GALVANIC PROCESSES WASTES UTILIZATION AS MAIN COMPONENTES OF CERAMIC PRODUCTION[1]

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Abstract

It was developed a new type of ceramic based on the galvanic process wastes – galvanic mud and surface cleaning glass rejects – in combinations with foundry sand and natural clay. All components are presented in more or less equal weight proportions. Such compositions of this initial components allow to obtain rather high flexion resistance (till 13.5 MPa), low values of water absorption (0.86-1.54%), solubility (Cr, Fe, Ni and Cu <0.05 ml/L, Zn and Al<0.10 ml/L) and lixiviation (Cr and Ni<0.05 mg/L, Zn <0.10, Fe=0.06 mg/L). XRF, XRD, SEM tests were performed for all initial components and final product compositions and structures. High chemical resistance in acid and alkaline environment, low lixiviation and solubility levels, allow the use of new ceramics as bricks and tiles, as covering of floor of chemical industry. In addition to economic factors the total galvanic waste elimination are strong and advantageous aspects for the utilization of the new ceramic materials.

Key-words: Galvanic sludge recycling; Surface cleaning glass rejects; Ceramics; Solubility; Lixiviation.

UTILIZAÇÃO DE RESÍDUOS DE PROCESSOS GALVANICOS COMO COMPONENTES PRINCUPAIS DE PRODUÇÃO DE CERÂMICAS

Resumo

Foi desenvolvido um novo tipo de cerâmica baseado em resíduos de processo galvânico – lodo de galvanização eletrolítico e vidro de jateamento, combinado com areia de fundição e argila natural. Todos componentes são misturados em proporções de peso mais ou menos equivalentes. Foi obtida a resistência à flexão até 13.5 MPa, baixos valores de absorção de água (0.85 – 1.54%), baixa solubilidade (Cr, Fe, Ni e Cu < 0.05 ml/l, Zn e Al < 0.10 ml/l), baixa lixiviação (Cr e Ni<0.05 mg/l, Zn <0.10, Fe=0.06 mg/l) e alta resistência química em meios alcalinos e ácidos. Ensaios de FRX, DRX e MEV das estruturas explicam as propriedades alcançadas das cerâmicas. Estas propriedades permitem o uso das cerâmicas na fabricação de tijolos e revestimento de pisos, especialmente para indústrias químicas. Os fatores econômicos da eliminação total do resíduo galvânico são aspectos fortes e vantajosos para a utilização da nova cerâmica.

Palavras-chave: Lodo galvânico; Vidro residual; Areia de fundição; Metais pesados; Lixiviação; Solubilização; Cerâmica vermelha.

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1 INTRODUCTION

Galvanic processes are one of the most widely-distributed industries all over the world. The wastes of these industries usually contain high values of heavy metals, like Ni, Zn, Cr, Sn, Cu, Pb, Sb, etc. Significant quantity of recent publications demonstrates that ceramic production is a highly promising method for heavy metals inertization and reduction of the environment pollution. Usai[1] informed, that the massive reuse of some industrial wastes containing heavy metals and/or by products in Sardinia (Italy) as raw materials in the ceramics industry is the aim of intensive experimental research carried out for 20 years. They were used for production of ceramics, such as bricks, paving tiles and others.

It was indicated[2] that yellow sludge contain hydroxides of several hazardous heavy metal ions, i.e., Cr, Fe, Cu, Zn and Pb. They proved, that soda-lime silicate glass is a very effective medium for stable solidification of heavy metal ions, and that the "glass wastes" can be reused for this purpose. In additional, the waste glass could be prepared from glass bottles used for commercial drinks.

It were vitrified[3] the bottom ashes with high content of heavy metals from two different municipal solid waste incinerators at 1400 C. The obtained glass, mixed with other wastes from metallurgical and mineral industrial wastes, was used as raw material for the production of glass-ceramic tiles. Two different mixtures were used for the tile production: (a) glass from bottom ashes plus corundum-based waste from an aluminum foundry and (b) glass from bottom ashes plus kaolin-based waste from the kaolin ore extraction process.

Naga and El-Maghraby[4] made a study to predict the suitability of Cu-slag as a flux for the production of sintered ceramic tiles. The sintered ceramic tiles having high bulk density, considerably lower firing temperature and reasonable tensile strength could be prepared by firing batches containing 30 wt% Cu-slag for 1 h at 1.175°C.

It was reported[5] the effect of several processing parameters, such as mixing time, the calcinations temperature and duration, the relative amounts of sludge and the physical aspects of the sample (powdered or pressed pellets) on the fixing level of relative species (SiO_2, SO_4, Zn, Ni, Ca, Cu, Cr) by leaching in different media. Relative amount of galvanic sludge in the mixture, changing from 1 to 10 wt.% (Table 1).

Balaton, Gonçãlves and Ferrer[6] successfully used 2% and %% of galvanic sludge with some mixtures of two types of natural clay. They roasted them with temperatures 850º, 900º and 950º C.

It were investigated[7] a possibility of utilization of tannery sludge with high content of heavy metals in mixtures with clay. Results of solubility and lixiviation tests permitted to recommend the use only 10% of this type of waste.

Another way of heavy metals of galvanic treatment process inertization was proposed. The authors[8] used a binding matrix containing calcium silicate 2CaO·SiO2 and sulphoaluminate 4CaO·3Al2O3·SO3, and CaSO4. The waste was disposed of in a hazardous wastes landfill to prevent the risk of Cd, Cr and Ni release.

Asavapisit and Chotkland[9] tried to bind galvanic sludge by the mixture of 30% of lime and 70% of pulverized fuel ash, activated by added till 8% of Na_2SiO_3 or Na_2CO_3. They received rather high strength and Pb, Cd and Cu were not found in

the toxicity characteristic leaching procedure leachates. But Cr, Zn, and Fe detected and in some cases Cr exceed US EPA allowable limits.
This work presents a more efficient method of two types of galvanic wastes (with total heavy metal content near 53%) neutralization as raw material for producing of environment friendly ceramic materials.

2 SUJECTS OF THE RESEARCH

In this research were used the following industrial wastes: galvanic sludge (GS), metal cleaning glass waste (GW) and foundry sand (FS). As a plasticizer of the mixtures of these wastes local clay was used as the only natural component extracted from a deposit in the Metropolitan Region of the city of Curitiba.
The GS and GW used in this work were obtained on the galvanic Plant "Tecnoplating" in Curitiba, Brazil. The sample of FS was obtained from one of machine construction enterprise near city of Curitiba, Brazil.

Table 1. Chemical composition of the raw materials under study (by XRF).

	Components, wt %.				
	Galvanic sludge		Wastes under study		Clay
	Under study	Magalhaes et al (5)	Glass waste	Foundry sand	
SiO_2	12.53		75.50	98.75	54.58
CaO	6.03	5.60	8.46		
MgO	2.80		3.04		1.53
Al_2O_3.	2.29	29.66		0.31	21.40
Fe_2O_3	4.31		0.69	0.41	8.33
P_2O_5	8.22		0.02		0.17
MnO					0.12
Na_2O	2.70		10.13		
K_2O	1.44		8.5 ppm		4.98
SO_3	8.94		0.26		
Cr	28.53	2.20	0.02		
Zn	20.28	1.36	0.07		
TiO_2			0.07		0.95
Cu	0.53	1.03			
Se	0.31				
Co	0.26				
Ni	0.24	7.12			
W	0.21				
Sn	0.21				
Pb	0.21		0.02		
Sr			0.02		
I_2O_3			0.92		
Zr				0.09	
C.L.	41.82		0.45	0.53	7.91

There is a considerable variation in the chemical and mineralogy compositions of the industrial wastes under study.
The main components of the galvanic sludge studied, Table 1, are heavy metals (Cr -28.53 e Zn - 20.28 wt. %) totalizing up to 50.78% of the composition.
The comparable GS[5] has only 11.71% of heavy metals. They present also in GW and FS, but in less quantity (1.21%). The total amount of heavy metals in both wastes totalizes 51.90%. On the XRD diffractograms are well visible two halo of amorphous materials with their centers approximately on 35^0 and 60^0 of 2θ of λCuK-α.
The GW mainly represented by micro-sphere of glass, safe or broken during the metal surface cleaning, has predominately in its composition SiO_2 - 75.50% with rather high content of Na_2O – 10.13% as flux, extremely valuable for ceramic production. It is presented one strong and vast amorphous halo from 12^0 till 38^0 of 2θ of λCu K-α on the diffractogramas (XRD) of initial GW. Only very weak peaks of crystalline structure of Quartz SiO_2 were found.
Chemical composition of FS is almost the same, as the composition of the initial natural sand (SiO_2), but with small inclusions of Fe_2O_3, Al_2O_3, C, heavy metals, etc.
Natural clay under study is represented by quite common pottery red clay for bricks production. Mostly it contains SiO_2, Al_2O_3 and Fe_2O_3.

3 RESEARCH GOALS

1. To investigate the possibilities of using of galvanic wastes (GS and GW) as raw materials for ceramic production with the binding of their heavy metals till the level, permitted by Brazilian and international sanitary legislation.
2. To research the processes of the new ceramic structural formation with obtaining of suitable mechanical properties.
3. To develop new ecologically safe method (compositions and technologies) of construction materials producing on industrial-scale for complete utilization of galvanic wastes.

4 SAMPLES PREPARING AND RESEARCH METHODS

The samples of the materials were obtained by homogenizing of dry initial components, initially dry with fineness up to 0,5mm, by humidification of the mixtures till the optimal humidity conditions (10-12%) and by compression under the pressure 20 MPa for 1 minute. The sizes of the rectangular samples were 60x20x10 mm. After the drying with temperature 100^0C till the constant weight the samples were roasted for 4 to 6 hours with different temperatures.

5 RESEARCH RESULTS

Table 2 shows the changes in the resistance to rupture by flexion of the ceramics with different temperature, duration of roasting and percentages of raw materials with strong predominant role of the industrial wastes mentioned above.
The data on the Table 2 show that all of developed materials have rather high resistance to rupture by flexion. The best resistance (13.5 MPa) has ceramic M9 with

50% of galvanic wastes value (GS and GW). With the increasing of the roasting duration resistance is not growing up, as it was expected. One of the possible reasons is additional boiling up of the material and pore formation, well visible on the SEM micrographs, Fig. 2-B.

Table 2. Resistance to rupture by flexion (on three points) of the developed ceramics with different temperatures and the duration (in hours) of roasting.

№ of ceramics	Samples' compositions, wt. %				Resistance to rupture by flexion, MPa		
	GS	GW	FS	Clay	1100^0C	1120^0C	1150^0C
M6	20	25	30	25	10.4 (2h) 11.0 (4 h) 9.9 (6h)	- 10.0 (4h) -	11.9 (2h) - -
M8	25	20	25	30	10.2 (2 h) 10.9 (4h) 11.7 (6h)	- 11.7 (4h) 10.0 (6h)	11.0 (2h) 11.2 (4h) -
M9	25	25	20	30	13.5 (2h) 12,8 (4h) 12.0 (6h)	- 11.5 (4h) -	- - -

The linear deformation of all three samples' compositions after all technological procedures (drying and roasting) was between 8.72 and 9.00 % and the meanings of water absorption were among 0.86 and 1.54%.
Comparison of the diffractograms of M8 sample before the roasting (Fig. 1, curve A) and after roasting with temperatures 950^0 during 2 hours (Fig. 1, curve B) and 1120^0 during 6 hours (Fig. 1, curve C) helps to explain the physico-chemical processes during the mixture calcinations with its transformation to ceramics. It is well visible complete disappearance of Illite peak near the 10^0 of 2θ, strong decreasing of the intensity of Quartz peak near $21^0$of 2θ with its partly transformation to Cristobalite near 22^0, appearance of Magnetite and Hematite between 30^0 and 35^0 of 2θ.

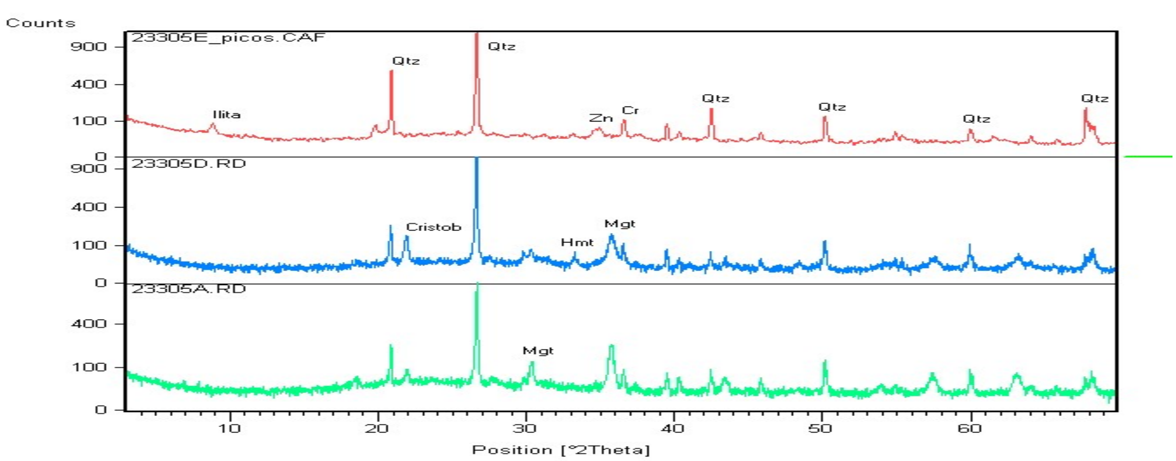
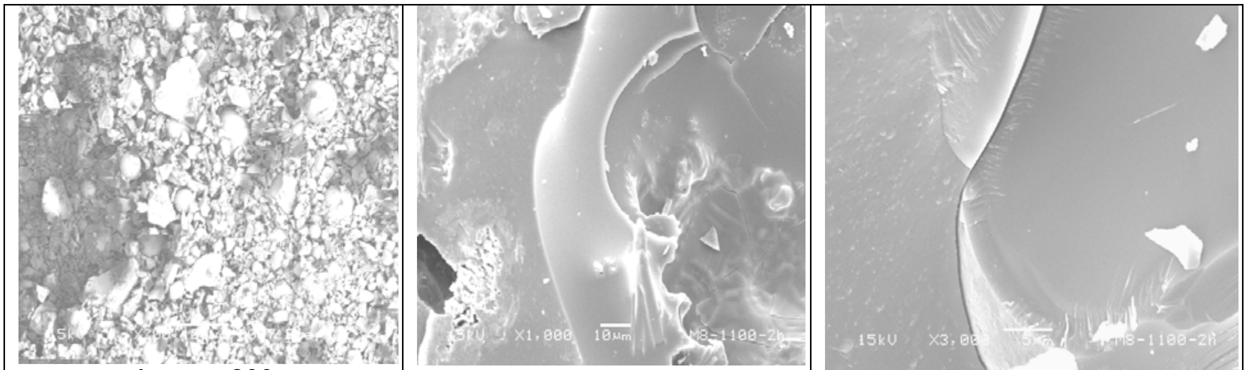


Fig. 1. Comparison of XRD diffractograms of M8 sample: curve A - before the roasting, curve B - after roasting with temperatures 950^0 during 2 hours and curve C - after roasting with 1120^0 during 6 hours.

SEM micrographs of initial mixture of components before the roasting (Fig 2-A) show the presence of separated particles of different sizes and forms. GW particles are noted among them as micro-spheres. After baking the micro level of the surfaces of the samples (Fig. 2-B and C) presented by glass-like new formations, very different from initial one.



A x 200 B x 1,000 C x 3,000

Fig 2. SEM micrographs of the surfaces of the samples: A - of initial mixture of components before the roasting; B and C - glass-like new formations after the roasting.

All these facts can be interpreted as the complete destroying during the roasting of some initial crystal structures (completely – of Illite, partly – of Quartz) and transferring of significant part of them to amorphous condition. The best evidence of such conclusion give SEM analyses. Such transformation explains rather high value of resistance to rupture by flexion, low lixiviation and solubility of heavy metals from obtained ceramics (Table 3).

Table 3. Lixiviation and solubility of heavy metals from developed ceramics.

Metals	Lixiviation		Solubility	
	Obtained results, mg/L	Standards limits, mg/L	Obtained results, mg/L	Standards limits, mg/L
Cr total	< 0.05	5.0	< 0.05	0.05
Fe	0.09	*	< 0.05	0.3
Ni	< 0.05	*	< 0.05	*
Zn	< 0.10	*	< 0.10	5.0
Al			< 0.10	0.2
Cu			< 0.05	2.0

*Note: * - demands are not still developed by Brazilian Standard NBR-1004.2004.*

The comparison of experimental values of heavy metals lixiviation and solubility from developed ceramics with demands of Brazilian Standard NBR-1004.2004 show a big (till 100 times) advantage of obtained results.

Experimental lixiviation and solubility tests of main part of heavy metals showed lower sensibility values than the Analyze of Atomic Absorption. Its is expected than , that the demand to others heavy metals’ lixiviation and solubility tests will have similar reserve of advantage.

5 CONCLUSIONS

1. The results of this research show that wastes from the galvanic industry, with high amounts of heavy metals (up to 52 wt %), can be used as valuable raw materials in up to 40-45% for production of environment friendly new construction materials, such as bricks, paving tiles and others.
2. The obtained results of new ceramic materials investigations demonstrate that rather high (till 13.5 MPa) values of resistance to rupture by flexion can be explained by destroying of some crystal structures of raw components (completely of Illite and partly of Quartz) and partial transition of crystal substances to amorphous glassy formations, well visible on representative SEM micrographs.
3. Such transformation to glassy materials explains very low (till 100 times less than standard's demands) lixiviation and solubility of heavy metals from obtained ceramics.
4. The developed materials can be highly economically attractive because of the utilization of industrial wastes for producing of construction materials. A considerable decrease in the costs is further enhanced by: a) low prices of the raw materials - industrial wastes; b) additional benefits are expected to be much higher because of the payments for utilization of industrial wastes.
5. The wide-scale use of the method is environmentally effective, because the most important advantage of this method is the use of industrial wastes that contaminate the environment and reduces open-quarry extraction of natural construction materials.

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