ZINC RECOVERY FROM WASTES USING SPENT ACID FROM SCRAPPED LEAD ACID BATTERIES

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Abstract

Kovohute Pribram is a plant recycling lead wastes, lead acid batteries in particular. Relevant new recycling technologies are being gradually developed. Outdated technology of smelting lead plates has been replaced by a new technology based on processing of entire batteries in a blast furnace according to the process developed by know-how of German Varta company. The classical Harris refining has been substituted by the oxygen refining. New technologies aimed at utilization of related wastes arising from refining lead bullion in Kovohute Pribram are being developed in house. At present, a new technology of utilization of spent battery acid for extracting zinc from various wastes has been developed. Zinc oxide dross from alkaline refining of lead bullion, during which residual zinc from the preceding vacuum de-zincing is removed as well as waste zinc galvanic sludges (a product of neutralizing precipitation of metals from industrial wastewaters with lime) were treated.

In this study, the new developed technology yielding basic zinc carbonate - a valuable raw material for zinc electrowinning, is described together with the first experience of applying the developed method to processing zinc wastes on a pilot scale. Most of the equipment used in the past to regenerate alkali solutions originating from Harris refinery was utilized in the practical realization of this new technology.

1. Introduction

The lead production and its processing has a long-time tradition in the Czech Republic. The origin of this production is connected with the treatment of ores rich in silver and lead from famous mines situated in the local area, which is in the central Bohemia, 60 km from Prague, in the town of Pribram. These ores were processed in the silver metallurgical work, which was first mentioned in written form in 1311.

The current plant was built in 1786 and produced lead and silver from ores until 1972 but currently it serves as a secondary plant only [1]. A classical blast furnace for the treatment of lead concentrates was replaced by a new blast furnace built in 1997 according to Varta (Germany) technology for the treatment of whole batteries with boxes; the classical wet alkaline Harris refinery was replaced in 1999 by a new oxygen refinery; the hydrometallurgical plant no longer works, but it is still possible to use it.
The current technology comprises crushing of scrap batteries and pouring out sulfuric acid – a waste, which is currently treated by neutralization. The batteries are subsequently mixed with other lead wastes (most of them originating from the production of new batteries), such as returned slag, coke, lime, metallic iron and iron oxides and are smelted in the blast furnace into raw lead [2]. The lead bullion is then refined in a refinery, where Sn, Sb and As are removed by a direct oxygen refining. Parkes's method is used for the recovery of precious metals. Finally, vacuum de-zincing is applied for zinc removal both from the silver crusts and lead bullion. Finished products are soft lead, hard lead and lead-calcium alloys.

The plant is looking for methods to improve efficiency or ecological consequences of the process. Many new technologies have been applied recently, such as carbonate leaching of PbCl₂ - flue dust from the blast furnace and returning the obtained PbCO₃ back to direct smelting in the blast furnace, electrosrap treatment and some others. To minimize production of the wastes utilization of spent battery acid for the zinc recovery from wastes of own or external production being considered at present.

2. Aim of the project

Main intention of this study is to exploit two kinds of wastes produced in the plant - spent battery sulfuric acid and zinc oxide dross, together with external zinc wastes, such as zinc galvanic sludges. Zinc oxide dross arises during alkaline refining of lead bullion (a modification of the former Harris refining) during which the residual zinc from the preceding vacuum de-zincing is removed. The developed method of utilizing spent sulfuric acid and zinc wastes followed two aims: to yield zinc compounds suitable for zinc electrowinning and not to produce any secondary dangerous wastes.

3. Theoretical background

Permanently increasing global demand for zinc metal in the last years together with decreasing zinc production from ores results both in strong increase in world prices of zinc metal and also in increasing zinc production from secondary resources. At present, approximately 70% of the zinc produced originated from mined ores and 30% from recycled or secondary zinc [3]. Various secondaries and wastes containing zinc are generated in metallurgical or metal plating industries such as galvanizing, casting, smelting, scrap recycling and several others. Zinc present in the secondaries is in the form of metal, oxides and/or alloy and is associated with different levels of impurities depending on their source. Sulfuric acid leaching has been frequently used for the zinc recovery from wastes containing zinc oxides or zinc hydroxides [4]. Such type of leaching is very advantageous due to rapid and efficient zinc dissolution in dilute solutions of sulfuric acid even at laboratory temperatures, whilst dissolution of most impurities is depressed. Species contained commonly in zinc-bearing wastes react with sulfuric acid according to the reactions given below:

\[
\begin{align*}
\text{ZnO} + \text{H}_2\text{SO}_4 & \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} \\
\text{PbO} + \text{H}_2\text{SO}_4 & \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} \\
\text{FeO} + \text{H}_2\text{SO}_4 & \rightarrow \text{FeSO}_4 + \text{H}_2\text{O} \\
\text{ZnO, Fe}_2\text{O}_3 + 4 \text{H}_2\text{SO}_4 & \rightarrow \text{ZnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{O} \\
\text{Ca}[\text{Zn}]_{32}\text{OH} + 3 \text{H}_2\text{SO}_4 & \rightarrow \text{CaSO}_4 + 2 \text{ZnSO}_4 + 8 \text{H}_2\text{O} \\
\text{CaO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}
\end{align*}
\]
Calcium and lead sulfates formed remain in the leach residues due to their limited solubility in $\text{H}_2\text{SO}_4$. Iron can be removed without significant zinc loses by hydrolytic pH-controlled precipitation up to pH = 4 under oxidative conditions using the processed wastes as a neutralizing agent:

$$\text{FeSO}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3$$
$$\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3 \text{H}_2\text{SO}_4$$

Zinc sulfate solutions are suitable intermediate for preparation of zinc sulfate electrolytes or precipitation of zinc compounds namely of zinc carbonate using sodium or potassium carbonate as a precipitation agent:

$$\text{ZnSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{ZnCO}_3 + \text{Na}_2\text{SO}_4$$

Zinc carbonate is a suitable raw material for zinc electrolysis or ZnO production. Precipitation of zinc carbonate, which is completed up to pH = 8.5 provided chloride free compounds even if zinc is separated from chloride-containing acid solutions [5].

4. Results of laboratory experiments

As the goal of laboratory leaching, precipitation tests were performed to establish optimum conditions for efficient zinc recovery from zinc oxide dross and waste galvanic sludges using a minimum amount of sulfuric acid and to depress precipitation of impurities into zinc carbonate - the product of the investigated process.

Chemical composition of treated wastes, zinc oxide dross from alkaline refining lead bullion in Kovohute Pribram and neutralizing zinc waste galvanic sludges from metal plating industry - is given in Table 1. According to the results of XRD analysis zinc oxide dross consisted of three dominant phases, ZnO, PbO and NaOH, as well of small amount of lead metal, whilst galvanic sludges were amorphous.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of elements [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>Oxide dross</td>
<td>9-11</td>
</tr>
<tr>
<td>Galvanic sludge</td>
<td>21</td>
</tr>
</tbody>
</table>

Sulfuric acid obtained in Kovohute Pribram from spent lead batteries, which was used for leaching of zinc wastes is characterized in Table 2. This acid contained about 130g $\text{H}_2\text{SO}_4$/l.

<table>
<thead>
<tr>
<th>element</th>
<th>Zn</th>
<th>Fe</th>
<th>Pb</th>
<th>As</th>
<th>B</th>
<th>Cd</th>
<th>Cu</th>
<th>Sb</th>
<th>Sn</th>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>c [mg/l]</td>
<td>80</td>
<td>990</td>
<td>2</td>
<td>3</td>
<td>320</td>
<td>28</td>
<td>24</td>
<td>50</td>
<td>2</td>
<td>45</td>
<td>2</td>
<td>5</td>
<td>39</td>
<td>2</td>
</tr>
</tbody>
</table>

Leaching conditions, which were chosen in the agreement with the results of our previous studies [6, 7, 8] were as follow: 13% spent $\text{H}_2\text{SO}_4$, liquid-to-solid ratio (l:s) adjusted from 3:1 to 10:1, laboratory temperature, reaction time of 1h. During leaching, $\text{H}_2\text{O}_2$ was added to establish oxidative conditions and samples were withdrawn at selected time intervals to determine the reaction rate of zinc dissolution. Elemental
concentrations in the filtrates were established using AAS method. After the completion of leaching tests, leach residues were filtered, water-washed, dried, weighed and analyzed.

It was found that zinc extraction of more than 85% was achieved even for leaching the wastes at l:s > 5:1 and that the extraction is completed within 30 min, Fig. 1.

![Graph](image1)

**Fig. 1** Zinc dissolution from zinc oxide dross at 13% spent H$_2$SO$_4$, 20°C

Conditions of hydrolytic iron removal from leach liquors were chosen based on the determined dependency, illustrated in Fig. 2.

![Graph](image2)

**Fig. 2** Dependence of hydrolytic pH-controlled iron precipitation from zinc sulfate liquors using zinc waste as a neutralizing agent

In the agreement with the results from leaching and refining experiments both treated zinc wastes were processed according to the flowsheet illustrated in Fig. 3.
Compositions of leach residues and washed zinc carbonate precipitates are given in Table 3. According to the XRD analysis zinc carbonate precipitates consisted of a mixture of $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ and $\text{ZnCO}_3$. Leach residues from processing of zinc oxide dross comprised a mixture of $\text{PbO} \cdot \text{PbSO}_4$, $\text{PbSO}_4$, $\text{PbO}$ containing a small amount of $\text{Pb}$.

Table 3 Concentration of selected elements in leach residues and zinc carbonate precipitates

<table>
<thead>
<tr>
<th>Zinc oxide dross</th>
<th>Concentration of selected elements [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Zn}$</td>
</tr>
<tr>
<td>Leach residue</td>
<td>0.70</td>
</tr>
<tr>
<td>Zn- precipitate</td>
<td>58.50</td>
</tr>
<tr>
<td>Waste galvanic sludge</td>
<td>$\text{Zn}$</td>
</tr>
<tr>
<td>Leach residue</td>
<td>1.05</td>
</tr>
<tr>
<td>Zn- precipitate</td>
<td>58.03</td>
</tr>
</tbody>
</table>

5. Trial in industrial conditions

Based on results achieved from the laboratory treatment of zinc oxide dross and zinc waste galvanic sludge the developed method was applied to processing zinc waste galvanic sludge on a pilot- scale in a hydrometallurgical plant in Kovahute Pribram. Most of the equipment used in the past to regenerate alkali solutions originating from Harris refinery was utilized in the practical realization of this new technology:

- 17m³ tanks for operation with alkali water suspension
- pumps with piping systems
- stirrers
- a crane for manipulation

Zinc waste galvanic sludge, the composition of which is given in Table 1, was processed according to the flowsheet presented in Fig. 4.

Fig. 4 Flow sheet of zinc recovery from zinc galvanic sludge on a pilot scale

From 34 tons of zinc galvanic sludges (external wastes from metal plating industry) 10.1 tons of wet Zn(HCO$_3$)$_2$ containing about 23% H$_2$O was produced. Analysis of the dried product obtained is given in Table 4. It is evident, that recovered zinc basic carbonate precipitate is a promising raw material for electrolytic zinc metal production and it is still possible to reduce the content of problematic impurities, namely of chlorides by more intensive washing. Neutralizing sludge can be directly utilized in the blast furnace as a source of iron.

Table 4 Analysis of basic zinc carbonate obtained from zinc galvanic sludges

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
<th>Ni</th>
<th>Ca</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>[%]</td>
<td>38-40</td>
<td>0.2-1.8</td>
<td>0.2-0.9</td>
<td>0.1-0.2</td>
<td>1.3-1.5</td>
<td>0.7-1.0</td>
<td>0.1-0.2</td>
</tr>
</tbody>
</table>
6. Conclusions

The hydrometallurgical method developed in this study for processing zinc wastes containing zinc oxide or zinc hydroxide represents a feasible approach to zinc recovery from such types of wastes under industrial conditions. This technology, which enables even processing external zinc wastes provided zinc basic carbonate of sufficient purity for zinc sulfuric electrolytic process. Arising secondary wastes, such as leach residues can be directly utilized in Kovohute Pribram as a source of lead and/or iron in the blast furnace.

Treatment of zinc waste galvanic sludge on a pilot-scale confirmed the possibility to apply the proposed and verified technology to industrial zinc waste processing. In spite of high treatment costs, progressively increasing fees for wastes disposal make this recycling technology efficient and the current zinc prices make it even more attractive.

This study will be continued and focused on recycling of spent electrode materials from zinc portable batteries after their dismantling.

Acknowledgement

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References
