ISSN 1062-7391, Journal of Mining Science, 2020, Vol. 56, No. 1, pp. 142–148. © Pleiades Publishing, Ltd., 2020.
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MINERAL DRESSING

Removal of Copper from Underspoil Water of Mines by Cementation

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Received January 22, 2019
Revised November 26, 2019
Accepted February 4, 2020

Abstract—The author studied the process of copper removal from underspoil water at Blyavinskoe and Safyanovskoe copper ore deposits by cementation by iron. The influence of pH, consumption of cementation agent impurity ions Fe^{3+}, Al^{3+} and Ca^{2+}, as well as timing on the cementation performance was analyzed. The mechanism of the process was determined, and by-reactions resulting in over-consumption of cementation agent were revealed. The studies of the material constitution of cemented copper showed that the concentrate quality worsened because of the joint settling of basic aluminum and calcium sulfates. The obtained results make it possible to draw the conclusion on applicability of cementation for removal of copper from underspoil water.

Keywords: Underspoil water, copper, cementation, iron, settling.

DOI: 10.1134/S1062739120016588

INTRODUCTION

As traditional sources of nonferrous metal raw materials became significantly depleted, the share of oxidized and mixed copper ore involvement in processing has increased in recent decades in the world. Close attention is paid to oxidation zones of dumps, cut-off grade sulphide ores and overburden rocks as potential manmade copper deposits.

The most typical representatives of these deposits in the Urals and Trans-Urals are Blyavinskoe and Safyanovskoe deposits of pyritic ores. Blyavinskoe copper-pyrite deposit is located in the Orenburg Region, Safyanovskoe—in the Sverdlovsk Region. Significant reserves of cut-off grade ore and overburden rocks in these deposits (copper content 0.4–0.8%) are stored and subjected to weathering. Water-soluble sulphates formed in the process of their induced oxidation [1 – 4]. Copper sulphates have commercial significance [5, 6]. An X-ray diffraction analysis carried out at the Uralmekhanobr Institute determined that these sulphates were mainly represented by the phase, which is similar to chalcanthite in structure ($CuSO_4 \cdot 5H_2O$) [7, 8]. The presence of chalcocyanite ($CuSO_4$), bonnatite ($CuSO_4 \cdot 3H_2O$) and butite ($CuSO_4 \cdot 7H_2O$) is noted [7, 8]. These minerals are found in the form of light gray and white sinter aggregates with a bluish and greenish shade. Currently, with atmospheric precipitations from dumps, acid solutions are drained and copper passes into them. Neutralization stations dispose of these drains, while nonferrous metals are irretrievably lost. Processing solutions to remove copper may be economically feasible [5–8]. Copper is traditionally removed from acid underspoil, mine and pit waters by cementation by metallic iron to obtain copper concentrate [9 – 11]. The process runs in conformity with the the reaction equation [12]:

$$Fe + CuSO_4 = Cu\downarrow + FeSO_4. \tag{1}$$

This paper studied the copper concentrate removal from underspoil water by cementation. The conditions for its preparation were investigated, providing the highest quality and recovery.

1. MATERIALS AND METHODS OF STUDY

The underspoil water of Blyavinskoe depoit with the following composition was used, g/l: 3.0 Cu, 0.05 Zn, 0.57 K, 0.08 Na, 0.82 Mg, 1.05 Al, 8.85 Fe(III), 1.12 Fe(II), 0.15 Mn, 0.63 Ca, 0.70 Si (pH 2.5) and acid water of Safyanovskoe deposit characterized as follows, g/l: 0.17 Cu, 1.8 Zn, 1.65 K, 0.05 Na, 4.20 Mg, 0.84 Al, 0.23 Fe(III), 0.21 Mn, 0.60 Ca, 0.53 Si (pH 2.8).

Waters are brines having a complex salt composition, with a high concentration of aluminum, alkaline and alkaline-earth metals. The copper content in solutions corresponds to a wide range of concentrations characteristic of waters of a given genesis. The water composition is typical for acid effluents of copper ore mining enterprises [1 – 7].

For cementation, PZhR5.200.26 iron powder as per GOST 9849-86 standard was used. Cementation was carried out with agitation in a laboratory reactor 2 l in capacity. At the end of the experiment, the solution was sedimented with a 0.1% Magnaflock M338 flocculant solution (10 ml/l) for 1 h, then it was decanted, precipitate was washed with a large excess of water (10:1 by weight), filtered, dried and weighed. Copper was determined by atomic absorption method using the M 12-27.19-2013 procedure. According to the results of precipitate and filtrate analysis, the balance of copper was drawn. Settling was performed with intensive agitation on an ES 800 laboratory agitator. In agitation, Reynolds criterion (Re) was about 15 000.

2. RESULTS AND DISCUSSION

The dependence of cementation indices on process duration was studied, which varied in the range of 0.25-4.0 h. The possibility of reducing precipitate consumption by increasing the contact time was studied (Fig. 1). The optimum duration of cementation was determined as $\tau = 0.5$ h. A further increase in contact duration is impractical—reverse dissolution of cement copper is observed. Thus, if the test lasts $\tau = 4$ h, the formed cement copper dissolves almost completely. The reverse copper dissolution is not accompanied by a change in iron valent state in solution. This process can be explained by the interaction with ambient oxygen according to the scheme [12]:

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O. \quad (2)$$

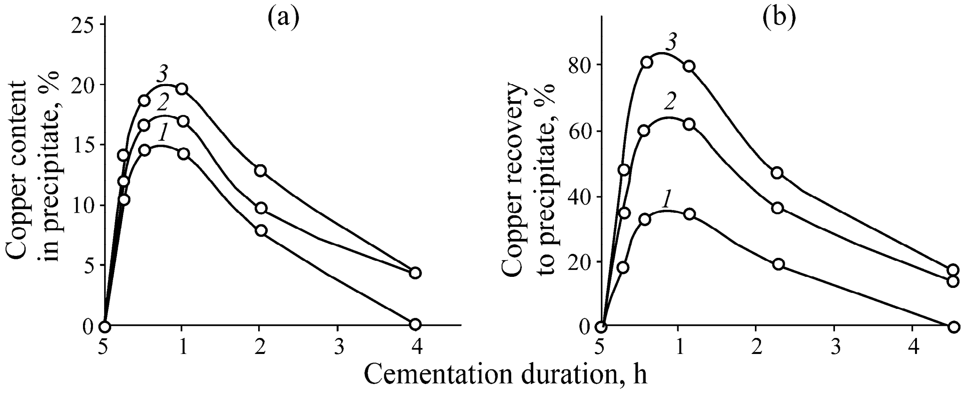

Fig. 1. Dependence of (a) content and (b) removal of copper from underspoil water of Safyanovskoe deposit to precipitate on the process duration with different iron powder consumption, g/l: 0.56 (*1*); 0.85(*2*); 1.20 (*3*).

Further cementation experiments were carried out with a time duration $\tau = 0.5$ h. To retain copper in precipitate phase (shifting the equilibrium of reaction (1) to the right), an excess of unreacted iron is required.

The results of determining the optimum consumption of cementation agent are presented in Fig. 2. The stoichiometric amount of iron per cementation reaction is about 0.88 kg per 1 kg of copper in solution. The results significantly exceed the theoretical reaction rate (1): copper recovery of at least 90% is ensured at a consumption of 4–9 kg/kg (for Blyavinskoe and Safyanovskoe deposits, respectively). This can be explained by the following fact. Solutions contain large amounts of impurity iron (III). Iron is consumed additionally during cementation according to the reactions [12, 13]:

$$\mathrm{Fe} + \mathrm{Fe_2(SO_4)_3} = 3\ \mathrm{FeSO_4}, \tag{3}$$

$$\mathrm{Fe} + \mathrm{H_2SO_4} = \mathrm{FeSO_4} + \mathrm{H_2}\uparrow. \tag{4}$$

The analyzes performed on Fe (III) (by complexometric titration method [14]) determined that copper settles completely only after deep reduction of iron (III) according to reaction (2): cementation mother solution of the above optimum conditions contains only trace amounts of iron (III) (less than 0.005 g/l). In addition, in accordance with reaction (4), an increase in pH from 2.5–2.8 to 4.0–4.2, respectively, is observed in the cementation process. The content of free sulphuric acid decreases from 0.5 to 0.1 g/l (determined titrimetrically, by the method with iron complexation by fluorides [14]).

The experimental consumption of iron almost completely (with a residual error of no more than 5%) corresponds to the stoichiometry of reactions (1)–(4) taking into account the remainder of unreacted iron in the precipitate phase. This allows predicting the consumption of iron powder knowing the chemical composition of original copper solutions. Experimentally achieved high powder consumption is determined by predominant contribution to indirect reduction of iron (III) according to (3).

Under these conditions 97% of copper is removed (content in mother solution—0.03 g/l). For the water of Safyanovskoe deposit, this value is 1.5 g/l, and removal reaches 94% (residual copper content in solution—0.01 g/l). Further increase fails to produce recovery gain. These consumption values correspond to the maximum copper content in the concentrate. The maximim achieved copper content for the water of Blyavinskoe deposit is 22.4%, for Safyanovskoe—17.8 %.

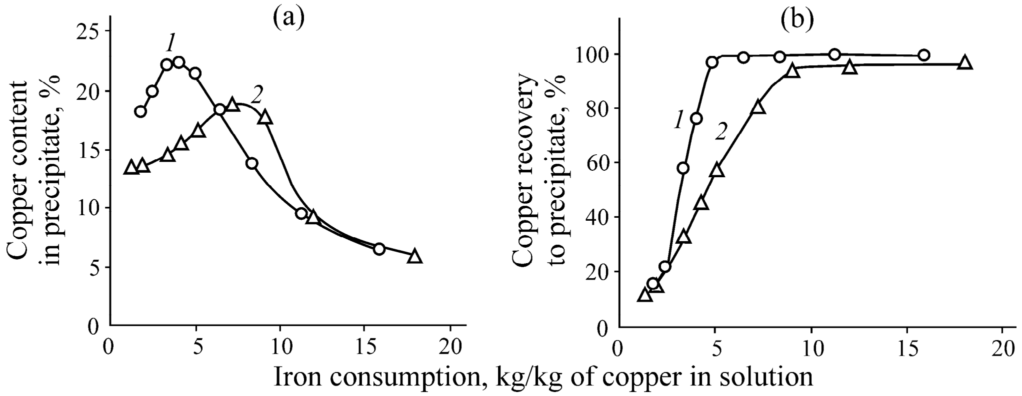

Fig. 2. Dependence of (a) content and (b) removal of copper from underspoil water of Blyavinskoe (*1*) and Safyanovskoe (*2*) deposits to precipitate on specific iron consumption.

Table 1. Chemical composition of washed cement copper obtained by settling in iron powder, %

Component	Components in precipitate obtained from underspoil water	
	Safyanovskoe deposit	Blyavinskoe deposit
Fe	36.59	10.50
Cu	17.79	22.40
Al	4.28	9.88
S	2.81	9.64
Si	0.90	3.00
Ca	1.25	1.30
Mg	0.79	0.77
Na	0.19	0.07
Mn	0.18	0.15
Zn	0.14	0.16
K	0.04	0.04

The copper content in precipitate weakly depends on the original concentration of copper in the solution and is low enough. The material composition of precipitates was studied to develop methods for their enrichment by copper. The chemical composition data indicate that precipitate is significantly contaminated with hydrated sediments (Table 1). The presence of iron 10.5–36.6% is also noted. This is due to the fact that excessive unreacted iron is required for the deep copper settling in accordance with reaction (1).

The X-ray diffraction analysis of precipitates was carried out using a Shimadzu XRD-7000 diffractometer. The diffraction pattern was recorded in cobalt monochromatic radiation at angles in the range of 5–95°. The obtained diffraction patterns for concentrates from both deposits are fundamentally identical in appearance. Figure 3 shows the diffraction pattern of a precipitate from Safyanovskoe deposit.

The X-ray patterns were decrypted using the IPS-6 software. Based on the data of X-ray diffraction and chemical analyzes, the phase composition of copper precipitate (Table 2) and in the X-ray pattern (Fig. 3) was determined. Iron in precipitate is predominantly in metallic form.

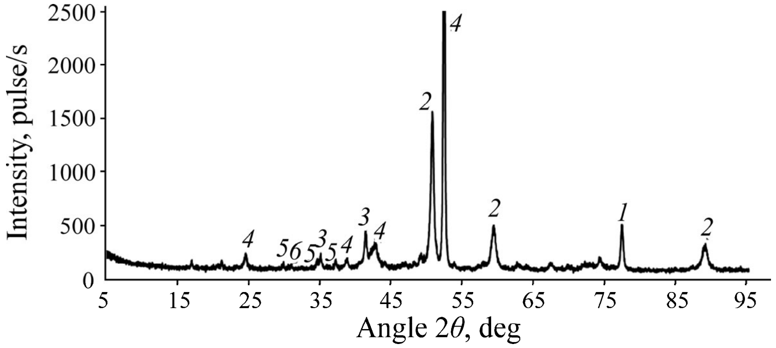

Fig. 3. X-ray pattern of precipitate sample with mineral phase peaks: *1*—iron; *2*—copper; *3*—cuprospinel; *4*—goethite; *5*—bassanite; *6*—wustite.

Table 2. Phase composition of cement copper (after washing), %

Component	Phases in precipitate obtained from underspoil water	
	Safyanovskoe deposit	Safyanovskoe deposit
Iron	36	10
Copper	17.8	22.4
Basic aluminum sulphates (amorphous)	27	45
Cuprospinel	8	12
Goethite	5	6
Bassanite	4	5
Wustite	2	2

Low copper content in the product (17.8–22.4%) is explained not only by the need to maintain an excess of iron, but also by the presence of a large amount of basic aluminum sulphates in the precipitate, which is confirmed by chemical analysis data. Settling at pH of about 4 [13], basic aluminum sulfates cannot be removed by water washing. This, in turn, leads to precipitate quality deterioration. Using X-ray diffraction analysis, we failed to find the main aluminum sulphates, which can be explained by their X-ray amorphous properties. As follows from the data obtained, precipitate is largely contaminated with iron oxides and calcium sulphate. Iron oxides are identified as cuprospinel ($CuFe_2O_4$), goethite (FeOOH) and wustite (FeO). Calcium sulphate settles as a compound similar to bassanite in structure ($CaSO_4 \cdot 0.5H_2O$).

To improve the precipitate quality, it was proposed to enrich it with wet magnetic separation methods. Magnetic separation was carried out on a 25-T magnetic analyzer. The field strength in the experiment was maintained at a level of 1500 Oe. The experiments did not allow distinguishing the nonmagnetic fraction: precipitate completely transferred to the magnetic product.

To explain the magnetic properties obtained, precipitate thin sections were studied using a Zeiss EVO MA 15 electron microscope. The appearance of precipitate grains is shown in Fig. 4a. Distributions of components over precipitate grain surface were performed using an EDX X-max X-ray fluorescence attachment (Fig. 4b, c, in white). Ultrafine intergrowth of grains of the formed iron-based copper phase is obvious: the linear sizes of copper particles are less than 1 μm [11]. The copper phase is concentrated mainly in the surface layer of iron particles.

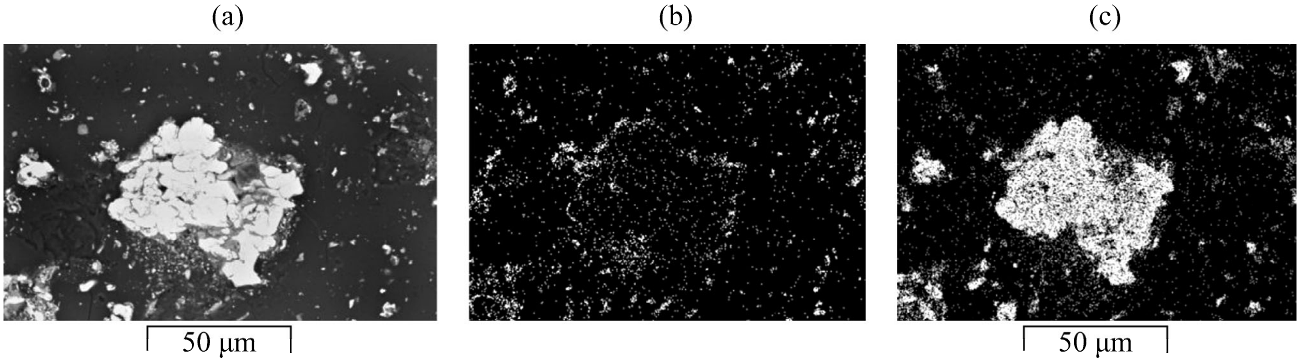

Fig. 4. (a) Typical thin section of precipitate grains (image in reflected electrons) and distribution maps of (b) copper and (c) iron superimposed on precipitate grain image.

During cementation settling, the data obtained by an electron microscope indicate the processes similar to copper electroplating on the iron surface: a thin surface phase of copper is formed, which is firmly bound to the iron matrix. Copper particles do not practically separate from the matrix. The formation of a close chemical bond between settling copper and metallic iron is confirmed by the occurrence of cuprospinel phase.

The resulting product meets the requirements of GOST R 52998-2008 for copper concentrate. Recovery of copper from solutions by cementation is a promising method for additional copper removal at copper pyritic ore mining enterprises.

Good condensability and filtrability of cement pulps was determined in studying their process properties. The linear velocity of pulp clarification was about 2 m/h. No significant reverse dissolution of copper was noted during condensation. Vacuum filtration of cement copper proceeded with a filter capacity in solids of 1.0–1.2 t/(m^2·h) and cake moisture content of 11–12% (at vacuum gage pressure of 0.8 MPa). Used fabric—belting (product no. 2030)

Cementation is recommended for industrial use to remove copper from underspoil water. The technology is characterized by simple implementation. Process flow diagram includes the following operations: copper settling in powder, condensation, vacuum filtration to obtain cake, drying of cake to obtain copper concentrate no lower than grade KM7 according to GOST R 52998-2008. Cementation mother solution is sent to a neutralization station.

CONCLUSIONS

Copper concentrate removal by cementation from underspoil water of complex salt composition, with a copper content ranging from 0.17 to 3.0 g/l was studied. Copper concentrates meeting the requirements of GOST R 52998-2008 for a grade not lower than KM7 were obtained experimentally. The conditions for obtaining copper concentrate were optimized. When studying the material composition of concentrate, factors affecting its quality were revealed. The possibility of preliminary determination of cementation agent consumption was shown using calculation of the solution composition.

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