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PILOT-INDUSTRIAL TESTING OF THE TECHNOLOGY FOR HYDROMETALLURGICAL DE-ZINCING OF THE COPPER CONCENTRATE FROM UCHALINSKY MINING AND CONCENTRATING WORKS

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Today the copper, zinc and, partially, pyrites concentrates are produced in the course of processing of the copper-zinc ores at the Urals concentrating plants. But complex substantial composition of the ores creates the problems in obtaining of the high quality concentrates from the ores with subsequent metal extraction with usage of the modern concentrating technique and technology. Coefficient of complexness of use of the copper-zinc raw minerals is about 20% lower than the last one in processing of the copper or lead-zinc ores.

The biggest losses of the zinc (12–15%) at Uchalinsky concentrating plant take the place in the copper concentrates. It means that the losses of the metal at Uchalinsky plant only are about 15 thousand tons every year. Besides, the zinc compounds influence negatively on the metallurgical process of copper producing.

The autoclave leaching (AL) is one of the effective methods of direct opening of the minerals. It ensures high extraction in the case of processing even of the low-grade copper-zinc raw minerals.

The methods of AL have been studied for many years in the leading scientific institutes: Urals Polytechnical institute, Gyntsvetmet, Gypronickel, IMET named by Baikov A. A., VNIItsvetmet and others. It has been studied the following processes of AL of the copper-zinc products: sodium, ammoniac, sulfurous, neutral [1–4] (i. c. 1788050).

The neutral method has been chosen as the most efficient among the listed above methods of AL. The neutral method allows separation of copper and zinc in the course of processing of the sulfide copper-zinc polymetallic concentrates in the single apparatus, in the single technological process. The technology is characterized by low materials and energy consumption.

Technology of hydrometallurgical treatment of the copper-zinc products is worked up conformably to specific object, since it depends considerably on ratio of copper and zinc content in the object.

It is known that 95–96% of zinc and 10–15% of copper are passed into solutions in the course of leaching of the copper-zinc concentrate under the temperature 185–200°C and pressure 0.3–0.5 MPa (by oxygen). Indicated regime is suitable for the concentrate contenting about 20% of zinc and 9% — copper. At the same time selectivity of zinc leaching decreases when the ratio of content of Zn and Cu in the concentrate decreases lower than 2. In the sample of the concentrate of Uchalinsky GOK the ratio is about 0.2. So, conditions of leaching of the copper concentrate were determined proceeding from above mentioned circumstance.

It has been determined in the laboratories (NPO "RIVS" JSC, IMET named by Baikov A. A.) the

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principal parameters of leaching (the claim 2006101197/02 of the iventors certificate).

Adopted technological scheme involves following principal operations:

- preparing of the pulp of the copper concentrate with the certain density and loading of the pulp into autoclave;
- autoclave leaching of zinc from the copper concentrate with supply of oxygen (air) under the temperature higher than 180°C and hydrothermal sedimentation of copper from obtained zinc solution;
- separating of the liquid and solid phases with obtain of the copper concentrate and polluted zinc solution;
- educing of the indium concentrate from the zinc solution;
- cleaning of the zinc solution from Fe with obtain of the easily filtered sediments;
- cleaning of obtained solutions from cadmium with obtain of the zinc-cadmium cake;
- sedimentation of zinc in the form of carbonate hydroxides;
- tempering of carbonate hydroxides with obtain of pure zinc oxide.

It has been created at Uchalinsky GOK experimental-industrial unit for testing of technological scheme of removal of zinc from the copper concentrate (fig. 1).

Taking into account the fact that all technological operations are carried out on the equipment of the same type it has been chosen for experimental-industrial tests the scheme of the apparatuses shown at the fig. 2.

The general look of experimental-industrial unit for zinc removal from the copper concentrate is shown at the fig. 3, the general look of the laboratory autoclave — at the fig. 4.

Chemical composition (%) of the studied sample of the copper concentrate of Uchalinsky plant is given below:

Copper	19.11
Zinc	3.82
Sulfur	88.7
Ferrum	43.14
Lead	1.58
Antimony	0.072
Cadmium	0.011
Gold (g/t)	4.8
Silver (g/t)	83.8

According to results of X-ray phase and petrographic analysis the sample is presented in common by chalcopyrite, sphalerite, pyrites and some non-metallic micaceous minerals type vermiculite (fig. 5).

Distribution of the classes of coarseness in the studied sample is following: +74 μm — 0.7%; –74 +44 μm — 1.9%; –44 μm —97.4%.

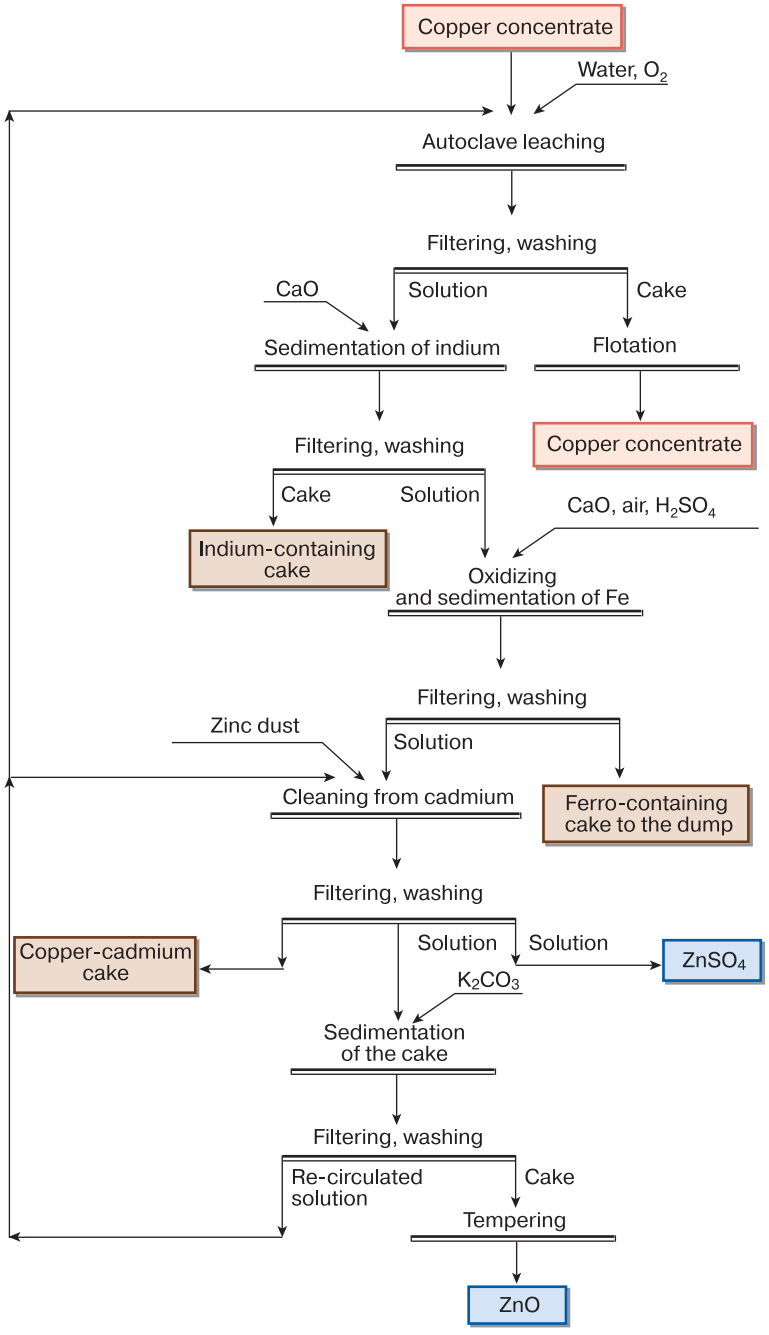

Fig. 1. Technological scheme of removal of zinc from the copper concentrate

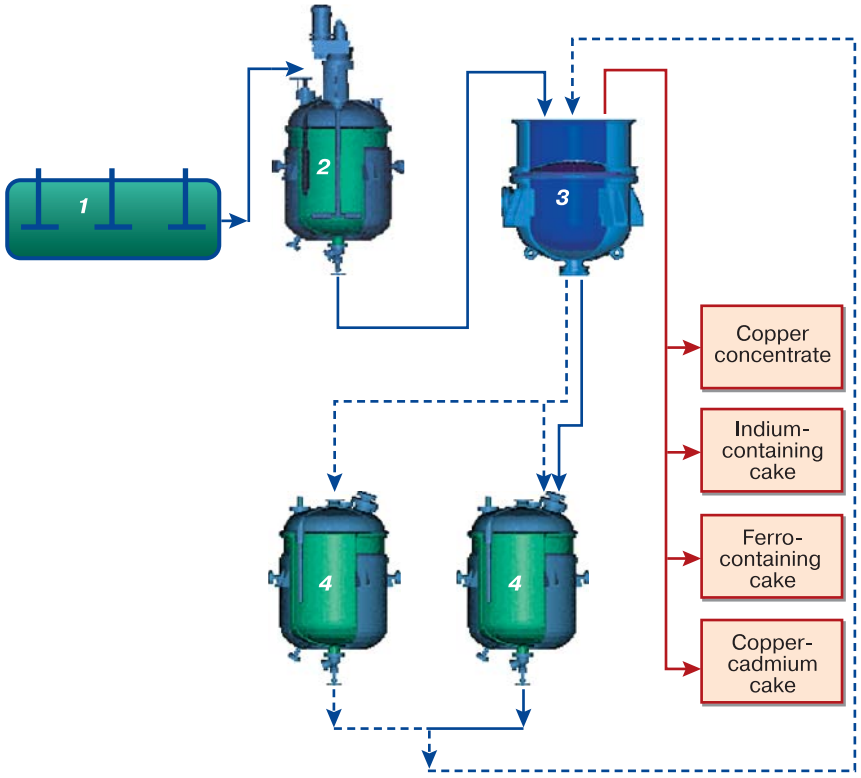

Fig. 2. Scheme of the chain of the apparatus
1 — autoclave; *2* — reactor; *3* — filter; *4* — tank

Fig. 3. Experimental-industrial unit for zinc removal from the copper concentrate
1 — autoclave, *2* — reactor, *3* — filter, *4* — tank

Fig. 4. Laboratory autoclave 25 liters capacity
1 — casing of the water cooling of electric drive of the mixture; *2* — distributor of the water cooling, *3* — frame of the autoclave, *4* — tubular heat exchanger of cooling of the autoclave

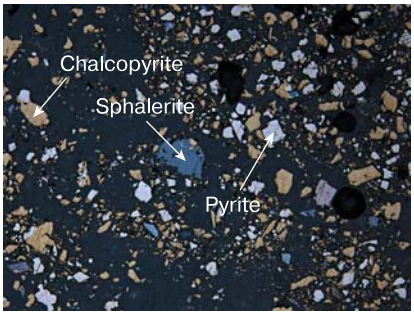

Fig. 5. Initial copper concentrate. Reflected light (magn.200)

Autoclave zinc removal from the copper concentrate with hydrothermal sedimentation of copper

Method of the work. For every test of AL it has been prepared the sample including 15 liters of water and 6 kg of the copper concentrate. Prepared pulp was mixed carefully and was loaded into autoclave with the operating mixers. Temperature of the pulp in the autoclave was increased up to 170–175°C by means of the heater. After that it has been fed oxygen, and pressure in the autoclave has been increased up to 1.5–1.55 MPa. Temperature has been kept automatically within the diapason 185–192°C. After two hours feeding of oxygen has been stopped. Hydrothermal sedimentation of copper passed into solution took the place during 1–1.5 hours after stopping of oxygen feeding.

When the temperature of the autoclave decreases to 100°C the pulp is unloaded and sent to the press filter. Liquid and solid phases were analyzed for content of the principal components.

It has been carried out more than 20 tests of AL. Average results of the tests are given below:

Output of the copper concentrate (%)	80.65 (73.85)
Content in the copper concentrate (%):	
Cu	23.68 (26.16)
Zn	0.59 (0.45)
Fe	32.28 (–)
Content in the zinc solution after autoclave leaching, g/l:	
Cu	0.21 (1.77)
Zn	12.59 (19.2)
Fe	44.53 (56)
Cd (mg/l)	41.68 (57)

Note: It is given in the brackets the results after addition in the process of 8 liters of re-circulating solution

Copper extraction into concentrate reached to 99.9% in the course of AL.

Educing of indium from the zinc-containing solution

Educing of indium, gallium and germanium from the zinc-

containing solutions by means of hydrolysis is fulfilled under pH = 2.5–3. Degree of sedimentation of indium is more than 95%. Solid hydrate sediment, containing indium, is easily filtrated and may be sent to the zinc plant as a high-grade product.

In 2007 indium content in the dispatched by Uchalinsky GOK copper concentrate was about 20–25 g/t. It means that every year it is passed to the copper plants about 6–7 tons of indium, and they are lost irrevocably, though indium has the high price at the international market.

Removal of the two-valent and trivalent ferrum, arsenic and antimony from solutions

As a result of the oxidizing AL of the copper concentrate and hydrothermal sedimentation of copper, and after educing of indium from solutions by hydrolysis almost all passed into solution ferrum is in the two-valent form. It is known, that for purifying of the zinc-containing solutions from the ferrum, it is necessary to convert the last one to the trivalent compound. After that Fe is educed from solution in the form of different sulfate hydroxides. But the pulps, obtained in the process, are filtered badly and are thickened very badly.

At the zinc plants content of Fe in the solutions is 1–1.5 g/l Fe(III) and 0.2–0.5 g/l Fe(II). The last one is oxidized be feeding of the manganese ore or manganese-contenting mud. Obtained solutions content 130–150 g/l of zinc and are characterized by the rather small concentration of Fe (1.5–2 g/l). The last one is easily removed by hydrolytic purification of the solutions with pH = 4.5–5.4 and does not hamper process of sedimentation and filtering of the pulp.

At the same time in this course of autoclave oxidizing leaching of the copper concentrate considerable amount of Fe is passed into solutions (probably owing to decomposition of chalcopyrite). Its concentration reaches 40–60 g/l. After hydrothermal sedimentation of copper almost all amount of Fe is in two-valent state.

Oxidizing of the great volumes of the Fe-ions by the manganese ore will lead to considerable consumption of the last one, to accumulation of the Mn-ions in solution, to increase of density of solutions and to total discomposure of the processes of sedimentation and filtering.

So, it has been used the method (i. c. 468522) of oxidizing of the Fe-ions in solution by air or by oxygen with obtain of the easily filtering crystalline sediments of the complex sulfate hydroxides of Fe. Arsenic and antimony are removed completely from the solution with above mentioned sediments.

Method of the work. Technological experiments were carried out by the following means: 20 liters of solution (after sedimentation of indium) were poured into the reactor with the mixer and heated to 50–60°C. Air was fed through the dispersant. The unit is supplied with pH-meter. Value of pH of the pulp in the course of oxidizing was kept in diapason 4.2–4.5 by means of feeding of the lime milk. The samples were selected every 0.5 hour for monitoring of the process by content of the ions Fe(II).

Depending on content of Fe (II) in initial product (25–60 g/l) the residual concentration of the Fe-ions (equal to 0.1–0.3 g/l) was reached in 2.5–3.5 hours (fig. 6).

After that it was carried out recrystallization of the sediment with obtain of the crystalline easily filtered compounds.

As a result of the oxidizing operation and sedimentation of Fe it is obtained the cake that is the mixture of gypsum and yarosite. It is formed about 8.5 kg of the cake of the 20 liters of initial product containing 52 g/l of Fe. Mass share of the principal components in the cake are (%): Zn – 0.88; Fe – 16.9; S – 14.2.

Thus, removal of Fe permits to solve the following tasks:

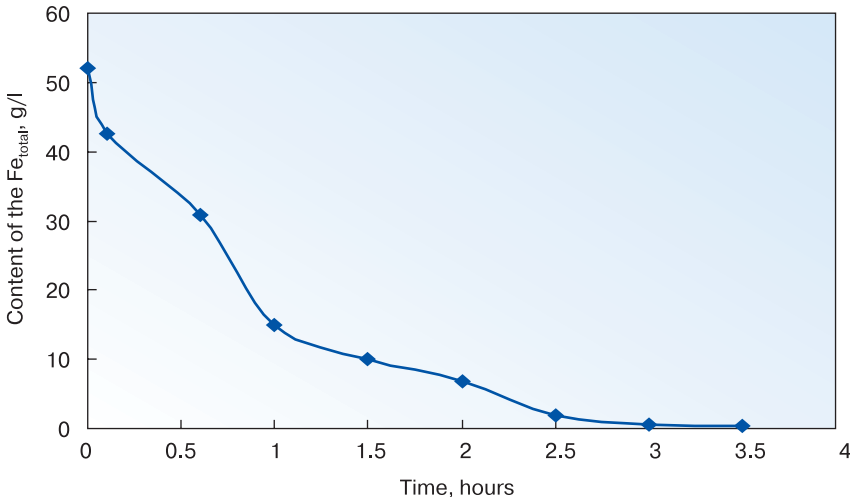

Fig. 6. Kinetics of oxidizing of the two-valent Fe

- obtain of the zinc-containing solution;
- arrangement of circulation of solution for increase of the zinc concentration in the last one;
- removal of arsenic and antimony from solution.

Obtained ferro-containing cake may be used as a component of the stowing compounds (pat. of RF 830824 and 2001118530).

Removal of cadmium from solution

Cleaning from Fe, arsenic and antimony zinc-containing solution is neutralized up to pH = 5.2÷5.4 and subjected to cementation with the zinc dust for sedimentation of cadmium and the rests of copper according to known, used at the all zinc plants technology.

After copper-cadmium cleaning the solutions do not content of the copper ions. Concentration of cadmium decreases to 0.5 mg/l.

Separating of commercial zinc compounds

Cleaned from admixtures of Fe, arsenic, antimony, cadmium, copper and others metals the zinc-containing solution (solution of zinc vitriol) may be used for needs of the concentrating plant.

For separation of zinc from solution in the form of carbonate hydroxide and oxide it is carried out the operations of sedimentation and tempering.

Method of the work. Solution of $ZnSO_4$ (10 g/l) and sedimentation substance — solution of K_2CO_3 (100g/l) — in correlation 1:1.1 were loaded by the small portions into thermostatic cell under the temperature about 50°C and with the constant mixing.

Owing to increase of pH value of the solution up to 8–8.5 after addition of the sedimentation substance, it has been added 3% solution of the sulfuric acid for decrease of pH up to ~5.

Period of sedimentation is about one hour (beginning from feeding of the latest portion of K_2CO_3). The fallen sediment has been filtered at the vacuum filter and washed with the small amount of water. The sediment is white fine-crystalline powder. Degree of its sedimentation from solution reaches 97.5%. In accordance with results of X-ray phase analysis of the powder dried under the temperature 100°C it consists of the mixture of zinc hydrocarbonate, mainly of $Zn_5(OH)_6$, $(CO_3)_2$, containing about 36% of zinc.

After tempering during one hour under the temperature 500°C the sediment has decomposed completely with forming of pure zinc oxide.

Conclusions

It has been carried out in the semi-industrial scale testing of technology of removal of zinc from the copper concentrate of Uchalinsky concentrating plant with separating of zinc as commercial products — zinc vitriol and zinc oxide (extraction 85–90%).

In the course of testing it has been obtained following results:

- copper content in the copper concentrate increases from 19.1 to 25% (extraction 99%) with simultaneous decrease of content of zinc from 3.8 to 0.5%;
- concentration of copper in the zinc-containing solution does not exceed 0.1–0.5 g/l;
- arsenic and antimony are removed completely from initial raw materials into the ferro-containing cake.

Application of the autoclave leaching in the metallurgical producing of copper will allow;

- decrease of amount of the slag;
- prevent of forming of speiss;
- decrease of viscosity of the slag and correspondingly the losses of copper, gold, silver;
- decrease of throw out into surrounding of the compounds of arsenic and antimony.

4. Preliminary calculations confirm high technical-economic efficiency of the worked up technology and rapid recoupment of the capital investments.

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