

## New Pyrometallurgical Bullion Lead Refining Process

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**Abstract:** After the primary or secondary lead production the bullion lead is remelted and charged into a vessel with following refining process. The removing of arsenic, antimony and tin takes place by salt slags or oxidizing gases like air or pure oxygen. Due to the increasing lead price Messer Austria GmbH and in cooperation with the institute of Nonferrous Metallurgy at the University of Leoben developed a new process named OXIPOT for the refining of Tin, Arsenic and Antimony. The OXIPOT process bases on the bottom purging technology with a ceramic or steel purging device. This leads to an increased retention time of the refining products due to the deeper bath level and an optimized specific reaction volume concerning the bubble size. This paper describes the process, pilot plant, thermodynamic calculations for the optimization concerning the selectivity of element removal.

### Introduction

Not only the lead price also the environmental restrictions are increasing. The issue of the new process for lead refining was an economical and ecological reason for the Messer Group therefore the refining by pure oxygen or oxygen/inert gas mixtures for the refining selectivity of the impurities and the higher reaction kinetic by a deeper bath was forced. The goal of highest efficiency will be reached by following points:

- Selectivity refining period of Tin, Antimony and Arsenic by optimizing the oxygen partial pressure
- Formed oxides (Tin, Antimony, Arsenic, Pb) could be directly recycled in the process or could be sold Arsenic products
- No residues for landfill
- Easily removal of the built oxides by a siphon tap hole system
- Lower refining times
- High economic efficiency by usage of technical gases instead of salts

## **State of the art of lead fire refining**

Apart from gold and silver, lead bullion contains many other metallic impurities including antimony, arsenic, copper, tin and zinc.

### **Removal of copper**

Copper is the first of the impurities to be removed and a liquation process is used. The lead bullion is melted and held just above its melting point when solid copper rises to the surface and is skimmed off. Sulphur stirred into the melt facilitates the operation by producing a dry powdery dross, which is more readily removed.

Once copper has been removed, there are a number of processes available for the extraction of the other impurities from the bullion. These include pyrometallurgical techniques where elements are removed one or more at a time in several stages and electrolytic processes that deal with most of the impurities in one operation. Although electrolytic methods are used in large scale production, they only account for the smaller part of the world refined lead production, the pyrometallurgical techniques being more widely employed [4], [5].

### **Removal of antimony, arsenic and tin**

After the removal of copper, the next step is to take out antimony, arsenic and tin. There are two methods available - the softening process (so called since these elements are standard hardeners for lead) or the Harris process [4], [5].

#### The softening process

This is carried out in a reverberatory furnace or cattle in which the lead is melted and agitated with an air blast, oxygen enriched air [1] or lances with pure oxygen and cooled with nitrogen, carbon dioxide or argon [2]. Another process is the VARTA process. They pump the melt into a separate vessel and treat them with pure oxygen [3]. This causes preferential oxidation of the impurities, which are then skimmed off Arsenic a molten slag [4], [5].

#### Harris process

This employs a molten flux of sodium hydroxide and sodium nitrate or some other suitable oxidizing agent. Using a rotary stirrer, the molten bullion and the flux are churned into a whirlpool, which thoroughly mixes them at the vortex. Sometimes, instead of the stirring method, lead is pumped out from the bottom of the pot and sprayed on to the top of the flux cover through which it passes owing to its greater density. After some hours, the impurities have left the lead and are suspended in the alkali flux in the form of sodium antimonate, arsenate and stannate and any zinc has been removed in the form of zinc oxide. This flux is then separated from the softened lead and the impurities are extracted in a separate process [4], [5].

### **Removal of gold and silver**

After the removal of antimony, arsenic and tin, the softened lead may still contain silver and gold and perhaps bismuth. The removal of the precious metals by the Parkes or Port Pirie process depends on them both being more soluble in zinc than in lead [4], [5].

### **Removal of zinc**

The removal of the precious metals results in the contamination of the lead with zinc, which must then be removed. This can be done either by oxidation with gaseous chlorine or by vacuum distillation. This latter process involves melting the lead in a large kettle covered with a water cooled lid under vacuum. The zinc distills from the lead under the combined influence of temperature and reduced pressure and condenses on the underside of the cold lid [4], [5].

### **Removal of bismuth**

The only likely remaining impurity is bismuth, though it is not always present in lead ore. It is easily removed by electrolysis and this accounts for the favoring of electrolytic methods in Canada, where it is a frequent impurity. Where pyrometallurgical methods of refining are used, bismuth is dealt with by adding a calcium-magnesium alloy to the molten lead, causing a quaternary alloy of lead calcium-magnesium-bismuth to rise to the top of the melt where it can be skimmed off [4], [5].

### **Electrolytic processes**

In the Betts process, massive cast anodes of bullion are used in a cell containing an electrolyte of acid lead fluosilicate and thin cathode "starter sheets" of high purity lead. The lead deposited on the cathodes will still contain tin and perhaps a small amount of antimony and these must be removed by melting and selective oxidation. For many years the Betts process was the only one that removed bismuth efficiently.

A more recently developed electrolytic process, first used in the 1950s in Italy, employs a sulphamate electrolyte. This is claimed to be an equally efficient refining method with the advantage that the electrolyte is easier to prepare [4], [5].

### **Lead refining in secondary lead industry**

Once smelting is complete, the molten lead is removed from the smelting furnace and can be cast into large blocks (called pigs) weighing 1.5 to 2.5 tonnes. These are transferred to the refining kettles which are top-access pots sunk into the refinery floor. Alternatively, in more modern plants, the molten lead is pumped directly from the smelting furnace to the refinery pots thus saving on time and energy in remelting.

The principal impurities which are removed in secondary lead refining are copper, tin, antimony and arsenic. Copper can be removed in a similar fashion to that outlined for primary lead. Some companies use iron pyrites and Sulphur which works at a higher temperature and can also remove any nickel present. The other elements are removed by a

modified Harris or softening process. Bismuth and silver levels tend to be slightly higher than in primary lead but are rarely removed [4], [5].

By combining a number of the processes described above to build up a complete refining scheme, it is possible to produce lead of a very high degree of purity. Most major refiners will supply bulk quantities of lead of 99.99% purity and for very special purposes it is possible to reach 99.9999% purity by additional processing [4], [5].

### Influence of the Bath Depth on the Refining Stage

The lead refining process is influenced by the reactions between the gas bubbles and the melt. Furthermore, the melt turbulence results in multiple advantages including thermal and chemical homogenization of the melt, an increased boundary layer between the formed oxides and metal and a higher chemical purity. The most important factor influencing the chemical reaction efficiency between the gas and melt is the residence time of the bubbles in the melt. This residence or ascending time is influenced by the bubble diameter and the bath height above the gas inlet (

Figure 1). The residence time  $t$  was calculated using equation 1 [7] and the terms are detailed in Table I.

$$t = \frac{1.08}{\sqrt{g} \cdot \sqrt[6]{p_0 \cdot V_0 \cdot \rho_L \cdot g}} \cdot \left( \sqrt[6]{p_0^7} - \sqrt[6]{(p_0 - \rho_L \cdot g \cdot x)^7} \right) \quad (1)$$

	Unit	Definition
$p_0$	Pa	Pressure over the discharge opening
$V_0$	cm <sup>3</sup>	Reaction volume
$V_x$	m <sup>3</sup>	Depth (x) dependent bubble volume
$g$	m/s <sup>2</sup>	Gravitational constant
$\rho_L$	kg/m	Melt density

Table I: Definitions and units of terms in equation (1)

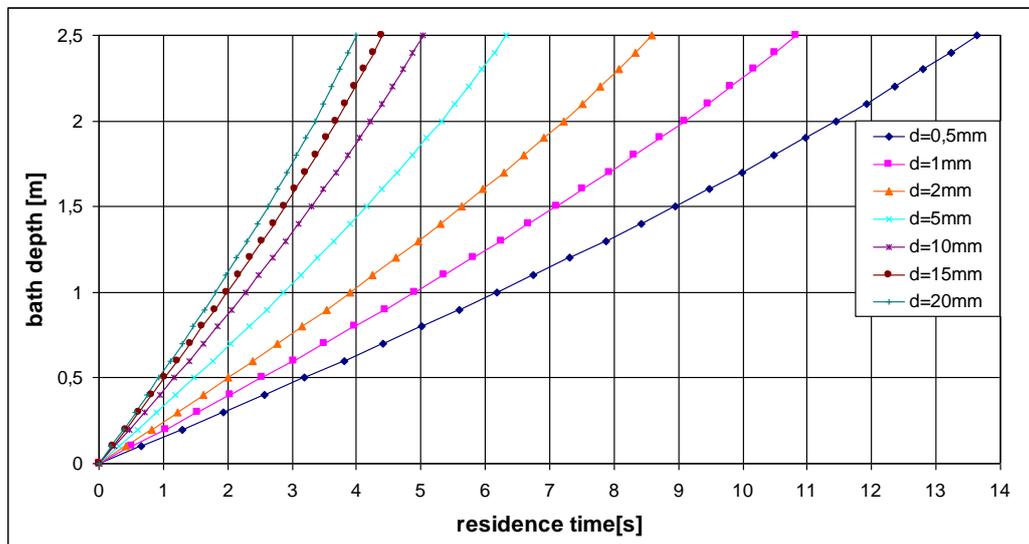


Figure 1: Residence time influenced by the bubble diameter ( $d$ ) and bath height above the tuyere.

In the case of chemical reactions in the melt, a small bubble diameter is essential because the residence time is longer than with larger bubbles. The form of the bubble is also crucial, and an elliptical bubble increases convection in the melt and the mass transport is increased. The gas bubbles formation in a water model Arsenic reference in the refining vessel is shown in Figure 2.

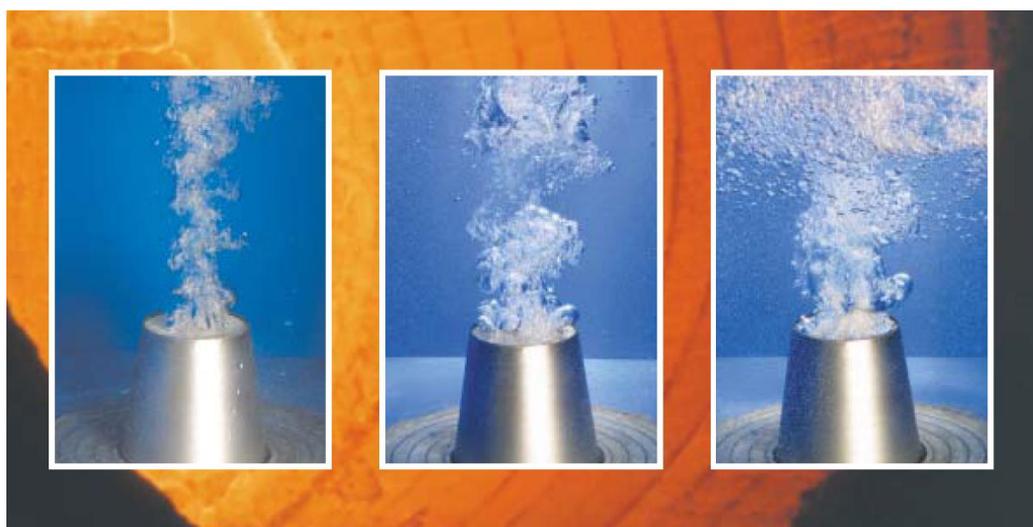


Figure 2: Ceramic purging plugs and gas bubbles formation in the water model over different gas flow rates [6]

## Modeling of Bath Movement During the Refining Stage

CFD simulation of the refining stage was performed using Fluent 6.2 3D and the following formulations were employed: The VOF model (2-phase ) for the phases, the Discrete Phase Model for gas, and the RNG k-epsilon model for the turbulence. The retention time of the simulated particles and the flow in the reaction vessel is shown in. The flow isn't symmetric around the axis. For the simulation, gas bubbles of 1 mm diameter were used but no formation of oxides was calculated therefore a failure is in the simulation. But we wanted to know the flow in the vessel. We used a purging plug temperature of 2000 °C for the heating of the melt over the chemical reaction. Since the CFD modelling did not depict the chemical reactions in the bath, the simulation of all parameters, the formation of oxides, the chemical kinetic and the flow of the melt were not interacted together .

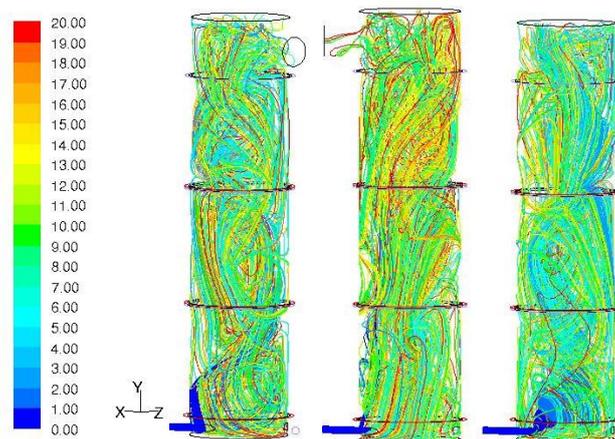


Figure 3: Retention time and flow of simulated particles at the different inlets (0, 120 and 240°)

## Refining by selective oxidation of Tin, Antimony and Arsenic

The main goal of the new refining process is the ecological issue by the selective oxidation of Tin, Arsenic and Antimony by the adjustable flow rate of the gas and the lead melt, the modifiable partial pressure and temperature. The thermo dynamical calculations were done with Factsage with a temperature range of 350 °C and 650 °C and a bullion lead composition of 1 wt% Antimony, 0.5 wt% Arsenic, 0.5 wt% Tin. Tin is removed by low oxygen partial pressure in the melt over the full temperature range. At temperatures between 350 °C and 550 °C Antimony is removed at a lower oxygen partial pressure in the melt than Arsenic. At temperatures over 550 °C the Antimony oxidation is removed to higher oxygen partial pressure in the melt therefore the Tin and the Arsenic could be selective removed by the oxygen (Figure 4).

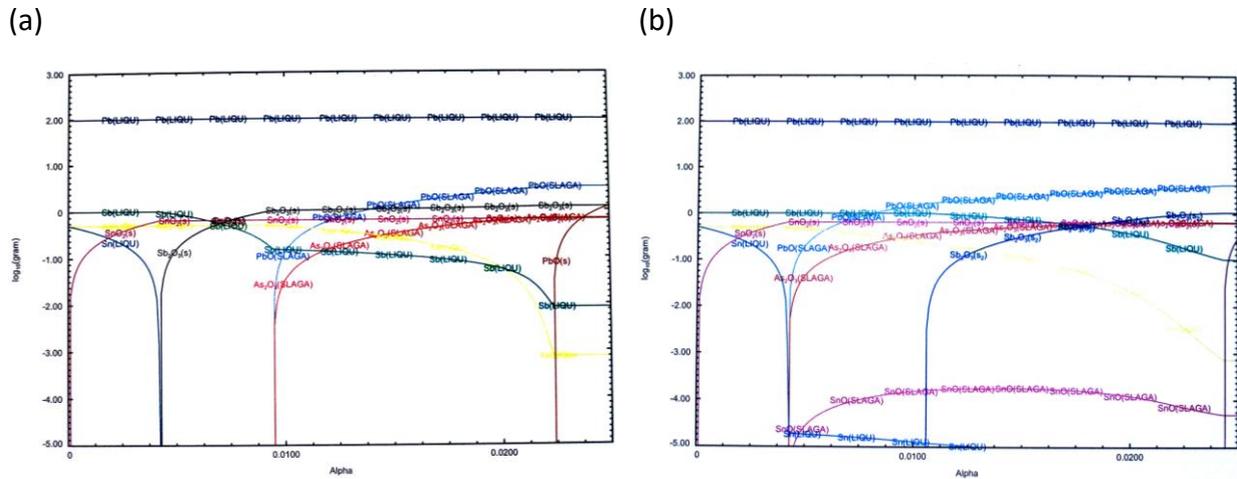


Figure 4: Thermo dynamical calculations of the lead bullion melt at a temperature of 350 °C (a) and 650 °C (b)

## The OXPOT Pilot Plant

The bullion lead comes at the bottom into the refining vessel and flows over a oxidation media inlet system. At this point, the lead and the impurities react with the injected oxygen containing gas and form oxides. These oxides will be transported with the melt over a circulating movement to the top of the vessel and there the melt and the oxides will left the vessel to a separation unit or the reefing kettle.

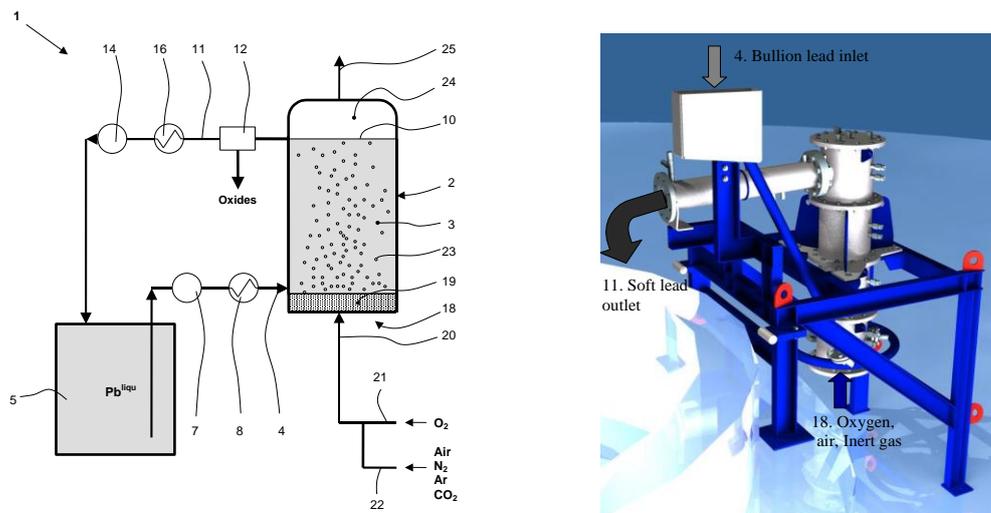


Figure 5: Scheme of the OXPOT lead refining apparatus (1), 2. Refining vessel, 3. Bullion lead, 4. Bullion lead inlet, 5. Kettle, 7. Bullion lead pump, 8. Heating device, 11. Soft lead outlet, 12. Soft lead and oxides (Tin, Arsenic, Antimony)separation unit, 16. Cooling device, 18. Oxidation media inlet system, 23. Gas bubbles

## **Conclusion**

The Messer Group is the world largest family owned technical gas supplier. Therefore the development and optimization of devices, which use for example oxygen or technical gases, is the main goal. The second goal is the ecological responsibility to the environment of the Messer Group and the lead companies. The usage of pure technical gases instead of salt slags lead not only to an ecological benefit also the economical benefit for the customers were delivered with this development. The costs of landfill will increase and the quality of the secondary material like batteries will decrease in the next years and Zero-Waste-Technologies will be very important. To reduce the by products or to sell the formed oxides to the tin or antimony industry is the main advantage of the OXYPOT process by lowering the production costs.

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