

Separation of metals from technological solutions Copper production

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ABSTRACT

At the copper smelting plant of JSC Almalyk MMC, technological solutions containing 60-90 g/l of copper and 15-25 g/l of nickel are formed in the process of copper sulfate production. The technological solutions were investigated using physical and chemical treatment methods. The analysis of the pH value of the deposition of metal hydroxides. These solutions undergo deep electrolysis of copper. Nickel is not extracted due to the lack of cost-effective technology. In the work, the possibility of separate extraction of copper and nickel from technological solutions using the methods of precipitation with milk of lime is studied. To facilitate mixing of the solution, the copper-containing precipitate is separated from the solution by two-stage precipitation. In two stages of precipitation with the addition of milk of lime at pH = 5.5-6, the degree of deposition of copper and nickel is 98% and 6.5%, respectively, which allows nickel to be extracted from the solution. Found technological solutions can be applied in other industries related to the processing of copper-containing products.

Key words: Solution, concentration, settling, quick lime, gypsum, metal, extraction, extractant.

1. INTRODUCTION

In copper production, technological solutions are formed containing copper, nickel, iron, zinc, cobalt, and other metals. These metals need to be separated from each other and removed from solutions. Savings and a sharp decrease in the level of losses of non-ferrous metals in the production of copper are among the priorities of the modern development of metallurgical production.

Considering that their solution must meet environmental requirements, the development and implementation of alternative technologies for processing copper waste, which makes it possible to extract all valuable components, is relevant. One of the valuable components of copper waste is nickel [1, 2].

The technological process of the production of copper sulphate of the Copper Smelting of Almalyk MMC JSC consists of series of sequential technological operations: preparing the electrolyte solution for processing, the loading granules into the oxidizer towers, neutralizing acidic solutions in the oxidizing apparatus, purifying the neutralized solutions from iron and arsenic, filtering the

solutions, evaporating the purified solutions, crystallizing the purified solutions, centrifuging, jointing, drying, packing and shipment of copper sulfate.

The electrolyte solution is a technological raw material for the production of copper sulphate, which is obtained from the refining shop of gold and silver (Gold and silver refining workshop) and the copper electrolysis shop. The electrolyte from should have a mass concentration (g/dm³): copper - 20÷40, nickel - 3÷5, sulfuric acid - 100÷140. The electrolyte from the copper electrolysis workshop should have a mass concentration (g/dm³): copper - 30÷50, nickel - 3÷5, sulfuric acid - 120÷180.

2. METODOLOGY

In [3], it was found that the selective and combined extraction of copper and iron impurities from a nickel electrolyte contains: 1.24 Cu (II), 0.89 Fe (III), 82.7 Ni (II) by extraction. At a temperature of 40°C, the extraction (in percent by weight) of the starting nickel does not exceed 0.1-6% at 3<pH<6, while the iron recovery is 83-99% at pH = 3-6, and copper - 80-96% at pH = 5-6, the highest separation coefficients of these metals with nickel are observed. With a mixture of oleic acid and triethanolamine in kerosene, it is possible to selectively extract predominantly iron at pH = 3-4 (no more than 2% nickel is recovered) and copper at pH = 5-6 (no more than 6% nickel is recovered) from nickel electrolyte joint extraction of iron and copper at pH = 5-6 (in this case, no more than 6% nickel is extracted). The authors of [4] proposed the separation of copper and nickel from solutions by sorption by contacting the solution with N- (2-hydroxypropyl) picolylamine resin. At very low pH s, the chemical affinity of copper for Bis-PA resins is orders of magnitude greater than for HPPA resins. Within pH 2, the resin has a high chemical affinity for nickel and copper, but almost no chemical affinity for cobalt, in contrast to the selectivity of the long-standing Bis-PA resin, which at the same pH strongly binds all three metals.

In [5], a method is proposed for separating nickel from copper by foaming flotation with naphthenic acid in kerosene and separating the resulting foam product into the aqueous and organic phases. In this case, the foamed flow extraction of nickel and copper is carried out collectively at pH = 7.8-8.25, and the organic phase of the resulting foamy product is treated with an aqueous solution of sulfuric acid at an equilibrium pH = 3.7-5.0 and a temperature of 60-70 °

C. followed by separation of the mixture into aqueous and organic solutions. In this case, the separation of nickel and copper is carried out in the process of sulfuric acid treatment of the organic phase of the foam product of the collective foam flotation, i.e., in the process of selective re-extraction of nickel. The deposition of metals from solutions of sulfuric acid leaching of oxidized nickel ores was carried out by the hydrolytic method [6].

In the range of pH = 7–9.5, complex precipitates containing nickel, cobalt, and manganese were obtained. The purification of nickel solutions from impurities by the precipitation method was studied. The issues of processing solutions with the release of nickel concentrate as a commercial product were resolved. The authors claim [7] that the use of caustic alkalis or premium lime (fluff), soda, limestone, chalk, marble, dolomite, and others, which mainly give carbonate ions to the solution, is not desirable for the deposition of copper. In the first case, carbonate ions will not reach for the formation of the necessary salt, in the second, hydroxyl ions. The author investigated in [8] the patterns of reduction of copper (II) ions by hydrazine. Despite the significant reduction potential of hydrazine ($E^0_{N_2/N_2H_4} = -0,23 - 0.23$ V for an acidic medium, $E^0_{N_2/N_2H_4} = -0.16$ V for an alkaline medium), upon reduction of Cu (II) aqua-hydroxyl complexes in the absence of a stabilizer do not lead to obtaining copper and Cu_2O .

When treating wastewater from heavy metals, mainly regenerative or oxidative processes, are used. Ozone is an ideal oxidizing agent in terms of “ecological” purity. The use of ozone for wastewater treatment of metallurgical enterprises has been little studied. After ozonation, metal ions precipitate in the form of insoluble hydroxides [9].

A series of experiments [10] were carried out on the extraction of nickel from acid waste solutions by precipitation using various precipitating reagents: sodium carbonate (Na_2CO_3), sodium sulfide (Na_2S), ammonium hydrosulfide (NH_4HS), sodium hypophosphite (NaH_2PO_2), dimethylglyoxime and sodium hydroxide ($NaOH$). The highest degree of nickel deposition from solutions was shown by dimethylglyoxime, which is used in analytical chemistry for the qualitative and quantitative determination of nickel. According to the stoichiometric ratio of the chemical reaction, 2 kg of dimethylglyoxime is necessary

for the deposition of 1 kg of nickel. Based on the cost of the reagent, further processing of the sludge is difficult.

The liquid extraction method takes place in a slightly acidic medium, excess acidity was neutralized with calcium carbonate (limestone), while iron precipitated, which was separated by filtration, and copper and zinc remained in solution. Then, copper was extracted from the solution with VK 992 extractant manufactured by the People’s Republic of China (Lix 64 analog), kerosene was used as an extractant diluent. Extraction was carried out for 5 minutes [12]. To purify mineralized industrial water by ion flotation was proposed to use the new GLIPET reagent (a mixture of polyethylene terephthalate: with glycerin) that allows improving the quality of purified water (from 98.5 to 99.99%) from metal cations Cu, Zn, Fe, Ni, Pb, Cd. Besides, the use of GLIPET reagent for flotation treatment of mineralized industrial waters of mining enterprises is environmentally safe and technologically affordable, it allows the disposal of solid household waste polyethylene glycol terephthalate (PET packaging) and uses in the cleaning process. It is recommended to use purified water from metal cations Cu, Zn, Fe, Ni, Pb, Cd for recycling water supply at mining and processing enterprises [13].

Precipitation of iron and silicate compounds with calcium oxide, after complete oxidation of iron, it was precipitated to separate iron and silicate compounds and obtain a pure solution of nickel and cobalt sulfates mixed with copper sulfate, which remained in solution after cementation. It should be noted that with an increase in the pH of the solution after bio regeneration, gel formation was not observed, since, possibly, silicates immediately formed a rather compact precipitate together with iron and calcium compounds. After separation of the precipitate of iron, silicates, and calcium by vacuum filtration, the resulting solution was evaporated to determine the composition of the compounds remaining in it [14].

3. OBJECTS AND METHODS OF RESEARCH

The source of the formation of metal-containing technological solutions (figure 1).

The results of the chemical and phase analysis of the technological solution are given in the table. 1.

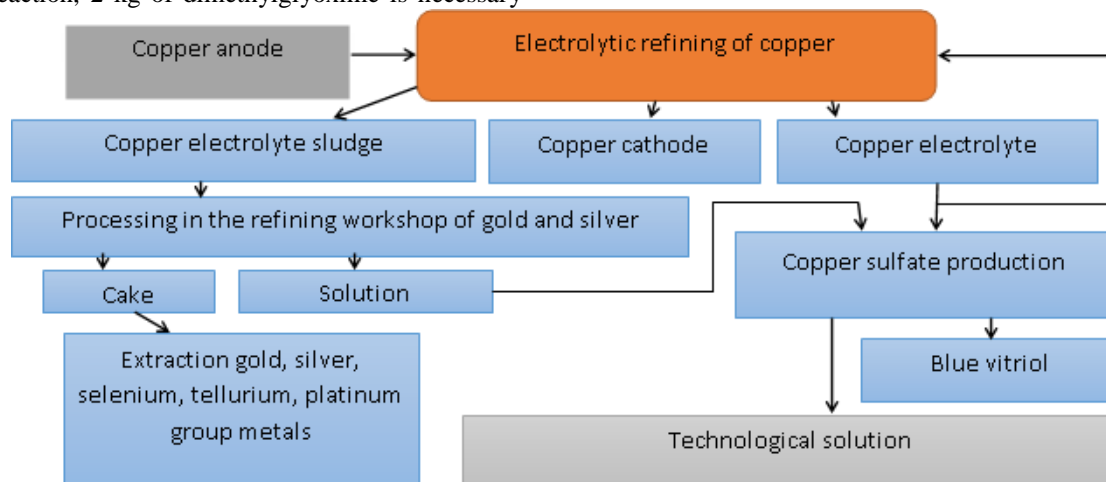


Figure 1: The technological scheme of processing copper anodes

Table 1: Chemical and phase analysis results

Analyzed product	Chemical composition, g/dm ³				
	H ₂ SO ₄	Cu	Zn	Fe	Ni
Technological solution	8,1	68,8	0,245	0,063	16,2
	H ₂ SO ₄	CuSO ₄	ZnSO ₄	FeSO ₄	NiSO ₄
	8,1	172	0,607	0,171	42,56

4. RESULTS

4.1. Separation of metals by precipitation in the form of sparingly soluble compounds.

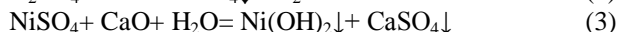
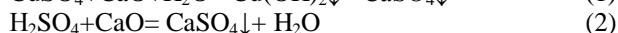
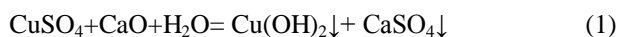
To extract metals and reduce the acidity of the solution, a lime precipitation method was studied, which forms sparingly soluble compounds that precipitate (table. 2).

The technological solution (pH = 1.5-2) is treated with milk of lime (T:W = 1:5) at a temperature of 50-60⁰C, the high copper content in the solution contributes to the formation of a large volume of sediment and mixing is

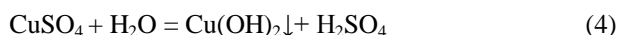
complicated. To facilitate the mixing of the solution, the copper-containing precipitate is separated from the solution by two-stage precipitation. At the first stage, the clarified milk is added to pH = 4.5 with a duration of 0.5 hours, and the solution settles. At this time, 65-75% of the copper is precipitated as hydroxide. In the second stage, additional clarified milk is added to the purified solution, mixed for 0.5 hours, and neutralized to pH = 6-6.5. Here, up to 99.1% of copper is precipitated as hydroxide. In the process, initial neutralization reactions occur:

Table 2: Metal hydroxide precipitation pH values

Material composition	The beginning of the deposition at the initial concentration of the deposited		Almost complete precipitation (residual concentration less 10 ⁻⁵ M)	The beginning of the dissolution of the precipitate (precipitation ceases to be complete)	Complete dissolution of the precipitate
	1 M	0,01 M			
Fe(OH) ₃	1,5	2,3	4,1	14	-
Al(OH) ₃	3,3	4,0	5,2	7,8	10,8
Cu(OH) ₂	4,2	6,5	7,1	14	-
Zn(OH) ₂	5,4	6,4	8,0	10,5	12-13
Pb(OH) ₂	6,4	7,4	9,0	10,5	-
Fe(OH) ₂	6,5	7,5	9,7	13,5	-
Ni(OH) ₂	6,7	7,7	9,5	13,2	-

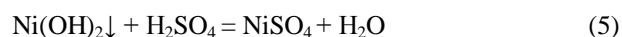


With a change in the pH of the solution, hydrolytic precipitation of metals begins. When the solution medium reaches $6.5 \leq \text{pH} \leq 4.5$, copper sulfate is hydrolyzed:



At pH = 4.5, nickel sulfate is not hydrolyzed, and the following secondary reaction occurs in the solution -

primary nickel precipitated in the form of hydroxide (reaction 9) under the influence of acid re-enters the solution:



4.2. The result of the study of the extraction of metals by deposition in the form of sparingly soluble compounds.

With an increase in the pH of the solution, complete precipitation of copper and zinc and partial precipitation of iron are observed (Fig. 2-4, table 3).

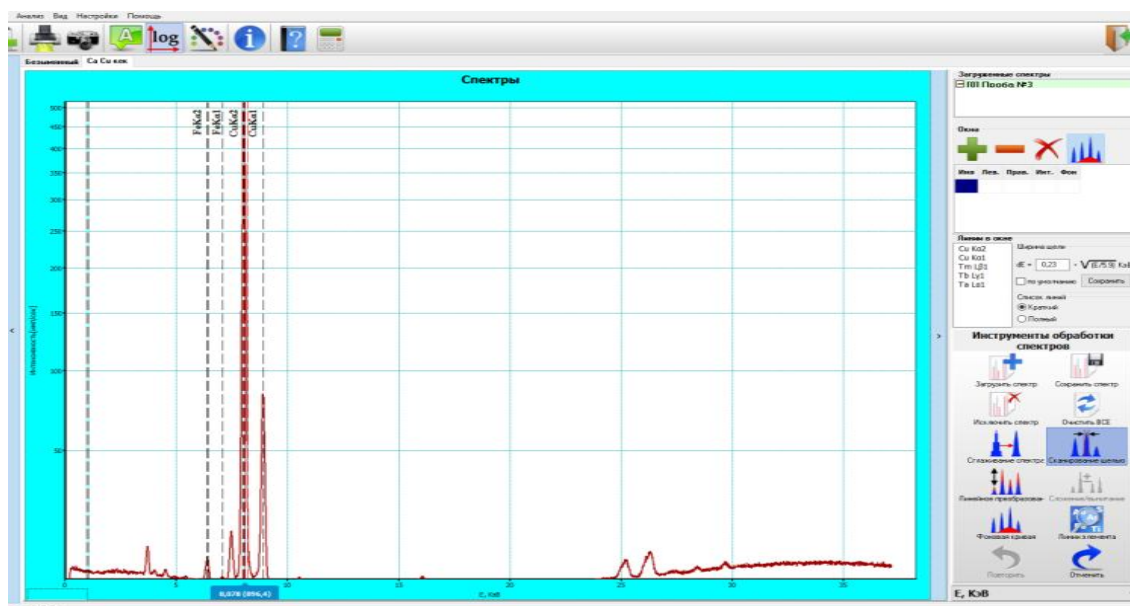


Figure 2: Spectra of sediment after processing technological solution using milk of lime

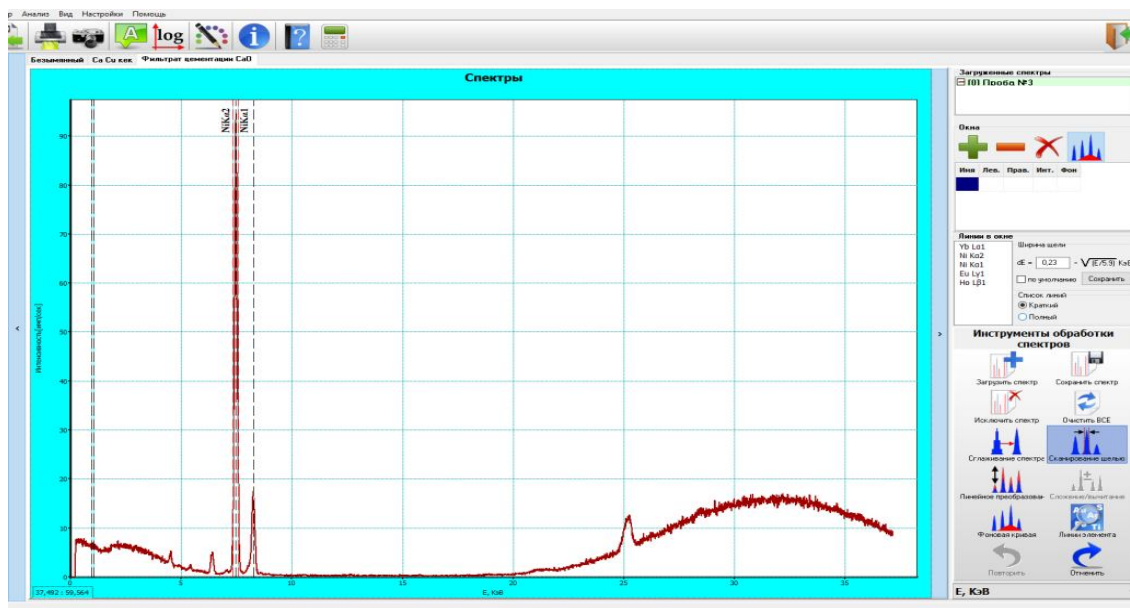


Figure 3: Spectra of the solution after processing the technological solution using milk of lime

Table 3: The results of the deposition of metals using lime at pH medium

Name and pH of the solution	Me ⁿ⁺ , g/dm ³				Recovery, %			
	Cu	Ni	Fe	Zn	Cu	Ni	Fe	Zn
Stock solution	68,8	16,2	0,063	0,245	0	0	0	0
pH = 4,0	38,5	16,2	0,063	0,244	44,04	0	0	2,4
pH = 4,5	20,2	16,1	0,063	0,23	70,64	0,62	0	6,1
pH = 5,0	6,35	15,9	0,062	0,22	90,77	1,85	1,59	10,2
pH = 5,5	1,45	15,4	0,061	0,14	97,89	4,94	3,17	42,86
pH = 6,0	0,91	15,1	0,06	0,085	98,67	6,79	4,76	65,3
pH = 6,5	0,61	14,6	0,035	0,02	99,11	9,87	44,4	91,83
pH = 7,0	0,34	7,3	0,022	0,01	99,5	54,9	65,08	95,9

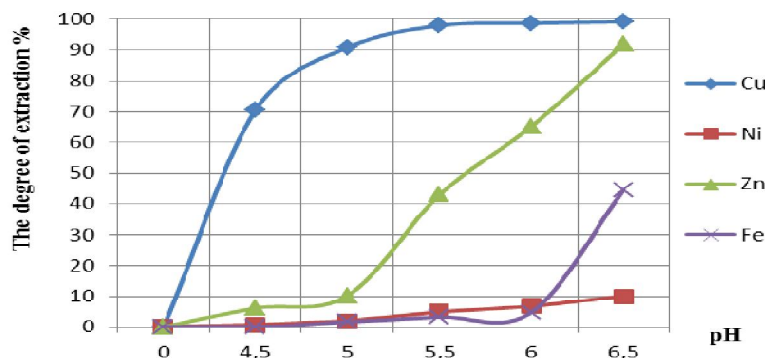


Figure 4: The dependence of the degree of extraction of metal ions at different pH environments.

5. CONCLUSION

In two stages of precipitation with the addition of milk of lime at pH = 5.5-6, the degree of deposition of copper and nickel is 98% and 6.5%, respectively, which allows nickel to be extracted from the solution.

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