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Viability for the production of inorganic pigments from galvanic sludge

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Abstract
The residue from the treatment of effluents from the galvanizing industries is called galvanic sludge and has potentially toxic metals in it. Incorrect disposal of galvanic sludge can cause damage to the environment and health. The work sought to evaluate the feasibility of using galvanic sludge in the production of inorganic pigments. Characterization of the residue was carried out using atomic absorption spectroscopy, X-ray fluorescence, moisture determination, sieve granulometry, fire loss, thermogravimetry, and differential thermal analysis. The results obtained bought the possibility of p production of pigments with galvanic sludge.

Keywords: waste characterization, galvanic sludge, inorganic pigments

1. Introduction
The National Policy on Solid Waste refers to the need to take advantage of waste arising from human activities and should be disposed of properly, only unused waste [1]. Every industrial process generates waste that is sometimes toxic, making its disposal and reuse a strategic issue. Galvanization is a surface treatment in which the formation of a coating layer occurs, by immersing the part in a solution containing the desired ion [2-3]. The process consumes large amounts of water for electrolytic and chemical baths, which after the treatment of effluents, generate sludges of difficult disposal [4]. Galvanizing mud presents alkaline and transition metals, potentially toxic to humans and the environment [5]. The implementation of environmental policies has made the industries seek viable means for the recycling and stabilization of the metals present in the sludge [6-7].
However, the traditional destination of the galvanic residue continues to be the shipment to industrial landfills, an onerous alternative and that, although it minimizes the occurrence of environmental accidents, does not effectively impede them [8].
The paper aims to evaluate the feasibility of recycling the galvanic sludge by incorporating it into the production of inorganic pigments. The production of inorganic pigments is an opportunity to reduce costs with disposal in landfills and reduce the risk of contamination of the environment and man. As specific objectives are the characterization of galvanic sludge utilizing physical-chemical analyzes and the comparison of results with existing pigments.

2. Bibliographical Review
2.1 Surface treatment
Among the most critical sectors concerning the emission of pollutants into the environment is the galvanic industry, being responsible for the generation of waste containing heavy metals [9]. The term electroplating refers to the process of depositing a thin layer of metal on a part by immersion in a bath which is intended to embellish, protect against corrosion or increase the strength of the material [10].
Before deposition, the part is pre-treated to ensure excellent adhesion, which consists of the removal of oils, oxides, paints, surface fouling, and other impurities, based on three operations: polishing, degreasing, and etching [11].
It then goes on to the coating process, which runs in tanks containing acid or alkaline solutions. The baths can be electrolytic, in which metallic deposition occurs through electric current, or pure immersion, without the use of electricity [12].
Finally, the part goes through the washing process to remove the film from concentrated chemicals adhering to the elements after the coating baths.
Waste from the galvanic activity is atmospheric emissions through steam losses in heated baths, liquid effluents used in chemical baths, pretreatment products, washing water and solid waste, such as packaging of chemicals and sludge derived from treatment units, these being the most representative [12].

2.2 Galvanic sludge
Waste generation is inherent in any industrial process and requires adequate treatment and disposal following environmental laws, giving priority to recycling [13].
Classified as Waste Class I - Hazardous, according to ABNT NBR 10004: 2004, galvanic sludge results from the effluent treatment of the metal treatment surface industry [14]. It is generally in the pasty state, containing from 60% to 75% water after passing through the filter press [15]. Disposal or improper storage of this waste can cause damage to the environment and health. According to Amaral (2015), this is mainly due to its toxicity and bio accumulative effect [12].
The main obstacle to the treatment of galvanizing sludge is the lack of uniformity in the percentages of each element and in the immobilization of metals, which is the leading way of reducing the environmental impact caused by the residue [16]. The final disposal of the galvanic sludge has been carried out in industrial landfills [17]. Around 100,000 tons of valuable metals in the form of galvanic sludge are wasted a year only in China [12].
New technologies have been studied for the disposal of galvanic sludge to prevent the deposition in landfills, such as the incorporation in bricks [18] cement hardening

accelerators [19], immobilization in vitreous material [20] inclusion in red ceramics) [12].
Existing techniques for extraction of metals from galvanic sludge are based, for example, on sulfation and leaching with thiosulphate [21] and pyrometallurgy [22].
The reuse of galvanic sludge as an inorganic pigment increases the life cycle of hazardous waste, contributing to environmental preservation and adding value to an economically under-expended liability [22].

2.3 Incorporation of galvanic sludge in the manufacture of pigments

They use galvanic sludge with high concentrations of chromium (III) for the production of ceramic pigments in pink and green colors. The raw materials used together with the residue were SiO_2 and $CaCO_3$, as well as $Na_2B_4O_7$ and NaCl for green and SnO_2 $LiBO_2$ for pink [23].
Inorganic pigments made from galvanic sludge (rich in Fe_2O_3, SO_3, CaO, and NiO) and kaolinite obtained from 15 samples in proportions (sludge: kaolinite) 1:0, 0:1, 1:1, 1: 2 and 2:1 [24].

Inorganic pigments developed from the galvanic sludge, whose main elements were iron, nickel, chromium, and zinc. The residue was dried at 105 °C and characterized by X-ray fluorescence, atomic absorption, leaching/solubilization test, pH, moisture, thermal analysis, and X-ray diffraction. The slurry was ground and calcined at 520 °C for 2 hours. The precursor formulation of the pigment was 33.33% Cr_2O_3, 33.33% Fe_2O_3 and 33.34% ZnO [11].

3. Materials and Methods

The research involved technical visits to the company that transferred the galvanic sludge to the study, located in the municipality of Novo Hamburgo. The visits aimed to survey the processes that originated the waste (pre-characterization), according to the requirement of ABNT NBR 10007:2004 [25].
Samples were collected directly from the press, removing material until approximately 1 kg daily for five days. The samples were stored in plastic bags and identified. The sample analyzed with SEM according to figure 1.

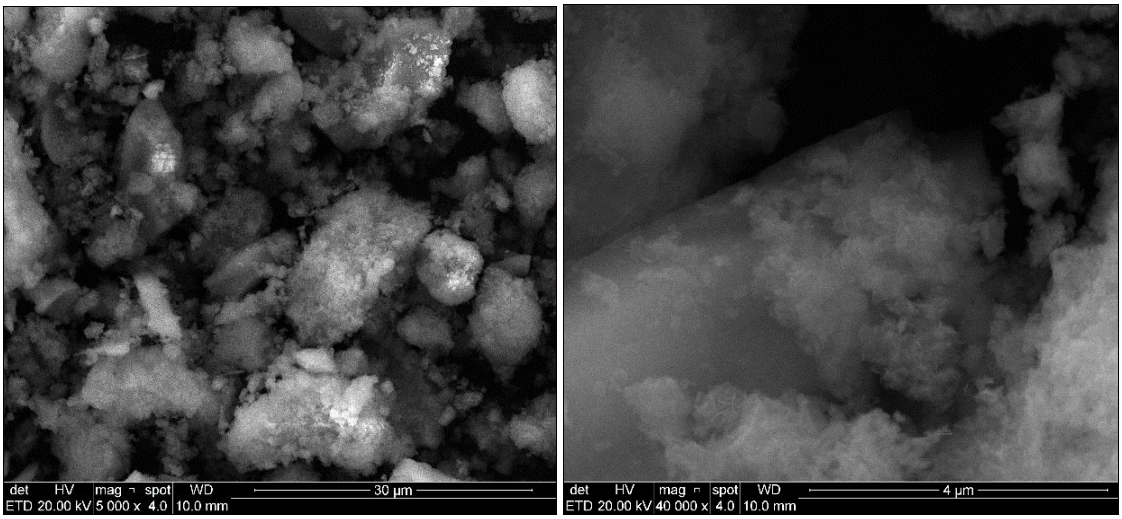

Fig 1: SEM result of the galvanic sludge sample

Subsequently, 300 grams of each sample was reserved. The rest of the material was mixed manually and quartered. One of the four parts was separated for analysis, while the others were stored.
The analysis of Atomic Absorption Spectroscopy, as well as the analyzes of X-ray Fluorescence, Moisture, Sieve Granulometry, Fire Loss, Thermo gravimetric, and Differential Thermal Analysis, were carried out.

3.1 Drying

The samples, corresponding to the five days sampled and to the quartet, were placed in the oven with a temperature of 105 °C for 24 hours for the removal of water from the sludge. The analyzes of X-ray fluorescence, sieve granulometry, fire loss, differential thermal analysis, and thermogravimetry performed from this material.

3.2 Atomic Absorption Spectroscopy

The spectrometer length used a flame atomic absorption spectrometer. Through this method, the concentration of copper and iron in the material was determined. The analysis of Atomic Absorption occurred in triplicate; the average concentration obtained is presented in Table 1.

Table 1: Results of the quantitative analysis of *Cu* and *Fe* elements for the quartered sample

Element	Concentration
Copper	6.895mg/g
Iron	1.712mg/g

The sludge in the study did not present high concentrations of copper and iron in its composition, indicating the efficiency of the filtration system of the baths.

3.3 X-Ray Fluorescence

The X-ray Fluorescence assay performed for the six samples, previously dried, using an energy dispersion spectrometer presents the results found in the X-Ray Fluorescence analysis according to Table 2.

Table 2: Composition of samples

Identification	Majority items (more than 50%)	Minority items (between 50% and 5%)	Trace elements (less than 5%)
Sample 07/19/18	Zn	Si, Al	Ca, Cu, Ni, S, Se, Fe, P, K, Cr
Sample 07/20/18	-	Zn, Si, Al, Ca, Cu	Ni, Mg, S, Fe, Se, P, K, Sr
Sample 07/23/18	-	Zn, Si, Al, Ca, Cu	Ni, Mg, S, Fe, Se, P, K, Sr
Sample 07/24/18	-	Zn, Si, Al, Ca, Cu	Ni, Mg, Se, S, Fe, P, K, Sr, Cr
Sample 07/25/18	Zn	Si, Al	Ca, Cu, Mg, Ni, Se, S, Fe, P, K, Sr
Quartered sample	-	Zn, Si, Al, Ca, Cu	Mg, Ni, S, Se, Fe, P, K, Sr, Cr

The lack of uniformity in the galvanic slurry composition was verified through the analysis, taking into account the variations in the coating process. The demands that the company receives have different specificities, directly influencing the generated effluent. The element with the highest concentration in the sludge studied was zinc, which can serve as a raw material for the manufacture of inorganic pigments. However, other commonly used elements (Iron and Chromium) are presented only as traces. The characterization of galvanic sludge by X-ray Fluorescence is joint. Borgo (2005) found mainly the presence of Copper and Zinc [7]; Milanez (2003) Iron, Nickel, Chrome, and Zinc [11]. The predominant element found by Boss *et al*. (2011) was iron [4]; already for Pinto (2012) was Zinc and Iron [25]. While for Amaral (2015), it was Copper [12].

3.4 Humidity

The principle of the method of determining the moisture content consists of the elimination of the water by controlled heating and verification of the mass difference. The analysis was performed in duplicate for the six samples according to CEMP - n° 105 [26].

Twelve alumina crucibles with 30 grams of sample were sent to the oven at 105ºC until constant mass. From the third weighing, the mass, to the nearest decimal place, has stabilized.

However, also from the third weighing, the thousandths and tenths of a thousandth (last two digits after the comma) increased. A possible justification for the event is the hygroscopic nature of the material, which, after reaching a constant mass, absorbs moisture from the environment. Silica (SiO_2) and copper sulfate ($CuSO_4$) are examples of materials with this property. The average water content of the galvanic slurry obtained is shown in Table 3.

Table 3: Average percentage of water in the galvanic sludge

Identification	07/19/18	07/20/18	07/23/18	07/24/18	25/07/18	Quart.
Moisture content	53.15%	62.50%	64.85%	53.95%	51.30%	58.69%

The moisture values obtained represent that, despite the treatments performed in the galvanic sludge and its passage through the filter press, water is the main constituent of this residue. The other authors that determined the percentage of water in the galvanic sludge found the values of 26.7% (BOSS *et al*., 2011), 30.35% (MILANEZ, 2003), 37.66% (ALVES and SEO, 2014), 85, 7 and 84.1% (AMARAL, 2015).

3.5 Mass Loss

The determination of fire loss consists of the burning, decomposition, and elimination of organic materials present in the sample. The analysis was performed for each of the six samples in triplicate, according to CEMP - n° 120 [27].

The performance of the test was as follows: eighteen alumina crucibles received 1 gram of sample each. The whole was brought to the muffle at 950 °C for 4 hours. At the end of the heating period, the crucibles were weighed again for comparison with the initial mass. The determination of Fire Loss occurs in triplicate for the six samples, the values found, as well as the calculated average is in Table 4.

Table 4: Result of the fire loss determination, in percentage

Identification	1 st	2nd	3rd
Sample 07/19/18	32.56%	32.61%	37.51%
Sample 07/20/18	32.20%	32.65%	41.53%
Sample 07/23/18	33.04%	33.23%	33.42%
Sample 07/24/18	35.84%	34.76%	33.81%
Sample 07/25/18	34.72%	34.73%	34.85%
Quartered sample	35.69%	35.86%	35.97%

The results indicate that the galvanic sludge analyzed has considerable quantities of organic matter, with average values close to 35%. The literature shows that for Lemos (2009), the fire loss was exponential, ranging from 9 to 15% between 100 and 900ºC. Borgo (2005) obtained value equal to 0.53%.

3.6 Thermogravimetry and Differential Thermal Analysis

The material heated in a temperature range between 25 °C and 900 °C, under a heating rate of 10 ° C in-1. The interpretation of the results of Thermogravimetry (Graph of Figure 2) was made simultaneously with those of the Differential Thermal Analysis (Graph of Figure 3), since the first curve indicates the variation of the mass of the sample (losses and gains), while the second curve allows identifying the reactions and phase transitions.

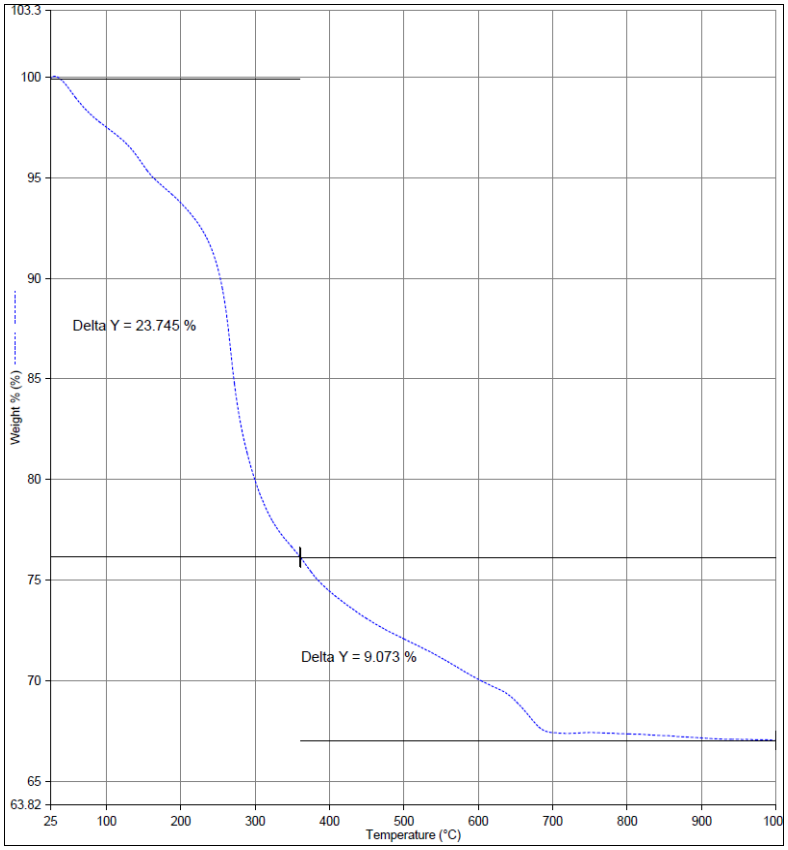

Fig 2: Result of mass loss determination, in percentage

The graph of figure 2 shows a continuous mass fall to 700ºC, equivalent to 32.818%, indicating that at higher temperatures, no organic matter remains. The reduction of the mass was similar to that found during the determination of Loss to Fire. An acceleration of the mass loss occurs after 350ºC, a behavior similar to that pointed out by the authors Casali *et al*. (2002) during the thermo gravimetric analysis of the titanium dioxide pigment [28].

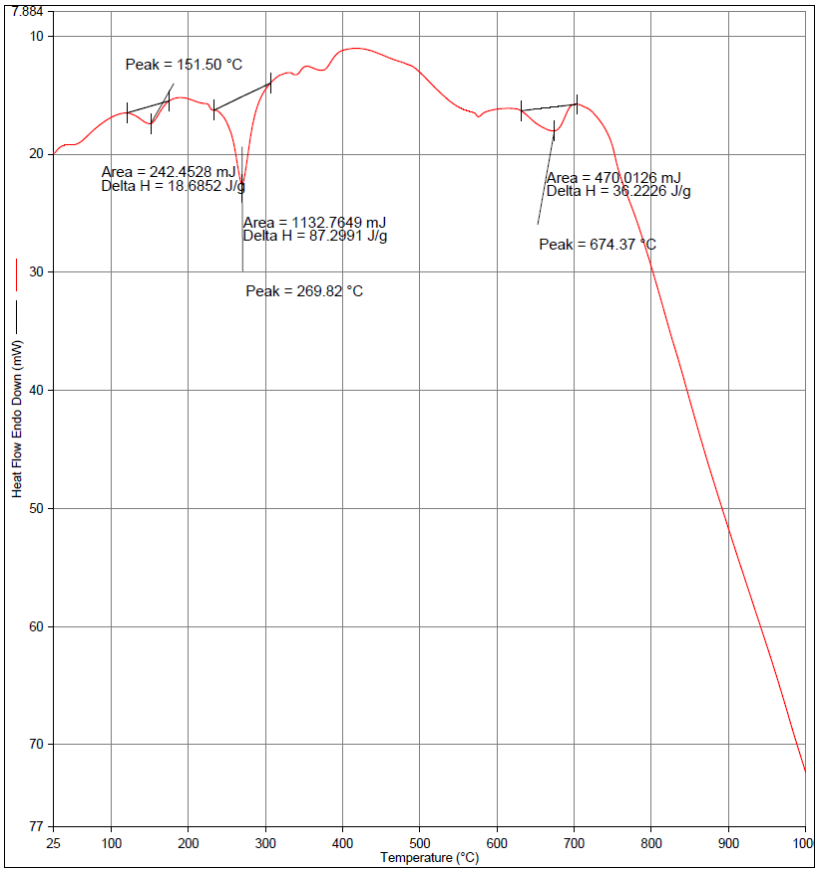

Fig 3: Differential Thermal Analysis Curv

In the graph of figure 3, we have three endothermic peaks in evidence. The first one occurs at 151.5 ° C, probably related to the elimination of surface water. The second peak occurs at 269.82ºC, referring to the decomposition of the organic material with the release of H2O and CO2. The third occurs at 674.37ºC and may be associated with the process of carbonate decomposition, water loss, and organic waste. Similar results were found in galvanic sludge studies performed by Rocha, Zorel, and Lando (2017) and Santos *et al*. (2006) [29].

3.6 Granulometry by Screen

The test performed for the six samples occurred in duplicate only for the quartered sample. For the analysis, 25 grams of sample previously dried by beaker was used. The samples sieved according to CEMP norm No. 081 - Determination of the granulometric distribution and modulus of fineness [30]. Tables 5 and 6 relate the mesh aperture to the percentage of mass retained in each sieve during the Granulometry by Sieve test.

Table 5: Result of the fire loss determination, in percentage

Screens (mm)	Mesh (mm)	Retention Mass (g)	Accumulated Mass (g)	Past Mass (g)	Retained (%)
4	4.75	6.05	0.00	25.50	23.73
6	3.35	2.30	8.35	17.15	9.02
12	1.70	6.61	14.96	10.54	25.92
20	0.85	6.43	21.39	4.11	25.22
30	0.60	1.72	23.11	2.39	6.75
40	0.42	0.83	23.94	1.56	3.26
50	0.30	0.49	24.43	1.07	1.92
70	0.21	0.26	24.69	0.81	1.02
100	0.15	0.23	24.92	0.58	0.90
140	0.10	0.05	24.97	0.53	0.20
200	0.07	0.08	25.05	0.45	0.31
270	0.05	0.20	25.25	0.25	0.78
Background		0.04	25.29	0.21	0.16

Table 6: Results of the grain size test of quartet sample B

Screens (mm)	Mesh (mm)	Retention Mass (g)	Accumulated Mass (g)	Past Mass (g)	Retained (%)
4	4.75	8.83	0.00	25.00	35.31
6	3.35	3.22	12.05	12.95	12.88
12	1.70	5.91	17.96	7.04	23.64
20	0.85	4.18	22.14	2.86	16.72
30	0.60	0.99	23.13	1.87	3.96
40	0.42	0.47	23.60	1.40	1.88
50	0.30	0.29	23.89	1.11	1.16
70	0.21	0.23	24.12	0.88	0.92
100	0.15	0.12	24.24	0.76	0.48
140	0.10	0.12	24.36	0.64	0.48
200	0.07	0.10	24.46	0.54	0.40
270	0.05	0.13	24.59	0.41	0.52
Background	-	0.01	24.60	0.40	0.04

During the analysis, there were losses, so the percentage retained was not equal to 100%. Galvanic slurry did not show uniform grain size. For application as a pigment, it is necessary to pre-grind the galvanic sludge to reduce it to dimensions between 0.1 and 10 μm as specified by Bondioli *et al*. (1998) [31].

4. Conclusions

The present paper presented the characterization of the galvanic sludge through physical-chemical analysis and the evaluation of the feasibility of incorporating it in the production of inorganic pigments.

The relevance of the theme lies in the recycling of hazardous waste, which entails excessive costs with its disposal, as well as the risk of contamination to the environment and man [32].

X-ray fluorescence indicates that the main constituent of the galvanic sludge analyzed is zinc, present in pigments such as zinc white (ZnO). The moisture analysis reveals that water corresponds to more than 50% of the composition of the residue.

Besides, the galvanic sludge behaved like the titanium dioxide pigment during the thermogravimetric analysis.

The results obtained by the characterization show that the incorporation of galvanic sludge in the formulation of inorganic pigments is a viable alternative since it presents in its composition elements frequently used for this application. The literature shows successful cases of pigments synthesized from galvanic sludge.

5. Acknowledgements

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