Chemistry for Sustainable Development **13** (2005) 483–490

Hydrometallurgical Schemes of Lead Concentrate Processing

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(Received July 14, 2004)

Abstract

The work is focused on the most developed hydrometallurgical methods of lead and its compounds processing, using sulphuric and hydrochloric acids. Major drawbacks of these techniques, that hamper industrial use, are shown. In particular, the barriers caused by the low solubilities of lead sulphate and chloride. The usefulness of hydrometallurgical flowsheets involving nitric acid for lead-containing raw materials processing was shown. The advantages include: high degree of metal extraction (up to 96–99 %), almost complete reagents regeneration. Under the testing conditions the methods had demonstrated superior to pyrometallurgical processes ecological safety.

INTRODUCTION

Nowadays, almost all of the lead-containing minerals are converted into metallic products by means of pyrometallurgical processes. The basic of them is a reduction fusion of the preliminary agglomerated lead concentrate, followed by the crude metal fining [1]. Example of such a technique is "Imperial Smelting" method of lead-containing raw material processing.

Partially, lead is synthesized from the high grade (with Pb mass ratio more than 65 %) metallic concentrates using various sorts of reaction fusion. On the whole, lead processing can be divided into three major groups: 89 % is processed using blast smelting, 9 % – "Imperial Smelting" and the last amount of lead is produced either by reaction fusion or concentrate fusion in suspension state.

In 1985 a new process had been developed – fusion in KIVTSET-TSS apparatus [2]. But efforts in that direction in CIS at present time had ceased, because of the different managerial problems. Still, this method was regarded as the most forward-looking in industry.

In the meantime, the techniques described above have some drawbacks, intrinsic for all pyrometallurgical processes:

– Initial materials have to contain relatively big ratio of initial metal (according to the standard documentation at least 30 %).

– Multistep synthesis leads to a reduced extraction degree, so that the best achievable parameters are 91–93 %. But during the process Pb is partially converted into different types of intermediate products. The latter demands specially designed process flowsheets. Eventually this makes the produce more expensive, because of the additional costs.

– During the prior treatment some concomitant metals are concentrated in intermediate products, the following extraction of these metals demands additional process flowsheets and is, in fact, a very difficult and complicated task.

– The process is not ecologically safe, because of the abundant emission of gases, including sulphuric compounds. These gases can not be readily converted into H_2SO_4 or other products because they contain insufficient sulphur concentration and catalytic poisons. Additionally, due to the high dispersity of raw materials, considerable amounts of them are lost in a form of dust (up to 10 %), thus complicated and expensive separating systems are needed.

The facts presented above highlight the importance of developing of alternative methods. In particular, hydrometallurgical schemes of lead and its compounds processing have important ecological advantages. The majority of works in that scientific field is concentrated on hydrometallurgical processes based either on sulphuric or hydrochloric acids, therefore it is possible to divide the schemes to chloride and sulphate, respectively.

CHLORIDE HYDROMETALLURGICAL FLOWSHEETS

Chloride hydrometallurgical schemes are based either on the temperature dependence of lead chloride solubility or on ability of oxidized lead compounds to dissolve, forming complex structures, in concentrated solutions of alkaline or alkaline earth metals chlorides. A great variety of reagents were proposed to convert lead sulphate into chloride: gaseous chlorine [3–8], hydrochloric acid (without oxidizing agents [9–11], and with them [12–15]), different sorts of chloride-containing salts [16–20]. Given that, chlorinating agents are able to provide sufficient lead extraction degree only at high concentrations or elevated temperatures, many scientists were interested in less active oxidizing agents, in particular, chloride solutions of multi-valency metals. One of the most important examples of that type of compounds is iron chloride. The possible applications of it were investigated by researchers in different countries such as USA, Japan, Norway and France [21–24]. In CIS the main scientific investigations had been made in Irkutsk Polytechnic Institute [25], Metallurgy and Concentration Institute of AS, KazUSR [26] and MISS [27]. As a result of this work, several technological schemes were presented. Their main difference lies is the way of metal–solution separation.

One of the most developed schemes is considered to be a method proposed by the USA Mining Department [22]. This process flowsheet consists of lead leaching by a solution mixture of hot iron chloride and NaCl, the latter agent is used to increase lead chloride solubility (Fig. 1). After solution cooling the pure lead chloride precipitate is formed. The marketable metal is produced using flux electrolysis of the lead chloride with an eutectic LiCl, KCl mixture. Chlorine gas formed during the electrolysis is used for reagent regeneration. This method was tested on an experimental plant with 230 kg per day productivity. In comparison to contemporary techniques this process is more conformable with ecological issues and, in addition, facilitates the lead fining procedure. Major disadvantages of the method include uneconomical consumption of energy and need to withdraw big solution volumes. The latter procedure is intended to prevent concomitant impurities accumulation when recycled electrolyte is used for newer portions of raw material.

Analogous technological scheme was tested in France on a semi-industrial scale plant, with lead sulphide concentrates as the raw materials. The process included electric precipitation of the powder lead from solutions, purified after leaching [23]. Electrolytic lead formation and iron chloride regeneration proceeded simultaneously.

Norwegian company Elkem had jointly with Falkonbrindge (Canada) developed the process flowsheet of an uninterrupted complex lead sulphides concentrates conversion. The process using iron (III) chloride, involves leaching at 105–115 °C which resultes in an extraction to the solution of 99 % of copper, zinc, lead and up to 95 % of silver [24]. Solutions are cooled to produce pure lead chloride crystals (contain about 0.1 % of iron, copper and zinc), then lead chloride is electrolyzed forming free metal. After the lead chloride crystallization, copper electric precipitation takes place at temperature 70 °C and current density 1–1.5 kA/m^2. Copper powder (125–500 μm) precipitates on the electrolysis bath bottom. Next step is a solution zinc extraction using tributyl phosphate. As a whole the described process is a closed cycle scheme and satisfies environment protection claims. The first testing set, based on this process flowsheet with 1500 kg per day productivity was started up in 1980. The plant produces lead bars, cathodic zinc and copper powder.

Authors of the patent [28] suggested copper (II) chloride as a chlorinating agent. This method for the first time was used in 1983 for the

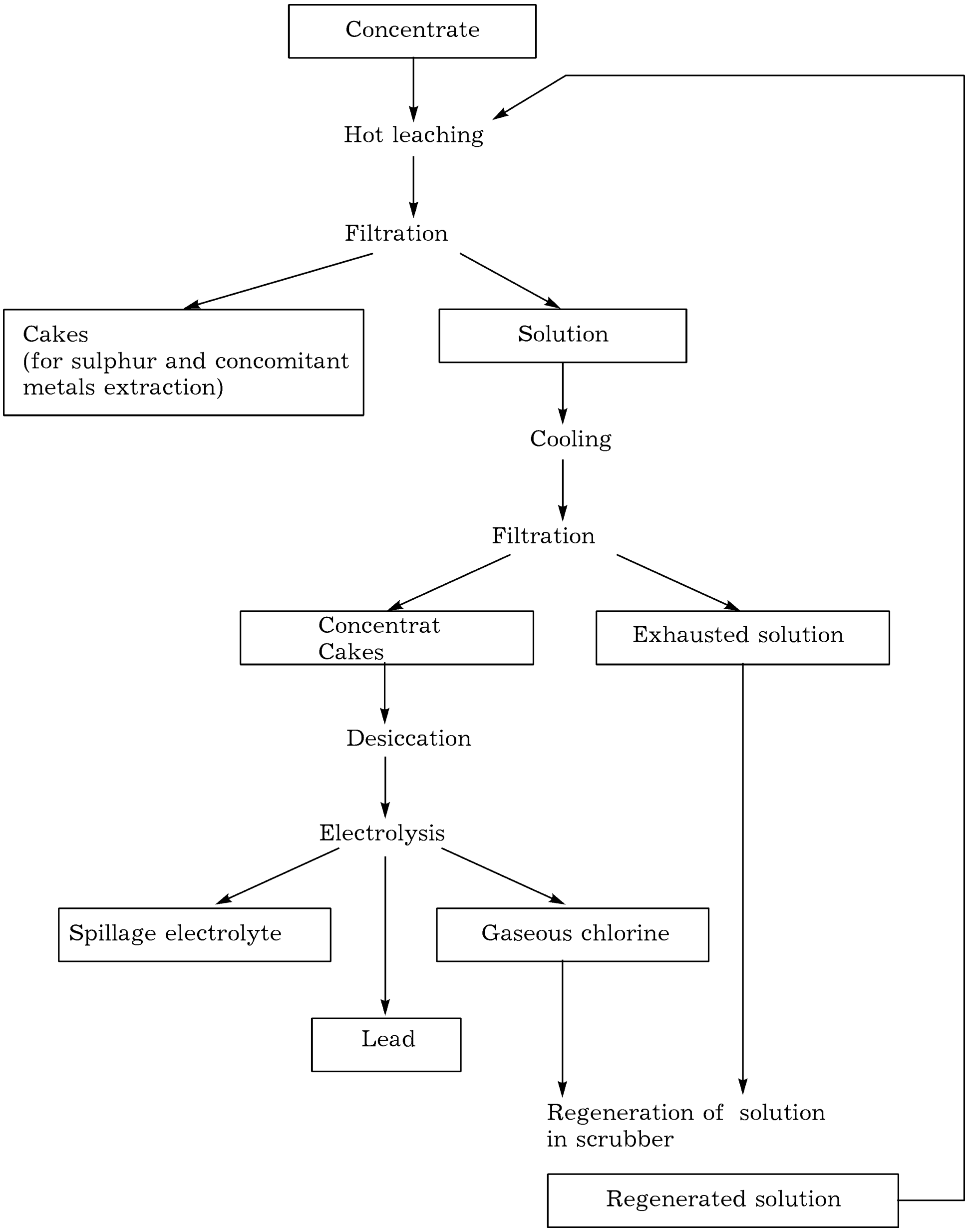

Fig. 1. Technological flowsheet of lead concentrate processing proposed by USA Mining Department [21].

processing of hardly-concentrated ores of Kayeli (Turkey) and Teyna (Ireland) [29]. The process is comprised of ore grinding down to 2–5 μm and treatment with solution (118 kg/m^3 of copper chloride and 205 kg/m^3 of sodium chloride, needed to facilitate lead chloride dissolution) for 2 h in the temperature range 80–106 °C. Solution extracts 98 % of lead and zinc and about 80 % of copper. Unfortunately, no information had been provided concerning reagents regeneration, therefore the practical usefulness of this technique is dubious.

So, the results, obtained for chloride hydrometallurgical flowsheets of lead-containing compounds processing, are satisfactory. Given that the extraction degree is very high for this type of technological schemes, there is a strong possibility of practical utilization. However, almost every method constitutes of the stages involving gaseous chlorine emission, this gas is a very corrosive and toxic substance, especially in humid air and at elevated temperatures. Therefore the process is insecure from the ecological point of view, causing additional expenses for special impermeable gear construction and sophisticated protective measures for the personnel.

SULPHATE HYDROMETALLURGICAL FLOWSHEETS

Sulphate hydrometallurgical flowsheets – the methods involving sulphuric acid as a main processing reagent, are well studied because of the availability and cheapness of the reactant. In addition relatively low (in comparison with other non-ferrous metals) lead sulphate solubility results in better selectivity of these hydrometallurgical schemes. However, until 1950 every developed process flowsheets consisted of sulphates and hydrogen sulphide formation stages, while only reactants concentrations and temperature were varied [29]. This researches lead to a conclusion of almost no prospect usefulness of these techniques in industry. Such a conclusion was made because of the following factors. First, as lead sulphate has low solubility its separation from gob would be very hard. This obstacle can be met using chloride salts, but this would be, in fact, another chloride scheme accompanied by all the deteriorating factors of this type of process flowsheets. In addition, sulphate ions utilization problem also occurs.

At the end of 1960's interest for sulphate technological schemes was revived because of the attempts to use organic complex-forming compounds as lead sulphate vehicles. The techniques developed by Sherit Gordon company (Canada) are of main interest in this field [30] (Fig. 2). The proposed technological flowsheet is composed of the following stages: autoclavic lead sulphide to sulphate oxidation; amine lead sulphate leaching at room temperature; CO treatment of amine solution resulting in a formation of lead carbonate ("white lead"); amine solution is regenerated using lime, after which the basic lead carbonate is reduced by carbon or electrochemically on insoluble graphite electrodes.

However, these techniques have important drawbacks:

– Solutions regeneration is accompanied by a considerable (up to 20 % for each turn) loss of expensive reagents.

– During the process the sulphur bound with lead can not be conserved, and is irreversibly lost.

– Till the present time no investigations had taken place on the problem of circulating amine solution purification (as it would inevitably accumulate impurities).

– No purification scheme for the solutions, made after sulphatization procedure, is known.

– Lead formation in a basic carbonate reduction reaction is a pyrometallurgical process involved with considerable mechanical losses.

A little bit more effective, than a previous one, is a cementation technique of lead extraction from solution [31]. The possibility to obtain highly pure lead had been shown, in principal, but the corresponding technological flowsheet is so complicated (first of all, because of the facilities used) that the process was not established in an industrial scale.

Other lead sulphate vehicles were tested along with amines: xylites, glycols, glycerin [32, 33], ammonia-ammoniumsulphate solutions [34] – but there was no significant meliorating effect observed.

The general conclusion is as follows: both chloride and sulphate hydrometallurgical lead processing flowsheets were not accepted by the industry, despite their high raw material utilization degrees. This fact can be explained, first of all, by the low lead sulphate and chloride water solubility. Whatever complex-forming substances are used to increase solubility of the initial lead-containing salt, it eventually makes the processes of lead extraction and solutions regeneration much more complicated.

HYDROMETALLURGICAL FLOWSHEETS INVOLVING NITRIC ACID

Nitric acid is an active sulphide mineral oxidizing agent, taking into account the high lead nitrate solubility, it becomes clear why using this acid one can reach good results in development of hydrometallurgical flowsheets for lead raw material processing [35]. In an experiment as oxidizing agents both nitric acid and its compounds were tested. In order to prevent formation of nitrose gases, raw

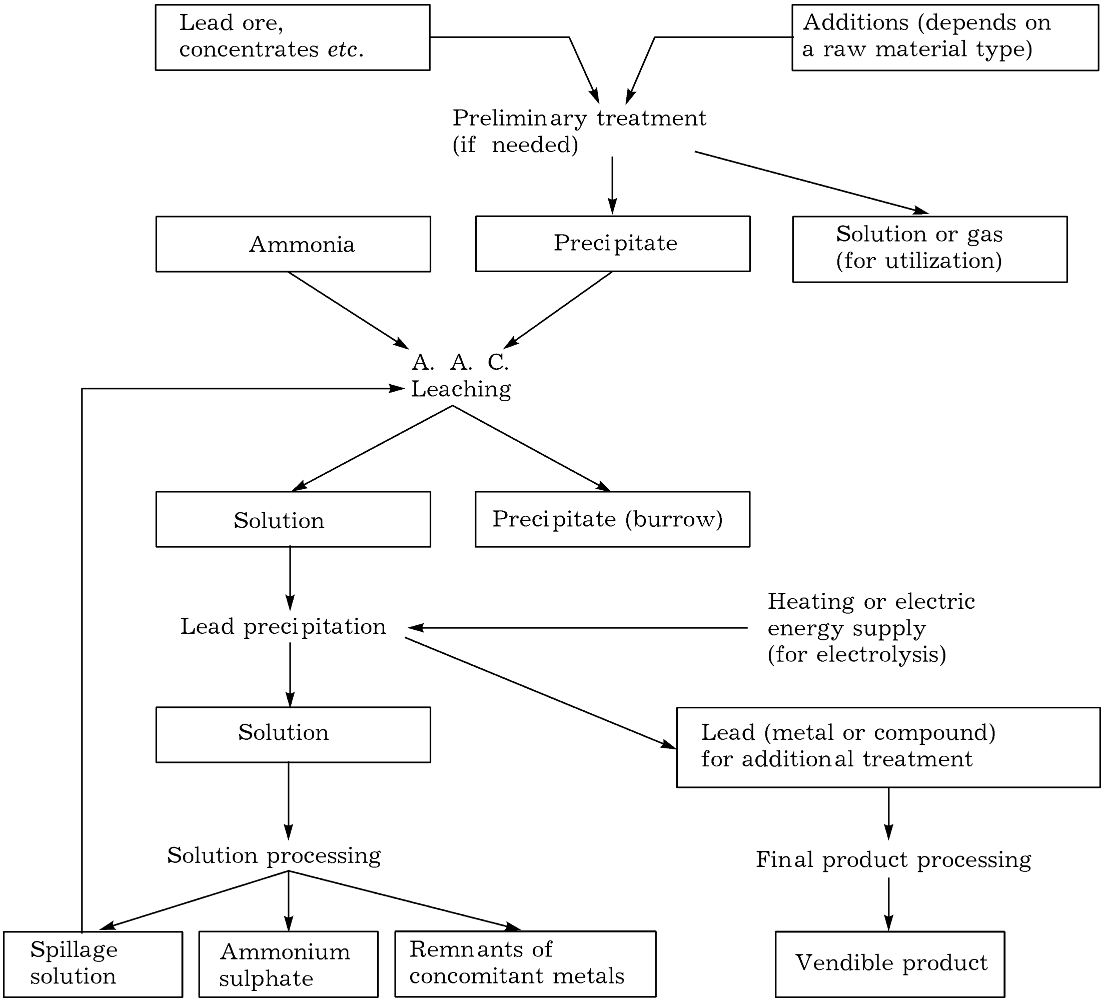

Fig. 2. Technological flowsheet of lead-containing raw materials processing, using leaching in ammonium sulphate ammonia solution [30].

material treatment is made in an oxygen atmosphere, for this purpose a special apparatus was developed. It was shown that nitrogen oxides percentage in air did not exceed background values. Different ways of solution regeneration were tested, along with methods of lead withdrawal from technological circle either in form of a metal, or different lead-containing substances: sulphate, nitrate and oxide. The process is accompanied by almost total solution regeneration. It was shown, that lead extraction reaches up to 92–96 % at galena oxidation degree 98–99.5 %. The optimal conditions for the process were established. One of the possible technological flowsheets is depicted in Fig. 3.

It was shown that degree of lead extraction into solution can be increased up to 96–99 % using a two-staged initial raw material treatment with an intermediate carbonization of cakes. Apart from an increase of the lead extraction degree, this procedure makes it possible to convert, almost without improvements, oxidized, both secondary lead materials and middling products (such as, zinc extraction cakes, lead powder, cable and accumulator industry wastes, lead processing plant waste water tailings). Another valuable potential of the scheme is an additional sulphur extraction from cakes that makes raw material utilization more complex, extraction degree can be increased up to 98.5–99.5 % with sulphur withdrawal in an environmentally safe form, *i.e.* elemental sulphur. Intermediate carbonization flowsheet was tested on concentrates from almost all of the fields in

USSR (including hardly-concentrated ores from Yayremskoe field), and foreign countries fields: Santa Lucia (Cuba) and Kayeli (Turkey). Increase of the lead and zinc extraction was 15 % and 22 %, respectively.

Laboratory results were proved in a semi-industrial scale testing on the VNIITSvetmet (Ust' Kamenogorsk) plant with 1–1.5 t per day productivity [36]. Corresponding discharge coefficients for reactants were determined. Special apparatuses were developed. An approximate economical benefit from this technique for 100 000 t of lead per year is 4.84 mln rubles (1987 rubles value), and that is without taking into account the positive environmental effect.

Cakes, produced after lead extraction, are complex materials, concomitant metals can be separated using standard metallurgical methods. For example, during the testing session was shown the possibility of zinc extraction from cakes using flotation separation of sulfide zinc concentrate followed by standard processing of these concentrates. Technical saltpeter can be derived from spillage solutions using evaporation after heavy metals have been precipitated by carbonates.

CONCLUSIONS

As a whole, the economical effectiveness of hydrometallurgical flowsheets for lead-containing materials processing had been proved. The testing that took place during the investigation showed ecological safety of the mentioned schemes in comparison with pyrometallurgical processes. However, only the factory-scale testing of these techniques could

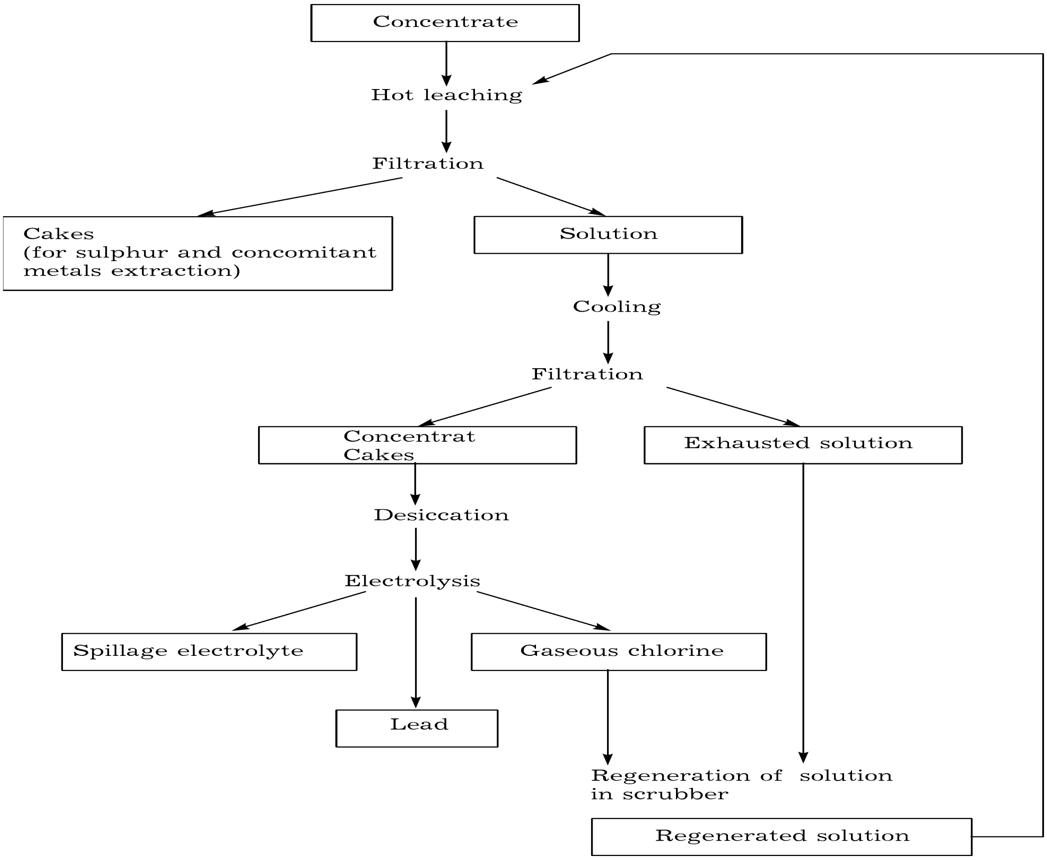

Fig. 3. Hydrometallurgical processing flowsheet of lead-containing raw materials, involving nitrates [36].

have helped to answer all the questions concerning industrial use of the processes.

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