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Removal of toxic metals from industrial sludge by fixing in brick structure

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HIGHLIGHTS

- ▶ Sludges generated in hot galvanizing are used as supplement in heavy clay bricks.
- ▶ Sludges contain toxic metals fixed within mineral structure during bricks firing.
- ▶ Strength drops with sludge share while porosity and water absorption increase.
- ▶ Amounts of most analyzed microelements are not detectable during leaching in water.

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ABSTRACT

The aim of this study was to test utilization possibilities of industrial sludge in masonry industry, as well as risk of toxic elements leaching potential. Sludge is generated in a hot-dip galvanizing process after waste water neutralization. This waste is considered to be hazardous due to the presence of toxic elements, which can be fixed within heavy clay matrix after thermal treatment. Relatively large amounts of toxic metals were found in used raw materials, but their leachability reduces to a negligible level after firing at 1020 °C. The results show that sludge can be used to produce eco-friendly bricks.

1. Introduction

Since building materials are produced using existing natural resources, there is a great influence in damaging of the environment due to their continuous exploitation. Also, the cost of construction materials is increasing incrementally, thus it is essential to find functional substitutes for conventional building materials. In view of the importance of energy saving and conservation of resources, efficient recycling of industrial waste is now a global concern [1]. Traditional building materials on the basis of heavy clay allow combining with different wastes without significant modification of the production process and final product usage. The properties of bricks such as compressive strength, durability and leaching characteristics must harmonize with the growing demands of quality [2–7].

Hot-dip galvanizing industry is one of the industries which produces numerous pollutants and causes serious environment contamination [4,5,8]. The removal of oxides from metal surfaces by cleaning with acid solution is one of the key steps in the metal finishing industries, a process called "pickling" [6,7,9]. Pickling solutions are considered spent when the acid concentration in them decreases by 75–85%, which is accompanied by metal content increase. The composition of spent baths from steel pickling in hot-dip galvanizing plants differ greatly depending on usage period, but they mainly contain zinc (II) (up to 120 g/l), iron (mainly iron (II), up to 204 g/l), traces of lead, chromium and other heavy metals (max. 500 mg/l), and also hydrochloric acid (10–80 g/l) [6,9,10]. Mixed solution of metal wastes can be much more toxic than simple solution of corresponding metal of higher concentration. Other pollutants such as cyanide and certain organic compounds are also present in metal finishing wastewaters which are highly toxic, even at low concentrations in water. If this waste is untreated, due to the presence of suspended solids, biodegradable organics and trace metals, these solutions are rendered as highly hazardous [7]. Steelwork plants in European Union produce about 300,000 m^3/year of pickling solutions and 150,000 t per year is stored [6]. Regeneration of spent pickling solutions is a crucial issue regarding both environmental protection and economy of the process [6,9]. Many methods have been developed to recover zinc from wasted pickling solutions as reported in [4,5,9,10], or HCl [6,7]. Valuable compounds recovery process is very difficult due to physicochem-

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ical complexity of the waste solution, where the target species are present in a heterogeneous mixture with different amounts of non-desirable compounds (oils, residual acid, impurities, etc.) [5]. Pickling solutions are neutralized using bases, generating solid waste–sludge, containing metals in the form of hydroxides [11].

Intensive investigations have been done towards encapsulation of sludge toxic metals using wide variety of materials, involving cement, polymers [12,13], and ceramic-based materials [1–3,12–18]. It is considered to be an effective low expense technique for toxic species fixation in usable products, or simple way to reduce the residue volume for further disposal. Not much has been reported on the emission of toxic elements during production of bricks and their leaching behavior from the heat-treated bricks, in combination with ceramic-technological characteristics of final products [1,2,15].

Thermal treatment is now-a-days being employed for stabilization of heavy metals. The stabilized mass obtained by this process could be utilized as building material or disposed off through land fillings without toxic metals leaching susceptibility. The use of relatively high temperatures promotes compounds decomposition of easily leachable species, such as hydroxides, and the formation of more stable oxides. Depending on the firing temperature and the nature of components, reactions between those compounds and Si/Al-based ceramic oxides might occur, leading the formation of flogopites, vilemites, forsterites and glassy phases. Experimental limitations of this method are generally imposed by the chemical complexity of the galvanic sludge, involving the presence of volatile species such as chlorides, or remaining soluble species like sulphates. High levels of calcium, arising from the use of lime in the acid neutralization, might also promote the chromium oxidation, increasing the hazardous character. The formation of $CaO{\cdot}CrO_3$ is then predicted [13].

The aim of this work was to test utilization possibilities of sludge in the masonry industry, as well as the risk level of toxic metals leaching (Pb, As, Cr, Zn, Ni, Cu and Ba) after bricks production and in the case of application or disposal. The technical quality of solid laboratory bricks was also evaluated. The samples were made of usual clayey raw material from Serbian brickyard with addition of two hot-dip galvanizing industry sludges. After firing at different temperatures, physical and mechanical properties were compared, as well as porosity development and toxic metals content. Two hot-dip galvanizing factories from Serbia considered in this research produce about 600,000 kg of sludge annually [11]. The usage of this sludge as secondary raw material in brick industry could bring economical and environmental benefits, avoiding the costly process of waste purification and reducing negative impact to the environment.

2. Materials and methods

2.1. Samples

Research was conducted on laboratory samples made of masonry clay from brickyard on the south of Serbia. Sample I was a representative, with no additives, whose characteristics were varied by adding Sludge I and Sludge II sampled from two hot dip galvanizing Serbian plants. Representative Sample I is enriched with Sludge I and Sludge II in the quantity of 3 and 6 wt.%, giving: Sample II with 3 wt.% of Sludge I, Sample III with 6 wt.% of Sludge I, Sample IV with 3 wt.% of Sludge II and Sample V with 6 wt.% of Sludge II. The choice for the share of sludge addition was based upon our preliminary studies and experience, since it was expected that mechanical strength of products would more significantly drop with the higher percentage sludge addition.

Laboratory samples were produced in the form of tiles ($120 \times 50 \times 14$ mm), hollow blocks with vertical voids ($55.3 \times 36 \times 36$ mm, cavities around 50%) and cubes ($30 \times 30 \times 30$ mm). Hollow blocks were ratable to industrial products dimensions. Samples were formed using laboratory extruder (*Händle*) in the usual laboratory procedure [19], dried to constant weight at 105 ± 5 °C, and later fired at 870 °C, 920 °C, 970 °C and 1020 °C (Fig. 1). Average heating speed to achieve temperature of 610 °C was 1.4 °C/min, and later 2.5 °C/min until the final given temperature was reached, at which the samples were treated for 2 h. One more positive effect of the investigated samples was dead load of the structure decrease, since weight loss during thermal treatment was lower in about 0.7–1.2 wt.%, depending on the firing temperature and the sludge share.

2.2. Analyses

2.2.1. Raw materials characterization

Major and trace elements content were determined using EDXRF (XRF spectrophotometer ED 2000 – Oxford). The source of excitation is X-ray tube with a silver target anode. Energy-dispersive Si (Li) detector is cooled with liquid nitrogen, and processor is SMART digital pulse.

Representative soil (Sample I) used in the investigation went through DTA/TG analysis using SDT Q600 (TA Instruments) device in a dynamic nitrogen atmosphere. The temperature was risen from a room temperature to 1000 °C, with a rate of 20 °C/min.

XRD analysis was performed on Sample I with Philips PW-1050 diffractometer (λCu-K_α radiation and scanning speed of 0.05 °C/s).

2.2.2. Ceramic and technological tests

The laboratory hollow blocks compressive strength is tested in a laboratory hydraulic press, according to standard SRPS EN 772–1 [20]. Water absorption was evaluated by soaking samples in water for 24 h, according to standard SRPS EN 771–1 [21].

Porous structure of the laboratory samples was tested by mercury porosimetry method. Experimental measurements were made on the device Porosimeter 2000 (Fisons Instruments). The program software Milestone 200 was used for the data calculation (Fisons Instruments).

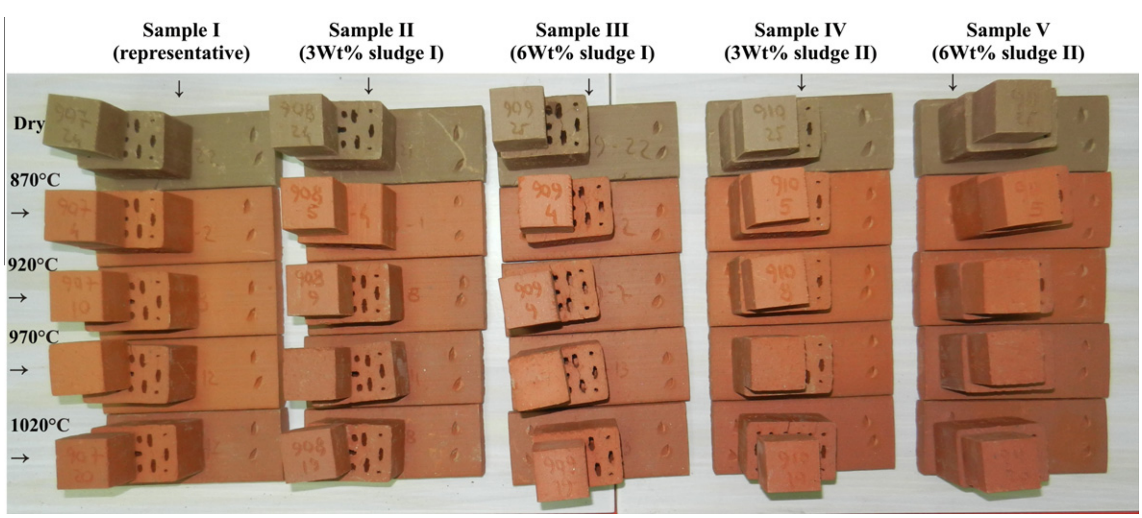

Fig. 1. Appearence of laboratory samples: tiles, blocks and cubes.