Lead and Lead compounds in Precious Metals Refining

1. Introduction

Precious metals (Gold, Silver, Platinum, Palladium, Rhodium, Ruthenium, Iridium and Osmium with the 6 last metals commonly called *Platinum Group Metals* (PGMs)) are rare non-ferrous metals with a high monetary value. Besides jewelry and investment, the Precious Metals ('PM') have a wide variety of industrial uses (electronics, automotive, catalysts, alternative energy, healthcare, photography, glass and mirrors…). Because of their rareness and high monetary value, industry aims to maximally recover PM from all applications, as well as from residues and scrap materials produced during industrial activities.

The input materials for PM refining contain various precious metals at highly variable concentrations. The PMs are selectively isolated and concentrated from the input material before the actual refining process is initiated and PMs in their metallic forms or as PM compounds are produced.

Base metals like lead, nickel and copper are widely used as scavenger and collector of PMs (Figure 1). In the Metal Wheel, it can be seen that lead metal is a good carrier metal for PMs (reducing conditions), but that it loses this property when present as lead compound (e.g. oxidizing conditions). Under oxidizing conditions, lead oxides are an excellent carrier metal for metals like copper, cobalt or germanium. This different carrier metal capacity under reducing vis à vis oxidizing conditions will be important in the 4 cases discussed below in more detail.

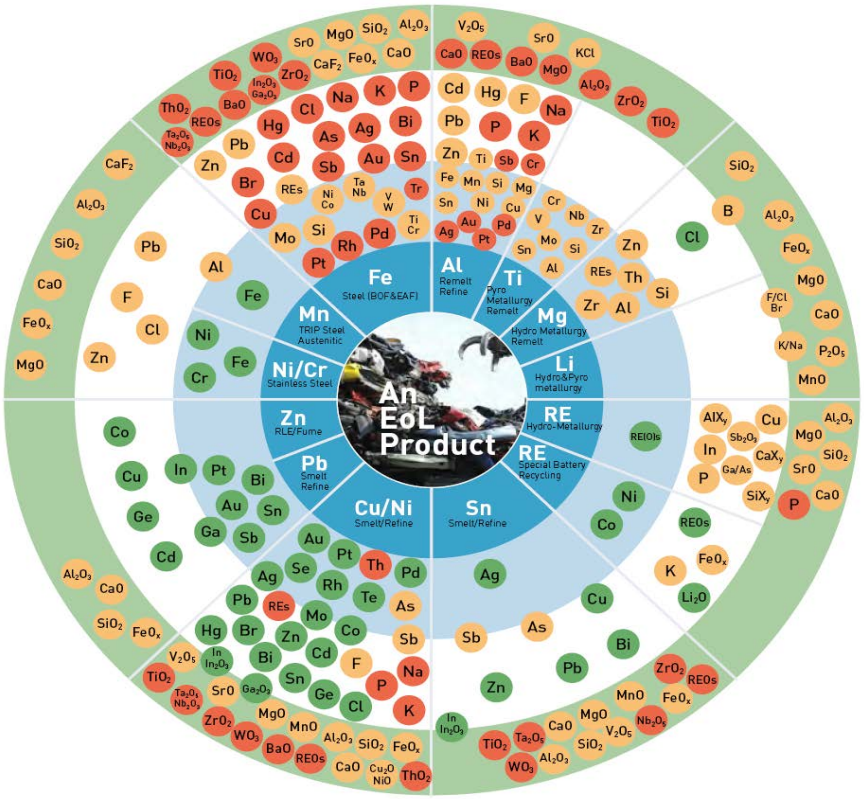

Figure 1: Metal wheel illustrating carrier function of base metals. The base metals are included in the dark blue ring, and the metals for which they can act as carrier metal (metals in green circles) are mentioned in the corresponding pie segment. The light blue band contain element that dissolve in the carrier metal when in metallic form, and white band contains compound metals (*Figure taken from UNEP (2013) Metal Recycling: Opportunities, Limits, Infrastructure*).

When acting as carrier metal, the optimal amount of required lead depends on the PM content in the material, and can thus be calculated once the PM content in the material is known.

Lead monoxide (PbO; CAS 1317-36-8; EC 215-267-0; Reg # 01-2119531110-62-xxxx) can be intentionally added during the PM refining process. During smelting (reducing environment), it is transformed to metallic lead and acts as PM scavenger/collector (cfr. Cases 1 and 3 below). In Case 2.2, however, lead is added (as metallic lead and/or lead compounds) as reactant to form a slag. Hereby, all lead is transformed to PbO in a pyrometallurgical process (oxidizing environment) and a slag is formed which:

-collects all impurities (non-PMs), and

-is separated from a purified PM concentrate.

This PM concentrate continues to the next steps of the PM refining process.

In the following sections, the utilization of Pb and PbO in the PM Refining industry is illustrated via four cases. For each case individually, PMCs interpretation is given if 1/ this can be considered a use of Pb/PbO *stricto sensu*, and if so, whether 2/ this use is considered an intermediate use (or not) in that specific case.

2. Lead in PM refining – process description and interpretation as intermediate use

1. Common steps for Cases 1 to 3

The initial process steps for the four cases described below are similar.

These steps consist of:

1) *mixing* of the (various) input material(s),
2) *process* steps of the input material (smelting and/or refining) and
3) *isolation* of a PM rich fraction and another fraction void of PM.

Typically, a combination of waste materials and REACH registered UVCBs is used as input material e.g. '*Materials for reclaim, PM with or without supports'* (Reg # 01-2119543879-20-xxxx) or '*Slimes and sludges, precious metal refining*' (Reg # 01-2119543718-30-xxxx). Note that the waste material ceases to be waste when used as input material for PM refining.

Lead can be present as metallic lead or as lead compounds, and is a constituent of these input materials. Depending on the conditions in the processes (reducing vs oxidizing), lead speciation might change.

From these processes, there is always a PM-rich fraction formed that is going on to the PM refining, and another fraction(s) that is further processed to recover other non-PM metals or that is treated as waste.

2. Case 1: PbO used in order to produce a PM rich UVCB

Process description

In Case 1, a PM rich fraction which is formed and isolated after smelting (reducing environment), and is registered as UVCB '*Lead bullion, Platinum Group Metals rich*' (Reg # 01-2119517585-35-xxxx). This UVCB is used as a feed material in the hydrometallurgical upgrading of PMs, and contains predominantly lead with lower concentrations of PMs, silver and gold and other non-ferrous metals in varying concentrations.

The silicate slag phase formed (void of lead and PM) is registered as UVCB '*Slags, precious metal refining'* (Reg # 01-2119535124-49-xxxx).

The PM rich UVCB is exposed to a nitric acid leaching process. Initially, lead will be present as metallic lead. However, as the leaching process progresses, lead will be dissolved and the aim is to have a full conversion of metallic lead to lead compounds at the end of the process. The PM rich residue of this leaching process is registered as UVCB '*Slimes and sludges,*

precious metal refining' (Reg # 01-2119543718-30-xxxx). This UVCB will go to the final PM refining and contains trace amounts of lead, as higher concentrations would interfere with the further PM extraction and purification.

The leaching solution only contains lead compounds, but not as lead monoxide. The solution is not REACH registered as it is not isolated. Via further process steps, a lead intermediate under SCC is produced which is registered as '*Reaction products of lead chloride or lead sulphate with alkaline solutions*' (Reg # 01-2119531554-42-xxxx) which is re-used and mixed with new input material.

Use of lead monoxide

During the initial steps of the PM refining process (described in section 2.1), lead is intentionally added to the input material if insufficient lead is present in the input material. If available, described lead intermediate is added. However, if this intermediate is not sufficiently available, lead monoxide is supplementary added to optimize the total lead content in the input material.

Regulatory interpretation of lead monoxide

As described, the lead monoxide is intentionally added to the input material during the initial process steps, and is completely consumed and converted into metallic lead during the smelting step. After cooling, the PM rich UVCB (containing Pb in metallic form) is separated from the slag. Both the PM rich UVCB and the slag are REACH registered as UVCB. Afterwards, a leaching process is performed, re-dissolving metallic lead to lead compounds (not as lead monoxide) as described in section 2.2 'Process description' (leading to generation of a leaching solution (not REACH registered as not isolated) and a lead intermediate under SCC (registered as '*Reaction products of lead chloride or lead sulphate with alkaline solutions*').

Conclusion: PMC considers the use of PbO in order to produce a PM rich UVCB as an intermediate use of lead monoxide.

3. Case 2: Pb(PbO) as carrier metal in the refining of PM (and non-PM)

3.1. Case 2.1: Pb/PbO present in input material

Process description

In Case 2.1, focus is on the lead which is present in the input materials (as metallic lead and/or lead compounds), i.e. as UVCB constituent (cfr. section 2.1).

The input materials are mixed and undergo several process steps (such as smelting and electrorefining). This results among others in an impure Pb intermediate, which contains silver

and other non-PMs. This impure Pb substance is registered as a UVCB under REACH (Pb bullion; 01-2119517450-50-xxxx). The Pb is present as Pb metal. The Ag is separated from the Pb by adding Zn, thus forming an alloy (Pb/Ag/Zn) floating on the molten Pb bath. This is removed as a skimming (cfr. Parkes process).

In this process, Pb is necessary to form a skimming in order to be removed from the molten Pb bath and to be further treated in the PM refining process. This skimming is registered as a UVCB under REACH ('*Zn, desilvering skims*'; Reg # 01-2119517451-48-xxxx).

Presence of lead monoxide

Lead monoxide is unintentionally present in the input material. PbO is transformed to Pb metal and the majority hereof is refined to pure Pb during the Pb refining process.

Regulatory interpretation of lead monoxide

As described, the lead monoxide is unintentionally present in the input material as UVCB constituent. The lead monoxide is therefore not a substance per se, and this case is not considered a use of PbO.

Conclusion: PbO is part of the input material (UVCB constituent) and refined to lead during a lead refining process. As such, PMC considers this case not as a use of PbO stricto sensu, and therefore as not relevant for the intermediate discussion.

3.2. Case 2.2: Pb/PbO added to form a slag

Process description

In Case 2.2, the PM-rich fractions from several (refining) streams (e.g. lead or copper refining) are considered and combined as feed material for PM refining process. All these fractions:

- underwent earlier process steps,
- had in these steps a base metal like lead or copper as carrier metal,
- are intentionally separated from other fractions (void of PM) that are each further processed or treated as waste,
- might contain lead as (minor) constituent in a UVCB.

These PM rich fractions are registered as UVCB under REACH (e.g. '*Slimes and sludges, PM refining*' (Reg # 01-2119543718-30-xxxx) or '*Zn desilvering skimms'* (Reg # 01-2119517451-48-xxxx).

The UVCBs are used as feed material in the pyrometallurgical operation for PM refining. During this process, lead is intentionally added as a Pb/PbO-rich UVCB. The Pb is transformed to PbO during the operation (oxidizing environment), and PbO remains as PbO. The main

purpose of Pb/PbO addition is to collect the impurities (non-PMs) in a slag, and a purified PM concentration is formed.

The slag (containing PbO and other non-PM materials) is isolated and registered as UVCB under REACH ('*slags, PM refining*' (Reg # 01-2119535124-49-xxxx)). This slag material is re-introduced in the initial mixing step before the pyrometallurgical operation for PM and non-PM refining.

The PM concentration is registered as UVCB under REACH e.g. '*Doré'* (Reg # 01-2119543724-37-xxxx) and treated further during PM refining. This PM concentration does not intentionally contain lead (only impurity at low ppm level) as lead would interfere with the further PM extraction and purification.

Use of lead monoxide

During the pyrometallurgical operation for PM refining, additional lead is intentionally added to the feed material (void of lead). This lead is added as Pb and/or PbO as UVCB constituents to enhance slag formation. Due to the oxidizing conditions during pyrometallurgical operation, all lead is transformed to PbO and separated via a slag (containing non-PM impurities) from a PM-rich concentration.

Regulatory interpretation of lead monoxide

The lead (Pb and/or PbO) which is intentionally added as UVCB constituent during pyrometallurgical operation is completely converted into PbO, and forms the basis of slag formation. The PM concentration is separated from the slag which contains the lead (in the form of PbO) together with other metallic elements (i.e. non-PMs). The PM concentration and the slag are registered as UVCBs under REACH. The slag is re-introduced in the initial mixing step.

Conclusion: ***PbO is intentionally added as UVCB constituent, and is completely transformed to PbO as constituent of another UVCB. PMC considers this case not as a use of PbO stricto sensu, and therefore as not relevant for the intermediate discussion.***

4. Case 3: PbO when used in fire assay (lab use)

Process description

Case 4 describes a laboratory use. Sampling and elemental analysis of (input) materials is an essential task for the PM refining industry to understand and determine the content of the recycling feed. The fire assay is the most commonly used lab assay for this purpose. Lead monoxide is added to a test sample at a fixed amount. The sample is smelted, lead monoxide

is reduced to lead metal and acts as PM scavenger and collector. The lead-PM rich fraction is separated from a slag containing impurities. The slag does not contain lead and PM.

The lead-PM-rich fraction is smelted again and lead is removed by cupellation. During this process, metallic lead is re-oxidized and volatilized to lead monoxide and a PM prill is isolated. The PM prill is send for further analysis.

None of the fractions are registered under REACH, and are re-introduced into the process or treated as waste.

Use of lead monoxide

Lead monoxide is intentionally added to a sample, to act as PM scavenger/collector under reducing conditions.

Regulatory interpretation of lead monoxide

During the smelting step, lead monoxide is completely consumed and converted to metallic lead. The lead-PM fraction is isolated, and the PM are further separated from the carrier material via cupellation. During cupellation, metallic lead is re-oxidised to lead monoxide which is captured with industrial filters and further treated at dedicated facilities. In some cases, some lead monoxide may be retained in the vessel, which is either recovered and reused or is discarded as hazardous waste.

The fire assay is a use meeting the definition of *Scientific Research and Development* (cfr. REACH Art 3(23)). However, some legal entities use lead monoxide in the fire assay in quantities >1 tonnes/y. As such, the exemption from authorization as described in REACH Art 56(3) does not apply for those legal entities exceeding this threshold, as described e.g. in ECHA *Guidance on Scientific Research and Development (SR&D) and Product and Process Orientated Research and Development (PPORD)* (Version 2.1, October 2017).

Conclusion: PMC considers this use of PbO in the fire assay NOT as intermediate use. Although this use is exempted from Authorisation for legal entities using <1 tonnes PbO/y, this exemption does not apply for tonnages exceeding this threshold.

3. Conclusion

As described above, PMC considers

- **Cases 1 as intermediate use of PbO**: lead monoxide is intentionally added to the process, completely consumed and separated from a PM concentrate via a slag. In both cases, lead becomes a constituent of a REACH registered UVCB.

- **Case 2.1 and 2.2 not as a use of PbO, and therefore not relevant for the intermediate discussion**: lead monoxide is part of a REACH registered UVCB which:
    - serves as input material for the initial mixing and process steps (no intentional addition) in case 2.1
    - is intentionally added during the pyrometallurgical operation and become constituent from another REACH registered UVCB in case 2.2.
- **Case 4 as no intermediate use of PbO**: lead monoxide is intentionally added in a laboratory use, converted to metallic lead during smelting but re-converted to lead monoxide during a final cupellation step. According to PMC's interpretation, this use is prone to authorization if used >1 t/y by a legal entity.