Journal of Environmental Chemical Engineering 4 (2016) 753–761

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Red ceramics from composites of hazardous sludge with foundry sand, glass waste and acid neutralization salts

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ARTICLE INFO

Article history:
Received 21 April 2015
Accepted 20 July 2015
Available online 22 July 2015

Keywords:
Water treatment plant sediments
Minerals sintering
Chemical interaction
Mechanical properties
Ceramics structure formation
Environmental engineering

ABSTRACT

This study is aimed at the development of new compositions of municipal water treatment plant sludge with foundry sand, glass waste and acid neutralization salts for red ceramics production. The chemical and mineralogical compositions of the raw materials and structure formation processes of the ceramics made from only industrial wastes were studied using XRF, XRD, SEM, EDS, LAMMA and AAS methods. The initial mixtures of these components were sintered at 900, 950, 1000, 1050 and 1100 °C for 6 h. The results indicate that the ceramics had flexion resistance strength up to 18.4 MPa (sintered at 1050 °C), low values of water absorption and linear shrinkage. It was shown that high values of mechanical properties can be attributed mainly to the synthesis of glassy structure formation with small inclusions of new minerals, namely corundum Al_2O_3, hematite Fe_2O_3, lazurite $Na_6Ca_2(AlSiO_4)_6(SO_4,S,Cl)_2$, mullite $3Al_2O_3{\cdot}2SiO_2$, nepheline $(Na,K)AlSiO_4$ and quartz SiO_2. The results of leaching and solubility tests by AAS are significantly lower than the requirements of the Brazilian standards, which demonstrates a reliable binding of heavy metals from the waste used as raw materials into insoluble compounds.

Introduction

The objective of solid waste recycling is to reduce raw material consumption, thus minimizing pollution problems and treatment costs. This paper explores the development of construction materials using the following recycled industrial solid wastes: municipal water treatment sludge (WTS) in composite with foundry sand (FS), glass waste (GW) and acid neutralization salts (ANS), without inclusion of any traditional natural components such as clay or clay–sand mixtures.

Davis [1] calculated that in Europe, dry weight WTS averages 90 g per person per day or 10 million tons annually. The Council Directive of EEC demonstrated [2] that the quantity of the solids fraction usually varies due to the different methods of the WTS processing. An increase in the WTS quantity of up to 1–2% of the total wastewater discharged occurred due to growth in the number of new wastewater treatment plants all over the world [3]. Dramatically increased demands for water due to technological advancement, population growth, and urbanization will greatly stress the natural water cycle [4].

A worldwide common practice of WTS treatment is to discharge directly into the landfills [5]. EEC [2] prohibited the use of untreated sediment in agriculture unless it is injected or incorporated in the soil for the protection of the environment. Moreover, the term treated sediments is defined as the material that "has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as to significantly reduce its fermentability and the health hazards resulting from its use" [2]. WTS usually includes grit, screenings and sediment suspensions of inorganic and organic substances, including typical coagulants—hydrated alumina oxides and iron oxides [6]. The majority of WTS is characterized by a high content of heavy metals (e.g., Ni, Zn, Cr, Sn, Cu, Pb, Sb), which are hazardous environmental pollutants and whose negative impact has been studied extensively [5,7].

All WTS could be, and should be, used as raw materials for production of different environmentally friendly and economically efficient products [6,7]. The mineralogical composition of WTS is particularly close to that of clay [8]. These processes can include some chemical and physical methods (e.g., freezing, heating or ultrasonic treatment) [9]. Dewatered and dried WTS can be used to

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http://dx.doi.org/10.1016/j.jece.2015.07.015
2213-3437/

remove phosphorus during wastewater treatment and can subsequently be used as fertilizer [10]. Kyncl [11] described possible alumina recovery in the WTS and its reuse for treatment of municipal wastewater. Anyakora [12] used WTS by adding 90% of natural clay to produce the brick; Chihpin et al. [13] used WTS ash at a 5% replacement level as a brick-making raw material through the sintering process. Kizinievič [14] analyzed the influence of WTS (from 5 to 40 wt.%) on the physical and mechanical properties, structural parameters as well as mineralogical composition of the ceramics sintered at 1000 °C and 1050 °C. Algam et al. [15] investigated the use of WTS (10–50 wt.%) used cement in the production of paving tiles with WTS for external use. John et al. [16] successfully used WTS as an additive to cement mortars. Alonso-Santurde et al. [17] concluded that green sand from the foundry industry can be used to replace the clay content in construction materials, and these foundry sand-based ceramics improved some results for salt solubility.

Among the most promising methods of heavy metals inertization (Cr, Fe, Cu and Pb) is ceramic production [18], using silicate glass as an effective flux. The method of glass wastes utilization as flux was developed for many materials, some of which had a heavy metals content up to 52 wt.% [19,20]. Guidance work was developed to minimize the waste generated from automotive batteries recycling with the neutralization of the sulfuric acid, which contains small percentages of heavy metals [21].

The goals of this research were to develop new environmentally friendly composites for ceramics production from industrial wastes that have acceptable mechanical properties using WTS as a principal component (up to 60 wt.%), to study the processes of the new materials structure formation in order to regulate their mechanical and chemical properties, and to develop waste-less technologies or to adapt current ones for production of new ceramics at laboratory level.

These objectives are in line with the 3rd Principle (Less Hazardous Chemical Syntheses) of the Twelve Principles of Green Chemistry [22]: “Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment”.

Materials and methods

Raw materials

All of the raw materials used in this study were collected at local industrial enterprises of Paraná State, Brazil: WTS was provided by the municipal company of water treatment SANEPAR, GW was obtained from a glass treatment workshop, ANS was provided by an automobile lead-acid accumulator (car battery) recycling plant, and FS was acquired from a local metallurgical plant.

This experimental research was performed in three steps: physicochemical characterization of the raw materials (WTS, GW, ANS and CSM); preparation of the TS containing different proportions of the wastes; and characterization and evaluation of mechanical, chemical and mineralogical properties of the ceramics from new compositions at different temperatures of sintering.

The WTS displayed the highest Al_2O_3 (24.46%) and Fe_2O_3 (13.00%) content. The FS had the highest value of SiO_2 (91.65%), followed by GW (76.04%), while the ANS contained the highest values of Na_2O (39.72%) and SO_3 (25.38%), although the GW also had a high Na_2O content (8.75%) (Table 1).

ANS had the highest value of calcination loss (C.L. of 44.64%) because of its large SO_3 (25.38%) content; SO_3 is the product of neutralization of sulfuric acid. WTS also had a significant C.L. (39.77%) due to high content of humus and fertilizers, as well as iron or alumina sulfates. Moreover, all of the industrial wastes used in this study for raw material contained heavy metals and toxic organic impurities. WTS had 0.32% of Cl, 0.12% of Ba and 0.03% of Br; GW had 0.11% of Pb and 0.27% of Cr; ANS had 0.25% of Sn, 0.38% of Sb, 0.58% of Zn, 1.18% of Cu, 0.47% of As, 1.25% of Pb, 0.18% of Ba, 8.24% of Cl and 0.04% of Br with a total content of extremely hazardous elements of 12.57%. Therefore, they are classified as Class I (dangerous) and Class II-A (no inert) materials, according to the Brazilian standards [24]. The values of leaching of metals (Table 2) from all of the wastes used as raw materials in this study significantly exceed the permitted national sanitary norms, in particular for As (from WTS and ANS), for Ba (from WTS, GW and FS), and for Pb and Cr from all components.

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

Oxides	Oxides contents (wt.%)			
	WTS	GW	ANS	FS
SiO_2	17.01	76.04	0.34	91.65
Al_2O_3	24.46	0.85	–	1.53
TiO_2	0.40	–	–	0.13
Fe_2O_3	13.00	2.24	0.36	1.96
MnO	3.20	–	–	0.24
MgO	0.15	2.50	–	0.14
CaO	0.30	8.20	–	0.26
Na_2O	<0.02	8.75	39.72	0.08
K_2O	0.18	0.44	1.16	–
P_2O_5	0.44	–	0.40	0.19
SO_3	0.61	0.26	25.38	0.12
C.L.[a]	39.77	0.34	44.64	3.70
Σ	99.55	99.62	99.43	100.00

[a] C.L.: calcinations' loss.

Analysis of the experimental results for the rates of metals leaching and solubility showed an greatly exceeded the sanitary standards (Tables 2 and 3) for all raw materials under study. In particular, the metal solubility from WTS exceeds the Brazilian norm for Pb by 2734 times, 4873 times for Cr, 31,422 times for Mn; the metal solubility from ANS is 2180 times the Brazilian norm for Mn and 1847 times for Pb.

Table 2
Results of leaching tests of the waste raw materials under study.

Elements	Leaching of raw materials (mg/L)				Limits [24]
	WTS	ANS	GW	FS	
As	17.69	1.43	0.86	0.14	1.0
Ba	93.37	54.87	92.72	24.23	70.0
Pb	29.82	12.41	1.024	2.172	1.0
Cr	179	981	14.61	9.87	5.0

Table 3
Results of solubility tests of the raw waste materials under study.

Elements	Solubility of raw materials (mg/L)				Limits [24]
	WTS	ANS	GW	FS	
Al	23.17	19.34	0.45	13.62	0.2
Ba	8.15	4.19	37.11	97.43	0.7
Pb	27.34	18.47	1.205	5.375	0.01
Cu	43.15	23.78	463.25	9.34	2.0
Cr	243.67	15.18	42.57	14.25	0.05
Fe	3.583	1.485	82.13	74.33	0.3
Mn	314.22	217.97	37.58	43.19	0.1
Zn	387.28	153.17	46.84	133.83	5.0