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EFFICIENT UTILIZATION OF ZINC, LEAD, AND COPPER CONTAINING BY-PRODUCTS

JÜRGEN ANTREKOWITSCH – STEFAN STEINLECHNER – GUSTAV HANKE

Chair of Nonferrous Metallurgy, Montanuniversität Leoben, Austria

Abstract: The importance of metal by-products and residues for the sake of metal supply is discussed. Some of the residues are already recycled, however, the worldwide recycling rates are still below 50% because of a lack of optimized processes, as well as missing information and data about the materials. The assessment of metal-bearing by-products and economic considerations are of high importance to allow an efficient utilization of these secondary resources in future.

Keywords: *metal by-products and residues, optimized technology, assessment of metal-bearing by-products*

1. PRIMARY AND SECONDARY RAW MATERIALS

Investigating the development of primary metal resources nowadays, a tendency becomes obvious that can be summarized by two trends: the decrease of metal grades and the increase of unwanted impurities. The statistics in *Figure 1* illustrate the metal grade decrease with two examples, one for the base metals zinc and lead and one for the special or minor metal gold.

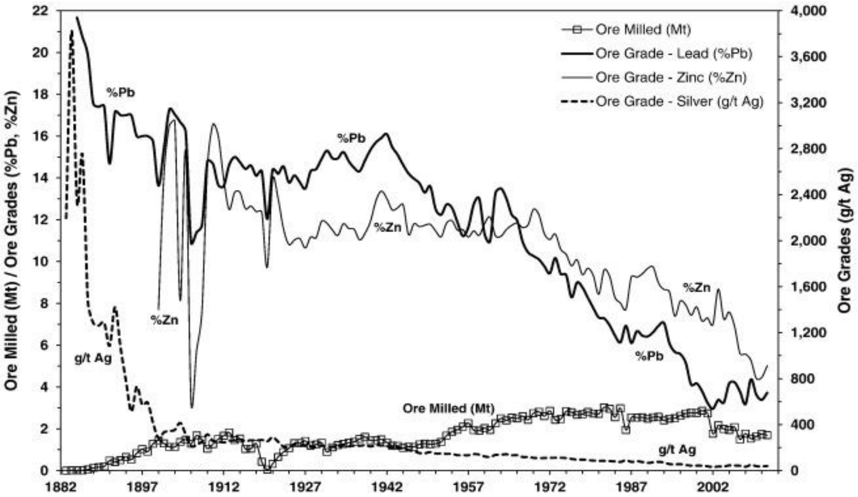

Figure 1
Decrease of metal grades in lead, zinc and gold ores [1]

The development of zinc and lead *(Figure 1*, left*)* clearly shows a decrease from about 10% in the 1970s to about 4 to 6% in 2016. This must be seen as a relevant change, especially considering that only a moderate development of smelting technologies took place within this time span. The same is true for gold resources, which dropped from the well-known 10 ppm content in the past to 2–4 ppm within the same period [1, 2].

In parallel, increasing iron values in zinc ores have become apparent, leading to much higher amounts of residues. These currently have to be landfilled due to a lack of reprocessing methods, thus causing an environmental problem due to residues which will have to be solved in the future. In case of gold, the multi-metal containing resources make economical gold extraction difficult, which is often caused by a lack of efficient recovery methods for the associated valuable metals. Additionally, more and more refractory type gold ores, often associated with arsenic, show reduced gold recovery due to a shortage of suitable liberation technologies.

Alternative metal supply by recycling might offer a certain compensation for declining ore qualities. However, as can be seen from *Figure 2*, the recycling rates of most of the metals are still relatively low. The illustration highlights the fact that the recycling rates of most of the important metals are far below 50%, raising the question of why there seems to be a certain limit in secondary metal production, even though recycling – especially of metallic scrap – is highly developed and applied in most regions of the world.

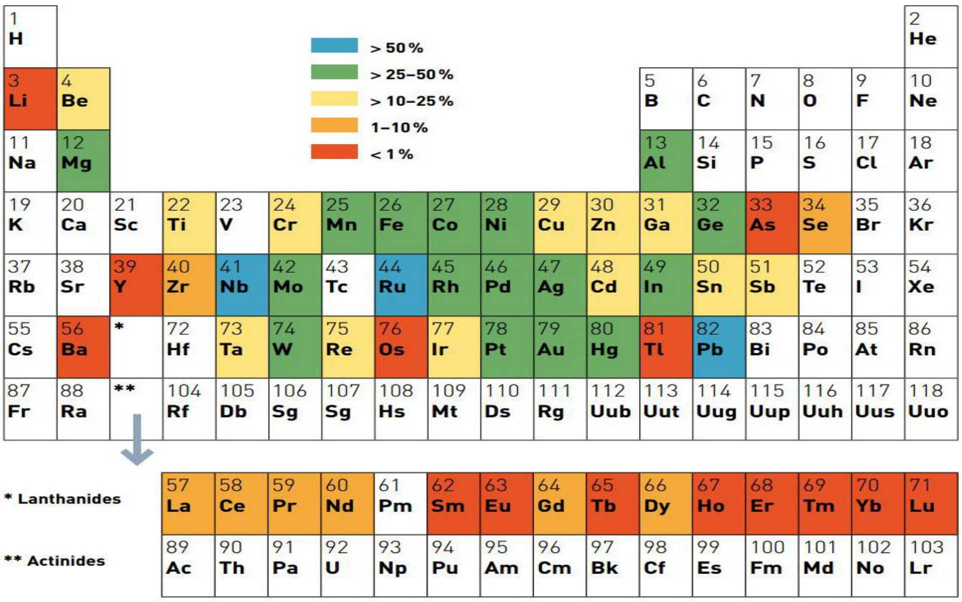

Figure 2

Recycling rates of various metals [3]

When having a closer look into metal processing circuits, it becomes obvious that several circumstances prevent higher recycling rates and make the dream of a circular economy, which is quite popular at the present time, unrealistic for this field of industry:

- The process used for metal production always produces a not so small amount of residues, often called by-products, which are often landfilled, even though they contain interesting amounts of valuable elements.
- Collection of the materials is difficult. Especially in Europe, many scraps and other secondary raw materials leave the continent via legal and illegal ways and cannot be seriously implemented into recycling circuits.
- Also, during recycling processes wastes are generated that contain valuable metals.
- In course of processing, part of the targeted metal is transferred into a form (e.g. low metal containing slag) out of which no recovery is possible due to energetic and thus economic reasons.

2. RAW MATERIALS LEAVING EUROPE

Europe nowadays faces the difficulty that even when raw materials are present, no matter if primary or secondary ones, they often leave Europe and are not available any more for metal production. Typical examples are automobile scrap, electronic scrap, and residues from the lead and zinc industry, but also copper and gold concentrates, to name just a few. This means that Europe has difficulties producing its own raw materials to become more independent, while available raw materials cannot be kept in Europe and are treated elsewhere.

The reasons for this strange situation can be listed as follows:

- high costs for energy
- high costs for labor
- strict environmental legislations
- strict safety regulations
- complicated approval and permission procedures
- lack of new or improved processing concepts that might be able to compensate for the above difficulties.

Of course, European citizens must be happy to live in a region of the world with highest safety and environment standards, but we must realize that this contributes to a lack of competitiveness with countries in Africa or Asia. Therefore, many European raw materials are treated outside Europe, which cannot be the beneficial strategy for the future.

In this context, a relatively new metal source, industrial by-products, have to be discussed, asking the question of whether they could represent an interesting raw material for Europe.

3. BY-PRODUCTS

For many decades, residues from metal production, such as slag, dust and sludge have often been qualified as waste that was simply dumped. This fact was – at least at that time – accepted by industry and involved authorities. Except for metal producing companies, no market participant really recognized that metal-bearing wastes were often landfilled to an amount that was more or less as high as the metal production itself. In the 1980s and 90s, the first environmental concerns called more attention to such dumps and residues. Nevertheless, due to inadequate technologies and low metal prices the interest in processing residues to recover valuables was still very low.

During the past few years, multi-metal recovery from concentrates has developed for both primary ores and secondary materials. In addition, minor metals contained in such residues have become important for daily life in industry. In other words, metals that did not have a real value in the past nowadays may essentially contribute to economic viability when recovered from residues.

In combination with increased metal prices and the need for special and rare metals in various highly sophisticated technologies (e.g. the electronics industry), more attention must be paid to such residues, which often represent a potential secondary resource. Currently, recycling rates are still low and huge amounts of residues are dumped annually.

Recycling is mainly based on scraps, where the elements in focus are available as pure metals. However, scraps have a defined volumetric limit and their treatment is already optimized to a certain level. As a matter of fact, considering the continuously dropping grades in primary ores, implying that new sources need to be exploited, recycling rates must be improved in the near future, as described above. As an important solution to this problem, by-products of various metallurgical processes (see *Figure 3)* already dumped or continuously being produced, have started to move into the focus of interest of both industry and research.

Screening the metallurgical area, residues emerging from the lead, zinc and copper industries must be considered. Processed ores commonly contain a high number of critical and valuable metals at the same time. Typical by-products are produced either in hydro-metallurgical or pyro-metallurgical process routes, as shown in *Figure 3*. Some of the contained metals are recovered to a certain amount by primary metallurgical processes but the bulk ends up in different waste streams.

Very often sludge from hydrometallurgical operations and dust from pyrometallurgical operations offer a significant number of metals at concentration levels that might be of economic interest. In addition, some recycling processes of highly diversified and contaminated scraps (e.g. car bodies or waste electric and electronic equipment) generate complex by-products.

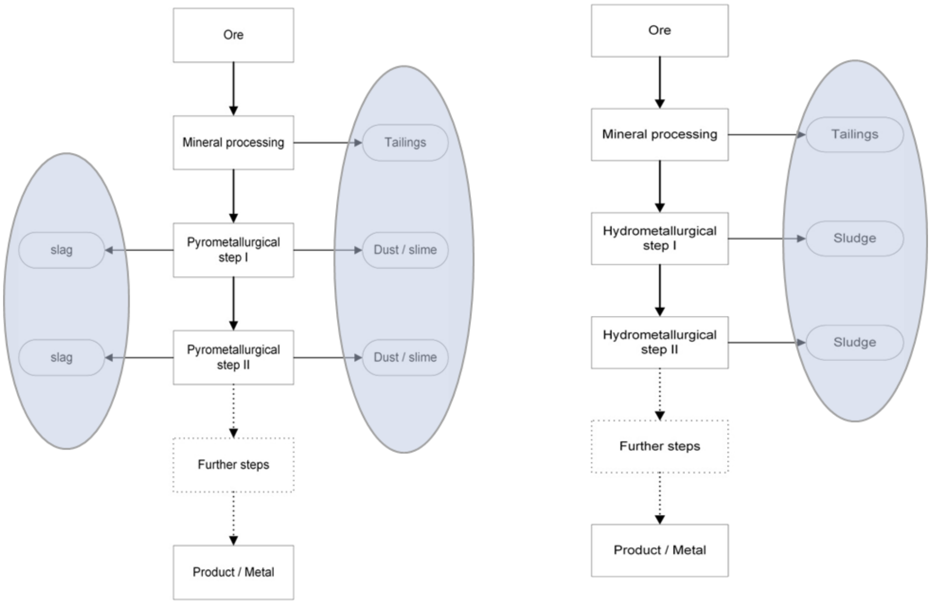

Figure 3
By-products of metallurgical processes

Figure 4 illustrates the possible recoverable elements but also shows the high overall metal content available in currently produced residues.

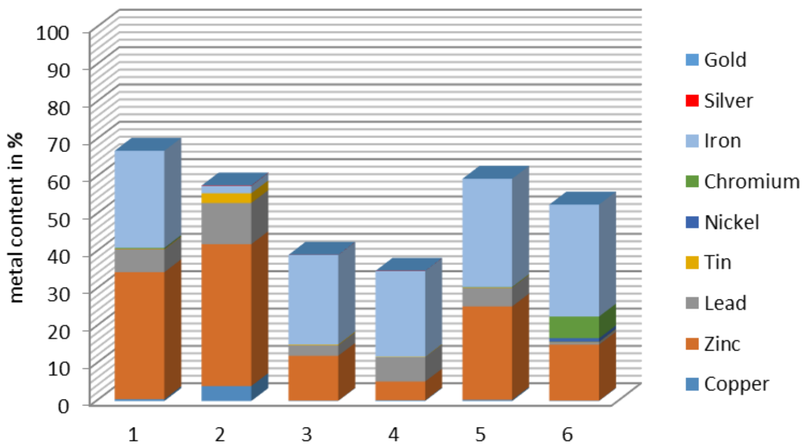

Figure 4
Examples for different residues and their metal content (except PGM) out of own investigations
(1 – Electric Arc Furnace steel mill dust, 2 – Dust from copper recycling, 3 – Slags from lead industry, 4 – Jarosite from zinc industry, 5 – Dust from cupola furnaces, 6 – Stainless steel production dust)

These residues can be found worldwide in huge quantities, either on dumps dating from the end of the last century or being currently produced, and they form an interesting secondary resource of metals with high availability. Due to the long European history in mining and metallurgy, such landfilling sites and producing mills are still present and have to be considered as 'part of the market' [4, 5].

Some of the residues described in *Figure 4* are already recycled to a certain extent. However, also for these secondary materials the worldwide recycling rates are still well below 50% for two main reasons:

- the lack of optimized processes
- missing information and data about the materials.

Both factors are responsible for the inefficiently utilized potential on secondary resources [4].

Another reason for the weak exploration and use of residues is the lack of any guideline or competence describing how to evaluate residual materials. This is partly due to the lack of adequate databases. For primary materials like metal ores, codes exist that serve as accepted and applied guidelines for a qualified evaluation by following pre-defined steps, leading to a "bankable feasibility study". Such guidelines currently do not exist for secondary materials. A consequent "stepwise approach" must be applied right from the beginning of the project.

4. Assessment of metal-bearing by-products

Montanuniversität Leoben has started to develop guidelines for the assessment of specific metal-bearing by-products to allow a clear perspective on how valuable typical materials are.

Two main areas are important from the technical point of view: 4.1. "Characterization of by-products" and "Processes development and product quality".

4.1. Characterization of by-products

Depending on the feed material used and the treatment technology applied, various residues with different properties emerge that can be distinguished by their origin or properties. Some of the residues mentioned above have already been investigated to a certain extent with respect to characterization and a first evaluation.

Detailed geochemical and mineralogical characterization of metallurgical residues is of highest importance in order to develop appropriate mineral processing recipes and then appropriate metallurgical methods to recover all metals of interest. Hence, the following questions need to be answered:

(1) Which particles contain the metals to be recovered?
(2) What is their particle size, shape and texture, i.e. zoned grains, coated grains?
(3) How intensive/complex are incorporated phases intergrown in different particle fractions?
(4) What is the concentration level of metals in the major particles?
(5) Presence and concentration of deleterious elements (such as As, Cd, Hg)?

In order to separate minerals or metallurgical phases by means of mineral processing techniques with physical, physical-chemical and/or chemical methods it is necessary to know the relevant phases regarding the key aspects mentioned above. In the end, the size, shape, structure and the chemical and mineralogical composition define a particle [6].

Deriving from these parameters, the density, optical, electrochemical, thermal, chemical and mechanical characteristics of any particle can be determined. As the way of managing a metallurgical process and its actual parameters highly affect the residues – not only in composition but also in structure – the variance of the residues' properties with regard to mineral processing characteristics is large, even for an existing plant in operation. In analogy to primary mineral deposits, processing results may vary widely if these changes are not taken into account. Thus, the residue has to be investigated and characterized properly.

Based on that, the main goal is to generate a basis for assessing possible metal or metal compound recycling methods. Additionally, the different metallurgical possibilities for treatment – hydro- or pyro-metallurgical – need to be determined. These results are mandatory for evaluating possible process steps to generate products from the residues. To generate this information, the main properties such as melting behavior, volatilization behavior, reducibility, and solubility need to be determined in advance by using special metallurgical characterization procedures.

4.2. Process development and product quality

To cope with the continuously stricter environmental legislation along with a shortage of critical metals in Europe, the process development for treatment of secondary resources and the optimization of existing processes are two major concerns. The challenge of the years to come is to minimize newly generated residues and at the same time to achieve maximum product quality within the recycling process. In addition, the quality of the products influences the targeted market and achievable revenues. Therefore, state-of-the-art processes have to be continuously adapted regarding energy consumption, mass-balancing and further improvement of the product quality. A specific geochemical, mineralogical and metallurgical characterization creates the basis for improving such existing processes. Thus, it will be possible to obtain higher product qualities and lower amounts of newly generated waste streams.

As demonstrated by several investigations carried out at Montanuniversität Leoben, the residues are not at all homogenous. Hence, it is not possible to recycle such residues as one combined single input stream. In order to increase the recoverable metal grade and to reduce the content of substances that hinder the metallurgical process, some separation by physical/mechanical techniques is required. If such a process shall be developed systematically rather than by trial-and-error, the residue must be characterized properly in terms of its properties relevant for a separation process.

Fractional analysis is the standard tool in mineral processing for assessing the amenability of primary mineral resources to be upgraded to saleable products of defined and consistent quality. Taking into account the heterogeneity of the residues, it is expected that some upgrading is possible, which may pay off during recycling. Fractional analysis yields the optimum results for separating a given feed material by assuming perfect separation. It thus also serves as a benchmark for assessing the performance of an existing process. The possible benefits of assessing and processing the residues in a similar way to primary mineral resources are obvious. As some common properties of the residues (e.g. the generally fine particle size distribution of dusts, just to name one) are problematic in fractional analysis, the methods require further adaptations.

In order to find the suitable processing chain, tests need to be carried out. Once a residue is tested, the obtained data will be collected and condensed in a database, which acts in future assessments as a decision support tool. Although similarities within the same type of material (e.g. slags, dust) can be found, each residue is generated in slightly different processing routes with varying input material. This leads to variable extraction yields, consumable consumption, energy input, obtained product quality, etc. Based on the experimental results the database will grow, and the more materials are cataloged, the more accurate the data for the assessment becomes.

One major disadvantage of past attempts in recycling by-products was that often just one single metal was recovered while possible further valuable metals were distributed into newly generated wastes and were therefore lost for production. Pyrometallurgical concepts allow the recovery of valuable metals by applying different basic operations: forming a volatile phase, where e.g. zinc or lead can be collected as oxides in the off-gas, or forming a liquid metal phase, where e.g. iron or lead act as an efficient collector for various minor metals. In combination with mineral processing steps, where a separation of metal containing fractions could be realized prior or subsequent to a metallurgical step, targeted multi-metal recovery can be realized. For hydrometallurgical approaches the dissolution of a larger number of elements followed by selective precipitation, again combined with mineral processing, would offer multi-metal recycling. However, also a combination of hydro- and pyro-metallurgy could lead to appropriate solutions [6].

Given the situation that for some by-products recycling techniques do not exist, and that the majority of methods recover only one metal, such an approach must be regarded as an essential novelty.

4.3. Economic considerations

Within the investigations also a model for economic verification was established and different dumps worldwide have been investigated. Within this evaluation very promising dump sites have been detected, as well as residues of poor quality.

Economic analyses were done for different materials and metal prices. As already mentioned above, gold and silver contribute in a very important way to the overall revenues of the various process concepts. However, the key message is that multi-metal recovery is essential for the economic stability of a recycling process and allows a higher flexibility regarding varying metal prices.

5. SUMMARY

By-products from the metallurgical industry can play an important role as a secondary resource for different metals in the future. Detailed evaluation and assessment of the materials is important for successful utilization, offering interested parties a reliable information tool similar to already existing guidelines for primary resources. Important steps towards such an assessment concept are advanced characterization of the by-products combined with sophisticated processing concepts, which in certain cases might be already available but may benefit from new developments. Especially the idea of recovering more than one metal from by-products would allow economical and ecological utilization of such wastes and will form an important strategy for the future.

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