EVALUATION OF TECHNOLOGICAL PROPERTIES OF CLAY CERAMICS WITH GALVANIC SLUDGE AS RAW MATERIAL

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ABSTRACT

This work investigates the possibility to obtain conventional ceramic-based clay added with galvanic sludge, soda-lime and borosilicate glasses. Initially, increasing levels of galvanic sludge in clay were added at 2%, 5%, and 10%, and burned at 900ºC, 1000ºC, and 1100ºC, respectively. Thereafter, the formulations were analyzed with the addition of 2% sludge and contents of 5%, 10%, and 15% for both glasses. These formulations were burned at 1100ºC. The ceramic bodies were obtained by uniaxial pressing and characterized, after burning, to flexural strength, water absorption, and linear shrinkage. In addition, the immobilization of hazardous elements present in sludge was evaluated by leaching tests and solubilization. An improvement at the mechanical properties with the addition of glass, especially with the addition of borosilicate glass was observed. Moreover, leaching and solubilization tests showed that the increasing addition of glass led to a reduction of heavy metals.

Topic 4: Ceramic Materials

Keywords: waste, sludge galvanic, ceramic materials

1. INTRODUCTION

All countries, no matter the location or international status, produce millions of tons of waste a day, justifying the mandatory creation of mechanisms that bring awareness, development, and deployment of new technologies to reverse this situation [1].

In the last decades, environmental considerations emerged as a major concern to most developed countries, and studies for the reuse of waste have been done.

Currently, considering the environmental legislation, the need of recycling encourages large and small companies to seek alternative solutions on recycling, which, in turn, ends up adding value to the end product [2].

The sludge produced in the physical-chemical surface treatment in electroplating plants is classified as eco-toxic wastes [3]. This is due to the high mobility of metals such as chromium, nickel, copper, and zinc present in these wastes. According to the Brazilian legislation the sludge resulting from the electroplating process is classified as hazardous waste - Class I [4].

The residue incorporation in red ceramic is currently an environmentally correct solution for the removal of a wide variety of solid wastes [5-6] because of the use of relatively simple processing techniques, the low technical performance required by the products, and the presence of a significant amount of impurities on the ceramic final structure.

The stage of burning, vital for the consolidation of the particles, allows: (a) the volatilization of hazardous compounds, (b) the change of the chemical characteristics of materials, and (c) the immobilization of hazardous and potentially toxic elements by setting the glassy phase.

In ceramic processing, it is essential to be able to obtain a relationship between some processing parameters, such as raw material, shaping, and burning conditions (time and temperature), and the final properties desired. These properties need to be controlled in order to obtain a microstructure suitable to cope with the service conditions for which the material is intended. The use of industrial waste, such as the galvanic sludge investigated here, as raw-material added to clay does not change such relationship. However, the immobility on the ceramic body of dangerous elements present in this waste should be considered. These elements cannot migrate from the ceramic body to the environment in quantities which could affect its integrity.

In this context, the present work searched for subsidies that lead to the understanding of the phenomenon that controls the obtaining of ceramic bodies with the typical properties obtained from clays doped with galvanic sludge. Moreover, the detention of chemical elements through the vitrification temperature of the ceramic body during its burning was also determined.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Electroplating sludge (ES): the sludge used was a result from the electroplating process used in an industrial treatment of metal parts in Porto Alegre, Brazil. The red clay (RD) is processed as industrial raw material in the region of Nova Santa Rita, Brazil. The soda lime glass (SL) was obtained from scrap drink packaging was used and the borosilicate glass (BS) from laboratory glass scrap. These materials were characterized for chemical composition by X-ray fluorescence. Results are presented in Table 1 and are given in oxides. The sludge has Cr and Cd, which, among other elements, leads to the classification of 'hazardous waste'.

Table 1. Chemical composition (by X-ray fluorescence) of thegalvanic sludge, red clay, soda lime and borosilicate glass.

Oxides	Sludge (%w)	Clay(%wt) (%)	SL Glass (%wt)	BS Glass (%wt)
Cr_2O_3	27,85	-	-	-
Al_2O_3	16,20	13,28	1,62	2,48
SO_3	13,29	-	-	-
CaO	12,77	0,29	12,95	3,11
MgO	9,55	2,06	1,11	3,65
Na_2O	4,94	0,20	12,49	7,84
SiO_2	3,56	67,54	70,24	73,42
CdO	3,35	-	-	-
Fe_2O_3	2,41	4,95	0,64	0,09
Cl	1,62	-	-	-
Rh_2O_3	1,41	-	-	-
NiO	1,30	-	-	-
K_2O	0,43	2,76	0,71	0,89
TiO_2	0,33	0,64	0,10	-
CuO	0,31	-	-	-
ZnO	0,16	-	-	-
SnO_2	0,12	-	-	-
PbO	0,12	-	-	-
P_2O_5	0,11	0,03	0,05	-
Co_2O_3	0,04	1,11	-	-
SrO	0,03	0,06	-	-
MnO		0,04	0,06	-
B_2O_3	-			6,93
BaO				1,50
Weight loss	3,5	8,17	-	-

2.2. Methods

Initially the raw material was dried in an electric oven at 110 ± 5 ° C to remove residual moisture, and then milled in planetary mill to be 100% passing the sieve 80 ABNT (180μm).

The experimental work was conducted in two stages: (i) development of formulations with mud and red clay burned at temperatures of 900ºC, 1000ºC, and 1100ºC, as showed in Table 2; (ii) development of formulations with 2% by weight of sludge, clay, SL glass, and BS glass, and burned at 1100ºC as showed in Table 3. The addition of clay and the burning temperature were defined according to the results obtained in the previous step.
All formulations tested were pressed at 40MPa and burned for 2h with heating rate of 150ºC/h. Samples were characterized for linear shrinkage [9], water absorption [10], and mechanical strength [11]. The immobilization of elements such as Cr and Cd was analyzed by solubilization and leaching tests, according to Brazilian technical norms NBR 10005, 10006, and 10004 [7,8,4].

Table 2. Ceramic mixes formulated with galvanic sludge and red clay.

Mixtures	Sludge (%wt)	Red Clay (%wt)
RC	-	100
2S98RC	2	98
5S95RC	5	95
10S90RC	10	90

Table 3. Formulations developed with galvanic sludge, red clay, and SL and BS glasses.

Mixtures	Sludge (%wt)	Red Clay (%wt)	SL Glass (%wt)	BS Glass (%wt)
2S5SL	2	93	5	-
2S10SL	2	88	10	-
2S15SL	2	83	15	-
2S5BS	2	93	-	5
2S10BS	2	88	-	10
2S15BS	2	83	-	15

3. RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the effect of linear shrinkage, water absorption, and mechanical strength as function of sludge addition and burning temperature of ceramic bodies, respectively. As expected, there was an increase of linear shrinkage with the increase of burning temperature. The increased amount of sludge used also contributed to greater shrinkage, except for formulations burned at 1100ºC when the retraction was constant at around 7%, independent of the sludge added. Regarding water absorption, there was a reduction with an increase in the burning temperature. In burning carried out at 900ºC, no influence on the incorporation of the water absorption was observed. At 1000ºC, the increasing content of waste led to an absorption reduction. At 1100ºC, the lowest water absorption was observed, about 2.6%, with the addition of 2% of sewage sludge; higher levels led to increased water absorption.
Considering mechanical strength, the best result was obtained for the formulation with 2% weight addition of clay, burned at 1100ºC, with values above 30MPa. A higher sludge addition to this same temperature showed a fall in the same parameters with values even lower than for the pure clay. At lower burning temperatures, the results were not significant. The results obtained in a higher burning temperature may indicate an effect of melting in some of the oxides. At this temperature, there was likely to be a partial melting of galvanic sludge, filling part of the residual porosity, which would have contributed to the increase of mechanical strength and reduced water absorption. This effect can be checked by micrographs in Figure 4, where a considerable reduction in the residual porosity with the burning temperature increasing from 900ºC to 1100ºC, was observed. Furthermore, the ceramic bodies made of 2% of clay showed a higher densification compared to other formulations - 5% and 10% - when burned at 1100ºC, as shown in the micrograph in Figure 5.

None of the tests, leaching or solubilization, exceeded the design limits of Cd and Cr established by the NBR 10004 for the leaching test (NBR 10005) (Table 4). However, all formulations presented in the sludge added with soluble extract (NBR 10006) showed values greater than those established by the same standard for Cd.
To decrease the amount of Cr and Cd leached/dissolved, formulations were developed with the use of glass, trying to hold the dangerous elements in its structure. These formulations were developed from the formulation with 2% of clay and some levels of glass.

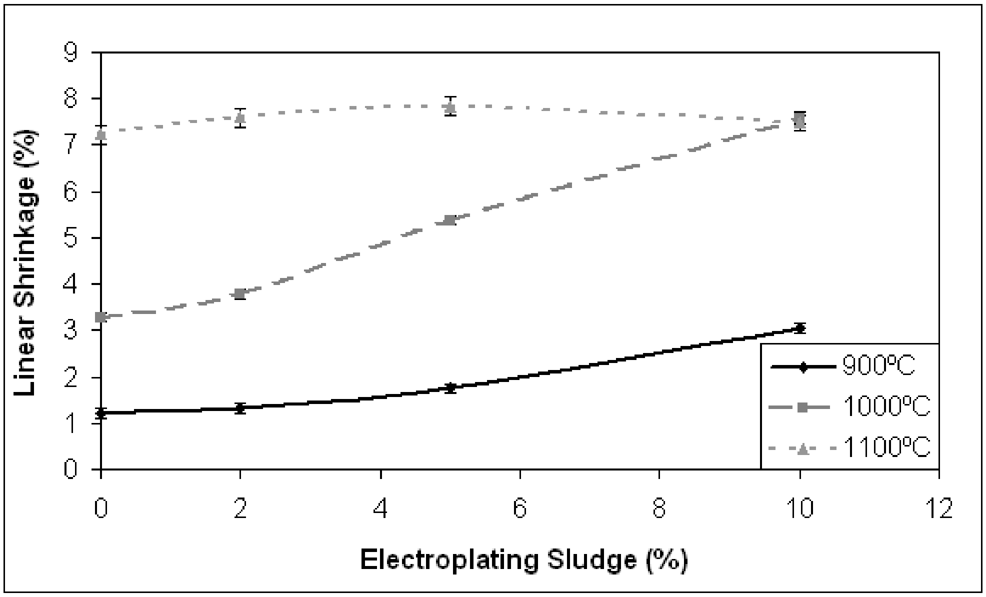

Figure 1. Linear shrinkage as function of galvanic sludge addition.

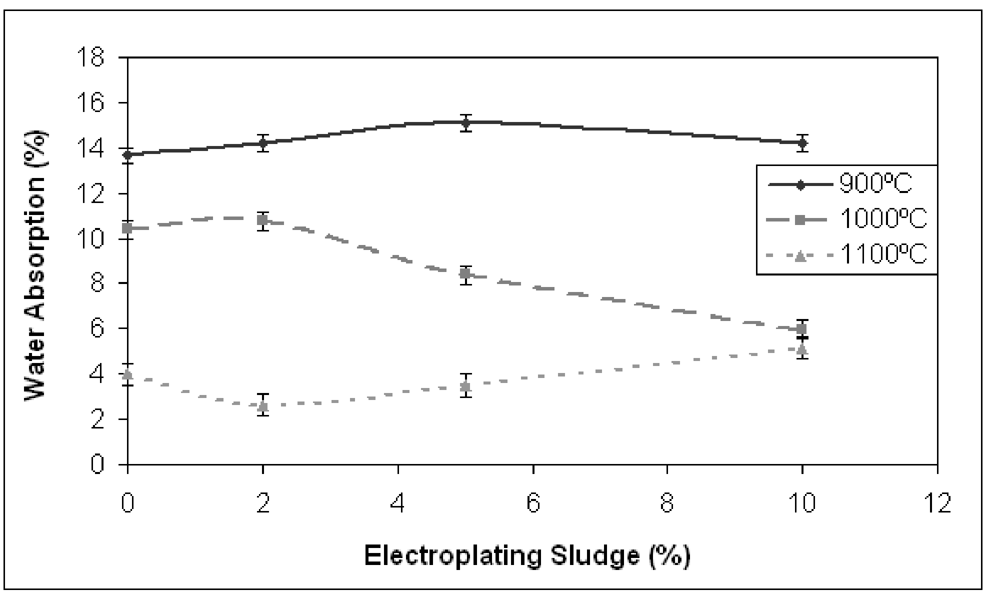

Figure 2. Water absorption as function of galvanic sludge addition.

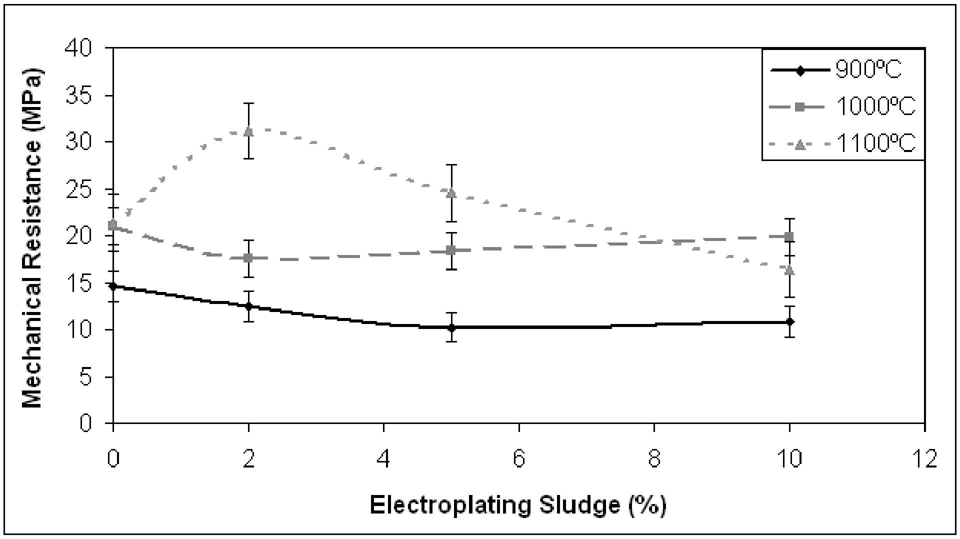

Figure 3. Mechanical resistance as function of galvanic sludge addition.

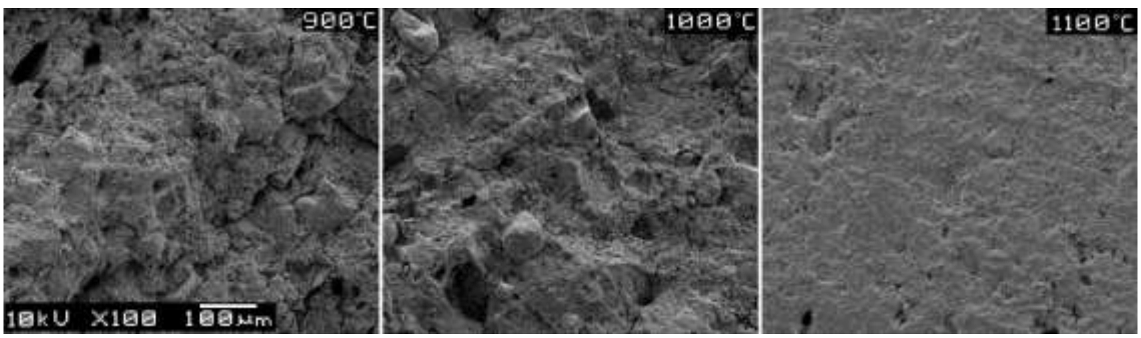

Figure 4. Micrograph of the ceramic bodies with 2wt% of galvanic sludge burned at (a) 900ºC, (b) 1000ºC, and (c) 1100ºC.

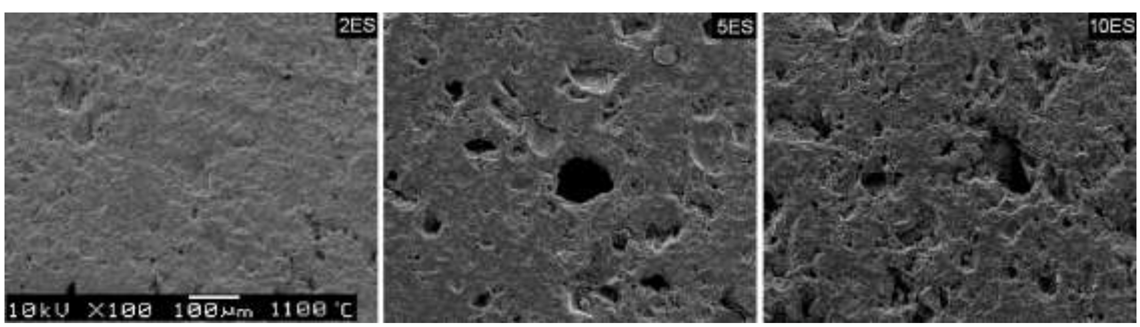

Figure 5. Micrograph of the ceramic bodies with galvanic sludge in (a) 2wt%, (b) 5wt%, and (c) 10wt% burned at 1100ºC.

Table 4. Evaluation on the amount of chromium and cadmium released during the solubilization and leaching tests for the mixtures with galvanic sludge and clay.

Mixtures	Leaching		Solubilization	
	Cd (<0,5mg/L)	Cr (<5mg/L)	Cd (<0,005mg/L)	Cr (<0,05mg/L)
100RC	0,003	0,02	0,002	0,028
98RC2ES	0,013	0,225	0,005	2,1
95RC5ES	0,026	1,95	0,005	6,27
90RC10ES	0,095	3,94	0,004	17

Results presented in Figures 6, 7, and 8 show the influence of the addition of glass on the mechanical properties. We observed an increase in linear shrinkage with the increased addition of both glasses, however, this is more evident in the addition of BS glass. Regarding water absorption, there was a reduction of this parameter in relation to ceramic bodies without glass. The addition of BS glass led to a significant reduction of absorption, i.e., to values below 0.2%, with no significant change with the glass content variation. About mechanical strength, SL glass led to a reduction in this parameter, although the variation of its content has not reflected such results. However, the addition of BS glass increased the mechanical strength of ceramic bodies which changed from an average of almost 30MPa to 40MPa with the addition of 5% of glass. Higher levels showed a decrease in mechanical strength, which can be explained by the micrographs presented in Figure 9. There was an increase in the porosity by adding increasing levels of glass. This effect was quite evident to the bodies based on ceramic BS glass. Probably for the formulation with 5% BS glass, there was a combination of wetting of particles by flow of glassy phase and particle rearrangement leading to further densification of the ceramic body and therefore higher values of mechanical strength. The decrease observed could be attributed to excessive glazing on ceramic body, leading to the formation of a glassy phase with coalescence of pores. For these formulations, a reduction in the amounts of dissolved cadmium and chromium was observed in the tests of leaching/solubilization, whose results are in Table 5. However, Chrome still exceeded the limit set by the NBR 10004.

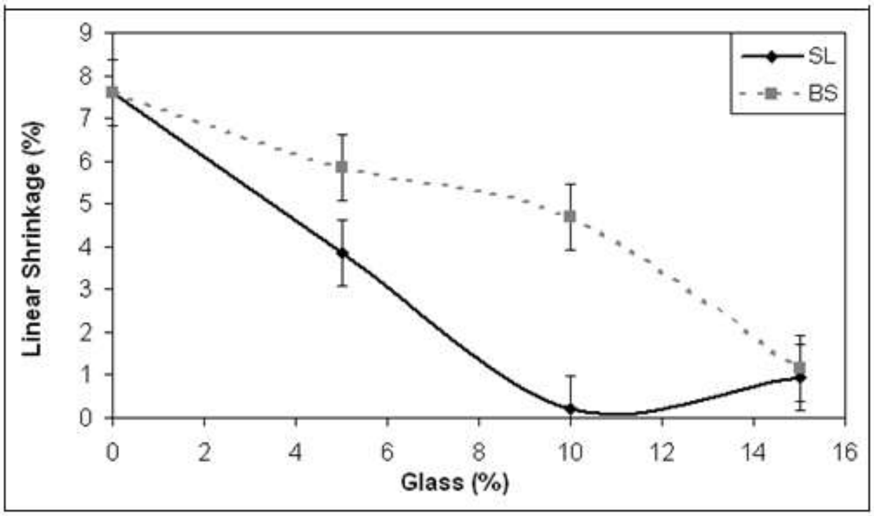

Figure 6. Linear shrinkage as function of borosilicate and soda-lime glasses addition.

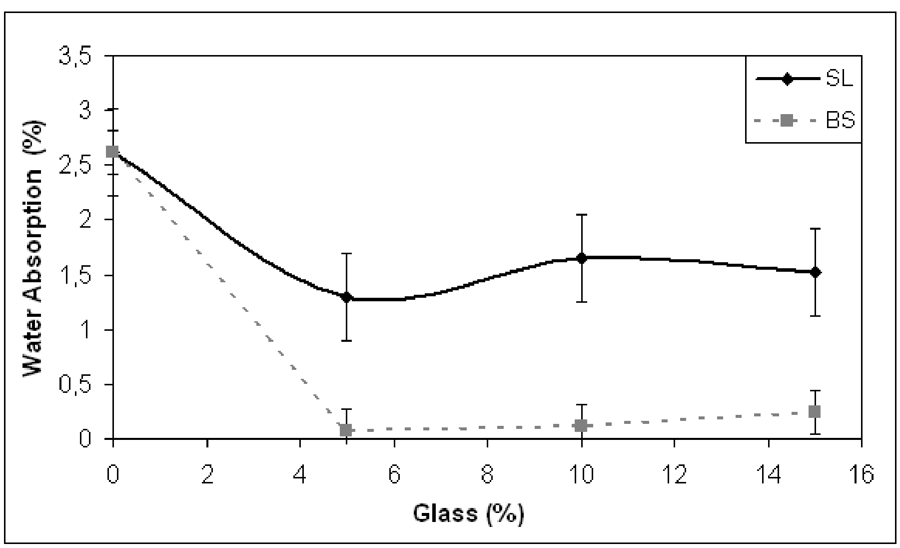

Figure 7. Water absorption as function of borosilicate and soda-lime glasses addition.

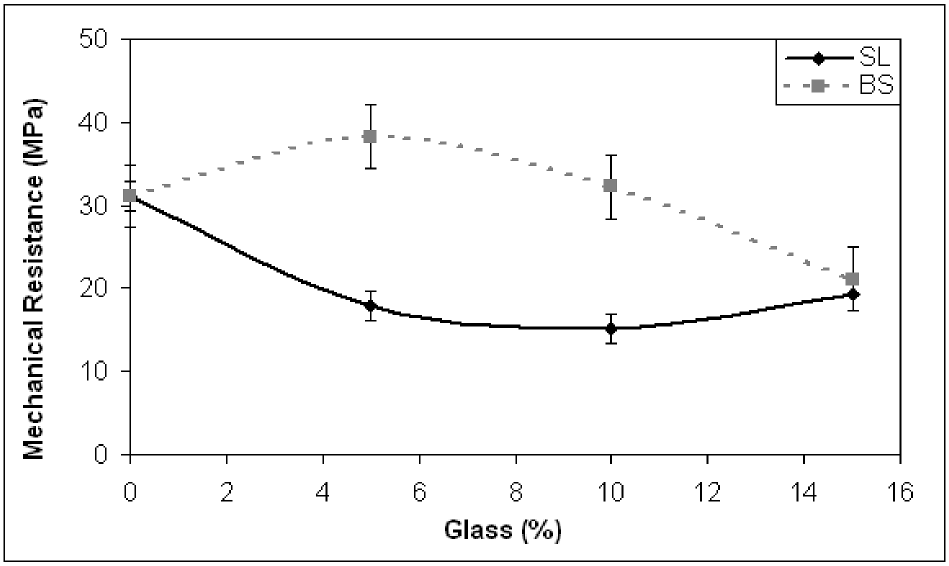

Figure 8. Mechanical resistance as function of borosilicate and soda-lime glasses addition.

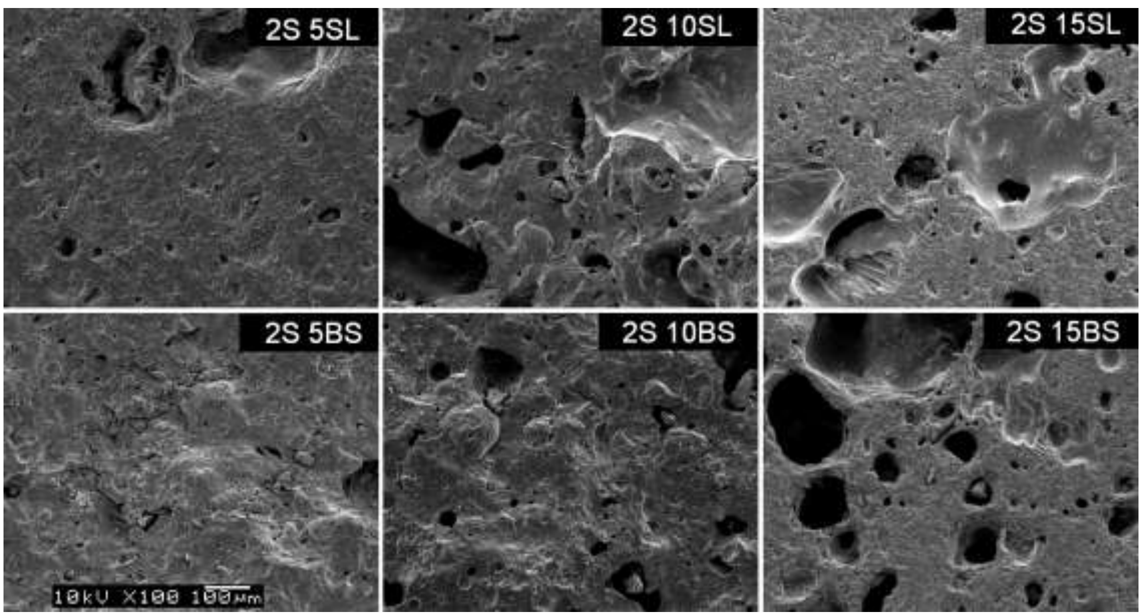

Figure 9. Micrograph of the ceramic bodies formulated with 2% of galvanic sludge and 5%, 10%, and 15% borosilicate and soda-lime glasses burned at 1100ºC

Table 5. Evaluation on the amount of chromium and cadmium released during the solubilization and leaching tests for the formulations with clay, galvanic sludge, and glass.

Mixtures	Leaching		Solubilization	
	Cd (<0.5mg/L)	Cr (<5mg/L)	Cd (<0.005mg/L)	Cr (<0.05mg/L)
2ES5SL	0.054	0.156	0.006	0.596
2ES10SL	0.078	0.082	0.005	0.391
2ES15SL	0.118	0.081	0.007	0.317
2ES5BS	0.005	0.09	0.002	0.43
2ES10BS	0.016	0.07	0.002	0.31
2ES15BS	0.014	0.05	0.002	0.22

4. CONCLUSION

The possibility to develop ceramic products using galvanic sludge as raw material was verified. The best technological results were obtained with the addition of 2% by weight of sludge and 5% by weight of BS glass. Regarding the immobilization of cadmium and chromium, the addition of glass resulted in a reduction of their amounts in soluble and leachate extracts. Thus, BS glass is more efficient than SL glass, although chromium has extrapolated the solubilized limit established by NBR 10004. These results classified the products obtained as a Class II A - not inert. Therefore, further investigations are needed on the mechanisms responsible for hazardous element immobilization.

5. REFERENCES

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