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Environment friendly ceramics from hazardous industrial wastes

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Abstract

This paper reports on recycling mixed industrial wastes (exhaust metallurgical dust, spent foundry sands, galvanic glass microspheres, and acid inertization salt) into environmentally friendly composite ceramic materials. The only natural component of the compositions developed is clay and sand mixture, which is a traditional raw material of local brick factories. All industrial wastes under study have high contents of heavy metals, such as Pb, Br, Sr and Cr. The main goal of this research is development of eco-friendly construction materials based on hazardous industrial wastes to reduce waste disposal at dumps that chemically contaminate the environment. This would prolong service life of industrial landfills and essentially reduce exploitation of natural raw materials. Samples containing 75–85% of industrial wastes fabricated at 950–1010 °C have flexural strength values of up to 14 MPa. The values of leaching and solubility of the heavy metals are hundreds of times less than those permitted the national standards of Brazil. Physicochemical studies of the samples confirm the formation of a glassy structure with inclusion of newly formed minerals (Sodium Anortite, Thenardite, Hematite and Mullite). This structure can explain the mechanical and chemical characteristics of the new ceramic materials.

Keywords: B. Composites; B. Impurities; C. Mechanical properties; Leaching and solubility

1. Introduction

Among the industrial and municipal wastes, some are extremely hazardous due to the high content of dangerous components, such as concentrated heavy metals. One of the most toxic are exhaust metallurgical dusts (EMD), which are a matter of global concern. There are investigations [1] on EMD of ore minerals containing a composition of hazardous substances, such as sulphides and arsenides of Cu, Pb, Zn, Ni and alloys of Pb and Pb–Cu (Legnica Głogów, Poland). It has been reported on an efficient method to prevent industrial air pollution [2] where a filter made up of coal and EMD (containing Zn/Pb) is used to absorb another type of EMD (containing H_2S/SO_2) released at briquette combustion.

It was calculated [3] that the specific amount of EMD emitted by crude steel production is of the order of 2 wt%. Worldwide, it gives yearly around 5 mln tons of EMD, which contains near 1 mln tons of zinc [4]. Similar percentage of zinc (7–20% or even more), depending on raw materials, are confirmed by others researchers [5–7]. It was determined [4,8] that chemical compositions of EMD involve such perilous elements as Zn 22–40%, Ni 0.03%, Pb 3.0%, Cu 0.25%, Cr 0.12%, Cd 0.08%, and in smaller quantities Hg, As, Cl, F, etc. In general, such wastes are simply disposed at landfills (60%) or reduced with coke in Waelz kilns to produce impure zinc concentrate. The cost of EMD disposal in the USA is $200 mln per year [9–11].

There is a patented method [12] for treating high-temperature exhaust gas from metallurgical furnace by adding a reducing agent that is active at oxygen concentrations of 1 vol% or below and at temperatures of 800 °C or above.

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Another method [13] permits both to minimize heat damage by metallurgy exhaust gas and to effectively remove EMD [reaching EMD concentrations of less than 20 mg/N m] by combining a sack dust collector and a finned tube heat exchanger. Exhaust gas recovery is also concerned within the methods [14,15] for recycling metal and carbon dust into molasses-bound pellets that are useful in sintering of iron ore. According to studies [16], if manganese EMD is recycled to the ferroalloy furnaces via the sinter plant, the overall zinc input will increase by 51–143%, depending on charging materials. Existing works report on successful use of GGM in red ceramics production [17,18] where it is used as flux component for galvanic sludge and oily diatomite waste utilization.

This paper experimentally proves the possibility of green chemistry realization by recycling EMD and other industrial wastes, such as galvanic glass microspheres (GGM), spent foundry sands (SFS), and acid inertization salt (IS), into ceramic materials containing up to 85 wt% waste raw materials. No attempts to use so wide range of industrial wastes in combination with EMD have been made so far. However, this would help to minimize both environmental pollution and exploitation of natural materials, to prolong the service life of industrial landfills, and to develop high performance construction materials with advantageous mechanical and chemical characteristics.

The objectives of this research are to develop new ceramics on the basis of foundry wastes (EMD and SFS) with inclusion of other wastes (GGM and IS) in order to reduce ceramic production costs and decrease the use of natural resources; to study the physicochemical processes of structure formation of new materials for optimizing their mechanical and chemical properties; to develop wasteless technologies or to adapt current ones for production of new materials at laboratory level.

These objectives are in line with the 3rd paragraph (Less Hazardous Chemical Syntheses) of the Twelve Principles of Green Chemistry: “Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment”.

2. Experimental sections

2.1. Materials

All the raw materials used in this study were collected at local industrial enterprises of Paraná state, Brazil: EMD—metallurgical plant, SFS—machine construction plant, GGM—galvanizing company (sandblasting waste), IS—recycling firm of a lead-acid batteries plant. Traditional raw material composed of clay and sand mixture (CSM) was provided by local brick factories.

Optimal humidity of the mixtures was between 10% and 12%. Humid mixtures were pressed at 10 MPa in rectangle form of $60 \times 20 \times 10$ mm and dried at temperature of 100 °C till constant weight. Than the samples were baked at different temperature regimes: at 1010 °C during 1, 3 and 6 h and at 950, 980, 1000, 1020 and 1030 °C during 6 h.

2.2. Methods

The raw materials and final ceramics were characterized by various established complementary methods and procedures. Chemical composition was studied by X-ray Fluorescence (XRF); mineral composition by X-ray diffraction (XRD) with the radiation λCu-$K\alpha$, a deciphering of the obtained diffractograms was performed under the program High Score with the data bank PDF-2; morphological structure by scanning electron microscopy (SEM); chemical microanalyses by Energy Dispersive Spectroscopy (EDS) and by laser micro-mass analysis; solubility and leaching of metals from liquid extracts by atomic absorption analysis (AAA) on Perkin Elmer 4100 spectrometer; granulometric composition by laser diffraction particle size distribution analysis; mechanical resistance by three-point flexural resistance strength tests by universal testing machine of EMIC, model DL10000; water absorption (WA); linear shrinkage (LS).

The values of mechanical properties and standard deviations were obtained as an average of 10 samples' measurements.

3. Results and discussion

3.1. Raw materials used

The SFS display the highest SiO_2 content (91.15%), followed by GGM (76.31%) and EMD (71.57%) (Table 1). The CSM show the highest value of Al_2O_3 (24.13%) while the IS contains the highest values of Na_2O (18.67%) and SO_3 (29.39%) although the GGM also has a high Na_2O content (8.75%).

All of industrial wastes under study are extremely hazardous, because they contain, besides principal elements (Table 1), dangerous heavy metals and poisonous organic impurities, such as Pb (0.69%), Cl (4.56%) and Br (0.02%) in IS; Sn (3.78%), Zn (2.18%), Cr (1.32%) and Zr (0.04%) in EDM; Pb (0.11%), Zn (1.06%), Cr (0.29%) in GGM; Cr (0.11%) in SFS. Therefore, they are Class I and II-A materials, according to the Brazilian standards [19]. The values of leaching and solubility of heavy metals from all the wastes used as raw materials in this study significantly exceed (Table 2) the permitted national sanitary norms [20,21].

Table 1
Contents of principal elements in the chemical compositions of the components (XRF data).

Materials	Compositions (wt%)						
	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	SO_3	MgO
EMD	71.57	12.74	8.34	1.47	1.23	0.87	1.41
SFS	91.15	2.18	1.89	0.25	0.13	0.18	0.23
GGM	76.31	0.85	2.24	8.75	8.31	0.26	2.5
IS	0.19	–	0.20	18.67	–	29.39	–
CSM	53.29	24.13	3.32	–	0.33	–	0.31