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Extraction of copper from the waste of the Karagayly concentrator under the action of an electric hydro-pulse discharge depending on the pH of the medium in the cell

In the work, the waste of the Karagayly concentrator was processed at the experimental hydro pulse discharge (HPD) laboratory set-up in order to transfer the copper contained in them (0.11–0.14 %) into the solution and then partially precipitate it in the process of pulsed electrolysis. Pulp from waste (waste + water 1:1) was poured into the cell, then an acidic medium was adjusted to the value pH = 1.0–3.0 using a mixture of reagents. Under the action of electro-hydro pulse the process of pulsed electrolysis occurs simultaneously. Then the lid was tightly closed and a hydro-pulse discharge (HPD) was performed for 5–20 minutes. Under the action of the discharge, all the metals contained in the pulp went into solution and simultaneously precipitated, except for copper ions, which remained in the solution and partially deposited on the cathode. As a result, after processing the pulp with HPD, 20 solutions with a precipitate were obtained. All solutions and precipitates were studied on a copper content by an atomic absorption spectrometer. The optimal conditions for the extraction of copper into solution, namely, the duration of discharge HPD for 20 minutes at pH = 1 and presence of silicate and phosphate ions, were established. All interfering ions of other metals remain in the sediment, since copper is to the right of other metals in the galvanic series.

Keywords: waste, copper, hydro-pulse discharge, pH medium, cell, pulp, sediment, solution.

Integrated use of mineral resources and the development of technologies for their complete processing, providing access to high quality products, taking into account the demand of external and internal markets is one of the most important areas of the mining and metallurgical complex of Kazakhstan [1]. To date, the state of the mining industry in Kazakhstan is characterized by the lack of significant capital investments in the industry, the lag in the development of the mineral resource base, the deterioration of geological and mining conditions for the development of deposits. The increase in production and processing volumes will be possible only through the development of new fields and the involvement of imbalance ores, dumps and waste after enrichment in the complex processing.

Worldwide, the process of mining and processing of metal ores is associated with the formation of a large amount of waste of various aggregative states. Currently, they contain billions of tons of ore processed. Further accumulation of waste from the mining complex is fraught with serious environmental degradation in the Republic of Kazakhstan. In this regard, the question of creating new environmentally friendly technologies for mining focused on their maximum usage [2].

The main advantage of non-ferrous metallurgy of Kazakhstan is the presence of its own mineral resource base. Kazakhstani ores containing non-ferrous metals are complex and have a complex structural and mineralogical composition. They include a wide range of rare and trace elements. At the same time, the structure, physical, chemical and other characteristics of Kazakhstani ores during mining, enrichment and metallurgical processing require an individual technology for each field. Existing technologies in Kazakhstan in the production of non-ferrous and rare metals do not fully meet the modern requirements of ecology, economics and integrated using of mineral raw materials. At present, the possibility of recycling the valuable components of metallurgical wastes is negligible, and the extraction of these components into such wastes is incomplete [3].

In Kazakhstan, the State Program of Industrial and Innovative Development of the Republic of Kazakhstan for 2015 — 2019 has been implementing, in order to ensure the sustainable development of the country. The program highlights the main problems of the metallurgical industry, namely:

- depletion of the resource base;
- low complexity of the raw materials used;
- a high degree of depreciation of fixed production assets;

- high degree of environmental pollution;
- technological lag;
- lack of integrated complexes with a full production cycle from mining to production with a high degree of product readiness;
- low capacity and distribution of the internal market;
- high energy, labor and material consumption of products.

In order to solve these problems, the state policy in the development of the mining and metallurgical complex of the country provides for:

- the organization of production of final products of high processing on the basis of base metals by small and medium-sized enterprises;
- stimulation of reducing the share of exports of ores and concentrates to ensure the integrated processing of mineral raw materials.

The promising areas of technological development of non-ferrous metallurgy are the production of pure metals (aluminum, copper, gold, and titanium) and products from them (wire rod, wire, rolled products, profiles and alloys, as well as jewelry) [4].

One of these technologies is the use of electro-hydraulic effect (EHE) to extract non-ferrous metals from mining waste, by passing energy-consuming enrichment technologies. In the series of electro-physical technologies, including laser, ultrasonic, plasma, electronic, electroerosion, electro-hydraulic technologies occupy a separate niche. Electrohydraulic (EH) technologies are based on the use of EH-effect (effect of Yutkin) [5].

EH-effect is a set of phenomena observed in a high-voltage pulsed discharge in a liquid (usually in water). There are only a few studies of electrolyte solutions [6].

High-voltage pulsed discharge in a liquid is accompanied by light and electromagnetic radiation, the formation of shock, ultrasonic and sound waves of a wide frequency range, pulse pressure (with an amplitude reaching tens of thousands of atmospheres under certain conditions), powerful hydrostream with cavitations [7, 8].

In our work, the waste of the Karagayly concentrator was processed at an experimental hydro pulse discharge (HPD) laboratory set-up in order to transfer the copper contained in them (0.11–0.144 %) into the solution and then was partially precipitated in the process of pulsed electrolysis. The presence of other metals in the waste is as follows: Zn — 0.12 %, Ni — 0.08 %, Fe — 0.04 %, the rest is less than 0.01 %. Metals standing to the left in the galvanic series are stronger reducing agents than metals to the right. They displace the latter from solutions of salts. For example, the interaction of $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ is possible only in the forward direction. Zinc displaces copper from an aqueous solution of its salt. At the same time, if a compound with which zinc forms an insoluble precipitate is present in the solution, for example OH^- , CO_3^{2-} , SiO_3^{2-} , PO_4^{3-} ions, then zinc ions precipitate, and copper ions or metallic copper remain in solution. These processes and the effects of HPD allow copper ions to be transferred into solution and partially precipitate pure copper on the cathode.

Experimental

Test Specifications:

- capacitance of the storage capacitor $C = 0.4 \mu\text{F}$;
- switch operating voltage $\sim 30 \text{ kV}$;
- energy storage of about 200 J;
- geometry of the anode of conical shape to the top of the cone covered with an insulator with a base diameter of 10 mm;
- the cathode was a cylindrical cell with a diameter of 120 mm and a height of 100 mm with a tip in the center of the bottom with a base diameter of 10 mm and a height of 12 mm;
- pH 1.0–3.0.

Pulp from waste (waste + water 1:1) was poured into the cell, then an acidic medium pH = 1.0–3.0 was adjusted using a mixture of reagents (reagents are selected for each type individually); in this case, under the action of an electro-hydro pulse, at the same time there is a process of pulsed electrolysis. Then the lid was tightly closed and a hydro-pulse discharge (HPD) was performed for 5–20 minutes. Under the action of the discharge, all the metals contained in the pulp went into solution and were simultaneously precipitated, except copper ions, which remained in solution and partially deposited on the cathode. As a result, after pro-

cessing the pulp with HPD, 20 solutions with a precipitate were obtained, which were filtered through a paper filter (red ribbon).

All solutions and precipitates were studied on a copper content by an atomic absorption spectrometer. The data are given in the Table.

Table

The output of copper from the pulp into the solution, depending on the pH of the medium and the duration of discharge HPD, % ($P = 0.95$)

No.	pH	Time, minutes							
		5		10		15		20	
		Sediment	Solution	Sediment	Solution	Sediment	Solution	Sediment	Solution
1	3.0	80.1±3.8	18±1.3	78.9±3.5	21±2.3	71.3±5.3	22±1.4	72.2±2.7	26±2.3
2	2.0	75.4±4.1	23±1.5	70.1±2.9	28±1.9	68.7±4.2	31±1.6	69.0±4.3	32±3.3
3	1.0	62.2±2.2	37±2.4	49.6±3.6	49±2.6	48.4±2.6	53±2.9	42.3±2.6	61±4.6
4	0.5	65.5±1.8	33±2.6	45.8±1.4	41±1.5	56.8±2.5	42±3.4	53.6±3.2	46±3.6

Note. The discrepancy between the percentage of copper in solution and sediment is due to the partial deposition of pure metal on the cathode.

Conclusions

A discharge of more than 20 minutes is not profitable, both in terms of energy consumption and as well as increasing the output of copper. Further lowering the pH below 0.5 does not increase the yield of copper in the solution. The optimal conditions for the extraction of copper into solution are the duration of discharge HPD for 20 minutes at pH = 1, in the presence of silicate and phosphate ions. All interfering ions of other metals remain in the sediment, since copper is to the right of other metals in the galvanic series, and the reagents in the pulp contribute to their conversion into insoluble sediments. The mechanism of action of HPD in an acidic medium formed by a mixture of reagents is not completely clear and requires further research.

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Ұяшықтағы орта рН тәуелді электр гидроимпульстік разряд нәтижесінде Қарағайлы кең байыту фабрикасы қалдықтарынан мысты алу

Қалдықтардың (қалдық + су 1:1) қоспасы ұяшыққа күйылды, содан кейін реагенттер қоспасы арқылы қышқыл орта рН = 1,0–3,0 жеткізілді; (реагенттер әр жағдайда жеке тандап алынады), бұл жағдайда электрхимиялық импульстің әсерінен импульстік электролиз процесі бір мезгілде жүреді. Содан кейін

какпақ тығыз жабылып, 5–20 мин бойы гидроимпульстік разряд жүргізілді. Разряд беру кезінде қоспа құрамындағы мыстан басқа барлық металдар ерітіндіге өтеді және бір мезгілде тұнады. Ерітіндіде қалған металдар жартылай катодта тұнады. Нәтижесінде қоспаны ГИР-мен өңдеуден кейін тұнбасы бар 20 ерітінді алынды. Барлық ерітінділер мен тұнбалардағы мыстың құрамы атомдық-абсорбциялық спектрометрмен зерттелді. Мысты ерітіндіге шығару кезіндегі ең жақсы шарттар силикат және фосфат иондарының қатысуымен $\text{pH} = 1$, ГИР разрядының ұзақтығы 20 мин болды. Барлық кедергі жасаушы металл иондары тұнбада қалады, себебі химиялық элементтер кернеу тізімінде мыс басқа металдардың оң жағында орналасқан. Қышқыл ортаға ГИР-дің әсер ету механизмі толығымен анықталмаған және әрі қарай зерттеуді қажет етеді.

Кілт сөздер: қалдықтар, мыс, гидроимпульстік разряд, pH орта, ұяшық, қоспа, ерітінді, тұнба.

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Извлечение меди из отходов Карагайлинской обогатительной фабрики при действии электрического гидроимпульсного разряда в зависимости от pH среды в ячейке

В статье проведена обработка отходов Карагайлинской обогатительной фабрики на опытной лабораторной установке гидроимпульсного разряда (ГИР) с целью перевода, содержащейся в них меди (0,11–0,14 %) в раствор и затем частичное осаждение ее в процессе импульсного электролиза. В ячейку заливалась пульпа из отходов (отходы+вода 1:1), далее с помощью смеси реагентов формировалась кислая среда $\text{pH} = 1,0\text{--}3,0$ (реагенты подбираются для каждого вида индивидуально), в этом случае при действии электрогидроимпульса одновременно происходит процесс импульсного электролиза. Затем плотно закрывалась крышка, и производился гидроимпульсный разряд в течение 5–20 мин. При действии разряда все содержащиеся в пульпе металлы переходили в раствор и одновременно осаждались, кроме ионов меди, которые оставались в растворе и частично осаждались на катоде. В результате после обработки пульпы ГИР были получены 20 растворов с осадком. Все растворы и осадки исследовали на атомно-абсорбционном спектрометре на содержание меди. Оптимальные условия извлечения меди в раствор — продолжительность разряда ГИР 20 мин при $\text{pH} = 1$, в присутствии силикат и фосфат ионов. Все мешающие ионы других металлов остаются в осадке, так как в ряду напряжений химических элементов медь стоит правее других металлов.

Ключевые слова: отходы, медь, гидроимпульсный разряд, pH среды, ячейка, пульпа, раствор, осадок.

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