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EXPERIMENTS REGARDING SOLUBILIZATION OF SLAG BRASSES WITH H_2SO_4

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Abstract: In this paper, the purpose of the experiments is to determinate the solubilization conditions for the maximum reduction of precipitated CuO and ZnO, and optimization of the process, defined by the minimum consumption of acid solubilization solutions and the maximum yield for the extraction of Cu and Zn oxides. The objectives that we want are related to possibilities to increase the valorization of brass and bronze slags, solutions and maximum yield of Cu and Zn oxides extraction, and completing the Cu and Zn extraction technology from brass slags.
Keywords: brass dross, H_2SO_4 hydro-solubilization, electrolysis, recycling

1. INTRODUCTION

Today, the recycling field is a key element of covering the copper demand, relying on its good property, namely, infinite purity during the recycling process. The degree of capitalization of metals contained in added-value equipment and materials is different. The higher the added value of the equipment, the more they contain smaller amounts of metals, thus involving higher costs as well. International trade with recycled resources emerged at a rapid pace as a result of local costs of separating product materials and resources in countries such as India and China, with the result leading to a geopolitical strategic recycling problem. [1,10-12] The development of high-strength and highly conductive brasses is necessary to satisfy new demands posed by the electronics industry, automotive, and aerospace applications and household appliance development [2,3,13,14]. The lead isotope analyses suggest different provenances of the raw materials used for making the brass objects, thus the different origins of the ores may hint that the brass wire and sheet were imported to the workshops in which the objects were manufactured. [4] Tzer-Ming Jeng, Sheng-Chung Tzeng, and Yi-Chen Chen, investigated the heat transfer characteristics in the asymmetrically heated rectangular channels fully filled with porous materials. Air was used as the coolant. The porous materials were packed by brass beads with average diameters (*d*) of 2, 4 and 6 mm. [5] Brasses are essentially copper and zinc alloys, they also contain other alloying elements such as lead, silicon, aluminum, iron, tin, manganese, nickel or arsenic whose presence and content are responsible for the wide variety of properties inherent to these materials.[6]

2. MATERIALS AND METHODS

Copper and copper-based alloys form a large group of important construction materials for outdoor applications due to their appealing visual appearance, desirable mechanical and physical properties. [7-14]

The brass/bronze dross is a fine powder - 90 % < 1,2 mm, dark gray or dark brown colored, and usually results from the brass / bronze slag processing stream after the sieving or milling in the Pontzen mill. The material is a mixture of metal oxides powder of Cu, Zn, Al, Si, Fe, Mn, etc. and a metallic fine particle suspension of the metal from which the metal batch was dispersed.

Figure 1. Brass/Bronze dross

Parameters are the variables X and Y, where:

- X = the amount of solution / kg;
- Y = the concentration of the solution;
- Output parameter is pH.

At 1 kg of dust containing CuO and ZnO, is dissolved in 4 different regimes in 4 reaction vessels, each vessel returning the amount of 0.25 kg of dust with this content. In 4 glass / plastic bottles, 0.25 kg of oxidized ash, with the same composition, homogenized, dried at 0.5% humidity, and the same granulation <0.5 mm are introduced. The four combinations are presented below (Table 1).

Table 1. The four combinations

1	X_1Y_1- 1000 gr solution	30% H_2SO_4	700 gr water - 300 gr acid
2	X_1Y_2- 1000 gr solution	15 % H_2SO_4	850 gr water - 150 gr acid
3	X_2Y_1- 600 gr solution	30 % H_2SO_4	420 gr water - 180 gr acid
4	X_2Y_2- 600 gr solution	15 % H_2SO_4	510 gr water - 90 gr acid

Figure 3. The four reaction vessels for the solubilization of the brass according to the experimental plan after the completion of the solubilization Phase 1

Figure 4. Detail for experimental variants X1Y1 and X1Y2 after Phase 1 solubilization

Figure 5. The four reagent vessels assembly after the second solubilization phase

Figure 6. Precipitation of the solid phases in the acidic solution of CuSO4 and ZnSO4.
1. Acid solution with Cu and Zn sulfate;
2. Precipitated neutral-sludge oxides

Four glass bottles with these codes were labeled into which the solution corresponding to the code was introduced. The solution was mixed from two to two hours for eight hours and allowed to decant. In each of the four reaction vessels, a clear blue-green solution and a copper-colored precipitate (reddish) were obtained, over which a black precipitate was deposited, as shown in Figures 3-7.

3. PRECIPITATED RED BRASS DUST

The pH of the solution was measured, with an electronic pH meter accurate to 3 decimal places, resulting in the following values for the four reaction vessels (Table 2). Since the pH values were very low, the solubilization reaction was continued by adding another 50 gr of brass dross to each reaction vessel. The solution was stirred for two hours in eight hours, precipitated for eight more hours, the pH was again measured, the new values being presented bellow (Table 3).

Table 2. Values for the four reaction vessels

No	Solution	PH	%
1	X_1Y_1	- 0,994	10,139
2	X_1Y_2	-1,19	6,92
3	X_2Y_1	-0,959	11,034
4	X_2Y_2	-1,602	4,21

Table 3. The new values for the four reaction vessels

No	Solution	PH	%
1	X_1Y_1	-1,070	-8,6
2	X_1Y_2	-1,34	-5,57
3	X_2Y_1	-1,071	-8,58
4	X_2Y_2	-2,565	-2,45

The electrolyte solution having H_2O, H_2SO_4, $CuSO_4$ and $ZnSO_4$ composition was separated. The precipitate solution was separated, the precipitate was washed in each of the dishes with 200 grams of H_2O and left to sediment. After clarifying the solution, washing solution 1 was separated and its acidity was measured, the mean pH of the solution being 2,751.

The second step of washing the precipitates was carried out with 200 grams of H_2O and allowed to precipitate. After the precipitation, the washing water was separated and, with it, the black sediment. It was separated by several washes of the water stored in step 2 to completely separate the black precipitate from the red one. The red precipitate is a brass powder that has been attacked by H_2SO_4, existing in the brass dross.

The black precipitate represents oxides associated with slag and oxidic impurities. Precipitation of copper from Cu sulfate in the solution was carried out by introducing a quantity of Zn splinters of purity R1 - 9.8%. The acidic solution of copper sulfate and zinc-electrolyte was weighed.

Zn splinters were added into each of the vessels in several steps as follows:

— addition of Zn splinters was made until the solution became completely white, the reaction being as follows:

$$CuSO_4 + Zn = ZnSO_4 + Cu$$

— the Zn splinters are consumed by neutralizing sulfuric acid by the reaction:

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4$$

The crystallographic structure of brass dust was analyzed by X-ray diffraction (XRD), using a Pananalytical diffractometer equipped with a Cu target (λ = 1.5418 Å) radiation tube, operating at an acceleration voltage of 30 kV and current intensity of 25 mA. The chemical composition obtained from spectroscopic X-ray fluorescence analysis by wavelength -WDXRF is shown in Table 4.

The obtained XRD diagrams show, as expected, the predominant presence of the brass-specific peaks (ICDD 00-050-1333 and 03-065-6321). The main elements formed compounds identified by XRD. The complete list of compounds is presented in Table 5.

After the diffraction on the brass dust, two main compounds - the α and β-phases of the Cu-Zn alloy, were observed. Thus, from the list of characteristic peaks, it can be noticed that the main peaks of the Cu-Zn alloys in α-phase of this nature are found around the values of 2θ ≈ 42.3° - the main peak, having a distance d between the planes of ~ 2.133 Å.

The values of 49.27°, 72.24 ° and 87.45 ° of the angles 2θ represent the other characteristic peaks of the α phase.

Figure 7. Precipitated brass powder after separation from the solubilization solution and after the drying operation

Table 4. Chemical composition obtained by WDXRF

Nr. Crt	Element	Concentration
1	Zn	39,41%
2	Cu	23,55%
3	Al	5,08%
4	Si	4,92%
5	Pb	1,61%
6	Fe	0,87%
7	Ca	0,44%
8	P	0,27%
9	K	0,17%
10	S	0,15%
11	Mn	0,10%
12	Sn	0,08%
13	Cl	0,05%

Table 5 . List of compounds

Nr. Crt.	Compound	ICDD
1	α Cu-Zn	00-050-1333
2	β Cu-Zn	03-065-6321
3	Pb	01-073-7078
4	Al-Fe-Si	00-052-0917
5	Al-Cu-Fe-Si	01-070-8942

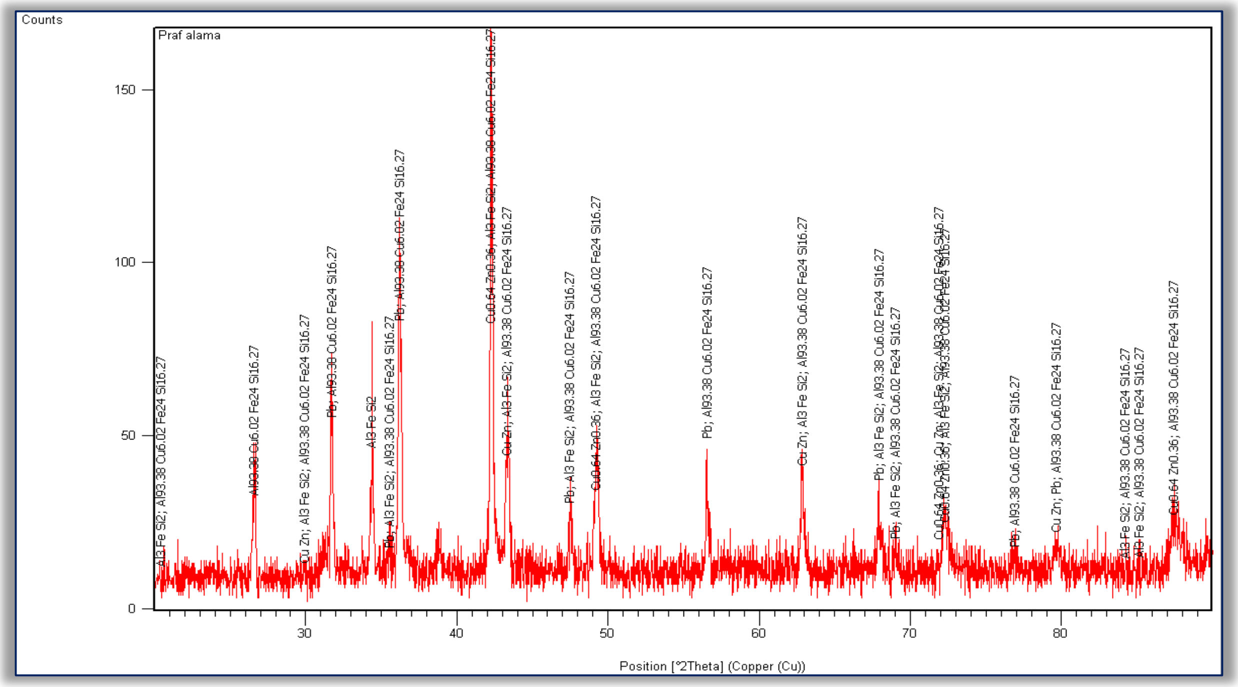

Figure 2. Crystallographic structure analyzed with radiation diffraction

Lead, by its existence as a secondary element in the Zn ore, often appears in brass-type alloys. It is possible for brasses to form complex compounds such as Al-Fe-Si or even Al-Cu-Fe-Si due to their chemical composition. Moreover, if we take into consideration elements such as C and O which do not appear in the analysis of the chemical composition, compounds that are more complex than those mentioned above can be obtained.

Table 6. Chemical composition of brass dross

Chemical composition of brass / bronze dross	
Zn	39,41%
Cu	23,55%
Al	5,08%
Si	4,92%
Pb	1,61%
Fe	0,87%
Ca	0,44%
P	0,27%
K	0,17%
S	0,15%
Mn	0,10
Sn	0,08
Cl	0,05%

3. RESULTS AND DISCUSSIONS

The resulting precipitate in each vessel was separated from the aqueous Zn sulfate solution. The resulting precipitate is Cu powder. The precipitate is washed and, as the case may be, the Zn residues left unreacted are separated by tweeze ring and afterwards are weighed and subtracted from the amount of Zn used to precipitate Cu sulfate.

The Cu powder precipitate is weighed. After drying, the Cu powder is weighed out again and is calculated on the basis of the Zn balance that reacted. The amount of black slurry separated from the solution to the 2nd wash step is dried and weighed. The amount of brass powder precipitate is weighed out. The total balance of material is given by:

- the amount of precipitated brass
- the amount of neutral slurry
- the amount of copper precipitated by reaction with Zn
- the amount of Zn sulfate in the aqueous solution.
- the amount of residual sulfuric acid

The results are presented in Table 7.

Table 7. Results of the four solubilization tests

Samples	Electrolytic solution mass [grams]	Zn splinters mass [grams]	Brass powder mass [grams]	Oxidic slam mass [grams]	$ZnSO_4$ solution Mass [grams]
X_1Y_1	933	53	165	19	828
X_1Y_2	946	31	168	15	960
X_2Y_1	498	23	164	17	658
X_2Y_2	493	17	168	22	435

4. CONCLUSIONS

Conclusions of the experiments on the optimal area of solubilization and precipitation conditions show that X_1Y_2 is the most efficient variant of sulfuric acid solubilization of brass dross, the arguments being, as follows:

- It consumes the smallest amount of acid at the same amount of solubilized oxides;
- It has the lowest amount of residual acid in the final solution, which is desirable for reducing the consumption of metal zinc used for CuO precipitation;
- It has the lowest consumption of metal zinc for precipitation;
- The final solution has a concentration of g / l of acid and of $ZnSO_4$ of the values closest to the solution for the electrolysis of metal zinc, respectively 35,6 and 100,06 g / l;

The presence of ZnO and CuO, PbO, may interact with acid rains, pollute the soil, have high potential to penetrate the soil and reach groundwater and therefore their storage is not recommended. It has been shown that extra metal extraction is possible by hydrometallurgical means such as: brass, electrolytic purity copper and electrolytic purity metal zinc.

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