STUDY OF ZINC-LEAD-CONTAINING CAKE LEACHING FEATURES

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The research subject is an intermediate product of zinc production containing lead, zinc, iron, copper, and silver. Thermodynamic analysis is performed for all probable transformations during sulfuric acid leaching, and a Purbe diagram is plotted. The study of uncovering lead-containing middlings is performed in two stages: the first is leaching with sulfuric acid with density 250 g/dm^3 (S:L = 1:4) at 80ºC for 2 h. At the second stage, washed cake is leached with a complexing solution (Trilon B) with the aim of maximum zinc transfer into the liquid phase. Conditions are selected on the basis of test results for process optimization by an experimental planning method, and from analysis of response surface, modeling the dependence of the degree of leaching on pulp density and complexing agent concentration.

Keywords: *zinc-lead cake, leaching, sulfuric acid, Purbe diagram, complexing agent, optimization.*

One of the main lead-containing intermediate products is zinc production lead cake, whose treatment is economically and ecologically expedient.

Lead cakes are formed in zinc production during leaching of Waelz-oxides. Oxides of zinc, lead and also compounds of iron, copper, silver, tin, nickel, and other metals are present within them. With sulfuric acid leaching, these components are transferred into solution, a ferrites, zinc silicate, and minerals of barren rock do not dissolve, contaminating and impoverishing the lead cake formed [1].

Quite a considerable amount of well-known work is devoted to hydrometallurgical processing of lead-containing raw material, including leaching in acid, alkaline, and salt solutions [2–9].

Results are given in this work for exploratory experiments for studying the possibility of using organic solvents during zinc cake leaching, containing lead, zinc, and silver. The chemical composition of the lead cake was, wt.%: Pb – 13.51; Zn – 9.14; Fe – 7.72; Cu – 0.042; Ag – 268 g/ton.

At the first leaching stage, experiments were performed for sulfuric acid extraction of oxides, ferrites, and silicates of zinc-containing phases.

Tests for leaching the test intermediate product were carried out in a standard unit, consisting of a thermostatically controlled reactor with a mechanical stirrer and a pH meter. Pulp was filtered and the cake and solution metal content was determined.

Probable reactions occurring at the surface of a dissolving particle during zinc-lead cake leaching with sulfuric acid are:

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O,$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O,$$
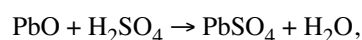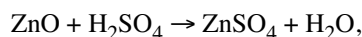
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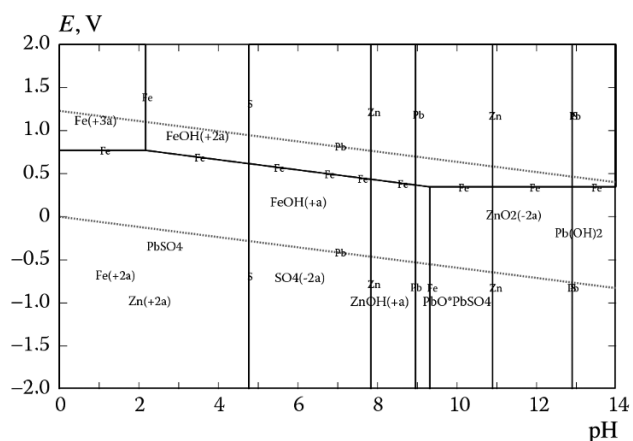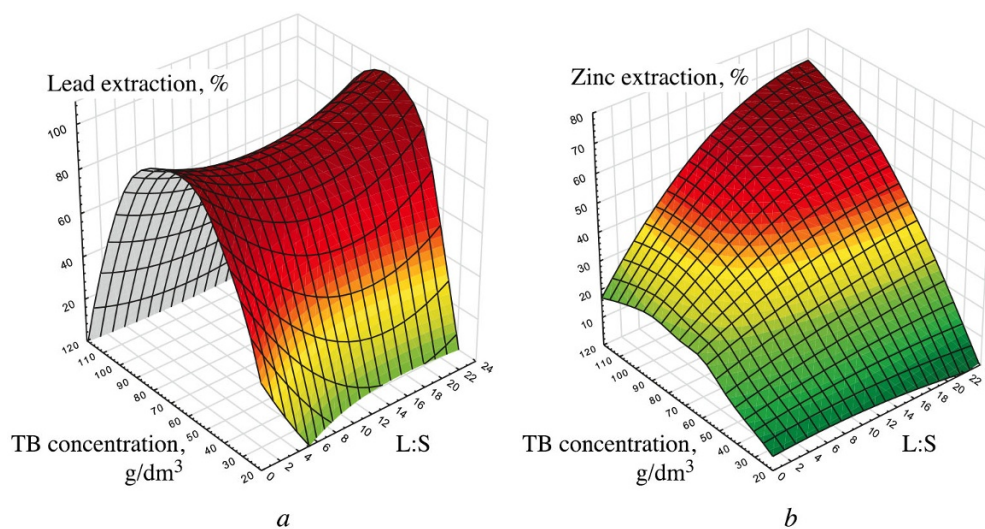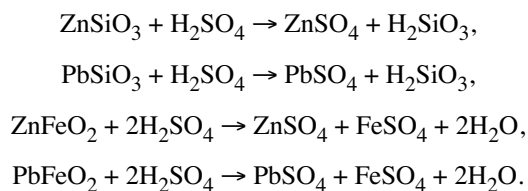
Fig. 1 Purbe diagram for the Zn–Pb–Fe–S–H$_2$O system.

Fig. 2. Dependence of lead and zinc extraction into solution on pulp density and solvent concentration during leaching with Trilon B solution (TB).

$$ZnSiO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2SiO_3,$$

$$PbSiO_3 + H_2SO_4 \rightarrow PbSO_4 + H_2SiO_3,$$

$$ZnFeO_2 + 2H_2SO_4 \rightarrow ZnSO_4 + FeSO_4 + 2H_2O,$$

$$PbFeO_2 + 2H_2SO_4 \rightarrow PbSO_4 + FeSO_4 + 2H_2O.$$

On the basis of these reactions, the main solid phase and ions were determined, forming heterogeneous systems corresponding to the actual composition (cake – sulfuric acid), which are used for calculating Purbe diagrams, specifying the equilibrium condition of leaching products in relation to pH and redox potential (Eh). The Purbe diagram for the Zn–Pb–Fe–S–H$_2$O system is given in Fig. 1. Analysis of the Purbe diagram showed that with sulfuric acid leaching of lead cake there is probably occurrence of reactions with formation in solution of nonferrous metal, silver, and iron sulfates. Effective reaction of zinc compounds with sulfuric acid is only possible in the acid pH range with an initial Eh potential not less than 1.0 V, and this corresponds to an initial sulfuric acid concentration of 1 mole/dm^3.

TABLE 1 Dependence of Lead and Zinc Extraction into Solution during Leaching with Trilon B Solution under Different Conditions (experiment planning matrix) at pH = 7

L:S (X1)	Trilon B concentration (X2), g/dm^3	Lead extraction, %	Zinc extraction, %
8	40	83	34
20	40	19	8
8	60	89	39
20	60	93	58
8	80	92	44
20	80	97	62
4	100	64	37
8	100	96	49
20	100	98	64

The main form of lead present in solution is sulfate, whose solubility is $1.3 \cdot 10^{-4}$ mole/dm^3. In a weakly acid region (pH $\geq$ 3.5–4.0) formation of iron hydroxyl compounds is probable, which also form a new solid phase, increasing the amount of residue. Formation of new solid phase at the surface of particles of dissolving cake determines the intradiffusion control of this stage.

At the second leaching stage, the solvent used was disodium salt of ethylenediaminetetraacetic acid (EDTA), whose concentration was varied within the limits of 20–140 g/dm^3. Temperature (25ºC) in tests was kept constant, L:S = (4:1)–(8:1), leaching duration 1 h. After leaching pulp was filtered, the solution was analyzed for lead and zinc content using a mass spectrometer with an inductively coupled plasma. Residue from leaching was subjected to twofold filter-repulping washing with distilled water (L:S = 1) at 25ºC, and the duration of each washing was 15 min. Residue washed after leaching was dried and analyzed for lead, zinc, and silver content.

On the basis of results obtained, an experimental planning matrix was formed (see Table 1) within which values of lead and zinc extraction were adopted for response function Y. Variable parameters: X1 is the ratio of ethylenediaminetetraacetic solution (Trilon B) and original cake (L:S = 4–20), X2 is complexing agent concentration (40–100 g/liter) with fixed pH = 7, whose value was selected by experiment from results of potentiometric titration. With the aim of optimizing leaching parameters, in the STATISTICA 7.0 program a surface was plotted specifying the dependence of extraction into solution on Trilon B concentration (x) and pulp density (y) in a neutral medium with pH = 7 for lead and zinc (Fig. 2).

The surface describing reciprocal effect of L:S and solvent concentration has two marked regions of maximum (96–98%) extraction of lead into solution: with high values of L:S and high solvent concentration. The saddle nature of the dependence for extraction ion concentration (see Fig. 2*a*) is probably caused by the complexing product solubility limit with a maximum solvent concentration. Extraction of lead into saturated solution of the reaction product is slowed down by diffusion of lead ions through a concentrated film of complex at a cake surface.

The surface describing zinc extraction into solution in relation to pulp density (L:S) and solvent concentration (see Fig. 2b) demonstrates the results of the reciprocal effect of two factors on response function. A maximum is uniformly reached with an increase in values of both factors. Maximum zinc extraction (with pH = 7) in an actual expression reaches 58–62%, which is registered in zinc complexonate solubility limits.

Conclusions

1. Leaching intermediate product with sulfuric acid makes it possible to extract zinc from oxide, ferritic, and silicate phases, and lead forms a new solid sulfate phase, increasing its content within residue.

2. Lead extraction into solution on leaching with Trilon B reaches 96–98%, and is only limited by the solubility of the complexone formed.

3. The effect of Trilon B on lead and zinc extraction into solution is described by a rectilinear relationship: with an increase in solvent concentration there is a proportional increase in component extraction. The maximum Trilon B concentration, equal to 100 g/liter, was selected from consideration of reaction product solubility: with an increase in solvent concentration there is a proportional increase in component extraction.

4. As follows from data obtained, pulp dilution leads to an increase in lead and zinc extraction up to 96 and 52%, respectively, at pH = 7. A reduction in pulp density to values of L:S = 20:1 in an neutral medium leads to a sharp increase in lead extraction into solution at room temperature, i.e., to values close to 100%.

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