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The Technology of Lead Production from Waste

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In this study the pyrometallurgical and hydrometallurgical processing of lead recovery from waste was investigated. Lead is the softest of the technically important base heavy metals. It is easily rolled and moldable, so it is possible to produce wire rod and tubes as well as sheets and foils. Lead consumption is linked to the manufacture and use of lead-acid batteries and is estimated to account for 85 % of production (Figure 1). Other applications of lead include roofing materials and radiation protection. As regards the environmentally safe production and recycling of base materials, this metal has another positive property: it can be almost fully recycled as often as required without any loss of quality or value. The use of lead in certain applications is limited by several EU regulations. Other uses for lead, which include pigments and compounds, cable sheathing, ammunition and petroleum additives, have been in decline. The use of lead metal in rolled and extruded products such as lead sheets has been fairly stable over the years. The aim of this work is to give a short review of lead-containing waste streams and examine current and future possibilities of obtaining lead from primary and secondary raw materials in EU.

Keywords:

Lead – Recovery – Secondary lead – Technology

Die Technologie der Bleiproduktion aus Abfällen

In dieser Studie werden der pyrometallurgische und der hydrometallurgische Prozess der Rückgewinnung von Blei aus Abfällen untersucht. Blei ist das weicheste der technisch relevanten Schwermetalle. Es ist leicht formbar und kann sowohl als Kabel und Rohre als auch als Platten und Folien Verwendung finden. Die Nachfrage nach Blei ist an die daraus erzeugten Produkte gebunden und die Herstellung von Bleiakkumulatoren wird auf 85 % der gesamten Produktion geschätzt (Abbildung 1). Andere Anwendungen von Blei sind Dächerbau und Strahlungsschutz. Im Hinblick auf umweltfreundliche Produktion und Recyclingfähigkeit hat Blei eine andere positive Eigenschaft: Es kann fast vollständig und beliebig oft ohne Qualitätsverlust recycled werden. Der Gebrauch von Blei in bestimmten Anwendungen ist durch EU-Richtlinien begrenzt. Der Trend anderer Verwendungen von Blei, wie beispielsweise als Pigmente und Verbunde, Kabelummantelungen, Munition oder als Zusatz in Benzin, ist rückläufig. Die Verwendung von Blei in gewalzten und extrudierten Produkten wie Bleiplatten verlief die letzten Jahren stabil. Ziel dieser Arbeit ist es, einen Überblick über Abfallströme mit Bleigehalt zu geben und die aktuellen und zukünftigen Möglichkeiten der Rückgewinnung von Blei aus Primär- und Sekundärmaterialien in der EU zu erarbeiten.

Schlüsselwörter:

Blei – Rückgewinnung – Sekundärblei – Technologie

1 Introduction

Lead is a strategically important metal resource for the industrial development and global economy. Lead is usually found in ore with zinc, silver and copper and is extracted together with these metals. The main lead mineral is galena (PbS). Other common varieties include cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Refined lead is derived from primary material in the form of lead or mixed metal ores and concentrates, and secondary material in the form of scrap and residue. The balance between primary and secondary production has shifted since 1998, and in 2011 secondary sources accounted for more than 77 % of EU production [1].

EU countries produced 343,900 t of lead concentrate, in 2014 the main producers being Poland (1.5 %), Sweden and Turkey. Total world mine production in 2014 was reported as 5.4 mill. t. World refined lead metal production in 2014

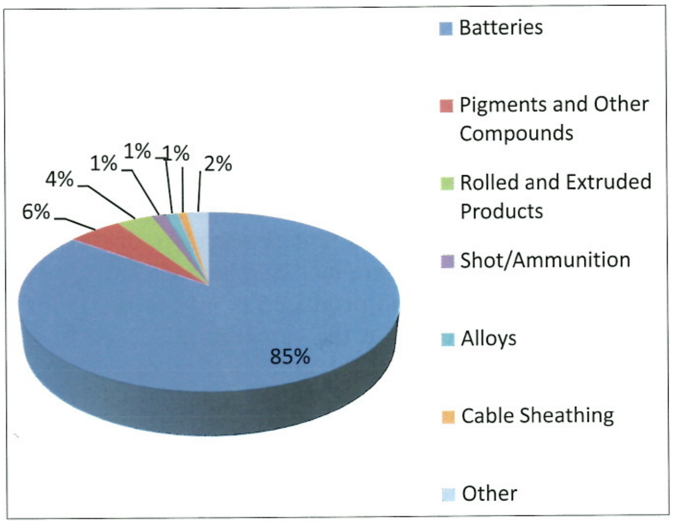

Fig. 1: Principal uses worldwide 2012

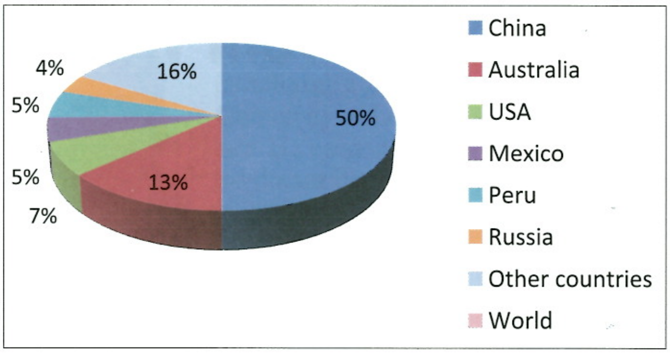

Fig. 2: World mine production of lead 2014

was reported as 10.6 mill. t. China was the world's largest producer of mined lead in 2014, with 50 % of the total world output. The second largest was Australia (13 %), followed by USA (7 %), Peru (4 %) and Mexico (4 %) (Figure 2). China was also the world's largest producer of refined lead in 2014, with 45 % of the total world Output. The second largest were the USA (11 %), followed by India (5 %) and Germany (4 %) (Figure 3) [2].

The secondary refining industry now supplies the majority of lead consumed. Lead-acid batteries are the main source of scrap for secondary refining. The secondary lead industry is characterised by a large number of smaller installations, many of which are independent. There are approximately 30 secondary smelters/refiners in the EU producing from 5000 t/a to 65,000 t/a. They recycle and refine scrap generated in their local area. The number of these refineries is decreasing as the large multinational companies, and the major battery manufacturing groups as well, acquire the smaller secondary facilities or set up their own recycling operations [3].

Umicore, Belgium produces a substantial amount of refined lead. Its capacity is 125,000 t/a. Though different grades were produced in the past, current production contains mostly 99.99 % lead [4].

Boliden, Sweden, produces lead from mines (62,000 t in 2015), lead smelters (26,000 t in 2015) and lead alloys (45,000 t in 2015) from recycled batteries in Bergsöe. Annual total production is around 70,000 t. At the Rönnskär smelter in Skelleftea, lead is extracted from concentrates from Boliden's own mines, as well as from external suppliers. The material contains minimum 99.97 % of lead and is characterized by its low content of silver and bismuth. The metal is cast into ingots weighing 42.5 kg each. At Boliden Bergsöe in Landskrona, lead is extracted and refined from scrapped batteries and other lead-containing recyclables. Bergsöe is one of Europe's largest recyclers of lead batteries. Its main products are lead and lead alloys. Approximately 60 % of the lead produced is sold to the battery industry in Europe, while the remainder is used in the manufacture of e.g. lead sheet and radiation shields [5, 6].

Lead production at Aurubis, Germany, produces refined lead in bars with a lead content of at least 99.985 % Pb. Aurubis produces 30,000 t/a of lead. The metal is employed in the production of rechargeable batteries and sheathing for deep-sea cables [7].

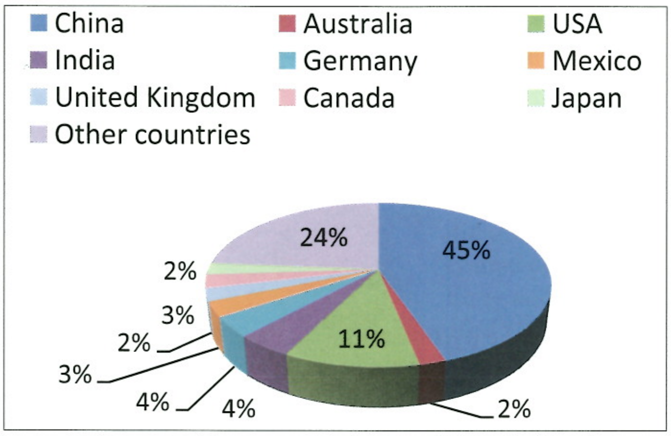

Fig. 3: World production of refined lead 2014

2 The technology of lead production

2.1 Primary lead production

There are two basic pyrometallurgical processes available for the production of lead from lead sulphide or from mixed lead and zinc sulphide concentrates: traditional sintering/smelting in a blast furnace or Imperial Smelting Furnace (ISF); and direct smelting.

Traditional two-stage process: The first stage is to remove the sulphur from the lead ore by roasting the ore in the air. The lead-bearing mineral is converted to lead oxide, and sulphur dioxide gas is released (Equation 1):

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \qquad 400\text{-}900\ °C \qquad (1)$$

The second stage is to reduce the lead oxide to metallic lead using carbon (coke) as both the reducing agent and heat source. The lead-oxide rich sinter from the first stage is placed in a blast furnace along with coke and limestone or some other flux (such as silica or iron oxide) (Equation 2).

$$2PbO + C \rightarrow 2Pb + CO_2 \qquad 900\ °C \qquad (2)$$

A variation of the traditional blast furnace is the Imperial Smelting Process. This operates in a similar way, but allows lead and zinc to be removed simultaneously, the lead in liquid form, and the zinc distilled off as vapour.

Direct smelting: The sintering stage is not carried out separately. Several processes are used for the direct smelting of lead concentrates and some secondary material to produce crude lead and slag: Ausmelt/ISASMELT sometimes in combination with blast furnaces, Kaldo (TBRC), the QSL (bath furnace) integrated processes and electric furnace (used for processing primary lead concentrates together with secondary materials). The Kivcet integrated process is also used and is a flash smelting process.

Hydrometallurgical Processes (which include electrolytic processes) are an alternative approach in obtaining and purifying metallic lead. These offer the advantage that, unlike traditional smelting operations, harmful lead fume and sulphur-containing gases are not evolved (although in modern plants, pollution control systems can reduce emissions to low levels). Hydrometallurgical methods are generally regarded by the industry as a much cleaner approach than pyrometallurgy, and may become important in the future.

The principle for all such methods is that anodes of impure lead are dissolved into an electrolyte and pure lead is deposited on the cathode. At present, this approach is not economical for primary production, except possibly in rare cases where there is a very cheap source of electricity. Electrolytic methods are sometimes used to refine lead which contains relatively small amounts of impurities [8].

2.2 Secondary lead production

Secondary production – the production of lead from scrap, rather than ore is distinct from primary production. There are many plants which are dedicated to production of only secondary lead, while other plants are designed to produce primary lead. However, the processes involved are very similar, and a number of primary production plants now take some scrap as part of their feed material, i.e. produce partly secondary lead, a trend which is likely to increase. Secondary lead can be indistinguishable from primary lead provided it is subjected to sufficient refining steps.

2.2.1 Recovery of lead from lead-acid batteries

Composition of typical lead-acid battery scrap with the content of lead is: lead (alloy) components (grid, poles, etc.) 25 to 30 wt.-%, from this Pb 96 to 98 % and Sb 2 to 4 %, Ca 0.5 %; electrode paste ($PbSO_4$, PbO, PbO_2 and Pb) 35 to 45 wt-%, from this $PbSO_4$ 60 %, PbO (PbO_2) 20 to 30 %, Pb 1 to 2 %. There are two common processes:

Blast furnace recycling process

Only compounds of lead or very crude lead mixtures (such as pastes from batteries, or oxidised lead dust and dross obtained from other operations) need to be smelted. Smelting is not required for clean scrap lead. Smelting was traditionally performed in a blast furnace in a similar way to the extraction of primary lead. The furnace is charged with lead-rich feed, metallurgical coke and possibly hard rubber battery casing [1].

This procedure was developed by the German company VARTA that makes batteries. The procedure is based on the processing of whole batteries after removal of the sul-

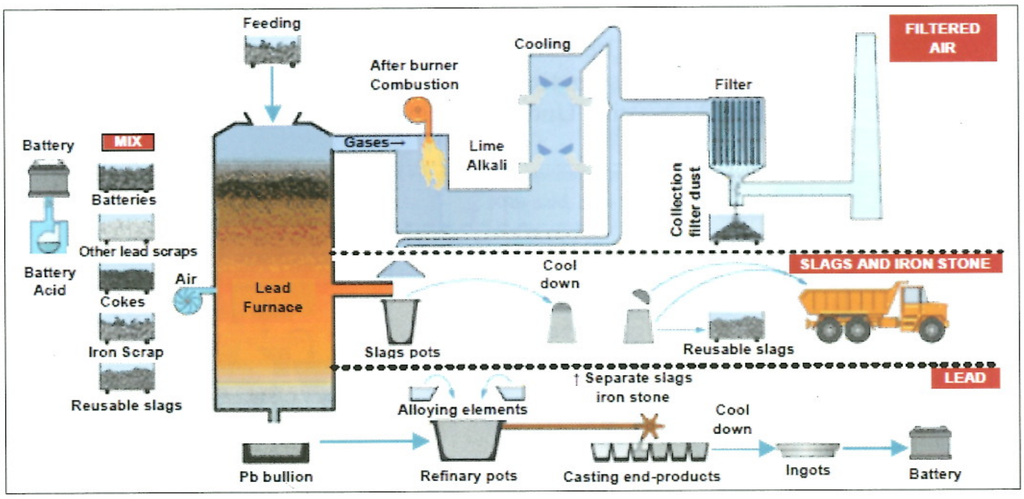

Fig. 4:
Typical shaft furnace battery recovery process [1]

Fig. 5:
A – bullion lead; B – refined lead; C – ingots: slag with matte; D – matte [10]

furic acid in the shaft furnace. This technology is used not only in Germany, Belgium, Russia, Sweden, but also in the Czech Republic. Significant producer of lead from waste in the Czech Republic applying the VARTA process is Kovohuty Přibram, Czech Republic (Figures 4 and 5) [9, 10].

Mechanical battery separation processes followed by smelting Examples of mechanical separation processes are the MA and CX (Engitec) processes (Figure 6).

The recycling process is divided into the following stages, in which there are strict quality controls for ensuring the regular course of production and achieving maximum product quality: batteries crushing, Materials sorting; high quality polypropylene, Pb < 1500 ppm, materials sorting; heavy plastics (ebonite, PVC, ABS, etc.), materials sorting; high quality materials > 96 % (poles and grids); supply of materials for furnace (lead paste, plates/grids, anthracite, iron, sodium carbonate); casting (furnace) at 1000 °C; molten lead paste for processing/refining; casting (ingots); production of lead (99.99 %) and lead alloys. The desulphurization reaction can be carried out by addition of sodium carbonate, sodium hydroxide or ammonium bicarbonate (Equations 3 and 4).

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \quad (3)$$

$$PbSO_4 + 2NaOH \rightarrow Na_2SO_4 + PbO + H_2O \quad (4)$$

2.2.2 Recovery of lead from residues and from flue-dusts from copper smelting

An example for the mentioned pyrometallurgical copper production from secondary raw materials is the company Kovohuty, Krompachy, Slovakia. Copper is smelted in a shaft furnace, converting and fire refining is the next operation of copper anode production. The resulting anode copper is electrolytically refined to cathode copper in the company Montanwerke Brixlegg AG, Austria. As by-products slag and flue dust are generated. The content of individual elements of interest is shown in Table 1. Lead is expelled at a temperature of 900 to 1000 °C in the shaft furnace in the form of PbO and $PbSO_4$ and PbS particular. Only a very small part of Pb is expelled in metallic form.

The following techniques are applied to recover lead and tin in secondary copper smelters:

- Use of a second reduction stage, where lead and also tin are reduced with steel scrap or tin cans in a TBRC process. The tin is refined by crystallisation before the second vacuum distillation stage.
- Use of flue-dust from the secondary copper converter (sometimes also from the blast furnace) as a feed material. Under reducing conditions, zinc is volatilised and

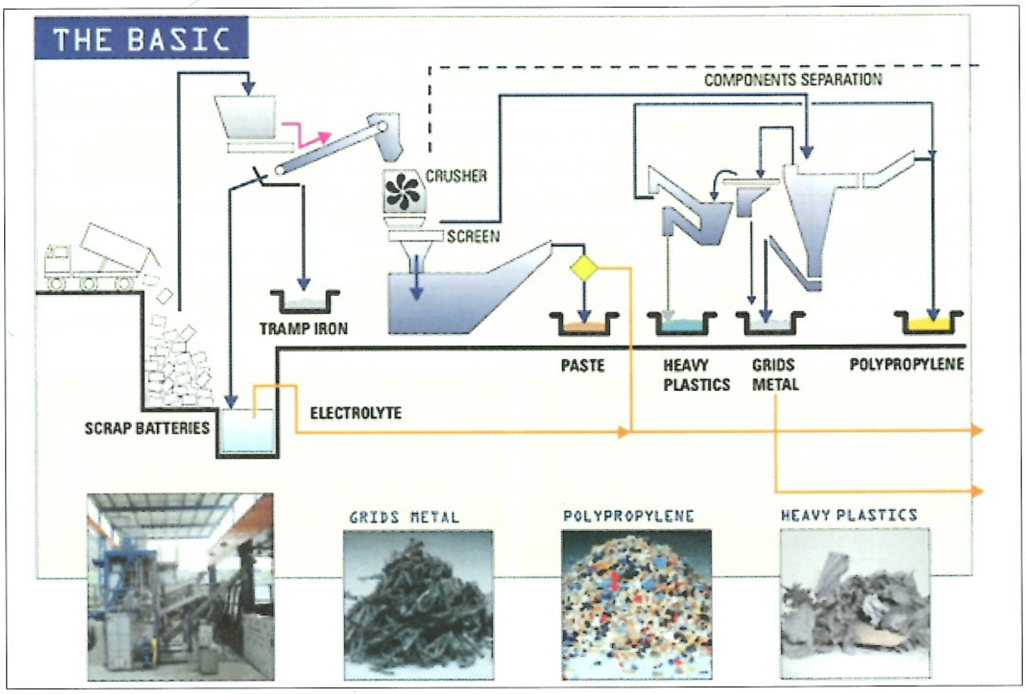

Fig. 6:
Engitec technology [11]

Table 1:
The chemical composition of by-products from secondary copper processing (Kovohuty, a.s., Krompachy, Slovakia) [wt.-%] [12]

Operation		Pb	Sn	Zn	Cu	Use
Smelting (shaft furnace)	slag	0.36-1.2	0.38-0.8	0.5-12 ZnO	0.7-1	Artificial stone for construction works
	dust	5-15	0.4-10.3	45-60	0.7-3	Production of zinc sulphate – closed at the moment
Oxidation process (converter)	slag	8-12	10-12	10-15	30-45	Recovered material to shaft furnace
	dust	4-30	2-20	45-55	0.4-1.5	As pellets to shaft furnace
Copper refining (anode furnace MAERZ)	slag	0.2	1-2	2-4	10.75	Recovered material to shaft furnace
	dust				4-20	As pellets to shaft furnace

recovered as oxide, while lead and tin are produced in the form of an alloy.

- Use of tin-lead alloy furnace technology in a multistage reduction process to produce black copper, tin-lead alloy and iron silicate slag from the KRS or TBRC converter slag.
- Use of a rotary rocking furnace to recover lead from the flue-dust from primary copper smelting.
- Use of electric furnaces for complex secondary materials such as those containing lead/copper, i.e. dusts, drosses, slags, slimes, copper alloy scrap, low-grade matte, lead/copper concentrates and other lead/copper bearing materials [1].

Multi-metal recycling with the Kayser Recycling System (KRS) is done at the Aurubis recycling center in Lünen (Figures 7 and 8). Pyrometallurgical preparation – smelting and refining – takes place in the KRS. The central operation is a submerged lance furnace (ISASMELT) which is almost 13 m high. A special feature is the use of a submerged combustion lance, which is immersed into the furnace from above and supplies the process with heating oil, oxygen and air. The reduction process is very fast in the submerged lance furnace. Charging times are short. The iron silicate sand extracted in that step of the process has a very low residual copper content. Copper, nickel, tin, lead and precious metals contained in the raw materials are enriched in an alloy with a copper content of about 80 %. In a 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. During the KRS process, zinc is enriched in the KRS oxide, a flue dust.

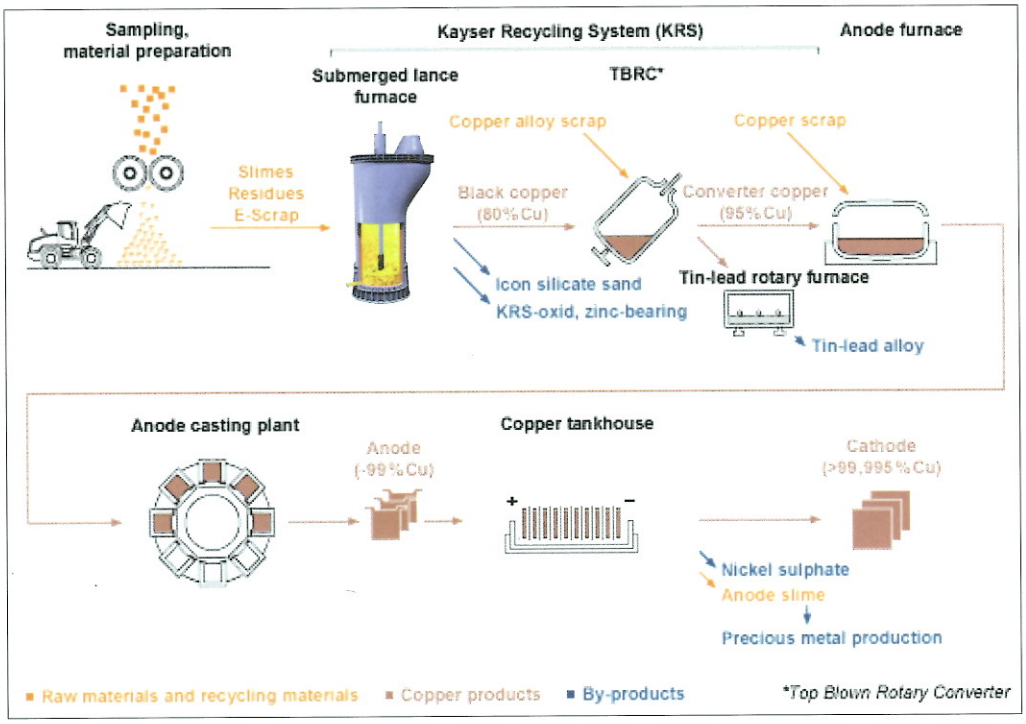

Fig. 7: Copper production at Aurubis, Lünen, Germany [14]

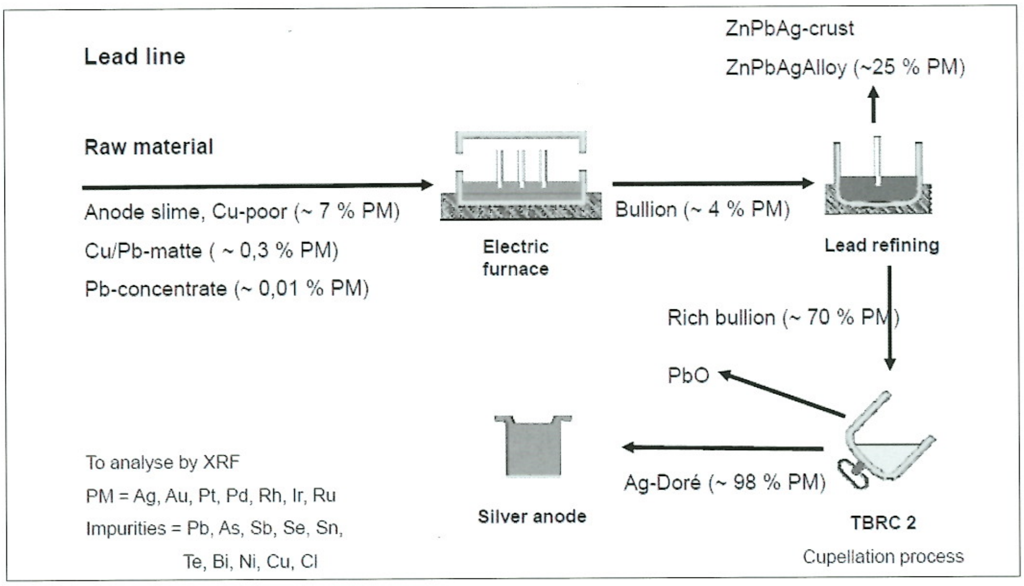

Fig. 8: Lead production at Aurubis, Lünen, Germany [15]

Copper scrap, electronic scrap and residues are used at Aurubis Hamburg. These secondary materials are processed in a modern electric furnace in various melting campaigns. The most important target is the pyrometallurgical separation of lead and copper and the enrichment of precious metals. 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

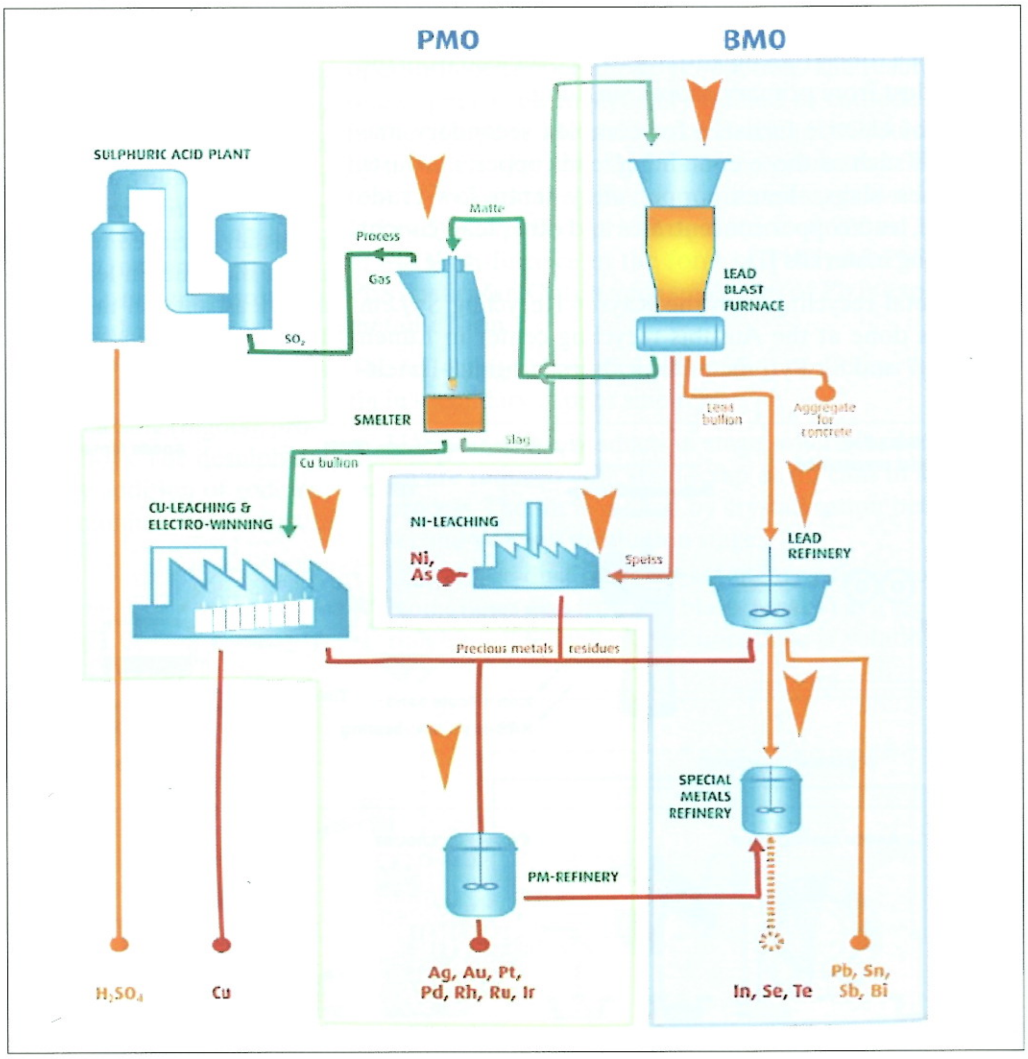

Fig. 9:
Umicore, Hoboken Belgium – Xstrata ISASMELT Technology, Lead Blast Technology [14]; Precious Metals Operations (PMO), Base Metals Operations (BMO)

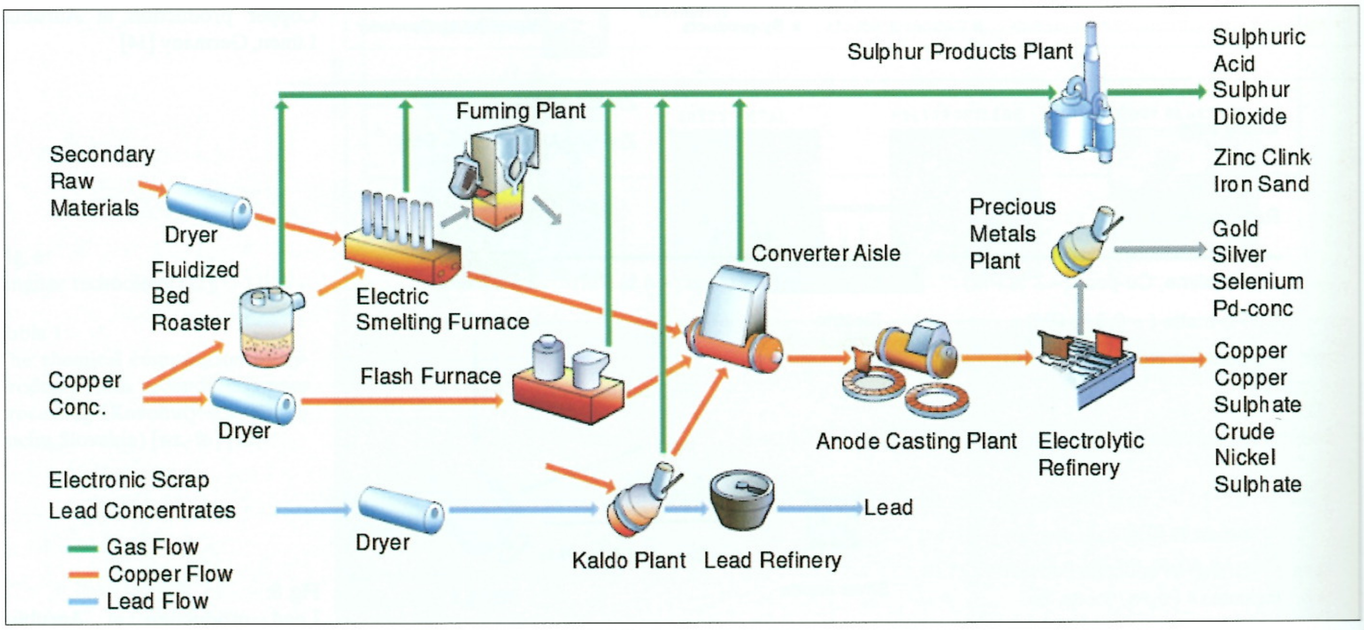

Fig. 10: Outotec Kaldo Technology at Boliden, Rönnskär, Sweden, [6]

bullion, lead-bismuth alloy, antimony concentrates and tellurium concentrates. The precious metals are fortified in a so-called rich lead, which has a precious metal content of about 70 % [13].

At Umicore there are two metals line processes: Precious Metals Operations (PMO) and Base Metals Operations (BMO) – a two-stage batch smelting and converting process. Copper matte remains in the furnace (ISASMELT) for Converting Stage. High lead slag from the furnace is a sub-product for the Base Metals Operation Plant (BMO) Converting Stage main products: converting slag remains in the ISASMELT furnace for the next cycle (Figure 9).

Boliden, Rönnskär, Sweden, – the Kaldo furnace is essentially a slightly leaning cylinder which rotates during the smelting process. The material is fed in and tapped out through the mouth of the furnace. There is no need to put any energy into the furnace: the plastic in the raw material provides sufficient energy for the smelting process (Figure 10).

2.2.3 Recovery of lead from steel scrap

One of the products from the manufacture of iron and steel is dust. The European Union currently produces mainly steel in basic oxygen furnaces (65 %) and in electric arc furnaces (35 %). The difference is mainly in zinc, as well as some heavy metals, if necessary, calcium and lead as well. Due to the high content of Fe in dust (over 30 %), this can be classified as secondary raw material. From the mineralogical study it shows that in the sample of interest most metals are present as franklinite $ZnFe_2O_4$, zincite ZnO, magnetite Fe_3O_4, calcite $CaCO_3$ and quartz SiO_2. Lead is present in phase PbO but also PbSO/$PbSO_4$ form.

The advantage of hydrometallurgical processes is their higher flexibility. Hydrometallurgical processes are also more economical because of lower capital and operating costs. In addition, hydrometallurgy offers the possibility of getting valuable metals from the dust or sludge. There are also environmental benefits in comparison with pyrometallurgy because of no problems associated with off-gases, dust nuisance and noise. However, hydrometallurgy does not offer a solution to the steelmaking waste processing by only one versatile way. The leaching methods are individual and depend not only on the type of the processed waste but on the physical, physico-chemical, chemical and mineralogical properties as well. Research in the field of hydrometallurgical processing is becoming more and more intensive. It is mainly because of the need to process complex raw materials, environmental aspects and also due to the legislative pressure for environmental protection. The content of individual elements of interest is shown in Table 2 [16-18].

Table 2: Chemical composition of dust [wt.-%]

	Fe	Zn	Pb	Ca
BOF (dust from converter)	47.7	2.74	0.18	6.8
EAF (dust from electric furnace)	29.66	18.96	1.94	4.42

For acid leaching a number of acids may be used e.g. acetic acid, sulfuric acid and others. Acid leaching is more effective than alkaline, but Fe, which dissolves causes problems for the subsequent processing of these solutions. Economically, it is appropriate to use sulfuric acid leaching. For practical reasons it is appropriate to infuse normal conditions, the lowest possible temperature and a low acid concentration, which is sufficient to dissolve the metal of interest. Preferred feature of acid leaching is the ability to use more diluted solutions. The disadvantage is that the solution passes through the portion of the iron. In the alkaline digestion are transitioning non-ferrous metals (Zn, Pb, Cd) in the solution. Iron does not pass to the solution and the solid phase remains in the leaching residue. The method for processing dusts requires the use of relatively concentrated solutions and may cause technical problems. In recent years, various industries have begun to successfully implement advanced technologies, which include technology using microwave radiation.

3 Conclusion

Lead production that is part of a complex metallurgical process to recover copper and precious metals remains unaffected. This paper described various waste containing lead and industrial waste generated in the different processes: recovery of lead from lead-acid batteries VARTA and CX (Engitec) technologies, recovery of lead from residues and from flue-dusts from copper smelting and also recovery of lead from steel scrap Xstrata ISASMELT and Outotec Kaldo Technologies. Some of these plants already meet most of the regulations in the EU Industrial Emissions Directive rules for the Best Available Techniques in the non-ferrous metals industry, which will become mandatory as of 2020.

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References

[1] Best Available Techniques (BAT) Reference (2014): Document for the Non-Ferrous Metals Industries Final Draft: 1242.

[2] Brown, T.J. et al. (2014): European Mineral Statistics. – British Geological Survey; 2010-2014: 378.

[3] International Lead Association (2012): http://www.ila-lead.org/lead-facts/lead-uses-statistics.

[4] Battery Recycling at Umicore (2016): http://www.umicore.com/en/industries/recycling/umicore-battery-recycling/.

[5] Boliden (2016): Metals for modern life. – http://www.boliden.com/Documents/Press/Publications/Metals%20for%20modern%20life/337-6514%20Metals%20for%20modern%20life%202016_EN.pdf: 32

[6] Borell, M. (2015): Rönnskär Smelter – A versatile and environmentally well adopted Non Ferrous Metal smelter. – http://www.georange.se/upl/files/111436.pdf: 41

[7] Aurubis (2016): Recycling at Aurubis. – https://www.aurubis.com/en/en/corp/products/page-recycling.

[8] Thornton, I., Rautiu, R. & Brush, S. (2001): Lead – the Facts. – http://www.ila-lead.org/UserFiles/File/factbook/chapter4.pdf: 192.

[9] Kunický, Z. & Vurm, K. (2014): 700 let stříbra a olova v Příbramsku, Kovohutě Příbram, 2011, ISBN 978-80-260-0451-6; Best Available Techniques (BAT) Reference Document for the Non-Ferrous Metals Industries, Final Draft: 1242.

[10] Trpčevská, J. & Laubertová, M. (2015): Metal waste and its treatment; ISBN 978-80-553-2365-7: 130.

[11] Lead-acid batteries complete recycling (2016); http://www.engitec.com/it/lead/.

[12] Kovohuty Krompachy, Slovakia (2014): Internal documents.

[13] Wood, J. et al. (2011): Secondary copper processing using Outotec Ausmelt TSL Technology. Conference: MetPlant 2011 Plant Design & Operating Strategies – World's Best Practice: 9.

[14] Modern, Flexible and Clean Technologies for Recovery and Recycling of Valuable Materials (2012). – 2nd International Workshop on Metals Recovery from Mining Wastes – M2R2: 37.

[15] Steffen, M. (2009): From Anode slime to silver-doré. – The LBMA Assaying & Refining, Seminar Aurubis AG, Hamburg, Germany.

[16] Havlík, T. et al. (2012): Acidic leaching of EAF steelmaking dust. – World of Metallurgy – ERZMETALL **65**, 1: 48-56.

[17] Havlík, T. et al. (2012): Leaching of zinc and iron from blast furnace dust in sulphuric acid solutions. – Metall **66**, 6: 267-270.

[18] Trpčevská, J. et al. (2010): Characterization of the bottom dross formed during batch hot-dip galvanizing and its refining. – Acta Metallurgica Slovaca. Roč. 2010, č. 3: 151-156.

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