IOP Conf. Series: Materials Science and Engineering **127** (2016) 012024 doi:10.1088/1757-899X/127/1/012024

Analyzing the Technology of Using Ash and Slag Waste from Thermal Power Plants in the Production of Building Ceramics

A G Malchik[1,a*], S V Litovkin[1,b], P V Rodionov[1,c], V V Kozik[1,2,d], M A Gaydamak[1,e]

[1] Yurga Institute of Technology, National Research Tomsk Polytechnic University Affiliate,
652050, Yurga, ul. Leningradskaya 26
[2] National Research Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia

E-mail: [a*]ale-malchik@yandex.ru, [b]protoniy@yandex.ru, [c]rodik-1972@yandex.ru, [d]vkozik@mail.ru, [e] vip.trd777@mail.ru

Abstract. The work describes the problem of impounding and storing ash and slag waste at coal thermal power plants in Russia. Recovery and recycling of ash and slag waste are analyzed. Activity of radionuclides, the chemical composition and particle sizes of ash and slag waste were determined; the acidity index, the basicity and the class of material were defined. The technology for making ceramic products with the addition of ash and slag waste was proposed. The dependencies relative to the percentage of ash and slag waste and the optimal parameters for baking were established. The obtained materials were tested for physical and mechanical properties, namely for water absorption, thermal conductivity and compression strength. Based on the findings, future prospects for use of ash and slag waste were identified.

Introduction

The development of fuel and energy complex and construction industry, building of new towns and population centers, environmental and related social issues directly or indirectly depend on the disposal of coal-burning residuals - fly ash and slag. In the time of the Soviet Union, fly ash and slag were not separated and disposed of, using a hydro transport system, in impoundments and landfills, causing large amounts of slag waste within or close to cities. This problem is particularly pressing in Russia because of harsh climatic conditions, as well as disagreement of production time and potential consumption of coal-burning byproduct solids.

The share of coal burnt for producing electrical energy is 94% in Poland, 93% in South Africa. 78% in India, 77% in Australia, 70% in China, 67% in the Czech Republic, 62% in Greece, 52% in Germany, 50% in the USA, 17% in Denmark, 33% in the UK, over 27% in 15 European countries. The share of coal in energy production was 37% worldwide ten years ago. Such a low share of coal in the energy production was associated with the signing of the Kyoto Protocol, which required reducing emissions of carbon dioxide into atmosphere. However, due to unstable prices for oil and gas and their limiting availability, this share is now about 40%, with an apparent trend to grow [1,2,3].

According to the Energy Strategy of Russia for the period up to 2020 with the fundamental principles thereof approved by the government in 2000, a steady growth of electricity consumption is scheduled as much as 2-3% annually. It is planned to develop environmentally friendly power plants using renewable energy sources, including wind, tidal, geothermal and biofuel power stations, micro hydro power stations, and etc. But totally these sources will give 0.01% of generated energy. Thermal power plants will remain the foundation of the power generation industry, with their relative share in the total power capacity being at 67 - 70%.

The energy production using fossil fuels such as coal, shale oil, peat and other is inevitably accompanied by the formation of ash and slag waste; and fly ash is usually 70 to 90% of total balance in terms of waste solids formed during the coal burning. The share of costs estimated for handling waste is about one third of the cost of energy produced [1].

The problem of processing and recycling ash and slag waste, as well as making researches with the purpose of innovative processing technologies is being tackled in many countries. In Russia, the following experts are involved in dealing with ash and slag waste: I.S. Kozhukhovsky (CJSC "Energy Forecasting Agency"), V.Ya. Putilov (MPEI), V.V. Zyryanov (Nanopowder Technology Ltd.), B.L. Vishnya (Ural Energy Engineering Center), Yu. K. Tselykovsky (All-Russia Thermal Engineering Institute), R.V. Shevtsov (Territorial Generation Company 11).

Currently, no more than 5- 10 % of ash and slag waste is used in various construction and production sector countrywide. The residue is being stored in the ash and slag disposal areas without use. With this, the disposed ash and slag waste is not reduced, and it is likely to increase taking into account the growing demand for electricity and insufficient development of alternative sources for its generation.

Ash and slag materials in terms of their chemical and mineralogical composition are largely identical to natural mineral raw materials. Their use in the industrial sector, construction industry and agriculture is one of the strategic solutions to environmental problems in the area of operation of thermal power plants.

The aim of this work is to study physical and chemical properties of ash and slag waste, to determine its possible use as a secondary energy source to reduce anthropogenic impacts on the environment, to explore the possibility of obtaining ceramic materials with adding ash and slag waste.

Equipment and devices used in studies

Samples for the study were heat treated in a muffle furnace LOIP LF-15/11 – 61; a laboratory mixer BL-10 was used for mixing samples. Particle size analysis was performed using a device Analizette 22 MicroTec Fritsch GmbH (Germany). The samples were tested for ultimate compression strength in accordance with the requirements of GOST 10180-90 using a laboratory press PM-20MG4. The activity of radioactive nuclides was determined using a gamma-radiometer RKG-AT1320. Weighting was performed on a laboratory balance BK-600. The samples were dried in an electric oven SNOL-F-67/350-I2P before baking, and a cubic mould FBS-70 was used for forming the samples.

Results and discussion

A composition of ash and slag waste is determined by the quantitative ratio of contained in the material minerals that are dependent on initial mineralogical composition of fuel used.

The chemical composition of ash gives an idea of the composition of minerals in coal. Coal ash is typically presented by the overwhelming majority (96%) of oxides of silicon, aluminum, iron, calcium and magnesium. It contains sodium and potassium compounds only in small amounts. Some coals and ashes have a little precious metal (gold, silver, and platinum) as well as rare and trace elements.

The main compounds of ash are oxides SiO_2, $A1_2O_3$, FeO, Fe_2O_3, CaO, MgO. Sulfates $CaSO_4$, $MgSO_4$, $FeSO_4$ are presented in small amounts. Phosphates and alkali metal oxides K_2O, Na_2O are contained in ash to an even less degree. Ash and slag waste may have biogenic (fluorine, manganese, cobalt, lead, copper, etc.). and toxic (boron, vanadium, arsenic, strontium, beryllium, etc.) elements.

Chemical compositions of ash produced in burning different solid fuels vary within a wide range of limits,%: SiO_2 10 – 68; Al_2O_3 10 – 40; Fe_2O_3 2 – 30; CuO_2 2 – 70; MgO 0 – 10; Na_2O and K_2O 0 – 10. Besides, ash contains a small amount of compounds of germanium, vanadium, arsenic, mercury, beryllium fluoride partially passing into water.

IOP Conf. Series: Materials Science and Engineering **127** (2016) 012024 doi:10.1088/1757-899X/127/1/012024

Knowing a chemical composition of ash and slag waste is a prerequisite for discussing its properties and making a conclusion on its possible use in various economy sectors.

To determine the chemical composition of ash and slag waste, the ash samples were taken from electric filters and dumped ash according to the procedure RD 34.09.603-88 "Guidelines for the organization of monitoring compositions and properties of ash and slag supplied by thermal power stations to consumers."

The samples were tested to determine ash chemical composition and activity of radioactive nuclides.

The radionuclide activity was determined in accordance with GOST 30108-94 "Building materials and products. Determination of specific activity of natural radioactive nuclei". A gamma-radiometer PKG-AT1320 controlling the radio nuclides of potassium (^{40}K), radium (^{226}Ra) and thorium (^{232}Th) was used to determine the specific activity. The radioactivity measured at the Yurga thermal power plant showed the following results: ^{40}K – 526 Bq/kg, ^{232}Th – 72 Bq/kg, ^{226}Ra – 37 Bq/kg. The specific activity is calculated in accordance with the following formula:

$$A_{\mathrm{eff}} = A_{\mathrm{Ra}} + 1{,}31A_{\mathrm{Th}} + 0{,}085A_{\mathrm{K}} \quad (1)$$

where A_{Ra} , A_{Th} , A_{K} are the specific activities of radium, thorium and potassium respectively, Bq/kg.

The calculated value of ash and slag waste activity at the Yurga thermal power plant is 175 Bq/kg that does not exceed the requirements of construction standards, qualifying ash and slag waste as the first class building material; this means it can be used in all types of construction.

Chemical analysis was performed using an X-ray fluorescence spectrometer Quan`X of the Common Use Center at Tomsk Polytechnic University. The results are shown in Table 1.

Table 1 - Chemical composition of ash from Yurga power generating plant

Compound	Ash waste		Electric filter	
SiO2	55,7	56,25	50,4	50,74
CaO	6,8	6,84	13,96	13,57
Al_2O_3	21,83	21,84	20,52	20,6
MgO	1,95	1,65	1,55	1,67
MnO	0,09	0,1	0,1	0,09
Fe_2O_3	7,44	7,4	8,55	8,53
FeO	6,69	6,66	7,69	7,68
K_2O	3,53	3,44	1,35	1,31
TiO_2	1,11	1,28	0,97	0,81
SO_3	0,72	0,68	0,87	0,82
BaO	0,44	-	0,5	0,59
P_2O_5	0,38	0,4	1,08	1,1
SrO	-	0,1	0,16	0,19

The main chemical compounds contained in the ash are oxides of silicon and aluminum; the content of iron oxide present is high as well, the content of calcium oxide in the ash waste samples is lower than that in the electric filter samples. Free calcium oxide is likely to react with the carbon dioxide, which is dissolved in the water used to transport the ash through a pipeline, to form calcium carbonate.

With the purpose to specify the possible use of ash and slag waste, it is required to define such criteria of classification as: acidity index, basicity, silica module and quality factor

The acidity index $M_{к}$ is calculated on the basis of the following formula:

$$M_{к} = \frac{SiO_2 + Al_2O_3}{Fe_2O_3 + CaO + MgO} \quad (2)$$

The acidity index is 2.9 for the electric filter samples and 4.7 for the ash and slag waste samples.
The basicity module M_o is defined according to the base-acid ratio:

$$M_O = \frac{CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3} \quad (3)$$

The basicity module is 0.2 for the electric filter samples and 0,16 for the ash and slag waste samples.
The silica module M_c is calculated as the ratio of silicon oxide to the sum of aluminum and iron oxides:

$$M_C = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (4)$$

The silica module is 1.7 for the electric filter samples and 1,9 for the ash and slag waste samples.
The quality factor K shows the ratio of oxides increasing the hydraulic activity to oxides reducing it:

$$K = \frac{CaO + Al_2O_3 + MgO}{SiO_2 + TiO_2} \quad (5)$$

The quality factor is 0.7 for the electric filter samples and 0.54 for the ash and slag waste samples.
The results obtained suggest that the ash and slag waste is of an acidic type of ash. Acidic ashes are characterized by unstable chemical composition, a small amount of free calcium oxide and a high content of silicon oxide. Such types of ash do not have distinct bonding properties which are possible with calcium oxide that forming the hydroxide in water. Drying in air, hydroxide absorbs carbon dioxide from the air and converts into calcium carbonate that makes the product hard.
Particle-size distribution is one of the main indicators of raw materials. The greater the content of micro-dispersed particles, the higher ductility of a material is. Consequently, raw material has a higher bonding property that positively influences strength performance of products made; and a particle size composition is important for determining the adsorption capacity of a material [2,4,5].
The results of the particle-size distribution are represented in Figure 1. The analysis showed that 60% of particle size is 10 to 70 microns.

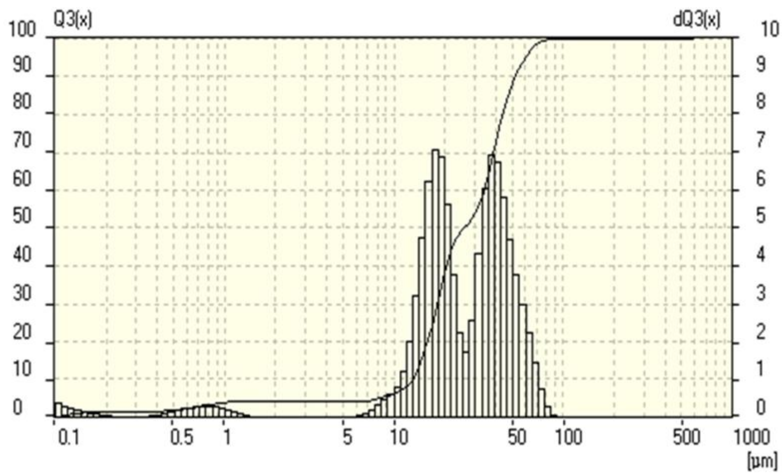

Figure 1 – Particle-size distribution of ash and slag waste

The next stage of the work was to make samples of ceramic bricks with the addition of ash and slag waste. Under laboratory conditions, ceramic bricks with different percentage of ash and slag waste were made by the soft–mud moulding process followed by baking at various temperatures. For illustrative purposes, all the data are summarized in Table 2 and Figures 2, 3 and 4. The figures are the graphs to show the dependency of baking temperatures on proportions.

Table 2 - Physical and mechanical properties of ceramic bricks at various baking temperatures and different percentages of ash and slag waste

Content of ash in clay, %	Heat conductivity, W/m °C				Water absorption, %				Ultimate compression strength, kg/cm^2			
	Temperature, °C				Temperature, °C				Temperature, °C			
	700	800	900	1000	700	800	900	1000	700	800	900	1000
0	0,84	0,85	0,85	0,85	11	10	9	8	60	80	90	110
5	0,83	0,84	0,82	0,85	17	17	15	10	70	96	100	115
10	0,83	0,81	0,82	0,81	18	18	16	12	72	104	110	120
15	0,77	0,79	0,74	0,76	20	19	17	14	75	106	115	125
20	0,77	0,69	0,73	0,71	24	23	18	16	70	90	105	115
25	0,55	0,6	0,57	0,61	27	25	20	18	65	85	95	110

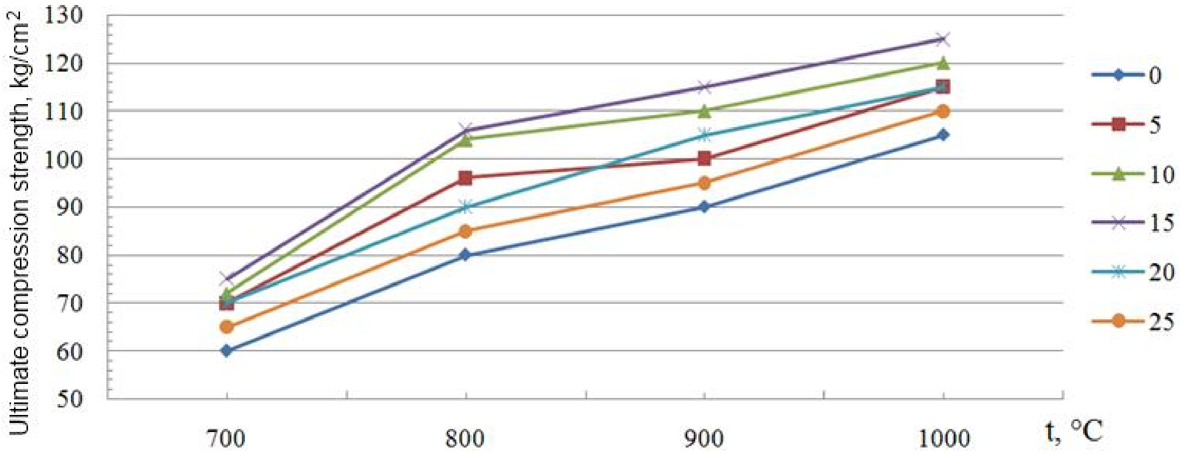

Figure 2 – Backing temperature dependence of the ultimate compression strength.

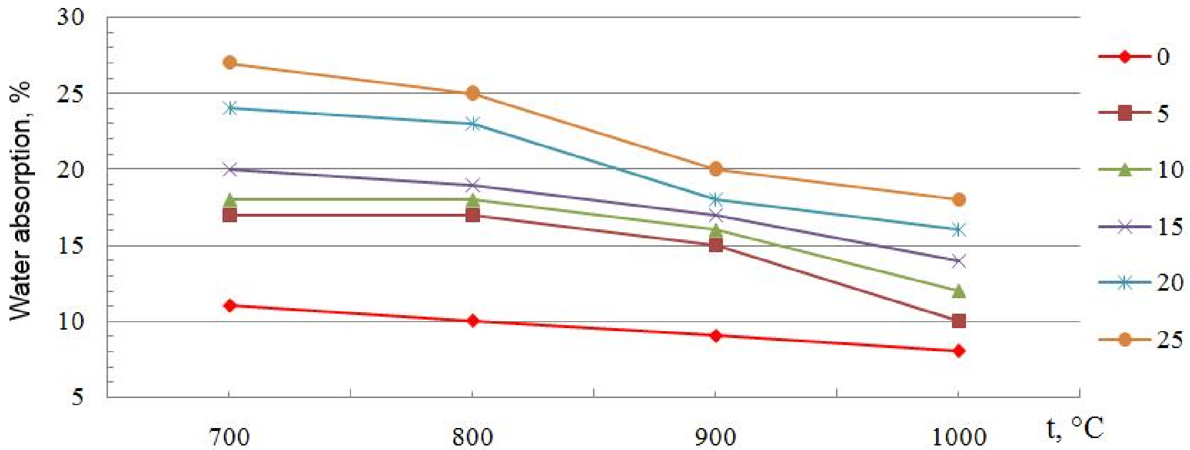

Figure 3 - Backing temperature dependence of the water absorption capacity.

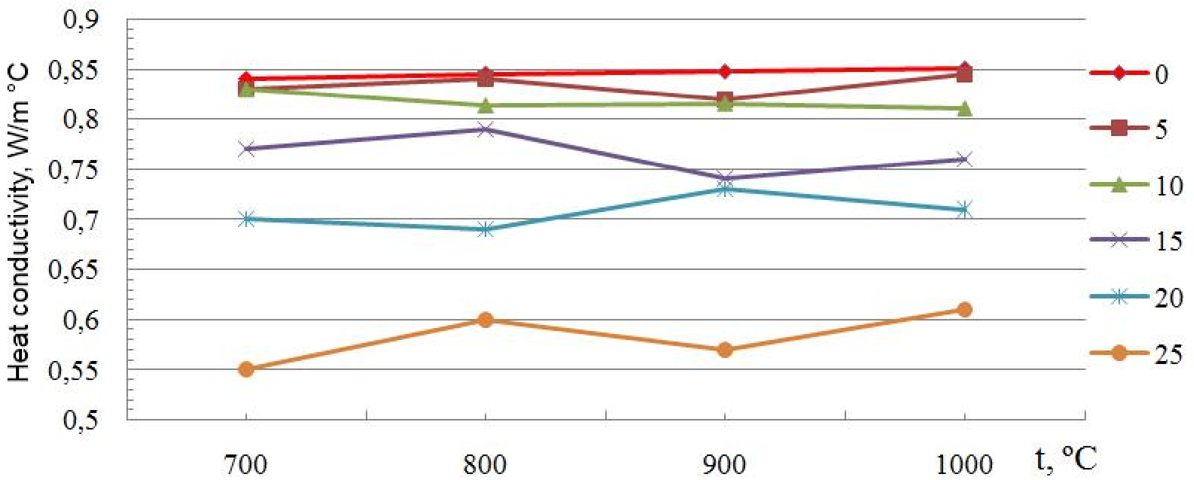

Figure 3 - Backing temperature dependence of the heat conductivity capacity.

Conclusions

The studies found that the heat conductivity, the ultimate compression strength and the water absorption capacity depend on both the amount of ash added and baking temperatures. The greater the ash and slag content in bricks, the lower their heat conductivity is. The water absorption capacity increases with an increase in ash content. The ultimate compressive strength also decreases with increasing the ash content in ceramics. The optimum percentage of adding ash and slag waste is fifteen percent at a baking temperature of 1000 ° C.

It has been established, if ash and slag waste is of an acidic type, it does not have self-sustained bonding properties and require adding curing agents.

The analysis of the particle-size distribution showed that 60% of particle size is 10 to 70 microns; the material is finely dispersed and can be used as a filler in the production of construction mixes and ceramics.

References

[1] Putilin E I Obzornaja informacija otechestvennogo i zarubezhnogo opyta primenenija othodov ot szhiganija tverdogo topliva na TJeS [Survey of domestic and foreign experience in using waste from burning solid fuels by thermal power stations] / E I Putilin, V S Tsvetkov. - Moscow: Soyuzdornii, 2003 - 60 p

[2] Zyryanov V V Zola-unosa – tehnogennoe syr'e [Fly ash – industry-related raw materials] / V V Zyryanov, D V Zyryanov Moscow: OOO IPTz “Maska”, 2009 - 320 p.

[3] Dik E P, Mashkovich K I, Vasilchenko Z A, Komponentnyj sostav zoloshlakovyh othodov TJeC // *Novoe v rossijskoj jelektrojenergetike [Chemical composition of ash waste from thermal power plant // New in Russian power sector]* 2003 No.5. – 40 p

[4] Spirin E K, Lugovtsova N Yu, Khomich O I Special features of VP-1Ap anion exchanger behavior under deep silicifi cation // *Russian Journal of Applied Chemistry*. – 2012 – Vol. 85 – p.921-925.

[5] Torosyan V F , Torosyan E S , Sorokin P D, Telitsyn A A Updating of sewage – purification facilities of electroplating enterprises with counterflow ion-exchange filters // *IOP Conference Series: Materials Science and Engineering*. – 2015 – Vol. 91, Article number 012077. – pp 1-8

[6] Bespalov V I, Prirodoohrannye tehnologii na TJeS: uchebnoe posobie [Environmentally freindly technologies at thermal power plants: Workbook] / V I Bespalov, S U Bespalova, M A Wagner. - Tomsk: Publishing House of Tomsk Polytechnic University, 2010 – 240 p.

[7] Putilov V Ya O roli i meste nauki v reshenie problemy obrashhenija s zoloshlakami TJeS [The

role and place of science in addressing the issue of treating ash and slag from thermal power plants] / V Ya Putilov, I V Putilova. Warsaw: Energoizdat, 2010 – 320 p.
[8] Gavrilov V I Toplivno-transportnoe hozjajstvo i zoloshlakoudalenie na TJeS [Fuel and transport facilities and ash and slag removal at TPP] /V I Gavrilov Moscow: Energoizdat, 1987. 168 p.
[9] Borisenko L F Perspektivy ispol'zovanija zoly ugol'nyh teplovyh jelektrostancii [Prospects for the use of ash from coal-fired power plants] / L F Borisenko, L M Deltsin, A S Vlasov. - Moscow: ZAO "Geoinformmark", - 2001 -68 p.
[10] Tymoshchuk N S Primenenie zoly i shlaka Burshtynskoj GRJeS v zhelezobetonnyh izdelijah dlja dorozhnogo stroitel'stva [Use of ash and slag from Burshtyn TPP in concrete products for road construction / N S Tymoshchuk, I.S. Bobyk. - Moscow: Mir, 1991 – 70 p.
[11] Bazhenov Yu M, Schebenkin P F, Dvorkin L I Primenenie promyshlennyh othodov v proizvodstve stroitel'nyh materialov[Use of industrial wastes in the production of construction materials]. - Moscow: Stroyizdat, 1986 -120 p.
[12] Bozhenov P I Kompleksnoe ispol'zovanie mineral'nogo syr'ja dlja proizvodstva stroitel'nyh materialov [Multiple use of mineral raw materials for the production of construction materials] / P.I. Bozhenov. - Moscow: Stroyizdat, 1963 - 170 p
[13] Tabin Rushad S 2011 Experimental Studies on Lime-Soil-Fly Ash Bricks (International journal of civil and structural engineering, volume 1, № 4)
[14] Obada Kayali 2005 High Performance Bricks from Fly Ash. (USA, Kentucky, Lexington World of Coal Ash, April 11-15)
[15] Henry Liu 2009 Environment Properties of Fly Ash Bricks, (USA in Lexington World of Coal Ash Conference – May 4-7)
[16] Kevan D Sharp. 1993 Fly ash for soil improvement: proceedings of sessions sponsored by Committees on Soil Improvement and Geosynthetics of the Geotechnical Engineering Division of the American Society of Civil Engineers in conjunction with the ASCE Convention in Dallas (Texas, October 24-28)