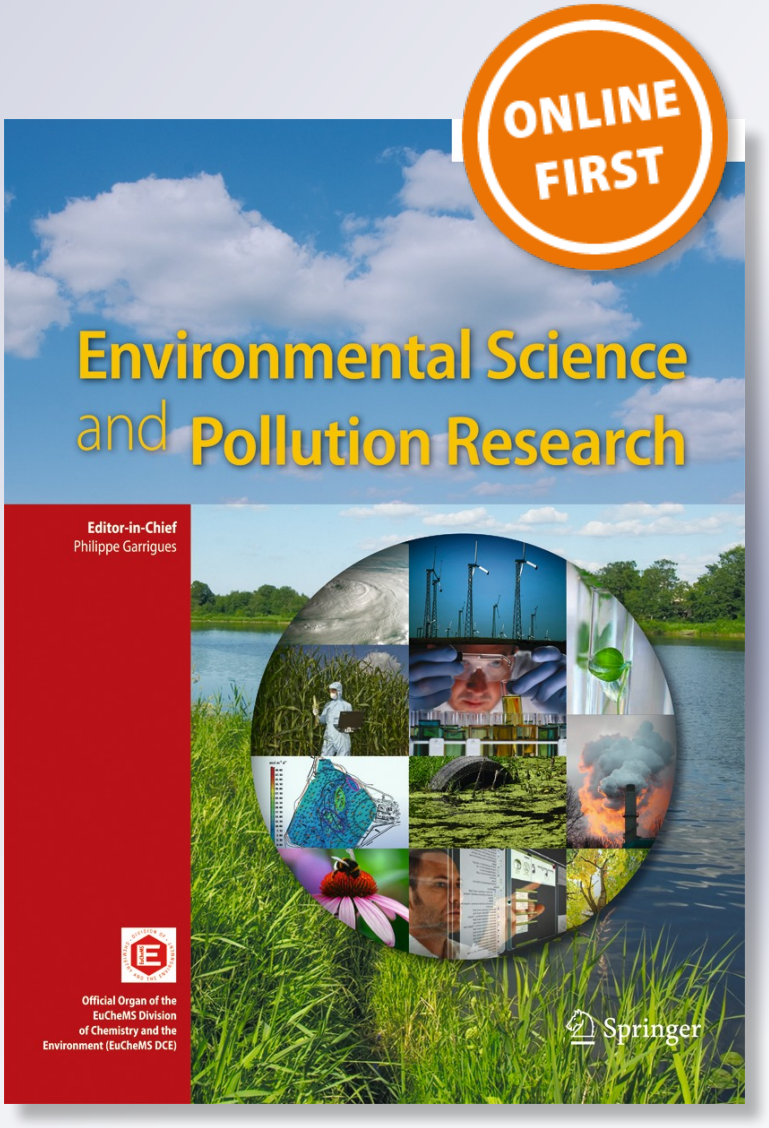
Preparation and characterization of green bricks using pharmaceutical industrial wastes

M. Yamuna Rani, D. Bhagawan, V. Himabindu, V. Venkateswara Reddy & P. Saritha

Environmental Science and Pollution Research

ISSN 0944-1344

Environ Sci Pollut Res
DOI 10.1007/s11356-015-5191-2



Springer

Environ Sci Pollut Res
DOI 10.1007/s11356-015-5191-2

Preparation and characterization of green bricks using pharmaceutical industrial wastes

M. Yamuna Rani [1,3] · D. Bhagawan [1,3] · V. Himabindu [1,3] · V. Venkateswara Reddy [2,3] · P. Saritha [1,3]

Received: 16 March 2015 / Accepted: 10 August 2015

Abstract This paper reports on recycling of industrial wastes (three pharmaceutical industrial sludges) into environmental friendly value-added materials. Stabilization/Solidification (S/S or bricks) process was applied to make a safer way for the utilization of pharmaceutical waste. The additives in this study include binders (cement, lime and bentonite) and strengthening material (pulverized fuel ash (PFA), silica fume and quarry dust) was used at different compositions. Bricks were cured for 28 days, and the following analysis-like compressive strength, leachability of heavy metals, mineralogical phase identity by X-ray diffraction (XRD) spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermal behaviour by thermogravimetric-differential thermal analysis (TG-DTA) had done. All the bricks were observed to achieve the standard compressive strength as required for construction according to BIS standards. Metal concentration in the leachate has reached the dischargeable limits according to Brazilian standards. Results of this study demonstrate that production of bricks is a promising and achievable productive use of pharmaceutical sludge.

Responsible editor: Philippe Garrigues

✉ V. Himabindu
drvhimabindu@gmail.com; Yamuna.m218@gmail.com

[1] Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad 500 085, India

[2] Department of Civil Engineering, JNTUH College of Engineering, Jawaharlal Nehru Technological University, Hyderabad 500 085, India

[3] Civil Engineering Department, Malla Reddy Engineering College, Hyderabad 500 085, India

Keywords Solidification/Stabilization · Pharmaceutical sludge · Compressive strength · Metal leachability

Introduction

The hazardous waste discharged from industries such as pharmaceutical industry is of primary concern in the recent decade, due to its toxic nature. Pharmaceutical industry often generates high-strength wastewater as well as sludge with varying quality and quantity parameters depending upon their raw materials and manufacturing processes (Nithyanandam and Saravanane 2013). Perpetual storage of hazardous wastes needs to be converted into non-hazardous forms by suitable pre-treatments (Aydın and Aydın 2014). Land filling, incineration, solidification/stabilization (S/S) and co-processing for cement industry are the disposal methods in practice. S/S method is the most preferable method for managing the pharmaceutical sludge in a sustainable manner due to its stability.

Stabilization/Solidification (S/S) is a method where the different types of industrial wastes can be managed and particularly suited to those of heavy metal-containing wastes (DellOrso et al. 2012). Stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile or toxic forms, while solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives (Montanes et al. 2014).

In recent decades, several types of waste materials were assessed as raw materials for brick making: lightly contaminated harbour sediments (Hamer et al. 1999; Hamer and Karius 2002; Karius and Hamer 2001), waste bricks

Published online: 19 August 2015

Table 1 Reactant materials used for study

S. No	Material	Purpose of use	Characteristic
1	Pharmaceutical industry waste	Needed to treat	Hazardous
2	Cement	Binder	Construction compound
3	Lime	Binder	Coagulant compound
4	Pulverized fuel ash	CO-binder	Hazardous
5	Bentonite	Binder	Coagulant compound
6	Silica fume	Strength increaser	Hazardous
7	Quarry dust	Strength increaser	Hazardous

(Demir and Orhan 2003), limestone dust and wood sawdust (Turgut and Murat Algin 2007), processed waste tea (Demir 2006), reservoir sediments mixed with fly ash (Hsu et al. 2003), dried sludge collected from industrial wastewater treatment (Liew et al. 2004; Lin and Wenig 2001; Weng et al. 2003), incinerated sewage sludge ash (Anderson et al. 1996; Anderson et al. 2002; Wiebusch et al. 1998), fly ash (Lingling et al. 2005), granite sawing waste material (Menezes et al. 2005), water treatment residual with excavation waste soil (Huang et al. 2005), steel dust (Dominguez and Ullmann 1996) and kraft pulp production residues (Demir et al. 2005). As a consequence, it is imperative to develop a new alternative for conventional solid soil bricks. Fortunately, preparation of hollow bricks based on the solid waste (Jianfeng et al. 2008), especially fly ash (Lingling et al. 2005, Dondi et al. 2002), has gained fast development in recent years.

The main objectives of this research is to develop new ceramics on the basis of pharmaceutical wastes (three industries) with inclusion of other wastes (fly ash, silica fume and bentonite) in order to reduce ceramic production costs and decrease the use of natural resources.

Table 2 Composition of the bricks

Sludge (%)	Fly ash (%)	Silica fume (%)	Cement (%)	Lime (%)	Bentonite (%)	Quarry dust (%)
10	30	30	10	10	5	5
15	30	25	10	10	5	5
20	30	20	10	10	5	5
25	30	15	10	10	5	5
30	30	10	10	10	5	5
35	20	15	10	10	5	5

Materials and experimental methodology

Three different pharmaceutical industrial wastes were collected from effluent treatment plants (ETP) of the pharmaceutical industries which were located in Hyderabad, India. The three samples were indicated as samples A, B and C. These samples belong to the industrial process of the acetophenone manufacturing, bulk drug formulation and processing industries, respectively.

The materials and their purpose of use in brick production were given in Table 1. The sludge were collected from industrial sites and dried in a hot air oven for 24 h at 105 °C and ground to less than 9.5 mm in size to aid workability of the sludge-ash-binder mixture during casting. The bricks were prepared in triplicates using three binders (cement, lime and bentonite). The PFA and binders were mixed in a pan mixer, and after 5 min, it was blended with water. To this blended mixture, the industrial by-products such as silica fume and quarry dust were added.

The prepared admixes were filled in the moulds which was having the internal dimensions of 50 mm×50 mm×50 mm and kept under moist condition for 24 h. The bricks were kept for curing for 28 days. The composition of the briquetting materials were reported in Table 2.

The X-ray diffraction (XRD) patterns are recorded on a D8 Advance XRD (Bruker Ltd.). A diffraction angle (2 h) between 10 and 90° and a scanning rate of 4/min is applied to analyse the crystal phases of the samples.

For toxicity characteristic leaching procedure (TCLP) analysis, the solid samples were manually crushed to <1 cm and leached using an extraction buffer of acetic acid and sodium hydroxide (pH 4.93±0.05) at a liquid/solid ratio of 20:1. The extraction (at 25±2 °C) was performed by shaking the material for 18 h. Subsequently, the leachate samples were filtered, and the resultant TCLP extract (filtrate) is analysed for heavy metals using atomic absorption spectroscopy (model: Atomic Absorption Sens AA Spectrometer).

Seiko SII TG/DTA 7200 is used for observing the thermal decomposition behaviour of the sludge. The weight and temperature calibrations of the instrument was made using the reference weight and according to the sensor calibration of the instrument, respectively.

The compressive strength of the composites was determined, according to SIST EN 12390-3:2009 after 28 days of moist curing, on 50-mm cube samples of the composites, prepared according to SIST EN 12390–2:2009.

PerkinElmer Fourier transform infrared spectroscopy (FTIR) was used for functional group identification of the bricks at a wavelength number ranged from 4000 to 400 cm^{-1}.

Table 3 Initial characterization of the pharmaceutical sludges

S. No	Parameter	Results		
		Sample A	Sample B	Sample C
1	Colour	Brown	Light yellow	Light yellow
2	State	Solid	Solid	Solid
3	pH	7.2	11.2	8.9
4	Density (g/cm^3)	0.82	0.98	0.65
5	Ni (mg/kg)	23	103	46
6	Cu (mg/kg)	23	103	62.5
7	Zn (mg/kg)	26.5	134.5	91.5
8	Pb (mg/kg)	45	94.5	133.5
9	Fe (mg/kg)	142	97	41
10	Co (mg/kg)	5	19	24.5

Results and discussion

The initial characterization of the samples was given in Table 3. From Table 3, it was observed that the concentration of the Zn, Cu and Pb was above the standard disposable limits, so that the pharmaceutical sludge needs to be treated properly before its dispodsal (Singh et al. 2007). So this sludge was used for the production of bricks which simultaneously minimizes the environmental pollution. The prepared bricks were given in Fig. 1.

Mechanical properties of the brick products

Mechanical property of the bricks was evaluated in terms of unconfined compressive strength (UCS). The UCS were measured and represented in Figs. 2 and 3, and it was observed that the maximum UCS was at the lower (10 %) concentration of the sludge in brick composition.

Fig. 1 Bricks prepared by pharmaceutical sludges

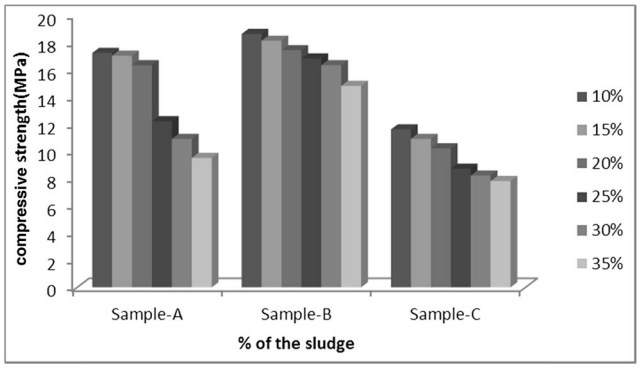


Fig. 2 Compressive strength of bricks without cure

Brick curing with water lasted for 28 days, and the maximum UCS of samples A, B and C was observed to be 20.9, 24.5 and 14.9 MPa, respectively, where the air dried bricks showed 17.2, 18.6 and 11.6 MPa, respectively. The compressive strength of the bricks increased in direct proportion to additive dosage (silica fume and fly ash). The reduction in UCS with increasing of sludge concentration was observed which might be due to the weakening of physical and chemical bonds between the components at the formation stage of bricks (Vsevolod et al. 2014). All the bricks met the Brazilian standards (NBR, standards) class C (>4.0 MPa) bricks required UCS (Vsevolod et al. 2014), Indian minimum required UCS standards (<10 MPa) (IS: 3495–1976), Bureau of Indian Standards (BIS) (2005) and Bureau of Standards (IS: 12894–2002).

TG-DTA of the bricks

The thermogravimetric thermal analysis (TG-DTA) of the sludges was carried in the temperature range between 100 and 800 °C (Fig. 4). The gravimetric loss of all the brick was observed to be dividable into three zones, where the first

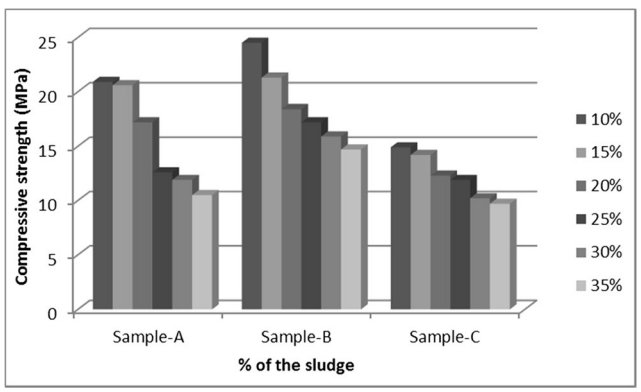
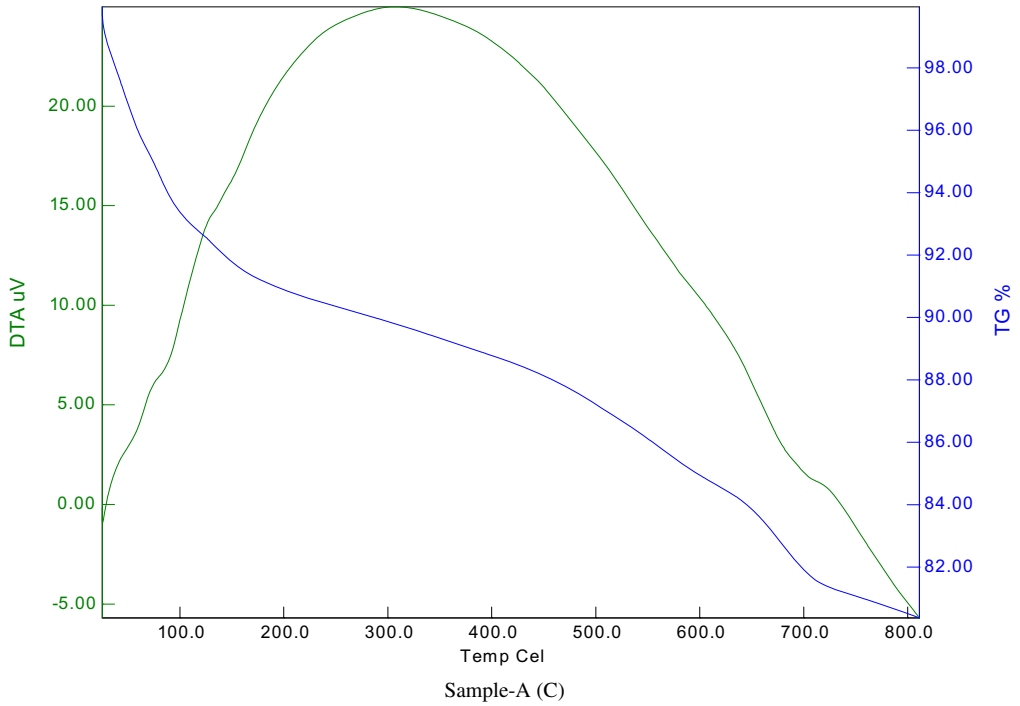
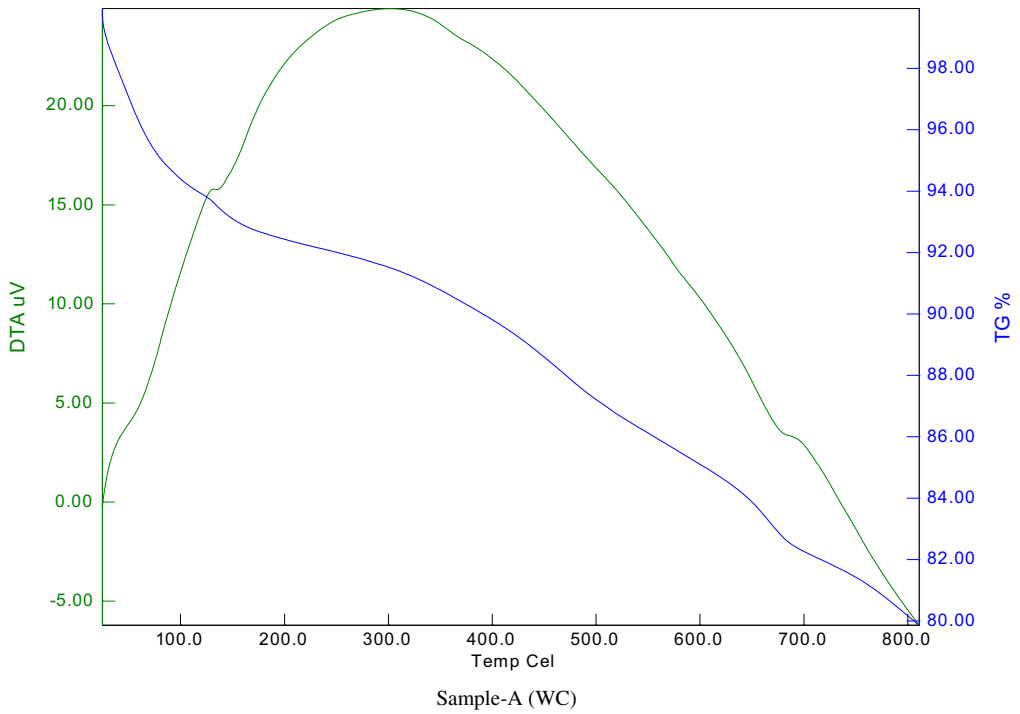


Fig. 3 Compressive strength of cured bricks

zone of the mass loss might be attributed to the evaporation of physically and chemically bounded water, whereas the second zone of the mass loss might be due to the decomposition of the stable hydrates of the calcium aluminates and calcium silicates (Altwair et al. 2011). The final zone might be due to the decomposition of the

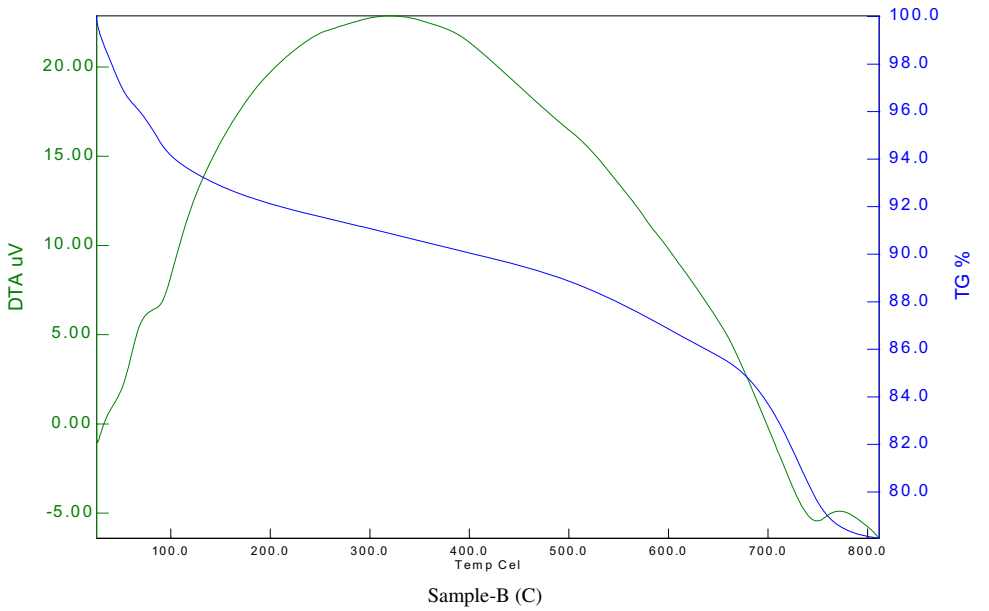


Sample-A (C)

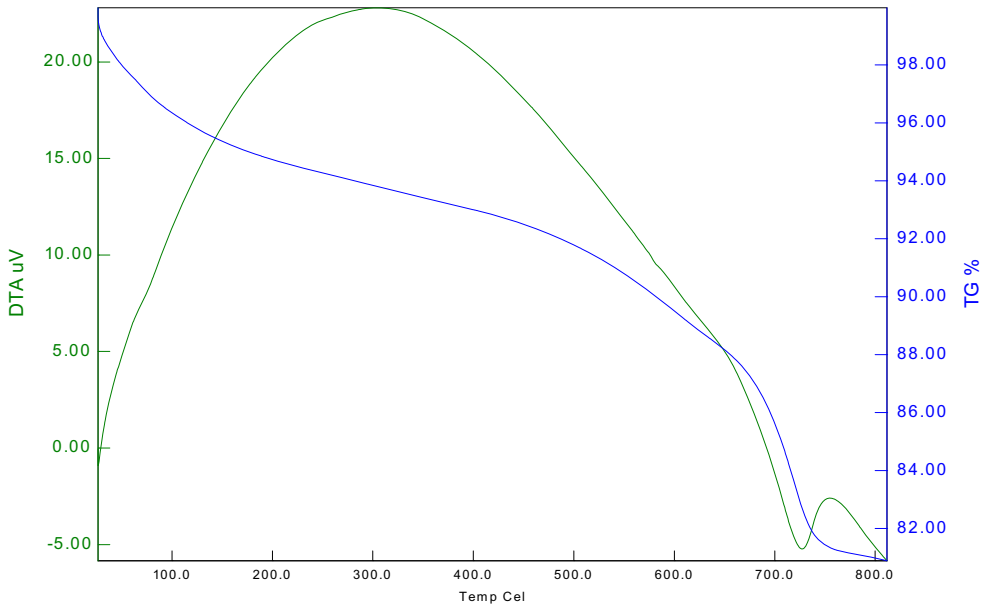


Sample-A (WC)

Fig. 4 Thermogravimetric-differential temperature analysis of S/S products of samples (a, b and c). *(C)* brick with curing, *(WC)* brick without curing



Sample-B (C)



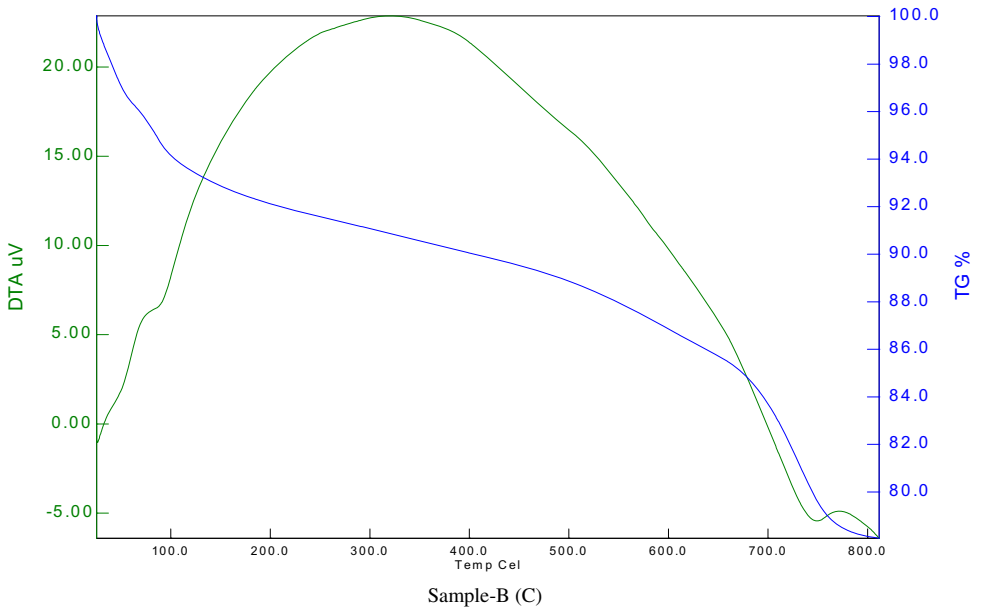
Sample-B (WC)

Fig. 4 continued.

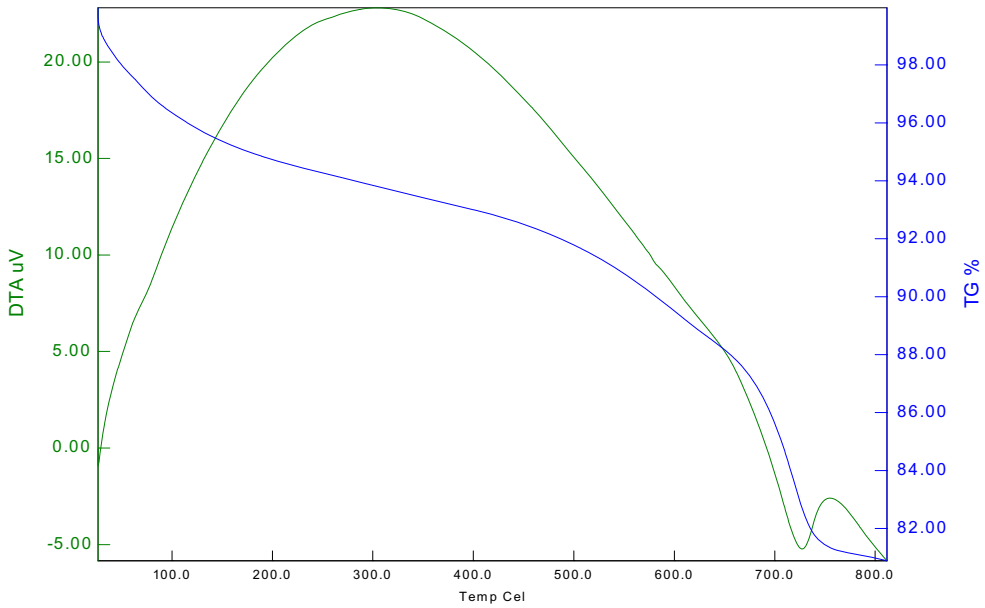
calcium carbonates at 780 °C (Altwair et al. 2011). However, weight loss between temperature range of 223.3 and 520.3 °C is due to decomposition of partially burnt organic compounds. Differential temperature analysis represented an exothermic peak at 750 °C and an endothermic peak at 300 °C in all the three samples. Only 20 % of the weight loss was observed in the TG analysis. This 20 % weight loss might be attributed to metal hydroxide decomposition and ingredient organic matter (Milica et al. 2012).

Leachability test of the products

Metal leachability of the bricks was evaluated by the method TCLP (Method 1311) (US Environmental Protection Agency 1994; Kadir et al. 2010) and (Cu, Zn, Fe, Ni, Co and Pb) concentrations were given in Table 4 and also compared with standard limits set by USEPA (Environmental Protection Agency 1994, 1996). The metal concentrations of TCLP were observed to be very low which might be due to the presence of



Sample-B (C)



Sample-B (WC)

Fig. 4 continued.

silicate matrix C–S–H and C–A–H as long as free silicate and aluminates (Liu et al. 2011). The organic content of the samples and leachate reduced tremendously. This reduction might be due to the hydroxide ions, which were released from calcium hydroxide and other phases in the bricks under aqueous condition and also contributed the alkalinity to the leachate (Liu et al. 2011).

Table 4 Leaching and solubility of metals from the samples of composition

Sample	Ni	Fe	Co	Cu	Zn	Pb
A	0.03	1.03	0.64	0.4	0.2	1.9
B	0.52	0.95	0.32	0.3	0.7	1.6
C	1.23	1.54	0.56	0.1	0.4	1.7

Mineralogical analysis of the products

X-ray diffraction (XRD) was used to determine the mineralogical properties of the bricks (Fig. 2). The

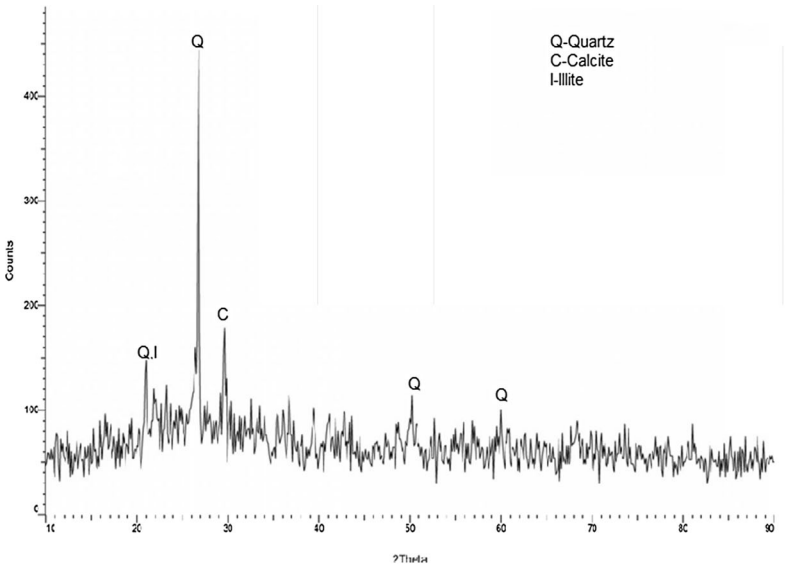


Plate-I

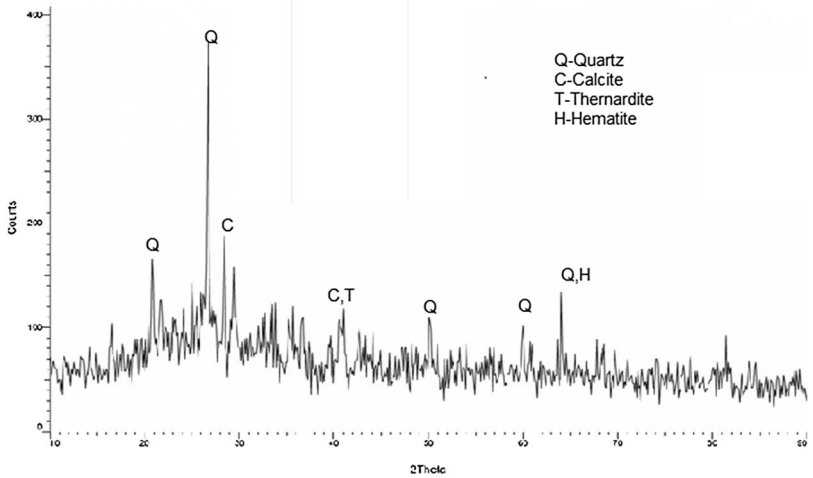


Plate-II

Fig. 5 XRD pattern of S/S products of samples (a, b and c). *Plate I* sample A brick without curing, *Plate II* sample A brick with curing, *Plate III* sample B brick without curing, *Plate IV* sample B brick with curing, *Plate V* sample C brick without curing, *Plate IV* sample C brick with curing

crystalline phases of the bricks (Fig. 5) showed the presence of the following minerals: quartz SiO_2, calcite $CaCO_3$, illite $KAl_2(Si_3Al)O_{10}(OH)_2$, thenardite Na_2SO_4 and hematite Fe_2O_3. The main crystalline phase of these matrices was quartz and calcite. Intensity of quartz peak (21° and 27° (2θ)) was observed to be strong in all brick samples. Calcite peak (29° and 39° (2θ)) was also observed in all samples but the intensity was lower than that of the quartz peak. The presence of calcite is attributed to the carbonation of samples during the curing and brick preparation process (Liu et al. 2011).

The efflorescence (trace to moderate) was observed in the sample B brick due to the presence of highly soluble sulphate thenardite (Na_2SO_4) (Vsevolod et al. 2014). There was no efflorescence observed in the remaining two industrial sludges (samples A and C).

FT-IR spectra of S/S products

The functional group pattern of the samples was studied using FTIR scanning, which was given in Fig. 6. The considerable broad band located at 3700–2200 cm^{-1} and 1700–1600 cm^{-1}

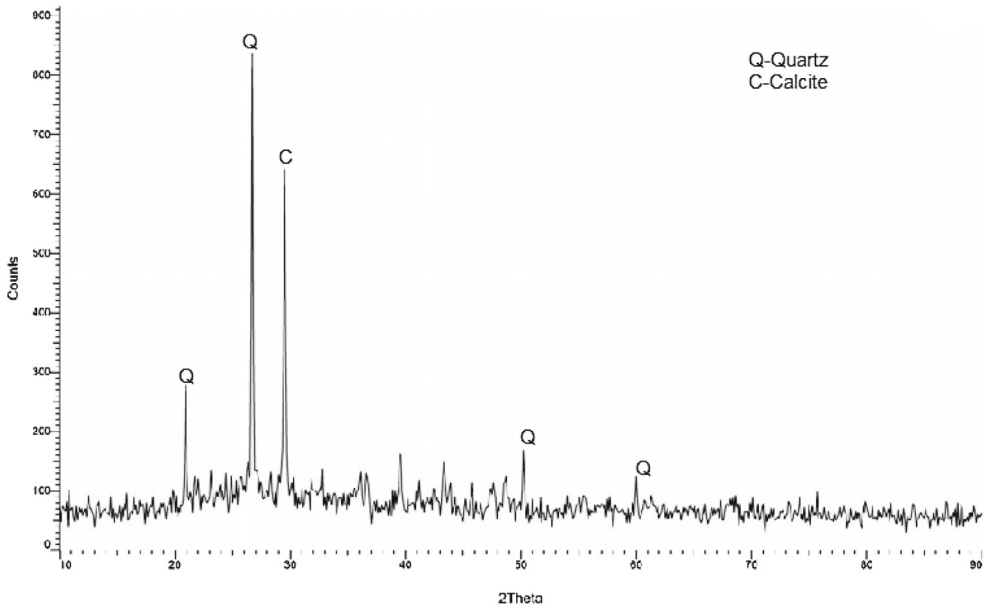


Plate -III

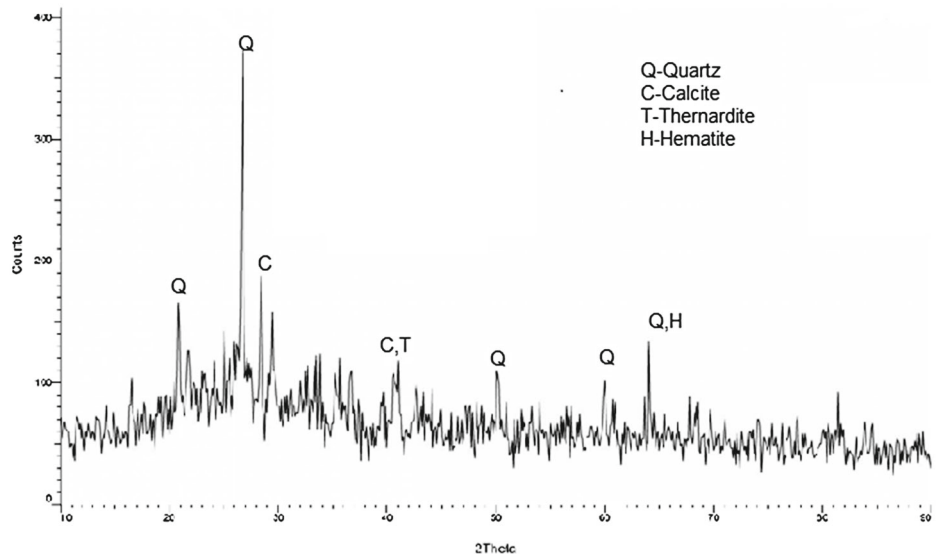


Plate -IV

Fig. 5 continued.

were assigned to O-H stretching and H-O-H bending, respectively, which might be due to the presence of weakly bounded water molecules adsorbed on to the surface or trapped in large cavities of the brick. The spectra peak at 1460 cm^{-1} represents the presence of sodium carbonate (Kornkanok et al. 2012). The peaks at the region 1200–1000 cm^{-1} and 807 and 475 cm^{-1} correspond to asymmetric stretching, symmetric stretching and bending modes of bulk Si-O-Si, respectively (Liu et al. 2012). The peak at 1630 cm^{-1} belongs to aromatic C-H bond (Onal et al. 2007).

Conclusions

1. From this study, it was concluded that the pharmaceutical sludge could be used for the production of construction

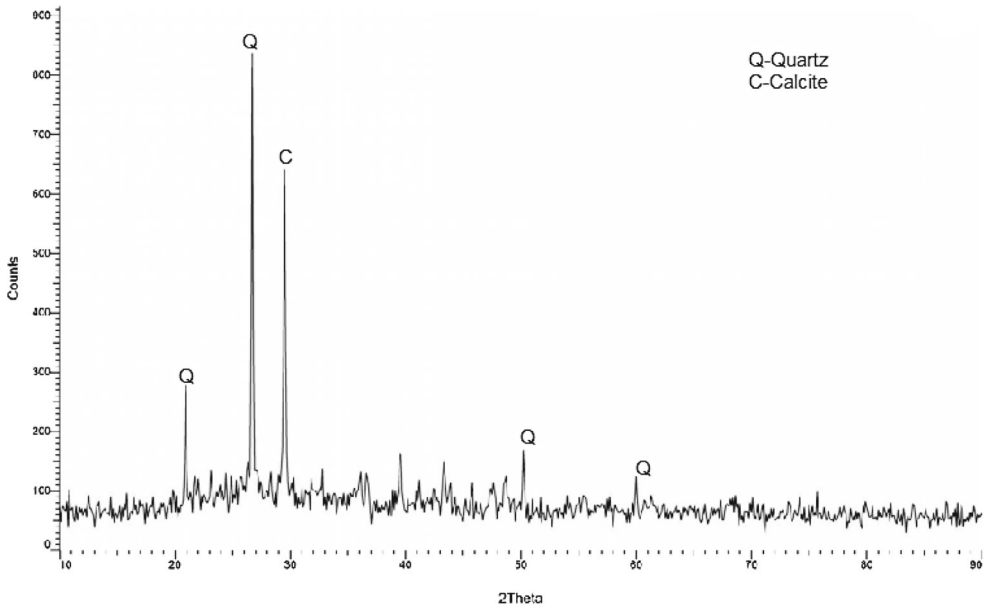


Plate -III

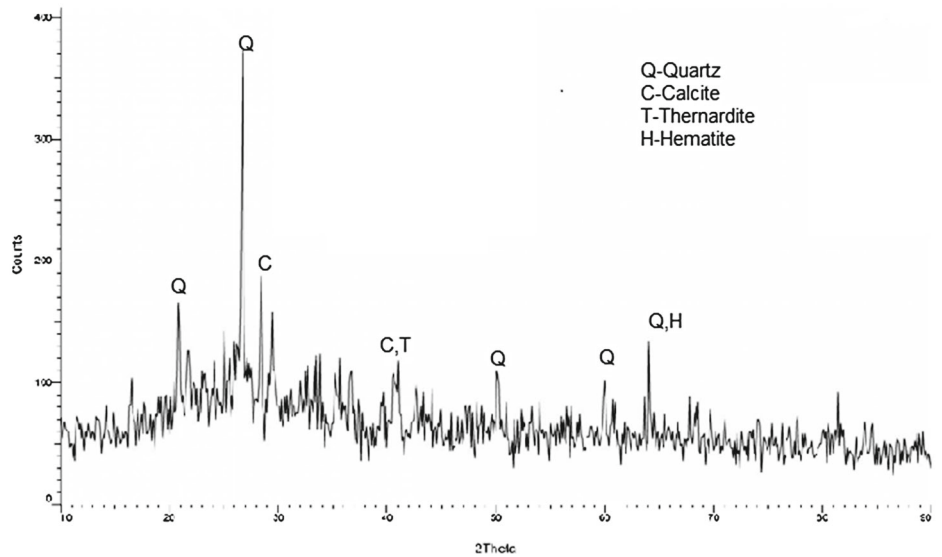


Plate -IV

Fig. 5 continued.

materials. Ten percent of sludge in the brick mixture provides good compressive strength.

2. Studies of XRD, TG-DTA and FTIR were evidence for the formation of new materials.

3. Despite the content of heavy metals in the raw materials, leaching and solubility tests of the new products show advantageous values as compared to the Brazilian standards. Solidification/Stabilization will reduce the release of metals from the solid waste.

4. The use of this method is highly profitable, in view of the fact that the use of common industrial wastes significantly reduces the cost of the end production in comparison to traditional natural materials and essentially reducing the exploitation of natural raw materials.

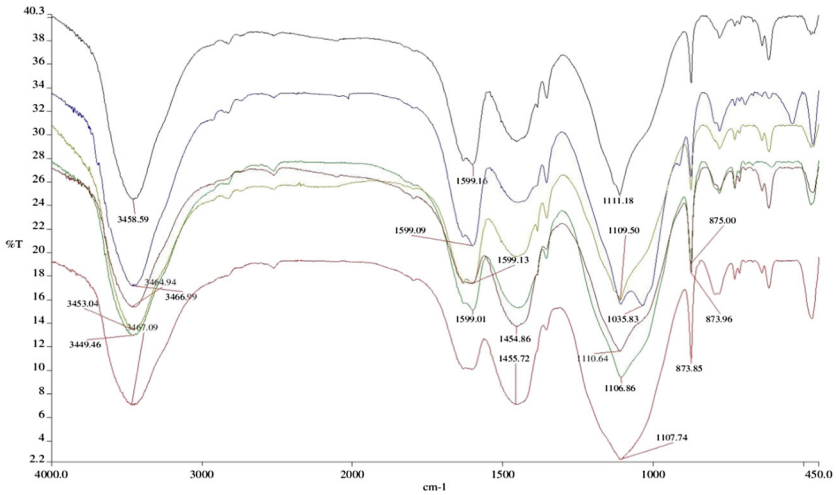


Plate-I

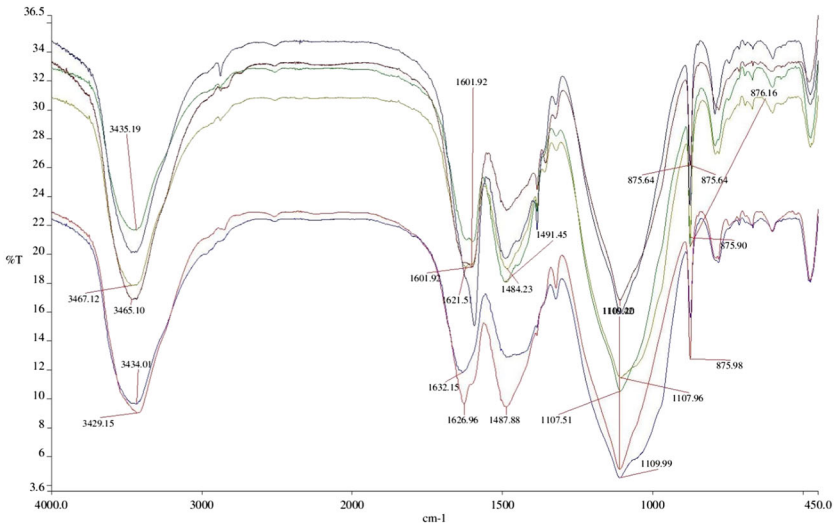


Plate-II

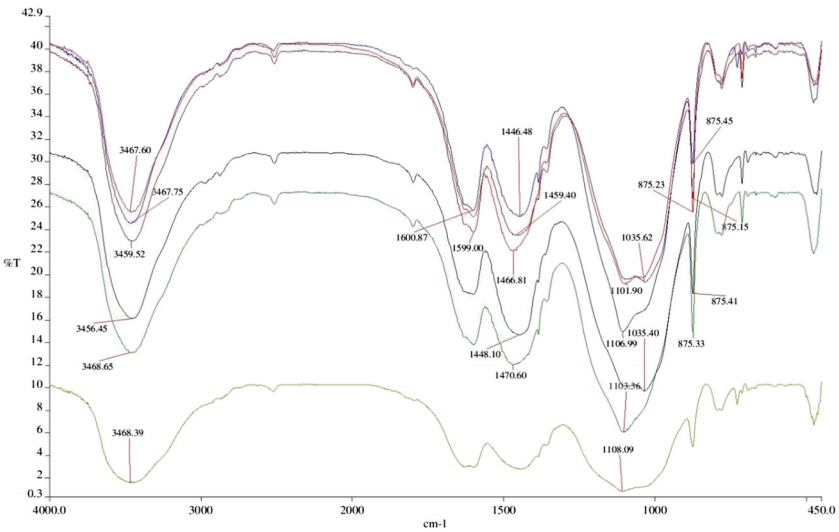


Plate-III

Fig. 6 FTIR analysis of the brick products of samples (a, b and c). *Plate I* sample A, *Plate II* sample-B, *Plate III* sample C

References

Altwair NM, Johati MAM, Saiyid SF (2011) Strength activity index and micro structural characteristics of treated palm oil fuel ash. Int J Civ Environ Eng 11:100–107

Anderson M, Skerratt RG, Thomas JP, Clay SD (1996) Case study involving using fluidised bed incinerator sludge ash as a partial clay substitute in brick manufacture. Water Sci Technol 3–4:195–205

Anderson M, Elliott M, Hickson C (2002) Factory scale trials using combined mixtures of three by-product wastes (including incinerated sewage sludge ash) in clay building bricks. J Chem Technol Biotechnol 77:345–351. doi:10.1002/jctb.593

Aydın AA, Aydın A (2014) Development of an immobilization process for heavy metal containing galvanic solid wastes by use of sodium silicate and sodium tetraborate. J Hazard Mater. doi:10.1016/j.jhazmat.2013.12.017

Bureau of Indian Standards (BIS) (2005) Fourth edition Reprint, UDC 666.762.712.

DellOrso M, Mangialardi T, Evangelista Paolini A, Piga L (2012) Evaluation of the leachability of heavy metals from cement-based materials. J Hazard Mater. doi: 10.1016/j.jhazmat.2012.04.017

Demir I (2006) An investigation on the production of construction brick with processed waste tea. Build Environ 41:1274–1278. doi:10.1016/j.buildenv.2005.05.004

Demir I, Orhan M (2003) Reuse of waste bricks in the production line. Build Environ 38:1451–1455. doi:10.1016/S0360-1323(03)00140-9

Demir I, Baspınar MS, Orhan M (2005) Utilization of kraft pulp production residues in clay brick production. Build Environ 40:1533–1537. doi:10.1016/j.buildenv.2004.11.021

Dominguez EA, Ullmann R (1996) Ecological bricks made with clays and steel dust pollutants. Appl Clay Sci 11(2):237–249. doi:10.1016/S0169-1317(96)00020-8

Dondi M, Guarini G, Raimondo M (2002) Orimulsion fly ash in clay bricks—part 2: technological behaviour of clay/ash mixtures [J]. J Eur Ceram Soc 22:1737–1747. doi:10.1016/S0955-2219(01)00494-0

Environmental Protection Agency (1994) Records of decision analysis of superfund sites employing solidification/stabilization as component of the selected remedy. USEPA, Washington, DC

Hamer K, Karius V (2002) Brick production with dredged harbour sediments. An industrial-scale experiment. Waste Manag. DOI: 10.1016/S0956-053X(01)00048-4

Hamer K, Waschkowitz C, Isenbeck-Schroter M, Schulz HD (1999) Harbour sediments for brick production. Ressourcen-Umwelt-Management, Schriftenreihe der Gesellschaft fur Umwelt Geowissenschaften (GUG), Koln, pp 223–240

Hsu YS, Lee BJ, Liu H (2003) Mixing reservoir sediment with fly ash to make bricks and other products. In: International ash utilisation symposium. Center for Applied Energy Research, University of Kentucky, Paper#89.

Huang C, Pan JR, Liu Y (2005) Mixing water treatment residual with excavation waste soil in brick and artificial aggregate making. J Environ Eng 131(2):272–278. doi:10.1061/(ASCE)0733-9372

Jianfeng WU, Fangwen LI, Xiaohong XU, Xianli SU (2008) Preparation of eco-environmental protection bricks from lake sludge. Preparation of Eco-environmental Protection 23:912–16. doi:10.1007/s11595-007-6912-2

Kadir AA, Mohajerani A, Roddick F, Buckeridge J (2010) Density, strength, thermal conductivity and leachate characteristics of lightweight fired clay bricks incorporating cigarette butts. Int J Civ Environ Eng 2:179–184

Karius V, Hamer K (2001) PH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks. Sci Total Environ. doi:10.1016/S0048-9697(00)00889

Kornkanok Boonserm, Vanchai Sata, Kedsarin Pimraksa, Prinya Chindaprasirt (2012) Improved geopolymerization of bottom ash by incorporating fly ash and using waste gypsum as additive. Cement Concrete Comp. doi: 10.1016/j.cemconcomp.2012.04.001.

Liew AG, Idris A, Samad AA, Wong CHK, Jaafar MS, Baki AM (2004) Reusability of sewage sludge in clay bricks. J Mater Cycles Waste Manage 6:41–47. doi:10.1007/s10163-003-0105-7

Lin DF, Wenig CH (2001) Use of sewage sludge ash as brick material. J Environ Eng 127(10):922–927

Lingling X, Wei G, Tao W, Nanru Y (2005) Study on fired clay bricks with replacing clay by fly ash in high volume ratio. Construct Build Mater 19:243–247. doi:10.1016/j.conbuildmat.2004.05.017

Liu Z, Chen Q, Xie X, Xue G, Du F, Ning Q, Huang L (2011) Utilization of the sludge derived from dyestuff-making wastewater coagulation for unfired bricks. Constr Build Mater. doi: 10.1016/j.conbuildmat.2010.10.012.

Liu Y, Guo Y, Gao W, Wang Z, Ma Y, Wang Z (2012) Simultaneous preparation of silica and activated carbon from rice husk ash. J Clean Prod. doi:10.1016/j.jclepro.2012.03.021

Menezes R, Ferreira HS, Neves GA, de Lira LH, Ferreira HC (2005) Use of granite sawing wastes in the production of ceramic bricks and tiles. J Eur Ceram Soc 25:1149–1158. doi:10.1016/j.jeurceramsoc.2004.04.020

Milica Arsenovic, Zagorka Radojevic, Slavka Stankovic (2012) Removal of toxic metals from industrial sludge by fixing in brick structure. Constr Build Mater. doi: 10.1016/j.conbuildmat.2012.07.002.

Montanes MT, Sanchez T, Roux MS (2014) The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium. J Environ Manag. doi:10.1016/j.jenvman.2014.04.026

Nithyanandam R, Saravanane R (2013) Treatment of pharmaceutical sludge by Fenton oxidation process. Int J Chem Eng Appl. doi:10.7763/IJCEA.2013.V4.325

Onal Y, AkmilBasar C, Sarıcı ozdemir C, Erdogan S (2007) Textural development of sugar beet bagasse activated with ZnCl2. J Hazard Mater. doi: 10.1016/j.jhazmat.2006.07.07

Singh IB, Chaturvedi K, Morchhale RK, Yegneswaran AH (2007) Thermal treatment of toxic metals of industrial hazardous wastes with fly ash and clay. J Hazard Mater. doi:10.1016/j.jhazmat.2006.06.112

Turgut P, Murat Algin H (2007) Limestone dust and wood sawdust as brick material. Build Environ 42:3399–3403. doi:10.1016/j.buildenv.2006.08.012

USEPA (1996) Hazardous waste characteristics scoping study. US Environmental Protection Agency, Office of Solid Waste, United States

Vsevolod Mymrin, Ricardo A C Ribeiro, Kirill Alekseev, Elena Zelinskaya, Natalia Tolmacheva, RodrigoCatai (2014). Environment friendly ceramics from hazardous industrial wastes. Ceram Int. doi: 10.1016/j.ceramint.2014.02.014.

Weng CH, Lin DF, Chiang PC (2003) Utilization of sludge as brick materials. Adv Environ Res 7:679–685. doi:10.1016/S1093-0191(02)00037-0

Wiebusch B, Ozaki M, Watanabe H, Seyfried CF (1998) Assessment of leaching tests on construction material made of incinerator ash (sewage sludge). Investigations in Japan and Germany. Water Sci Technol 38:195–205