synthetic polysulfide together with zinc sulfate. The composition of polysulfide for ore crushing has been changed in accordance with changes in the composition used for polysulphide flotation.

Flotation reagent has the following regime with polysulfide: $ZnSO_4$ — 5.3 cm^3 — 1.0% solution, sodium butyl xanthate — 1.5 cm^3 — 0.1% solution, foaming agent T-90 — 5 g/t, flotation time — 5 minutes.

In order to determine the effect on flotation of synthetic polysulphide components, the experiment #0 (grinding and flotation without sulphidizer) was carried out.

The reagent regime of the experiment #0 is the following:

Grinding: 87 g of ore, 22 cm^3 of water, $ZnSO_4$ — 5.3 cm^3 — 1.0% solution, grinding time — 3 minutes.

Flotation: $ZnSO_4$ – 5.3 cm^3 – 1.0% solution, sodium butyl xanthate — 1.5 cm^3 – 0.1% solution, foaming agent T-90 — 5 g/t, flotation time — 5 minutes.

A reagent regime experiment using synthetic polysulfide reagent regime is similar to the experiment #0. The composition and supply amount of the grinding and flotation in synthetic polysulfide, and the experimental results are shown in the Table 1.

These results have demonstrated that the use of synthetic polysulfide sulfur as a substitute for sodium can increase the copper extraction to concentrate by 8.98% (experiment #5) and will increase the selectivity index by 1.7% (experiment #7). Correlation analysis was carried out in order to determine the significance of the polysulfide components and consumption influence on flotation process. The first phase was conducted in order to determine the influence of polysulfide components and the quantity on the extraction to concentrate of copper, zinc and selectivity. The analysis results using the Fisher criterion are shown in the Table 2.

These data demonstrate that the amount of sulfur in the polysulfide K_s — 0.89 has the greatest impact on copper recovery in the concentrate. Addition of active polysulphide sulfur atoms (have the affinity with sulfide minerals lattice) into the pulp during the grinding process together with sulfur atoms (not substituted in the lattice) form thiochain (surface layers enriched with sulfur) leads to increase of copper recovery. The formed thiochain

Table 1

Results of experiments with various polysulfide composition

Composition and amount of polysulfide supplied to the mill and flotation	Product name	Output, %	Content, %				Extraction, %				Selectivity index for Cu and Zn
			Cu	Zn	Pb	Fe	Cu	Zn	Pb	Fe	
Experiment #0	Concentrate	38.95	2.10	5.50	1.20	25.30	50.76	62.56	65.69	79.51	49
	Tailings	61.05	1.30	2.10	0.40	4.16	49.24	37.44	34.31	20.49	
Basic experiment	Concentrate	29.24	4.8	4.21	1.31	24.16	85.3	34.7	61.4	67.4	83.7
	Tailings	70.76	0.34	3.27	0.34	4.81	14.7	65.3	38.6	32.6	
S — 30%, NaOH — 61%, Sulfonic acid — 9%, into the mill 5 cm^3 — 0.5% solution in flotation 3.6 cm^3 — 0.5% solution	Concentrate	33.528	4.49	4.2	1.81	26.62	88.65	37.57	71.72	76.87	83.9
	Tailings	66.472	0.29	3.52	0.36	4.04	11.35	62.43	28.28	23.13	
S — 30%, NaOH — 61%, Sulfonic acid — 9% into the mill 10 cm^3 — 0.5% solution in flotation 7.2 cm^3 — 0.5% solution	Concentrate	34.012	4.46	4.34	1.59	26.08	89.84	39.75	73.2	76.72	83.4
	Tailings	65.988	0.26	3.39	0.3	4.08	10.16	60.25	26.8	23.28	
S — 36%, NaOH — 54%, Sulfonic acid — 10% into the mill 5 cm^3 — 0.5% solution in flotation 3.6 cm^3 — 0.5% solution	Concentrate	41.908	4.8	4.32	1.29	24.63	94.28	46.82	73.82	84.5	81.9
	Tailings	58.092	0.21	3.54	0.33	3.26	5.718	53.18	26.18	15.05	
S — 44%, NaOH — 44%, Sulfonic acid — 11% into the mill 5 cm^3 — 0.5% solution in flotation 3.6 cm^3 — 0.5% solution	Concentrate	40.922	4.86	4.22	1.3	24.72	93.35	45.87	75.01	85.26	81.9
	Tailings	59.078	0.24	3.45	0.3	2.96	6.655	54.13	24.99	14.74	
S — 44%, NaOH — 44%, Sulfonic acid — 11% into the mill 10 cm^3 — 0.5% in flotation 7.2 cm^3 — 0.5%	Concentrate	33.628	4.37	3.68	1.23	26.72	86.69	32.92	62.75	76.49	85.4
	Tailings	66.372	0.34	3.8	0.37	4.16	13.31	67.08	37.25	23.51	
S — 50%, NaOH — 25%, Sulfonic acid — 6%, H_2O —19% in grinding 5 cm^3 — 0.5% in flotation 3.6 cm^3 — 0.5%	Concentrate	33.913	2.63	4.33	1.12	14.78	88.23	40.39	61.49	70.59	82.1
	Tailings	66.087	0.18	3.28	0.36	3.16	11.77	59.61	38.51	29.41	

Table 2
Calculation results of correlation coefficients

Name of indicator	Correlation coefficients K_n		
	Extraction to concentrate		Selectivity
	Cu	Zn	
Quantity S in polysulfide	0.89	–0.61	0.85
Quantity NaOH in polysulfide	0.84	–0.81	0.93
Quantity polysulfide-amide	0.84	–0.79	0.91
Quantity polysulfide in H_2O	0.07	–0.12	0.10
Quantity polysulfide fed to the grinding	0.66	–0.83	0.80
Quantity polysulfide fed into the flotation	0.71	–0.87	0.85

increase the hydrophobicity of the minerals copper and zinc, thereby increasing their floatability. The quantity of sodium hydroxide and the sulfonic acid in polysulfide has the less influence to copper recovery than the quantity of sulfur. The amount of polysulfide in grinding K_{grind} — 0.66 has even less impact on copper recovery.

The quantity of polysulfide K_{flot} — 0.71 supplied to the flotation has a greater effect on copper recovery than the quantity of polysulfide supplied to grinding. The amount of sodium hydroxide KNaOH — 0.93 in polysulfide has the greatest impact on the selectivity of the process. The second highest influences are the amount of sulfonic acid K_{amide} — 0.91 in polysulfide, and the amount of sulfur K_s — 0.85.

The quantity of polysulfide supplied in the process affects the selectivity index as following:

– in the first place, there is the amount of polysulfide K_{flot} — 0.85 supplied to the flotation and secondly the amount of polysulfide K_{grind} — 0.80 supplied to the milling;

– quantity of water used for polysulphide does not affect the copper recovery and selectivity.

The presence of positive values of aforementioned factors indicates a positive effect of increasing the content of these components in the polysulfide and an increase in its consumption in the process. The analysis allows us to determine the effect of polysulfide components on copper recovery and selectivity without giving a comprehension of the polysulfide components effect on the main technological indicators of flotation.

The Table 3 has been derived in order to provide the comprehension of polysulfide components impact on selectivity index and copper and zinc recovery.

The changes in selectivity index, copper and zinc recovery depending on the content ratio of polysulfide sulfur and sodium hydroxide are shown in the Fig. 2.

As seen in the Fig. 2, the maximum selectivity index of 85% is achieved at the ratio of sulfur to the caustic sodium as 1:1.1. In this case copper recovery of 87 and 32.5% zinc extraction can be achieved. The maximum copper extraction up to 95% is achieved at the ratio of

Table 3
Correlation of the components and process indicators

The ratio of components included in the polysulphide	Extraction concentrate, %		The selectivity index
	Cu	Zn	
S/NaOH			
2	88.23	40.39	82.1
1.71	85.90	40.48	80.79
1	86.69	32.92	85.4
0.67	94.28	46.82	81.9
0.49	89.84	39.75	83.4
0.38	83.46	40.60	79.37
0	50.76	62.56	49.00
S/sulfonic acid			
3.33	89.84	39.75	83.4
3.60	94.28	46.82	81.9
3.67	86.69	32.92	85.4
8.33	88.23	40.39	82.1
2.50	83.46	40.60	79.37
12.00	85.90	40.48	80.79
0	50.76	62.56	49.00
NaOH/sulfonic acid			
6.78	89.84	39.75	83.4
5.40	94.28	46.82	81.9
3.67	86.69	32.92	85.4
4.17	88.23	40.39	82.1
6.50	83.46	40.60	79.37
7.00	85.90	40.48	80.79
0	50.76	62.56	49.00

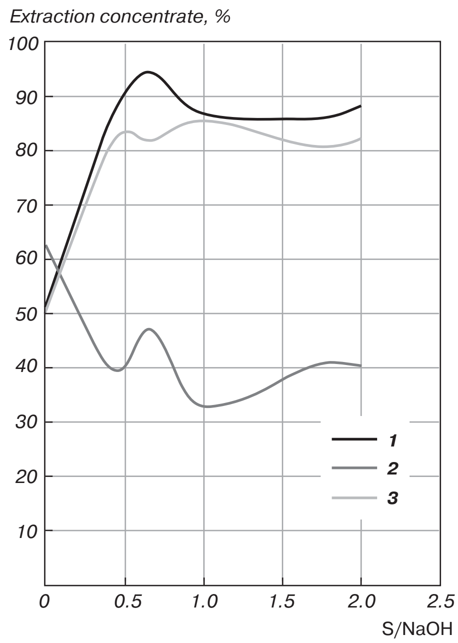

Fig. 2. Dependence of selectivity ratio and extracting copper and zinc concentrate on the content of sulfur and sodium hydroxide in the polysulfide:
1 — Cu; *2* — Zn; *3* — selectivity

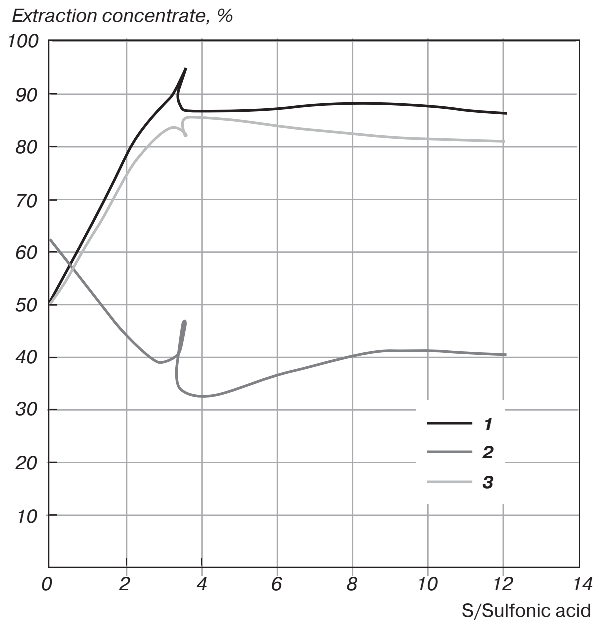

Fig. 3. Dependence of selectivity index and copper and zinc recovery by varying the ratio of sulphur and sulfonic acid in polysulfide:
1 — Cu; *2* — Zn; *3* — selectivity

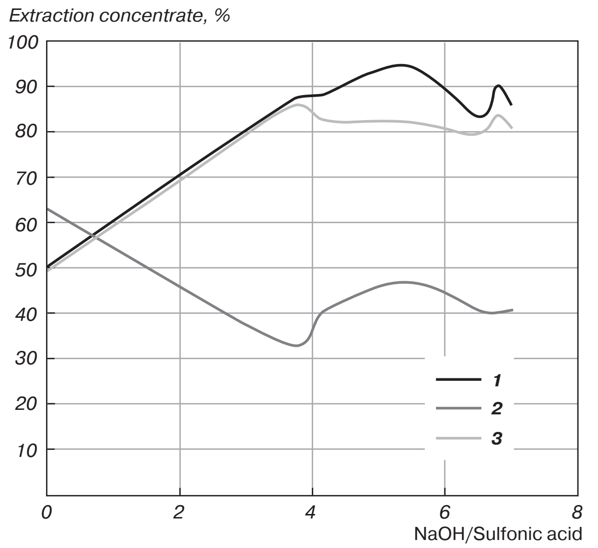

Fig. 4. Dependence of selectivity index and copper and zinc recovery by varying the ratio of sodium hydroxide and sulfonic acid in polysulfide:
1 — Cu; *2* — Zn; *3* — selectivity

Table 4
Results of calculation of correlation coefficients

Indicator	Correlation coefficients		
	Extraction concentrate		Selectivity
	Cu	Zn	
S/NaOH	0.52	–0.38	0.50
S/sulfonic acid	0.44	–0.28	0.41
NaOH/sulfonic acid	0.91	–0.75	0.94
Quantity of polysulfide feed in grinding	0.66	–0.83	0.80
Quantity of polysulfide feed during flotation	0.71	–0.87	0.85

1:0.6, wherein the zinc recovery is 47% and selectivity index is 81%. The dependence of selectivity index and copper and zinc recovery by varying the ratio S /Sulfonic acid and NaOH/sulfonic acid are shown in the Fig. 3 and 4.

As can be seen from Fig. 3 and 4, other factors (except the specified ratios), not accounted in the data charts, influence the selectivity index and copper and zinc recovery. Additional correlation analysis has been accomplished in order to determine the effect of the ratio of components and quantity of polysulfide in the feed process. The results of calculation of the correlation coefficients are presented in the Table 4.

As seen from the calculations, the ratio of NaOH/sulfonic acid is equal to 0.91–0.94, and has the greatest influence on selectivity ratio and copper recovery. On the basis of the analysis results, we can conclude that optimal ratio for synthesized polysulfide is NaOH/sulfonic acids greater than 7 but not more than 8.0, because the increase of sodium hydroxide will decrease the proportion of sulfur. At a ratio of NaOH/sulfonic acid of 1:7.5, ratio of S/NaOH is 1:1.05. This ratio provides a higher copper recovery and a higher selectivity.

Conclusion

The research on the use of synthetic polysulfide as a substitute for sodium sulfide suggest the possibility of its using for flotation ore separation. Moreover, the synthesized polysulfide has to have the ratio of NaOH/sulfonic acids greater than 7 but not more than 8.0, because the increase of sodium hydroxide will decrease the proportion of sulfur. At the ratio of NaOH/sulfonic acid of 1:7.5, the ratio of S/NaOH is 1:1.05.

This ratio provides a higher copper recovery and a higher selectivity. Our enlarged laboratory tests on synthetic polysulfide in the flotation of polymetallic ore from Irtysh deposits confirmed the possibility of its use as a substitute for sodium sulphide.

In the future, the copper extraction may be conducted using a pyrometallurgical or hydrometallurgical treatment [11, 12].

P. Balaz (Slovak Academy of Sciences, Slovakia) and K. K. Mamyrbaeva (Satbayev University, Kazakhstan) were also the participants in this work.

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NFM

On the issue of loparite ore as a source of rare-metal and rare-earth elements and increasing its dressing efficiency

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A unique source of rare-metal and rare-earth elements is loparite ore, mining and processing of which are carried out at Lovozersky Mining and Processing Plant (MPP). The improvement of the enterprise's processing figures has to do with an increase in recovery of fine-graded particles, losses with which amount to 60–70% of the plant's overall loss. An increased load on the outmoded facilities and a low efficiency of slimes preparation to dressing are the causes of the losses such as these.
The implemented investigations are based on the optimization principle, consisting in well-directed forming the products, characterized by homogeneity of the particles on some physical attribute, and timely removing them from the process.
Proposed was a method of primary slimes separating from the feed at the 1st dressing stage by means of fine screening. An influence of slimes removal onto the indexes of spiral separation at the 1st dressing stage has been investigated. There has been shown a possibility of obtaining the final tailings with loparite content of about 0.1% at the yield up to 75% from the operation feed even at this stage. The granulometric characteristics of the screening product (feeding of a slime branch) as well as loparite distributuion and grains shape have been studied.
The indicators achieved in dressing of this product according to a gravity scheme with the use of spiral sluices and table concentrators are 1.5–2 times higher than that of processing the plant slimes of current production.
There has been developed a process flowsheet for primary slimes gravity processing, which comprise spiral separation at a sluice, cleaning of the obtained products on table concentrators and centrifugal concentrator. According to the proposed scheme, the expected loparite recovery into gravitation concentrate will be about 75% with loparite content not less than 51%. Overall loss with tailings will amount to 25% with loparite content of no more than 0.6%.

Key words: loparite, slimes, gravity concentration, fine screening, grain size grade, recovery, spiral sluice, concentration table, concentrate, tails.

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