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# PROPOSAL FOR IMPROVEMENT OF CURRENT TECHNOLOGY OF PROCESSING OXIDE ASHES

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**Abstract:** This paper presents a study on the current technological flow of the copper oxidic ash processing from both economically and technologically points of view, which brings major improvements compared to the classical technology. The material balances made at 1 ton of crude brass/bronze slag, show a casting of ingoted and refined metal with standard brand characteristics of approximately 570 kg of metal. Otherwise, without the separate manual materials, it is found that around 500 kg of dust is a waste that usually drops out of brass or bronze dross.
**Keywords:** oxidic ash, copper, technological flow, melting

## 1. INTRODUCTION

The increasing demand of zinc and copper in the world has required intensive studies for the recovery and extraction of these metals from different sources. [1,5,8,9]

Copper slag is a byproduct of the pyro-metallurgical smelting of copper concentrate.[2,6,7] Trade in internationally recycled resources emerged as a result of local costs of separating product materials and resource growth at a rapid pace in countries such as India and China, with the result leading to a geopolitical strategic recycling problem. [3] The amount of electronic waste produced today is very high and has increased in a rather short time. Several studies have been recently carried out concerning the use of ammonia as an infiltration agent in solid Cu waste. [4, 6] Copper recycling also includes copper recovery from residual processes such as slag, dust or sludge. Copper melting slags typically contain between 1.5 and 8% copper, depending on the process used. Piro and hydrometallurgical methods have been proposed for the treatment of dust and the recovery of precious metals.[10] Copper production technologies can be classified into pyro-metallurgical and hydrometallurgical technologies. The application of technology depends on the country's energy and raw materials resources. In table 1 are presented the heavy copper, brass and bronze wastes and the source of the equipment they come from.

Table 1. Heavy copper, brass and bronze wastes and the source of the equipment they come from [7]

| Class | Details |
|---|---|
| A mixture of brass and bronze | This class includes assorted clean brass and solid bronzes |
| Radiators (pure) / Auto | This includes car radiators made up of a mixture of brass, copper and iron. Does not include aluminum radiators. The usual composition is 70% copper, 3-3.5% tin, 7-8% lead and 10-11% zinc. |
| Radiators (impure) Auto | Includes copper and brass metal radiators. Does not include iron or aluminum elements. |
| Heating radiators | It includes copper and pure brass heating radiators. |
| Bronze aluminum bodies | It may comprise a solid aluminum bronze alloy with a typical analysis of 78-90% copper, 1-5% iron, and 8.5-11.5% aluminum and may include up to 5% nickel. |
| Solid manganese bronze bodies | It includes manganese and bronze alloy wastes containing at least 55% copper and maximum 1% lead. |
| Brass / Wire | This class includes brass wire nodules from shredding operations. |
| Insulating wire / Brass | Brass insulating wire consisting of brass plastic wire. |
| Connectors / Wire | Includes covered or uncovered plates of electrical cable connectors. |
| Iron Bronzes and Brass | Includes solid bronze and brass with a maximum of 10% iron. |
| Other categories of brass and bronze | Includes bronze and brass materials, which are not included in other categories. |

Modern technologies for processing oxide ash are optimized by reducing fuel consumption, using oxygen-enriched air or technical oxygen, reducing aggregates in the process stream, recycling and recovering all intermediate products, and introducing a high degree of mechanization and automation. [5,11] Hydrometallurgical processes currently provide about 25% of the world's copper production from mining raw material processing and are mainly applied to oxide ores and less sulphurous ores. The main technological phases are: preparation of raw materials (crushing, milling or preparation of mine holes, settlement of pits or piles, etc.), solubilisation, purification of solutions or their concentration by extraction with organic solvents and extraction of copper from solutions by cementation, electrolytic extraction or reduction from solution.

## 2. MATERIALS AND METHODS

An important achievement with regard to metal recycling is that it represents a succession of technological processing steps. If a certain stage is not performed correctly, the efficiency of the whole process decreases. [7,8,13] Valuable metals like copper, zinc and lead have been successfully recovered from brass melting slag by applying hydrometallurgical treatments. [14]

The recovery line of Cu, brass and bronze in the dross, consists of the following installations:

1. primary processing plant of oxidic wastes by grinding in Pontzen mills
2. primary machining plant for copper turning, INTAL type
3. primary treatment plant for copper waste in pieces
4. melting plant
5. refining plant
6. casting machine with inclined tape

The technology applied here differs from the classical technology by the presence of the following elements:

- using the ash dryer;
- introduction of manual separation;
- using the flame fixed crucible;
- using the slag mixing system with metal bath.

The benefits of current technology are:

- obtaining a molten Cu-Zn alloy containing Fe, Al, Mn, Pb, Sb, Sn, as low as possible in the final phase of the preparation and before refining;
- fully recovering molten metal losses into slag and recycling of slag and reduction of Zn losses in gas during development;
- elaboration of metal with a specific fuel consumption as low as possible and without combustion products contaminating the composition of metal batch or slag;

Stages of the classic process of processing copper oxide are represented by:

- direct grinding in the Pontzen ball mill and dust separation;
- melting raw material in a rotary kiln with capacity of 30-50 t (fuel used fuel oil, light liquid fuel or $CH_4$);
- melting the slag resulting from the batch (12-45%) and the exhaust with a metal content of 12-20%;

This process has the advantage that productivity of the oven is very high 35-40 t/h with the duration of a batch being 18-20 hours, and the disadvantages that the refining of the material is cumbersome due to the poor mixture of slag and metal bath and an alloy with a high impurity content of more than 3.5% being obtained, which makes its use very restricted, also, Zn losses by evaporation are very high 3-7% of the total Zn content of the batch and fuel consumption is high 90-100 l fuel / t metal or 120-140 m$^3$ $CH_4$ / t m.

The equipment used in the metallurgical process flow of the slag brasses are:

1. Fraction separation screen> 80 mm.
2. Pontzen ball mill.
3. Air intake system
4. Tubular furnace for drying oxidic ash
5. Magnetic separator of drum type

In the following, it will be presented a way to minimize the losses in the classic technological flow of oxidic ash processing, by using sulfuric acid. The optimized technological flow proposed is presented below: the equipment and the technology for obtaining the copper oxide powder through the hydrometallurgical processing of copper ashes, as well as the regeneration of the sulfuric acid involved in the process. The technological flow is shown in Figure 1. The technological flow and the necessary equipment to obtain the copper oxide powder through the hydrometallurgical process and the sulfuric acid recovery part for its reuse in the industrial process have been established.

Table 2. General data of the technological flow

| | |
|---|---|
| Productivity | 650 kg/month |
| | 65 kg/cycle |
| Number of cycles | 10 cycles /month |
| Solution of dissolution | Solution of sulfuric acid, 15% mass concentration, solution / solid ratio - 4/1 |
| First matter | Oxidic-ash - copper or brass slag |
| The composition of usual copper slags derived from brass charge | CuO: 25-45 % |
| | ZnO: 5-35 % |
| | $SiO_2$: 2-15 % |
| | $Fe_3O_4$: 5-10 % |
| | $Al_2O_3$: 0,5-2 % |
| | Grain of copper ash : 95 % < 1,2 mm |
| | Density :2,5 – 2,7 kg/dm$^3$ |

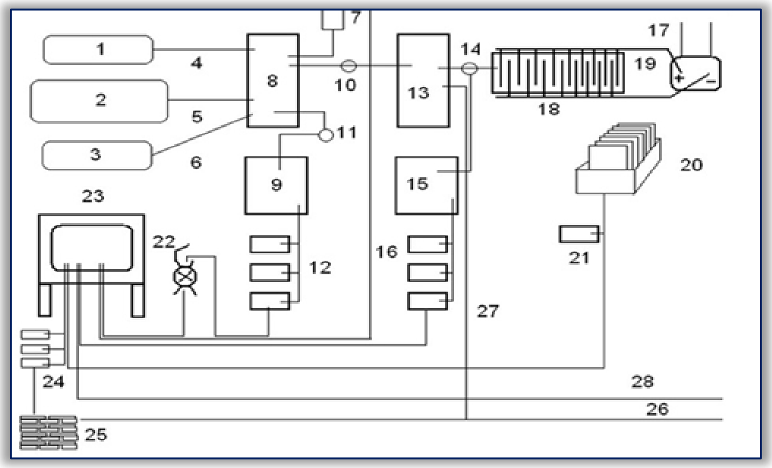


Figure 1. Main elements of the working technology involved in the technological flow
1. Sulfuric acid tank with 40% concentration; 2. Residual solution reservoir of $H_2SO_4$ - $ZnSO_4$ -$H_2O$; 3. Washing water tank; 4. Sulfuric acid feed path; 5. Recirculated -regenerated feed path; 6. Route for washing water; 7. Ash tank with feed path - helical conveyor; 8. Sulfuric acid ash pool and suspension agitation systems; 9. Stage III water storage tank; 10. A transfer system of $CuSO_4$- $ZnSO_4$-$H_2O$ solution with a liquid pump; 11. Reaction ash transfer system and wash water in the settling tank 9; 12. Steel trays for storage and drying of ash decanted with moisture of about 25 - 30%; 13. Reaction tank of the $CuSO_4$ - $ZnSO_4$ - $H_2O$ solution for the production and decantation of copper dust; 14. $ZnSO_4$-$H_2O$ solution transfer system; 15. In the washing water storage tank; 16. Steel trays for storage of wet copper powder; 17. DC power supply for supplying the electrolysis battery with a dimensioned current characteristic to provide an anode-cathode voltage of 3 - 5 V and a current density of about 8 - 10 A / $dm^2$; 18. Anode cathode electrode battery - aluminum cathode - stainless steel 3 mm; 19. Fitted on copper bars with a section to ensure a current density of max 5 A / $mm^2$; 20. Storage and washing of stainless steel cathodes with Zn deposit; 21. Stainless steel tray for fixing Zn stainless steel cathodes during melting; 22. Disintegration mill of reacted and dried copper ash; 23. A room-type furnace with electrical resistance for reacted copper ash drying functions, drying and / or oxidation of copper powder, Zn smelting on stainless steel cathodes; 24. Ceramic or graphite forms for casting Zn ingots; 25. Zinc ingot storage; 26. Delivery of Zn ingot for direct capitalization; 27. Zn splinters recirculation for the Cu powder reaction; 28. Route of copper or copper oxide displacement after the oxidation treatment in the electric furnace 23.


Figure 2. DC power supply for electrolysis supply of $ZnSO_4$ solution for metal zinc extraction


Figure 3. Sulfuric acid tanks and electrolyte waste solution intended for the solubilization of brass dross


Figure 4. Electrolysis battery with 5 PbSb anodes and 4 stainless steel cathodes with dimensions: 4.5 x 2.8 dm for the Zn extraction from the $ZnSO_4$ solution


Figure 5. Screw feeder for fractional introduction of brass dross into the acidic solution for solubilization

Figure 6 shows the overall image of the brass dross processing section on metallic precipitation solubilization - electrolysis sequences for metallic Zn extraction with a production capacity:

- 750 kg / month Cu powder
- 550 kg / month Electrolytic metal Zn
- 3200 kg / month brass powder

## 3. RESULTS AND DISCUSSIONS

It is necessary to make a set of experiments, to determine the optimum conditions. One of the problems commonly encountered in ash solubilization is of the presence of a fairly large amount of CuO and ZnO, which does not react with sulfuric acid, although the solubilization reaction is at equilibrium. There is also a large amount of unreached $H_2SO_4$ in the solution. On an industrial scale, this causes a major disadvantage, because it reduces the yield of the extraction process, which produces an extra recirculation of quantities of solutions and materials. If the concentration of the precipitate is not controlled, there is a risk of throwing large amounts of CuO and ZnO into the waste slurry.


Figure 6. Overview of the brass dross processing section on the solubilization - metal precipitation - electrolysis sequences for the metallic Zn extraction

Although in the industrial practice the hot solubilization process is used at 60-70°C, it is considered to be a very large financial effort in the case of the solubilization of large quantities of materials. Configuring the structure and capacity of a production unit for the processing of brass and bronze scrap is mainly based on setting the minimum production level to cover non-profit-generating expenses called the breakeven. This level allows the determination of the minimum output for which all expenses can be covered. Under this level, the activity is bankrupt and generates losses continuously. Above the calculated minimum, it works with profit generation. In table 3, it is represented brass ingot evaluation costs.

Table 3. Brass ingot evaluation costs

| Cost | Brass ingot cost / 1 ton of slag brick | | | Brass ingot cost (Dust Additive, Electrolytic Zn) / 1 ton of slag brick | | |
|---|---|---|---|---|---|---|
| | Quantity Kg | Price €/ UM | Costs € | Quantity | Price €/ UM | Costs € |
| Slag brass /bronze | 1000 | 550 | 550 | 1000 | 550 | 550 |
| Zn r1 for alloying | 22 | 1850 | 40,7 | 22 | 1850 | 40,7 |
| Comb. CLU 3 | 34.3 | 600 | 21 | 34.3 | 600 | 21 |
| Refining stream | 8,8 | 1200 | 10.56 | 8,8 | 1200 | 10.56 |
| Electricity | 22 | 75 | 1.7 | 22 | 75 | 1.7 |
| Transport | | | 40 | | | 40 |
| Used ingots | | | 27,5 | | | 27,5 |
| Refractory materials | | | 15 | | | 15 |
| Workmanship | | | 45.1 | | | 45.1 |
| | Total | | 751.8 | Total | | 751.8 |
| Administration 20% | | | 150 | | | |
| | Total | | 901.2 | | | |
| Sulfuric acid | | | | 0.33 | 800 | 264 |
| Electricity | | | | 210 | 75 | 18 |
| Stainless steel cathodes | | | | | | 20 |
| | | | | | | 15.2 |
| Transport | | | | | | 36.2 |
| Workmanship | | | | Total | | 1105.2 |
| Administration 20 % | | | | | | 221 |
| Brass poured into ingot | 440 | 3000 | 1320 | 440 | | 3000 |
| Cu dust | | | | 41 | | 5500 |
| Brass dust | | | | 310 | | 3000 |
| Electrolytic Zn | | | | 60 | | 1850 |
| Total income | | | 1320 | | | 2586 |
| Gross profit | | | 419 | | | 1260 |

In figure 7, it is represented the Gant diagram, for the entire flow of brass dross processing on the solubilization – Cu- electrolysis precipitation phases, which is related to the technological flow, shown previously in figure 1.

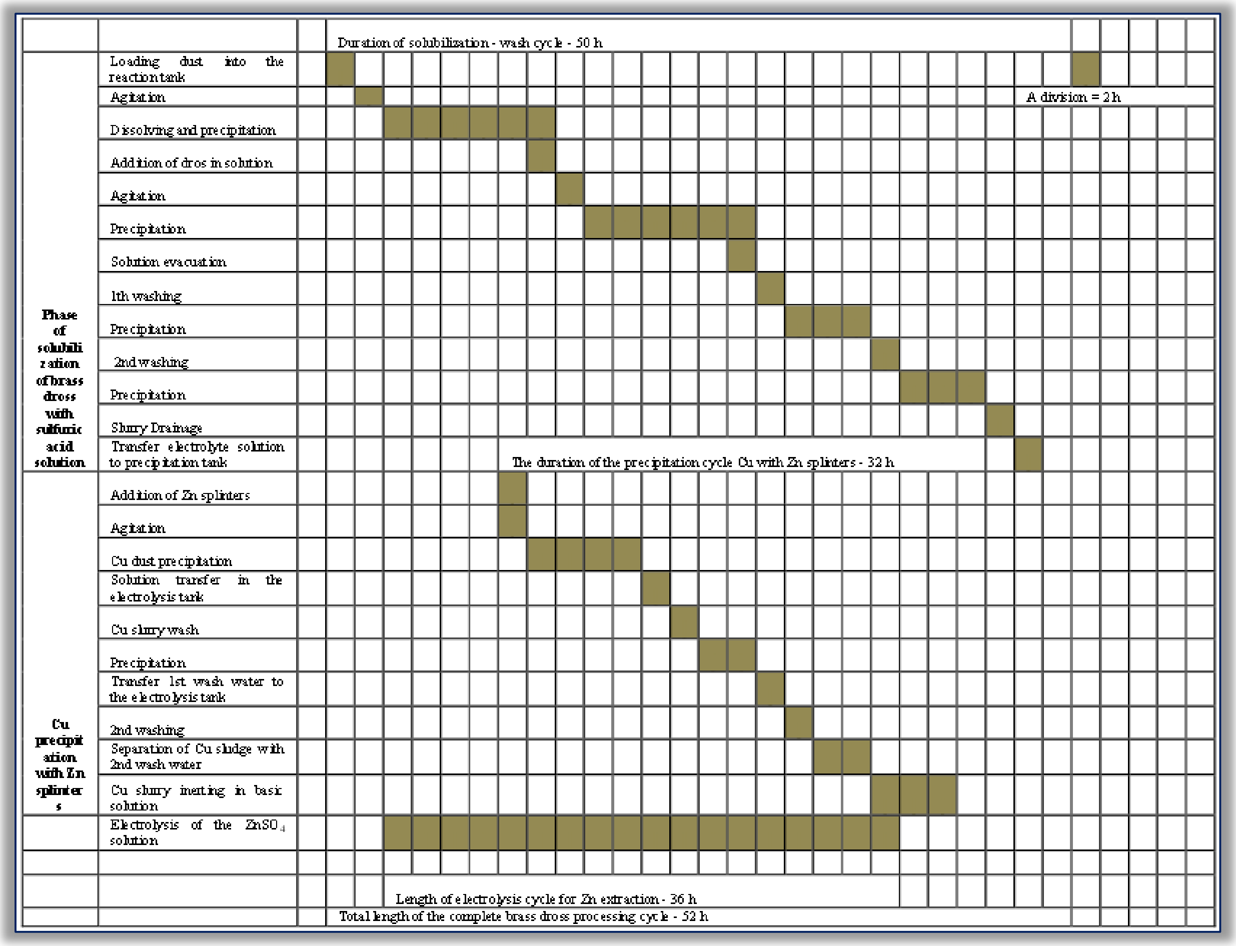


Figure7. Operation diagram for the entire flow of brass dross processing on the solubilization – Cu- electrolysis precipitation phases

## 4. CONCLUSIONS

The paper presented a synthesis of a study on the current technological flow of the copper oxidic ash processing from both economically and technologically points of view, which brings major improvements compared to the classical technology. The processing of the raw brass / bronze slag by mechanical extraction of the metallic fraction, melting and casting it into ingot can be done with a profit of approx. 420 €/t slag processed under the consumption and labor conditions specified in the above data. The application of this technology shows that effective metal removal is only 44% and results in a significant amount of waste - brass / bronze dross that is normally discarded or has a lower use without the recovery of useful metals still present therein. Thus, 570 kg of material is lost, but the most important aspect is that the presence of heavy metals in both oxide and metallic conditions results in hazardous waste material. The presence of ZnO and CuO, PbO, may interact with acid rains, pollutes the soil, have high potential to penetrate the soil and reach groundwater and therefore their storage is not recommended.

It has been shown that, by hydrometallurgical means, more metallic materials can be extracted such as: brass, electrolytic purity copper and electrolytic purity metal zinc. The mass balance on these materials shows that another 410 kg of metal can be recovered from the 570 kg of slag. It is therefore important to show that the resulting waste is reduced from 570 kg to approx. 150 kg. Chemical analyzes made on this waste show that it is composed of common soils inert oxides characterized as non-hazardous waste, if, it is well neutralized after exhausting from precipitation with sulfuric acid. Recoverable metal balance with potential for extra capitalization compared to the 440 kg metal cast in ingot is: brass-310 kg; dust Copper-41kg; electrolytic Zn-60 kg. There is an increase in the gross profit achieved by applying the two technological sequences from 419 € / t raw slag to 1266 € / t raw slag.

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