Environmental valuation of the galvanic solid waste generated in a chroming process.

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Abstract

The galvanic process consists on the deposition of a thin layer metal on a metallic or plastic substrate in order to prevent the action of corrosion, increasing the thickness, hardness and wear resistance and giving a more attractive appearance. This deposition occurs by immersing the parts in tanks containing acid or alkaline solutions.

The metallic coating process generates large volumes of effluents that may contain cyanide, heavy metals, solvents, surfactants, oils and greases.The effluents must be sent for the treatment systems in order to attend the Brazilian environmental standards regulations. This effluent treatment is responsible for the generation of galvanic solid waste, also called galvanic sludge, consisting mainly of metals such as chromium, nickel and copper. The storage of this sludge before treatment and final disposal represents a concern as a passive environmental due to its toxicity.

The electroplating arouse concern for the potential environmental risk and in this context this paper intends to give his greatest contribution, discussing one of the main environmental impacts of this process, the waste generated. Moreover, the present study evaluated the economic and environmental value of solid waste from an electroplating company.

The economic value of environmental resources was calculated by summing the costs of wastewater treatment process, the final destination of the galvanic waste and losses of the metal coating process.

Considering all the costs incurred for de company so it does not pollute the environment (costs of wastewater treatment process end the final

destination of the galvanic waste) and the values of the losses in the productive process, the economic value of the environment resources is US$ 16,107.64[1] per year.

With this value is expected the change of vision of what the waste has no aggregate value, not only by the fraction of heavy metals in the sludge, but also the costs of effluent treatment. This process when operated incorrectly causes excessive production of sludge, which raises the costs of storage and end disposal, as can be seen in the analyze of ICP-AES e XRD.

Introduction

The galvanic process consists in depositing a thin layer of metal on a metallic or plastic surface, by chemical or electrochemical means. The goal of the surface treatment process is to prevent corrosion of certain metals, increase the thickness, hardness, resistance to wear and the conductivity of the surfaces, addition to reduce the incidences of stains and grant to the products more attractive appearance. (VEIT, 2006; TOCCHETTO, 2004; BRAILE; CAVALCANTI, 1993).

In Brazil, the galvanic process was initiated to attend decorative requirements of parts to bicycles, harness of horse, belt buckles, trays, teapots and jewelry. The coming of the auto industry favored the development of galvanic industries, encouraging the professionalization and introducing, from 1920, new technologies, standards and quality requirements.

The technical galvanic service, in almost its totality, is processed in tanks containing acid or alkaline solutions. There are two types of baths, electrolytic baths, where metallic deposition or the cleaning of metal parts are made by means of electric current and immersion baths simple, not using the electric current (BRAILLE; CAVALCANTI, 1993).

The scheme of the electroplating process consists in the following steps: pre-treatment →treatment →post-treatment (PACHECO, 2002; SENAI-RS, 2002).

The pre-treatment process consists in preparing the surface to be treated, by mechanical and/or chemical means, so that the coating can have

[1] 1 Brazilian Reais = 1,885 U.S. dollar on 23/04/2012

good adhesion, uniformity and appearance. The mechanical pre-treatment is aimed to remove burrs, grooves, irregularities, among others, by means of abrasive materials. The presence of layers of oxide, oil, grease, dust, among others, affects the metal deposition, making it necessary a chemical pre-treatment, which is divided into degreasing and pickling.

In the treatment stage occurs the metallic deposition by chemical or electrochemical means. In the electrochemical baths the part is connected to the negative pole of a direct current source, making it cathode, in which the deposition occurs. The treatment can develop in a sequence of baths. For example, for the chroming, the part is initially bronzed, then nickeled, and finally, the part receives a layer of chrome.

Finally, in the post-treatment, the parts can go through the washing and/or drying processes to be forward to packaging, storage and shipment.

The metallic coating process generates large volumes of effluents that may contain cyanide, heavy metals, solvents, surfactants, oils and greases. The effluents must be sent for the treatment systems in order to attend the Brazilian environmental standards regulations. This effluent treatment is responsible for the generation of galvanic solid waste, also called galvanic sludge.

According to Milanez et al. (2005), this galvanic sludge has received special attention due to the nature of its constitution based on alkali and transition metals, especially chrome, nickel and copper.

This work performed the characterization of the galvanic sludge by analytic-instrumental techniques to quantify the concentration of chrome, nickel and copper. The function of this characterization was to evaluate the environmental economic value of the solid waste coming from an electroplating company.

Background

The metallic coating process generates large volumes of effluents with a high concentration of metal compounds, acids, additives and metal sludge. The treatment systems are designed to meet the environmental legislation, preventing the discharge of pollutants that may cause harm to human health and to the environmental quality.

The treatment systems are based on the transformation of contaminants in suspension or dissolved in inert gases and sedimentary solids (SILVA et al., 2007; TOCCHETTO, 2004).

The collect and transportation of alkaline effluents and acid effluents are carried out separately, mainly for security reasons. When the process uses cyanide or chrome based compounds, its effluents treatment must contain a step of pre-treatment, where anions cyanide and chromate are treated by oxidation and reduction respectively (SILVA et al., 2007; TOCCHETTO, 2004).

The mixture of alkaline effluents containing cyanide with acid effluents may generate hydrogen cyanide (HCN), which under ambient conditions is a toxic gas. The reduction of hexavalent chrome to trivalent chrome occurs only in the presence of reducing agents and at pH below 3. The current of pre-treated effluent are attached and forwarded to the next step in the treatment process, called neutralization (BRIDGE, 2002; BRAILE; CAVALCANTI, 1993).

The most common method to remove heavy metal is the precipitation. Heavy metals precipitate in the form of hydroxide when treated with sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$). This precipitation occurs in pH at around 8.5. The galvanic sludge is the precipitated that accumulates at the bottom of the decanter and pass through a dehydration process, which may be by filter-press, drying bed, among others. (TOCCHETTO, 2004).

As the study focuses galvanic sludge, they analyzed the ABNT NBR of collection (10.007/04), classification (10.004/04) and storage (12.235/92), the national policy of solid waste and the solid waste policy in São Paulo state.

The ABNT NBR 10.004/04 classifies solid waste about its potential risks to the health and to the environment, so they can be properly managed. The residues are classified into two groups: Class I – Hazardous and Class II- Non-hazardous, being that this last one, is divided into: Class II A- not inert and Class II B- Inert. Therefore, the risk that the galvanic sludge provides must be classified as Class I.

The rule ABNT NBR 12.235/92 determines the condition for storage of any hazardous solid waste (Class I) in order to protect health and the environment. The ABNT NBR 10.007/04 aims to establish the requirements for sampling of solid waste, being used to collect the galvanic sludge.

The Law 12.300/06 establishes policy for the state of São Paulo solid waste, defining principles, objectives, guidelines and tools for the integrated and shared management of solid waste, directing for the prevention and control of pollution, for the prevention and recovery of the environmental quality and to promote public health.

The Law 12.205/10 establishes a national policy of solid waste and lay out their principles, instruments and objectives, as well as guidelines for the integrated management and for the solid waste management, including the hazardous waste.

Methodology

The study was conducted in two stages which, although complementary, they were reported individually due to their characteristics.

The first stage involved a technical visit to a chroming company, where galvanic sludge was collected and a questionnaire was applied in order to identify the process of metal deposition, the effluents treatment, the ways of galvanic sludge disposal and the costs of this final disposal.

The applied questionnaire is an adaptation of the one used by the project of mobile units from the surface treatment sector (PRUMO/TS). This project, according to Mattos et al. (2007), is a program that aims to improve the processes and products of micro, small and medium enterprises by means of utility vehicles equipped with laboratorial equipment.

After the questionnaire, the collection of solid waste was held, according to the guidelines of the ABNT NBR 10.007/04 regarding sampling of solid waste. This collection was made directly in the storage barrel, by removing material until approximately 1 kg. The material was stored in a plastic bottle with identification label, to be analyzed later.

The second step consisted of the characterization of the galvanic solid waste through analytical instrumental techniques and the use of data obtained through the questionnaire and the characterization of the galvanic waste and for the realization of the environment economic valorization of this waste.

The material collected in the company, before being sent for chemical and physical-chemical analysis, was taken to the greenhouse with a temperature of 105º C for 24 hours to remove the liquid fraction (water) from the sludge. The galvanic sludge, after dried, received a heat treatment of 600º C and 1000ºC. The material calcination at these temperatures was held for the analysis of the X-Ray Diffraction, in order to identify the occurrence of variations in the galvanic sludge crystal structure at high temperatures.

The characterization of the galvanic solid residue was performed by chemical and physic-chemical analysis. The chemical characterization was through qualitative and quantitative technique, such as X-Ray Fluorescence (XRF) and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP – AES), respectively. After the chemical analysis, was performed to study the galvanic sludge physic-chemical properties, and the technique applied was the X-Ray Diffraction (XRD).

The environmental economic valuation performed in this study was obtained by the sum of all costs incurred to prevent the company from disobeying the laws and polluting the environment.

The total cost (C_T) of the economic value of the environmental resource was calculated on an annual basis by the sum of the expenses arising from the effluents treatment process (C_{Treat}), the disposal of the galvanic waste (C_{Dest}) and the losses of the metal plating process (C_{Losses}), as shown in equation 1.

$$C_T = C_{Treat} + C_{Dest} + C_{Losses} \quad (1)$$

The costs of the effluent treatment plant and storage of galvanic sludge are arising from the consumption of chemical products used to treat effluents, from the skilled labor to operate the treatment plant and the purchase of barrels, according to ABNT NBR 12.125/92 specifications, for the storage of galvanic sludge until its final destination. The variable C_{Treat} is the sum of these costs incurred to the company.

The correct disposal of galvanic waste has high costs for the generator companies. The value of the parcel C_{Dest} was obtained through the questionnaire applied in the chroming industry.

The determination of the cost of the metallic elements (C_{Losses}) existing in the galvanic solid residue was performed in three steps. The first step was multiply the percentage of the elements of interest (chrome, copper and nickel), obtained by means of characterization, by total of galvanic sludge generated to determine its mass in the residue. The second step consisted in performing the stoichiometric calculation to determine the mass of the components regarding the mass each metallic element in the residue, and the third step was to calculate the values of the bath components lost by its market price.

Results and Discussions

The collection of data relevant to the study was performed by a visit to the chosen company, where a questionnaire was applied and the galvanic solid residue was collected. The questionnaire was applied to identify the metal plating process, the effluent treatment system, the amount of galvanic waste generated and its disposal costs.

The components used in these chromium plating baths are shown in table 1. This table also shows the monthly consumption in kg of each of these components, along with its respective costs.

Table 1 – Bath used in the galvanic process

Baths	Bath Composition	Monthly Consumption (Kg)	Cost (US$)
Degreaser	Caustic Soda	100	111.4
Stripper	-	250	145.90
Acid Activatior	Sulfuric Acid	298	268.75
Alkalin Copper	Sodium Cyanide	70	315.65
	Copper Cyanide	25	305.05
Acid Copper	Copper Sulphate	200	424.40
	Sulfuric Acid	100	90.20
Níquel Watts	Nickel Sulphate	25	330.90
	Nickel Chloride	10	187.80
	Boric Acid	5	11.25
Decorative Chromium	Chromic Acid	100	893.90
	Sulfuric Acid	2	1.80
Total		1.185	3,087.00

The liquid effluents generated in the metal plating baths are forwarded to the effluent treatment plant, which operates in a continuous regime. The effluents are collected and sent to the station by two collection network, such as, the acid and the alkalis effluent collecting. The steps of treatment and the chemical products used are shown in figure 1.

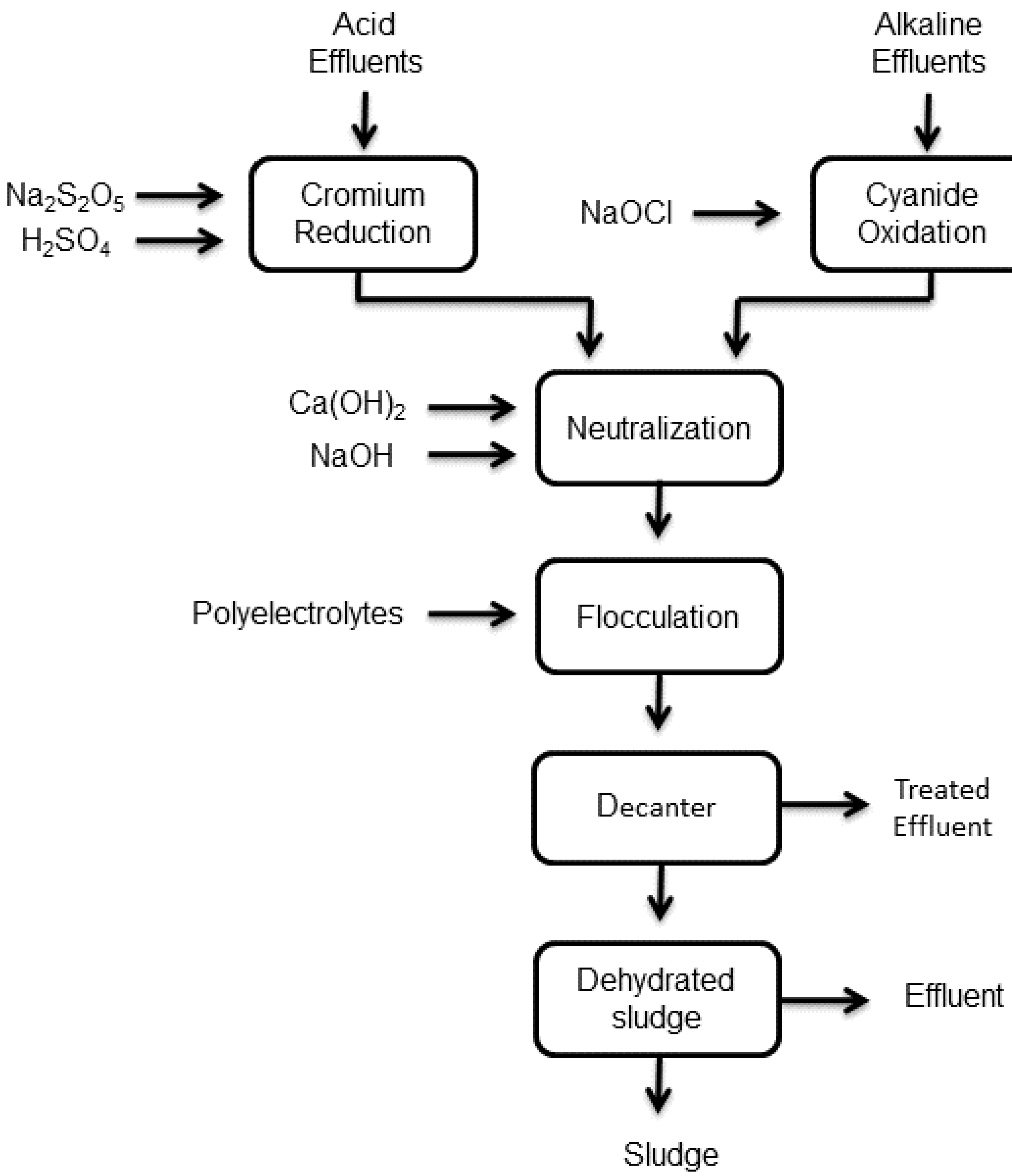

Figure 1 – Flowchart of the Effluent Treatment Process.

The acid effluents are sent to a treatment vessel in which the chromium is reduced by the addition of sodium metabisulfite ($Na_2S_2O_5$) and sulfuric acid (H_2SO_4). The alkaline effluents are sent to a tank of cyanide oxidation, where sodium hypochlorite (NaOCl) is used. These two types of treated effluents are sent to a neutralization tank, where the metals are precipitated by addition of calcium hydroxide ($Ca(OH)_2$). The pH adjustment for the neutralization is done by adding sodium hydroxide (NaOH). After the neutralization the effluent is forwarded to the flocculation tank where the addition of polyelectrolyte results in the formation of flakes which are removed in step decantation.

The treated effluent is sent to the sewage disposal system and the sludge produced at the bottom of the tank passes through the filter-press to be dehydrated before being stored. This storage is held in iron barrels with plastic bags. Nowadays, the allocation of galvanic solid residue is held by an outsourcer company (Ecológica Nova Era Indústria e Comércio Ltda), which holds the collection of industrial waste and moves it to a final location at a cost of US$ 291.80 per tonne.

Galvanic Sludge Characterization

The galvanic sludge, before being sent to chemical and physic-chemical analysis, passed through the drying process at 105º C for 24 hours. With the wet and dry mass of sludge, the moisture content of this residue was estimated in 63.5%. This measurement confirms the high moisture content of the galvanic sludge cited in literature, which are on average of 60%. An efficient dewatering process would be able to reduce the amount of sludge generated, by reducing the costs of storage and disposal.

The first analysis performed was an X-Ray Fluorescence to detect the main elements present in the residue. The result is presented in order of prevalence in table 1.

Table 1 – Galvanic sludge qualitative characterization.

Prevalence order	Elements
Prevalences	Calcium and Sulfur
Average proportions	Copper, Chrome, Iron and Nickel
Traits	Sílica, Magnesium, Phosphorus, Zinc.

From the qualitative analysis it was performed an quantitative analysis Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to obtain the exact contents of elements present in the galvanic sludge. The result of ICP-AES is shown in table 2. As the galvanic solid residue is very heterogeneous, the analysis was not able to detect all the elements present, shown in table 2, only the most relevant to the study and/or that present risk to the environment.

Table 2 – ICP-AES analysis result

Element	Weight (%)
Ca	22.60
Cr	3.34
Fe	1.57
Ni	0.58
Cu	3.71
Zn	1.43
Ba	0.01
Pb	0.01
Total	**33.25**

After the chemical analysis, X-Ray Diffraction was performed to study the physic-chemical properties of galvanic waste. In the diffractograms patterns obtained, it was observed the formation of compounds with increasing of temperature.

The result of the sample treated at 105ºC, demonstrates that the most abundant element in the residue at this temperature is the hydrated calcium sulphate ($Ca(SO_4).(H_2O)_{0.5}$), followed by calcium carbonate ($CaCO_3$) and copper sulfide and iron ($CuFeS_2$), as seen in Figure 2. At 600ºC occurred the dehydration of calcium sulphate ($Ca(SO_4)$), as shown in Figure 3, and the formation of Calcium chromate ($Ca(CrO_4)$). In the analysis at 1000ºC it was detected the calcium sulphate as predominant and the formation of chromium oxide and copper ($CuCrO_2$), phosphate iron oxide ($Fe(PO_4)_2O$) and cuprous chloride (CuCl). However, due to the high temperature, the calcium carbonate decomposed, and these results are presented in figure 4.

According to the results of ICP-AES analysis, the amount of calcium present in the residue is 956.90 kg. This whole mass is derived from the calcium hydroxide used in the neutralization step of the wastewater treatment system. The X-Ray Fluorescence analysis found that this element at 105ºC is in the form of calcium carbonate and hydrous calcium sulfate, popularly known as plaster, used in building constructions and in medicine (orthopedics). But, there aren´t any technologies or viable economic applications that allow the recycling or recovery of hydrated calcium sulfate.

These results demonstrate that the treatment system does not operate properly. Creating a sludge volume bigger than necessary to treat effluent, giving the company an unnecessary consumption of chemicals products, storage and final disposal.

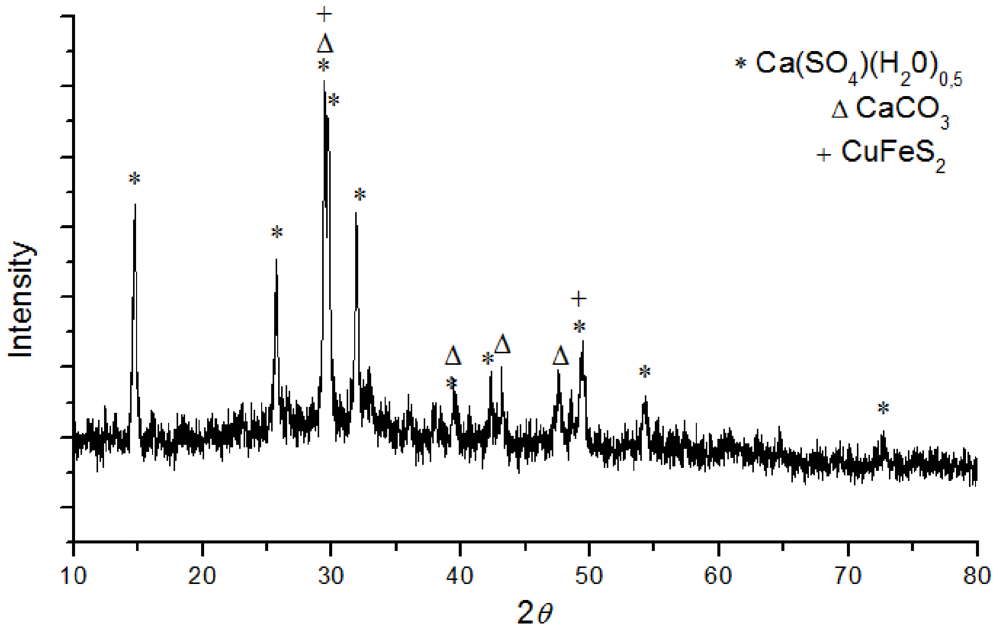

Figure 2 – Diffractograms patterns of sample treated at 105°C.

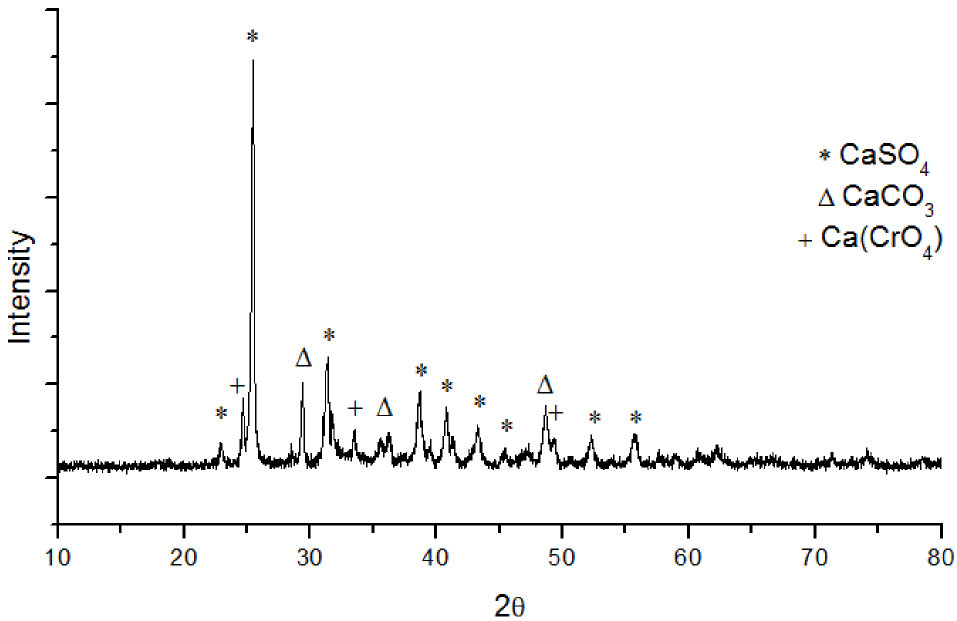

Figure 3 – Diffractograms patterns of sample treated at 600°C.

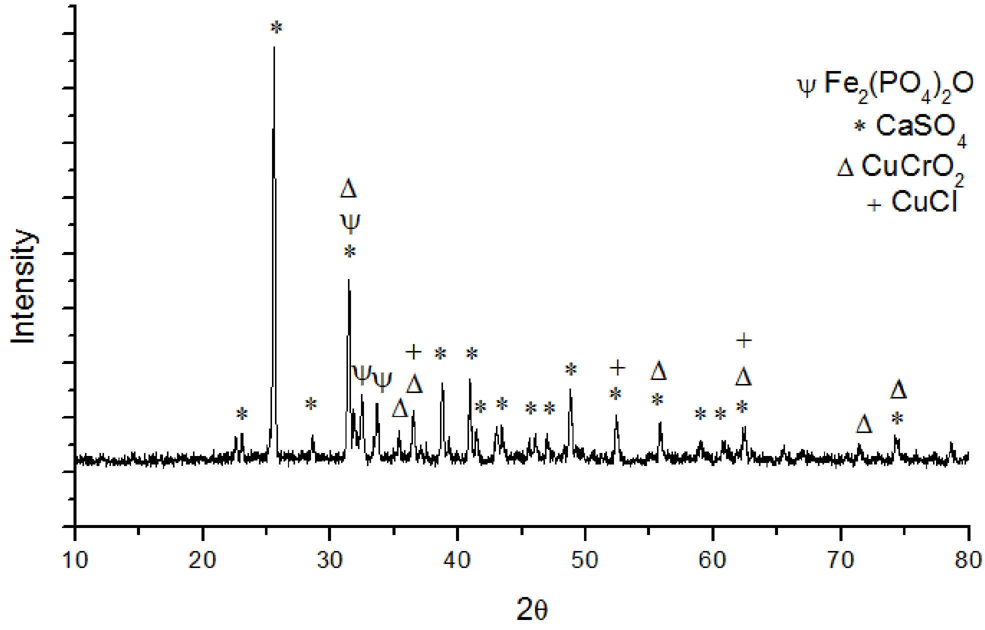

Figure 4 – Diffractograms patterns of sample treated at 1000°C.

Environmental Valuation of the Galvanic Waste

The environmental economic valuation was carried out according to the methodology presented. The cost of the effluents treatment plant were obtained by questionnaire applied in the company, which quantified the costs of products used in the treatment and their respective masses, spending on barrels and plastic bags and the salary of the chemical technician responsible for the station. The result of this portion C_{Treat} is shown in table 3.

Table 3 – Cost of the effluents treatment station.

C_{Treat}	Anual Consumption	Anual Cost (US$)
Chemical Products used	3,147.04[2] (Kg)	1,430.00
Chemical Technician Responsable	1[3] (un)	4,788.85
Barrels with plastic bags	58 units[3] (un)	1,907.70
Total		**8,126.55**

The value of the disposal cost has been obtained through the questionnaire applied in the chromium plating industry. The data used were the

[2]Quantity expressed in kilograms. (Kg)
[3]Quantity expressed in unity. (un)

annual generation of galvanic sludge (11.6 tonnes) and the cost that the outsource company charges for the residue disposal (US$ 291.80/tonne), resulting in an annual cost (C_{Dest}) of US$ 3,384.61 for the company.

To determine the cost of metallic elements present in the galvanic solid residue, it was first measured the mass of the elements present in the residue by multiplying the ICP-AES analysis to the total of dry galvanic sludge (4,234 kg), and the result is shown in table 4.

Table 4 – Mass of elements in the galvanic sludge.

Element	Weight (%)	Mass Elements in the Resídue (Kg)
Ca	22.60	956.88
Cu	3.71	141,42
Cr	3.34	66,47
Fe	1.57	24,51
Zn	1.43	157,08
Ni	0.58	60,55
Ba	0.01	0,42
Pb	0.01	0,57
Total	**33.25**	**1,407.90**

The determination of the bath elements for the elements in table 4 was necessary to quantify how much each component contributed to the total percentage of the element in the residue. This value was calculated based on the mass of the components used in each bath, and the result is shown in table 5.

Table 5 – Mass of the elements of interest in the galvanic sludge.

Element	Percentage of the Elements in the Residue (%)	Bath composition	Percentage of elements Divided by Baths (%)	Mass of the Elements in the Residue (Kg)
Cu	3.71	$Cu(CN)_2$	0.56	23.56
		$CuSO_4$	3.15	133.52
Ni	0.58	$NiSO_4$	0.40	16.67
		$NiCl_2$	0.18	7.84
Cr	3.34	CrO_3	3.34	141.42
Total				**323.01**

The mass of the bath composition lost in the process was determinated by performing the stoichiometric calculations that converted the mass elements, presented on table 5, again the bath mass components, and the result of this calculation is presented on table 6.

Table 6 – Mass of the components in the galvanic sludge baths.

Bath composition	Mass of the Residue Elements (Kg)	Mass of the Bath Mass Components Present in the Residue (Kg)
$Cu(CN)_2$	23.56	42.86
$CuSO_4$	133.52	335.34
$NiSO_4$	16.67	43.95
$NiCl_2$	7.84	17.32
CrO_3	141.42	271.96
Total	**323.01**	**711.43**

By quantifying the mass of bath components present in the galvanic solid residue, we performed the calculation of the cost of losses in the production process (C_{Losses}). These costs are related to products purchased for the chroming process, but that due to the losses during the process, are sent to the treatment plant and become galvanic sludge. The C_{Losses} value is the sum of the loss of all bath components, resulting in a value of US$ 8.619,39, according to table 7.

Table 7 – Total value of the process inefficiency.

Bath Composition	Mass of Bath composition Present in the Residue (Kg)	Price by Kilograms (US$)	Value Lost with Residue (US$)
$Cu(CN)_2$	42.86	12.20	522.91
$CuSO_4$	335.34	2.12	711.61
$NiSO_4$	43.95	13.24	581.78
$NiCl_2$	17.32	18.78	325.30
CrO_3	271.96	8.94	2,431.04
Total	**711.43**		**4,572.63**

In table 8, the loss in the metal plating process generates a yearly loss to the company corresponding to about 18% of the cost to obtain the products.

Table 8 – Comparing consumption and losses in the process.

Bath	Composition	Anual Consumption (Kg)	Anual Cost (US$)	Mass Present in the Residue (Kg)	Value Lost in the Residue (US$)
Cobre	$Cu(CN)_2$	300.00	3,660.48	42.86	522.91
	$CuSO_4$	2400.00	5,092.84	33.,34	711.61
Níquel	$NiSO_4$	1.200.00	3,970.82	43.95	581.78
	$NiCl_2$	300.00	2,253.58	17.32	325.30
Cromo	CrO_3	120.00	10,726,80	271.96	2,431.03
Total		**4,320.00**	**25,704.52**	**711.43**	**4,572.63**

Considering all the costs incurred for the company so that it does not pollute the environment and the values of losses in production, the economic value of environmental resources (C_T) is US$ 16,083.79 per year, as observed in table 9.

Table 9 – Result of the environmental economic valuation.

Parcelas dos Custos	Valor Total Anual
C_{Trat}	US$ 8,126.55
C_{Dest}	US$ 3,384.61
C_{Perdas}	US$ 4,572.63
C_T	**US$ 16,083.79**

According to Mattos (2007) the PRUMO/TS project serves about 30 chroming companies in the east city of São Paulo. Extrapolating the value obtained by valuing to the 30 companies, the economic value of the natural resources to the east is US$ 482,513.70.

Conclusions

The environmental economic valuation performed in this study confirms the environmental economic potential of the galvanic residue. The compilation of the results obtained through the questionnaire, and the chemical and physic-chemical analysis proceeded in an economic environmental value of US$ 16,083.79 per year for the company studied.

From the results presented, the reduction of losses of the process would result in economic earnings, once it would reduce the consumption of chemical products and the generation of waste, and environmental, with the reduction of the quantity of hazardous elements in the galvanic sludge. In case this reduction in loss is not possible, there are techniques for recovering of elements of interest, for example, by combined sulfidation and oxidation treatment, that recovers chromium, copper and nickel.

The residue moisture content is 63.5%. This means that the largest portion of what is being sent as sludge is water. The main action to reduce the amount of sludge generated is the decrease of this fraction of moisture. As the dehydration process used in the company is the filter press, just by handling it the right way would be able to reduce the moisture in the sludge.

The moisture content of the residue is 63.5%. This means that the largest portion of this sludge is being forwarded as water. The main action to reduce the amount of sludge generated is the decrease of this fraction of moisture. As the dehydration process used in the company is the filter press, handling it correctly would be enough to reduce the moisture in the sludge.

With this value it´s expected a change view that the residue does not have aggregated value, not only by the fraction of heavy metals in the sludge coming from loss of the chroming process, but also for the wastewater treatment. This process, when operated incorrectly causes excessive production of sludge that leads to the increasing in the costs of storage and final disposal, as it can be seen in ICP-AES and XRD analysis.

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