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Industrial sewage slurry utilization for red ceramics production

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HIGHLIGHTS

- New construction materials include sewage slurry of industrial processes.
- The slurry contains Ni 3%, Zn 5%, Pb 1.3%, Sn 0.7%, Cr 4%, Cu 3.8%.
- The values of flexural strength of ceramics sintered at 850 °C reach till 12 MPa.
- Water absorption value is 13% and dilatation between 12% and 13%.
- Leaching and solubility of ceramics permit their use as tiles, bricks, blocks.

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ABSTRACT

This paper reports on ceramic materials based on hazardous industrial sewage slurry containing galvanic glass waste and clay–sand mixture. The slurry waste has high contents of heavy metals (Ni – 3.24%, Zn – 5.28%, Pb – 1.32%, Sn – 0.67%, Cr – 4.28% and Cu – 3.78%), organic components (pitches, oils, paints, inks, etc.), and water (56.35%). The ceramics is sintered at temperatures of 700, 750, 800 and 850 °C to provide flexural strengths of up to 12.5 MPa, coefficients of thermal expansion 6.1–9.0% and water absorption of 11.95–13.20%. The minerals that survive sintering are only Quartz SiO_2 and Hematite Fe_2O_3. Analyses of ceramic samples demonstrate their amorphous glassy nature, presence of Na–Anortite $(Ca,Na)(Si,Al)_4O_8$, Thenardite Na_2SO_4 and Mullite $Al_6Si_2O_{13}$, and strong chemical binding of the heavy metals within insoluble structures (leaching and solubility tests).

1. Introduction

Galvanic processes are one of the most widely-distributed industries all over the world. Their wastes are characterized by high contents of heavy metals, e.g., Ni, Zn, Cr, Sn, Cu, Pb, Sb, etc. which are extremely hazardous environmental pollutants whose negative impact is profoundly studied [1]. All of these wastes could and should be used as raw materials for production of different environmentally friendly and economically efficient products. Among the most promising is the ceramic production as a method of heavy metals inertization.

Yellow sludge contains hydroxides of several hazardous heavy metal ions, i.e., Cr, Fe, Cu, Zn and Pb. It is well known that soda-lime silicate glass is a very effective flux and therefore it is very efficient medium for stable solidification of heavy metal ions, thus, the "glass wastes" can be reused for this purpose. Additional waste glass could be prepared from glass bottles used for commercial drinks. It is reported on production of green glass by melting yellow sludge together with synthetic soda-lime silicate brown glass. This technique is aimed to stabilize hydroxides of heavy metals (Cr, Fe, Cu and Pb) [2].

Another method involves sintering at 1400 °C bottom ashes from two types of municipal solid wastes having high contents of heavy metals. The obtained glass, mixed with other metallurgical and mineral industrial wastes, is 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 [3]. Naga and El-Maghraby [4] study the suitability of Cu-slag as a flux for the production of sintered ceramic tiles having high bulk density, considerably low firing temperature and reasonable tensile strength. It is prepared by firing at 1175 °C a 30 wt.% slag material containing a variety of substances (SiO_2, SO_4, Zn, Ni, Ca, Cu, Cr). Effect of processing parameters, such as mixing time,

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calcination time and temperature, relative amounts of sludge (1–10 wt.%) and physical aspects of samples (powdered or pressed pellets) on fixing process has been shown [5]. Balaton et al. [6] successfully use galvanic sludge (2% and 5%) in mixtures with two types of natural clay sintered at temperatures of 850, 900 and 950 °C. Basegio et al. [7] study the possibility of utilizing tannery waste of high heavy metal content in mixtures with natural clay. Solubility and leaching tests result in a recommendation of only 10% of such waste. Another way to neutralize heavy metals from galvanic waste, proposed by Cioffia et al. [8], involves binding matrix containing, Calcium Silicate $2CaO{\cdot}SiO_2$, Calcium Sulphoaluminate $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, and Pure Anhydrous Calcium Sulfate $CaSO_4$, synthesized with the use of powdered tuff, bauxite, calcium carbonate and sulfate. Currently, the waste is disposed to a landfill to prevent the risk of Cd, Cr and Ni release.

Asavapisit and Chotkland [9] try to bind galvanic sludge using a mixture of lime and pulverized fuel ash (30% and 70%, respectively) activated by addition of Na_2SiO_3 or Na_2CO_3 till 8%. The material shows rather high strength. As for leaching tests, Pb, Cd and Cu are not found in the leachate but Cr, Zn, and Fe are detected and, moreover, in some cases Cr exceeds the US EPA allowable limits.

A number of new efficient methods (compositions and technologies) for industrial and municipal waste utilization are developed and patented at the Federal Technological University of Paraná (UTFPR) in Brazil [10,11]. Among 77 types of wastes studied, there are galvanic slurries containing high levels of heavy metals (up to 52 wt.%) [11]. The mentioned work is rather close to the present one.

The goals of this research are: to develop new environmentally friendly compositions of ceramics for utilizing industrial slurry as a valuable component of construction materials that have acceptable mechanical properties; to study the processes of the new materials' formation in order to improve their mechanical and chemical properties; to decrease the production cost of construction materials without losing their mechanical properties.

2. Materials and methods

2.1. Materials and preparation of test samples (TSs)

Raw materials under study are industrial sewage slurry (SS), glass waste (GW) from metal cleaning before galvanic process, and mixture of red pottery clay with sand (CSM), all provided by local industrial enterprises of Paraná state, Brazil.

Preparation method of ceramic samples of various compositions (Table 1) involves homogenizing a mixture of the initial components (water contents of 12–14%), compressing at 3 MPa (wet samples are rectangular, 60 × 20 × 10 mm in size), drying to constant weight at 100 °C, sintering for 6 h (temperatures of 700, 750, 800 or 850 °C), and cooling by natural convection. Production conditions correspond to real ranges at local brick plants.

2.2. Methods

The raw materials and the ceramic samples were characterized by various complementary methods. Chemical compositions were studied by X-ray fluorescence (XRF) on Philips/Panalytical PW 2400; mineral compositions – by X-ray diffraction (XRD) on Philips PW 1830; morphological structures – by scanning electron microscopy (SEM) on FEI Quanta 200 LV; chemical micro analyses – by method of energy dispersive spectroscopy (EDS) on Oxford (Penta FET-Precision) X-ACT; solubility and leaching of metals from liquid extracts – by method of atomic absorption analysis (AAA) on Perkin Elmer 4100 spectrometer; granulometric composition – by laser diffraction particle size distribution analysis on LA-950 HORIBA Analyzer; mechanical resistance – by three-point flexural strength (FS) on EMIC universal testing machine; water absorption (WA) – on Instrutherm BD 200; linear shrinkage (LS) – on Mitutoyo. Besides, bulk density measurements were carried out. Values of mechanical properties and standard deviations were obtained as an average of 10 samples' measurements.

Table 1
Substantial compositions of developed ceramics.

Comp. no	Compositions (wt.%)		
	SS	GW	CSM
1	4	6	90
2	4	8	88
3	6	10	84
4	8	10	82
5	8	6	86
6	0	10	90
7	0	0	100

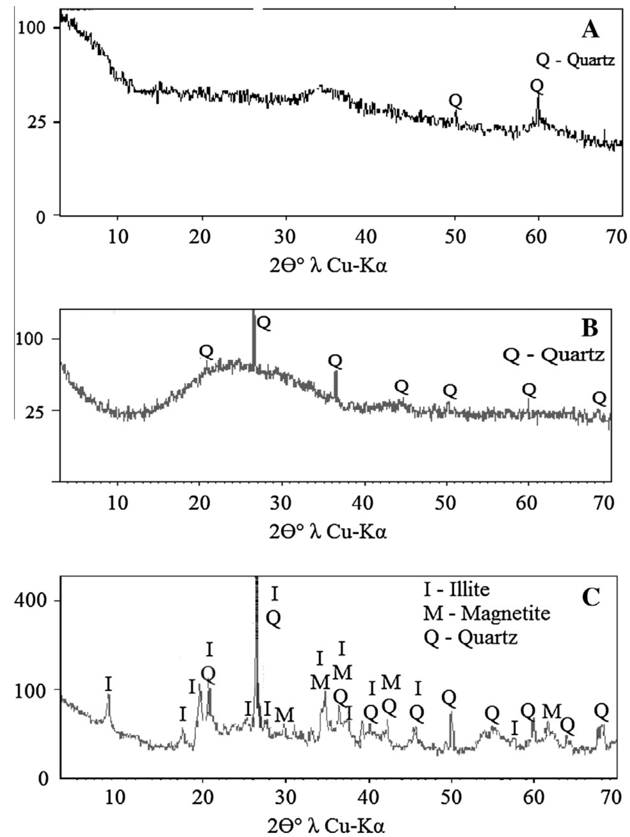

Fig. 1. Diffractogram patterns of the raw materials used: (A) sewage slurry, (B) glass waste; and (C) mix of clay and sand.

2.3. Calculations

The flexural strength of the TSs was measured according to the ASTM [12], using the equation:

$$RF = \frac{3PL}{bh^2} \quad (1)$$

where RF – flexural strength (MPa), P – maximum load supported (kgf), L – distance between the supports (mm); b – sample's width (mm), h – sample's height (mm).

The values of water absorption were measured according to the ASTM [13], using the equation:

$$W_A = [(M_{SAT} - M_D)/M_D] \times 100 \quad (2)$$

where M_{SAT} – mass of the water saturated by sample after 24 h of immersion, M_D is – mass of dry sample after sintering.

The values of apparent specific gravity were obtained according to the ASTM [13], using the equation:

$$BD = Md/(Mw - Mi) \quad (3)$$

where BD – bulk density (g/cm^3); Md – mass dry sample after sintering (g); Mw – mass wet sample (g), Mi – mass of sample, immersed in water (g).