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Complex Processing Of Lead-Containing Technogenic Waste From Mining And Metallurgical Industries In The Urals

Khakimov Kamol Djurayevich

Independent Doctorate Student, Karshi Engineering And Technology Institute, Republic Of Uzbekistan, Karshi, Uzbekistan

Eshonqulov Uchqun Kxudoynazar O'g'li

Independent Doctorate Student, Karshi Engineering And Technology Institute, Republic Of Uzbekistan, Karshi, Uzbekistan

Amanov Tolib Sirozhevich

Uzbek Institute Of Geotechnical And Non-Ferrous Metallurgy Research And Project Search "O'zgeorangmetliti" Engineer Of The Mining Department Of The State Unitary Enterprise, Uzbekistan

Umirzoqov Azamat Abdurashidovich

PhD scholar of the department of Mining, Tashkent City, 100095, Tashkent State Technical University named after Islam Karimov, Uzbekistan

ABSTRACT

The current economic situation forces copper smelters to refuse to process man-made waste (slags, dusts, cakes, etc.). Lead-and zinc-containing solid waste accumulates in significant quantities on the territory of factories, in so-called "temporary " dumps, and is often stored on the sites of enterprises. Attempts to sell lead-containing industrial products encounter difficulties related to low prices on the part of lead monopolists, problems with the preparation and transportation of industrial products, environmental and other restrictions.

KEYWORDS

technicsogen waste, economic effective, combined technology, which includes recycling X raw materials, industrial products, water-soluble compounds, carbon dioxide, selectively transfer results to the solution, gidrometallurgical processing.

INTRODUCTION

Russia has been left without primary lead production plants. the latter is used in the electrical, chemical,

and nuclear industries, as well as in the production of automobile batteries and fuel anti-detonators. The

lagging lead mining base and the need for significant capital investments hinder the construction of a large

enterprise for the extraction and production of primary lead [1].

Chemical composition of dusts from Ural copper smelters in the CIS, %

The company, the smelting unit	Element				
	Zn	Pb	As	Cu	Fe
<i>Sredneuralsky copper smelter:</i>					
kiln	11,3	2,1	3,3	9,3	19,8
reverberatory furnace	6,9	1,5	2,2	11,8	27,50,3
converter	31,7	25,5	2,2	1,7	0,3
<i>Vanyukov oven:</i>					
coarse dust	4,0	0,8	0,4	10,0	21,0
fine dust	12,0	4,5	1,4	5,5	12,0
<i>Kirovgrad copper smelter:</i>					
reverberatory furnace	2,4	2,9	3,5	9,7	18,3
<i>Shaft furnace:</i>					
coarse dust	25,7	3,8	0,1	12,5	9,7
fine dust	43,4	4,8	0,1	0,4	1,2
<i>Converter:</i>					
coarse dust	15,7	7,4	0,1	31,4	7,8
fine dust	38,5	14,2	0,2	1,8	0,2
<i>Krasnouralsky copper smelter:</i>					

kiln	3,8	1,7	4,3	12,2	21,3
<i>Reverberatory furnace:</i>					
coarse dust	8,9	3,0	—	9,9	22,9
fine dust	21,6	4,1	1,4	3,8	—
<i>Sukholozhsky plant of secondary non-ferrous metals:</i>					
reverberatory furnace	48,8	1,3	—	3,3	0,9
induction furnace	31,2	0,9	—	3,7	0,5

However, only copper smelters in the Ural region have accumulated significant reserves of lead in man-made waste. Taking into account the expansion of recycling of battery scrap, it is possible to reduce the lead deficit in Russia. Environmental safety, economic efficiency, minimal capital investment, and the possibility of creating new jobs are taken into account when choosing the technology for creating lead production. The main technogenic wastes of copper smelters are lead-containing dusts of smelting units and cakes obtained by sulfuric acid leaching of zinc dusts.

MATERIAL AND METHODS

The Kirovgrad copper smelter (KMK) had a fairly complete scheme for processing dusts, where granulated zinc vitriol was obtained from Converter dusts. About 400 kg of lead-tin cake (20-25% humidity) was produced at the KMC per ton of zinc sulfate, which is currently difficult to sell. Solasmonocolores Ural copper-smelting enterprises is given in the table, it depends on the type of feedstock, design of the melting unit and the characteristics of the technology of specific enterprise [2]. Dust with a high zinc content is usually subjected to sulfuric acid leaching, and zinc oxide or its salts are obtained from the solution purified from impurities; lead and tin are concentrated in the cakes.

The composition of cakes typical for the practice of the Sredneuralsky copper smelter (SUMZ) and the Kirovgrad copper smelter (KMK) is given below:

Cu Zn PbSn Fe As CYM3 0,2—0,5 8—12 42—46 —
0,4—0,5 1,7—2,1 KMK 1,5—2,0 5—8 40—45 10—15
0,5—1,0 0,4—0,5

Processing such raw materials for lead or its alloys is economically feasible, but there is no consensus on the optimal technology yet. The literature discusses issues related to individual technological operations, provides specific arguments in defense of certain solvents, and offers options for improving outdated technological techniques [3]. One of the important conditions when choosing a technological scheme for processing lead cakes is their phase composition. According to our data, lead in them is represented by 50-60% in the form of sulfate, 35-45 % — in the form of oxide; the rest of the lead is bound in complex oxide compounds (silicates, Arsenates, antimonates, etc.). Copper is represented by 75-85% oxide compounds, 15-20 % — sulfide, 3-4 % — sulfate. Zinc is contained in cakes mainly (by 65-70 %) in silicate form, in the form of sulfate (15-20%) and free oxide (5-10%). Almost all the tin in sincovich presented an amorphous modification metalbands acid.

In most of the recommendations, the main operation for processing lead industrial products is smelting for rough lead with its subsequent pyrometallurgical refining. These mastered operations make it possible to obtain a sufficiently pure metal, provide high lead extraction and the removal of a significant part of the impurities (zinc, arsenic and iron). However, environmental restrictions are becoming a serious obstacle to the large-scale implementation of pyrometallurgical schemes [4]. The hardware design of melting and refining in boilers is cumbersome, and provides a complex scheme for dust collection and waste gas neutralization. The resulting products (slags, removals, secondary dusts, etc.) require improvement, which reduces the economic efficiency of production as a whole. In recent years, there has been a trend in world practice to use hydrometallurgical techniques for processing secondary non-metallized lead raw materials [5].

At the Department of metallurgy of heavy non-ferrous metals of USTU-UPI, several options for processing lead and lead-tin cakes were studied: leaching with Ethylenediamine solutions to produce lead carbonate; leaching of tin-lead cakes in solutions of the disodium salt of ethylenediaminetetraacetic acid to produce tin concentrate and a lead-containing solution directed to lead electroextraction; electro-leaching of lead cakes in solutions of sulfamic acid to produce cathodic precipitation of lead; reduction melting of cakes for rough lead followed by its electrolytic refining in fluoroborate and sulfamine electrolytes; carbonation of cakes with soda solutions followed by melting and electrolytic refining [6].

Since lead-containing compartments contain significant amounts of water-soluble compounds, the main operation of their hydrometallurgical processing is washing. This reduces the content of copper and zinc in the cake, which reduces the consumption of solvent. Complex compounds are promising solvents for lead oxide and sulfate forms.

Their advantages are high lead capacity, selectivity and the possibility of regeneration. In particular, the most studied solutions are Ethylenediamine (EP). Lead sulfate and oxide are dissolved in them according to the equations: $PbSO_4 + 2En = Pb(En)_2SO_4$; $PbO + En + H_2SO_4 = Pb(En)SO_4 + H_2O$.

For active dissolution of lead oxide, the presence of sulfuric acid in the solution or pre-sulfation of compartments is necessary [7]. After 20-30 minutes at 293 K and the ratio W:T = 10: 1 up to 90-95% of lead is extracted into the solution. Sulfide compounds, precious metals, iron oxides, bismuth, tin, and waste rock minerals remain in the insoluble residue [5]. The lower oxides of antimony and arsenic partially pass into the solution. For leaching CMC cakes, EP solutions with concentrations of 100-200 g/dm³ were used. In 120 min, only 48% of lead is extracted into the solution, which corresponds to the content of its sulfate form in the original cake. Introduction to the solution of up to 30 g/dm³ of sulfuric acid did not give positive results. Therefore, for effective use of Ethylenediamine as a solvent, pre-sulfatization is necessary, which will require additional acid-resistant equipment, increase the amount of harmful effluents and worsen working conditions.

RESULTS

The effective method for separating lead from purified Ethylenediamine solutions is to purge them with carbon dioxide, which ends with the deposition of lead carbonate, which, after washing and drying, is suitable for the production of chemical compounds, including for obtaining pure lead oxide used in the production of crystal [8]. When leaching cakes in solutions of disodium salt of ethylenediaminetetraacetic acid (EDTA), both sulfate and oxide forms of lead are dissolved; this allows processing lead-containing industrial waste without any preliminary preparation. The advantages of dissolution include environmental safety and the possibility of using equipment from available grades of structural steels. The nature of changes in the concentration of lead in the solution during leaching

indicates that the speed of the process slows down over time and is mainly determined by the density of the pulp. The final lead content in the solution depends only on the concentration of EDTA (the "capacity" of the solution for lead) and is about 40 g/dm³. When sulfate and lead oxide are dissolved, there is a region of unstable saturated solutions where a reversible reaction occurs: $PbSO_4 + n(ЭДТА)Na^+ = Pb(ЭДТА)_n + nNa^+ + SO_4^{2-}$. In parallel, crystallization occurs tilantongo complex of lead associated with the sulfate ion. According to our data, the best leaching results are achieved at an EDTA concentration of 140-150 g/dm³ and a ratio of W: T=(10-12): 1. the Optimal method for extracting

lead from a trilonate solution is electroextraction, which allows one operation to regenerate the solvent, extract copper and 95-96% lead from it. The cathode current output is 70-75 %, the bath voltage is 2.7-2.9 V, and the power consumption is 2800-3000 kWh/t of cathode sludge. It is rational to Deplete the electrolyte to a lead concentration of not less than 0.8-1.0 g/dm³ in order to avoid reducing the effectiveness of the solvent during repeated use in the leaching operation. The solid leaching residue of lead-tin cakes contains 92-95 % tin (IV) oxide; this product is suitable for producing tin metal or its compounds.

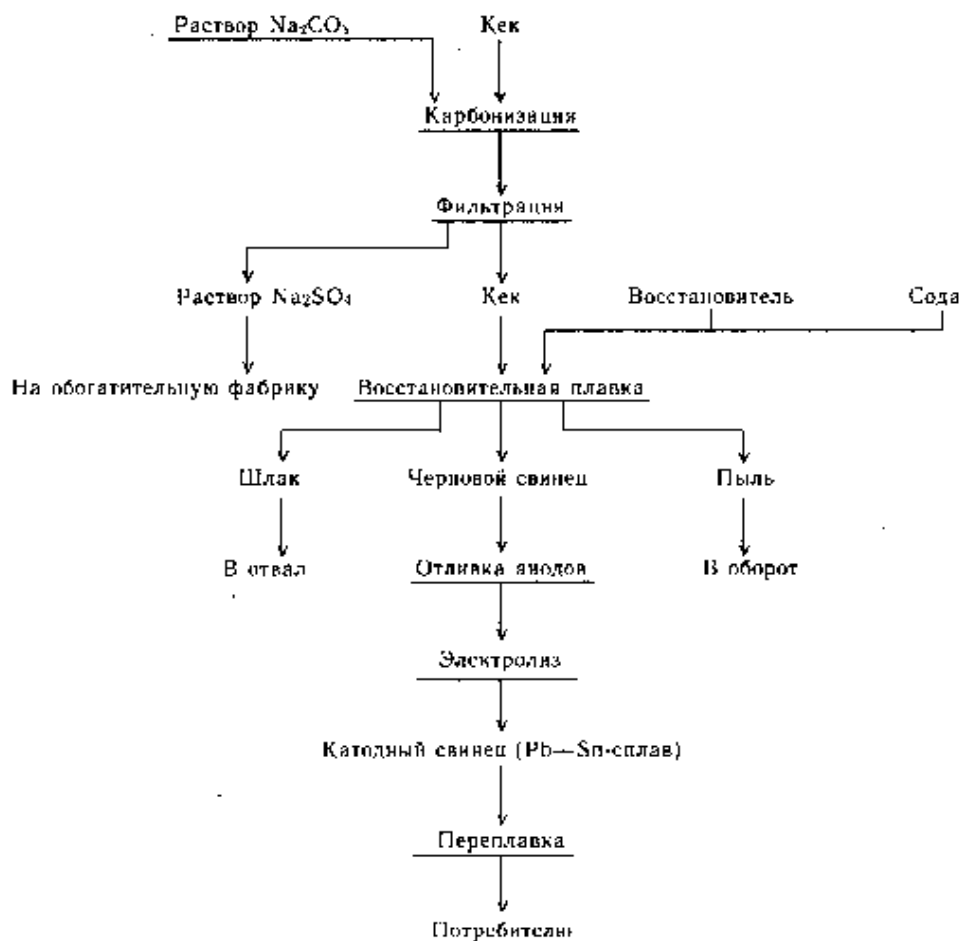


Fig. 1. Technological scheme for processing lead-containing cakes

The main disadvantage of direct leaching of cakes is the accumulation of sulfate ion in the solution, which negatively affects the performance of subsequent operations. The removal of the sulfate ion in the form of insoluble CaSO_4 is associated with additional operations and the production of gypsum industrial products, which complicate the technology [9]. Therefore, it is more rational to first remove sulfur from lead-containing waste, for example, by carbonizing the latter in concentrated solutions of sodium carbonate (potassium): $\text{PbSO}_4 + \text{Na}_2\text{CO}_3 = \text{PbCO}_3 + \text{Na}_2\text{SO}_4$. We found that the best results of carbonation are achieved at a concentration of Na_2SO_3 150g/dm³, W:T=5: 1, duration of 40-60 minutes. The final solution contained, g/dm³: 0.2 Si, 2.3 Pb, 0.4 Zn; cake after carbonation contained 53% Pb (97-98 % of the carbonate form) and 0.5% Si, zinc almost completely passed into the solution. The sodium sulfate solution obtained after carbonization is suitable for use in the scheme of flotation enrichment of ores. Under laboratory conditions, we have studied the variants of separate and combined leaching and electrodeposition processes in relation to carbonized lead and lead-tin technogenic products. In the first variant, cakes were leached in solutions of sulfamic acid (100-120 g/dm³) for 3 hours. The complexation reaction proceeds according to the scheme: $\text{NH}_2\text{SO}_3\text{H} + \text{PbCO}_3 = \text{NH}_2\text{SO}_3\text{Pb} + \text{H}_2\text{O} + \text{CO}_2$. The extraction of lead in solution is 80-85 %. After filtration, the solution is sent to the electrolyzer (DR = 150 A/m², U= 1.9-2.0 V). In the combined process of electro-leaching in a two-chamber electrolyzer with a tissue membrane, lead was deposited in the cathode cell, and the anode cell was fed with new portions of the original cake. In this case, the design of the electrolyzer did not provide reliable circulation of the solution through the tissue membrane and convenient unloading of the undissolved residue [10].

DISCUSSIONS

The discussed technologies for hydrometallurgical processing of lead-containing waste have a number

of common disadvantages: pre-water washing of cakes is necessary with the formation of significant amounts of toxic industrial water, the disposal of which is difficult; filtration of pulps after washing, leaching and other operations is difficult, especially when the content of tin oxide in cakes increases; electroextraction of lead from contaminated solutions leads to the formation of spongy sediments that require additional refining; most hydrometallurgical operations with lead-containing solutions require additional costs for safe maintenance [11].

CONCLUSIONS

For the processing of lead-containing industrial waste, combined technologies are interesting, the main operation of which is reduction melting for rough lead (Fig. 1). To avoid emissions of sulfur dioxide, cakes should be carbonized before melting according to the technology described above [12]. After drying and pelletizing, the carbonate product is processed in an electric furnace, and rough lead (95-97%) is obtained. In this case, 95-96% of lead is extracted into the rough metal, and 90-95 % of zinc passes into the gas phase. Rough lead is subjected to electrolytic refining in sulfamine (to obtain a cathodic Deposit of Pb—Sn-alloy) or fluoroborate (to obtain branded lead) electrolytes. Calculations have shown the effectiveness of the combined technology.

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