HAZARDOUS INDUSTRIAL WASTES AS THE MAIN COMPONENTS OF RED CERAMICS PRODUCTION

Vanderlei Mateus Tallini Jr
vanderleitallini@yahoo.com.br
Vsevolod Mymrine
seva@ufpr.br
Ricardo Augusto Cruz Ribeiro
ricardoribeiro@ufpr.br
Laboratory of Environment Technology, Federal University of Paraná (UFPR)
Laboratory of Environment Technology, Federal University of Paraná (UFPR)

Abstract: This research involved the development of new types of red ceramics from class I and II wastes, using different industrial residues such as sludge (WTP sludge, foundry sand, glass residues, residual salts) and clay. The chemical, mineralogical and structural compositions of the residues used as raw material and the new ceramic compounds were analyzed and studied using XRF, XRD, SEM and chemical microanalysis (EDAX). The results obtained indicate that the ceramic prepared with 70% of residues (composition 1), without the addition of sand and with the maximum clay content, presented the highest strength (20 MPa) at 1050°C. Composition 2, with a 5% lower clay content and a 5% higher sand content showed a significantly lower strength at all the temperatures tested. Increasing the proportion of sand to 15 and 20% in compositions 5, 6 and 7 led to a considerable increase in resistance at 1050°C in comparison to the other temperatures. The results showed high flexural strength and low values of water absorption and linear retraction, characterizing the good sintering of the materials and vitreous formation, ensuring low values of solubilization and leaching.
Keywords: WTP sludge, foundry sand, glass residues, residual salts and red ceramic.

INTRODUCTION

The industries gradual are searching new alternatives for the disposal of its solid residues, had to the pressures of the ambient agencies or for the fact to acquire ambient certifications to become more competitive in the market. The practical one of the recycling through the use of industrial residues as main component in the manufacture of materials of civil construction, can bring innumerable ambient benefits, therefore, it substitutes the use of natural resources for recycled residues. In accordance with (ÂNGULO et al.,2001) is esteem that the sector of the civil construction is responsible for the consumption of up to 75% of our natural resources, what becomes it a consumer in potential of great part of the residues generated in the different industrial sectors.

All industrial processes generates residues that are inherent to their industrial activities. In the galvanic industry, for example, in addition to the sludge that is generated with a high heavy metal content characteristic of the galvanic industry, glass residues are also generated. These glasses consist of microspheres used as abrasives for cleaning metal parts prior to chemical treatment.

The acid lead battery is a complex, composed industrial product to put distinct materials: metallic components, acid solution, plastics and polymers (JOLLY et al., 1994). The Brazilian Association of the Electric Industry and Eletrônica (ABINEE), in partnership with some producing companies of automobile batteries in Brazil, developed an orientation work to minimize the residues generated in the process of recycling of the automotivas batteries, being one of the recommendations of this study, to the sulfuric acid neutralization of. Automotive battery recycling plants generate salts in the process of neutralization of the battery acid before disposal. These salts contain low concentrations of heavy metals such as As and Pb, characterizing them as hazardous waste.

Manufacturing processes of molds for metal parts use sand known as foundry sand. An average of 800 to 1000 Kg of foundry sand is used for every 1000 Kg of parts produced.

Some authors also consider water treatment an industry because, to obtain treated water as the end product, sludge is generated in decanters and filters. The chemical composition of WTP (water treatment plant) sludge is highly varied, containing several metals and varying according to the type of coagulant and auxiliary agents used for treating water and the quality of the water collected. Due to its chemical composition, WTP sludge is a non-inert waste that requires a suitable final disposal. Currently, a major challenge for water treatment companies is to find economically and technically viable alternatives for disposing of WTP sludge without causing environmental impact at a low cost.

MATERIALS AND METHODS

The experimental research of this work was carried through in three stages: characterization of the substances cousins (WTP sludge, foundry sand, glass residues, residual salts and clay) preparation and study of the best test specimens, with different percentages of the residues in different temperatures of burning; e, finally, characterization and evaluation of the mechanical properties of the new ceramic composition.

The industrial residues that in this work had been used as substances cousins are proceeding from distinct companies. The WTP sludge was supplied by the company of sanitation of the Paraná (SANEPAR) of the station of treatment water Passaúna (Curitiba-PR) that it generates 12 approximately tons/day of this residue (ÂNGULO et al.,2001). The residual glass is proceeding from a galvanic industry that uses micron glass spheres for the cleanness of the metallic parts before the galvanic treatment. The residual salts are generated in the tanks during the process neutralization the acid solution, had been supplied by a recycle lead company of automotivas batteries in Londrina (PR).

The use of residual salts them in the composition ceramics has for purpose to solve the problem of discarding of the residue, beyond, to reduce the temperature of burning of ceramics, since it acts as one cast due its chemical composition. The foundry sand used in this work is proceeding from an industry of casting located in the city of Ponta Grossa (PR), that it uses foundry sand in the confection of the molds. After some cycles of use the sand becomes a residue. As only natural component of the red ceramic was used in small percentages clay preceding from São José dos Pinhais (RMC) that generally is used for local companies red ceramics production.

The chemical, phases mineralogical and structural compositions of the residues used as raw material and the new ceramic compounds were analyzed and studied using XRF, XRD, SEM and chemical microanalysis (EDAX). All the components used were oven-dried at 60°C, pulverized and sieved. The test specimens were prepared with different proportions of the components, homogenized, humidified to a level of 10% and compacted under a pressure of 23 MPa for 30 s, oven-dried at 100°C until their weights remained constant, and fired at temperatures varying from 900°C to 1050°C for 6 h. The samples were then subjected to several flexural strength, linear retraction and water absorption tests.

RESULTS AND DISCUSSION

The result of the chemical composition of the clay was studied with the use of the method of rays-x fluorescence and presented as being its main elements the SiO_2 - 53.29%, Al_2O_3 - 24,13, Fe_2O_3 - 3,32 and TiO_2 - 1,65. The result of the analysis of X-rays difratometric of the clay presented three typical mineral phases of clays: Quartz, Caulinita and Montmorilonita. The result of the chemical composition of reject it of glass (micron-spheres) is characteristic of some types of glass, therefore, presented one high text of SiO_2 - 75.15%, Na_2O - 10,69, CaO - 8,30 and MgO - 3,15%. Also the presence in small percentages of some metals (TiO_2, Cr_2O_3, Zn) proceeding from the cleanness of the metallic parts was evidenced.

In the X-rays analysis difratometric it was verified the chemical phases of the material that presented a difratometric with the very ample halo and few peaks of crystalline structures. The only crystalline peak, which separates the deep one in the area of 44,66° of 2θ it was deciphered as being the peak of metallic, deriving Iron of the impurities of the metallic parts.

Through the electronic microscopy of sweepings it was more evident that the residue is constituted basically of three materials: perfect glass spheres, abrasive particles of the spheres and other substances that had been identified as being assistant who the company uses to increase the power of abrasion and speed of cleanness. The chemical composition was gotten of two areas of the surface of the sample with the microanalysis method (EDX). The gotten result had of being calculated to deduct the high gold text during the metallizing of the sample for analysis MEV. The result presented one high Sodium text respectively (41,62 and 44,21%) and a low Potassium text (1,64 and 1,93%). Moreover, the material possesss one high Sulphur text (27,96 and 26,74%). The fact of the contamination of this substance exists cousin with Copper (11,07 and 6,58%) - product of the interaction of Cobre with the acid environment of the accumulators. Also it has a possible contamination with Lead and other metals weighed in low concentrations.

Through the use of the method of X-rays difratometric the mineral phase of these was searched leaves. The difratometric presents a great amount of peaks, that coincides completely or partially in the scale of 2, that it makes it difficult the decipher process. The identification and decipher of the peaks demonstrate the presence of two minerals: Thenardita Na_2SO_4 and Halita NaCl. The main constituent elements of the WTP sludge had been detected through the ray-X method fluorescence, that presented as being they are the oxides: of aluminum (Al_2O_3), silicon (SiO_2), iron (Fe_2O_3), titanium (TiO_2), manganese (MnO), calcium (CaO), sulphur (SO_3), sodium (Na_2O), potassium (K_2O) and (P_2O_5), as constant values in table I. Through the use of the method of X-rays difratometric it was searched the mineral phases that had presented two similar clay phases: Quartzo($Si O_2$) and Caolinita $Al_2 Si_2 O_5$.

After analyzing all the components and based on the theoretical knowledge on the formation processes of structures of ceramic materials a series of test specimens were prepared with different percentages, varying the total concentration of residues from 70% to 85%, from these, we selected the test specimens that had presented better mechanical resistance in the distinct temperatures of burning. The results of these tests and their respective firing temperatures are listed in the table I.

	WTP SLUDGE (%)	GLASS AND SALTS (%)	CLAY (%)	FOUNDRY SAND (%)	900°C-6h MPa	950°C-6h MPa	1000°C-6h MPa	1050°C-6h MPa
1	30	40	30	-	8,1	14,1	14,0	20.0
2	30	40	25	5	7.2	12.5	12,6	15.1
3	40	35	20	5	5.1	7.0	7,4	10.9
4	35	35	25	5	7.6	10.1	10,5	11.3
5	35	35	15	15	3,4	5,8	6,2	11.6
6	35	30	15	20	2,4	4,1	4,5	8.1
7	30	35	15	20	3,0	4,3	5,5	11.5

Table I - Result of resistance mechanics in different temperatures of burning.

The results obtained indicate that the ceramic prepared with 70% of residues (composition 1), without the addition of sand and with the maximum clay content, presented the highest strength (20 MPa) at 1050°C. Composition 2, with a 5% lower clay content and a 5% higher sand content showed a significantly lower strength at all the temperatures tested. Increasing the proportion of sand to 15 and 20% in compositions 5, 6 and 7 led to a considerable increase in resistance at 1050°C in comparison to the other temperatures. The results showed high flexural strength and low values of water absorption and linear retraction, characterizing the good sintering of the materials and vitreous formation, ensuring low values of solubilization and leaching.

This can be observed through the interpretation of x-rays difratometric that demonstrates a great height enters the line of base and the horizontal axle, and, the presence of small peaks in relation with the height of the deep one of the amorphous part of the material.

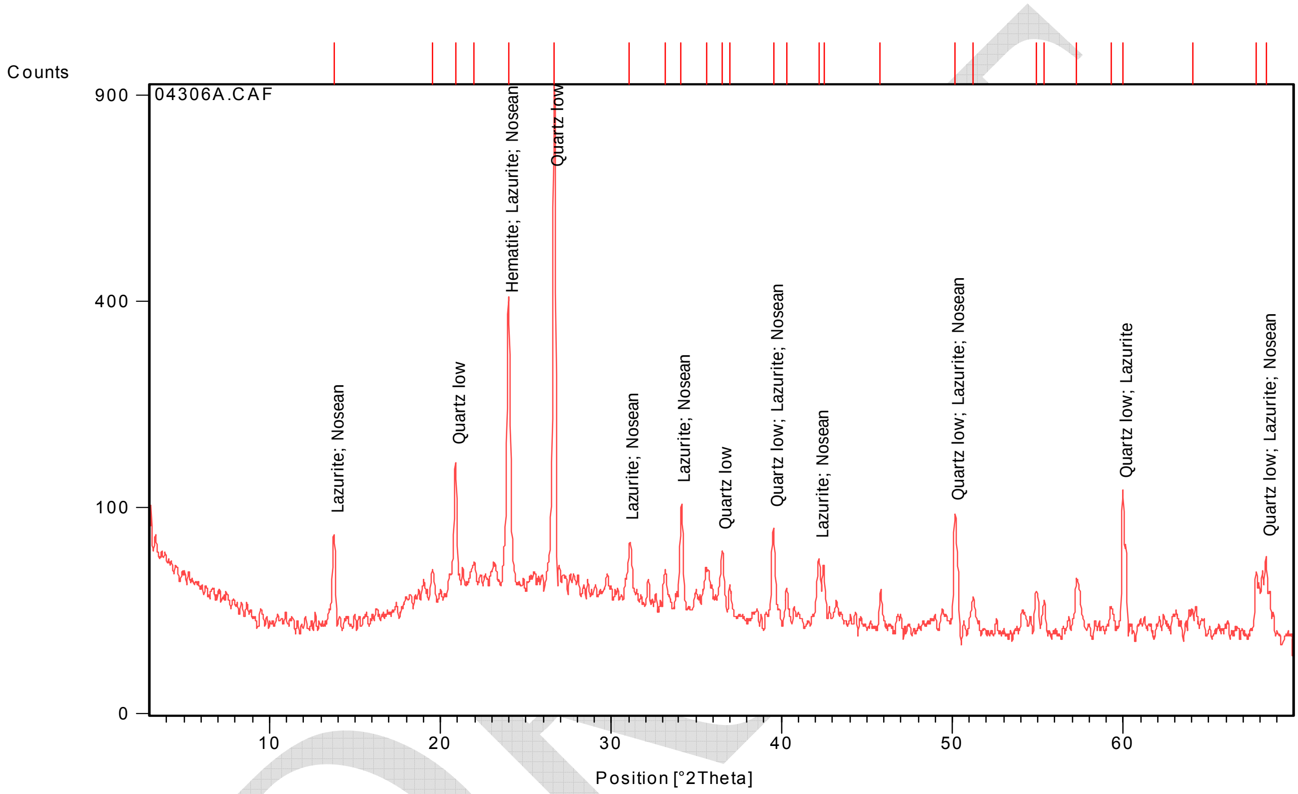

Figure 1: x-rays difratometric of the new ceramic

The glass structure is distinguished as being of predominant occurrence in the structure of the sample, due to height and characteristic of the deep one of the XRD. The high gotten values of resistance can be attributed in a large extent mainly to this predominant formation, even so there could be the synthesis of new minerals after the burning of the initial mixture, as: Lazurite (Na8.56 (Al6 Si6 O24) (S O4)1.56 S.44) , Nosean (Na8 Al6 Si6 O24 S O4) , Hematite (Fe2 O3) e Quartz low (Si O2).

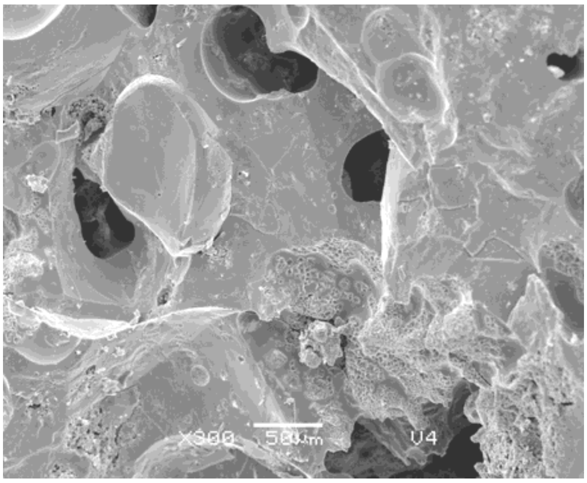

Figure 2 – Electronic microscopy of sweepings of Ceramics – 300 x

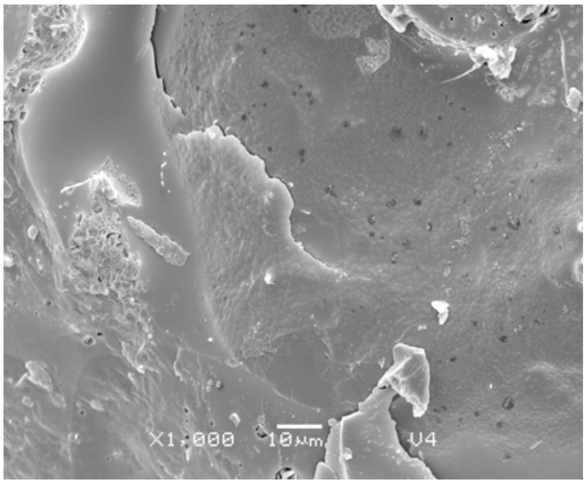

Figure 3 - Electronic microscopy of sweepings of Ceramics – 1000 x

Through the analysis carried through with the use of the method of electronic microscopy sweepings were possible to visually certify the interpretation of the analysis of x-rays difratometric, therefore, all the samples had presented different levels of vitreous formation and chemical interaction in the different temperatures. With the good level of vitrious form gotten is probable that it does not occur leaching and solubilization of the small heavy metal concentrations into in some of the residues.

CONCLUSION

1. The new ceramics presented one high value of resistance mechanics, much above of the demanded one for the norm, what it becomes possible and viable the use of these residues for the ceramics production.
2. Due to the high gotten values of resistance it was proven that the structures possess different levels of vitreous formation and porosity for the distinct compositions and temperatures of burning.
3. The different gotten levels of vitreous formation will guarantee that it does not have leaching and solubilization of heavy metals.
4. The values of the results of linear retraction and water absorption are small compared to the values gotten in the conventional ceramic industries.
5. The use of residues in the ceramic manufacture will make that it could have a reduction of the consumption of natural raw material.

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