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PROCESS of ZINC SULFATE SOLUTION PURIFICATION from COPPER and CADMIUM

Abstract: This paper is aimed to the solution of the actual problem on the involving into processing of low-grade zinc sulfide concentrate of Nikolayevsk deposit of Kazakhstan and the development of technology of its processing with produce the intermediate product – copper-cadmium solid precipitate – cake. The article presents the results of experimental studies of the process of purification from a copper and cadmium the zinc sulfate solution obtained after hydrolytic purification from iron, arsenium, antimony, lead and silicon of the solution after the autoclave leaching of low grade zinc sulfide concentrate of Nikolayevsk fields of Kazakhstan. It was determined that the determined conditions of the process of cadmium and copper cementation provide high degree of the purification of the test productive solution from copper and cadmium. In the purified solution copper and cadmium content is less than 2,98 g/dm^3, zinc – 221,4g/dm^3. The resulting intermediate product - copper-cadmium solid precipitate – cake is suitable for the production of copper and cadmium.

Keywords: X-ray analysis, atomic absorption analysis, process time, zinc dust, one-stage purification, cementation, copper-cadmium solid precipitate, cake, sulfide concentrate.

Introduction. In world practice feedstock used for production of zinc sulphide concentrates rich or conditioning zinc content (over 50 %) [1]. In this regard, the current challenge of zinc metallurgy in the Republic of Kazakhstan and abroad is the widespread involvement in the processing of low grade sulphide zinc concentrates as the primary type of raw material and the development of highly efficient technologies for their processing.

We carry out studies on the involvement in the processing of low-grade sulphide zinc concentrate Nikolayev fields of Kazakhstan, in particular, the way it was designed autoclaved leaching [2].

Average zinc sulfate solution of 10 experiments on the pressure leaching of low grade sulphide zinc concentrate Nikolayev fields of Kazakhstan contains significant quantities of impurities. Table 1 shows the chemical composition of the solution.

As a result, chemical and atomic absorption analysis sample solution averaged 10 experiments investigated concentrate leaching autoclave [3,4] that have passed in the solution with zinc (at 99,5-99,6 %) significant quantities of copper (in 84,55 %), cadmium (73,3 %) and iron (67 %), small amounts of arsenic (1,5 %), antimony (to 0,094 %), lead (1,97 %) and silicon (to 11,21 %) [2].

Table 1 - Chemical composition of the average zinc sulfate solution of 10 experiments on the pressure leaching of low grade zinc sulfide concentrate Nicholas Field

Sample of solution	Element content, g/dm^3						
	pH	Zn	Fe_{total}	Fe (III)	Fe (II)	As	Sb
after pressure leaching of the concentrate solution	1,1	134,0	11,6	10,21	1,39	0,0013	0,026
Sample of solution	Element content, g/dm^3						
	$S_{общ}$	SiO_2	Pb	Cu	Cd	Co	
after pressure leaching of the concentrate solution	34,57	3,21	0,11	7,54	0,90	<0,005	

As seen from Table 1, the solutions are representative of the content and recovery of zinc from them. However, the impurity content of the resulting zinc sulfate solution does not meet the requirements of Air Conditioning zinc-containing commercial product (metallic zinc or zinc oxide).

Based on literature data [5,6] we had selected and executed from a group of cleaning hydrolytic impurities: iron, arsenic, antimony, lead, silicon and the purified solution was obtained, which contains the following elements (Table 2).

Table 2 - Chemical composition of the zinc sulfate solution purification after the hydrolytic impurities from the iron group, arsenic, antimony, lead and silicon

Sample of solution	Element content, g/dm^3				
	Zn	Fe (III)	Si	Cu	Cd
after hydrolytic removal of impurities solution	186,05	0,0004	0,002	7,98	1,03

Table 2 shows that the solution contained significant amounts of copper and cadmium. The objective of these studies is the removal of copper and cadmium zinc sulfate solution obtained after hydrolytic cleaning solution from the autoclave leaching of low grade zinc sulfide concentrate Nikolayev fields of Kazakhstan from iron, arsenic, antimony, lead and silicon.

This process is based on the reduction of copper and cadmium in copper-cadmium solid precipitates and dissolution of zinc from zinc dust. For example, the chemistry of the process of cementation of copper and cadmium from zinc sulfate solutions is described by the following reactions (1-2):

$$Zn + Cu^{2+} = Zn^{2+} + Cu, \quad (1)$$

$$Zn + Cd^{2+} = Zn^{2+} + Cd. \quad (2)$$

At the simultaneous presence in solution of copper and cadmium copper will be cemented first. This is due to the fact that the number of elements in the copper has a more positive potential than cadmium, therefore cadmium is precipitated from solution is added to cement copper. Consequently, to ensure complete cleaning solutions of cadmium and copper in the experiments using excess zinc dust was provided by the theoretically required amount of [7,8].

Experimental part. *The methodology of the experiments.*

Experiments were performed in heat-resistant glass beakers. The solution was heated on an electric plate, maintaining the selected temperature and duration of the process. The solution temperature was controlled laboratory glass thermometer TLC-2; stirred solution of BP-8000 laboratory mixer with variable speed for n = 300 rev/min.

The chemical composition of the solution and solid precipitates was determined by chemical and atomic absorption methods of analysis, phase composition - the method of semi-quantitative XRD diffract meter X’Pert MPD PRO (PANalytical).

Terms of the cementation process. For experiments on single-step purification of copper and cadmium were taken 0,5 dm^3 solution purified from iron, arsenic, antimony, lead and silicon with a content of metals: Zn - 93,02 g, Cu - 3,99 g, Cd - 0 ,51 g; process temperature - 60 ^{0}C, cementation process duration - 30 min. In experiments using zinc dust Ridder metallurgical complex “Kazzinc” (99 % Zn), granule metric dimensions of which are class “-0,074 mm.” Consumption of zinc powder was 1: 2 with respect to the stoichiometric total amount of copper and cadmium in solution.

Results and Discussion. Research on one-step purification of the solution from the copper and cadmium cementation with zinc dust. After experimentation by one-stage solution purification of copper and cadmium were obtained 0, 44 dm^3 purified solution and 4, 05 g copper-cadmium solid precipitate.

The results of determining the chemical composition of the purified solution and copper, cadmium and zinc, copper and cadmium in the solid precipitate are shown in Table 3. Extractions of copper and cadmium in the solution and the solid precipitate after a single stage of cementation with zinc dust are presented in Table 4.

In the one-stage zinc dust cementation copper recovery (65,14 %) and cadmium (52,77 %) in the copper-cadmium solid precipitate is sufficiently high. Copper and cadmium in copper-cadmium solid precipitate: copper – 2,59 g (63,95 %), cadmium – 0,27 g (6,67 %).

Table 3 - Chemical composition of the solution and copper-cadmium solid precipitate from one-step cementation zinc sulfate solution

The content of elements:											
Cu				Cd				Zn			
in solution		in the solid precipitate		in solution		in the solid precipitate		in solution		in the solid precipitate	
g/dm^3	g	%	g	g/dm^3	g	%	g	g/dm^3	g	%	g
2,98	1,31	63,95	2,59	0,52	0,23	6,67	0,27	221,64	97,9	26,17	1,06

Table 4 - Extraction of copper and cadmium in solution and solid precipitate after a one-step cementation with zinc dust sulfate solution

Removing elements, %			
Cu		Cd	
in copper-cadmium solid precipitate	in solution	in copper-cadmium solid precipitate	in solution
65,14	32,85	52,77	44,44

Cadmium content of copper and cadmium solid precipitate small because of its low content in the initial solution. In fact, 94,7 % of the zinc consumed from stoichiometry. The excess of zinc was stoichiometrically required amount is provided to prevent the inverse transition of copper and cadmium from solution in the precipitate.

Figure shows a flow diagram of a one-step purification method of cementation with zinc dust solution of hydrolytic treatment.

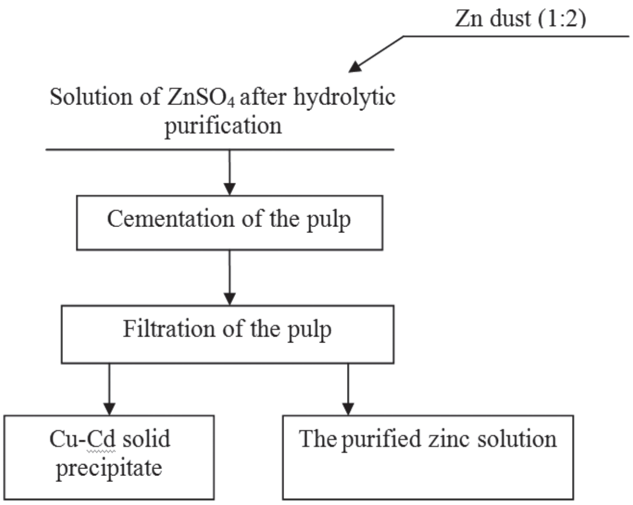

Figure – Technological scheme of one-step cementation of copper and cadmium from the zinc sulfate solution

Conclusions. Carrying out a one-step purification of cementing in a zinc sulfate solution from the autoclave leaching of low grade zinc concentrate of Nicholayev deposit yielded copper-cadmium solid precipitate, which can be sent to the production of copper and cadmium. The zinc sulfate solution after the single-step purification of copper and cadmium copper content was 2,98 g/dm^3, cadmium in solution – 0,52 g/dm^3, and the zinc content of the solution increased to 221,64 g/dm^3.

REFERENCES

1 Sadykov S.B. *Avtoklavnaya pererabotka nizkosortnykh tsinkovykh kontsentratov* (Autoclave processing of low-grade zinc concentrates). Ekaterinburg: UrO RAN. **2006**, 581. (in Russ.)

2 Zhunussova G.Zh., Bedelova Zh.D., Kalyanova O.A., Burshukova G.A. *Issledovanie protsessa sernokislotnogo avtoklavnogo vyshchelachivaniya tsinka iz nizkosortnogo sul'fidnogo tsinkovogo kontsentrata mestorozhdeniya Kazakhstana* (Investigation of the process of sulfuric acid pressure leaching of zinc from low-grade zinc sulfide concentrate deposits in Kazakhstan). *Vestnik KazNITU = Bulletin of the KazNRTU.* **2016**, *5.* 539-543. (in Russ.)

3 Kreshkov A.P. *Osnovy analiticheskoj khimii* (Fundamentals of Analytical Chemistry). *Vol.2.* Moscow: Khimiya, **1971**. 453. (in Russ.)

4 *Khimiko-spektral'nye metody. Instruktsiya № 155-KhS.* (Chemical and spectral methods. Instruction № 155-CS) *Atomno-absorbtsionnoe opredelenie medi, tsinka, kadmiya, vismuta, sur'my, svintsa, kobal'ta, nikelya, zheleza i margantsa v gornykh porodakh, rudakh i tekhnologicheskikh rastvorakh* (Atomic absorption determination of copper, zinc, cadmium, bismuth, antimony, lead, cobalt, nickel, iron and manganese in rocks and ores technological solutions). Moscow: VIMS, **1978.** 67. (in Russ.)

5 Pat. 2365641 RU. *Sposob ochistki sul'fatnykh rastvorov tsvetnykh metallov ot zheleza* (A method of cleaning non-ferrous sulfate solutions from iron metal) Shneerson Ya.M., Kozyrev V.F., Chugaev L.V.; opubl.27.08.**2009**, *Bul. 30.* 2. (in Russ.)

6 Pat. 2239667 RU. *Sposob okisleniya ionov zheleza v sul'fatnykh tsinkovykh rastvorakh*. (The process of oxidation of iron ions in the zinc sulphate solution). Kazanbaev L.A., Kozlov P.A., Kolesnikov A.V.; opubl. 10.11.**2004**, *Bul. 3.* 3. (in Russ.)

7 Pat. 2282671 RU. *Sposob ochistki sul'fatnykh tsinkovykh rastvorov ot primesej* (A method of purification of zinc sulfate solution from impurities). Kazanbaev L.A., Kozlov P.A., Kolesnikov A.V.; opubl. 27.08.**2006**, *Bul. 24.* 2. (in Russ.)

8 *Avtorskoe svidet*. (Invention Certificate) 1536828 RU. *Sposob ochistki tsinkovykh sul'fatnykh rastvorov ot primesej* (A method of purification of zinc sulphate solutions from impurities). Sharova T.F., Han O.A., Saprygin A.F.; opubl. 10.08.**1999,** *Bul. 5.* 3. (in Russ.)

ЛИТЕРАТУРА

1 Садыков С.Б. Автоклавная переработка низкосортных цинковых концентратов. – Екатеринбург: УрО РАН. 2006. – 581 с.

2 Жунусова Г.Ж., Беделова Ж.Д., Кальянова О.А., Буршукова Г.А. Исследование процесса сернокислотного автоклавного выщелачивания цинка из низкосортного сульфидного цинкового концентрата месторождения Казахстана // Вестник КазНИТУ. – 2016 – № 5 – С. 539-543.

3 Крешков А.П. Основы аналитической химии. Т.2. – М.: Химия, 1971. – С. 453.

4 Химико-спектральные методы. Инструкция № 155-ХС. Атомно-абсорбционное определение меди, цинка, кадмия, висмута, сурьмы, свинца, кобальта, никеля, железа и марганца в горных породах, рудах и технологических растворах. – М.: ВИМС, 1978 – С. 67.

5 Пат. 2365641 РФ. Способ очистки сульфатных растворов цветных металлов от железа / Шнеерсон Я.М., Козырев В.Ф., Чугаев Л.В.; опубл.27.08.09, Бюл. № 30. 2 с.

6 Пат. 2239667 РФ. Способ окисления ионов железа в сульфатных цинковый растворах / Казанбаев Л.А., Козлов П.А., Колесников А.В.; опубл. 10.11.2004, Бюл. № 3, 3 с.

7 Пат. 2282671 РФ. Способ очистки сульфатных цинковых растворов от примесей / Казанбаев Л.А., Козлов П.А., Колесников А.В.; опубл. 27.08.2006, Бюл. № 24, 2 с.

8 Авторское свидет. 1536828 РФ. Способ очистки цинковых сульфатных растворов от примесей / Шарова Т.Ф., Хан О.А., Сапрыгин А.Ф.; опубл. 10.08.1999, Бюл. № 5, 3 с.

ТҮЙІНДЕМЕ

Жұмыс Қазақстанның Николаевское кенорнының төменсортты сульфидты мырыш концентраттарын өңдеу мен мыс-кадмийлі қалдықты аралық өнімін алу технологиясын құру бойынша өзекті мәселені шешуге бағытталған. Мақалада автоклавты шаймалау үрдісінен кейінгі, темір, мышьяк, сурьма, қорғасын, күкірт және марганецтен гидролитикалық тазарту арқылы алынған сульфатты мырыш ерітінділерін мыс пен кадмийден тазарту үрдісін эксперименталды зерттеу нәтижелері келтірілген. Мыс пен кадмийді цементациялық тазарту үрдісінің технологиялық тәртіптері зерттелуші өнімді ерітіндінің мыс пен кадмий қоспаларынан жоғары дәрежеде тазартылуын қамтитындығы анықталды (ерітіндідегі мыс пен кадмийдің құрамы – 2,98 г/дм^3-ден төмен, ал мырыш мөлшері – 221,64 г/дм^3). Алынған мыс-кадмийлі қалдық аралық өнімі мыс пен кадмий өнірісінде қолдану үшін жарамды болып табылады.

Түйінді сөздер: рентгенфазалық талдау, атомды-абсорбциялық талдау, температура, мырыш шаңы, бірсатылы тазарту, цементация, мыс-кадмийлі кек, концентрат.

РЕЗЮМЕ

Данная работа направлена на решение актуальной задачи по вовлечению в переработку низкосортного сульфидного цинкового концентрата Николаевского месторождения Казахстана и разработке технологии его переработки с получением промежуточного продукта – медно-кадмиевого кека. В статье представлены результаты экспериментальных исследований процесса очистки от меди и кадмия цинкового сульфатного раствора, полученного после гидролитической очистки от железа, мышьяка, сурьмы, свинца и кремния раствора от автоклавного выщелачивания низкосортного сульфидного цинкового концентрата Николаевского месторождения Казахстана. Было определено, что установленные технологические режимы процесса цементации меди и кадмия обеспечивают высокую степень очистки исследуемого продуктивного раствора от меди и кадмия. В очищенном растворе содержание меди и кадмия составляло менее 2,98 г/дм^3, цинка – 221,64 г/дм^3. Полученный промежуточный продукт – медно-кадмиевый кек - пригоден для использования в производстве меди и кадмия.

Ключевые слова: рентгенофазовый анализ, атомно-абсорбционный анализ, цинковая пыль, одностадийная очистка, цементация, медно-кадмиевый кек, сульфидный концентрат.

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DEVELOPMENT of TECHNOLOGY and EQUIPMENT for DIRECT SMELTING of REFRACTORY LEDGE GOLD ORES of TERISKEY Ltd ORE MINING COMPANY

Abstract: This article presents the results of the works on improvement of the process parameters and development of the basic design elements of an electric furnace for processing of ledge gold ores from a number of deposits of Teriskey Ltd Ore Mining Company in order to create a pilot project for testing and implementation of a contractile pyrometallurgical selection process (CPS-process) for refractory gold-bearing materials in this enterprise. The design compositions were prepared based on previously completed studies on direct melt processes of the ledge gold ores from Teriskey Ltd deposits, i.e. three-, four- and five-component charges for the CPS-process. The ratio of individual components and their calculated compositions were determined. Constructional calculations of basic dimensions, design and technological parameters of individual components and systems of the pilot project were carried out. Thus, the basic parameters of a two-electrode electric furnace with the capacity of 200 – 300 kVA, the main equipment for the gas cleaning system, systems of feeding and preparation of the raw charge materials with the determination of the structure of load devices were found. Based on the initial data and production schedules of Institute of Metallurgy and Ore Benefication JSC, the project of above-mentioned pilot plant of CPS-process approved by the management of OMC Teriskey Ltd has been performed.

Keywords: matte, slag, gold, contractile pyrometallurgical selection, CPS - process, blending.

Introduction. It is known that more than 50 % of the available active gold reserves are characterized as hard for benefaction and containing contaminants, i.e. arsenic, antimony and carbon. According to experts, about 60 % of the current reserves can be included into the share of such ores. The gold metallurgy describes