WASTES: Solutions, Treatments and Opportunities
1st International Conference
September 12th – 14th 2011

SMALL SIZED PILOT SCALE EXPERIMENTS ON THE RECOVERY COOPER AND NICKEL HYDROXIDE FROM GALVANIC SLUDGE

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ABSTRACT
The present work, carried out within the project VALMETAIS, proposes a hydrometallurgical process for copper and nickel recovery from galvanic sludges produced by Ni/Cr plating plants. The procedure has been developed on laboratory scale and the results validation was verified in a small sized pilot scale.
The project starts with a leaching process of sludge in sulphuric acid solution in three stages followed by copper cementation step, using iron scrap as precipitating agent. It was found that metals dissolution was almost completed for the three stages of leaching process. Extraction rates of 99% for Cu and Ni were achieved under the leaching. The solid residue separated from the leaching solution is mostly constituted by gypsum ($CaSO_4$), and presents heavy metal content below 1%. Copper cementation process was performed at a pH of 2. Such pH level led to insignificant precipitation of other metals present in the leaching solution, particularly chromium. The recovery rate of copper is about 99% with a purity grade of 99% which enables its application as a commercial product. Nickel hydroxide precipitation was performed by adding sodium hydroxide solution. Results showed a successfully nickel hydroxide extraction obtaining 99% with a purity grade of more than 98%.
These evidences demonstrate the high potential of this methodology to treat and derive economic benefits from galvanic sludge. The end products cooper and nickel can be applied as a commercial product generating a profit and the gypsum based sludge from the leaching process can be reutilized as component of construction materials.

Keywords: Galvanic sludge, Hydrometallurgical process; Metals recovery; Pilot scale experiments

INTRODUCTION
Industrial units of surface metal plating generate wastewaters that need to be treated to produces good quality water to be recycled into the process. During the wastewater treatment, usually by physical-chemical methods, significant amounts of sludge are produced. For nickel and chromium plating processes the resulting sludge is classified as hazardous waste according to Council Decision 2000/532/CE and represents a potential source of environmental contamination. This classification is due to the high concentration of mobile/leachable species, such as heavy and/or transition metals like chromium and nickel [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]. These sludges are frequently sent to landfills with no valorization or economic benefits. This is clearly the least desirable option from both the environmental and economical points of view. For that reason available alternatives or appropriate routes that enable the valorization of those wastes with material recovery must be developed.
Different studies have been carried out in order to develop possible technologies for the chemical fixation of galvanic sludges in clay based ceramic materials, such as common formulations for tiles and bricks. The main mechanism for the inertization of phases with high levels of heavy metals in ceramic matrixes was described by Magalhães et al [5,6]. Alternatives technologies for

stabilization/solidification of galvanic sludges by asphalt emulsions [7] and the incorporation in Portland cement clinker [8,9] and silica and feldspar [10] have also been attempted and developed. Despite these technologies enable the formation of an effective physical and chemical barrier which reduces the leachibility of the soluble elements, they do not allow the recovery of valuable metals present in galvanic sludges. Several treatments routes have been proposed in literature to recover valuable metals contained in those sludges focused on pyrometallurgical or hydrometallurgical processes. The pyrometallurgical route is based on chemical reactions at high temperatures and allows recovery rates from 40 and 60% for the target elements Zn, Ni and Cu [11]. However, these processes present strong constraints since they can only be implemented to treat wastes within a confined composition regarding a maximum and a minimum content of selected elements [12]. Additionally the high energy consumption and the need of cleaning systems and collecting gases make the technique less attractive in relation to the hydrometallurgical route [13]. Hydrometallurgical processes for sludge valorization have been proposed by several authors [14-17]. Their works are related with acid or alkaline leaching, followed by distinct operations for metals recovery namely by solvent extraction (using di-(2-ethylhexyl)-phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex272)) and by electrowinning processes. Although the technologies summarized above are feasible processes for the management of galvanic sludges it is of great relevance the search and development of new technically and economically sound alternatives for the treatment and valorization of those sludges to recover valuable products as well as the optimization of the operating conditions under which all the steps of a valorization process should be performed.
In this context the project VALMETAIS aimed to develop a process in laboratory scale and validate the results in a pilot scale for 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. The hydrometallurgical solution proposed is based in sequential steps undertaken with lower operational costs than those required for the traditional extraction processes of solvent extraction and electrowinnning. The technical and economic feasibility of the whole developed process evaluated at a pilot scale 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) and CVR - Centro para a Valorização de Resíduos and W2V, S.A., as the technical partners for the Project. This work presents the most relevant results of copper and nickel hydroxide recovery from galvanic sludges in a small sized pilot scale.

HYDROMETALLURGICAL PROCESS TO RECOVER COOPER AND NICKEL HYDROXIDE

The hydrometallurgical process to recover nonferrous metals like copper and nickel hydroxide comprises different procedural steps, such as:

a. Leaching of galvanic sludge;
b. Recovery of copper by cementation;
c. Elimination of impurities;
d. Recovery of nickel hydroxide.

The experiments of this work were realized in a small sized pilot scale (figure 1). This pilot scale was built and its materials were selected according to the specifications identified in laboratory scale methodology. Thus, this pilot scale comprises all steps to leaching of galvanic sludge and for the recovery of copper and nickel hydroxide.

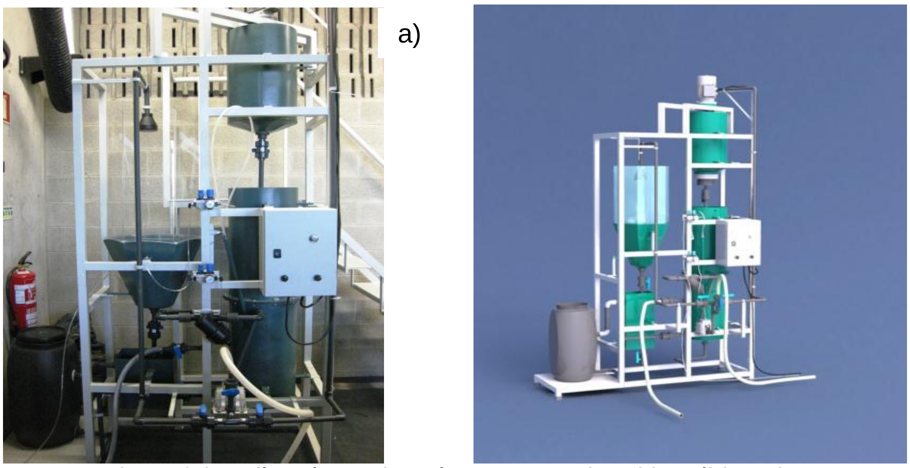

a) b)

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

METHODS AND MATERIALS

Characterization of galvanic sludge

For this study galvanic sludge produced by the physico-chemical treatment of wastewaters generated in an industrial unit of Ni/Cr plating were collected. Sludges have been characterized for their physic-chemical properties. The chemical composition of dried samples was determined by X-ray fluorescence (XRF, X Unique II Philips).

Methodology

The process begins with the leaching phase of galvanic sludges realized in three steps at room temperature and atmospheric pressure under constant agitation. The acid leaching for the dissolution of constituent metals of galvanic sludges was accomplished with sulphuric solutions. During leaching test cakes were collected and analyzed by X-ray Fluorescence Spectrometry (XRF).

In order to recover the copper from the obtained solution, a subsequent process of cementation has been studied with iron craps at room temperature and atmospheric pressure. For that operation, the solution obtained from the sulphuric acid leaching with a pH 2.0 was used. The chemical composition of the obtained cement was observed by SEM and determined by XFR.

Recovery of nickel hydroxide occurs for its precipitation through the solution concentrate in nickel and frees of others elements. For this was added a sodium hydroxide solution. The chemical composition of precipitated cake has been determined by XFR.

Small sized pilot scale

The cylindrical agitation tank has a diameter of 350mm and 500 mm in height, with a volume capacity of 30 L. All tanks are constructed in galvanized iron with 3mm thickness and coated with cid resistant painting. Mixing is promoted by a rotational engine (BONFIGLIOLI, model BN 71B6) connected to a horizontal shaft with three propellers in stainless steel to prevent corrosion induced by acid solutions. To adjust the speed of the propellers it was used a frequency converter (OMRON, model V1000) coupled to the engine. The filter tank has twice the volume capacity of the agitation tank and has a perforate plate to filter the solutions.

The cementation tank was built in the same materials as agitation reactor and has two main components: an upper tank and a bottom tank. In the first tank the re-circulated solution contact the iron straps and in second tank the cooper precipitates. The re-circulation of the solutions is ensured by a pneumatic membrane pump (VERSA MATIC, model E8PP6XPP9).

RESULTS

Table 1 shows the chemical composition of the selected galvanic sludge collected in an industrial unit of Ni/Cr. The results showed that galvanic sludges have high contents of valuable metals such as Cu and Ni, 6.0% and 9.9% respectively. Cr is also present in high contents and Ca to, consequence of the chemical physical process applied to the wastewater treatment. At the same time several other elements are present like Cr, Fe, P etc and their presence interferes on the leaching process through their co-dissolution together with the valuable metals, reducing the purity of the resulting liquor leach.

Table 1 - Chemical composition (FRX) of dried sludge (wt%)

Elements	Results [%]
Ca	9,1
Cr	13,6
Cu	6,0
Fe	3,9
Cl	0,4
K	0,1
Mg	0,5
Na	2,1
Ni	9,9
Pb	0,1
Zn	0,01
Al	0,1
P	8,0
S	2,5
Si	0,1
Sn	0,2
Sr	0,04

Leaching of galvanic sludge

Table 2 shows the chemical composition of the cake filtered and collected after leaching process in three steps. The results showed that cake is basically formed by $CaSO_4$ (gypsum) and the others elements are in residual values. This evidence proves that sulphuric acid leaching allows to dissolve almost all the initial present metals.

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

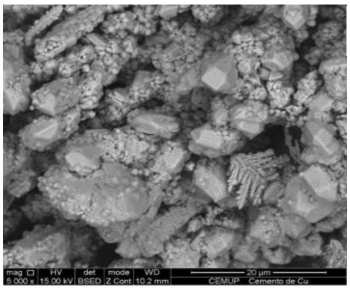
Elements	Results [%]
Ca	33,4
Cr	0,3
Cu	0,03
Fe	0,06
Ni	0,01
Sn	0,01
Al	0,04
P	0,7
S	24,5
Si	0,03
others	0,05

Recovery of copper by cementation

Table 3 shows the chemical composition of the cement collected after cementation step with iron scraps. The results showed a purity grade of 99% in cooper and an extraction yield of 99%.This high purity confirmed the efficiency of cementation with iron scraps. Figure 2 illustrate the obtained cement with 99% of copper in SEM determination and real overview.

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

Elements	Results [%]
Al	0,1
Cr	0,02
Cu	99
Fe	0,01
P	0,17
S	0,7
Si	0,04



a)

b)

Figure 2- Cement obtained by cementation with iron craps: a) SEM determination; b) real overview

Recovery of nickel hydroxide

Table 4 shows the chemical composition of the collected and filtered cake after nickel hydroxide recovery step. The results showed a purity grade of 98% in nickel hydroxide. Results also demonstrated an extraction yield of 99% which prove the adopted methodology.

Table 4 - Chemical composition (FRX) of dried nickel hydroxide recovery process (wt%)

Elements	Results [%]
Cu	0,01
$Ni(OH)_2$	>98
Mg	0,8
Al	0,2
P	0,1
Si	0,5

CONCLUSION

From the experimental work developed in the pilot scale it can be concluded that sulphuric acid proved to be an efficient leaching media 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. In the final of leaching process the galvanic sludges are converted into a material essentially constituted by gypsum. Thus is eliminated the need for landfill as hazardous waste which reduce the cost for its management. Gypsum can be also reused as raw-material in the production of construction materials.

The cementation procedure with iron scraps promotes with success the recovery of Cu from sulphuric leaching solutions with pH of 2 achieving 99% of extraction. Cement with a purity grade of 99% of cooper was obtained, which has a substantial commercial value.

The nickel hydroxide recovery step with a solution concentrate in nickel achieved an extraction yield of 99% and a purity grade of more than 98%. These results prove the efficiency of the methodology selected in this work.

Due to these factors it can be concluded that the methodology studied in this work besides presenting a way to treat galvanic sludge, presents also an added value through the commercialization and reuse of the products formed along the process.

Acknowledgement: The authors acknowledge to QREN (NORTE-01-0202-FEDER-005509) for the financial support granted.

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