COPPER AND ZINC RECOVERY FROM BRASS FILINGS OF METAL MECHANICS INDUSTRY FOR PRODUCING MICRONUTRIENTS BEARING CHEMICALS TO AGRICULTURE

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ABSTRACT

Copper and zinc are separately recovered in the form of substantially pure marketable products from secondary sources, such as metallic copper and brass scrap (*e.g.*, junked automobile radiators) and oxidized residues (*e.g.*, smelter flue dust), which contain relatively large proportion of copper and zinc and relatively small proportions of other non-ferrous elements, by an oxidative leaching releasing copper and zinc into solution. This technical contribution aims at defining, in bench scale, the operational parameters that allow to speed up the dissolution of brass filings, generated in the metal-mechanical industrial sector, through an oxidative leaching processes that release in the bulk chlorine gas. The leachate-bearing copper and zinc ionic species is treated for producing quite important chemicals that provide micro-nutrients used in agriculture, such as copper oxichloride $3Cu(OH)_2.CuCl_2$ and zinc sulphate ($ZnSO_4$).

KEYWORDS: brass filings; metal-mechanic; micronutrients; agriculture.

1. INTRODUCTION

Copper and zinc are separately recovered in form of substantially pure marketable products from low grade material, such as metallic copper and brass filings (*e.g.*, junked automobile radiators, brass filings etc.) and oxidized residues (*e.g.*, smelter flue dusts) (Ján Veres, Stefan Jakabsky and Michal Lovás), which contain relatively large proportions of copper and zinc and relatively small proportions of other non-ferrous elements, by an improved ammoniacal leaching procedure (Graham, Savage & Associates). The low grade material is leached with an aqueous ammoniacal solution (ammonium sulphate or ammonium carbonate solution), dissolving the copper and zinc and leaving an insoluble residue. The copper-zinc solution is treated with a liquid ion exchanger to produce a raffinate containing a zinc ammonium complex in solution, which is substantially completely free of copper. The liquid ion exchanger then is treated with an aqueous acid solution to form an eluant solution containing copper and substantially completely free of zinc and other metals. Substantially pure copper is recovered from the eluant solution; and the raffinate solution is treated to form a substantially pure zinc product. The copper and zinc depleted residual ammoniacal solution is recycled for re-use in the leaching operation. Another approach for recovering zinc and copper values, from copper bearing materials is leaching them with a mixture of nitric and sulphuric acids, after which the dissolved copper is cemented from solution by contacting it with iron. The solution, containing dissolved iron and zinc salts is reacted with ZnO to precipitate iron as ferric oxide, which is separated, leaving zinc sulphate in solution. Solid zinc sulphate is recovered from solution by evaporation, and then calcined to produce SO_2, which is recovered and recycled as H_2SO_4, and ZnO, which is reused in the process, any excess being recovered as a product (Robert N. Moore) (M. K. Jha., V. Kumar, R. J. Singh).

In this technical contribution the operational parameters that allow speeding up the dissolution of brass filings, generated in the metal-mechanical industrial sector, were defined, in bench scale, through an oxidative leaching processes that release in the bulk chlorine gas. The leachate-bearing copper and zinc ionic species is treated for producing quite important chemicals that provide micro-nutrients used in agriculture, such as copper oxichloride $CuCl_2.3Cu(OH)_2$ and zinc sulphate ($ZnSO_4$).

2. EXPERIMENTAL

2.1. Physical Characterization

The particle size analysis was accomplished, and, in accordance with the results of Table I, it was found that approximately 62% of brass filings is with particle size equal to or smaller than 65 mesh, which was easier to leach it in a mechanical stirred reactor as one is dealing with higher specific surface are for the digestion reaction to take place.

Table I. Results of the particle size analysis accomplished with brass scraps.

Tyler series (mesh)	Opening (mm)	Retained Weight (g)	Accumulated Retained Weight (g)	Accumulated Retained Weight (%)	Passing Retained Weight (%)
20	0.850	2.10	2.10	1.05	98.95
65	0.212	73.50	75.60	37.91	62.09
100	0.150	34.30	109.90	55.12	44.88
150	0.104	20.00	129.90	65.15	34.85
-150	-0.104	69.50	199.40	100.00	0.00

2.2. Technological Characterization

The brass filings sample, as seen in Figure 1, was homogenized and a representative fraction of it separated for chemical analysis of elements of interest. Following the chemical analysis, the original sample was submitted to a magnetic separation for removing the iron filings. The letter A means the original sample, the B the magnetic phase and C the non-magnetic phase.

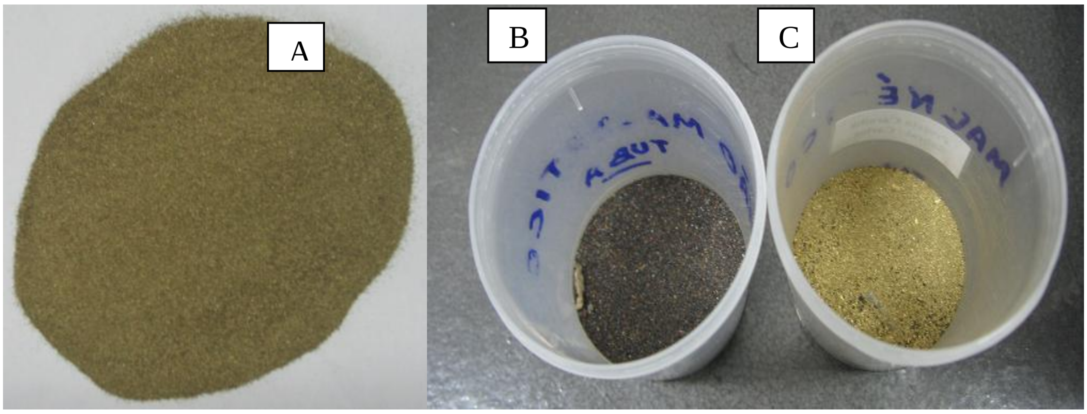

Figure 1. Physical aspect of a granular sample of brass filings.

The chemical and instrumental characterizations were accomplished by: scanning electron microscopy with punctual analyzer by energy dispersion (SEM/EDS). The scanning electron microscope used was a LEO S440, equipped with microanalysis system by energy dispersion Link ISIS L300 with detector of Shilhi Pentafet, thin window ATW II, for a resolution of 133 eV to 5.9 keV. All analyzes were performed with 20 kV accelerating voltage of electrons. The images were generated predominantly by electron detector retro-scattered (backscattered electrons detector - BSD), where the gray levels are proportional to the average atomic number of elements excited by electron beam during the scan, being, therefore, compositional images, with the lighter shades representing higher average atomic numbers phases. The resolution of the micro analysis by EDS is the order of 1 micrometer radius surface and a depth of the order of 1.5 to 5 μm, depending on the specific gravity of the material in the analyzed point.

The X-rays diffraction equipment used was a Siemens/Brucker - AXS D5005, equipped with Goebel mirror for parallel beam X-ray, graphite monochromator, when necessary, and solid state NaI detector. The radiation used was Cu Kα (40 kV/40 mA); the goniometer speed was 0.02° 2θ per step with counting time of 1.0 second per step. The interpretation was carried out by comparison with standards contained in PDF 02 (ICDD, 1996) in software Brucker Diffrac Plus.

The X-rays diffraction semi-quantitative analysis results of the chemical species constituents of brass filings, show that the brass scraps sample under study contains high copper and zinc contents, elements of interest in this study, a fact which is confirmed by chemical analysis by atomic absorption spectrometry (AAS), after digestion of a representative filings sample. Figure 2 shows a micrograph by SEM/EDS of the brass filings sample.

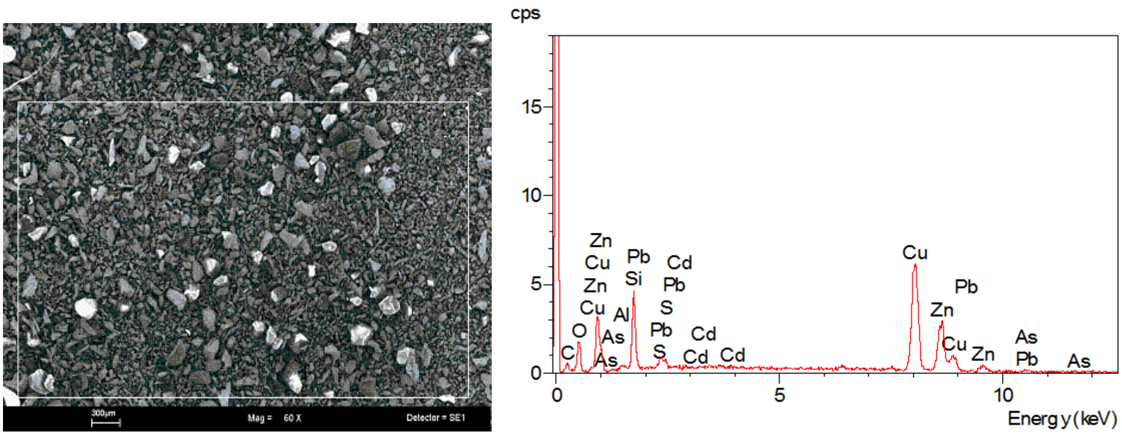

Figure 2. The SEM micrograph of a brass filings sample and corresponding EDS spectrum.

2.3. Chemical Characterization

In accordance with the atomic absorption spectrometry technique, the copper and zinc contents in the brass filings were 34.1% and 16.1% (m/m), respectively, apart from other metals have been detected.

3. TECHNOLOGICAL ROUTES

The routes developed in this study for the processing of brass shavings, source of copper and zinc, were from the acid leaching in reactor busy with adding periodic an oxidizing agent. Table II shows briefly the acid medium and the oxidizing agent used in the two routes proposed, as well as the main products obtained.

Table II. Technological routes and the respective products generated.

Route	Acid Medium	Oxidizing Agent	Products
Sulphuric	H_2SO_4	H_2O_2	$Cu(OH)_2$, $Zn(OH)_2$, ZnO
Chloride	HCl	NaClO	$3Cu(OH)_2.CuCl2$, $Zn(OH)_2$, ZnO

3.1. Chloride Route

3.1.1. Chloride Leaching

The chloride route is based on dissolving the metallic particulate material in hydrochloric acid solution with periodic addition of sodium hypochlorite (NaClO), an oxidizing agent, which releases chlorine gas when in contact with acidic solution.

The tests were accomplished according to a complete experimental design with two variables with three levels, where the acidic solutions used in the brass scrap dissolution tests contained 40 , 50 and 60% of 37% v/v (density 1.18 $g.cm^{-3}$) hydrochloric acid (HCl), while maintaining a solid/liquid ratio of 1:4, with regular addition of sodium hypochlorite (HClO), at 15% w/v, as oxidizing agent (75ml, 100ml and 125ml) directly into the acid solution, under mechanical stirring at 500 rpm and withdrawing aliquots for analysis in 2, 3 and 4 hours. The following reactions show how do brass scraps dissolution takes place:

$$Cu^o + NaClO + 2HCl \rightarrow CuCl_2 + NaCl + H_2O \quad (1)$$

$$Zn^o + NaClO + 2HCl \rightarrow ZnCl_2 + NaCl + H_2O \quad (2)$$

According to the chemical analysis the most effective copper and zinc dissolution conditions were 50% v/v HCl and 125 ml and NaClO within four hours of test, which meant an extraction of 99.97% of copper and 99.99% of zinc. The route for recovering copper and zinc from brass scraps follows the process and unit operations outlined in the flow chart of Figure 3.

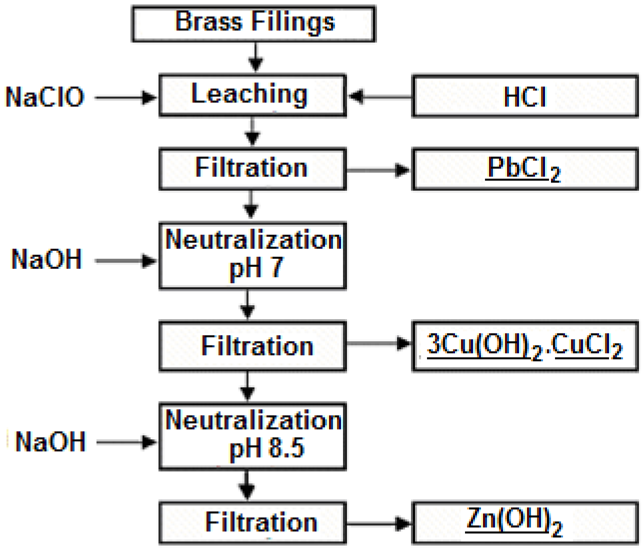

Figure 3. Process and unit operations for extracting copper and zinc from brass filings.

3.2. Sulphuric Route

3.2.1. Sulphuric Leaching

This route is based on the dissolution of metallic brass filings in sulphuric acid with periodic addition of hydrogen peroxide (H_2O_2), a soluble oxidizing agent that does not depend on the salinity of the aqueous phase and have water as final product. Once finishing the digestion of those filings, the leachate is treated with same process and unit operations depicted in the Figure 3 for producing the copper and zinc final solid chemicals as a fungicide and micro-nutrient, respectively.

The reactions, as follows, show how the dissolution reactions of metals of interest, out of brass filings, take place when in contact with hydrogen peroxide solution in sulphuric acid.

$$Cu^o + H_2O_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O \quad (3)$$

$$Zn^o + H_2O_2 + H_2SO_4 \rightarrow ZnSO_4 + 2H_2O \quad (4)$$

From a given leachate, either in hydrochloric acid or sulphuric acid, copper oxychloride ($3Cu(OH)_2.CuCl_2$) and copper hydroxide ($Cu(OH)_2$) were obtained, respectively, by precipitating them within the proper pH range (5.5 - 6.5). In this pH range zinc remains soluble. However, the pH of this solution should be raised up to 10.5 - 11, by adding NaOH solution, as shown in reaction 5, so as to precipitate other metallic impurities, remaining soluble the zinc in the form of zincate (ZnO_2^{2-}) from where can be re-precipitate, as $Zn(OH)_2$, by decreasing the pH.

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O \quad (5)$$

4. CONCLUSIONS

As conclusions one can say that:

- The production of inorganic copper and zinc salts out of the brass scrap dissolution proved very attractive;
- The hydrochloric acid leaching of brass scraps, adding sodium hypochlorite has shown promising results regarding the metals extraction efficiencies, where it was possible to dissolve 99.9% of copper and zinc present in the brass filings samples used over 4 hours tests;
- However, the sulphuric acid leaching of brass filings, adding hydrogen peroxide, presented a slower kinetics in comparison to the hydrochloric acid leaching with hypochlorite as oxidizing agent, fact that served as basis for the decision to consider that route in the scaling up of such process;
- The salts copper oxychloride and zinc hydroxide, after being chemically analysed have showed metallic contamination that are within the specifications of the competent environmental institution for being used as fungicide and micro-nutrient, respectively.

5. REFERENCES

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