

# UPGRADING OF SECONDARY LEAD SMELTING RESIDUE TO SECONDARY IRON ORE

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## Introduction

More than 85% of the total amount of secondary lead is produced using spent lead-acid batteries as a resource.<sup>1</sup> Metallic lead is recovered by high temperature reduction of the lead compounds (sulfates, oxides) present in the batteries<sup>1</sup>. This recycling process, however, also generates an estimated 200 000 tpa of solid residues in Europe.<sup>2</sup> As the residues are often considered hazardous wastes, they represent significant costs for companies as well as an environmental hazard for society. However, due to the high Fe and Pb content, the residues also have potential to be recycled into valuable resources. The MIP-ICON project “MaxiVIA” (Maximal Valorisation of iron rich waste streams) aims to valorise these iron rich residues by a combination of physical and chemical treatments. This paper focuses on the results obtained for a secondary lead smelter residue (matte) that initially contains circa 50 wt% Fe (as FeS, Fe<sub>3</sub>O<sub>4</sub>, FeO and metallic iron) and 5-7 wt% Pb (as PbO, PbS and metallic Pb). To use the Fe-rich matrix as a secondary pig iron ore, its Fe concentration had to be increased to at least 60 wt% Fe, preferably in oxidic form.

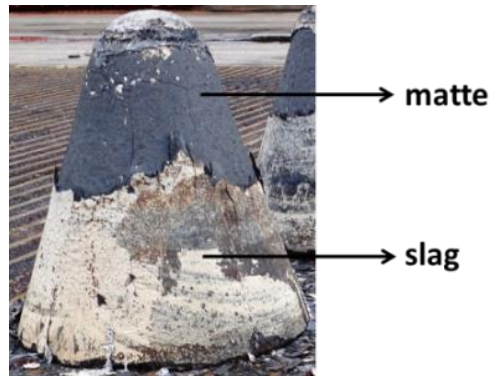
## Methodology

### Material

The material used in this study came from a company recycling lead-acid batteries. The recycling process is based on the reduction of lead compounds present in lead-acid batteries to metallic lead at temperatures higher than 1000°C. During the smelting process, three layers are formed in the furnace based on different densities. The bottom layer consists of metallic lead that is separated and further refined. The other two layers, matte (middle layer) and slag (top layer), are tapped into a “slag pot”. After cooling, the slag pot is turned over and the matte and slag (Figure 1) are separated physically with a jaw pulveriser.

A representative sample of the matte was collected on site by taking a total of 16 individual scoops (4 L each) at different locations across the material heap (estimated

volume 40 m<sup>3</sup>). The samples were transported to the laboratory in 20 L buckets (each containing 4 scoops) and subsequently mixed prior to further treatment.



**Figure 1:** Layers of the matte and the slag

## Methods

The sample was crushed to a particle size below 2 mm in a two-step process using *Retsch* crushers *Model BB300* and *Model BB200*, and sieved into a 1-2 mm fraction using a vibratory sieve shaker (*Model AS200*, *Retsch*). A handheld XRF analyser *Niton XL3t GOLDD+* (50 kV and 0.2 mA Ag anode, 120 s measurement time) placed in a mobile test stand, was used for elemental analysis. Mineralogical analysis was performed by an XRD diffractometer *X'Pert PRO* from *PANalytical* (Cu tube (fine focus), step size 0.04° in the 2Theta range of 2 to 120°). Obtained diffractograms were evaluated by the software *HighScore Plus* version 4.0.

Low intensity magnetic separation (LIMS) was performed by a handheld ferrite magnet (0.15 T). The handheld magnet was covered by a plastic bag for convenient removal of the magnetic fraction. The distance between the handheld magnet and the sample layer was kept constant to ensure reproducibility.

Wet high intensity magnetic separation (WHIMS) experiments were performed using a *Master Magnets Ltd.* WHIMS separator at maximal current (17.5 A). A stainless steel matrix with a gap of 0.96 mm was used for each experiment.

Oxidising roasting was performed in a chamber furnace (*Linn High Therm GmbH*), at a temperature of 600°C using a heating rate of 3°C/min, a dwelling time of 4 h and air oxygen at ambient pressure as oxidising agent. After roasting, the sample was milled for 5 minutes in a mortar to disintegrate agglomerates created during the roasting.

Leaching tests were carried out in a 60 ml polytetrafluoroethylene (PTFE) bottle with cap on 2.0 g solid samples. The sample was mixed in an L/S ratio of 8 with a solution of 0.5M nitric acid and 0.15M Fe(NO<sub>3</sub>)<sub>3</sub> in the bottle, which was stirred in a water shaking bath at 25°C for 1 h. The reagents used in this study were 68% HNO<sub>3</sub> (*VWR chemicals*) and Fe(NO<sub>3</sub>)<sub>3</sub> (98% purity, *Sigma-Aldrich*) with analytical grade. After each leaching experiment, the slurry was filtered by filter paper (*Whatman*) of 0.45 µm pore

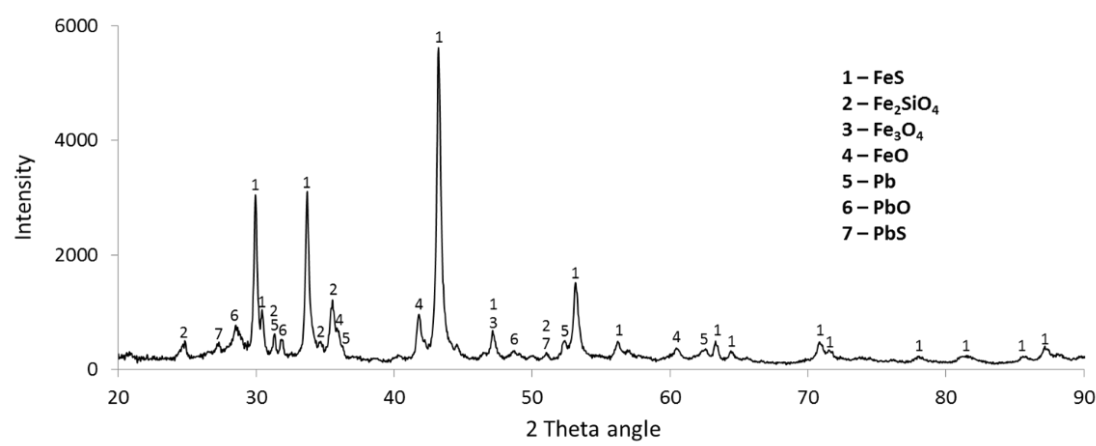
size and the filtrate obtained was analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, *Thermo Elemental*) to determine the amount of metal extraction.

## Results

The matte initially contains 50 wt% Fe and 7.0 wt% Pb, with minor concentrations of Cu, Ni and Zn (Table 1). The XRD analysis (Figure 1) showed that iron is mainly present as sulphide (troilite (FeS)), oxides (FeO, Fe<sub>3</sub>O<sub>4</sub>) and metallic iron. Lead was identified as PbO, PbS and metallic lead.

**Table 1:** Chemical composition of the matte

wt%	Fe	Pb	Cu	Ni	Zn	Sn	As	Si	S
Matte	50	7.0	1.3	0.17	0.48	0.23	0.08	3.3	20



**Figure 2:** XRD patterns of the matte (1-2 mm)

As shown in Table 2, the ferromagnetic fraction after LIMS (70 wt% of initial material) is slightly enriched in Fe (53 wt%), Pb (7.3 wt%) and S (27 wt%) compared to the original material. On the other hand, Si is enriched in the non-ferromagnetic fraction (30 wt% of initial), which is beneficial for subsequent leaching processes where formation of silica gel can severely hinder filtration<sup>3</sup>. The LIMS FM fraction was treated further by roasting and WHIMS. By these treatments, Fe content is increased to 61 wt%, sufficient for use as a secondary iron ore, with a strong reduction in S content. The remaining sulphur is due to the formation of PbSO<sub>4</sub> during oxidative roasting. The loss during WHIMS treatment (16 wt%) is caused by dissolution of soluble sulphates created during roasting and material loss during filtration.

To further increase the Fe content and reduce the residual sulphur in the final product, hydrometallurgical removal of Pb prior to roasting was investigated. The leaching tests were performed on the original sample, before enrichment by physical treatments. It

was found that leaching with HNO<sub>3</sub> in the presence of Fe(III) as an oxidant, can recover 90% of Pb at ambient temperature<sup>4</sup>. As 20% Fe is also leached, other leaching systems are recently being investigated to increase the Pb/Fe selectivity. By combining LIMS with atmospheric leaching, a final product can be made that contains more than 60% Fe. By further refining the product through oxidative roasting and WHIMS, a purity of 97% Fe oxides can be reached.

**Table 2:** Chemical composition of ferro-magnetic (FM) and non-ferromagnetic (NFM) fractions after different magnetic separation steps. Results are average of three measurements, standard deviations given between brackets

Fraction	Composition [wt%]				Yield [wt%]
	Fe	Pb	S	Si	
Original	50	7.0	20	3.3	100
LIMS FM	53 (0.5)	7.3 (0.1)	27 (0.4)	0.5 (0.1)	70
LIMS NFM	31 (0.5)	2.3 (0.1)	4.9 (0.2)	10 (0.4)	30
LIMS FM after milling and roasting	57 (0.1)	6.8 (0.1)	5.3 (0.1)	0.5 (0.1)	103.6% <sup>a</sup>
WHIMS FM <sup>b</sup>	61 (0.2)	5.7 (0.1)	4.0 (0.1)	0.5 (0.1)	63
WHIMS NFM <sup>b</sup>	56 (0.2)	7.9 (0.1)	4.4 (0.1)	0.5 (0.1)	21

a: Weight increase due to oxidation; b: input material is LIMS FM fraction after milling and roasting

## Acknowledgement

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