ATLANTIS PRESS
Atlantis Highlights in Material Sciences and Technology (AHMST), volume 1
International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019)

The Manufacturing of Structural Ceramics with the Addition of Non-Ferrous Slags

Gurieva V.A.
Modern construction materials and technologies
Orenburg State University
Orenburg, Russia
victoria-gurieva@rambler.ru

Ilyina A.A.
Modern construction materials and technologies
Orenburg State University
Orenburg, Russia
ilyina.a06@gmail.com

***Abstract* – The article deals with problems of using wastes in metallurgy. In particular, the use of slags formed after the extraction of nickel, copper, cobalt, gold and other metals will be described. The paper provides the results of a study, evaluating the viability of using slags of Yuzhuralnickel plant in Orenburg region in combination with low-melting clay of Alimsay field to produce ceramic bricks. The work provides a brief literature review of using industrial products to produce ceramic construction materials with certain properties in Russia and abroad. It also gives information about the study of the technological properties of feedstock and the development of compositions. In particular, it determines the influence of clay/slag charge composition on compressive strength, contraction, water absorption and density of experimental samples – bricks after baking in the interval of 950–1200 ºC.**

Keywords – construction materials; ceramics; nonferrous metals slags; industrial products; wastes; clay.

I. Introduction

Industrial processes, such as extraction and processing of sulphide (the content of nickel is 1–2%) and iron silicate (the content of nickel is 1–1.5%) ores as well as ferroalloy production result in big amounts of wastes that harm the environment. In some cases, a part of produced slag comes back to be used in steelmaking. However, the big amount of wastes is left non-demanded. That’s why new methods of industrial wastes recycling, including nonferrous metallurgy slags, have got great attention. These methods will allow to minimize the impact of wastes on the environment, clear the territories used for tailings, create new workplaces and etc. The use of industrial wastes in the production of construction materials, such as bricks, concrete, etc, allows to obtain efficient construction materials with necessary strength and simultaneously decrease the amounts of primary natural resources extracted.

The Ural region has a great concentration of mining and smelting facilities. Nonferrous metal plants usually have low (10–15%) yield with respect to the amount of extracted resources, which results in a lot of wastes. The most extracted metals in the Ural region are copper, nickel, vanadium, aluminum, chrome, and zinc.

In Orenburg region, copper and nickel industry prevails. This is due to the exploitation of large stocks of copper and nickel-bearing ores [1].

Yuzhuralnickel plant located in the Orsk city has a waste pile that covers approximately 240 thousand square meters of plant’s territory. Nearly 75% of this area is taken by dregs, representing a combination of carbonate Ca and nickel oxide hydrate (OH)2·nH2O with admixed cobalt, copper, iron, silicon, calcium, aluminum, magnesium and potassium in the form of oxides, sulphates and chlorides.

According to the evaluation carried out by the plant specialists based on the area and thickness of the deposit the stock of nickel and cobalt in the waste pile is 2790 and 218 tonnes respectively.

Nowadays there are almost no ceramic bricks manufacturers in Orenburg region due to the lack of quality stock. Clays, produced in the region are predominantly mixed-layer kaolin – montmorillonite clays with chlorite-illite additions. They mostly have average and moderate plasticity, low melting point. They are also prone to defect formation during forming and don’t need high temperatures for baking (more than 1100˚ C) [2].

Construction materials industry is a unique consumer of metallurgy waste. Both in Russian and abroad specialists place great emphasis on using different industrial wastes as improvement additives during the production of ceramic construction materials.

Let’s review some researches concerned with the use of wastes in construction materials production.

The authors of [3] justify the decrease in water absorption by lining bricks using granulated blast-furnace slag. Light tone ceramic mixture for lining bricks contains Cambrian clay, floured scrapes of autoclaved lightweight concrete and granulated blast-furnace slag with the following ratios of components %: Cambrian clay – 68–72; floured scrapes of autoclaved lightweight concrete – 4–6; granulated blast-furnace slag – 24–26.

The charge containing clay, granulated blast-furnace slag (20–25%) and floured scrapes of autoclaved lightweight concrete (15–20%) was offered to decrease the coefficient of heat transfer in ceramic bricks [4].

Currently, there exist researches by Bozhenov P.I., Prokofieva V.V, Gurieva V.A., etc. [5–8] that describe the use of slags and wastes of the mining industry as initial raw material components for manufacturing ceramic materials for walls. These wastes include tailings of apatite-nepheline and copper-nickel ores, copper-nickel manufacturing slags, tailings of jaspilites, vermiculate ores, serpentinites and etc.

Brazilian researchers from the Federal University of Ouro Preto offered to use the waste of Brazilian mining and smelting industry in the manufacturing of clay and chalk bricks [9].

Turkish researchers from Bartin University [10] studied the influence of ferrochromium slag, zeolite and their different combinations on physical and mechanical properties and microstructure of bricks. The mechanical strength of experimental samples with the addition of ferrochromium slag was higher than 7 MPa, while the heat transfer decreased to 42.3% in comparison with samples without additives. The results of the research showed the possibility of producing zeolite and slag bricks.

II. Methods and materials

The object of this research is the clays of Alimsay field and the slags of Yuzhuralnickel plant (Orenburg region).

During the experiment standard methods for the analysis of compositions and technological properties of raw materials were used. Mineralogical and chemical types of analysis were used to study the contents of clay material and slags. The particle size distribution of clays was determined by screening according to GOST 12536-2014. The preparation of raw materials, the formation of prepared mixtures, drying and baking of samples were carried out according to standard industrial methods.

III. Results

Copper and nickel-smelting slags are of great interest for construction and manufacturing of construction materials.

These wastes are usually used in small amounts as improvement additives to ceramic charge. The use of nonferrous metallurgy wastes is one of the efficient ways to save natural materials while recycling byproducts and protecting the environment.

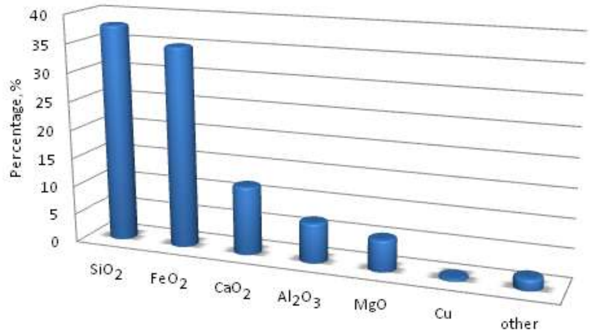
Waste slags have black color (fig. 1.2). They are not prone to degradation. The average density of slags is 3300–3800 kg/m^3, the water absorption is 0.1–0.6% and the compressive strength limit is 120-–300 MPa. Nickel slags have similar high physical and mechanical properties as copper ones. According to the chemical composition, all slags belong to acid raw material. Nickel granulated slags have almost no hydraulic activity despite the glassy phase.

Fig. 1. Samples of Mednogoskiy copper and sulfur plant slag, containing copper.

Fig. 2. Samples of Yuzhuralnickel plant slag, containing nickel.

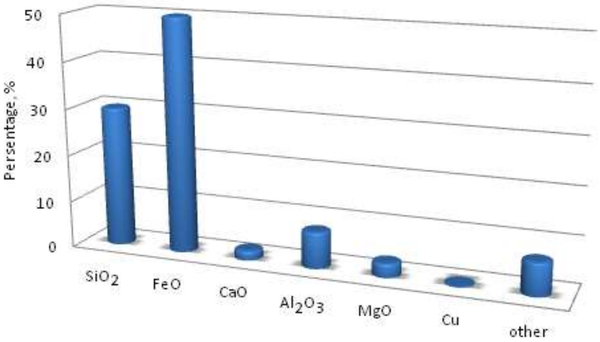
The diagrams show averaged chemical compositions of analyzed slags of copper-smelting plants (fig. 3) and nickel manufacturings (fig. 4).

The objective of the research is mathematical planning and development of models for rationally chosen compositions of charge with a maximum rational percentage of slag replacing clay.



SiO2	FeO2	CaO2	Al2O3	MgO	Cu	other
38	35	12	7	5,5	0,5	2

Fig. 3. Averaged chemical composition of copper-smelting plants.



SiO2	FeO	CaO	Al2O3	MgO	Cu	other
30	50	2	7,8	3	0,2	7

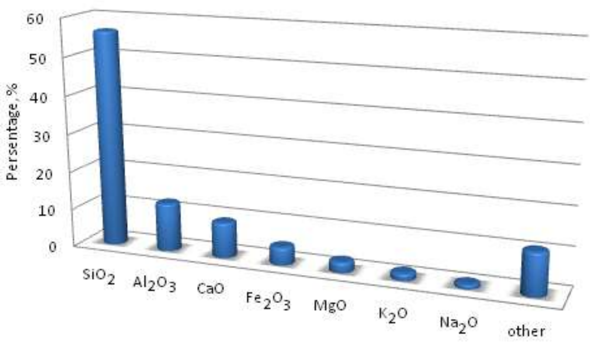
Fig. 4. Averaged chemical composition of nickel manufacturings.

This work analyses anthropogenic deposits of Yuzhuralnickel plant (Orenburg region) – aged nickel-bearing slags that didn't crystallined. This type of slag is not recycled by domestic or foreign enterprises as such wastes are hard to clean by traditional methods because of structural, textural, physical and chemical properties.

Slags have a complex structure with inclusions of nickel that vary from 0.5 to 6 µm. The results of studying the linear coefficient of X-ray absorption allowed to determine that nickel slags have complex multimineral composition, consisting of 5–7 mineral phases as basic components. The typical sizes of mineral aggregates are 20–30 µm in average and don't exceed 300 µm. Nickel slags are predominantly represented by sulphides of nonferrous metals and oxides of silicon and iron sulphide Fe-Cu (the average content of Cu is 54.91%) sulphide Fe-Cu-Zn (the content of Cu is 16.83 %). Slags are non-radioactive, fire and explosion-proof, low toxic products, pertaining to low-hazard substances.

The content of nickel in metal alloys varies from 2.05% to 79.48%. The electron microscopic investigation showed that 42% of copper prills in waste slag are inside the grains of anthropogenic pyrites. Thus the analysis of chemical, mineralogical and grain composition of enrichment products allows supposing their possible use as charge components during drying and liquid synthesis of ceramic material during baking.

The first stage of the experiment was to determine the chemical composition of clay from Alimsay field, represented in fig. 5. According to the level of alumina ($A1_2O_3$), this clay belongs to the group of acid argillous raw material and according to the content of iron oxide ($Fe_2O_3 > 3\%$), it belongs to the group with a high content of coloring oxides. The analyzed clay contains 56.5% of quartz (SiO_2) that decreases plasticity. According to the grain size, the clay belongs to clay-bearing soils.



SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	other
56,5	12,7	9,3	4,7	2,76	1,84	1,1	11,1

Fig. 5. Chemical composition of Alimsay field clay

By analyzing the chemical composition of the clay-bearing soil it is possible to predict its mineral composition. The low content of alumina indicates the low content of kaoline and montmorillonite. Other oxides indicate the presence of carbonate-bearing material in the form of calcite, magnesite, dolomite and the presence of gypsum, anorthite, albite, and argillite.

The samples from the clay of Alemsay field were produced using plastic forming and then used for analyzing baking properties. The diagrams in fig 6–8 show the results.

The obtaining of ceramic products with necessary properties depends on the content of a charge, its preparation, forming and thermal treatment [11–13]. Thus, to determine the dependency of qualitative characteristics of ceramic products from the composition of charge and its treatment when planning and carrying out the experiment. We proposed the following factors as determining the final properties of products;

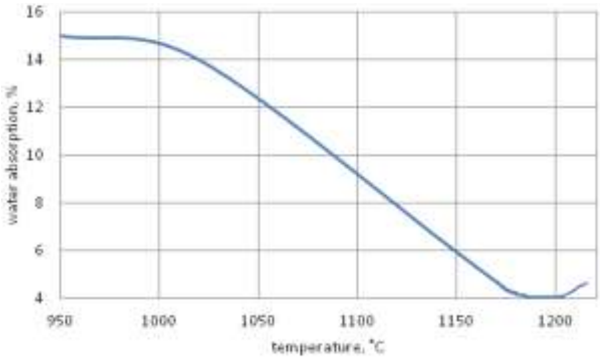


Fig. 6. Dependency between water absorption and the temperature of baking

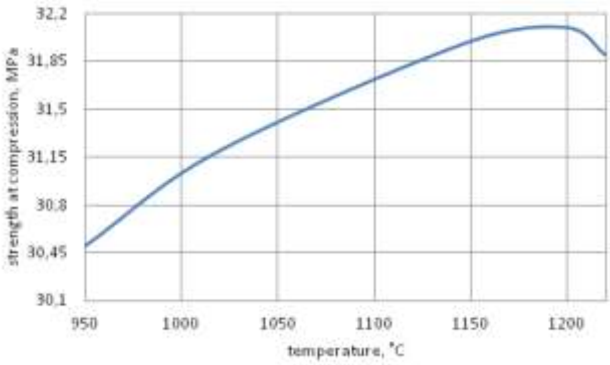


Fig. 7. Dependency between the compression strength limit and the temperature of baking

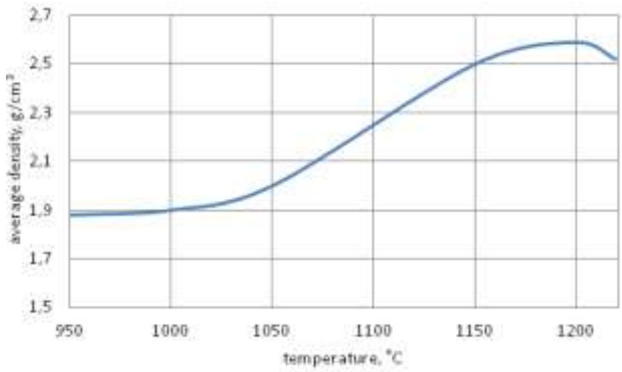


Fig. 8. Dependency between the density and the temperature of baking

The content of each component in ceramic charge (clay/slag, mass. %) and the temperature of baking (°C).

The baking of an airbrick with optimum composition forms its structure that determines a set of technical properties of ceramic products: strength, density, water absorption, contraction. These indicators, which characterize the degree of conversion of ceramic material into a stone-like piece, were used as main criteria of efficiency when optimizing the composition of the charge, containing slags of Yuzhuralnickel plant.

The compositions were developed according to the matrix for planing two-factor experiments. A mathematical model in the form of a second-order polynomial for each characteristic of a product was developed as a result of the experiment and processing of obtained data (see formula 1). The variability intervals are: the first factor is the baking temperature that equals to 900–1200˚C, the second factor is the content of slag in a charge that varies between 10 to 50%.

$$Y=a_0+a_1X_1+a_2X_2+a_3X_1^2+a_4X_2^2+a_5X_1X_2, \quad (1)$$

where a_0; a_1; a_2; a_3; a_4; a_5 are coefficients in the regression equation;

X_1–baking temperature, ºC;

X_2– the content of slag in a sample, mass. %.

The compression strength limit, MPa, water absorption, %, density, t/m^3, thermal contraction, % were used as parameters for optimization. The choice of the parameters is based on their close association with the structure of a ceramic product that influences heavily on working properties and durability of ceramic samples.

Ceramic samples were produced from nickel slags of Yuzhuralnickel plant and the clay from Alimsay field. High clay plasticity (P=24.4) justified the choice of a rational forming method, which was plastic forming in this case. The results of the experiment are shown on graphs (see fig. 9–12).

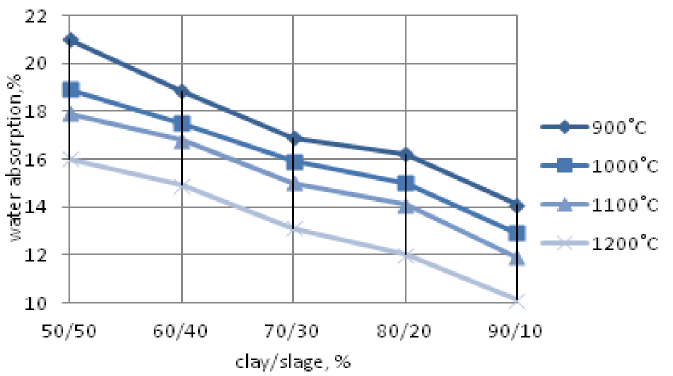


Fig. 9. Changes in water absorption depending on the clay/slag ratio

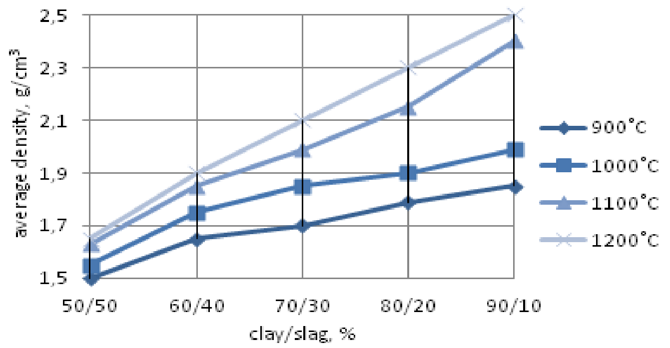


Fig. 10. Change in average density depending on the clay/slag ratio

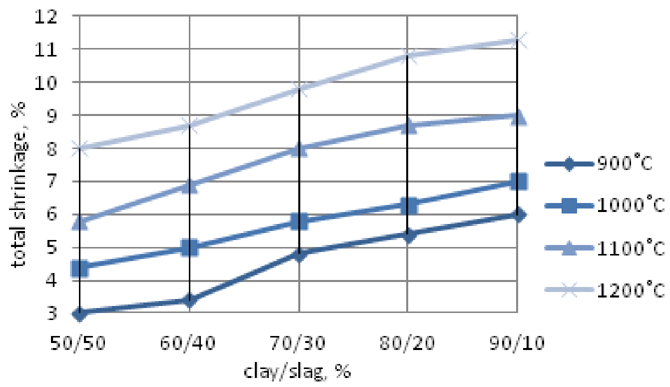


Fig. 11. Change in average contraction depending on the clay/slag ratio

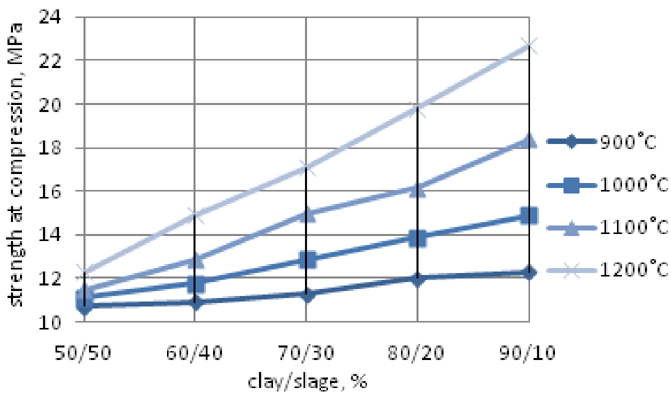


Fig. 12. Change in average compression strength depending on the clay/slag ratio

IV. Conclusion

The analysis of the results, shown on graphs 9–12, indicates that the increase in the amount of slags in a charge results in the increase of water absorption and determines the decrease in the limit of compression strength, contraction and average density. At 1100 ºC baking temperature the water absorption exceeds the recommended technological interval by 12–14%. These changes are connected with the transformation of the structure of original charge components during the process of thermal treatment: slags and aluminia-silicate raw material. At the 900–1200ºC baking temperature the fracturing in slags increases as well as their apparent porosity (fig. 13). The increase in slag content leads to the increase in apparent porosity and the water absorption of a ceramic product independently of the clay properties.

This research serves as a basis for further works aimed at developing resource-saving technology of manufacturing ceramic bricks with rational composition using low-melt clay and nonferrous metallurgy slags, used as multifunctional additive: a leaner at the stage of product forming and baking intensifier.

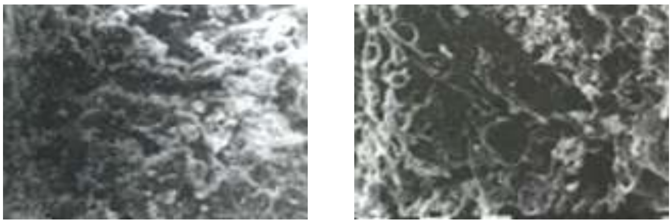


Fig. 13. Microstructure of ceramic brick samples (100 and 400x zoom) with the addition of nickel-bearing slags

References

[1] O.A. Kolodina, “Metallurgy of the Orenburg Region”, Geography, vol. 43, pp. 27–30, 2003.

[2] N.F. Solodkiy, A.S. Shamrikov, V.M. Pogrebenkov, Mineral and raw material base of the Urals for the ceramic, refractory and glass industries. Tomsk: Reference manual, 2009, 332 p.

[3] V.Z. Abdrakhimov, E.S. Abdrakhimova, “The use of slag from coal combustion in the Kansk-Achinsk basin in the production of ceramic materials based on inter-shale clay”, Ecology and Industry of Russia, pp. 36–39, 2014.

[4] V.Z. Abdrakhimov, Ecological, theoretical and technological principles of the use of phosphoric slag and slag material in the production of high-quality ceramic bricks. Novosibirsk, 2008, pp.20–24.

[5] V.V. Prokofieva, The Use of Associated Iron Ore Enrichment Products in Construction in the North. Leningrad, 1986, 176 p.

[6] V.A. Gurieva, Physical and chemical studies of the use of dunites in decorative and finishing ceramics. Orenburg, 2007, 133 p.

[7] P.I. Bozhenov, Complex use of mineral raw materials and ecology. Moscow: Publishing House of the Association of construction universities, 1994, 263 p.

[8] V.A. Gurieva, “Application of silicate-containing associated products of mining and processing plants in the production of ceramics”, News of universities, Construction, p. 596, 2008.

[9] L.F. Welington, E.L. Reis, R.M.F. Lima, “Incorporation of residues from the minero-metallurgical industry in the production of clayelime brick”, Journal of Cleaner Production, pp. 505–510, 2015.

[10] O.M.S. Gencel, E. Erdogmus, V. Koc, “Cay Properties of bricks with waste ferrochromium slag and zeolite”, Journal of Cleaner Production, pp. 112–113, 2016.

[11] L.B. Svatovskaya, L.L. Maslennikova, A.M. Slavina, N.A. Babak, O.A. Kapustina, “The mixture for the manufacture of ceramic bricks”, Russian Patent no. 241213, Byul. no. 5, 2011.

[12] L.B. Svatovskaya, L.L. Maslennikova, A.M. Slavina, N.A. Babak, T.I. Boykova, “Ceramic mass of light tone for the front brick”, Russian Patent no. 2433980, Byul. no. 32, 2011.