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On the Issue of Processing Hydroxide Arsenic Sludges of Copper Refining Production

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Abstract

The paper carried out X-ray phase analysis of arsenic sludge, whereby the following compounds were detected: $(CaSO_4) \cdot 2H_2O$, $Cu(OH)_2$, $Ni(OH)_2$, $Fe(OH)_3$, $Ca(OH)_2$, and $Zn(OH)_2$. The presence of arsenic (III) as calcium metaarsenite ($Ca(AsO_2)_2$) was also determined. Options for extraction of non-ferrous metals from multicomponent hydroxide raw materials containing significant amounts of arsenic were considered. Solutions of sulphuric acid, ammonium salts, oxyethylidenediphosphonic (OEDP), ethylenediaminotetraacetic acid (EDTA), alkaline metal tartrates were explored as reagent solvents. The values for the logarithms of the stability constants of copper (II), nickel (II), and calcium (II) complexes with appropriate ligands were presented. According to experimental data, the use of substances that ensure the copper and nickel extraction as complexes while maintaining $pH > 5$ allows for almost complete elimination of arsenic dissolution. It was experimentally proven that ammoniacal leaching and leaching in solutions of EDTA salts did not lead to arsenic contamination of the filtrate ensuring copper and nickel extraction from sludges. The use of EDTA and its salts also simplified technology and equipment selection for further solution processing. The findings led to the conclusion that the use of EDTA solutions at leaching of sludges of neutralising industrial solutions was promising.

Key words: hydroxide sludge, calcium metaarsenite, complexing agent, leaching, EDTA

INTRODUCTION

Large amounts of solid wastes that contain valuable components and are simultaneously highly toxic for the environment are annually generated at non-ferrous metallurgy enterprises. Sludges obtained by neutralisation of non-conforming process solutions are one of such wastes. Thus, in copper refining production, a fraction of acid production solutions containing both valuable components and impurities accumulated during the turnover in the technological scheme is withdrawn and subjected to neutralization with lime milk. Consequently, sludge comprising mainly non-ferrous metal hydroxides, gypsum, and arsenic compounds is formed after the separation of treated waste water. The typical composition of the sludge obtained during neutralization of spent electrolyte, %: 50–85 $(CaSO_4) \cdot 2H_2O$; 5 – 15 $Cu(OH)_2$; 5–10 $Ni(OH)_2$; 0.5 and 2 $Zn(OH)_2$; 1–5 $Fe(OH)_3$; 0–4 $Pb(OH)_2$; 1–6.5 $Ca_3(AsO_3)_2$; 0.5–3.5 SiO_2.

Copper content in sludges reaches 10 %, nickel – to 9 %, herewith, arsenic content is 0.5–3 %. Thus, these products are promising technogenic raw materials. Significant amounts of hydroxide sludges are accumulated in the Ural region, which makes relevant the issue of their disposal not only from the viewpoint of extraction of nonferrous metals but also a decrease in the environmental hazard on production. However, the complex chemical composition drives the need to search for a rational scheme of processing. When solving the objective, one should take into account the availability and possibility of regeneration of the reagents and instrumentation simplicity to ensure processing profitability, and also an opportunity of reducing the volume of highly toxic arsenic waste and extraction of valuable components into high-quality demanded products.

The use of pyrometallurgical methods of processing of similar raw materials requires large energy costs and does not ensure selective extraction of elements. Additionally, highly toxic dusts and gases that also require disposal are formed during pyrometallurgical processes.

Separative methods of enrichment are of little use, since they do not allow reaching the required selectivity and the degree of metal extraction using conventional methods. This is driven by the phase composition and peculiarities of the formation of compounds upon sludge generation. The use of methods of mechanoactivation for raw materials is economically inefficient.

The utilization of hydrometallurgy methods enables selective extraction of valuable components as commercial products and the removal of arsenic as a poorly soluble compound.

Selective extraction of valuable components into a solution suitable for their further processing is the major task when processing of solid multicomponent raw materials by hydrochemistry methods. Dissolution of metal hydroxides is not technologically complex and can be carried out by sludge processing by acid solutions, which ensures high degrees of extracting metals. A sulphuric acid solution was recommended as a solvent in a series of papers [1, 2]. Consequently, we managed to sufficiently transfer metals into sulphuric acid solutions that can be processed in traditional technological schemes of copper and nickel production. However, arsenic dissolution largely happens under acid leaching conditions, which imposes limits upon the introduction of the resulting solutions into the production cycle. Arsenic leaching in acid pH regions is driven by the formation of arsenous acid. Thermodynamics of the solubility of calcium arsenite was demonstrated on an example of its interaction with a sulphuric acid solution. The calculated change in Gibbs energy of this reaction is negative:

$$Ca(AsO_2)_2 + H_2SO_4 = CaSO_4 + 2HAsO_2(v) \quad (1)$$

$$\Delta G = -34.74 \text{ kJ/mol}$$

Thus, solvent selection should be carried out considering the prevention of production solution contamination with arsenic. The transfer of non-ferrous metals into a solution as complex compounds appears to be the most promising method of selective leaching.

An increase in end-to-end recovery of non-ferrous metals at copper refining production enterprises by the processing of the sludge formed at neutralisation of the technological solution with lime milk is the work purpose. Dealing with this challenge also allows for reducing volumes of arsenic-containing wastes.

EXPERIMENTAL

Materials

Ethylenediaminotetraacetic acid disodium salt, oxyethylidenediphosphonic (OEDP), ammonia, potassium sodium tartrate were selected as chelating agents based on literature data analysis, and also for reasons of the profitability of potential recycling scheme. The listed compounds ensure dissolution of both copper and nickel. High-level extraction of non-ferrous metals into a solution and simultaneously weak solubility of arsenic compounds should be regarded as the major efficiency criterion of reagents.

Trilon B. The EDTA complexes with transition metal cations are relatively well understood [3]. Double-charged 3*d*-metal cations form stable soluble complexonates with ML^{2-} composition. Copper complex has the maximum stability ($\log_{10}\beta(CuL^{2-}) = 18.8$) among them, and the stability of the rest decreases in the following order: $Cu^{2+} > Ni^{2+} > Zn^{2+} > > Co^{2+} > Fe^{2+} > Mn^{3+} > Cr^{3+} > V^{3+}$ ($\log_{10}\beta(VL^{2-}) = 12.7$).

OEDP. Alkyldiphosphonic acids showing high specificity of the interaction with a series of cations are of substantial interest. An important representative of these acids is OEDP comprising two phosphonic groups capable of complexation in highly acid medium and an oxyethyl group. Complexation processes begin in an acid medium (pH 1.0–2.5); complexes are destroyed at pH > 12.5 [4].

Ammonia. Owing to electron-donor properties ammonia molecules may enter into complexes as ligands. Thus, the introduction of the excess ammonia in solutions of d-metal salts leads to the formation of their amino complexes [5]. According to calculations of partial distribution of ionic forms, $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ ions should be considered predominant.

Seignette salt contains two hydroxyl groups and is able to form a complex compound with copper (II) hydroxide in an alkaline solution, sim-

TABLE 1

Stability constants of copper, nickel, and calcium complexes

Ligands	Form	Cu(II)	Ni(II)	Ca
Ammonia	$[\mathrm{Me(NH_3)}]^{2+}$	3.99	2.67	−0.2
	$[\mathrm{Me(NH_3)_2}]^{2+}$	7.33	4.79	−0.8
	$[\mathrm{Me(NH_3)_3}]^{2+}$	10.06	6.4	–
	$[\mathrm{Me(NH_3)_4}]^{2+}$	12.03	7.47	–
	$[\mathrm{Me(NH_3)_5}]^{2+}$	11.43	8.1	–
	$[\mathrm{Me(NH_3)_6}]^{2+}$	8.9	8.01	–
EDTA	$\mathrm{Me(edta)}^{2-}$	18.8	18.62	10.7
	$\mathrm{Me(Hedta)}^{-}$	11.54	11.56	3.51
OEDP	$[\mathrm{Me_1(oedph)_1}]^{2-}$	12.5	9.2	–
	$[\mathrm{Me_1(H_1oedph)_1}]^{-}$	6.3	5.1	6.04
	$[\mathrm{Me_2(oedph)_1}]$	16.9	12.2	15.59
	$[\mathrm{Me_2(H_1oedph)_1}]^{+}$	9.6	7.7	–
Tartrate	$[\mathrm{Me(tart)}]^{2-}$	3.00	–	2.98
	$[\mathrm{Me(tart)_2}]^{2-}$	5.11	5.42	9.01
	$[\mathrm{Me(tart)_3}]^{4-}$	5.76	–	–
	$[\mathrm{Me(tart)_4}]^{6-}$	6.20	–	–

Note.

ilarly to polyatomic alcohols [5]. Herewith, copper tartrate is able to dissolve in the presence of the excess alkali metal ions. This reagent is of interest considering the prevalence of tartrate solutions in galvanic productions [12].

Table 1 presents the stability constants of some copper, nickel, and calcium complexes [6, 7].

Methods

Neutralization sludge of the spent electrolyte of a copper refining shop was utilized as a study object (Fig. 1).

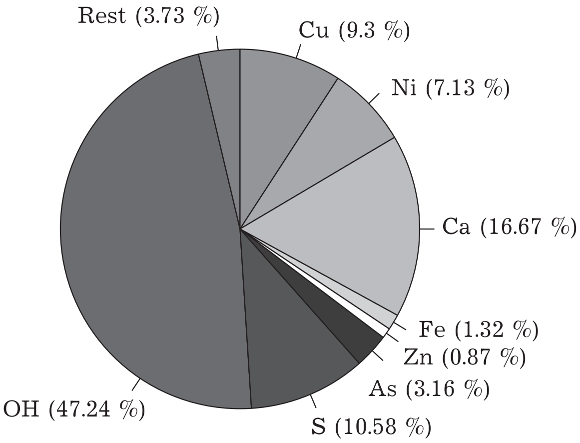

Fig. 1. Chemical composition of sludge.

X-ray phase analysis of the study object determined the presence of the following compounds: $(CaSO_4) \cdot 2H_2O$, $Cu(OH)_2$, $Ni(OH)_2$, $Fe(OH)_3$, $Ca(OH)_2$, $Zn(OH)_2$. Based on diffractograms, we managed reliably to determine, in which compound arsenic is found. Depending on the initial solution data under its thermodynamic neutralization conditions, calcium metaarsenite ($Ca(AsO_2)_2$) is a stable form. The determination of the latter in the obtained diffractogram can be complicated due to the proximity of the values of the interplanar distances with already determined substances present in large amounts.

All reagents used for the preparation of leaching solutions corresponded to chemically pure reagent grade or higher.

Solution concentration was selected in order to ensure the most stable forms of metal complexes [6]. Leaching was carried out at L/S = 1 : 5, contact time is 1 h at 25 °C and mechanical stirring. Table. 3. presents leaching conditions.

Copper and nickel content in the initial material was determined by complete dissolution of a sample of air-dry sludge in chemically pure concentrated nitric acid followed by analysis of the solution using atomic absorption spectroscopy (AAS) technique. Leaching products were also

TABLE 2

Rational composition of hydrate sludge

Compounds	Cu	Ni	Ca	Fe	Zn	As	S	O	H	Rest	Total
$(CaSO_4) \cdot 2H_2O$			13.23				10.58	31.75	1.32		56.88
$Ca(OH)_2$			0.91					0.72	0.05		1.68
$Cu(OH)_2$	9.30							4.65	0.29		14.24
$Ni(OH)_2$		7.13						3.86	0.24		11.23
$Ca(AsO_2)_2$			2.53			3.16		2.70			8.39
$Fe(OH)_3$				1.32				1.13	0.07		2.52
$Zn(OH)_2$					0.87			0.43	0.03		1.33
Rest										3.73	3.73
Total	9.30	7.13	16.67	1.32	0.87	3.16	10.58	14.24	2	3.73	100

TABLE 3

Leaching conditions

Conditions	Solvent				
	H_2SO_4	OEDP	TrB/H_2edta^{2-}	NH_4OH/NH^{4+}	Tartrate
Concentration, mol/dm^3	0.25	0.5	0.25	1	2
pH	0.3*	0.72	3.5[8]	9–9.5	6.3

* Calculated value

subjected to chemical analysis. The averaged values are 8.5 mass % for copper and 8 mass % for nickel.

RESULTS AND DISCUSSION

Figure 2 gives sludge leaching results. As expected, maximum extraction of copper, nickel, and arsenic was reached in sulphuric acid leaching. The results of the analysis of solutions for arsenic by AAS technique confirm a model for dissolution built on the basis of thermodynamic calculations.

High levels of copper and nickel extraction into a solution was obtained during leaching of sludge with OEDP solution. Alongside this, significant arsenic dissolution is observed, which complicates further solution processing. Leaching in solutions of EDTA, tartrates, and ammonium salts demonstrated lower extraction of non-ferrous metals. Herewith, the transfer of arsenic into a solution in case of leaching with ammonia and EDTA is significantly limited. Thus, the specified solvents are of most interest for further studies. Tartrate regarded in the work as a convenient reagent for obtaining demanded solutions in galvanic productions did not allow achieving a high degree of extraction of non-ferrous metals, and also did not demonstrate selective leaching of non-ferrous metals in the presence of arsenites.

From the standpoint of reagent consumption, the use of EDTA suggesting simple regeneration technique of complexing agent with obtaining solutions of non-ferrous metals suitable for further solution processing is more promising in the technological chain [9]. Nevertheless, in terms of increasing the degree of extraction of valuable components, the process requires optimisation.

Metal extraction from ammonia solutions is likely by several methods: ion exchange, precipitation as sparingly soluble compounds, distilling off ammonia, electrolysis [10–13]. Electrolytic extraction is the most promising method. However,

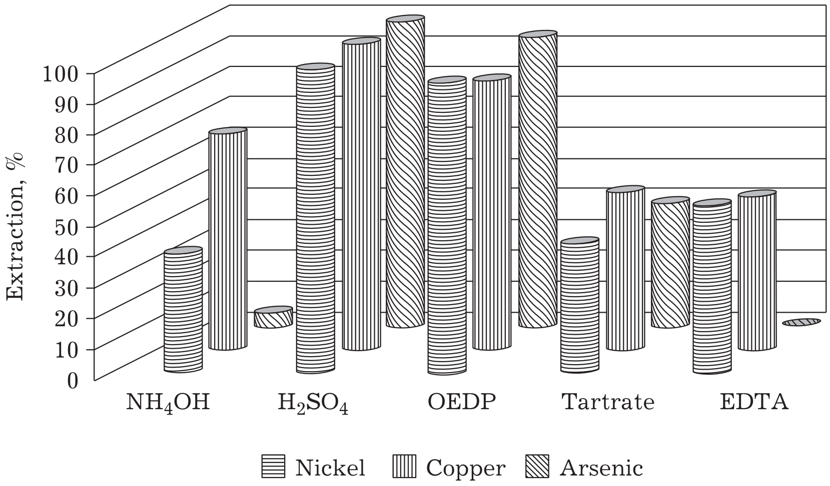

Fig. 2. Sludge leaching results in solutions of chelating agents and sulphuric acid.

	NH_4OH	H_2SO_4	OEDP	Tartrate	EDTA
Nickel	38.54	99.48	94.51	41.87	54.55
Copper	70.35	99.76	87.73	51.07	49.71
Arsenic	4.27	99.64	94.51	39.70	0.04

it requires the use of pressurized electrolysers and is characterised by increased power consumption.

CONCLUSION

The work studied a series of chelating agents ensuring the transfer of valuable sludge components into a solution. Sludge leaching in solutions of complexing agents at pH >5 allows almost complete elimination of arsenic transfer into a solution.

Thus, solutions of EDTA salts and ammonium salts allow extraction of non-ferrous metals from sludge not contaminating solutions with arsenic. Degrees of nickel and copper extraction reach 38.5 and 70.3 % under conditions described in the experimental part and 54.5 % and 49.7 % in case of the utilization of EDTA, respectively.

However, ammonia solutions have a number of disadvantages, such as the failure to reach high metal concentrations under a condition preserving high degree extraction condition, the need to use special hermetically sealed equipment. This causes the complexity of their processing and reagent regeneration.

Considering selectivities and degrees of extraction of valuable components, leaching in solutions of EDTA and its salts appears to be most promising.

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