# PRESENT STATUS IN THE RECYCLING OF INDUSTRIAL RESIDUES FROM LEAD, ZINC AND COPPER INDUSTRY AND THEIR POSSIBLE FUTURE CONTRIBUTION TO THE SUPPLY OF SELECTED MINOR ELEMENTS, LIKE SILVER

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**Abstract**

In the past the treatment of industrial residues from copper, lead or zinc industry focused in the majority of cases only on the recovery of one target metal. Mostly it is the focal metal produced in the industry the residue arises from. With this, valuable accompanying elements were often disregarded. Especially in copper, zinc and lead industry minor metals, like the group of precious metals but also others like indium or germanium, are interesting side-elements occurring in the concentrates next to the base metal itself. Although a recovery of these elements is partly considered in the base metal production, the presence in the corresponding residues in regard to their recycling is unvalued in a lot of processes until today. This offers the chance in future recycling concepts that these minor elements, like for instance silver, can contribute to the overall economic feasibility of potential new processes, even though they occur in significant lower amount as the base metal in the tailings, dusts, sludge or dusts of the corresponding industry. For example the annually produced and mainly land filled amount of leach residues from zinc industry contains roughly 500 tons silver next to other valuable elements, like zinc or lead. Thus, this paper tries to answer the question how recycling of such residues can contribute to the supply of minor elements, especially at the example of silver.

**Keywords:** Industrial residues, precious metals, recycling, lead, zinc, copper

## 1. INTRODUCTION

To maintain life's quality raw materials play a crucial role. As the distribution of base- as well as special-metals worldwide is not homogenously discrepancy between supplying and consuming countries are the consequence. Mainly the industrialized countries are responsible for a high amount of consumption of technologically important metals, like Ag, Au, PGM but also In and Ge for electronic goods. Silver as one of the precious metals is not defined as critical in the European Union at the moment. Nevertheless, the consumption due to its use in electronic equipment steadily increases. Together with the fact that silver is mainly produced as a by-product of other base metals also this element seems to get more and more important and critical. The same circumstance is true for indium, which can be seen in the following **Table 1**, within also the carrier element, share of production and the share on the total revenue in the relevant industry sector is shown.

As illustrated in the table shown above, the supply of minor and critical elements often is linked to the production of different carrier metals, like zinc, lead and copper. However, the demand of critical metal is not correlating with the production amount of carrier metal. Also taking into account that by-products and waste streams from this industry sectors therefore are potentially carrying these critical metals as well it becomes obvious why especially the waste streams from this industry sectors are more and more in the focus of research activities. Therefore, this paper examines residues generated from lead, zinc as well as copper production and their possible contribution to the supply of minor elements, like for instance silver.

**Table 1** Source of production of selected minor elements. Critical materials defined by the EU are underlined [1, 2, 3]

| By-product Metal | Sources of Production | Share of Production | Recovery Efficiencies | Max. Share of Total revenues |
|---|---|---|---|---|
| <u>Germanium</u> | Zinc | 70 % | ≈12 % | ≈2 % |
| | Coal | 25 % | - | - |
| Gold | Primary | ≈90 % | - | - |
| | Copper | ≈10 % | >99 % | ≈20 % |
| <u>Indium</u> | Zinc | 100 % | 25-30 % | ≈3 % |
| Silver | Lead-Zinc | ≈35 % | >95 % | ≈45 % |
| | Primary | ≈30 % | - | - |
| | Copper | ≈23 % | >99 % | ≈25 % |
| | Gold | ≈12 % | - | - |
| <u>Palladium</u> | Platinum | 60 % | 40-60 % | ≈15 % |
| | Nickel | 40 % | - | ≈15 % |
| <u>Platinum</u> | Nickel | 15 % | - | ≈10 % |

## 2. BY-PRODUCTS AND RESIDUES FROM COPPER-, LEAD- AND ZINC-INDUSTRY

In this chapter the zinc, lead and copper industry is introduced and evaluated onto their by-products and residue streams next to their possible contribution to the silver supply.

### 2.1. Zinc hydrometallurgy

The hydrometallurgical route processes the major part of sulfidic or oxidic zinc ore today. Although several new technologies were implemented, like the direct leaching of sulfidic ore or the solvent extraction, two main routes can be differed in the hydrometallurgical zinc winning. The following **Figure 1** illustrates the conventional two-step leaching and the one-step leaching under moderate acidity, applied in case of low iron containing zinc ores (see figure right side).

After the roasting, which is the reason for occurrence of zinc ferrite in the calcine, a neutral-leaching is carried out. As a result of present lead, zinc, silver and in some cases also other precious metals, which are insoluble under this moderate conditions, they can be found in the neutral leaching residue in case of the one-step flow-sheet. This generates, depending on the ore type, around 600-700 kg of neutral leaching residue per ton of zinc and up to 0.1 % silver [4].

A hot acid leaching is mandatory in case of high iron contents in the calcine and the formed zinc ferrite as a consequence. This additional leaching step with increased temperature and high acidic conditions dissolves the present zinc-ferrite spinel, which is far less soluble than simple zinc oxide. In case that there is no separate filtration step for the hot-acid-leaching residue, which carries typically lead, silver and $SiO_2$, the iron is directly precipitated onto the remaining material and therefore the lead, silver is contained in the iron-residue. Moreover, calcine used for neutralisation introduces further lead, zinc-ferrite and silver in the iron-precipitate. In case of a precipitated goethite, the residue can be utilized in some cases. Anyhow, a majority of zinc plants still use the jarosit process, which is dumped world wide till today. Literature reports that 500-600 kg Jarosite per ton of zinc are generated with up to 230 ppm Ag [5, 6] in this residue next to also present indium and possible other precious metals. Own investigations showed up to 300 ppm of silver and Indium in investigated dried filter cakes.

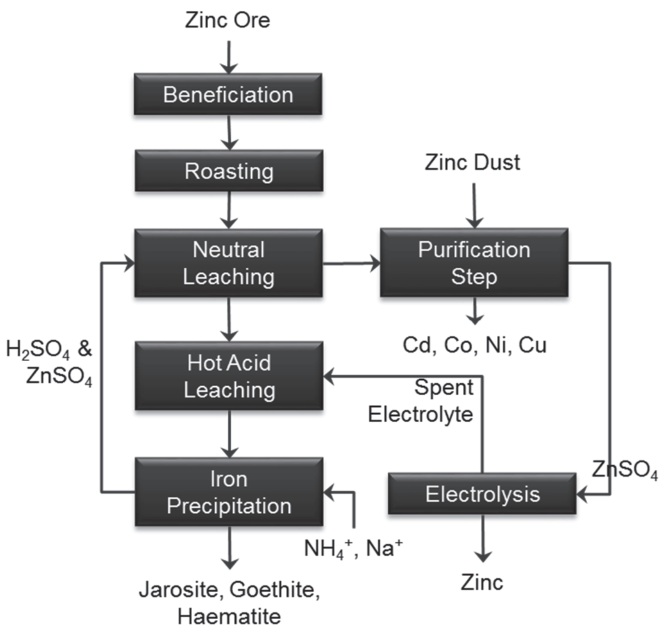


**Figure 1** (left flow-sheet) typical two-step zinc production (neutral followed by hot acid leaching) (right flow-sheet) one-step concept for low iron containing ores

## 2.2. Slags from primary lead production

Today a high number of facilities used for primary lead production are in use. Independent from the facility the principle is the same. Depending on the ore type, below **Figure 2** summarizes the general ways of direct production of lead-ores and the processing of mixed lead/zinc ores in a shaft furnace.

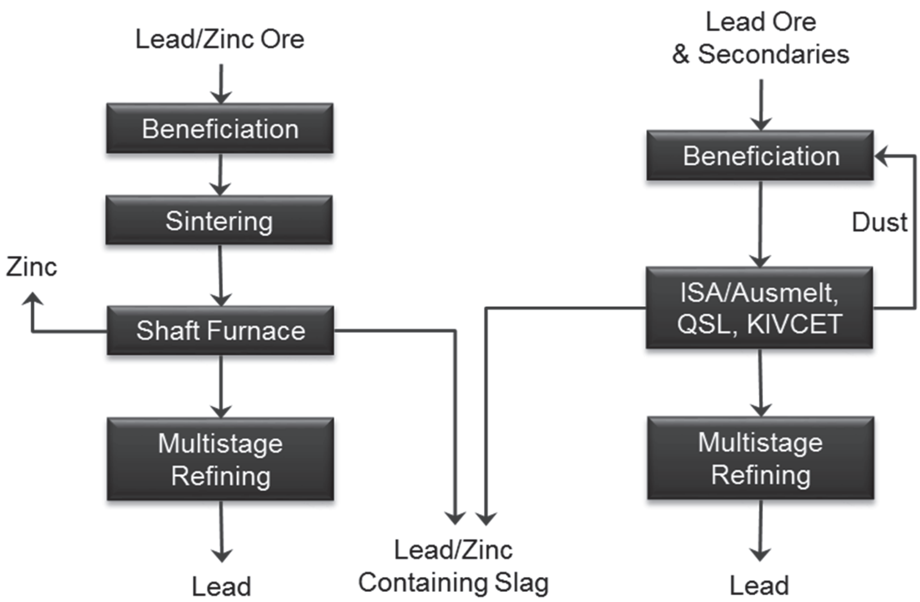


**Figure 2** Flow-sheet of primary lead production route

As shown above, the typical processing of lead/zinc concentrate is the route via the shaft furnace, producing zinc and lead as separate products in the so-called Imperial Smelting furnace. An average composition of a typically obtained slag from an IS furnace is shown in **Table 2**.

**Table 2** Average composition of generated slag from an IS furnace (wt.%) [7, 8, 9]

| | Zn | Pb | Cu | S | FeO | $SiO_2$ | CaO |
|---|---|---|---|---|---|---|---|
| **Slag** | 6 - 9 | 0 - 2.5 | 0 - 0.6 | 0 - 3.6 | 37 - 45 | 15 - 19 | 13 - 21 |

To avoid unwanted reduction of the iron present in the concentrate, the ratio of reducing agent and zinc has to be kept at a certain level, with the disadvantage of lead and zinc losses in the process slag. As a accompanying element of lead also silver can be expected in the losses. Own investigations showed silver contents of up to 150 - 200 ppm per ton of dumped slag. In average, the generated amount of slag is 0.65 to 1.00 times the amount of produced zinc [7, 8, 9].

If the ore is low in zinc, the lead is produced without the by-product zinc. Furnaces which are used are shaft furnaces with a pre-sintering step or a QSL-, Ausmelt- or other direct production furnaces. As a result of up to 3 % of zinc contained in the concentrate, which has to be removed from the process, the reduction potential is kept low. This leads to conditions which does not reduce the zinc oxide, leading to the presence in the taped slag. In former years the content had to be higher than 11 % zinc oxide in the slag for an economic treatment to recover the zinc from the taped slag via slag fuming. In case of lower amounts of zinc in the slag was dumped [8]. Own investigations showed that dumps with zinc contents up to 15 % exist next to significant amounts (up to 6 %) of lead and with this silver. The amount of generated slag per ton of lead fluctuates from lead production site to site because of different ore types, facilities and with this recovery rates between 400 - 600 kg per ton.

## 2.3. Copper production

As the main industry sector carrying out recycling of electronic scrap, a wide range of materials and with this elements can be found in the copper production routes. Due to the mentioned processing of complex materials, like WEEE, shredder material, different sludge, etc. an major input of other elements like zinc, lead, tin, halogens but also precious- and minor metals is the result. Based on the target of producing high grade copper, all of these introduced elements have to be removed again by generated slag-, dust- or slime phases during the smelting, reduction and converting step or also in the electrolytic refining. Consequently these elements get enriched in those phases and can form valuable "residues". Below **Figure 3** illustrates that the secondary copper production consist of four main steps, namely the melting and reduction, converting, fire refining and electrolytic refining step.

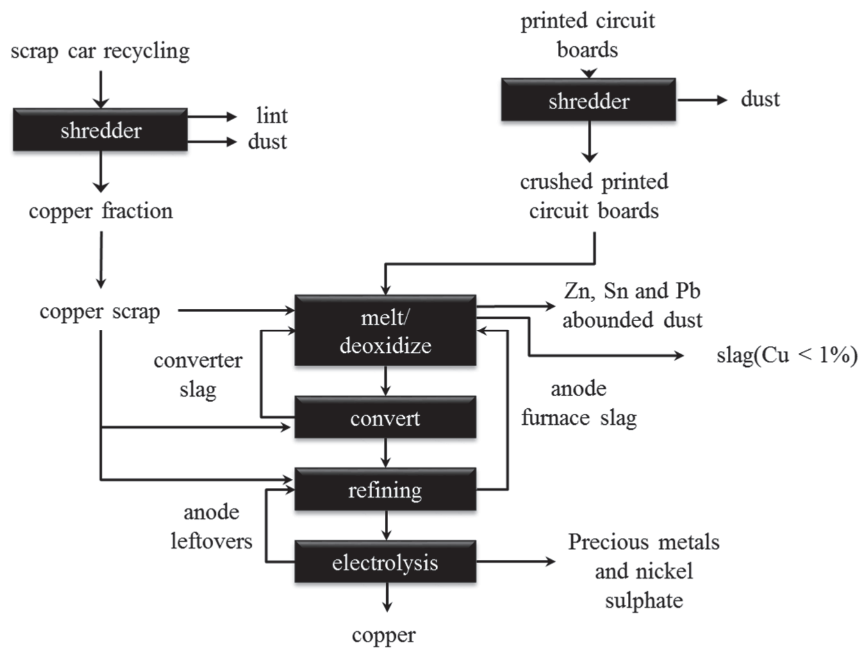


**Figure 3** Process flow-sheet of a typical secondary copper plant

Based on the purity of the input material it is charged in different steps, offering a wide range of materials to be recycled within the same process. It can be seen that an internal recycling of special fractions, like the converter slag takes place. Although the slag from the first step is very low in its copper content, some operators still do a floatation of these slags to recover still present small droplets of copper. However, a huge amount is dumped without treatment and therefore could be potential for copper, gold and silver recovery. The outlet for the precious metals is the generated anode slime, which is further processed worldwide so that this does not show new potential. An interesting residue is the emitted dust from the first two stages, which can be up to 60 kg per ton of produced copper. These dusts show high contents of valuables because of the presence of halogens in the input material (like PCBs), which are forming volatile compounds with different elements. This leads to evaporation and in consequence to the formation of dust in the bag house filters. This mechanism is the reason why next to lead and zinc also indium and precious metals are a constituent of the dust. This leads to strongly fluctuating chemical compositions of the dust, depending on the charged raw material, used process technology and operation parameters [10, 11].

Especially the content of the minor metals cannot be predicted exactly. **Table 3** gives an overview about a typical composition of the main elements in copper smelter flue dust from secondary plants.

**Table 3** Composition of a typical flue dust from secondary copper production in [wt.%] [10, 11]

| Zn | Pb | Sn | Cu | Cl | Br | F | S | Fe | CaO | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 35-45 | 10-15 | 2-5 | 2-6 | 3-5 | 3-6 | 0.5-1 | 1-2 | 1-4 | 2-3 | 1-3 |

The valuable main fraction is formed by elements like zinc, lead, tin and copper. But next to that up to 800 ppm silver beside gold and PGMs can be present, due to carry-over as well as formed volatile compounds. Because of the high content of halides in the residue the dust cannot be directly used in zinc metallurgy although a content of nearly 50 % zinc. Also the present copper, tin and lead would lead to increased purification efforts. Nevertheless, these dusts are showing high potential concerning the secondary production of precious metals but also secondary zinc oxide or sulfate [10, 11].

## 3. CONCLUSION

Concentrates from copper-, lead- or zinc-ores often carry elements like gold, silver, indium or PGMs as valuable side elements. As a result also residues from those industry sectors can carry them and therefore potentially contribute to a future supply of silver or other minor elements. Aside from residues which are treated inefficiently or dumped also by-products, like anode slimes from copper electrolysis, solution cleaning residues from zinc industry or by-products from lead-refining are directly utilized or further treated. However, also this area still shows an optimization potential. A summary of by-products and residues from copper, lead, zinc-industry is given in **Table 4**.

**Table 4** Status of precious metals recycling out of residues from lead, zinc and copper industry

| Base Metal | Copper | Zinc | Lead |
|---|---|---|---|
| **Mainly recycled** | Anode slimes | Neutral leach residues<br>Goethite | Matte |
| **Generally not recycled** | Slags from 1st step<br>Dusts from various steps | Jarosite | Slag<br>Speiss |

The reason why still today some of the mentioned materials are dumped is on the one hand the complexity of the materials and with these expensive processes and additionally on the other hand also the circumstance that in various processes only one metal is considered for recovery. Even though the potentially present amount of minor elements in the mentioned materials can be very low, in some cases only ppm, the contribution to the overall economics of a recycling process can be significant. Following **Table 5** summarizes this circumstance and tries to estimate the amount of silver contained in the discussed untreated residues of the lead, zinc and copper industry per year.

**Table 5** Potential sources of silver in untreated residues from copper, lead and zinc industry

| **untreated material** | **amount** | **silver** | **potential for:** | |
|---|---|---|---|---|
| | in 1 000 t | in t | **gold** | **PGMs** |
| Jarosite | 4 000 | 800 | yes (low) | |
| Goethite | 400 | 100 | | |
| Neutral leaching residues | 200 | 200 | yes (low) | yes (low) |
| Dust from sec. copper industry | 100 | 50 | yes | yes |
| Lead slag | 3 000 | 150 | | |

In total the estimated silver which gets dumped and would be available in those untreated residues is 1 300 tons of Ag annually, which is 5.1 % of the worldwide mine production. Not taken into consideration is the mine waste, like flotation tailings, etc. The average contents of gold and PGMs are relatively difficult to estimate in these residues, which is the reason why it is only mentioned in what residues there is a potential to find them. Nevertheless, it was shown that there is high potential of different secondary resources to contribute to the silver as well as other precious metals supply in future.

## ACKNOWLEDGEMENTS

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