Recovery of copper and nickel hydroxide from galvanic sludge – Pilot scale experiments

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Abstract

The present work has been developed under the scope of the project VALMETAIS and proposes a hydrometallurgical process for copper and nickel hydroxide recovery from galvanic sludges produced by Ni/Cr plating plants. In this project, the procedure has been developed at a laboratory scale and validated at a small sized pilot plant. The developed procedure includes a first stage of a counter-current sulphuric leaching process of sludges in three stages. Extraction rates of 99% for Cu and Ni were achieved under the leaching conditions above mentioned. The solid residue separated from the leaching solution is mostly constituted by gypsum (CaSO4) presenting a metal content below 1%. In order to recover selectively the copper from the leaching solution, a cementation process was carried out using iron scrap and performed at a pH of 2, which was achieved through adding new sludge to the filtered previous solution. The recovery rate of copper was 99%, producing cement with a high purity grade which enables its application as commercial product. Nickel hydroxide precipitation was performed by adding sodium hydroxide to the cemented solution purified. Results showed a successfully nickel hydroxide extraction rate of 99% and a purity grade of more than 98%.

These evidences demonstrate the high potential of the developed methodology in treating and obtaining economic benefits from galvanic sludge. The end products, namely the cooper and the nickel hydroxide, as well as the gypsum based sludge resulting from the leaching process, can be applied as commercial products or as component materials generating profits.

1- INTRODUCTION

Galvanic sludges are the solid wastes produced by the treatment of wastewaters generated in galvanic coating process by physical-chemical methods. During the wastewater treatment, significant amounts of sludge are produced. These sludges are considered hazardous according to Council Decision 2000/532/CE and are often disposed, mainly on landfills, without any economical or environmental benefits. This classification is due to the high concentration of mobile/leachable species, such as heavy and/or transition metals like chromium and nickel. The development of alternatives and viable ways that reduce the environmental impact and enable the recovery of valuable metals contained in those sludges such as copper, nickel or zinc, which content might reach 30% (wt.%, dry weight) are of utmost importance [1,2]. In fact, besides water (typical solids content is under 40%) and some soluble salts, the galvanic sludge is composed of metallic species and additives and its composition dependent of the processing conditions [3,4].

Several treatments routes have been proposed in literature to recover valuable metals contained in galvanic sludges. These technologies were focused on pyrometallurgical [5], electrowinning [6] or hydrometallurgical processes [7-9]. The high energy consumption, the inevitability of the existence of cleaning and colleting gases systems, together with the requirement of a certain content of metals contained in galvanic sludges makes pyrometallurgical and electrowinning processes less attractive when compared to the hydrometallurgical route [10,11].

In this perspective, the project VALMETAIS aimed to develop a new hydrometallurgical process to recover nonferrous metals, like nickel and copper, from galvanic sludges and to decrease the hazardous character and amount of the remaining waste before final disposal. For that purpose, the project was divided in laboratory scale experiments and in a pilot scale experiments for validate the results. Technical and economic feasibility of the whole developed process was also evaluated at a pilot scale plant. The obtained results allowed the establishment of an integrated solution able to be implemented in industry. This project was sponsored by the QREN (Quadro de Referência Estratégico Nacional), having CVR - Centro para a Valorização de Resíduos and W2V, S.A., as technical partners. This work presents the most relevant results of copper and nickel hydroxide recovery from galvanic sludges obtained in the small sized pilot plant scale.

2- MATERIALS AND METHODS

Selection and Characterization of galvanic sludges

For this study ten samples of galvanic sludges produced by the physical-chemical treatment of wastewaters generated by seven industrial units of Ni/Cr plating were collected in order to get a representative spectrum of their production in Portugal. Galvanic sludges have been characterized for their chemical properties. Chemical composition of samples was determined by X-ray fluorescence spectrometry (XRF, X Unique II Philips spectrometer) and by atomic absorption spectrometry (AAS, GBC 904 AA equipment).

Experimental Methodology

Small sized pilot plant scale experiments

After evaluating different operating conditions, the procedures showing the best results identified in laboratory scale were further verified and validated in a small sized pilot plant scale (Figure 1). This unit was projected, developed and constructed according to the specification in materials and in the developed methodology. All tanks were constructed in galvanized iron with 3mm thickness and coated with acid resistant painting. The cylindrical agitation tank has a diameter of 350mm and 500 mm in height, with a volume capacity of 30 L and mixing was promoted by a rotational engine (BONFIGLIOLI, model BN 71B6). Filter tank has twice the volume capacity of the agitation tank and has a perforate plate to filter the solutions. Cementation tank was built in the same materials as the agitation reactor and presents two main components: an upper tank and a bottom tank. In the upper tank the re-circulated solution contact with the iron scrap and in the bottom tank the cooper precipitates as cement. Re-circulation of the solutions was assured by a pneumatic membrane pump (VERSA MATIC, model E8PP6XPP9).

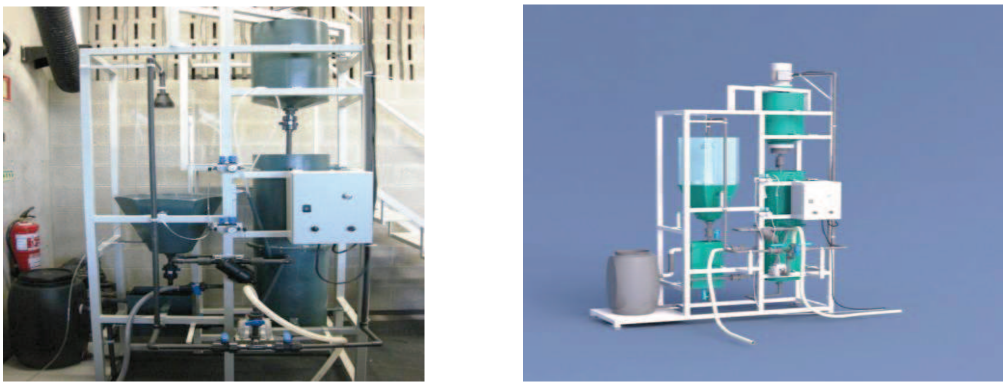

Figure 1: Overview of the pilot plant scale: a) real representation; b) SolidWorks representation

Leaching experiments

Leaching experiments were performed in three steps with sludge recirculation using sulphuric acid solution under stirring conditions at room temperature and under atmospheric pressure. Sulphuric acid leaching experiment has been carried out according to the following experimental conditions: 100g/L of acid concentration, 1:10 solid (dried and grounded sample) to liquid ratio, total digestion time of 8 hours for the three leaching steps and a stirring speed of 400 rpm. During leaching experiments, samples were collected and analysed by X-ray Fluorescence Spectrometry (XRF).

Recovery of copper by cementation

In order to recover copper from the obtained solution after leaching experiments, a subsequent process of cementation has been performed with iron scrap at room temperature and atmospheric pressure. The solution obtained from the sulphuric acid leaching with a pH 2.0 was used. Chemical composition of the obtained cement was determined by X-ray Fluorescence Spectrometry (XRF).

Nickel hydroxide recovery

Recovery of nickel hydroxide occurs by precipitation through the solution concentrate in nickel and frees of others elements. Nickel precipitation was accomplished by adding sodium hydroxide solution with a concentration of 200 g/L. Chemical composition of precipitated cake has been determined by X-ray Fluorescence Spectrometry (XRF).

3- RESULTS AND DISCUSSION

Selection and Characterization of galvanic sludges

Table 1 shows the chemical composition of the samples of galvanic sludges collected in the distinct industrial units (IU) of Ni/Cr plating selected for this study. Results show that galvanic sludges present high contents of metals such as Cu, Cr and Ni, in some cases higher than 10%. Calcium is also present in relevant contents, which is related to the physical-chemical process applied to the wastewater treatment. At the same time several other elements are present, namely Fe, Cl, Na, P among others, which presence interferes on the leaching process through their co-dissolution with the valuable metals, reducing the purity of the resulting liquor leach.

	IU1-1	IU1-2	IU2	IU3	IU4-1	IU4-2	IU5-1	IU5-2	IU6	IU7
Al	0,05	0,09	0,55	0,13	1,0	0,75	0,30	0,48	0,17	4,5
Ca	9,0	9,4	11,9	9,8	8,2	11,2	15,6	17,9	26,2	12,6
Cl	0,24	0,38	0,07	1,2	0,26	0,33	0,15	0,07	0,15	1,3
Cr	12,1	8,7	0,76	4,1	5,3	6,8	0,87	0,50	3,21	0,15
Cu	9,7	8,5	3,1	0,25	11,3	13,2	1,6	1,1	0,08	0,04
Fe	0,11	0,06	0,14	0,79	0,13	0,08	0,38	0,65	0,03	0,26
K	0,08	0,06	0,06	0,06	0,08	0,11	0,06	0,09	<0,05	0,12
Mg	0,10	0,53	0,35	0,80	0,14	0,11	0,24	0,33	0,73	0,50
Na	0,42	2,04	0,64	0,47	0,33	0,52	0,29	0,18	0,19	2,1
Ni	8,7	10,5	13,2	21,8	9,5	8,1	9,1	8,3	10,2	0,58
P	4,9	8,9	0,43	0,57	3,7	4,4	1,3	0,93	1,09	3,5
Pb	0,06	0,07	0,09	0,04	0,14	0,09	0,11	0,08	<0,01	0,01
S	1,4	2,5	9,2	3,7	1,1	1,8	7,0	8,8	4,7	2,8
Si	0,11	0,10	1,5	2,7	4,2	3,3	4,7	4,1	1,5	8,9

Table 1: Chemical composition (AAS and FRX) of dried sludges (wt%)

Based both on the characteristics of the sludges, as the content of valuable metals (copper and nickel) and in the amount of galvanic sludges produced by year in the different industrial units tested in this study, the selected sludge for subsequent treatment and study was the corresponding to the sample 2 of IU1.

Leaching experiments

Table 2 presents the chemical composition of the cake filtered and collected after the counter-current leaching process in three steps.

Element	%
Ca	33,4
Cr	0,3
Cu	0,03
Fe	0,06
Ni	0,01
Sn	0,01
Al	0,04
P	0,7
S	24,5
Si	0,03
Others	0,05

Table 2: Chemical composition (FRX) of dried cake (wt%)

The obtained cake is basically formed by CaSO4 (gypsum) and by other elements present in residual contents. This evidence proves that sulphuric acid leaching allows almost the total dissolution of the initial metals present in the sludges. The presence of undesirable metals co-dissolved during the leaching process of galvanic sludges could decrease the purity grade of the recovered metals. In this perspective, the developed methodology aimed to recover, selectively and separately, each one of the valuable metals of the sludge.

Recovery of copper by cementation

The chemical composition of the cement collected in the cementation step with iron scrap, table 3 displays a purity grade of 99% in cooper with an extraction rate of 99%.

Element	%
Al	0,1
Cr	0,02
Cu	99
Fe	0,01
P	0,17
S	0,7
Si	0,04

Table 3: Chemical composition (FRX) of the dried cement (wt%)

Nickel hydroxide recovery

Table 4 exhibits the chemical composition of the collected and filtered cake produced during the nickel hydroxide recovery step.

Element	%
Cu	0,01
$Ni(OH)_2$	>98
Mg	0,8
Al	0,2
P	0,1

Table 4: Chemical composition (FRX) of dried cake from nickel hydroxide process (wt%)

Results showed a purity grade of 98% in nickel hydroxide and an extraction rate of 99%, proving the efficiency of the adopted methodology for nickel recovery. It is also important to note that, at the end of the developed methodology for cooper and nickel hydroxide recuperation, the final effluent is free of metals. Table 5 shows the chemical composition of the final solution.

	Concentration (mg/L)	
	Cooper	Nickel
Solution before nickel hydroxide recovery	14	7500
Solution after nickel hydroxide recovery	0,3	1,6
Extraction yield [%]	97	99,9

Table 5: Chemical composition (EAA) of solution after nickel hydroxide recovery process (mg/L)

4- CONCLUSIONS

From the experimental work developed in the pilot scale, it can be concluded that sulphuric acid proved to be an efficient leaching medium for the first step of a hydrometallurgical process to recover the valuable metals present in galvanic sludges. Extraction rates of 99% for Ni and Cu were achieved for the studied operating conditions. Cementation procedure with iron scraps promotes efficiently the recovery of Cu from sulphuric leaching solutions with pH of 2, achieving 99% of extraction and the formation of cement with a purity grade of 99% in cooper, which has a substantial value and allows its commercialization. The nickel hydroxide recovery step achieved an extraction yield of 99% and a purity grade of more than 98%. These results prove the efficiency of the methodology selected in the present work. Based in these factors it can be concluded that the methodology developed and established besides presenting a way to treat galvanic sludges, presents also an added value through the commercialization and reuse of the products formed along the process. With the technology validation it has been possible to create a draft of a potential industrial scale layout facility for treat 1,5 ton day^{-1} of galvanic sludge (Figure 2). From the implementation of the purposed technology it would be possible to recover 28kg of nickel hydroxide and 15 kg of copper cement, for each ton of treated galvanic sludges.

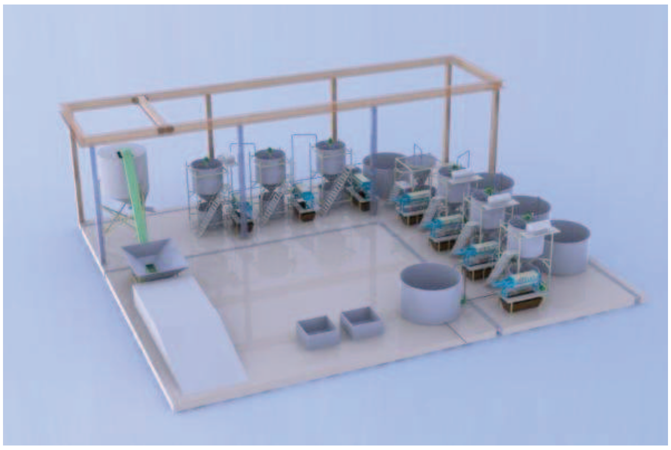

Figure 2: General overview of proposed industrial scale facility

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PRODUCTION OF METALLIC NANOPARTICLES, FROM INDUSTRIAL RESIDUES, BY THE USE OF DIFFERENT TYPES OF REDUCTION GASES

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Abstract

The need to enhance and reuse existing materials on secondary sources of metals has had quite an impact in recent times. Several processes and technologies had being studied for recovery of raw materials from industrial waste generated. This study focuses on the possibility of waste reducing, from the galvanic floor covering industry, with the aim of obtaining micro or nano-particles of nickel or a nickel based alloy.

Sludges from one galvanic treatment plant were used as base material in two conditions: as produced and after a hydrometallurgical treatment for metal concentration. Several reducing agents were used in this study: a synthesis gas from a polymer pyrolysis and solid polymer agents (PVC, HDPE and PP residues). Obtained products were characterised in terms of metallic particles production during the reduction treatment and by SEM/EDS analysis on the final products.

A simultaneous differential thermal and thermogravimetric equipment (DSC/TGA) was used for the study of the reduction process with a reduction gas obtained from the pyrolysis of chlorine free PVC derived char. The obtained results show that it is possible to obtain small metallic particles, in the range of 60 to 240 nm, at 800 ºC.

Reduction tests, by the use of a solid residue, were made in a laboratorial furnace with two independent heating zones. Best results were obtained with de-chlorinated PVC as a reduction agent with the production of metallic particles, in the range of 150 to 600 nm, at 800 ºC. For all the tested conditions the metallic particles were constituted by Ni and Cu with variable chemical composition.