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PROCESSING OF COPPER SMELTING SLAG USING SULFURIC ACID LEACHING: TECHNOLOGICAL ASPECTS AND SOLUTIONS

The article focuses on the study of the processes intended for copper smelting slag processing, in order to extract such valuable components as copper, zinc, iron and silica. Various options for slag leaching with the use of sulfuric acid as one of the most promising approaches are considered. Preliminary thermodynamic calculations confirmed the high probability of dissolution of metal oxides when interacting with sulfuric acid.

High-temperature leaching resulted in higher recovery rates for copper and other valuable metals. The use of sulfuric acid at the concentration of 50 g/dm³ in combination with the optimization of leaching parameters provided the high efficiency of valuable metal extraction–copper up to 76%, zinc up to 94% and iron in the form of oxide up to 92%. Acceleration of pulp filtering was achieved through two-stage re-pulping with hot water.

The study results confirm the prospects of hydrometallurgical methods of slag processing. It opens up opportunities for the development of more efficient technologies for processing copper smelting waste, aimed at maximum extraction of useful components at minimal costs.

Keywords: *copper slag, sulfuric acid, leaching, silicic acid, pulp, cake, thickening*
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Introduction

One of the key challenges of the present day is development and large-scale introduction of a processing technology for the non-ferrous metallurgy waste which are mostly hundreds million tons of slag accumulated for the decades of operation of metallurgical plants [1, 2]. Elaboration of effective hydrometallurgical technologies for slag processing is a top priority of integrated waste management aimed at recovery of non-ferrous metals and iron from waste, including copper smelting slag, as this can improve ecological and economic situation in the non-ferrous metallurgy industry.

Research and development in the field of non-ferrous metallurgy slag processing is still in progress, and embraces a wide range of theoretical and applied approaches. Processing of current slag can use various available treatment technologies [3–8], as well as pyrometallurgical [9–12] and hydrometallurgical [13–16] processes.

For the comprehensive recovery of silica, iron and non-ferrous metals from slag, the most efficient process in terms of energy, as well as current and capital costs is hydrometallurgical leaching. The main problems in slag leaching are connected with the difficulty of filtering of silica-bearing pulp. In connection with this, oxidation sulfuric acid leaching of copper smelting slag was carried out in the presence of hydrogen peroxide, under temperature of 70 °C and normal pressure [17]. In this case, oxidation of slag takes place simultaneously with the removal of iron from it. Subsequent extraction yielded to 80% Cu, 90% Co and 90% Zn in selective solutions.

It is also suggested [18] that hydrogen peroxide is the best oxidizer in leaching. For example, in leaching of slag under room temperature for 2 hours in the presence of this oxidizer, recovery of copper and iron reached 63.4% and 48.6%, respectively. Within the first 60 min of the reaction, the dominant process of was copper dissolution while iron dissolution prevailed later on. For intensifying sulfuric acid leaching of copper converter slag, potassium dichromate, being an efficient oxidizer, was additionally used [19]. In the other waste management research [20], aiming to eliminate pure reagents, sulfuric acid decomposition of slag used solution of sulfuric acid from process stages of copper–nickel production.

There are known methods of copper–nickel slag processing by hydrochloric acid leaching [21, 22]. According to these methods, hydrochloric acid at a concentration of 15–20% is first heated to 55–90 °C and then added with slag [21], or the slug pulp is preliminary prepared and introduced to the acid solution until its pH of 5.5–6.5 [22]. The finely dispersed particles of the pulp, with their extended surface, enable running of this process at room temperature [22]. The shortages of these approaches are the large consumption of acid, the need to heat the solution and the use of expensive acid-proof equipment.

In the light of these facts, development of a hydrometallurgical sulfuric acid technology for copper smelting slag processing at the comprehensive and high recovery of the whole range of the valuable components to marketable products is of special relevance at the moment.

For expanding the sources of raw materials and to increase the recovery of non-ferrous metals, the present research authors set the following tasks:

—to analyze the elemental and phase composition of copper smelting slag;

—to determine distribution of target components in solution and in precipitate from the analysis of thermodynamically probable reactions during sulfuric acid leaching of slag;

—to test the sulfuric acid slag leaching at different parameters of the process on a laboratory scale.

Research subject and methods

The subject of research is the copper smelting slag sampled from slagpiles of domestic production and having the following composition, %: 0.46 Cu; 0.69 Pb; 4.68 Zn; 36.08 SiO_2; 1.13 TiO_2; 5.81 Al_2O_3; 34.38 Fe_2O_{3total}; 9.73 CaO; 1.82 MgO; 0.95 Na_2O; 1.12 K_2O; 0.58 MnO; 0.07 H_2O.

The chemical and X-ray phase analyses of slag samples used standard procedures. The mineral composition of the sampled slag to 98% is zinc-bearing fayalite.

The thermodynamic analysis of possible reactions of interaction between sulfuric acid and the test slag components involved calculations in the license program Outotec Technologies HSC Chemistry ver: 8.1.5.

The test slag was ground to a size of –100 μm in a lab vibrating rod mill. Leaching of the ground slag samples 100 g in weight was carried out in a lab stirrer. At the first stage, sulfuric acid leaching was performed without heating of sulfuric acid solution at a concentration of 50 g/dm³ and

Table 1. Sulfuric acid slag leaching results

Feed	Total, g	SiO_2	FeO	CaO	Cu	Pb	Zn	H_2O	SO_3	Other
Slag	100	36.08	30.9	9.73	0.46	0.69	4.68	0.07	0	17.39
Solution H_2SO_4	950	–	–	–	–	–	–	904.4	45.6	–
Total	1050	36.08	30.9	9.73	0.46	0.69	4.68	904.47	45.6	17.39
Product	Total	SiO_2	FeO	CaO	Cu	Pb	Zn	H_2O	SO_3	Other
Cake	85.44	15.85	9.31	9.73	0.11	0.69	1.92	0.26	33.46	14.1
Content, %		18.55	10.90	11.39	0.13	0.81	2.25	0.31	39.17	16.502
Recovery, %		43.94	30.13	100.0	23.68	100.0	41.07	0.03	73.38	81.08
Pregnant solution	964.59	20.23	21.59	–	0.35	–	2.76	904.24	12.136	3.291
Content, %		2.10	2.24	–	0.036	0	0.29	93.74	1.258	0.342
Recovery, %		56.06	69.87	–	76.32	0	58.93	99.97	26.62	18.92
Total	1050.03	36.08	30.9	9.73	0.46	0.69	4.68	904.50	45.599	17.392
Discrepancy	0.03	–	–	–	–	–	–	0.029	–0.001	–

Table 2. Hot sulfuric acid slag leaching results

Feed	Total, g	SiO_2	FeO	CaO	Cu	Pb	Zn	H_2O	SO_3	Other
Slag	100	36.08	30.9	9.73	0.46	0.69	4.68	0.07	0	17.39
Solution H_2SO_4	1100	–	–	–	–	–	–	1048.3	50.6	1.1
Total	1200	36.08	30.9	9.73	0.46	0.69	4.68	1048.4	50.6	18.49
Product	Total	SiO_2	FeO	CaO	Cu	Pb	Zn	H_2O	SO_3	Other
Cake	59.504	8.49	2.32	9.73	0.11	0.69	0.3	0.05	22.13	15.684
Content, %		14.27	3.9	16.35	0.19	1.16	0.51	0.08	37.19	26.35
Recovery, %		23.54	7.51	100.0	23.91	100.0	6.41	0.03	43.74	84.83
Pregnant solution	1140.2	27.58	28.57	–	0.35	–	4.38	1048.1	28.45	2.81
Content, %		2.42	2.51	–	0.03	–	0.38	91.92	2.5	0.24
Recovery, %		76/44	92/46	–	76.09	–	93.59	99.97	56.23	15.2
Total	1199.7	36.07	30.89	9.73	0.46	0.69	4.68	1048.1	50.59	18.48
Discrepancy	–0.33	–0.01	–0.01	–	–	–	–	–0.3	–0.01	–

at a ratio L:S = 9.5:1. For the comparison with the room temperature leaching results, the further tests were executed at a temperature of 80 °C and using sulfuric acid solution with a concentration of 50 g/dm³ and at a ratio L:S = 11:1.

The elemental composition of the initial slag samples and leaching products was tested on the X-ray fluorescent analyzer SPARK-1 with Cu-cathode at the tube voltage U = 25 kV and exposure for 40 s, and on the portable geological analyzer Thermo Niton. The samples were tableted for the analysis.

Results and discussion

Thermodynamics of sulfuric acid leaching of copper slag. The thermodynamic analysis shows a high probability of reactions with formation of soluble iron, zinc and copper sulfates and insoluble silicic acid. $CuSO_4$, $ZnSO_4$, $FeSO_4$ and silicic acid are leached. H_2SiO_3 forms a gel over time. Sulfates of other metals ($PbSO_4$, $CaSO_4$, $MgSO_4$ are partly soluble) remain in cake of acid leaching [23].

Leaching without heating. Slag fraction 2–4 mm was pre-milled to the size of –100 μm for 5 min. Leaching conditions of the milled slag sample in a lab stirrer were as follows: milled sample weight—100 g; H_2SO_4 concentration—50 g/dm³, solution—900 ml; L:S = 9.5:1; duration—2 h; stirrer speed—300 min^{-1}. Leaching was carried out without heating of the solution, under room temperature, but within the first 10–15 min, the pulp temperature rose to 45–50 °C owing to the heat of exothermal reactions. Addition of sulfuric acid initiated formation of hydrogen sulfide through the reaction below:

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$

which shows that slag contains sulfides such as FeS, and, probably, Cu_2S and ZnS.

After leaching, filtering of pulp was complicated; some thickening of the pulp was observed in 12 h, with formation of a jellylike layer of silicic acid H_2SiO_3. Filtering was accelerated through re-pulping with addition of 500 ml hot water. The analytical data on slag and leaching products are compiled in **Table 1**. The implemented preliminary experiments demonstrate that the recovery of FeO (69.87%), Cu (76.32 %), Zn (58.93%) and SiO_2 (56.06%) from slag is possible and is sufficiently effective, and the efficiency improvement can be achieved by optimizing the technology and equipment factors.

Leaching with heating. Aimed to compare the results of leaching under room temperature, the ground slag samples were subjected to hot sulfuric acid leaching: slag sample—100 g; leaching temperature—80 °C; sulfuric acid concentration—50 g/dm³; solution—1000 ml; leaching duration—2h; stirrer speed—300 min^{-1}; initial ratio L:S = 11:1. During leaching, because of evaporation of water, the ratio L:S decreased to 7:1. The resultant pulp was a uniform thick mass which evaded settling and filtering for a few hours.

For optimizing the process of filtering, the pulp was subjected to two stages of re-pulping in graduated cylinders. The process conditions and product are described below:

—Stage 1: added hot water—325 ml; initial pulp—725 ml; final pulp volume—645 ml; thickening duration—7 h; clarified solution—180 ml;

—Stage 2: added hot water—200 ml; initial pulp—668 ml; thickening duration—2 h; clarified solution—127 ml.

Table 2 gives the analytical data on slag and hot leaching products.

It is necessary to emphasize that leaching generates much silicic acid, which hampers thickening and filtering of pulp, especially if the initial solution contains silicic acid to 100 g/dm^3 and has a low ratio L:S = 5:1. Hot leaching features a higher recovery of components as compared with leaching at the room temperature. For example, the recovery of iron oxide is 92.46%, zinc oxide is 93.59% and silica oxide is 76.44%. The temperature of the leaching solution has a minimum influence on the coper recovery which totals 76.09%.

Sulfuric acid leaching of slag results in the release of hydrogen sulfide. Recovery of sulfur in terms of oxide is more than 2 times higher in hot leaching than in leaching without heating. It is expedient to use oxidizers (pyrolusite, hydrogen peroxide, oxygen) to remove hydrogen sulfide. Solutions also contain arsenic which is to be removed in its non-toxic form, for instance, as calcium arsenate.

Conclusions

The implemented research proved high efficiency of sulfuric acid leaching of copper smelting slag under different temperatures, with recovery of large amount of valuable components such as iron, zinc and copper. The benefit of this technology is the zero need of heat expenses owing to exothermicity of reactions.

Leaching at the temperature of 80 °C boasts a substantial increase in the recovery of iron, zinc and silica oxides as compared with the process of leaching without heating, and has no essential effect on the copper recovery. Thickening and filtering of pulp is complicated by the formation of much silicic acid, which requires optimizing the process. Re-pulping with hot water added improves filtering. In this context, it seems necessary to develop a special technology for extracting silicic acid for the further marketable production of silica gel or carbon white.

On the ground of the obtained results, it is possible to recommend hydrometallurgical technologies with sulfuric acid leaching as a promising trend of integrated processing of copper smelting slag with a view to recovering silica and non-ferrous metals.

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