A Study of different cements and waste ceramic (CDW) on the process of Solidification/Stabilization (S/S) of galvanic sludge (GS)

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Abstract

In many countries, a large variety of industrial waste is generated each year. The control of the risks of water and soil pollution and degradation in areas where these wastes are deposited requires the improvement of waste management technologies. The S/S process involves adding a binder to promote solidification of the residue and the stabilization of the contaminants thereby increasing its environmental suitability. In this process the amount of binder required may be high, increasing the cost of the process. Moreover, the type of binder is also extremely important, because the success of the technique depends essentially on the waste-binder compatibility. In this study, the galvanic sludge (GS), generated during the surface treatment of metallic materials having chromium and nickel as major pollutants was treated. In order to ensure the stabilization of the heavy metals, two binders were used: Portland cement (PC) and calcium aluminate cement (CAC). In addition to a conventional solid matrix (composed of cement and sludge), construction and demolition waste (CDW) were used as an alternative aggregate to produce mortars. The results showed that the presence of sludge proportionally reduces the mechanical strength. The presence of CWD mortar, although it reduced the consumption of GS, also reduced of the consumption of cement and improved the mechanical performance. Leaching tests showed that samples made with both CAC and PC presented no hexavalent chromium.

Key words: wastes, sludge, blinders, solidification, stabilization, galvanic sludge, leaching tests,

1. Introduction

The plating process is a treatment in which certain materials, especially metal, undergo coating to acquire protection against the weather and handling, besides providing beauty, durability and improvement to surface properties in order to meet the needs and demands of the market. The purpose of plating is to prevent galvanic corrosion, increase the solidity and conductivity of the surfaces, and to make the products appear more attractive by depositing a thin metal layer on the surface of a material.

The principle of electroplating is the electrochemical deposition of a thin metal layer on an object being bathed by the action of a direct current in an electrolyte solution containing metal cations used for coating (called a galvanic bath). The metals that are normally appliedto produce galvanized coating are chromium, tin, copper, zinc, nickel, cadmium, lead and iron and for special purposes silver, gold or platinum are used. (Bednárik et al., 2005).

However, after a certain period, the galvanic bath becomes unusable and needs to be replaced, which ends up generating a lot of waste.Chemical precipitation is the most widely used method for the treatment of galvanic wastewater that is indicated in the literature (Bednárik et al., 2005). This conventional method for treating industrial wastewater containing metals in an aqueous solution is to increase the pH to values above 9.0; promoting conditions of low solubility of the metal hydroxidesthat are precipitated as hydroxides or various complexes. Due to the supersaturating conditions, colloidal solids form and require coagulation/flocculation steps duringthe separation phase of the residual liquid. A considerable amount of precipitate (galvanic sludge), usually classified according to Brazilian standard NBR 10004 as residue class I, as dangerous and toxic and is a waste product of the treatment process.

Because the galvanic sludge is classified as hazardous waste, it is discarded in large landfills and its disposal is costly. In addition to the cost, the scarcity of suitable landfillsis, in fact, the main problem. In Brazil in 2005, there were more than 4.500 galvanic companies, many of which (90%)were small companies (Matos, 2011).Moreover, the country has only sixteen industrial landfills and the state of Paraná has only one (ABETRE, 2000). Therefore, alternative methods of treatment are essential.

The solidification/stabilization (S/E) technique was developed in the 1960s for radioactive waste treatment. In the last decades, it has been used in the treatment of many industrial wastes, since it is possible through this process to improve physical characteristics, reduce leachability and to limit the solubility of their contaminants(Luz et al., 2006). The S/S process not only improves the physical and chemical conditions of the residue, it is also inexpensive compared to other treatment techniques because it includes cement and other byproducts (fly ash, ground granulated blast furnace slag) that are mostly used as building materials in construction. These aspects are extremely relevant, since the resultant solid matrix can reach an interesting performance level when it isused as building material (Hills and Pollard, 1997, Luz et al, 2006).

However, in this process, the identification of bindersthat are able to assume the fixation of contaminants is essential for the success of the technique.Portland cement (PC) is the main binder used in the S/S process. However, many heavy metals (mainly chrome) that are present in galvanic sludge are strong retardants of PC hydration, resulting in an increase in the leachability and solubility of the contaminants and a reduction in compressive strength.

Recently, the retention capacity for heavy metals of calcium aluminate cement (CAC) was also investigated. Navarro-Blasco et al. (2012) studied CAC pastes containing Pb, Zn and Cu and the leaching tests presented a 99.9% retention.

In other recent study, Coeli(2013) verified that the presence of Cr^{6+}strongly reduced the compressive strength of solid matrix (mortar), however the leaching tests showed the high efficiency of CAC regarding Cr^{6+} immobilization (> 90%) and also displayed both the capacity for hexavalent chromium retention and its reduction.

The high efficiency of the immobilization of Cr by CAC cement is related to $Cr^{6+}$and can be reduced to Cr^{3+},and its high alumina content means that it could replace Al in the majority of calcium aluminate hydrate phases (Navarro-Blasco, et al., 2012;Coeli, 2013).

The aim of this paper was to study the S/S of galvanic sludge(GS). GS was obtained from the chromium electroplating processand contains chromium as its main heavy metal. Based on the S/Stechnique, a new methodology was developed to encapsulate GSbased on calcium aluminate cement (CAC). The construction and demolition waste (CDW) of ceramic block was also utilizedto obtain a solidmatrix (MS).The properties of the solid matrix were evaluated by mechanical and environmental tests.

2. Materials and Methods

In the present study, GS came from a Brazilian industry, atPatoBranco, a city in the state of Paraná. The construction and demolition waste (CDW) (generated in Paraná) and calcium aluminate cement (CAC) were the materials used in the treatment of galvanic sludge. Portland cement (PC) was also used as a binder to compare the efficiency of CAC regarding the retention of chromium.

Table 1shows the chemical composition of dried GS, obtained by X-ray fluorescence. Among the contaminants, the presence of nickel and chromium was significant and approximately 15%. Other heavy metals (Cu, Ti, Zn, Pb) were present in smaller proportions. CaO was also present as the main elements in 14.8%. The water content of the GS was 80%, its pH reached 8.7 andits raw density was 1.20 g/cm3.

The construction and demolition waste (CDW) was obtained by grinding ceramic blocks to get particles smaller than 4.8 mm. The objective of including CDW to obtain the solid matrix was to reduce its disposition in landfill, to make the process cheaper and to improve the sludge and cement mixing. These aspects of GS and CDW are showed in Figure 1.

Table 1: Chemical composition of galvanic sludge (%)

Oxides	Galvnicsludge (GS)
NiO	14.8
CaO	14.8
Cr_2O_3	14.6
SO_3	12.9
Fe_2O_3	5.9
SiO_2	2.8
P_2O_5	1.6
Na_2O	1.0
Al_2O_3	0.8
MgO	0.5
CuO	0.3
Cl	0.1
CeO_2	0.1
TiO_2	0.1
ZnO	0.1
SrO	0.1
PbO	0.1
K_2O	0.1
Ignition loss	29.29

Figure 1: Galvanic sludge and grinding ceramic blocks (CWD) used in pastes and mortars

The solidification of GS using cement was elaborated in two parts:

- Paste: GS + Cement
- Mortar: GS + Cement + CDW

The pastes and mortars were composed of 66.7% pastes (containing 10, 20, 30 e 40% of GS) and 33% of CDW, as shown in Table 2. The water/cement ratio was 0.25 and 0.36 for pastes and mortars respectively.

Table 2: Proportion of cement, GS and CDW (%) in pastes and mortars

Solid Matrix	Paste		Mortar	
	GS	Cement	Paste	CDW
0%	0	100	66.7	33.3
10%	10	90	66.7	33.3
20%	20	80	66.7	33.3
30%	30	70	66.7	33.3
40%	40	60	66.7	33.3

The pastes and mortars were cast in prismatic molds (40 mm×40 mm×160 mm). After 24 hours, the samples were wrapped in wet paper, placed in plastic bags and maintained in a climate chamber (23^{o}C) until reaching the compressive strength (at 7 and 28 days).

Leaching tests were conducted according to Brazilian Standard NBR 10005 on crushed mortar samples (smaller than 9.5 mm) containing 40% of GS at 28 days (Figure 2). The samples were leached in water and an acid acetic solution (to achieve a pH of 2.88) at a water-to-solids ratio of 20 for 18 hours.

Figure 2: Leaching tests: PC and CAC crushed mortar samples at 28 days

3.Results and discussion

3.1 Compressive strength

The compressive strengths of solid matrices (pastes and mortars) containing galvanic sludge (GS) made with CAC cement are presented in Figure 3. In both solid matrices, the presence of GS resulted in a decrease in compressive strength, which was proportional to the amount of GS added. It was also possible to verify that when the amount of GS is low (0 and 10%), the pastes reached higher values than the mortars. However, as the amount of GS increases, this difference becomes lower as observed in a solid matrix containing 40% of GS. In this case, the opposite was observed: the mortar reached higher values than the paste, confirming the positive effect of CDW on the sludge mixing with cement.

In addition to better mechanical performance, mortars with 40% of GS containedless cement than pastes in their compositions, providing a cheaper process of treatment (Table 3).

Despite the compressive strength having strongly dropped with the presence of GS, all mortars reached an interesting mechanical performance.Figure 4 shows the results of mortars made with CAC compared with PC cement, with both containing 40% of GS, at 7 and 28 days. For CAC and PC cement, in both ages, the mortars reached higher compressive strengths than did the pastes. At 28 days, mortars made with CAC and PC reached 22 and 31 MPa respectively, showing a very high performance.

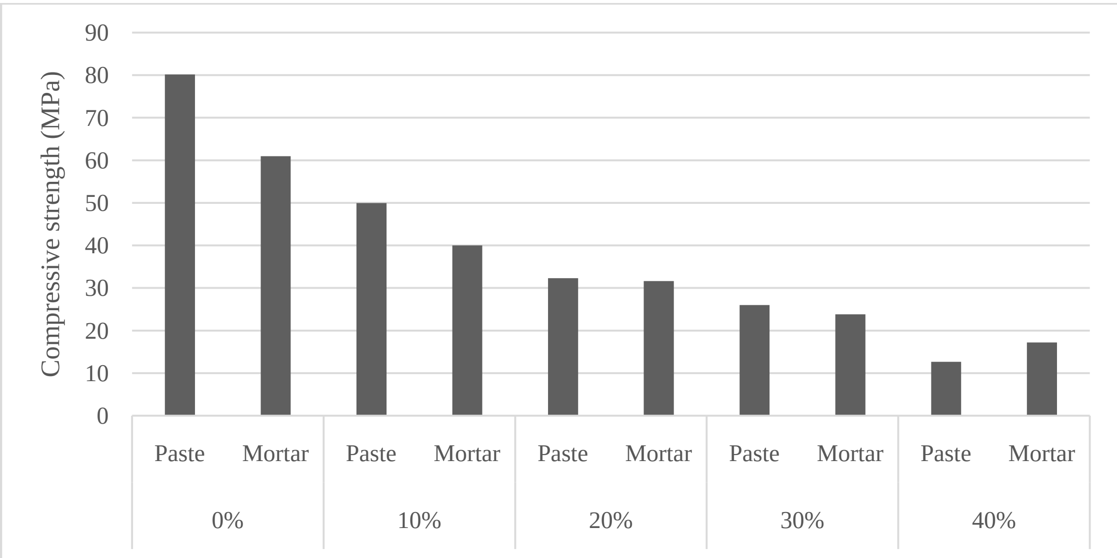

Figure 3: Compressive strength of pastes and mortars made with CAC cement at 7 days

Table 3: Consumption of cement and SG in pastes and mortars (kg/m3)

Solid Matrix	Paste		Mortar	
	GS	Cement	GS	Cement
0%	0	1638	0	1176
10%	156	1563	117	1167
20%	302	1509	228	1139
30%	440	1468	330	1101
40%	563	1408	434	1086

The positive effect on the CWD on the mortars made with both cementscan also be observed in Figures5 and 6. CWD was able to provide a better compacting and a better distribution of GS inside of the mortars.

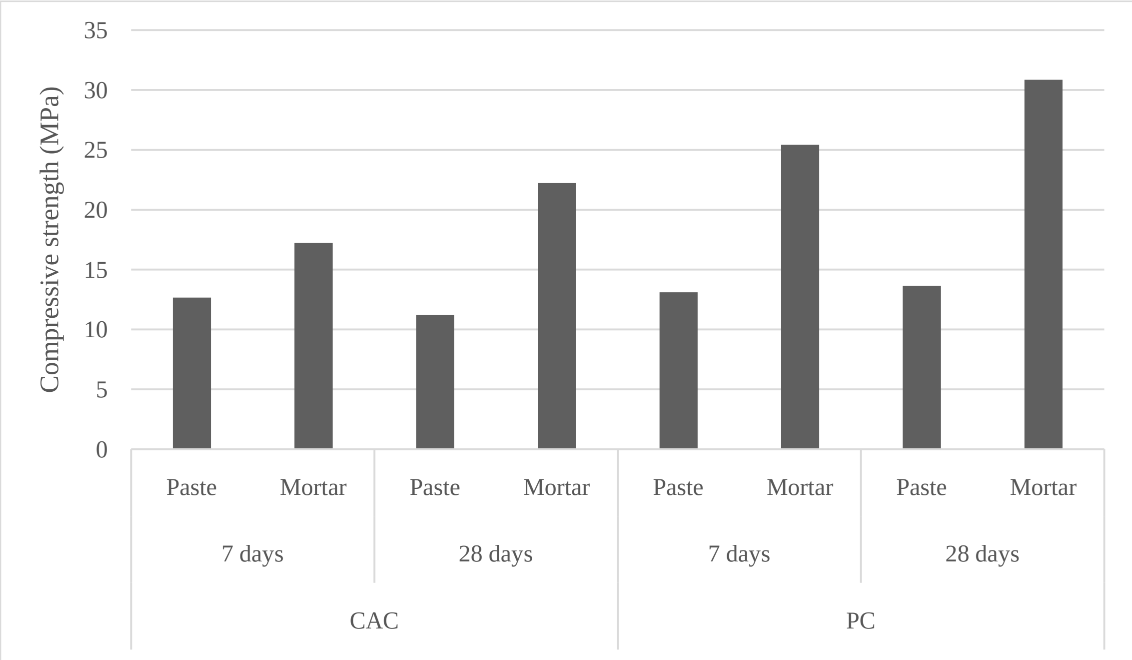

Figure 4: Compressive strength of pastes and mortars at 7 days made with CAC and PC containing 40% of GS

Figure 5: CAC matrix solid containing 40% of GS: Paste and Mortar

Figure 6: PC matrix solid containing 40% of GS: Paste and Mortar

3.2 Leaching tests

Leaching tests were carried out according to the Brazilian standard NBR 10005 on crushed mortars (<9.5 mm) at 28 days. Mortars containing 40% of sludge made with CAC and PC cement were leached in an acetic acid solution (AA) and de-ionized water (W) at a water-to-solids ratio of 20 for 18 hours. The hexavalent chromium was no identified and total chromium was only identified upper the standard limit (5 mg/l) in acetic acid solution as also observed for nickel (Table 4). The efficiency of retention was high for both metals and lightly higher for mortars made with PC.

Table 4: Results of mortars made with PC and CAC leached in acetic acid (AA) and water (W) at 28 days (mg/L)

Sample	**Chromium**		**Nickel**
	Total	**Hexavalent**	
PC – AA	34,5	<0,05	10,9
PC – W	<0,01	<0,05	<0,01
CAC – AA	43,3	<0,05	19,4
CAC – W	0,22	<0,05	<0,01

Table 5: Efficiency of stabilization processes.

Sample	**Total Chromium**	**Nickel**
PC – AA	89,98%	97,28%
PC – W	100%	100%
CAC – AA	87,42%	95,16%
CAC – W	99,94%	100%

4. Conclusions

Pastes and mortars prepared with sludge galvanic (SG) and construction and demolition waste (CDW) by grinding ceramic made with Portland and calcium aluminate cements (CAC) shows very interesting results.

The presence of SG in pastes containing both cements made mixing them difficult,suggesting a non-compacting solid matrix. Despite the compressive strength having lower values in proportion to the sludge content, the values achieved were very interesting.

The presence of CDW as alternative aggregate to compose the mortars improved the distribution of SG inside of the solid matrix and providing a better-compacted solid matrix and consequently a better mechanical performance. Despite the presence of CDW to reduce consumption of sludge, it also reduced the consumption of cement, making the process cheaper.

The strength values exhibited by the mortars made with 40% of sludge, 22 MPa and 31 MPa, for calcium aluminate (CAC) and Portland cement (PC), respectively, were very higher than the minimal value required by Brazilian Standard (NBR 15961) for structural concrete bricks of 6.0 MPa.

Leaching tests carried out on crushed samples showed avery good retention of both chromium and nickel, under water solution, and wereslightly higher for Portland cement.

S/S is an important treatment technique in waste management. This process is simple and reduces packaging, collection, transportation and treatment problems and, ultimately, the final disposal of hazardous waste in landfills. Good performance of the solid matrix can also lead to the recovery of these by-products reducing the consumption of non-renewable raw materials in the construction industry.

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