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POSSIBILITIES OF INCREASING THE EFFICIENCY OF THE TECHNOLOGY OF HYDROMETALLURGICAL PROCESSING OF LEAD CONCENTRATES

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ABSTRACT

The most developed hydrometallurgical technological schemes for the production of lead and its compounds, based on the use of sulfuric and hydrochloric acids, are considered. Their main disadvantages are shown, which prevent their introduction into practice, which is associated, first of all, with the low solubility of lead sulfate and chloride. The prospects of using hydrometallurgical schemes with the use of nitric acid for processing lead-containing raw materials to obtain lead and its compounds have been substantiated. Metal recovery reaches 96-99% with almost complete reagent regeneration. The tests carried out demonstrate greater environmental friendliness compared to pyrometallurgical.

INTRODUCTION

Currently, almost all lead from lead-containing mineral raw materials is obtained by pyrometallurgical methods. The main one is reduction mine smelting of pre-sintered lead concentrate and subsequent refining of the crude metal [1]. One of the varieties of this method is the production of lead from lead-zinc concentrate by the Imperial Smelting method. Lead is also partially obtained from rich (with a lead content of more than 65%) concentrates by reactive smelting in its various variants. In general, the mine smelting method produces more than 89% of the total lead, about 9% by the Imperial Smelting method, the rest of the lead is obtained by reactive smelting or smelting of concentrates in suspension.

METHODOLOGY

Since 1985, the development of a new pyrometallurgical process began - melting in the KIVCET-TsS unit and its varieties [2], but recently, for a number of organizational reasons, the volume of work in this direction in the CIS has

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decreased. At the same time, this method of producing lead is recognized as one of the most promising in world practice. Nevertheless, these methods have a number of disadvantages inherent in pyrometallurgical processes in general, including:

- The need to use raw materials with a relatively high (according to current regulatory documents at least 30%) content of the base metal.

- Multi-stage lead production and, consequently, a relatively low degree of direct metal extraction into a commercial product (at the most advanced enterprises of the industry, it is 91-93%). In this case, lead partially passes into various industrial products, the processing of which is carried out according to special technological schemes. The costs of additional removal of lead from these products are much higher than for the production of lead from concentrates, which leads to an increase in the cost of the products.- In the course of processing, a number of accompanying metals are concentrated in middlings, the extraction of valuable components from which requires the use of additional technological schemes. The latter is an independent complex technical problem and involves an increase in the overall level of production.

- Serious environmental hazard of production due to the formation of a large amount of gases, into which a significant part of the sulfur contained in the feedstock goes. The low sulfur content in the gases of lead production, as well as the presence of irreversibly acting catalytic poisons (for example, arsenic-containing compounds) in them, make it difficult to utilize sulfur in sulfuric acid and other products. In addition, due to the low dispersion of the feedstock, its significant dust emission occurs (up to 10% of the weight of the feedstock), which necessitates the construction of complex and expensive gas and dust treatment systems.

RESULTS AND DISCUSSION

In connection with the above, of particular interest are developments aimed at creating hydrometallurgical technological schemes for the production of lead and its compounds, as environmentally safer. The overwhelming majority of works are associated with the use of sulfuric and hydrochloric acids most widely used in the practice of hydrometallurgy; therefore, the developed technological schemes can be divided into chloride and sulfate.

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CHLORIDE HYDROMETALLURGICAL CIRCUITS

Chloride hydrometallurgical schemes are based on the dependence of the solubility of lead chloride on temperature, or on the ability of oxidized lead compounds to dissolve in concentrated solutions of chlorides of alkali and alkaline-earth metals with the formation of complex compounds. Various reagents have been proposed to convert lead from sulfide to chloride: chlorine gas [3-8], hydrochloric acid (both without oxidants [9-11], and in their presence [12-15]), various chloride salts [16-20]. Considering the fact that chlorinating reagents can provide sufficient completeness of the extraction of lead into solution only at high concentrations or elevated temperatures, the attention of researchers was attracted by mild oxidants - solutions of metal chlorides with variable valence: first of all, such a widespread metal as iron. The development of technological schemes using this reagent was carried out by researchers from the USA, Japan, Norway, France, and others [21-24]. In the CIS, a large amount of research in this direction has been carried out at the Irkutsk Polytechnic Institute [25], the Institute of Metallurgy and Enrichment of the Academy of Sciences of the Kazakh SSR [26], MISiS [27]. As a result, a number of technological schemes have been proposed, differing mainly in the methods of removing metals from solutions. The most developed of them and close to its implementation is the method of the US Mining Bureau [22], the technological scheme of which includes the leaching of lead with a hot solution of iron (III) chloride and NaCl, introduced to increase the solubility of the resulting lead chloride (Fig. 1). Upon subsequent cooling, the leached lead precipitates in the form of pure chloride, the electrolysis of a solution of which in a molten eutectic mixture of lithium and potassium chlorides produces a commercial metal. Chlorine released during electrolysis is used for reagent regeneration. The method was tested on a pilot plant with a capacity of 230 kg of lead per day. Compared to existing technology, this process is more environmentally friendly and, in addition, simplifies the lead refining procedure. As significant disadvantages, one should note the high power consumption and the need to remove a large number of solutions from the circulation (to prevent the accumulation of associated impurities in them when using circulating electrolyte for leaching lead from new portions of the feedstock).

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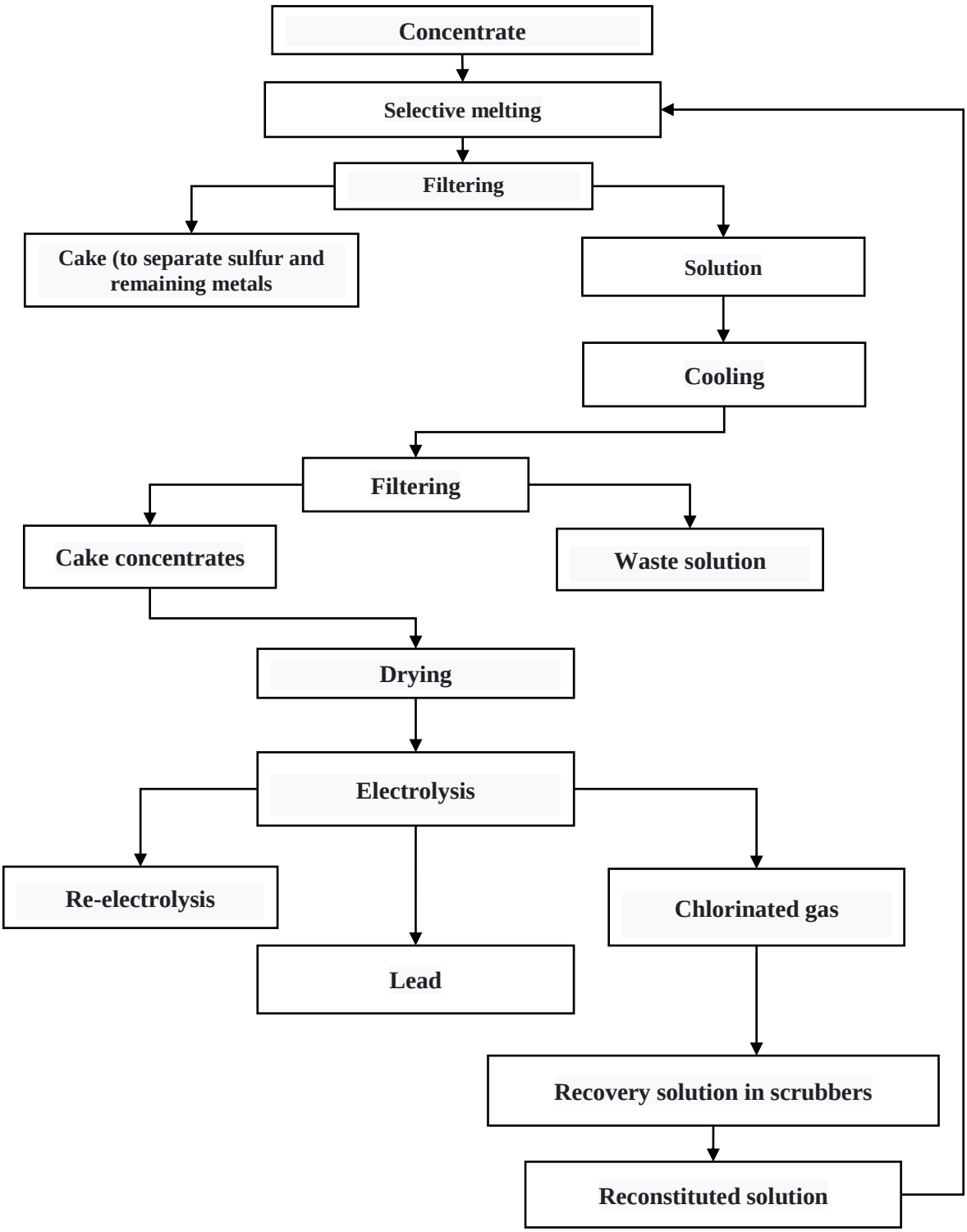
In France, a similar technological scheme was tested on a semi-industrial scale for processing lead sulfide concentrates with electrodeposition of powdered lead from solutions purified after leaching [23].

Simultaneously with the electrolytic release of lead, ferric chloride is regenerated. Elkem (Norway) together with Falkonbridge (Canada) have developed a continuous process for the processing of complex sulfide concentrates using iron (III) chloride, including leaching at a temperature of 105-115 ° C with extraction into solution up to 99% of copper, zinc, lead and up to 95 % silver [24]. Then the solutions are directed to crystallization of pure lead chloride containing about 0.1% of iron, copper and zinc, and electrolysis of the chloride melt is carried out to obtain lead. After crystallization of lead chloride from solutions, copper is electroplated at 70°C and a current density of 1-1.5 kA / m^2 and copper is obtained in the form of powder with a particle size of 125-500 microns, which is deposited on the bottom of the electrolysis bath. Zinc is extracted from solutions after electrolytic separation of copper with tributyl phosphate. In general, the process is carried out in a closed loop and meets the requirements for environmental protection. A pilot plant operating according to this scheme was first put into operation in 1980 and is designed to process 1,500 kg of raw materials per day. The plant produces pig lead, cathode zinc and copper powder.

The authors of [28] suggested using a solution of copper (II) chloride as a chlorinating reagent. In 1983, information appeared on the use of the proposed method for processing refractory ores from the Kayeli (Turkey) and Teina (Ireland) deposits [29]. It was shown that when grinding ore to 2-5 microns using solutions containing 118 kg/m^3 of copper in the form of chloride and 205 kg/m^3 of sodium chloride, introduced to increase the solubility of lead chloride, in the temperature range of 80-106°C in Within 2 hours, 98% of lead and zinc and about 80% of copper are extracted into solutions. However, the work does not indicate the ways of regeneration of the reagent, therefore, it is problematic to assess the prospects of the practical application of this method. In general, when using chloride hydrometallurgical schemes for processing lead-containing raw materials, satisfactory results were obtained, and the possibility of achieving a high degree of lead recovery opens up prospects for their application. However, in almost all of these methods, at one stage or another, gaseous chlorine is released, an extremely aggressive and highly toxic substance, especially in a humid atmosphere and at elevated temperatures. This makes the processes unsafe from the point of view of

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SULPHATE HYDROMETALLURGICAL SCHEMES

Sulfate hydrometallurgical schemes using sulfuric acid for opening the feedstock have been studied quite well, which is associated with the cheapness and availability of the latter. In addition, the lower solubility of lead sulfate in comparison with sulfates of other non-ferrous metals provides a greater selectivity of hydrometallurgical schemes based on this compound. However, up to 1950, sulfuric acid was used in all studies to obtain sulfates and hydrogen sulfide, varying only the concentration of the reagent and the temperature of the process [29]. As a result of the research, it was concluded that the application of these methods in industry is low. First of all, this conclusion is explained by the fact that, due to the low solubility of lead sulfate, its separation from waste rock is difficult, and the use of chloride salts for this purpose leads to one of the variants of the chloride technological scheme with corresponding technological difficulties. In addition, there are problems associated with the need to utilize sulfate ionsIn the late 1960s, interest in sulfate technological schemes began to appear again in connection with attempts to use organic complexing compounds as solvents for lead sulfate. Of greatest interest was the method developed by the firm "Sher-Rit Gordon" (Canada) [30] (Fig. 2). The proposed technological scheme includes the following stages: autoclave oxidation of lead sulfide to sulfate, amine leaching of lead sulfate at room temperature, treatment of the amine solution with carbon

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dioxide to precipitate basic lead carbonate ("white lead"), regeneration of the amine solution with lime and reduction of basic lead carbonate with carbon or electrolytic release of lead on insoluble graphite electrodes. However, this scheme has significant drawbacks:

- regeneration of solutions is accompanied by significant (up to 20% at each turn) loss of expensive reagents;
- there is a complete loss of sulfur associated with lead;
- there are no recommendations for the removal of associated metals from the circulating amine solution, which will inevitably accumulate in it;
- there is no scheme for cleaning solutions after sulfatization from impurities;
- obtaining lead by reducing its basic carbonate is a pyrometallurgical operation and leads to significant mechanical losses.

Slightly higher technical and economic indicators from the introduction of sulfate technological schemes are demonstrated by the cementation method for removing lead from solutions [31]. It was shown that it is possible to obtain high-purity lead, but the cumbersomeness of the technological scheme (associated, first of all, with the complexity of the hardware design) did not allow the introduction of this process into practice.

In addition to amines, other reagents have also been tested as solvents for lead sulfate:

xylites, glycols, glycerin [32, 33], ammonium-ammonium sulfate solutions [34], but their use did not lead to an improvement in technical and economic indicators.

In general, it should be noted that both chloride and sulfate acid hydrometallurgical schemes for processing lead-containing raw materials have not found their practical application, despite the high rates of raw material utilization. This is primarily due to the low solubility of lead sulfate and chloride in water. The use of complexing reagents to increase the solubility, regardless of their nature, significantly complicates the processes of lead removal from solutions and the regeneration of solvents.

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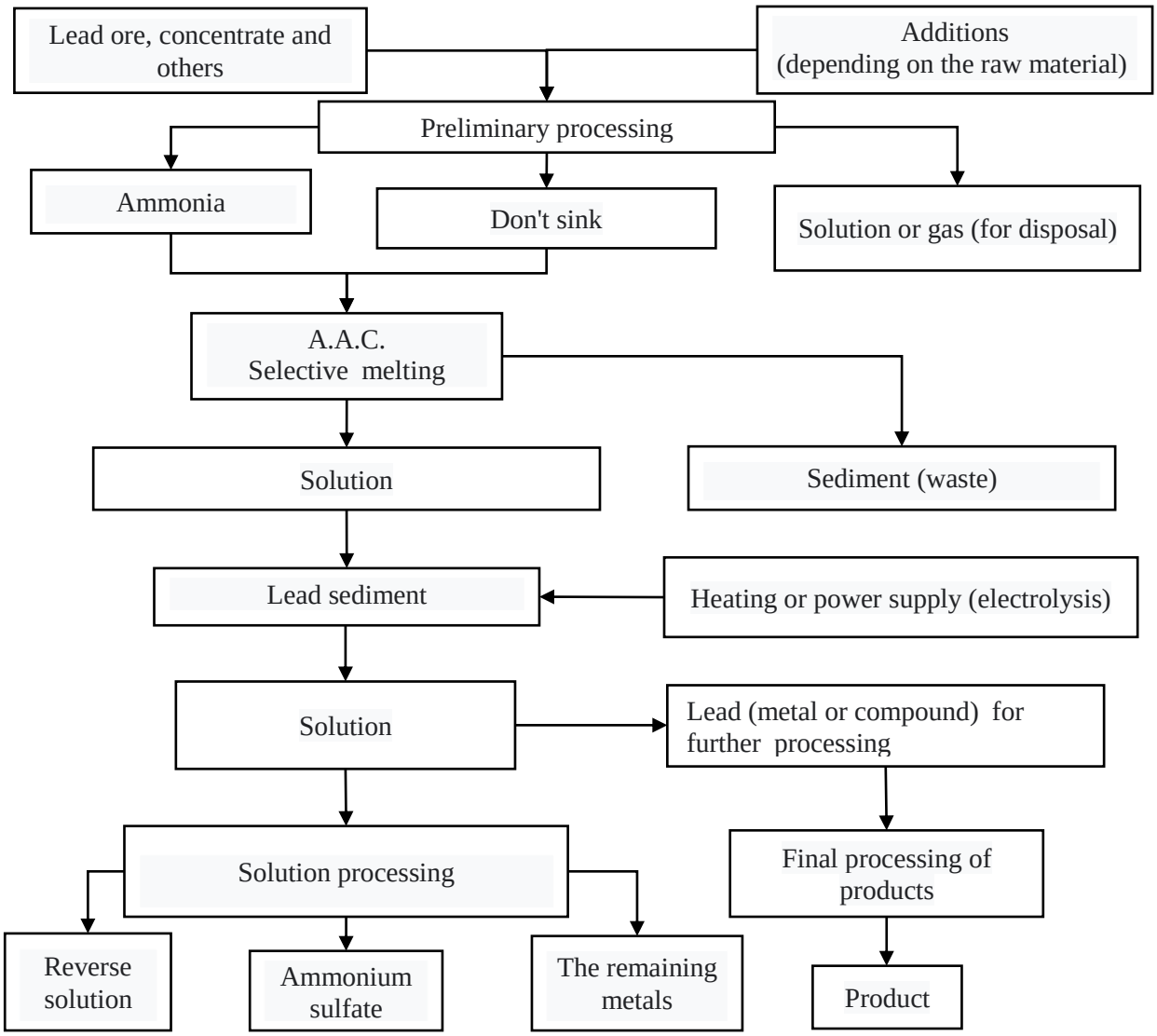


Figure:2. Scheme of processing of leadcontaining raw materials by leaching in an ammonia solution of monium sulfate [30].

HYDROMETALLURGICAL SCHEMES USING NITRIC ACID

Nitric acid is an active oxidizing agent of sulfide minerals and, in combination with the high solubility of lead nitrate, its use makes it possible to achieve good results when creating hydrometallurgical schemes for processing lead-containing raw materials [35]. Both nitric acid and its compounds have been tested as an oxidizing agent. To prevent the release of nitrous gases into the atmosphere, the autopsy is carried out in an oxygen atmosphere, for which a special apparatus has been designed. It was shown that the content of nitrogen oxides in the air does not exceed the background values. Various methods of solvent recovery with lead removal from the technological chain have been tested,

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both in the form of a metal and various lead-containing compounds (sulfate, nitrate or dioxide). In this case, almost complete regeneration of the solvent occurs. ... It has been shown that the degree of extraction of lead into solution reaches 92-96% with the oxidation state of galena 98-99.5%. The optimal conditions for carrying out operations have been determined. One of the developed technological schemes is shown in fig. 3.

It is shown that the extraction of lead into solution can be increased to 96-99% due to the use of two-stage opening of the feedstock using intermediate carbonization of cakes. In addition to increasing the degree of extraction of lead, this method of opening makes it possible, practically without changing conditions, to process in a single technological cycle both oxidized and secondary lead-containing raw materials and industrial products (cakes after zinc extraction, lead dust, wastes from the cable and battery industry, wastewater sludge from lead processing enterprises, etc. etc.). Due to additional extraction from sulfur cakes, the possibility of complex use of raw materials appears and a high (up to 98.5-99.5%) degree of lead extraction is achieved with sulfur removal to a safe level.

An ecological point of view, a form of elemental sulfur. The scheme with intermediate carbonization was tested on concentrates of almost all deposits of the USSR (including refractory ores of the Zhairemskoye deposit), as well as a number of foreign deposits of Santa Lucia (Cuba) and Kayeli (Turkey). The increase in the throughput of lead and zinc from the ore is 15 and 22%, respectively.

The results of laboratory studies were confirmed on a semi-industrial scale during tests at the Pilot Lead Plant of VNIItsvetmet (Ust-Kamenogorsk) on a unit with a capacity of 1-1.5 tons of raw materials per day [36]. Consumption factors for the reagents used have been determined. The hardware design of the processes has been developed. The estimated economic effect from the introduction of the proposed method in the production of 100 thousand tons of lead per year at 1987 prices was 4.84 million rubles. (not counting the effect of preventing environmental pollution).

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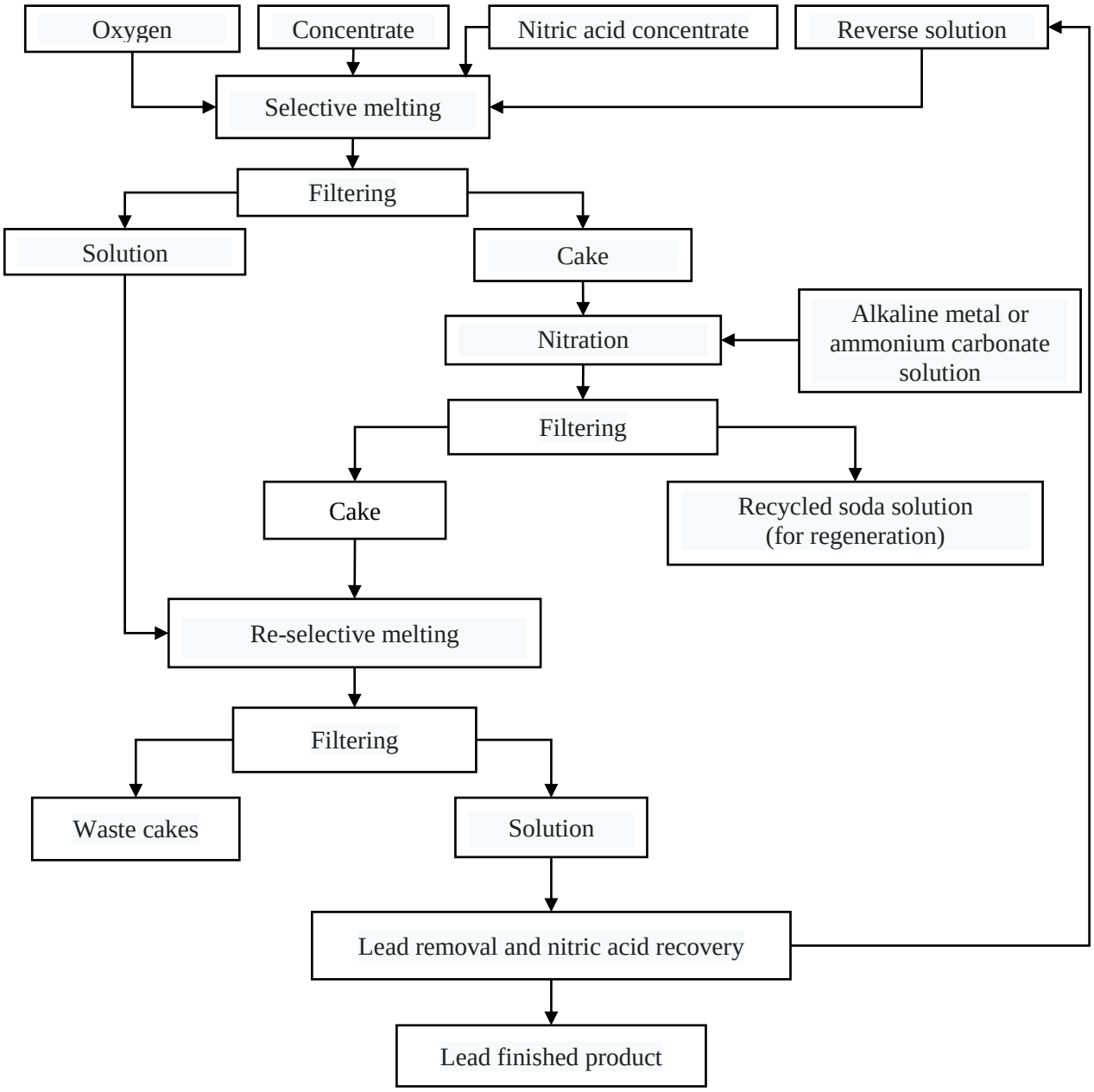


Figure: 3. Nitrate hydrometallurgical scheme for processing leadcontaining raw materials [36].

Cakes after lead recovery are common polymetallic raw materials from which the associated metals can be recovered by conventional metallurgical methods. In the course of tests, for example, the possibility of zinc extraction from cakes was shown by flotation separation of zinc sulfide concentrate and its subsequent processing using standard technology. The circulating solutions can be utilized after soda precipitation of heavy metals to obtain technical nitrate by evaporation [37].

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CONCLUSION

In general, the economic feasibility of using acid hydrometallurgical technological schemes for processing lead-containing raw materials can be considered proven. The tests carried out demonstrate the environmental safety of using these schemes in comparison with pyrometallurgical processes. However, to fully answer the questions, the solution of which is necessary for the implementation of the developed technological schemes into practice, it is required to conduct tests on an enlarged scale.

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