Separation of Copper from Technological Solutions to the Production of Copper Sulphate

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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 possibility of separate extraction of metals from solutions of copper and nickel using solutions of lime solution and other precipitants were studied.

KEY WORDS:solution, concentration, settling, quick lime, gypsum, metal, extraction, ion flotation, extractant.

I. INTRODUCTION

Nickel is found in nature mainly in the form of oxides, sulfides and silicates. Nickel ores are mined in approximately 33 countries of all continents, and they are smelted or refined in approximately 30 countries. Primary nickel is produced and used in the form of ferronickel, nickel oxides, nickel sulfate and other chemicals, as well as more or less pure metallic nickel. Nickel is also easily processed in many areas of its application, and large tons of recycled or nickel scrap are used as additives.

II. LITERATURE SURVEY

Statistics by INSG (International Nickel Study Group) show that the accumulation of nickel in the world since 1995 is 31.898 million tons [1].

This method [2] of the extraction of nickel from acidic solutions and deeper purification of using ion-exchange resins, weakly acid cation exchangers, including chelating cation exchangers. The capacity of weakly acidic cation exchangers for one or another ion, when adsorbed from solutions of complex composition, ceteris paribus, depends on the concentration of the ion in the solution, the pH of the solution in the resin phase and the affinity of the ion to the functional group of the cation exchanger, or its position in the selectivity series. The affinity of these or other ions to the functional groups of weakly acid cation exchangers, including chelate cation exchangers, is determined by both the property of the ion and the property of the functional group, and in the general case it obeys the following series of selectivity: $H^+>Cr^{3+}>Fe^{3+}>Al^{3+}>Cu^{2+}>Ni^{2+}>Zn^{2+}>Co^{2+}>Fe^{2+}>Mn^{2+}>Ca^{2+}>Mg^{2+}>Na^+$.

The work [3] describes the results of a study of the selective extraction of copper from a solution containing, g / dm3: copper - 2.4, nickel - 1.1, iron - 0.07, 10% L1X®984N. At pH 2.4, the maximum copper extraction and the minimum extraction of iron and nickel were achieved; the content of copper reextract was 10 mg/dm^3.After a three-stage extraction and re-extraction, an electrolyte of the composition, 30 g/dm^3 of copper and 200 g/dm^3 of sulfuric acid was obtained. The disadvantage of these methods is the sorption ability of copper ions is very close to the ability of nickel ions, therefore, both ions are sorbed together. The following process requires the separation of metals.

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 (Copper electrolysis workshop). The electrolyte from (Gold and silver refining workshop) 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/dm^3): copper - 30 ÷ 50, nickel - 3 ÷ 5, sulfuric acid - 120 ÷ 180.

The process of neutralizing sulfuric acid in solution occurs due to the oxidation of elemental copper. At the moment of passage of the aerated solution through the layer of granules, elemental copper dissolves according to the following reactions:

$$Cu + 1/2O_2 = CuO \qquad\qquad (1)$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O \qquad\qquad (2)$$

The neutralization process is periodic and is considered complete when the acidity decreases to pH = 3.5 and the mass concentration of copper in the solution reaches at least 130-160 g/dm^3. After neutralization, the solution is sent for purification from impurities of arsenic and iron: oxidation and hydrolysis of iron, partial evaporation, sedimentation and decantation of the solution.

The oxidation of acidified iron to oxide occurs with atmospheric oxygen, which is blown through a heated solution, and iron oxide sulfate is formed. The temperature of the solution before oxidation is 80 ± 100C.
Iron (III) sulfate is formed by the reaction:

$$2FeSO_4 + 1/2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \qquad\qquad (3)$$
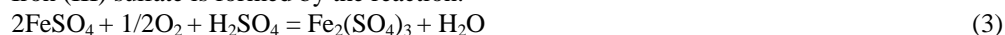
After the end of the oxidation operation at pH = 1 ÷ 2 in the solution, the hydrolysis process begins according to the reaction:

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4 \qquad\qquad (4)$$

The duration of the hydrolysis operation is three hours. The sedimentation and decantation of the solution should be at least two hours. The solution will be sent for filtration, and a purified solution is obtained. The pure solution is acidified with sulfuric acid to a concentration of 7 ± 15 g / dm3 and then pumped to a vacuum evaporator.

Evaporation of neutralized purified solutions to a density of 1.48-1.54 g/dm^3. The mass concentration of copper at the beginning of the operation is 130-160 g/dm^3, at the end of the operation 200-220 g/dm^3.Evaporated solutions are fed into the crystallizer. The crystallization process is periodic and is considered complete when the temperature of the solution in the crystallizer 24-32^{0}C is reached. The separation of crystals of copper sulfate from the technological solution is carried out in a centrifuge. The vitriol is sent to the drying drum for drying, and the mother liquor in the CEW (Copper electrolysis workshop) for use in the technology of producing cathode copper by electroextraction.

To conduct the process of electroextraction of copper, bathtubs are included in each circulation system, in which Pb-Sb anodes are hung instead of copper anodes. Oxygen is produced at the anode, and copper ions are discharged at the cathode. The solution is depleted of copper and enriched with acid. The electroextraction process is used, as a rule, to extract metal from more dirty solutions than during refining. This causes a reverse dissolution of the precipitate and, as a consequence, a reduced current and energy yield. The electrolysis of a solution with insoluble anodes is associated with an additional energy consumption, since the voltage during electrolysis with lead anodes rises to three volts, which per 1 ton of copper will be an energy consumption of 2500–3000 kW/h [4].

III. SIGNIFICANCE OF THE SYSTEM

The results of chemical and phase analysis are given in table. In this regard, the choice of technological solutions for the extraction of metals is of paramount importance. The following methods of metal extraction are used: mechanical, physicochemical, flotation, sorption, electrochemical, etc.
 The difficulty in processing the solution is associated with a high acid content. The pH values of the onset of precipitation of metal hydroxides, their almost complete deposition, as well as the onset of dissolution and completes dissolution of amphoteric hydroxide precipitates, which are necessary in all cases of choosing the optimal pH range in order to detect, separate and quantify polyvalent metal ions (Table 1, Fig. 1)

Table 1.
Results of chemical analysis

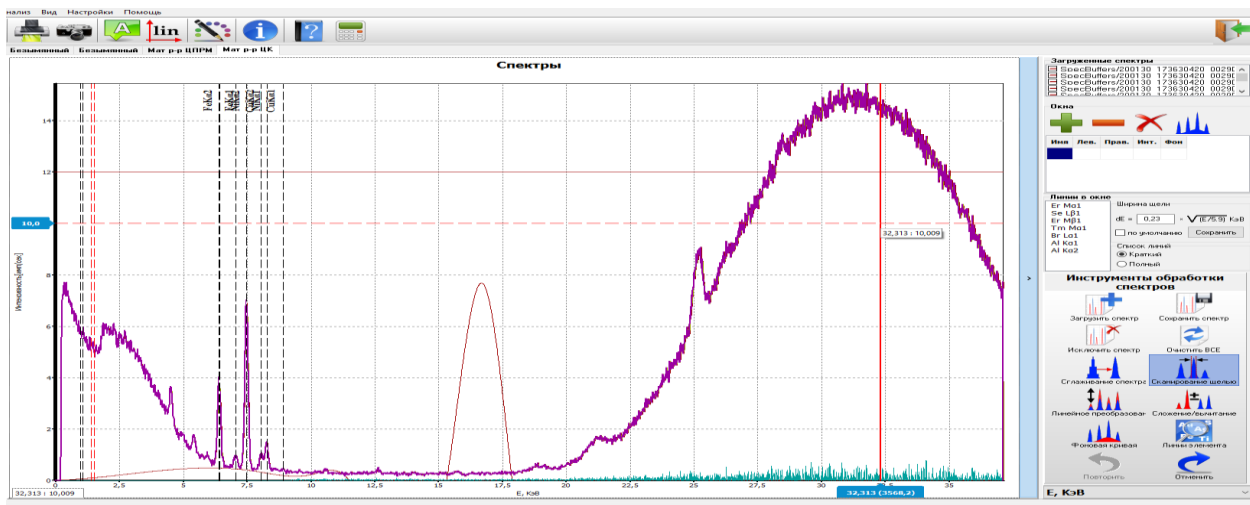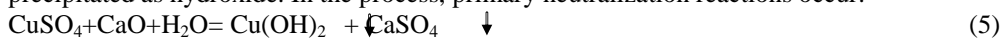| Analyzed product	Chemical composition, g/dm^3							
	H_2SO_4	Cu	Zn	Fe	Ni	Sb	Mo	As
Technological solution	8,1	68,8	0,245	0,063	16,2	0,34	0,002	0,14
The material composition, g/l	H_2SO_4	$CuSO_4$	$ZnSO_4$	$FeSO_4$	$NiSO_4$	$HSbO_2$	$HMoO_4$	$HAsO_2$
	8,1	172	0,607	0,171	42,56	0,445	0,0034	0,2

Fig. 1. Spectra of the qualitative analysis of the technological solution

IV. EXPERIMENTAL RESULTS

Precipitation - the allocation in the form of a solid precipitate from a solution of one or more components. For this, conditions are created when the system passes from the initial stable state to an unstable state and a solid phase forms in it.

The technological solution (pH = 1.5-2) is treated with lime solution (S:L = 1: 5) at a temperature of 50-60^{0}C, the high copper content in the solution contributes to the formation of a large volume of sediment and mixing is complicated. To facilitate mixing of the solution, the copper-containing precipitate is separated from the solution by two-stage precipitation. At the first stage, the lime solutionis 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 lime solutionis added to the purified solution, mixed for 0.5 hours and neutralized to pH = 6-6.5. Thus, up to 99.1% copper is precipitated as hydroxide. In the process, primary neutralization reactions occur:

$$CuSO_4 + CaO + H_2O = Cu(OH)_2 + CaSO_4 \downarrow \qquad (5)$$
$$H_2SO_4 + CaO = CaSO_4 + H_2O \qquad (6)$$
$$NiSO_4 + CaO + H_2O = Ni(OH)_2 + CaSO_4 \downarrow \qquad (7)$$

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

$$CuSO_4 + H_2O = Cu(OH)_2 \downarrow + H_2SO_4 \qquad (8)$$

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:

$$Ni(OH)_2 \downarrow + H_2SO_4 = NiSO_4 + H_2O \qquad (9)$$

Based on the research results, the technology of separation of copper and nickel from technological solutions is recommended (Fig. 2).

Table 2
The results of hydrolytic precipitation of metals using lime solution at pH medium

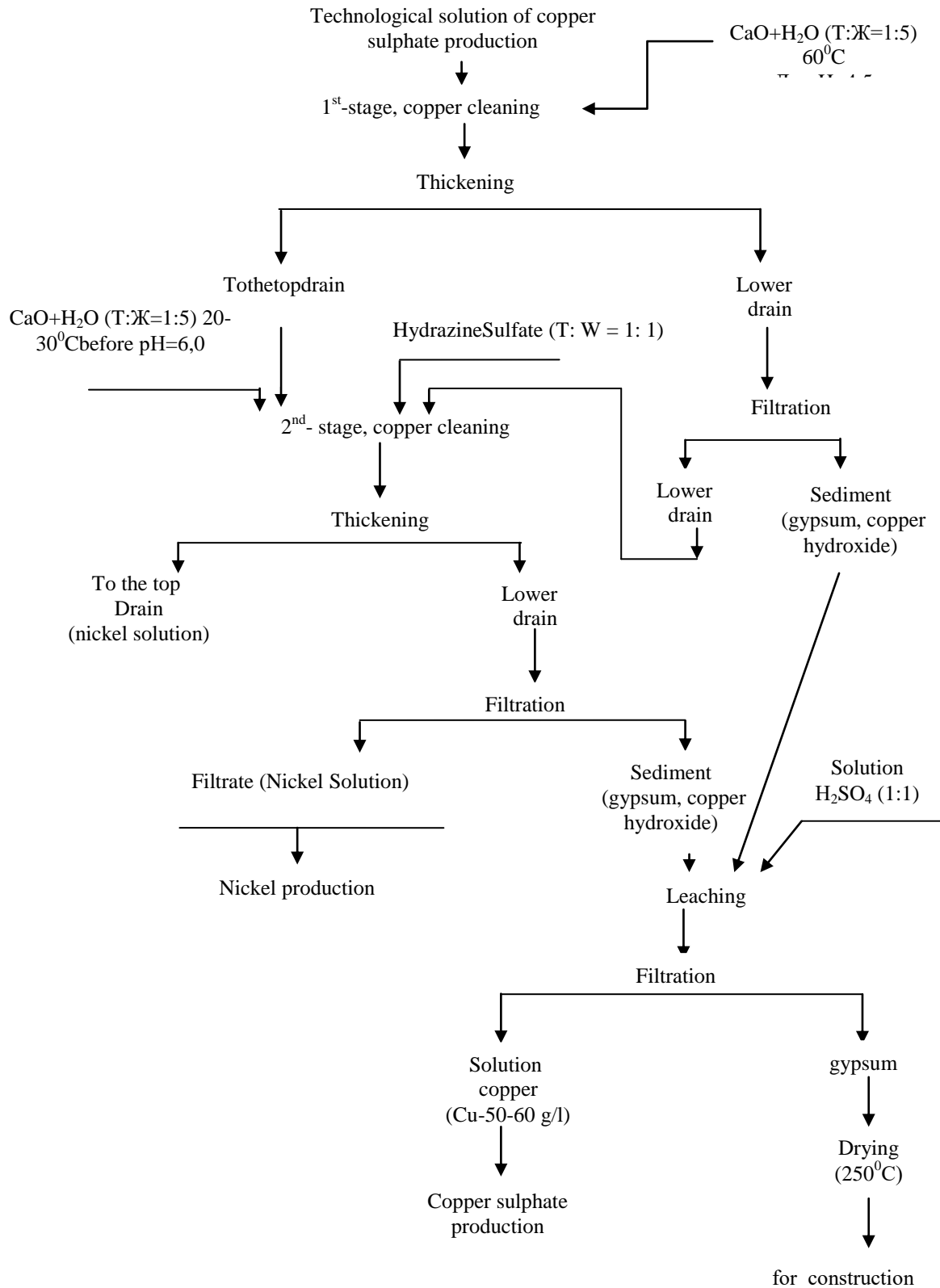| I. NAME AND pH OF THE SOLUTION	II. Me^{N+}, G/L				III. EXTRACTION, %			
	IV. Cu	V. Ni	VI. Fe	VII. N	VIII. U	IX. Ni	X. Fe	XI. Zn
XII. STOCKSOLUTION	XIII. 8,8	XIV. 6,2	XV. ,063	XVI. ,245	XVII.	XVIII.	XIX.	XX.
XXI. pH = 4,0	XXII. 8,5	XXIII. 6,2	XXIV. ,063	XXV. ,244	XXVI. 4,04	XXVII.	XXVIII.	XXIX. ,4
XXX. pH = 4,5	XXXI. 0,2	XXXII. 6,1	XXXIII. ,063	XXXIV. ,23	XXXV. 0,64	XXXVI. ,62	XXXVII.	XXXVIII. ,1
XXXIX. pH = 5,0	XL. ,35	XLI. 5,9	XLII. ,062	XLIII. ,22	XLIV. 0,77	XLV. ,85	XLVI. ,59	XLVII. 0,2
XLVIII. pH = 5,5	XLIX. ,45	L. 15,4	LI. 0,061	LII. ,14	LIII. 7,89	LIV. ,94	LV. ,17	LVI. 2,86
LVII. pH = 6,0	LVIII. ,91	LIX. 5,1	LX. ,06	LXI. ,085	LXII. 8,67	LXIII. ,79	LXIV. ,76	LXV. 5,3
LXVI. pH = 6,5	LXVII. ,61	LXVIII. 4,6	LXIX. ,035	LXX. ,02	LXXI. 9,11	LXXII. ,87	LXXIII. 4,4	LXXIV. 1,83
LXXV. pH = 7,0	LXXVI. ,34	LXXVII. ,3	LXXVIII. ,022	LXXIX. ,01	LXXX. 9,5	LXXXI. 4,9	LXXXII. 5,08	LXXXIII. 5,9

Technological solution of copper sulphate production

$CaO+H_2O$ (Т:Ж=1:5) 60^0C

1st-stage, copper cleaning

Thickening

Tothetopdrain

Lower drain

$CaO+H_2O$ (Т:Ж=1:5) $20-30^0C$ before pH=6,0

HydrazineSulfate (T: W = 1: 1)

2nd- stage, copper cleaning

Filtration

Lower drain

Sediment (gypsum, copper hydroxide)

Thickening

To the top Drain (nickel solution)

Lower drain

Filtration

Filtrate (Nickel Solution)

Sediment (gypsum, copper hydroxide)

Solution H_2SO_4 (1:1)

Nickel production

Leaching

Filtration

Solution copper (Cu-50-60 g/l)

gypsum

Copper sulphate production

Drying (250^0C)

for construction

Fig. 2. Recommended technology of the separation of copper and nickel from technological solutions

V. CONCLUSION AND FUTURE WORK

An implementation to achieve the production of nickel of normal quality is the improvement of production, which involves saving resources and reducing the mass of waste generated, which is achieved by the creation and implementation of internal drainage-free production and waste-free technologies.

The developed technological solutions can be the basis of innovative technologies for processing technological solutions formed in the production of copper sulfate and are recommended for use at enterprises in this industry. Found technological solutions can be applied in other industries related to the processing of metal-containing products.

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