DOI 10.24412/2181-1431-2023-3-65-70 Ostonov Sh.Q., Khujakulov N.B., Axtamov F.E., Sobirov D.N.

STUDY OF RECOVERY OF HEAVY NON-FERROUS METALS FROM WASTE WATER OF COPPER PRODUCTION

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Annotation. Today, the high level of development of techniques and technologies leads to an increase in the demand for the consumption of metals. The continuous growth of the production of heavy non-ferrous metals has led to an increase in the consumption of man-made waste, which is seen not only as a source of additional production of metals, but also as a factor in reducing the cost of finished products. In the coming years, JSC "Almaliq KMK" plans to increase the volume of copper production by 1.5-2 times, as a result of which the amount of man-made waste (slags, gases, dust, sludge, washing solutions, waste water, etc.) will also increase, which will be recycled. and performance requires a special approach. Having the metals in a molten state makes their separation somewhat easier. Because, as we know, the main expenses in the metallurgical industry are spent on the processes of preparation for processing. Waste water containing rhodanite ions was used in the separation of metals from the wastewater of the copper sulfate workshop.
Key words: copper sulfate, nickel, hydrometallurgy, ammonium rhodanide, copper sulfate, technological solution, mass spectrometer selectivity, electrolyte.

ИССЛЕДОВАНИЕ ИЗВЛЕЧЕНИЯ ТЯЖЕЛЫХ ЦВЕТНЫХ МЕТАЛЛОВ ИЗ СТОЧНЫХ ВОД МЕДНОГО ПРОИЗВОДСТВА

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Аннотация. Современный мир задаёт тенденцию высокого уровня развития техники и технологий, что соответственно приводит к росту потребности в потреблении металлов. Непрерывный рост производства тяжёлых цветных металлов привёл к увеличению потребления не только первоначального сырья, но и промышленных отходов. Они рассматриваются не только как источник дополнительного производства металлов, но и как фактор снижения себестоимости конечной продукции. В ближайшие годы в АО «АГМК» планируется увеличение производства меди в 1,5-2 раза, что в конечном итоге гарантирует рост количества промышленных отходов (шлак, газы, пыль, шлам, промывные растворы, сточные воды и т.д.). Технологические операции по их переработки требуют наличия основательных решений. Наличие металлов в расплавленном состоянии несколько облегчает их разделение. Ведь, как известно, основные затраты в металлургической промышленности идут на процессы подготовки к переработке. Стоит отметить, что сточные воды, содержащие ионы роданита, использовались для извлечения металлов из сточных вод медесульфатного завода.
Ключевые слова: сульфат меди, никель, гидрометаллургия, родант аммония, медный купорос, технологический раствор, селективность масс-спектрометра, электролит.

MIS ISHLAB CHIQARISH OQOVA SUVLARIDAN OG‘IR RANGLI METALLARNI AJRATISHNI O‘RGANISH

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Annotatsiya. Bugungi kunda texnika va texnologiyalarning yuqori darajada rivojlanishi metallar iste’moliga bo’lgan talabni ortishiga olib kelmoqda. Og’ir rangli metallarni ishlab chiqarishning uzluksiz o’sishi texnogen chiqindilarni iste’molini ko’payishiga olib keldi, bu nafaqat metallarni qo’shimcha ishlab chiqarish manbai, balki tayyor mahsulot tannarxini pasaytirish omili sifatida ham ko’rilmoqda. Yaqin yillarda "Olmaliq KMK" AJ mis ishlab chiqarish hajmini 1,5-2 baravar oshirishni rejalashtirmoqda, buning natijasida texnogen chiqindilar (shlaklar, gazlar,chang, shlam, yuvish eritmalari, chiqindi suv va boshqalar)ning miqdorini xam ortishiga olib keladi, ularni qayta ishlash esa maxsus yondashuvni talab qiladi. . Metallarni erigan holda bo’lishi ularni ajratib olishni bir muncha osonlashtiradi. Chunki, bizga ma’lumki metallurgiya sanoatida asosiy sarf xarajatlar qayta ishlashga tayyorlash jarayonlariga sarflanadi. Mis kuporos sexi oqova suvlaridan metallarni ajratishda Navoiazot 201-sex (tiomochevina ishlab chiqarish sexi) ning tarkibida rodanit ionlari bo’lgan chiqindi oqova suvlaridan foydalanildi.
Kalit so’zlar: mis sulfati, nikel, gidrometallurgiya, ammoniy rodanid, mis kuporos, texnologik eritma, mass-spetrometr tanlovchanlik, elektrolit.

Introduction. Treatment of waste water generated during production is considered one of the most problematic issues of our time and requires special attention. Water is one of the most important natural resources, but today, large amounts of harmful substances and toxic compounds are dumped into water bodies all over the world every day. As a result, the chemical composition of water is under the influence of negative changes, and as a result, it harms people's health and the state of the environment. Production of non-ferrous metals is one of the industries that consumes the most water. As a result of the wastewater generated in metallurgical production being neutralized and thrown into open water bodies, a number of valuable useful components - copper, zinc, cadmium, molybdenum, rhenium and other metals - are lost along with the wastewater. As a result of the researches, the complex extraction of metals from wastewater is one of the difficult problems to solve, the properties of which are related to the amount of many components that are close to each other, which makes their selective extraction difficult. it was found to reflect in itself. At the same time, in order to further extract valuable metals by returning wastewater to the main technological production, research and development works are being carried out to improve the technological processes aimed at the use of these wastes. Adsorption is widely used in wastewater treatment research. As an adsorbent, local wastes are used in researches: they include sawdust from oak bark and leaf litter [1], algae, as well as animal waste. Clays can also be used as a sorbent in the adsorption process [3]. Low-grade adsorbents include agricultural waste (waste from rice husk to wheat husk, egg shell, coconut shell, palm fruit, mushroom shell, ground nut (i peel, fruit peel, biochar) and industrial waste. Agricultural waste consists of lignin, cellulose, hydrocarbons, sugar, water and starch. These wastes can be used directly, they are first washed and put into the soil. They are then sieved to obtain the desired particle size used for adsorption tests Chemical precipitation is an effective and simple technology for wastewater treatment of heavy metals. Traditionally, strong alkaline reagents such as ammonia, lime, sodium hydroxide, sodium carbonate, and sodium sulfide are used to raise the pH of the wastewater. In this case, soluble heavy metal ions are converted into insoluble hydroxide, carbonate or sulfide compounds and precipitate in an alkaline environment. However, conventional reagents have several disadvantages: most of the heavy metal ions are present in acidic solution, and sulfide reagents in acidic solution can generate toxic hydrogen sulfide gas ¬, which is harmful to human health and the environment. has a harmful effect., [4] The authors studied the separation of metal ions by electrochemical methods from the solution formed by selective melting of Ni-Cu mixed ore. Electrochemical reactions of copper and nickel ions from sulfated copper-nickel solutions in an acidic environment were observed in the study. Since ozone is a strong oxidizing agent, it can be used to separate heavy non-ferrous metals from wastewater [5]. The efficiency of the process largely depends on the pH level of the treated solution [10]. An increase in the number of additives is observed during the processing of electrolytes of the copper electrolysis shop of "Almaliq KMK" JSC Copper smelting plant (MEZ) and decoppering solutions of the gold and silver refining shop in the copper sulfate shop. The results of the analyzes showed that the amount of nickel in the technological solutions of the copper sulfate workshop (Matochnye rastvory) reaches 15-25 g/l.Part of the nickel is included in the copper sulfate, and the resulting finished product sometimes does not meet the standard requirements. Cleaning of such a complex sulfate solution can be done electrochemically, with the help of precipitation reagents, ion exchange and some other methods [6]. Ammonium rhodanide was used as a reagent for separate separation of copper and nickel contained in the technological solutions formed during the production of copper sulfate. The dependence on temperature, time, solution concentration was investigated. [7]

Research part. Waste water containing rhodanite ions from Navoiazot 201 workshop (thiomochevine production workshop) was used as a precipitation reagent for the extraction of metals from the technological solutions formed in the production of copper sulphate by the precipitation method. First, we determined the composition of both wastewaters in a mass spectrometer.

Table 1

Analysis of elemental composition of technological wastewater.

Analyzed product	Chemical composition, g/dm3								
	l	a	n	e	i	u	n	s	b
Acidic wastewater from the vitriol workshop of the MPZ	2	70	4	70	0	2	3	,4	3
Washing solutions produced by rhodonite JSC "Navoiyazot"	5	00	,100	,8	,32	8	2	8	,6

In the study, we took samples of copper sulfate plant wastewater and thiourea production plant waste water in different ratios (1:9, 1:4; 1:2.5; 1:1.5; 1:1; 1.5:1) and mixed them. Mixing was done every 10 min using a glass rod. The procedure was carried out at room temperature.

Rhodanide ions react with metal ions as follows:

$$CuSO4 + 2CNS^- = Cu(CNS)2 + SO4^{-2} \quad (1)$$
$$Cu^{+2} + 2CNS^- = Cu(CNS)2 \quad (2)$$
$$NiSO4 + 2CNS^- = Ni(CNS)2 + SO4^{-2} \quad (3)$$
$$Ni^{+2} + 2CNS^- = Ni(CNS)2 \quad (4)$$
$$FeSO4 + 2CNS^- = Fe(CNS)2 + SO4^{-2} \quad (5)$$
$$CoSO4 + 2CNS^- = Co(CNS)2 + SO4^{-2} \quad (6)$$
$$ZnSO_4 + 2CNS^- = Zn(CNS)_2 + SO4^{-2} \quad (7)$$

After one hour, stirring was stopped and the solution was filtered. The composition of the filtered solution was determined. In this case, the filtering process was carried out on filter paper. The appearance and color of the filtered solution and the remaining precipitate were studied. The precipitates remaining on the filter were viewed under a NLSD-307B screen microscope at a magnification of up to 700 times. For this, the precipitate left in the filter was dried. 20 g was taken, crushed and studied microscopically.

Table 2

Results of the analysis of the mixing of AGMK copper sulfate workshop and Navoiazot wastewater in different proportions and the precipitation of metals (g/l)

Ratio A÷B	Fe	Ni	Cu	Zn	As	Sb
1÷0	270	20	22	23	1,4	63

0÷1	2,8	0,32	18	12	0.48	2,6
1,5÷1	0,5	0,003	37	0,26	0,078	0,612
1÷1	0,27	0,002	25	0,17	0,056	0,433
1÷1,5	0,21	0,0014	15	0,12	0,046	0,358
1÷2,5	0,15	0,0009	5,6	0,1	0,031	0,272
1÷4	0,0049	0,0006	0,00026	0,006	-	0,16
1÷9	0,0031	0,00022	0,000078	0,00056	-	0,069

A- Copper sulfate shop wastewater.
B- "Navoiazot" OA rhodanite wastewater

As can be seen from the table, the number of metals in the solution increases with the increase in the amount of copper sulfate workshop wastewater when mixed with Navoiyazot rhodanite waste water in different proportions. The number of metals in the sediment has decreased, which means that the amount of rhodanite wastewater has not been completely neutralized. It is desirable to obtain a larger amount of waste water with rhodanite compared to the waste water of the copper sulfate workshop. Mixing was carried out in different time intervals (between 10-60 minutes) and the amount of copper, zinc and nickel transfer to the bath was determined. In the process, the waste water of the Almalyk copper sulfate plant was mixed with the waste water of Navoiazot rhodanite in a ratio of 1:9. the results obtained during the experiment were included in table 3.5

Table 3.

Time dependence of the number of metals in solution.

Mixing time(min)	amount of metals in solution (g/l)		
	Cu	Ni	Zn
10	0.0096	0.0078	0.0012
20	0.0055	0.0025	0.00097
30	0.00018	0.00095	0.00078
40	0.000090	0.00034	0.00062
60	0.000078	0.00022	0.00056

Table 4

pH values of solutions

Primary wastewater			After mixing solutions		
№	Name	pH value	№	Mixing ratio	pH value
1	**Copper sulfate**	1.48	1	1:9	8.41
2	**Navoiyazot**	9.23	2	1:4	6.68
			3	1:2.33	2.08
			4	2.33:1	1.75
			5	4:1	1.65

The environment is acidic (pH=1.48) due to the presence of sulfate ions in the copper sulfate workshop wastewater. Due to the abundance of organic compounds in rhodanite wastewater, the environment is weakly alkaline (pH=9.23).

Table 5.

Dependence of metal precipitation on pH value.

pH value	Number of precipitated metals (%)		
	Cu	Zn	Ni
1.65	25.6	94	67

1.75	45.6	95	69
2.08	72.5	97.3	87
6.68	99	98	98.6
8.41	99.2	99	99

The results of the chemical analysis of deposition indicators using different values of pH in the deposition of metals in the technological solution are presented in Table 4, and based on the obtained results, a graph of the dependence of the deposition process on pH was created.

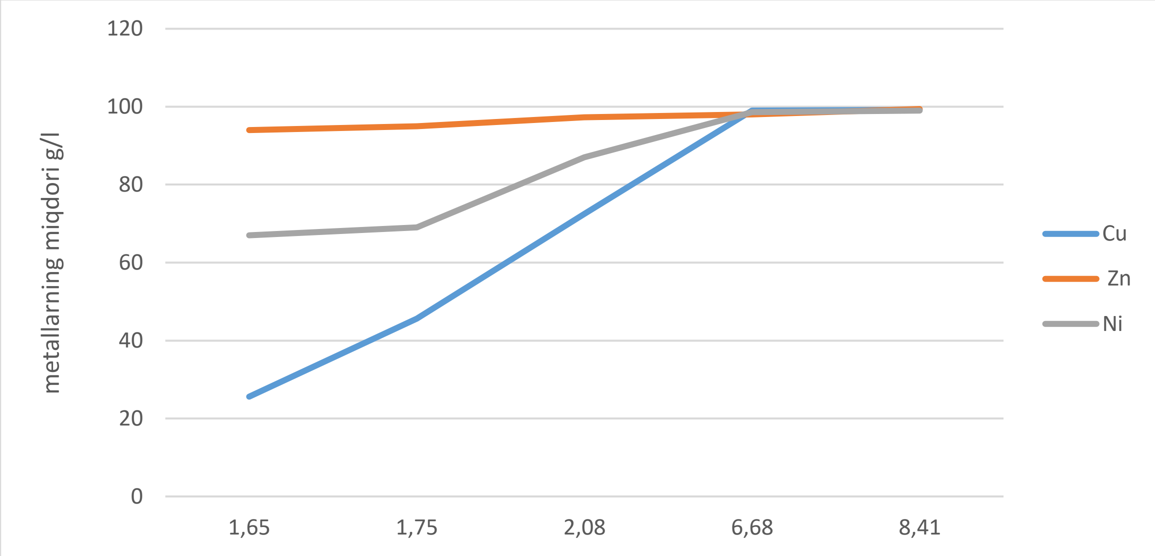

Fig. 1. Dependence of the precipitation of metals on pH.

As the pH value increases, precipitation of metals increases. In this case, 99% of copper (pH=8.41), 98.7% of zinc, and 97% of nickel were deposited.

Summary. During the separation of high-concentration metals (copper and nickel-zinc) contained in the technological solutions (Matochnye rastvory) produced in the production of copper sulfate, through waste water containing rhodonite ions from Navoiazot 201-shop (thiomochavina production shop) was conducted. According to the results of the research, the co-precipitation of metals in the solution was observed under different conditions. In this case, the maximum rate of precipitation of copper from the solution was 80%, the rate of precipitation of nickel from the solution was 94%, and that of zinc was 97%. The results of experimental studies show that metals precipitate in a significant amount in a short period of time (10-15 minutes). In addition, the amount of precipitate formed depends on the ratio of solutions. The lower the acidity, the faster the system stabilizes and the amount of sediment and metals in it increases.

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