Alternatives to lead in the assaying and recycling of precious metals?

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1. Introduction

This document collected some elements to inform the discussion about the possibility to substitute lead in the precious metals (PM) industry.

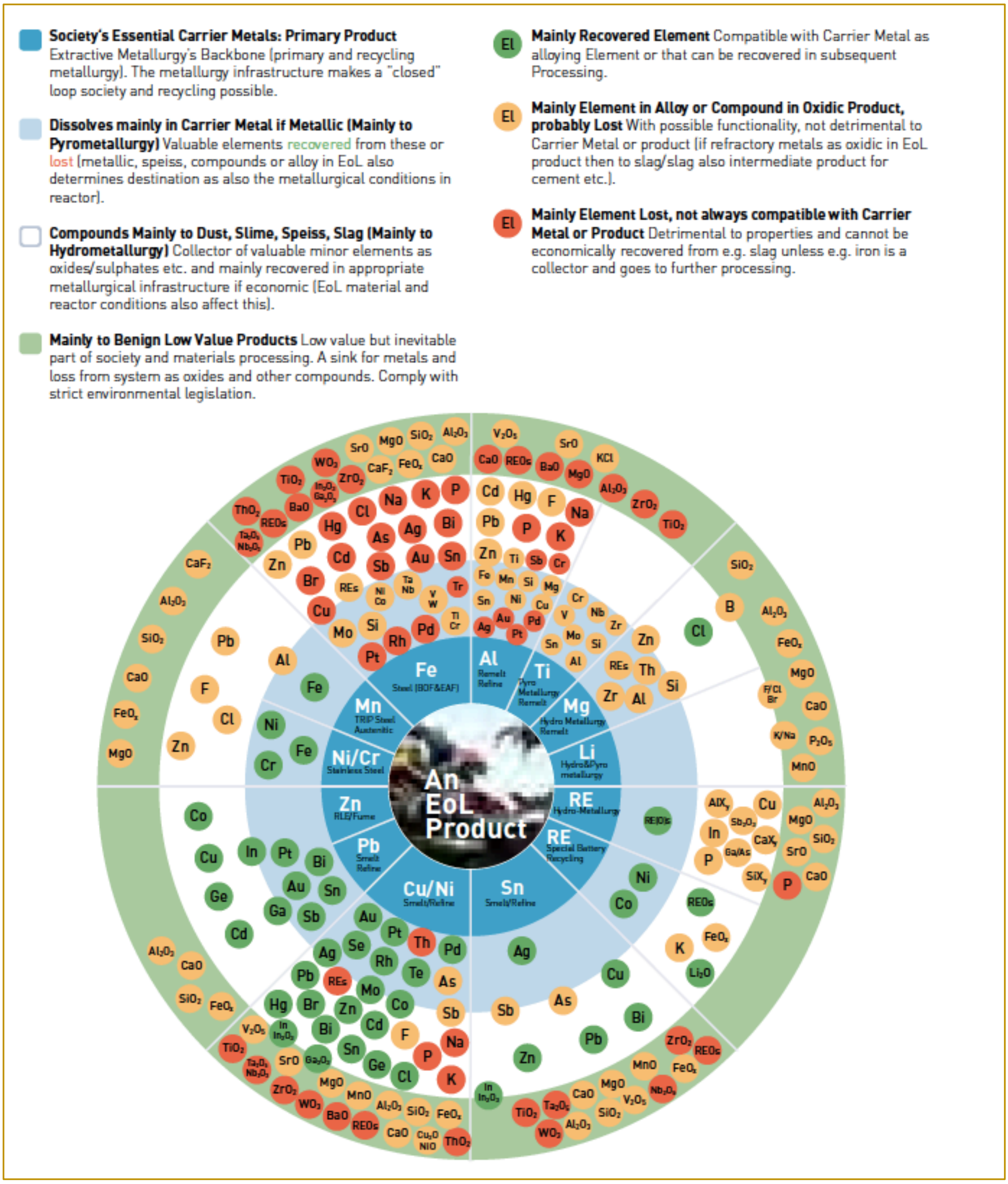
Lead as metal or oxide has two major functions in this industry:

1. As fluxing/collecting agent in the analytical method known as 'fire assay', lead makes a precise and mutually accepted determination possible of the composition in PM of materials proposed for refining or recycling.
   This technique is suited for a broad range of PM and PM concentration (even very low ones).
2. Lead acts as a collector metal in PM refining/recycling. It enables a resource and cost-efficient processing of a broad range of ores, non-ferrous metals industries' residues and various end-of-life materials that cannot be processed through a basic re-melt or chemical separation.

Any discussion of the role of lead in non-ferrous refining and recycling and in particular PM recycling will have to keep in mind the famous "Metal Wheel" of the 2013 UNEP report "Metal Recycling – Opportunities, Limits, Infrastructure" where the author depicts the destination of different elements in base-metal minerals as a function of interlinked metallurgical process technology.
Each of the slices represents the complete infrastructure for base- or carrier metal refining.
The authors indicate that the "*complexity of consumer product mineralogy requires an industrial ecological network of many metallurgical production infrastructure to maximize recovery of all elements in end-of-life products. (Reuter and van Schaik, 2012a&b; Ullmann's Encyclopaedia, 2005 as quoted in UNEP report)"*

As one can see, lead is part of a very small group of society's essential carrier metals able to usefully recover other metallic elements. These are essentially Cu, Ni and Pb. Two complex metallurgical operations are presented in this discussion note to illustrate that lead cannot be removed from these process flows. The carrier property of a metal is a key determining element in the development of any effective and resource efficient recycling process.

Not all PM recycling processes rely on lead as there are companies that specialise in the processing of waste material from PM processing industries as well as PM goods of certain composition ranges. In these cases, where the materials are less complex in composition, the recycling process may not necessitate the reliance on carrier metals such as lead.



From Metal Recycling – Opportunities, Limits, Infrastructure (UNEP – report 2b of the Global Metal Flows Working Group of the International Resource Panel of UNEP – 2013), page 30

2. Fire assay

1. Base concepts

Metallurgical assay is the analysis of composition of an ore, a metal or an alloy.
Several assaying methods exist depending on the type of material to be analysed and the objective of the analysis such as the preparation of the furnace charge to optimize the metallurgical process, the setting of the price to be paid for the material delivered to the plant, or technical support to customers. Metallurgical companies usually use various analytical methods such as e.g.:

- **Fire assay:**
  Also known as cupellation, it is the industry standard analytical method for determining the amount of gold and silver and PGM in a sample. Fire assay with lead or lead oxide (thiarge) is the oldest known assaying method and is the standard for commercial transactions in the PM industry.

  The fire assay method is used in commercial analyses throughout the PM production from ore to the final PM product: analyses of samples from exploration, ore and concentrates, raw metals, secondary raw materials and purification of PM.

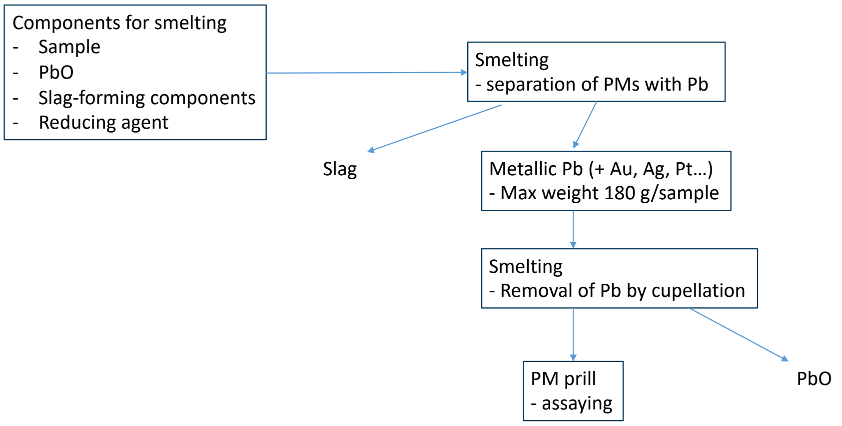
- **Wet chemistry:** Some complex materials require the classical wet chemistry approach, which is labour and time intensive, but needed for obtaining the most accurate results.

- **Spectroscopy:**
  - **Quantitative techniques:** This type of analytical techniques areused to determine impurities in PM materials. They may consist of Atomic absorption spectrometry (AAS) or Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-OES)
  - **Semi-quantitative techniques:** XRF (X-ray fluorescence spectroscopy) is a technique often used for a quick, semi-quantitative analysis of a material's composition, which might later on be refined through fire assay. Hand-held XRF devices allow, for example, a quick, on-the-spot and 'non-destructive' scan of finished goods.

The choice of analytical method depends on the type of material and the specific need to be addressed by the analysis. Some techniques allow a quick screening of materials or may be sufficient for companies addressing regular flows of homogeneous materials (such as processing scraps e.g.) whilst other techniques such as fire assay are more resource and time consuming but the recognized standard when complex and high value materials are concerned.

2. The fire assay process

The fire assay process can be summarized as follows:



Fire assay scheme (courtesy Boliden)

If the platinum group metals Pt, Pd, Rh are present, they dissolve in the molten lead and are collected in the gold-silver bead after cupellation. Their concentration in the gold after parting can be determined by spectrometry.
The lead assay is the reference assaying method for Au, Ag and the most industrially used PGM which are Pt, Pd and Rh.
Iridium, osmium and ruthenium, on the other hand, are largely lost during the standard lead assay and cupellation technique; if their presence is suspected, the nickel sulphide collection technique is often used to determine them.
Note that fire-assaying methods are also used to determine easily reducible base metals such as lead, bismuth, tin, antimony, and copper.

Illustration: State of the art fire assay lab (courtesy: C.Hafner)

3. Metals used in fire assay

Next to lead, bismuth, nickel sulphide are used as collecting metals, although other metals are referenced in the patent literature (Cu and Fe; Si, P, B; Cu, Ni and Fe). None of these techniques surpass the lead-based fire assay or to offer the technical and commercial comfort to the operators to switch away from the Pb-based approach which is also the most economic and simple.

Bismuth trioxide can be used instead of PbO (litharge) and has been investigated since the early 1900s up until the 1990s (cf. US copper mining and refining company Asarco patent in the 1990s).

Cost factors (Bi is up to 3 times more costly than Pb) but also issues with stability of duplicate sampling etc. have dissuaded companies to adopt this technique.

Nickel sulphide is used for collecting gold and the six PGM elements. It is a slow process that is expensive and requires a great care as it involves the use of highly toxic carbonyl nickel powder. The NiS matte button extracts the gold and PGM. Different treatment methods of the NIS button exist such as crushing and dissolution in HCl, filtering and spectrometric analysis of the PM residue on the filter.
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4. Concluding considerations on fire assaying

The highly recognized reliability of fire assays with lead/lead oxide means that companies prefer investing in state-of-the-art equipment (local exhaust ventilation and filters) to protect operators than to jeopardize the trust of their commercial partners.

Companies often use a combination of analytical techniques in function of the specific needs from initial screening to precise composition establishment to calculate what needs to be paid for the material. The more time- and resource consuming fire assay technique is only used when there is a technical and/or commercial need for it as alternative techniques may be quicker in providing (be it more rough / semi-quantitative) data on the materials.

Substitution therefore consists in either the choice for an alternative technology (calibration issues may reduce their usability for complex materials) or in resorting to an alternative collecting metal such as bismuth. For each company, substitution will have to prove to be technically, economically and commercially feasible in the knowledge that sampling and assaying are a critical reliability criterion for a PM processor and that these activities, which are core business components, may represent well over 10% of a recycler's operating budget!

3. Pb as collector metal in precious metals refining/recycling

1. Key concepts

Lead has always been an important metal for Europe's major non-ferrous metals refiners owing to the presence of lead in most zinc and copper ores and was thus indissolubly linked with copper or zinc smelting and refining. Low-lead or 'lead-free' ores have ceased to be sufficiently available more than a century ago, at the time of the first World War.
The use of lead as collector material to help produce a copper of sufficient purity (as such or for further electrolytic refining) dates back to the early days of industrial non-ferrous metals refining. Since then, companies have increasingly complexified their business models in line with the complexification of articles in the economy which at their end-of-life become a major, if not the only source of raw materials for the EU refiners.

2. Two illustrative cases

Two cases illustrate the complexity of contemporary metallurgy which by necessity (ore and end-of-life materials composition) is becoming an increasingly sophisticated multimetallic operation. The viability of such operations rests on the full use of the carrier metal properties of a limited number of base metals. There are other large and smaller operations in the EU where non-ferrous metals recycling processes rest on these basic principles and which also rely on lead.

AURUBIS

The core business of this world leader in copper refining is the production of copper cathodes from copper concentrates, scrap and recycling materials (copper refining). These are processed within the Group into continuous cast wire rod, shapes, rolled products and strips as well as special wire made of copper and copper alloys.
PM are an important product field of Aurubis as well.

Figure: Recycling at Aurubis (https://www.aurubis.com/en/products/recycling/metal-recycling)

The recycling processes at Aurubis depend on the consistency and chemical composition of the raw materials. Apart from copper, these materials are used to produce by-products such as PM, nickel, tin, lead and zinc.
Two major process routes are in place, both of them with lead playing a role at various stages, where it will collect tin and PM:

1. Multi-metal recycling with the Kayser Recycling System (KRS) at the Aurubis recycling center in Lünen:
Copper scrap, electronic scrap and residues are used as input material in the Aurubis recycling center in Lünen. The Kayser Recycling System is well suited for utilizing recycling materials with low copper and PM contents and very complex materials such as electric and electronic scrap.

Material preparation: If necessary, processing begins with sampling, followed by a material preparation step. Depending on consistency and composition, the raw materials are then crushed, treated in a material preparation plant or directly conditioned into input mixtures.
In this preparatory phase, the amount of lead and its speciation will be closely monitored to ensure it can display its collecting property during the ensuing process.

Smelting and refining: Pyrometallurgical preparation – smelting and refining – begins in the Kayser Recycling System (KRS).

1. *Submerged lance furnace (reduction process):* Copper, nickel, tin, lead and the PM contained in the raw materials are enriched in an alloy with a copper content of about 80 %.
   Lead's affinity with other metals (Sn, PM) contributes in the manufacturing of the alloy.

2. *Top blown rotary converter (TBRC):* The copper content is further enriched to 95 % and tin and lead are separated into a slag. The tin-lead slag is subsequently processed into a tin-lead alloy in the directly connected tin-lead furnace.
   Lead's affinity with tin allows both metals to be separated from the copper.

3. *Copper cathode production:* The 95% copper is further enriched with copper scrap to raise the copper concentration to a 99 % pure copper which is cast into copper anodes.

4. *Copper tank house process:* high-grade copper cathodes are produced in a quality identical to copper cathodes from primary copper production. Important by-products, **in particular gold and silver**, are enriched in the anode slimes. Nickel is extracted as crude nickel sulfate from electrolyte treatment.
   The collected by-products gold and silver will meet again with lead at a later stage in Hamburg.

2. PM and by-metal production at the Hamburg site of Aurubis:

1. *Secondary copper process (pyrometallurgical steps):* The basic material for Hamburg's secondary copper production process consists of a variety of **recycling materials rich in PM** as well as **intermediate smelter products originating both from Aurubis' production plants and from external metal smelters and PM separating plants.**
   In accordance with the requirements of the specific raw materials, these materials are processed in a modern electric furnace in various smelting campaigns. **The most important target is the pyrometallurgical separation of lead and copper and the enrichment of PM**.

   ⇨ *Lead refinery:* By-elements still existing during copper production, such as lead, bismuth, antimony and tellurium, are separated in the **connected lead refinery** and sold as lead bullion, lead-bismuth alloy, antimony concentrates and tellurium concentrates. The **PM are fortified in a so-called rich lead**, which has a PM content of about 70 %.

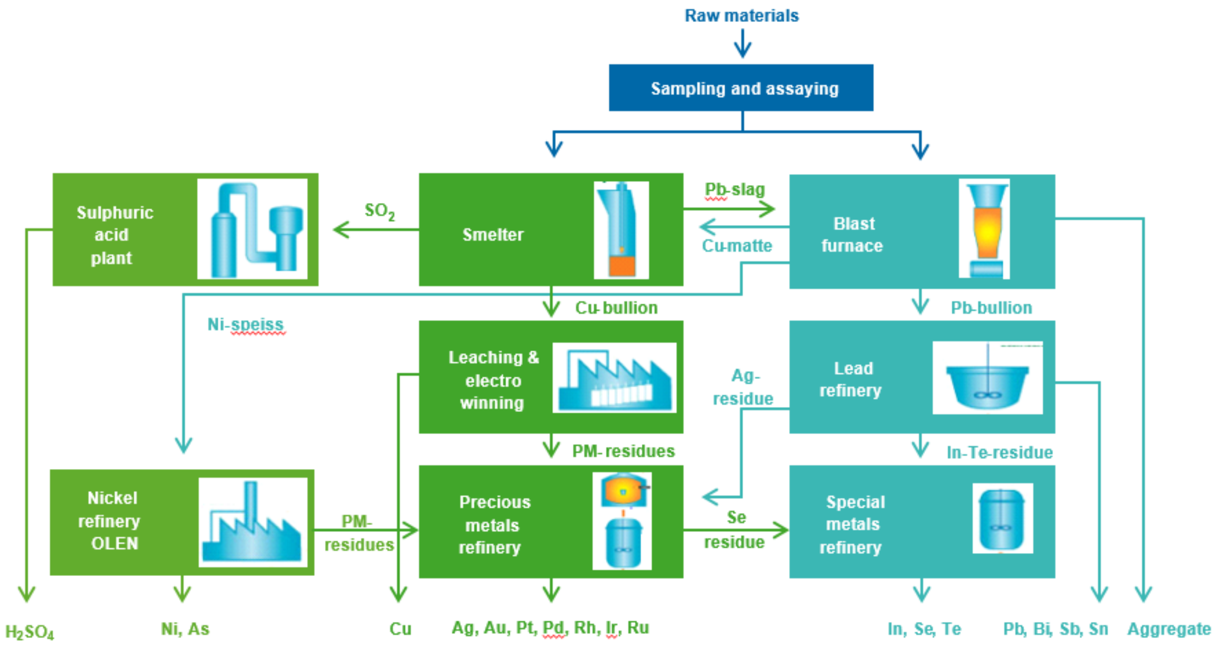
2. *Copper tank house process:* It produces PM-rich anode slimes

3. PM production plant: The **PM-rich anode slimes** and the **rich lead** from the lead refiner are processed together with all sorts of other materials such as PM-bearing sweeps and slag leading to the production of fine silver, fine gold and concentrates of the PGMs.

UMICORE PRECIOUS METALS REFINING

Initially a lead and PM refining plant, the Umicore Hoboken facilities moved into becoming a PMs recycler in the late 1990s.
Umicore Precious Metals Refining now operates the world's largest and most complex PM recycling facility in the world. This business unit of Umicore is the world market leader in recycling complex waste streams containing precious and other non-ferrous metals (more than 200 different types of raw materials).
The plant recovers and sells PM (silver, gold, platinum, palladium, rhodium, iridium, ruthenium), special metals (indium, selenium, tellurium), secondary metals (antimony, tin, bismuth) and base metals (lead, copper, nickel).

As is the case with Aurubis, the process flow at Umicore Precious Metals Refining is one that uses the collecting/carrier potential of Pb, Cu and Ni in synergy.



3. Concluding considerations on Pb as collector metal in PM refining/recycling

PM refining and recycling have historically always been linked with lead through either ore composition or metallic secondary raw materials composition.

The collecting/carrier properties of lead illustrated in the "Metal Wheel" explains why this metal plays a key role in effective and resource efficient PM recycling processes.

The metallurgical production infrastructure that European operators have developed over the last decades to maximize recovery of all elements in end-of-life products rests on a synergy of copper, lead and nickel as carrier metals.

A ban on having lead present and allowed to display its properties in these processes would, for these companies, mean

a) Disrupting the entire architecture of these resource and recovery efficient processes
b) Losing the capacity to continue recycling PM from complex end-of-life products and intermediates
c) Closing down parts if not all of the affected operations
d) Ultimately closure of these operations in the EU.

These consequences seem unavoidable as there is no carrier metal available that can be 'inserted' as a drop-in alternative in these processes. Considering the diversity of the materials being treated in the above-described processes, it has to be considered that several alternative technologies would have to be developed to recycle them separately, therefore increasing the costs of recycling and the overall entropy of the recycling process. Even if many of these different processes could be made technically feasible, only a few of them might be economically viable leading to a lot of the materials dropping out of the circular economy dynamics.

From a circular economy perspective indeed, one sees that this would have severe consequences for the PM supply chain within the EU. Those providing end-of-life and intermediate materials to these recycling operations would need to find alternative companies able to accept the PM-containing materials as it seems unreasonable to suppose that considering their contained value they would simply be disposed of in licensed sites. It is more likely that these materials could be sold or processed outside of the EU, representing a loss of value and resources to the EU economy.

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