EXTRUDED AND SINTERED CLAY CERAMICS CONTAINING STEEL-MAKING DUST

VAYOS KARAYANNIS

Department of Environmental Engineering, Technological Education Institute of Western Macedonia, Kila, 50100, Kozani, Greece, e-mail: vkarayan@teiwm.gr

In the present work, the feasibility of recycling a steel-making by-product into extruded clay-based ceramics is examined, with the emphasis put on their mechanical performance. Actually, the utilization of massive amounts of solid residues recovered in steel production plants worldwide, such as steel-making dust (electric arc furnace dust, solid waste from gas treatment), is of increasing importance. This fine powdery residue, however, contains several oxides (mainly iron and zinc oxide phases), and therefore it could be considered as secondary material for substituting traditional clayey materials in ceramics manufacturing. For the fabrication of extruded specimens, a laboratory pilot-plant simulation of the industrial processes was employed. Clays appropriate for standard brick manufacturing were selected as the base materials and characterized. Then, various clay/steel dust mixtures were prepared and mixed with water to form a plastic mass for extrusion of specimens. The extrusion procedure and drying behavior of specimens were optimized in order to obtain integral specimens possessing sufficient green density and strength for the subsequent sintering at 850, 950 and 1050°C, in a controlled furnace. The effect of the % by-product content, and also of the firing temperature, on shrinkage, bulk density, water absorption capability and mechanical strength of the fired specimens was investigated. According to the results, the addition of steel-making dust up to 15 wt. % in clay-based bricks is tolerable without significant variations in the mechanical performance, while the open porosity slightly increases, which could be of importance in terms of heat insulating behavior.

Keywords: Ceramics, extrusion, sintering, steel-making dust.

INTRODUCTION

The management and valorization of massive quantities of solid residues recovered in steel-making plants worldwide, such as electric arc furnace dust, electric arc furnace slag and ladle furnace slag, represents a significant issue.

In steel industry, the production of 1 ton of steel results to generation of 2-4 tons of various types of waste by-products (Das *et al.*, 2007), while 1 ton of stainless steel waste is produced per 3 tons of stainless steel making (Huaiwei and Xin, 2011). Therefore, taking into account the huge quantities of steel wastes, their utilization is environmentally and financially beneficial, the proper disposal and handling remaining both dangerous and expensive task. Blast furnace slag and steel slag are competitive raw materials in the mineral industry, and blast furnace slag utilization in the cement industry currently increases resulting in the reduction of the production cost. Furthermore, electric arc furnace slag is widely used in the road and pavement construction and is also recently studied for the development of vitreous ceramic tiles (Das *et al.*, 2007; Khan *et al.*, 2002; Sarkar *et al.*, 2010).

Particularly, the recycling of steel dust (electric arc furnace dust - EAFD) is very important, because it is one of the major steel by-products, included in the European Waste Catalogue (Commission decision 2000) with code no. 10 02 07* (solid wastes from gas treatment containing dangerous substances), and produced worldwide in large quantities (Krztoń 2010; Martins *et al.*, 2008; Tang *et al.*, 2008; Sofilić *et al.*, 2004). EAFD is generated from the volatilization of heavy metals when steel scrap is melted in the electric arc furnace. Volatilized metals are oxidized and subsequently solidified and detained in the form of fine powder in specially designed filters, which are placed in the EAF gas stream cleaning system (Salihoglu and Pinarli, 2008, Guézennec *et al.*, 2005, Kashiwaya *et al.*, 2004, Gritzan and Neuschütz, 2001). The use of EAF technology in the steelmaking industry has been increasing considerably over the last decades resulting in the production of significant quantities of solid residues. The world generated steel dust per year has been estimated to be around 3.7 million tons (Néstor and Borja, 2003).

Since EAF dust mainly contains zinc and other metals, it is recycled in USA for recovering zinc and lead from the industrial waste stream, utilizing the Waelz Kiln technology. Main product is Waelz oxide, which is transformed into zinc oxide, zinc sulfate or zinc metal by zinc smelters. Waelz iron product, an iron concentrate, is also produced (Steel Dust Recycling 2014). Moreover, this by-product is examined as an additive in asphalt cement mixtures for road construction (Alsheyab and Khedaywi, 2013). Nevertheless, EAFD contains several valuable oxides, and thereby it could be considered as secondary raw material for substituting traditional clayey materials in bricks manufacturing. On the other hand, huge quantities of clays are annually needed for the production of considerable amounts of fired ceramic bricks worldwide, and therefore, much research focuses on the utilization of alternative raw materials from various origins in clay mixtures at different combinations and proportions for the fabrication of conventional sintered bricks (Karayannis *et al.*, 2013). The recycling of steel-industry byproducts as raw materials in bricks production would contribute to the conservation of natural resources, from the environmental point of view. Moreover, the low cost of these solid wastes and even possible energy savings during clay/waste mixtures firing in bricks manufacturing should also be considered, particularly taking into account recent targets of the EU's energy policy (Vogl, 2013; Antoniadis *et al.*, 2014). So far, limited studies are reported on the utilization of steel-making dust in the fabrication of construction materials including ceramics, vitreous and glass-ceramic products (Lis and Nowacki, 2012; Machado *et al.*, 2011).

In the present work, the feasibility of recycling steel-industry waste byproducts into extruded clay-based bricks is studied, this being an undertaking of technological, environmental and economic interest. Specifically, EAFD was incorporated in clayey raw material mixture, and the effect of the % dust content as well as of the firing temperature on the physico-mechanical properties of the extruded and sintered brick specimens is examined.

EXPERIMENTAL

Raw Materials

Three clay samples from different deposits in Greece, considered representative of the main types of clayey raw materials utilized by the ceramic industry (A, B and C), were selected and characterized (XRF-analysis). The CaO content of the clay samples used ranges from 3.51 to 11.82 wt.%, but they contain no sulphur. The main mineralogical phases identified were albite, enstantite and illite.

Main constituents of the EAFD (red/brownish fine powder), which was used as a secondary raw material in the current research, are iron and zinc, this being in accordance with several other studies on the characterization of steel-industry dust. Certainly, each particular dust is site-specific. However, the zinc in the dust typically exists as zinc oxide (ZnO) and as a mixed zinc-manganese ferrite spinel or ZMFO ($(Zn_xMn_yFe_{1-x-y})Fe_2O_4$) (Pickles, 2010).

Specimen Preparation and Testing

80x43.5x18 mm specimens of were prepared employing a pilot-plant simulation of the industrial brick manufacturing processes (Spiliotis *et al.*, 2013): the clay samples were pulverized and mixed in proportions appropriate for standard brick fabrication.

Various clay/EAFD mixtures with 0-15 wt.% dust content were prepared and mixed with water to form a plastic mass for extrusion. The plasticity of the mass was evaluated using a thermo-balance. After gradually drying, a) in air for 24 h and b) subsequently in an oven at 105^oC for 48 h, the specimens were fired in a chamber furnace for sintering and consolidation. The first heating step of 500^oC, was reached after controlled heating at 1.7^oC/min for 5 h, followed by further heating at 4.5^oC/min up to a peak temperature. The specimens remained at the max. temperature only for 15 min to attain energy savings, and then they were cooled to room temperature in the furnace.

After optimizing the % EAFD content in the mixture by firing at 1050^oC, similar heating procedure was followed by lowering the maximum firing temperature to 950^oC and also down to 850^oC, to assess the possibility for attaining energy savings.

Shrinkage, bulk density, open porosity, water absorption (%), mechanical strength and thermal conductivity were determined on sintered specimens and studied in relation to the admixture percentage as well as to the firing temperature. In order to determine the water absorptivity, the sintered specimens were weighed before and after immersion in water for 2h. Mechanical behavior was assessed by 3-point bend testing. Tests were performed on 20 specimens of each composition and firing temperature, and the average values were reported in the results. Then the modulus of rupture (MOR) was calculated.

RESULTS AND DISCUSSION

Brick Specimen Preparation

Plasticity differences were observed when steel dust was added in various amounts in the clays, but they did not caused significant problems in the specimen preparation, which had the strength required to ensure safe handling in the subsequent fabrication steps. Hence, no additive was demanded to facilitate plastic extrusion of mixtures containing EAFD. Therefore the extrusion behavior of the green (unfired) specimens can be considered satisfactory. Drying behavior of the green specimens was quite satisfactory, and only limited shrinkage was observed during this first step of thermal treatment (drying in air). In all cases, the shrinkage appeared relatively restricted and remained within tolerable limits for standard brick manufacture. Upon firing up to 1050^oC, specimen coloring turns gradually from lighter to dark brown when the EAFD percentage in the raw material mixture is increased, due to its noticeable % iron content.

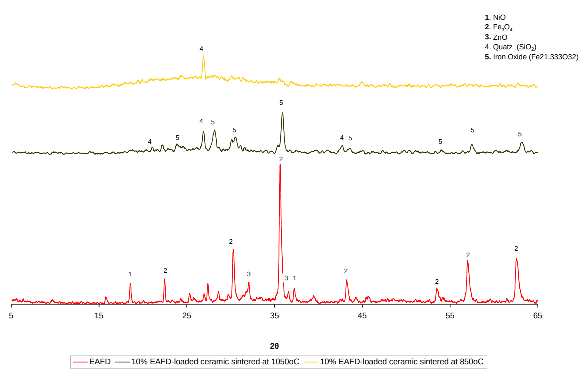

Figure 1. Typical XRD spectra of EAFD and 10 wt.% EAFD-loaded clay ceramics sintered at 850^oC or 1050^oC

Open Porosity - Water Absorption (%)

The influence of the % EAFD addition into the clays for specimens fired at 1050°C, as well as of the firing temperature for 10 wt.% EAFD-loaded specimens, on the open porosity and the % water absorption of the sintered ceramic specimens is depicted in Figs. 2a and 2b respectively. Fig. 2a shows that the open porosity does not vary significantly with the % EAFD content. The lower open porosity is determined when 10% EAFD is added into the clay mixture (1050°C). The trend in the results for the % water absorption presented in Fig. 2b is generally similar to that for the open porosity in Fig. 2a. Specifically, the water absorption of the bricks sintered at 1050°C slightly decreases as the EAFD amount in the mixture increases up to 10 %, while further waste addition (15%) leads to a slight water absorption increase. Regarding firing temperature effect on 10% EAFD specimens, it can be seen that the water absorption remains almost constant when the sintering temperature is increased from 850 to 950°C, but it clearly decreases when firing at 1050°C, following the decrease in porosity respectively.

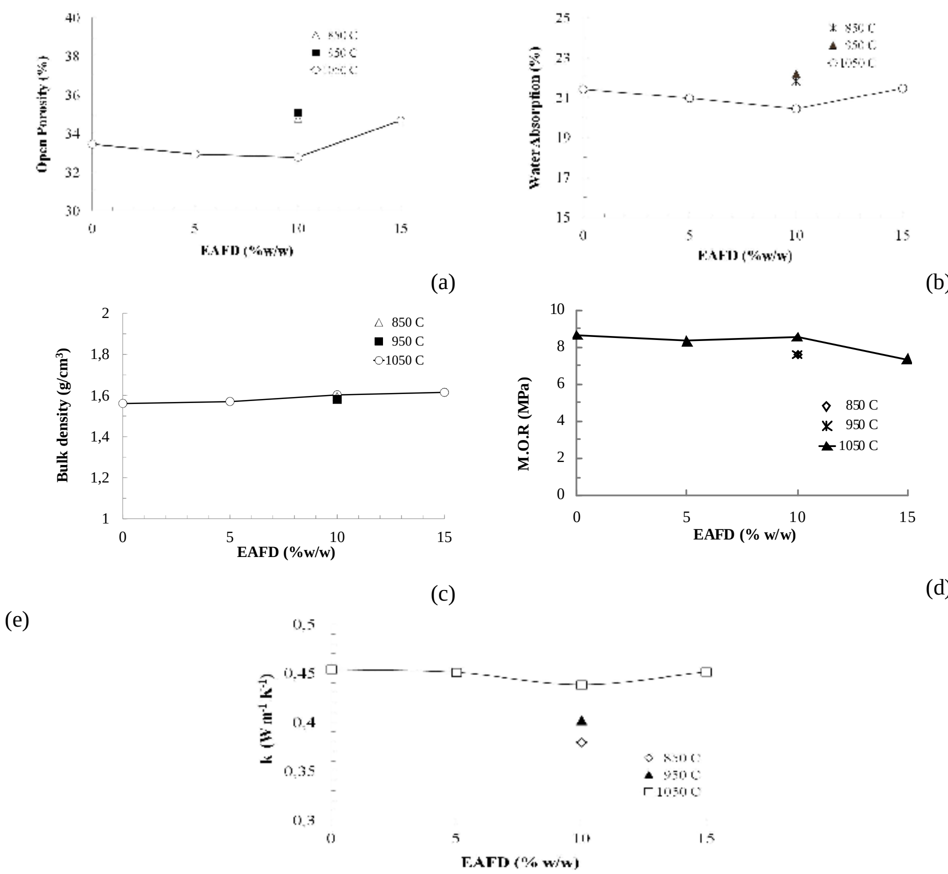

Figure 2. Effect of the % EAFD embodiment and also of the firing temperature on the open porosity (a), water absorptivity (b), bulk density (c), modulus of rupture (MOR) upon bend testing (d), and thermal conductivity (e) of sintered specimens

Bulk Density

The effect of the % EAFD addition into the clay mixture for specimens fired at 1050°C, as well as of the firing temperature for specimens containing 10 % EAFD, on the bulk density after sintering is presented in Fig. 2c. According to the results, bulk density of the sintered specimens is only slightly affected by the % EAFD content and the firing temperature. These findings are in accordance with the experimental results for the weight loss upon sintering, which does not vary substantially and lies approximately in the range of 9.5-10.5%.

Mechanical Strength (Modulus of Rupture)

The effect of the % EAFD addition into the clay mixture for specimens fired at 1050°C, as well as of the firing temperature for specimens containing 10 % EAFD, on the modulus of rupture (MOR) calculated upon three-point bending of the bricks is shown in Fig. 2d. The experimental data indicate that steel dust addition up to 10 wt.% into the clay mixture does not deteriorate the bending strength (expressed in terms of MOR) of the sintered bricks, while further waste addition (15 wt.%) leads to a noticeable decrease of approx. 15% in MOR. With regard to firing temperature effect, no difference in MOR is observed for a temperature increase from 850 to 950°C, but the MOR increases by approx. 12% when firing the specimens at 1050°C, which should be associated with the aforementioned decrease in open porosity at this firing temperature.

Thermal Conductivity

Use of ceramics as thermal insulators represents one of the main applications for this category of materials. The usefulness of a ceramic for these applications is largely fixed by the rate of heat transfer through it under a particular T gradient. The basic equation (1) to define thermal conductivity coefficient is (Kingery *et al.*, 1976):

$$dQ/d\theta = -(kAdT)/dx \quad (1)$$

where: dQ = the amount of heat flowing normal to the area A in time $d\theta$; $-dT/dx$ = the temperature gradient; k = thermal conductivity coeff., the proportionality factor, a material constant.

Fig. 2e shows how k of sintered bricks is affected by a) the % EAFD in the clay mixture (at 1050°C) and b) the firing temperature (for 10% EAFD-loaded specimens). It is apparent that k does not vary considerably with the EAFD addition up to 15% (1050°C) and remains relatively constant (around 0.45 $Wm^{-1}K^{-1}$). On the other hand, k increases when the sintering temperature of 10 wt.% EAFD specimens is increased from 850 to 950°C, and especially up to 1050°C. This variation in ceramic thermal conductivity should mainly be attributed to the corresponding decrease in open porosity.

CONCLUSIONS

- Extruded and sintered clay ceramics incorporating steel-making dust are successfully produced using brick manufacturing pilot-plant simulation procedures.
- EAFD (steel dust) embodiment up to 15 wt.% in clayey mixtures does not prevent an effective extrusion of ceramic bricks without significant variations in both their mechanical performance and thermal conductivity after sintering.
- EAFD does not act as a pore-forming agent in the ceramics so-produced, as only slight increase in the open porosity is obtained, even with 15 % dust addition into the clays. Further % admixture use would endanger the extruded product quality.

- Sintering of 10% EAFD-loaded clays at 850°C or 950°C results in ceramics with similar mechanical and thermal behavior. At 1050°C however, the MOR and thermal conductivity increase as a result of porosity reductions and higher crystallinity.

Acknowledgment

This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – Research Funding Program: ARCHIMEDES III. Investing in knowledge society through the European Social Fund.

REFERENCES

Alsheyab, M.A.T. and Khedaywi, T.S. (2013), "Effect of electric arc furnace dust (EAFD) on properties of asphalt cement mixture", *Resources, Conservation and Recycling*, 70, 38-43.

Antoniadis, I., Alexandridis, A. and Sariannidis, N. (2014), "Mergers and acquisitions in the Greek banking sector: An event study of a proposal", *Procedia Economics and Finance*, Article in Press.

Commission decision of 3 May 2000 (2000), *Official Journal of the European Communities*, L 226/3.

Das, B., Prakash, S., Reddy, P.S.R. and Misra V.N. (2007), "An overview of utilization of slag and sludge from steel industries", *Resources, Conservation and Recycling*, 50(1), 40-57.

Gritzan, A. and Neuschütz, D, (2001), "Rates and mechanisms of dust generation in oxygen steelmaking", *Steel Research*, 72(9), 324-330.

Guézennec, A.G., Huber, J.C., Patisson F., Sessiecq, P., Birat, J.P. and Ablitzer, D, (2005), "Dust formation in Electric Arc Furnace: Birth of the particles", *Powder Technology*, 157(1-3), 2-11.

Huaiwei, Z. and Xin, H. (2011), "An overview for the utilization of wastes from stainless steel industries – Review", *Resources, Conservation and Recycling*, 55(8), 745-754.

Karayannis, V.G., Moutsatsou, A.K. and Katsika, E.L. (2013), "Synthesis of microwave-sintered ceramics from lignite fly and bottom ashes", *Journal of Ceramic Processing Research*, 14(1), 45-50.

Kashiwaya, Y., Tsubone, A., Ishii, K. and Sasamoto, H. (2004), "Thermodynamic analysis on the dust generation from EAF for the recycling of dust", *ISIJ International*, 44, 1774-1779.

Khan, Z.A., Malkawi, R.H., Al-Ofi K.A. and Khan, N. (2002), "Review of steel slag utilization in Saudi Arabia. In: *Proceedings of the 6th Saudi Engineering Conference, KFUPM, Dhahran*, 3, 369-381.

Kingery, W.D., Bowen, H.K. and Uhlmann, D.R. (1976), *Introduction to Ceramics*, 2nd ed., Wiley.

Krztoń, H. (2010), "Quantitative phase composition of steelmaking dust from polish steel industry", *Diffusion and Defect Data Pt.B: Solid State Phenomena*, 163, 31-37.

Lis, T. and Nowacki, K. (2012), "Options of utilising steelmaking dust in a non-metallurgical industry", *Metalurgija*, 51(2), 257-260.

Machado, A.T., Valenzuela-Diaz, F.R., De Souza, C.A.C. and De Andrade Lima L.R.P. (2011), "Structural ceramics made with clay and steel dust pollutants", *Applied Clay Science*, 51, 503-506.

Martins, F.M., dos Reis Neto, J.M., da Cunha C.J. (2008), "Mineral phases of weathered and recent electric arc furnace dust", *Journal of Hazardous Materials*, 154(1-3), 417-425.

Néstor, G.G. and Borja, G.E. (2003), "The situation of EAF dust in Europe and the upgrading of the Waelz process", *Waste Treatment and Clean Technology*; 99(2), 1511-1520.

Pickles, C.A. (2010), "Thermodynamic modelling of the formation of zinc-manganese ferrite spinel in electric arc furnace dust", *Journal of Hazardous Materials*, 179, 309-317.

Salihoglu, G. and Pinarli, V. (2008), "Effect of surface area during stabilization of electric arc furnace dusts from steel foundries", *Environmental Progress*, 27(3), 339-345.

Sarkar, R., Singh, N. and Das, S.K. (2010), Utilization of steel melting electric arc furnace slag for development of vitreous ceramic tiles", *Bulletin of Materials Science*, 33(3), 293-298.

Sofilić, T., Rastovcan-Mioc, A., Cerjan-Stefanović, S., Novosel-Radović, V., and Jenko M. (2004), "Characterization of steel mill electric-arc furnace dust", *Journal of Hazardous Materials*, B109, 59-70.

Spiliotis, X., Papapolymerou, G., Ntampegliotis, K. and Karayannis, V. (2013), "Sewage Sludge & Pet Coke into clays: Effect on process & materials properties", in: *Proceedings of the 23rd International Mining Congress and Exhibition of Turkey, IMCET 2013*, 1, 373-380.

Steel Dust Recycling LLC. (2014), http://www.steeldust.com.

Tang, M.T., Peng, J., Peng, B., Yu, D. and Tang, C.B. (2008), "Thermal solidification of stainless steelmaking dust", *Trans Nonferrous Met Soc China*, 18, 202-206.

Vogl, F.X. (2013), "Ceramic roadmap 2050 - Whitewares' contribution", *CFI Ceramic Forum International*, 90(6-7), E34-E38.