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COMBINED METAL AND SLAG VALORISATION AT METALLO-CHIMIQUE

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Introduction

The Company

Metallo-Chimique NV is a part of the Metallum Holdings Group, which is active in trading, pre-treatment and recycling of complex scrap materials. The entity Metallum Group AG specialises in trading, warehousing and separation of ferrous and non-ferrous metals. It has divisions operating in Switzerland, Belgium, Spain and Hong Kong. The metallurgical operations of the Group are located in Beerse, Belgium (Metallo-Chimique NV) and Berango, Spain (Elmet s.l.u.).

The past five years saw significant investments in the Beerse plant, aimed at increasing capacity and metal recovery, while keeping a good environmental performance. The Metallo workforce in Beerse has grown consequently from 280 (in 2006) to over 400 (in 2014), despite the 2008-2009 crisis climate.

Figure 1: Aerial view of the Metallo-Chimque plant in Beerse

The Raw Materials

Metallo purchases mainly copper and tin bearing raw materials, around 400 000 tonnes per year. Non-ferrous metals are recovered and refined, either as pure metal (copper, tin, nickel, lead) or a valuable concentrate (zinc, antimony, precious metals). Metallo treats only secondary materials: intermediates and by-products of other non-ferrous companies and scrap from the consumer market:

- Scrap copper wire from copper wire production
- Electrical cabling from house demolition
- Electrical motors from household appliances
- Slags and sludges from messing and bronze smelting
- Slags from copper refining
- Scrap bronze from pumps, ships, sanitary conducts
- Tin foils from food canning industry
- Tin scrap from cans,
- Solder alloys from other refiners
- Metal fraction of electronic scrap (tin solder, copper, aluminium)

Figure 2: Typical raw materials as delivered for recycling. Tin ash and copper filtration residue (top left), bronze scrap (top right), mixed copper scrap (bottom left), copper refining slags (bottom right)

As can be seen in Figure 2, these raw materials come in very different shapes and sizes. Metallo is able to treat very fine materials, such as dry powders or wet sludges, as well as lumpy bigger sized materials such as slags or pump housings.

Mostly, the raw materials are metallic or oxidic. Sulphidic materials are not actively prospected, due to the limited scrubbing capacity for sulphur dioxide (SO2).

In copper and tin scrap, other metals such as lead, nickel and zinc are commonly present. They are often found as alloying element, or as a fine coating on copper or tin. These strongly intermixed metals cannot be separated any more by physical separation techniques, such as density, eddie current or magnetic separation. Chemical separation, mostly with pyrometallurgical techniques, is the preferred option.

Consumer products continuously evolve, also in chemical composition. Product performance is often improved by small additions, making the recycling a bit more challenging. For the recycler, this means continuous adaptation to his changing environment As an example, the ban on lead (for health reasons) has led to the development of bismuth-copper alloys. Bismuth however, is detrimental in the copper wire production, as it causes wires to break. So on one side, bismuth alloys are brought in for recycling, on the other side the product should be free of bismuth, which is almost impossible to remove from copper[1].

The increasing complexity of the scrap also challenges the chemical analytical techniques. Metals in alloys can interfere with each other and the use of different analytical techniques is often needed for one material. Impurities must be identified to optimise the treatment in the plant. Those factors have led to the investment in a new analytical laboratory (2014), located in next to the raw material storage.

Figure 3: New analytical lab (2014) located next to raw materials storage area

The Zero-Waste Recycling Process

To refine increasingly complex scrap, a complex flow sheet was gradually developed. It's not a straight line from scrap to pure metal, but many intermediates circulate from one furnace to another, from one department to another, to finally yield the desired products. Figure 4 is a simplified schematic of the metallurgical process.

Low-grade copper scrap is first treated in the Metallo or Elmet smelter. These versatile smelters can take many types of raw materials, from powder to lumps, wet or dry. The smelting process is carried out at 1200°C. At this temperature, water and other volatile elements are evaporated, while metal and slag are fully liquid. The liquid phases are immiscible and separate in two layers: slag on top, metal in the bottom of the furnace. The slag is called the copper smelting slag and the metal is black copper. Black copper is a 80% copper alloy with lead, tin and nickel as main alloying elements.

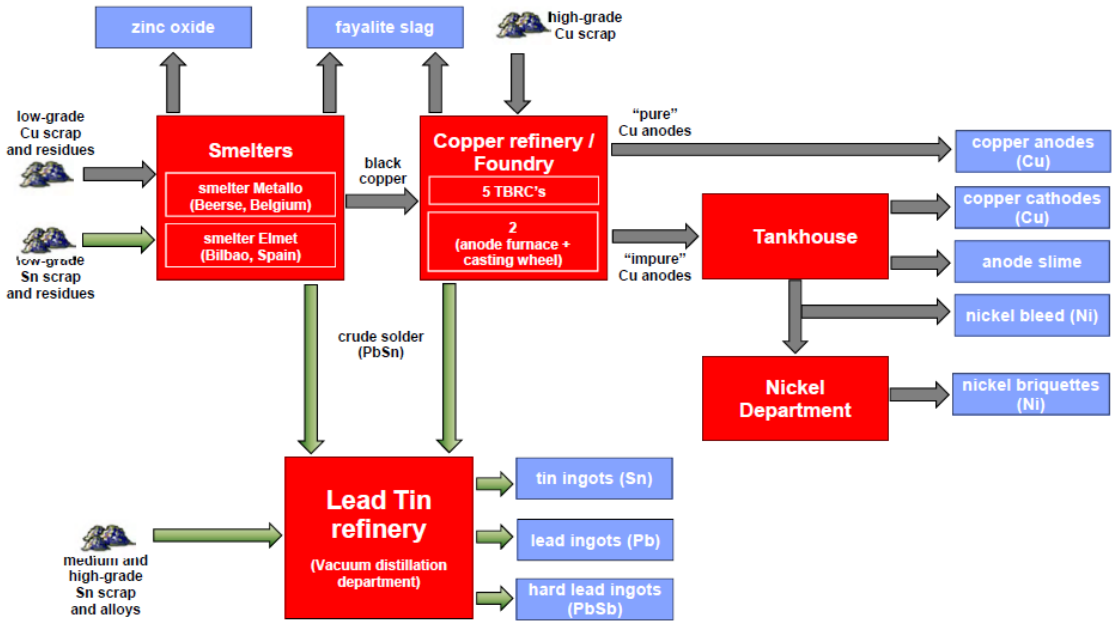

Figure 4: Metallo flow sheet, displaying inputs (black), outputs (blue) and production departments (red)

The Elmet smelter treats also low-grade lead-tin scrap to produce a crude solder. Crude solder is a 70% lead alloy with tin and copper as main alloying elements.
The black copper, together with high-grade copper scrap and low-grade tin scrap are fed to the Foundry. In this section, 5 TBRC furnaces co-operate to obtain the best possible separation of the metals of interest to Metallo. Top-Blown Rotary Converters are tiltable, rotating furnaces working typically around 1200°C. The heat is provided by an inserted burner. The rotation movement provides excellent mixing, which considerably reduces the reaction times between the slag, metal and additives in the furnace.

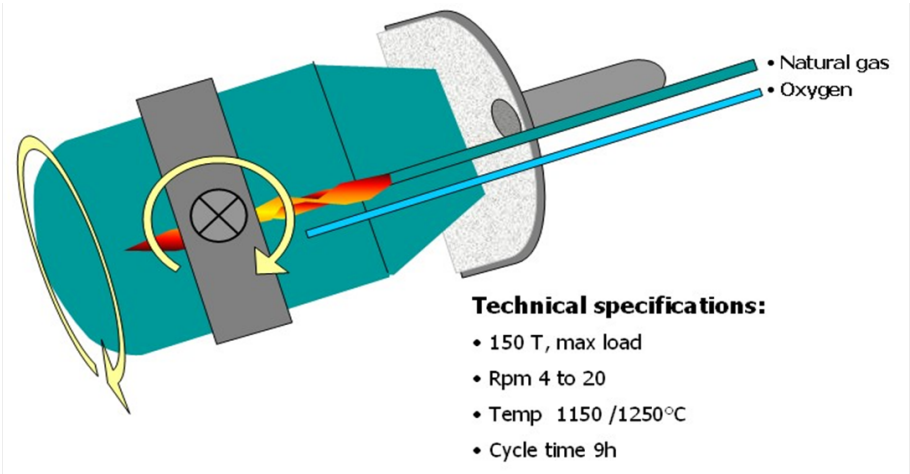

Figure 5: Working principle of TBRC furnace (Top-Blown Rotary Converter)

Copper is refined to anode quality and cast in anodes (99.3% Cu) for sale. Lead and tin are collected in a crude solder intermediate for the Lead-Tin refinery. Nickel is concentrated in impure copper anodes, for further treatment in the Tankhouse. Every furnace is equipped with a separate gas treatment section, consisting of afterburning, gas cooling, dust filters and if needed SO2 or dioxin captation.

The refining process in the Tankhouse is called electrolysis. An electrical potential difference is applied between anode and cathode, which are submerged in an electrolyte. Copper from the anode dissolves in the electrolyte and the copper ions are deposited as pure copper on a cathode. It takes 3 weeks to dissolve an anode, while the cathodes are “harvested” every week (see Figure 6).

Figure 6: Harvesting the copper cathodes from the electrolyte bath (principle)[2]

Impurities in the anode are not deposited and remain in the electrolyte (nickel) or as an inert sludge (precious metals). The process is specifically designed for the purification of impure copper anodes and the recovery of nickel in the electrolyte.
Grade B copper cathodes are produced, and the nickel is collected in the bleed solution. This bleed solution can be sold or used in the Nickel refinery to produce nickel briquettes, suitable for the production of stainless steel. The inert sludge, called “anode slime” is sold for further treatment in a precious metals refining plant.
The Lead-Tin refinery realises the separation between tin and lead-antimony. The applied processes here are smelting and refining in kettles and distillation in vacuum furnaces. Many different refining processes are needed to achieve end products of

desired purity. In the end, ultra-pure tin (>99.9%) is produced, as well as pure lead and lead-antimony alloys.

The Metallo process characterized by its “zero-waste” approach: no waste product from the production process has to be disposed of. Exhaust gases are cooled and purified. The generated filter dusts are recycled back to the process, or sold for their Zn content. Waste waters are cleaned and the resulting residue is re-used in the smelting process. The SO2 scrubber produces sulphuric acid, which is applied further in the Tankhouse.

The Products

Metallo is an important secondary copper producer and Europe’s largest tin producer. Other metals, commonly associated with tin and copper, are also valorised. The main products are listed here and displayed in Figure 7.

- Copper anodes (120 000 tonnes per year): sold for further refining in the customer’s tankhouse, to produce cathode quality copper.
- Copper cathodes (25 000 tonnes per year):
- Nickel (1000 tonnes per year): briquettes are used for the production of stainless steel, while the bleed is used by our customers to produce pure nickel sulphate.
- Tin (12 000 tonnes per year): Metallo’s electronic grade tin is of the highest quality. It is also particularly interesting for its low lead content and low alpha radiation, compared to primary tin from mining operations.
- Lead and lead-antimony (25 000 tonnes per year): mainly applied for the production of lead-acid batteries: the pure lead in the paste, the lead-antimony alloy for grids and connectors.

In quantity however, the most important product is copper smelting slag, commercialised as Metamix®. Metallo yearly produces 160 000 tonnes of this iron silicate (fayalite) slag, as a by-product. It comes in granules of about 1 mm, and consists mainly of inert oxides of silicon, calcium, aluminium and iron. This makes this slag very suitable for construction applications (sand replacement) and sand blasting applications. It’s sold for these applications at a (small) positive value. The content of copper, lead, tin and nickel added up is below 1%. From a metal recovery perspective, this slag is “depleted”: further refining would be uneconomical.

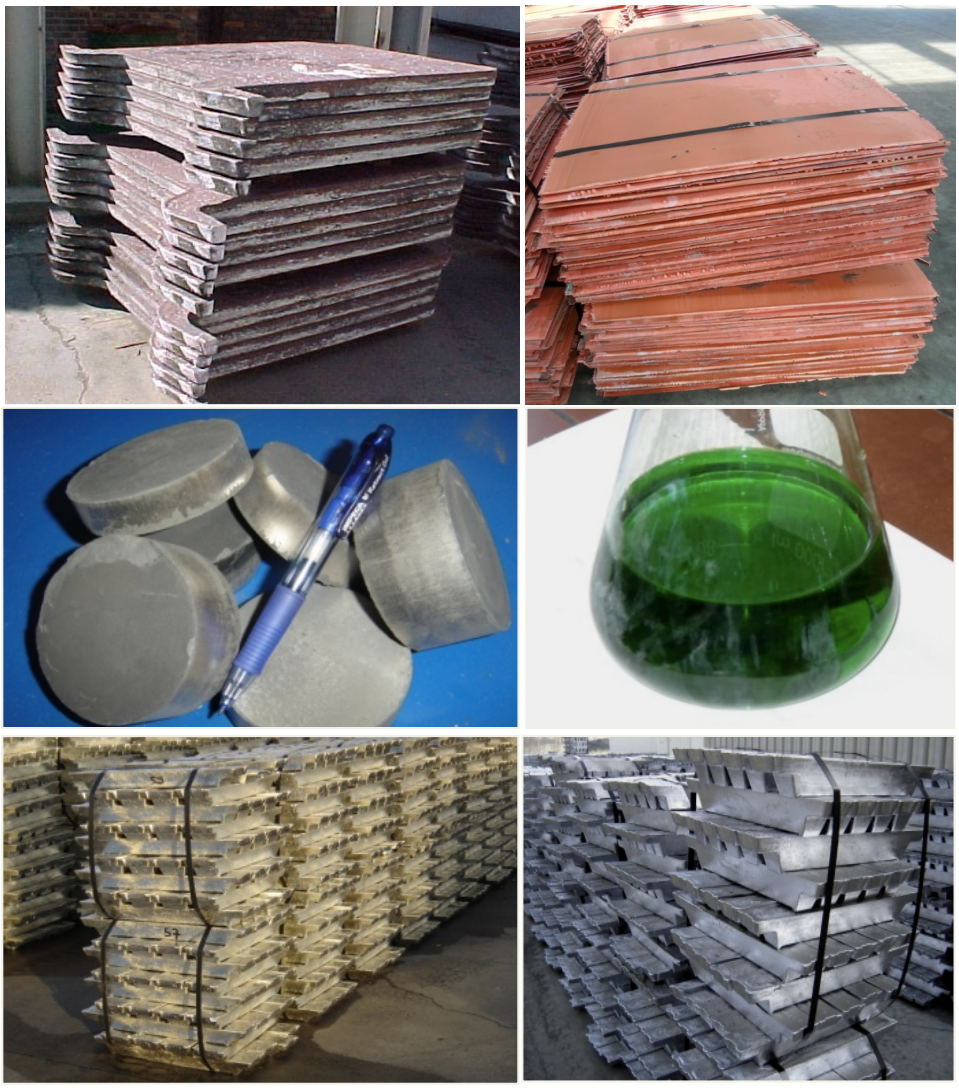

Figure 7: main products sold by Metallo: copper anodes (top left), copper cathodes (top right), nickel briquettes (middle left), nickel bleed (middle right), pure tin ingots (bottom left), lead-antimony ingots (bottom right)

In recent years, better valorisation options have been technically developed, as is demonstrated in the various Slag Valorisation Symposia. Non-ferrous slag is becoming more than an inert residue for replacement of natural sand or rock. It can be used as a material with interesting technical properties, for example as a binder for construction materials. This evolution could influence the metallurgical flow sheet and trigger the metal recycler to refine his by-product even further, yielding better overall recycling rate and a cleaner by-product.

Slag valorisation: a necessity for better metal valorisation

Classic scheme in the metal recycling industry: metal valorisation

In the metal recycling industry, metals are the only focus. This can be understood by looking at the value of most non-ferrous metals (see Table 1).

Table 1: LME (metals stock exchange) prices in January 2015

Metal	Price ($/tonne)
Copper	5 600
Tin	19 600
Nickel	14 500
Lead	1 850
Zinc	2 200
Silver (non-LME)	550 000

Price fluctuations and metal recovery rate greatly influence the revenue from a metal recycling operation. If a plant recycles 100 000 tonnes of copper per year, 1% increase in recovery rate yields 5.6 million dollars additional revenue. For metals such as tin and nickel the effect is even bigger.

This explains why in metal industry the main focus has always been on maximising and monitoring the recovery of metals. A slag, once depleted from metals, cannot generate the same order of revenues.

The role of zinc oxide in the slag

The Metamix® contains 4-6% of zinc oxide. This oxide is inert in normal conditions, but could be leached out in acid leaching conditions. In the long term, the leach stability of the slag could limit valorisation options. Reduction of the zinc content in the slag to around 1% would be beneficial for future valorisation.

Extraction of zinc from the slag would allow the refiner to sell a concentrated zinc product. Considering the value of zinc, around $ 2 200 per tonne (January 2015), this concentrate could be sold at a positive value.

Business model for zinc extraction from the slag

Further refining of the slag could add value in 2 ways:
- Selling of a zinc concentrate
- More value for ultra-clean slag

This value needs to pay for the extra processing cost. The common pyrometallurgical process for zinc recovery is the fuming process: slag is smelted at 1200°C (or even higher), with addition of a reducing agent (coke, gas, fuel). Zinc oxide is reduced to Zn(g), which evaporates from the slag and is collected as zinc oxide in the off-gas.
Typical features of the fuming process are: high energy demand for evaporation and reduction, high investment costs.

Metallo recently announced an investment of 36 million Euro to build a new installation for the further cleaning of the end slag: “The additional treatment will reduce the remaining metals in the slag to minimal levels, leading to an environmentally very attractive product. This will enlarge the field of applications, with a positive impact on the marketing possibilities and the value. The metals that are recovered will be valorized and brought back to the maximum in the value chain.” [3]

New scheme for low-grade materials: combined metal and slag valorisation

In this environment of high operational costs (energy) and capital investments (gas cleaning), the metal value is not enough to justify the investment. The “recoverable” metal content in Metamix® is simply too low. At this low metal content, the value of the remaining 95% of the slag can be more relevant. For the first time, the metal content of a product is not the only determining factor in the value chain.

Due to the low metal grade of the slag, adding value to the by-product has more impact in the business case than recovering more metals. The slag fuming practice could become the first operation designed to improve a slag product rather than recover more metals.

Ultra-clean slag: the new star product for metal recyclers?

High metal prices have always justified a single focus on metal value recovery. Investments in equipment and process development have always been aimed at improving metal recovery rates. Today, these rates are already very high, especially for the more valuable metals such as copper, nickel and tin.

When less valuable metals are present at lower concentrations, processing and investment costs are no longer covered by the difference between metal sales value ad purchasing cost. The value of the by-product starts to become significant in the business model for better metal valorisation. For less valuable metals, it is vital to increase the value of the slag to justify investments.

Metallo-Chimique is active in developing technical applications for clean slag. Given the importance of slag, the process can be changed to make a better final product. This way, slag is no longer an inert residue, but becomes a technical material with an intrinsic higher value. Of course, this better product should lead to better market value. That will probably be the biggest challenge, before we can say that slag becomes a product which deserves the same attention as today's star products: valuable metals.

Metallo-Chimique wants to tackle this challenge and –in partnership with other stakeholders- make slag valorisation a real added value for metal recycling. Metallo believes that slag valorisation will help to complete the material cycle and realise a more sustainable society.

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