

# Copper and zinc extraction from underspoil waters using sulfur solution in sodium hydroxide

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During the passage of atmospheric precipitates through the porous dump body, the products of oxidation of sulfide minerals are dissolved. As a result, underspoil waters with low pH values and a significant amount of dissolved metals are formed. For the most part, all types of the sewage produced by mining and processing enterprises (underspoil, colliery, pit, drainage) are combined before treatment, which leads to the formation of a common water yield with complex chemical composition. According to the existing practice, the combined flow is neutralized with lime milk, which leads to irretrievable losses of non-ferrous metals with mud after neutralization. The use of the sulfiding method as part of the tactics of locally autonomous processing makes it possible to obtain the copper and zinc commercial products suitable for further metallurgical processing. Previously, sulphides of biogenic or chemical nature, as well as hydrogen sulphide, have been used in extraction of metals in the form of sulphides. In this study, we have used sulfur solution in sodium hydroxide with a mass ratio of NaOH:S = 1:1 as an alternative to the old reagents. During the study, the sulfur consumption for copper and zinc extraction were determined. The impact of water pH on zinc extraction is shown. The pilot-scale tests have confirmed the results of laboratory studies. Proposed is a flow chart with the following main operations: copper extraction, zinc extraction and the zinc product conditioning. Copper concentrate with a copper content of 32.9% and zinc concentrate with a zinc content of 48% were obtained. In the resulting deposits, copper is in the form of covellite (CuS), and zinc is in the form of sphalerite (ZnS). Through metal extraction was 99.9% for copper and 99.5% for zinc.

**Key words:** sewage, acidic water, metal extraction, copper, zinc, sulfiding, sulfur, sodium hydroxide.

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## Introduction

The formation of underspoil waters largely depends on the dump volume and amount of atmospheric precipitates. Sulphide minerals in the porous dump body are intensively oxidized under the influence of aeration, microorganisms and solar radiation, resulting in the formation of soluble sulphate compounds of metals, which are washed out by atmospheric precipitates and seep to the base of the dumps [1–2].

Usually, all types of the sewage produced by mining and processing enterprises (underspoil, colliery, pit, drainage) are combined before treatment, which leads to the formation of a common water yield with complex chemical composition. According to the existing practice, the combined flow is neutralized with lime milk. Metal ions are deposited in the form of poorly soluble hydroxides, and sulphate ion is deposited as gypsum. The main disadvantages of lime softening are the formation of a large amount of gypsum, overgrowth of settling tanks and pipelines, and irretrievable loss of non-ferrous metals with mud after neutralization.

The significant content of non-ferrous metals in underspoil waters allows considering them as raw materials for extraction of metals. The processing of underspoil waters at the places of their formation will allow one to use simpler and more efficient technologies for extraction of metals to obtain products suitable for further processing [3].

When choosing a method for extracting metals from solutions, it is necessary to take into account the following aspects: the composition and volume of a starting solution, availability of reagents and materials, instrumentation and economic indicators of the process. Various physico-chemical processes are used to extract metals from sewage: sorption; extraction; ion exchange; cementation; galvanic coagulation; electroflotation, chemical deposition in the form of poorly soluble compounds and membrane technology [4–15].

The source of underspoil water is located at a considerable distance from settlements. The absence of central power supply determines the high cost of generating electricity from generators and limits the use of electro-

chemical methods. Application of sorption and extraction is difficult due to the low kinetics of the processes and need for water treatment (pH adjustment, presence of suspended matters). Low efficiency of copper extraction, contamination of the solution with iron ions, high cost and the need to prepare iron scrap limit the use of cementation as well. The main factors preventing from the use of membrane technologies are thorough water preparation, complexity in operation, high requirements for tightness of equipment, lack of selectivity, high cost and the necessity for membrane regeneration [1, 3, 5].

The indicators of the studied underspoil water during the year can vary in wide ranges: pH 2.37–3.79; copper content 24.79–444.15 mg/dm<sup>3</sup>; iron content 7.75–185.65 mg/dm<sup>3</sup>; zinc content 8.21–558.50 mg/dm<sup>3</sup>; sulphate-ion content 2236.10–9366.00 mg/dm<sup>3</sup>. The expected recovery of metals may amount to hundreds of tons. The content of non-ferrous metals (copper and zinc) in the underspoil water is uneven throughout the year. In this regard, it is necessary to use a technology that is insensitive to significant fluctuations in the concentrations of extracted metals, is able to provide selective separation in the acidic pH range and does not require complex instrumentation. That is the reason why the method of chemical precipitation in the form of sulphides was chosen to extract copper and zinc.

Previously, there were published the studies [16–23] in which sulphides of biogenic or chemical nature (Na<sub>2</sub>S, NaHS) as well as hydrogen sulphide (H<sub>2</sub>S) were used to precipitate metals in the form of sulphides. In this study, we have used a sulfur solution in sodium hydroxide as an alternative to the old reagents.

The aim of the work was to develop a technology for copper and zinc extraction from underspoil water by sulfiding into concentrates suitable for further metallurgical processing.

#### Materials and methods of analysis

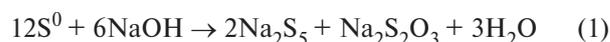
To prepare sulfur solution in sodium hydroxide there were used: commercial solution of sodium hydroxide (mass fraction of sodium hydroxide, %, not less than 44–46),

technical sulfur (mass fraction of sulfur, %, not less than 99.5) and distilled water.

Cu, Fe, Zn concentrations in filtrates and deposits have been determined by atomic absorption spectrometry on an Agilent Technologies 200 Series AA spectrophotometer. X-ray diffraction analysis of deposits was performed using a Shimadzu XRD-7000 diffractometer. X-ray fluorescence analysis of deposits was performed on an S4 Explorer Bruker AXS wavelength dispersive X-ray fluorescence spectrometer.

#### Preparation of sulfur solution in sodium hydroxide

Sodium hydroxide solution was heated to a temperature of 110–115 °C. Sulfur was loaded up to mass ratio of NaOH:S = 1:1. Reactions 1–2 may proceed in the solution:

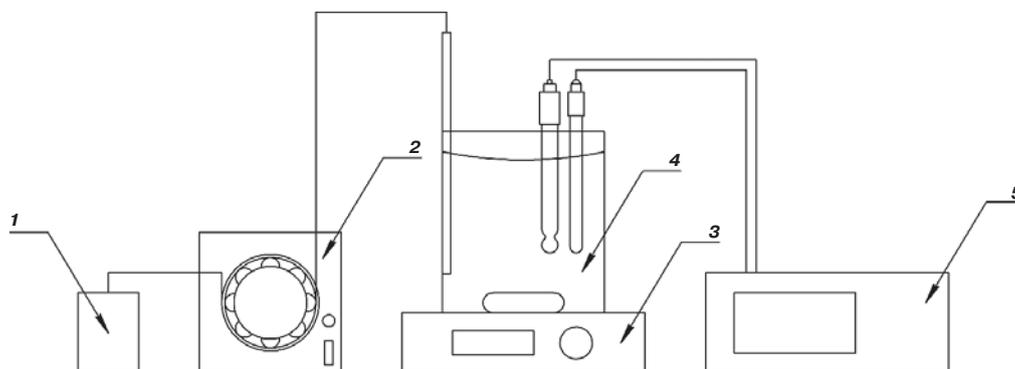


After loading sulfur, the resulting solution was stirred during heating for 30 minutes. To prevent crystallization, the solution was diluted with distilled water twice as much as the initial volume of sodium hydroxide.

#### Determination of sulfur consumption for copper extraction

Studies on copper extraction were carried out at room temperature using underspoil water of the following composition, mg/dm<sup>3</sup>: Cu – 250; Fe – 16; Zn – 510; pH = 3.03. The installation consisted of a glass reactor, a peristaltic pump, a magnetic stirrer and a pH meter (**Fig. 1**). The volume of sulfur solution in sodium hydroxide was calculated at the sulfur consumption indicated in **Table 1**. Underspoil water was poured into the reactor, while stirring with the help of a peristaltic pump, a solution of sulfur in sodium hydroxide was batched.

Suspended particles were formed in the solution. After batching, the resulting suspension was stirred for 3 minutes and filtered on a vacuum filter through Blue ribbon filter paper with a pore diameter of 2–3 μm. Metal



**Fig. 1.** Diagram of a laboratory installation:

1 – container with sulfur solution in sodium hydroxide; 2 – peristaltic pump; 3 – magnetic stirrer; 4 – glass reactor; 5 – pH meter

extractions (%) were calculated from the difference in metal concentrations in the filtrate and underspoil water.

It follows from the data in Table 1 that the extraction of copper, iron and zinc increases with an increase in the consumption of sulfur solution in sodium hydroxide. With sulfur consumption of 2.0 g per 1 g of copper, the extraction is 94% for copper, 12.5% for iron, and 5.7% for zinc. An increase in consumption to 2.3 and 2.7 g of sulfur per 1 g of copper provides an increase in copper extraction by nothing but 4.6% and 4.8%, respectively. Therefore, for further research, the sulfur consumption of 2.0 g per 1 g of copper was chosen.

#### Determination of sulfur consumption for zinc extraction

Studies on zinc extraction were carried out using decoppered water obtained taking into account the previously selected flow rate for copper extraction. The decoppered water composition was, mg / dm<sup>3</sup>: Cu – 1.6; Fe – 60; Zn – 490; pH = 2.75. First, the pH was determined, at which the efficiency of using sulfur solution in sodium hydroxide would be maximum. For this purpose, the pH of decoppered water was corrected by adding solutions of sodium hydroxide or sulfuric acid. Experiments on zinc extraction with pH adjustment were carried out with

consumption of 1.75 g of sulfur per 1 g of zinc. When determining the optimal pH, the obtained data (Table 2) showed that zinc extraction increases sharply from 46.9 to 81.8 in the range of pH values from 2.0 to 2.5, then reaches the maximum value of 89% at pH = 4.0. Low zinc extraction in the range from 2.0 to 2.5 is probably explained by decomposition of a sulphide-containing reagent, therefore the optimal pH for zinc extraction is a value above 2.75 at which the efficiency of using sulfur solution in sodium hydroxide will be maximum.

Zinc extraction increases uniformly as sulfur consumption increases. With sulfur consumption of 2.0 g of sulfur per 1 g of zinc, zinc extraction is 95.7%. An increase in sulfur consumption to 2.25 g of sulfur per 1 g of zinc raises zinc extraction by 4.1%. Therefore, for large-scale studies, the sulfur consumption of 2.0 g of sulfur per 1 g of zinc was chosen.

#### Large-scale laboratory tests

Large-scale laboratory tests were carried out in order to confirm the previously selected consumption values for copper and zinc extraction. The following equipment was used: a glass reactor 5 dm<sup>3</sup> in volume with a mixing device (YHCHEM Technology); a Masterflex C/L peristaltic pump and a filter unit.

Table 1

Results of experiments to determine the sulfur consumption for copper extraction

Material	Consumption, g S/ g Cu	pH	Content, mg/dm <sup>3</sup>			Extraction, %		
			Cu	Fe	Zn	Cu	Fe	Zn
Underspoil water 1	–	3.03	250.0	16.0	510.0	–	–	–
Filtrate 1	1.3	3.20	59.7	15.3	501.4	76.1	4.4	1.7
Filtrate 2	1.7	3.26	32.7	14.8	492.7	86.9	7.5	3.4
Filtrate 3	2.0	3.33	15.0	14.0	481.0	94.0	12.5	5.7
Filtrate 4	2.3	3.42	3.6	13.1	467.3	98.6	18.1	8.4
Filtrate 5	2.7	3.50	3.1	12.0	450.0	98.8	25.0	11.8

Table 2

Results of experiments to determine the sulfur consumption for zinc extraction

Material	Consumption, g S/ g Zn	pH	Content, mg/dm <sup>3</sup>			Extraction, %		
			Cu	Fe	Zn	Cu	Fe	Zn
Decoppered water	–	2.75	1.6	60.0	490.0	–	–	–
Filtrate 6	1.75	2.0	<0.1*	43.0	260.0	> 93.8	28.3	46.9
Filtrate 7	1.75	2.5	<0.1*	42.0	89.0	> 93.8	30.0	81.8
Filtrate 8	1.75	3.0	<0.1*	41.0	56.0	> 93.8	31.7	88.6
Filtrate 9	1.75	3.5	<0.1*	40.0	55.0	> 93.8	33.3	88.8
Filtrate 10	1.75	4.0	<0.1*	38.0	54.0	> 93.8	36.7	89.0
Filtrate 11	1.25	2.75	<0.1*	43.0	180.0	> 93.8	28.3	63.3
Filtrate 12	1.50	2.75	<0.1*	43.0	120.0	> 93.8	28.3	75.5
Filtrate 13	1.75	2.75	<0.1*	43.0	64.0	> 93.8	28.3	86.9
Filtrate 14	2.00	2.75	<0.1*	42.0	21.0	> 93.8	30.0	95.7
Filtrate 15	2.25	2.75	<0.1*	42.0	1.0	> 93.8	30.0	99.8

\*Less than the detection limit.

Underspoil water (5 dm<sup>3</sup>) was poured into a glass reactor; to extract copper, sulfur solution in sodium hydroxide was batched with a peristaltic pump. The copper-containing pulp was settled for 1 hour. The clarified part was decanted. The thickened part was filtered with formation of a copper-containing sulphide concentrate. The filtrate was combined with the clarified part and analyzed for the content of copper, iron and zinc.

Large-scale tests on zinc extraction were carried out in a similar way. In total, 15 dm<sup>3</sup> of underspoil water was processed. The results of the large-scale laboratory tests are presented in **Table 3**.

Extraction of metals into a copper-containing sulphide concentrate was, %: copper 99.5; iron 64.7; zinc 7.5. Large-scale laboratory tests have confirmed the possibility of obtaining a copper-containing concentrate with a copper content of 18.5%.

Extraction of metals into a zinc product was, %: copper – more than 0.47; iron 10.0; zinc 92.2. Through extraction was, %: copper – more than 99.9; iron – 74.7; zinc – 99.7.

### Pilot-scale tests

To test the technology in real conditions, the pilot-scale tests were organized directly at the deposit. The following equipment has been used: reactors 1 m<sup>3</sup> and 0.8 m<sup>3</sup> in volume equipped with a mixing device; submersible pump; a vacuum filtration unit with PTF-3 (ПТФ-3) polypropylene filter cloth. The process flow diagram of the tests is shown in **Fig. 2**. Underspoil water was supplied from a gathering pond (stand 1) to the reactor (stand 3) by a submersible pump (stand 2). The mixing device was turned on (stand 4), sulfur solution in sodium hydroxide was batched (stand 12). As the reaction progressed, the formation of a dark-colored precipitate was observed. Then the mixing was turned off, the resulting pulp was settled for an hour. The clarified part was decanted by a submersible pump (stand 5) into the reactor (stand 6). The thickened part was poured out through a tap (stand 7) into a storage tank and filtered on a vacuum filter to obtain a copper-containing precipitate. Stirring was turned on (stand 8) in the reactor (stand 6); sulfur solution in sodium hydroxide has been batched (stand 13). The formation of a light gray precipitate was observed. With the process completed, the mixing was turned off; settling has lasted for an hour. After pulp separation by a submersible pump (stand 9), the clarified part was pumped into the pit of the sewage disposal plant. The thickened part was poured out through a tap (stand 10) and sent for filtration to obtain a zinc-containing precipitate.

In the course of the pilot-scale tests, there were processed 2 m<sup>3</sup> of underspoil water. The composition of the products is presented in **Table 4**.

The actual sulfur consumption for copper extraction was 2.79 g of sulfur per 1 g of copper. Extraction of metals into copper-containing sulphide concentrate was, %: copper – 99.4; iron – 3.6; zinc – 6.1. The main elements of copper-containing sulphide concentrate according to X-ray fluorescence analysis, %: copper – 32.6; iron – 0.42; zinc – 0.19; oxygen – 9.2; sulfur – 56.92; the sum of impurity elements is no more than 0.67. The precipitate mainly consists of sulfur and copper sulphide (II) (**Fig. 3**).

Table 3  
Results of the large-scale laboratory tests

Material	pH	Content, mg/dm <sup>3</sup> (%)		
		Cu	Fe	Zn
Introduced for copper extraction				
Underspoil water 2	2.46	320.0	170.0	530.0
Obtained after copper extraction				
Water after copper extraction	2.75	1.6	60.0	490.0
Copper-containing sulphide concentrate	–	(18.5)	(5.45)	(1.36)
Introduced for zinc extraction				
Water after copper extraction	2.75	1.6	60.0	490.0
Obtained after zinc extraction				
Water after zinc extraction	3.3	<0.1*	43.0	1.7
Zinc product	–	(0.08)	(0.27)	(23.1)

\* Less than the detection limit.

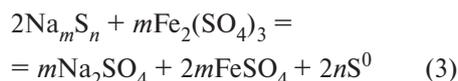
Table 4  
Results of the pilot-scale tests

Material	pH	Content, mg/dm <sup>3</sup> (%)			
		Cu	Fe	Zn	S
Underspoil water 3	2.1	170.0	55.0	330.0	–
Copper extraction					
Water after copper extraction	3.45	1.1	53.0	310.0	–
Copper-containing sulphide concentrate	–	(32.9)	(0.56)	(0.27)	(56.92)
Zinc extraction					
Water after copper and zinc extraction	3.47	<0.2*	0.93	1.7	–
Zinc product	–	(0.35)	(0.37)	(33.6)	(53.16)
Conditioning of zinc product					
Solution after conditioning	–	64.5	240.0	96.8	52.9
Zinc-containing sulphide concentrate	–	(0.46)	(0.30)	(48.00)	(29.12)

\* Less than the detection limit.

The extraction of metals into a zinc product was, %: copper — 0.5; iron — 94.7; zinc — 93.4. The gross composition of the zinc product according to X-ray fluorescence analysis is represented by elements, %: copper — 0.41; iron — 0.21; zinc — 35.71; oxygen — 9.9; sulfur — 53.16; the sum of impurity elements is no more than 0.61. Phase analysis has showed that the zinc product consists of sulfur and zinc sulphide (**Fig. 4**). The actual consumption was 2.01 of sulfur and 1.0 g of zinc.

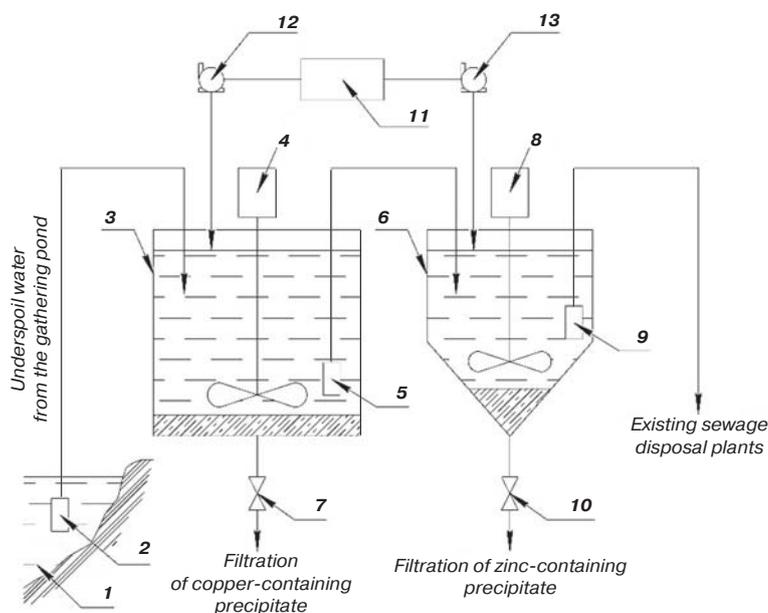
The increase in sulfur consumption and the increased sulfur content in the copper concentrate and zinc product can be explained by the reduction of trivalent iron with the formation of sulfur by reaction (3), as well as zinc and iron coprecipitation by the reagent decomposition at the pH of underspoil water equal to 2.1.



### Conditioning of zinc product

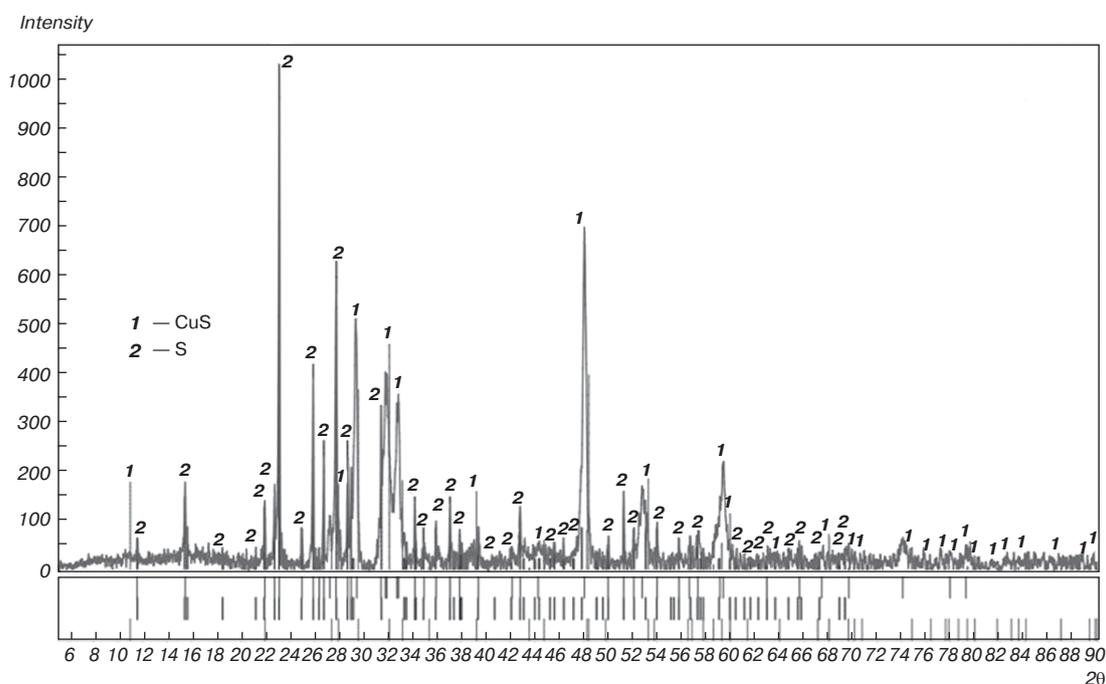
In order to improve the zinc product quality, an operation of its conditioning was carried out in a commercial solution of sodium hydroxide for 30 minutes at S:L = 1:4 and temperature of 95 °C. Passing of metals and sulfur into the solution after conditioning was, %: copper — 8.2; iron — 43.4; zinc — 0.2; sulfur — 61.7. Zinc-containing sulphide concentrate consists of the

following elements, %: sodium — 4.6; copper — 0.57; iron — 0.34; zinc — 50.17; oxygen — 14.1; sulfur — 29.12; the sum of impurity elements is not more than 1.1. X-ray diffraction analysis has showed that the main components of zinc concentrate are zinc sulphide; zinc oxide and sodium carbonate (**Fig. 5**).



**Fig. 2.** Process flow diagram of pilot-scale tests:

1 — gathering pond of underspoil water; 2 — submersible pump; 3 — reactor with a volume of 1 m<sup>3</sup>; 4 — mixing device; 5 — submersible pump; 6 — reactor with a conical bottom with a volume of 0.8 m<sup>3</sup>; 7 — discharge of copper-containing pulp; 8 — mixing device; 9 — submersible pump; 10 — discharge of zinc-containing pulp; 11 — container with sulfur solution in sodium hydroxide; 12, 13 — peristaltic pumps



**Fig. 3.** Diffractogram of copper concentrate

Based on the results of industrial tests, a process flow diagram has been developed (Fig. 6). It is proposed to be implemented between sites of underspoil water accumulation and the sewage disposal plant.

Underspoil water is supplied to copper extraction, where sulfur solution in sodium hydroxide is batched into tubing using a pump. In the tubing, sulfur solution in sodium hydroxide is mixed with underspoil water, and a suspension of copper-containing precipitate is formed. Then the resulting pulp is piped to a settling tank for

separation into clarified and thickened (copper-containing) parts. The thickened copper-containing part is filtered, and two products are obtained: copper concentrate and filtrate, which is combined with the clarified part.

The clarified part and filtrate are sent to zinc extraction, where sulfur solution in sodium hydroxide is batched into tubing by a pump in a similar way. The clarified part and filtrate with a suspension of zinc-containing precipitate are sent to a settling tank for separation into the clarified part and thickened (zinc-containing)

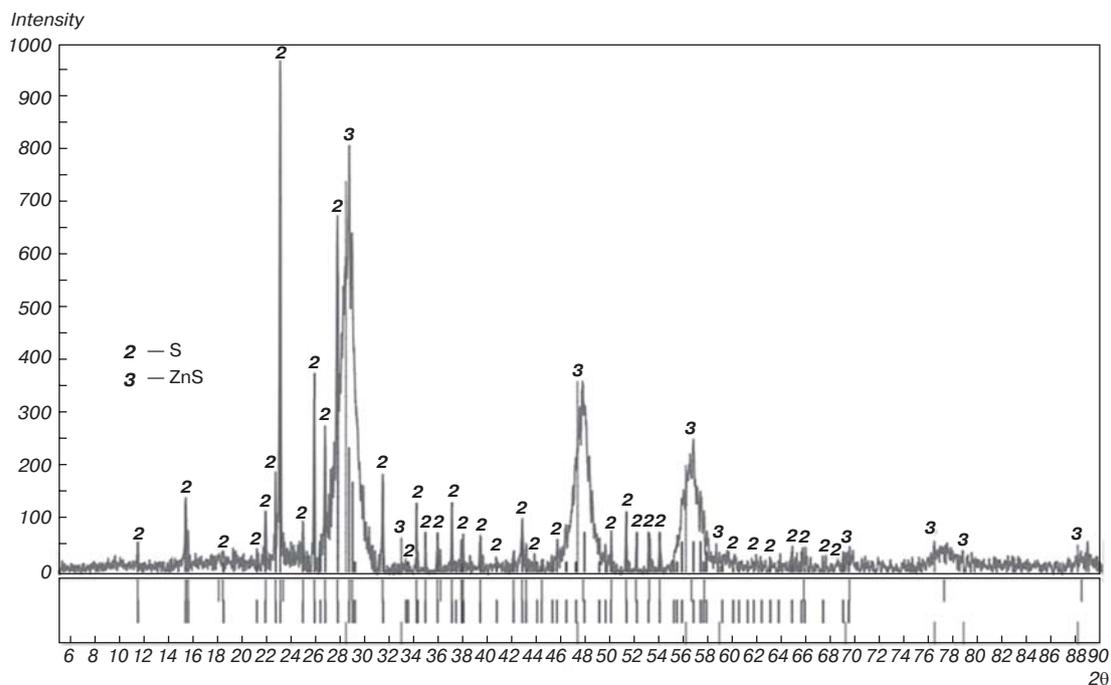


Fig. 4. Diffractogram of zinc product

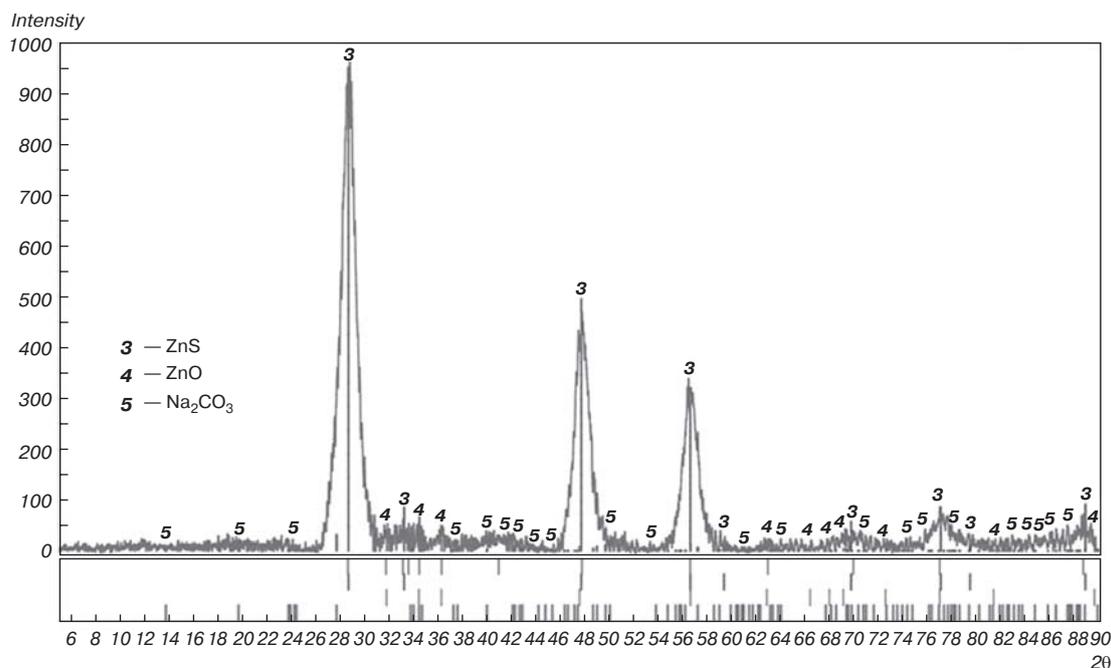


Fig. 5. Diffractogram of zinc concentrate

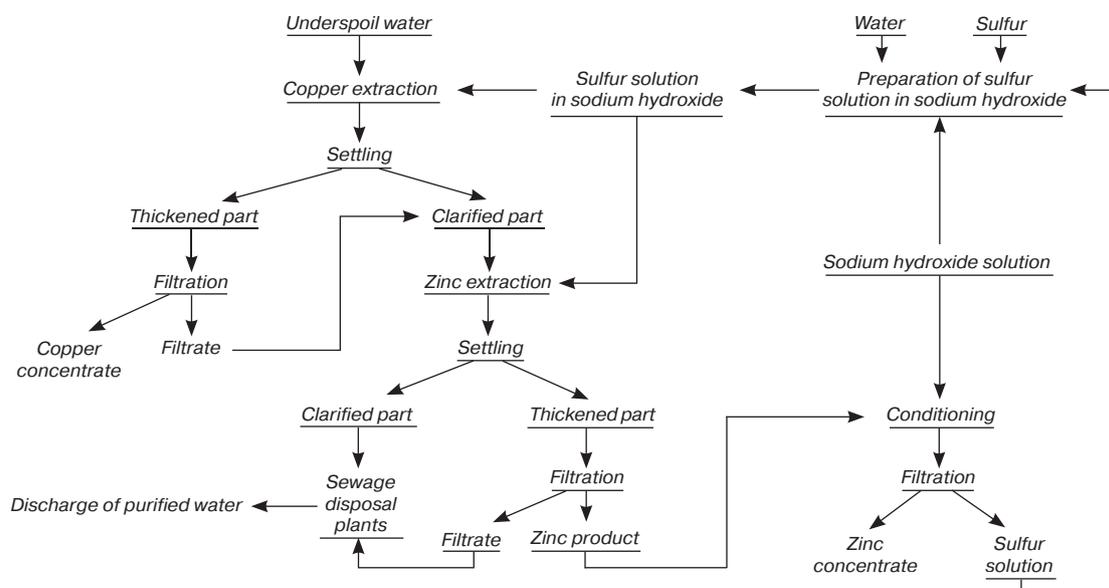


Fig. 6. Flow chart

parts. The zinc-containing thickened part is filtered to obtain the zinc product and filtrate, which is combined with the clarified part and sent to the existing sewage disposal plant.

The zinc product is conditioned for 30 minutes in a commercial solution of sodium hydroxide at a ratio of  $S : L = 1 : 4$  and a temperature of  $95\text{ }^{\circ}\text{C}$ . The conditioning operation is carried out in order to improve the zinc product quality and return the “washed” sulfur to the operation of preparing sulfur solution in sodium hydroxide. After agitating, the pulp is filtered to obtain zinc concentrate and sulfur solution in sodium hydroxide, which is strengthened with sulfur to a ratio of  $\text{NaOH} : \text{S} = 1 : 1$  and used to extract copper and zinc.

### Conclusions

This article proposes a technology for zinc and copper extraction from acidic underspoil waters of mining and metallurgical enterprises, which complements the existing purification system and allows extracting copper and zinc into the products suitable for further processing. The technology of copper and zinc extraction with sulfur solution in sodium hydroxide includes the following stages: preparation of sulfur solution in sodium hydroxide, batching of a sulfidizer into a flow for copper precipitation, settling of a copper product, batching of a sulfidizer into a flow for zinc precipitation, settling of a zinc product. Applying the conditioning operation makes it possible to improve quality of the resulting zinc product, as well as to use sulfur more fully for metal extraction.

Through extraction, %: copper up to 99.9; zinc up to 99.5. Passing of metals to the copper product was: copper — 99.4%; iron — 3.6%; zinc — 6.1%. Passing of metals to the zinc product was: copper — 0.5%; iron — 94.7%; zinc — 93.4%. The resulting precipitates are covellite

( $\text{CuS}$ ) and sphalerite ( $\text{ZnS}$ ). The content of elements in the copper product, %: zinc — 0.2; copper — 32.6; oxygen — 9.2; sulfur — 56.9. The content of the main components in the zinc product, %: zinc — 35.7; copper — 0.4; oxygen — 9.9; sulfur — 53.2.

The technology may be implemented between the sites of underspoil water accumulation and sewage disposal plant before discharge into the environment. The technology application will reduce the consumption of lime milk for neutralization, the amount of deposit formed due to copper and zinc extraction, as well as return to production the metals that are lost during the underspoil water treatment by hydrolytic purification.

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