YIT-ITEE IOP Publishing
IOP Conf. Series: Materials Science and Engineering **91** (2015) 012081 doi:10.1088/1757-899X/91/1/012081

Investigations of physicochemical properties of bottom-ash materials for use them as secondary raw materials

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Abstract. In this paper chemical content and particle size distribution of bottom-ash material are defined; results of differential thermal and X-ray analyzes are given; processes of phase transformations occurring during heating, are examined for possible use of the waste to produce ceramic products. Studies have shown that effective specific activity of radionuclides in the material under examination would have no effect on radiation safety of the finished product.

1. Introduction

On the Russian Federation territory there are more than 350 thermal power plants (TPP). Their proportion of generated energy is 70% from the national overall energy balance [1,2]. About 30% of TP plants burn coal [3]. When burning coal electric energy is generated, and also by-products, namely fly ash and slag, are formed. About 50 million tons per year of the bottom-ash are produced in Russia [1,4]. More than 1.5 billion tons of waste are accumulated at TPP ash disposals; their total area is 2000 km^2 [1,4]. By 2020, the proportion of coal burned at the TPP will increase to 40% [3]; that will cause further formation and accumulation of the bottom-ash wastes.

In Russia only 10% of bottom-ash annual content is recycled. For comparison, Germany utilizes about 100%, India - over 50% [5], Finland, Great Britain - 60%, USA - 25% [3]. In some foreign works it is reported that bottom-ash have been successfully used as the main component of ash bricks [6,7,8] as well as a fertilizer [9].

Taking into account further increase of coal burning and low level of waste recycling, a threat of ash disposal overflows arises, which will cause shutdowns of coal plant [5]. Open ash disposal areas pollute the environment. Dusting of ash has a negative impact on human health, flora and fauna.

In Russia, especially in Siberia, there are certain difficulties in the use of foreign techniques and practical recommendations for ash-and-slag utilization because they exceed actual capabilities of Russian economy. Therefore such recycling techniques are required that can adequately adapt national and international experience as well as have competitive advantages achieved by rational use of natural resources and investments [10].

The object of the examination is bottom-ash and slag materials (BAM) from TPP of Open Joint Stock Company "Yurga Machine Building Plant". The subject of the examination is to determine physical and chemical properties of ASM.

The aim of this work is to examine BAM physical and chemical properties, and its usability as a secondary resource to reduce the anthropogenic impact on the environment.

2. Experiments

To determine chemical composition of the bottom-ash waste, ash sampling was made. A total of 130 samples were selected. Chemical analysis was performed using X-ray fluorescence spectrometer KevexSpectrace's Quan`X. Analysis of the particle size distribution was performed using Analizette 22 MicroTec Fritsch GmbH (Germany) on the original software. Thermal characteristics were determined using a differential scanning calorimeter DSC 404 F3 Pegasus NETZSCH (Germany). The samples were roasted in a laboratory gradient furnace SP 30/13 (LAC (Czech Republic). The samples were tested for compressive strength with laboratory press PM-20MG4. X-ray diffraction analysis was performed using Rigaku 2500 D-max diffractometer with CuKα-radiation (λ = 1,5418 Å) in the range of 2θ = 10-80°. Identification was performed using catalogs PDF-2. Electron microscopy examinations were performed with JSM-5610 LV JEOL (Japan) scanning electron microscope. RKG-AT1320 gamma radiometer was used to determine the activity of radionuclides).

3. Results and Discussion

Tested ash and slag materials are fine mixtures, mainly gray-coloured. Averaged chemical composition is shown in Table 1. Bottom-ash chemical composition depends on mineral composition of burnt coals, and may differ significantly at different plants. Composition of the materials under investigation is characterized by a low content of calcium oxide, middle - of alumina and high - of iron oxide. Oxides of silicon and aluminum are the main components. This indicates presence of free calcium oxide in bottom-ash composition which, during disposal, reacts with the dissolved carbon dioxide to form calcium carbonate.

Ash samples were also taken from the precipitator. The ash from the precipitator contains twice as much calcium oxide. This indicates presence of free calcium oxide in bottom-ash composition which, during disposal, reacts with the dissolved carbon dioxide to form calcium carbonate. Presence of calcium carbonate is confirmed by XRD data (see Figure 1).

Table 1 Averaged chemical composition of bottom-ash sample.

Element	Ash disposal site,%		Precipitator, %	
	sample 1	sample 2	sample 1	sample 2
SiO_2	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

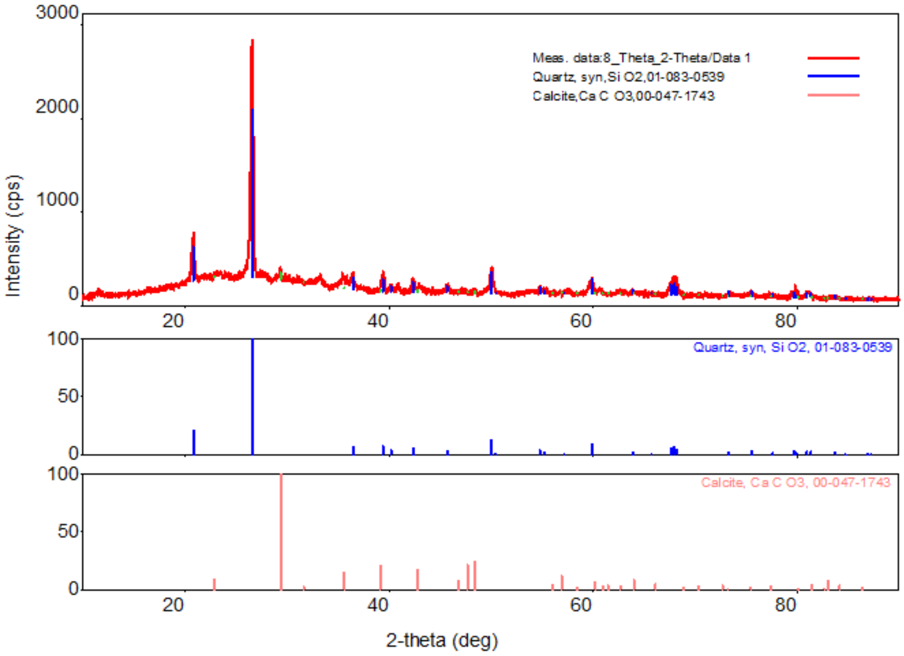

Figure 1. X-ray diffraction analysis of ash sample.

One of the main indicators of raw materials is their particle size distribution. A higher content of micro-dispersed particles increases ductility of the material. Therefore, if a raw material has a high cohesion, it improves the strength characteristics of the finished product; particle size distribution also specifies adsorptive capacity of the material.

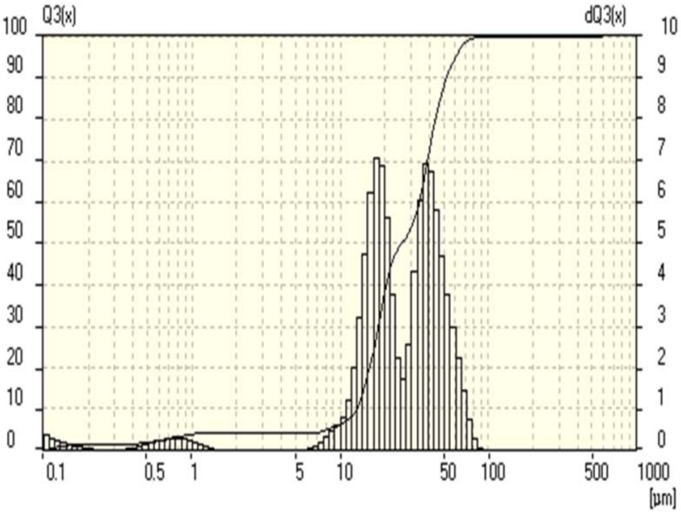

Figure 2. Particle size distribution in bottom-ash.

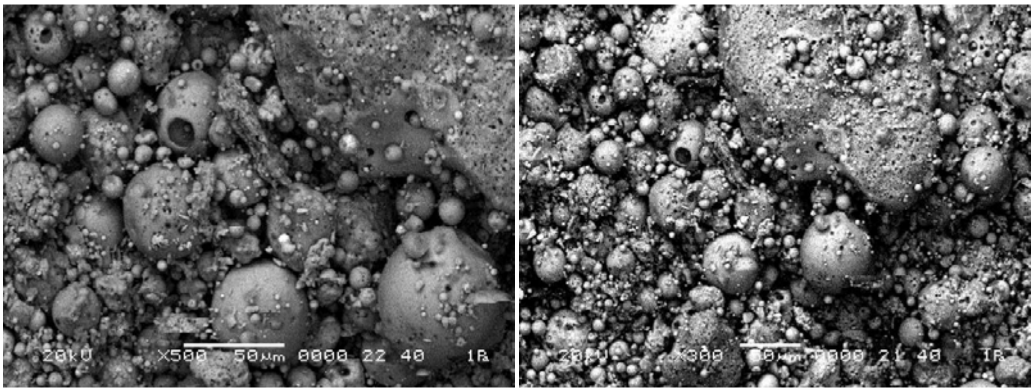

Figure 3. Microphotography of bottom-ash particles.

Results of the particle size distribution are shown in Figure 2. Analysis of particle size distribution shows that 60% of the particles have dimensional characters from 10 to 70 microns in size. Dimensions and morphology of the ash particles are shown in Figure 3.

The picture shows that the bottom-ash particles are beads and compactly shaped aggregates; the particle dimensions vary from 10 to 100 microns. Obviously, the material is very finely dispersed.

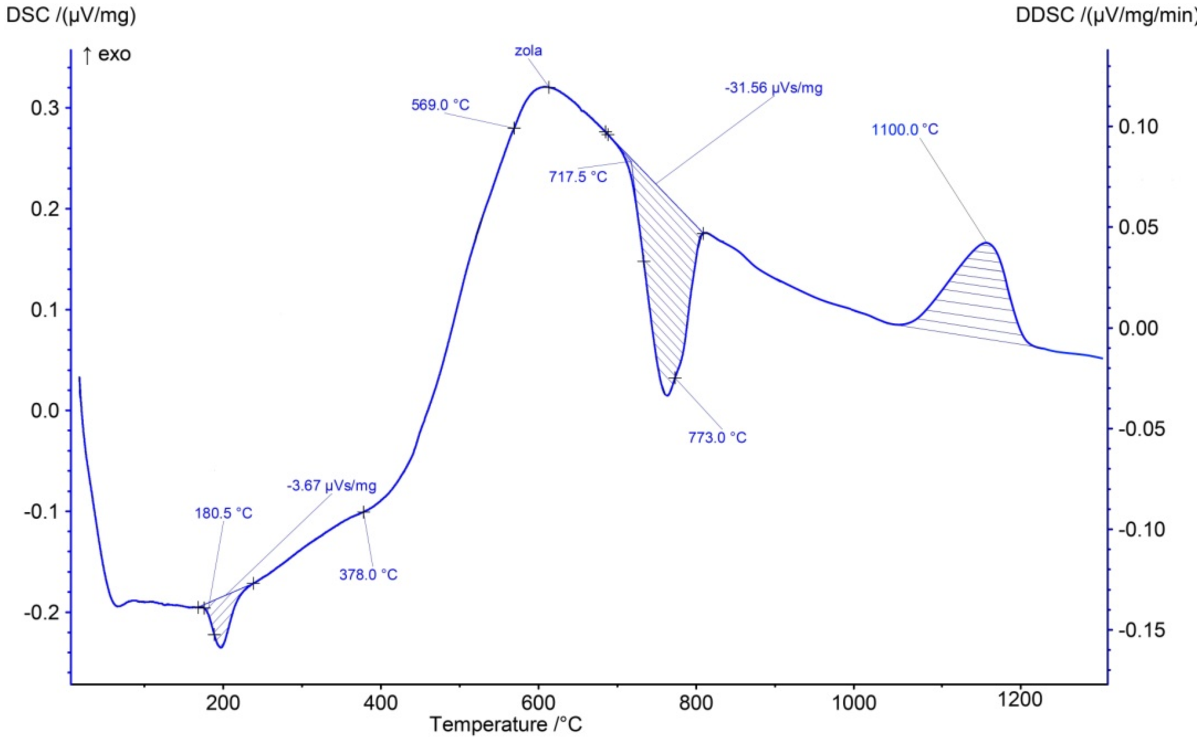

Figure 4. Bottom-ash DTA curve.

Differential thermal analysis (DTA) was performed to examine physical and chemical processes occurring in the ash during heating. On the DTA curve (Figure 4) there is a broad endothermic effect in 180°C area generated by removal of physically-bonded water and dehydration of hydroxides and hydroxide salts. At 180°C the bulk of physically and chemically bonded water is removed; the remainder is removed at a wider temperature range up to 750ºC; that proves the presence of stable OH- groups in the BAM. A small exothermic effect at 378ºC indicates the start of combustion of organic matter residues in BAM. Exothermic effect at 569ºC confirms presence of quartz; in this temperature range (530-580ºC, as described) quartz polymorphic inversion is observable, which is related to second-order phase inversions.

The next endothermic effect at 773ºC is caused by dissociation of magnesium components of dolomite. Exothermic effect at 1150ºC is caused by formation of mullite from free oxides $3Al_2O_3 + 2 SiO_2 = 3 Al_2O_3•2 SiO_2$. Mullite is the most thermodynamically stable form of the compound wherein some aluminum ions have quaternary coordination, others have sextuple coordination. Analysis of the resulting materials shows, that when ash-and-slag material undergoes heating to1000 – 1200ºC in oxidizing environment, mullite and α-quartz are produced mainly; this is confirmed by X-ray diffraction. For a more detailed examination of physical and chemical processes which occur during bottom-ash roasting, a multi-position heat treatment was performed in temperature range of 950 - 1100°C with steps of 50°C. The resulting sinter density increases with increasing of the processing temperature to 1100°C (Table 2).

Table 2. Influence of sintering temperature on material strength.

Temperature of heat treatment, °C	Strength, MPa
950	2
1000	2
1050	7
1100	15

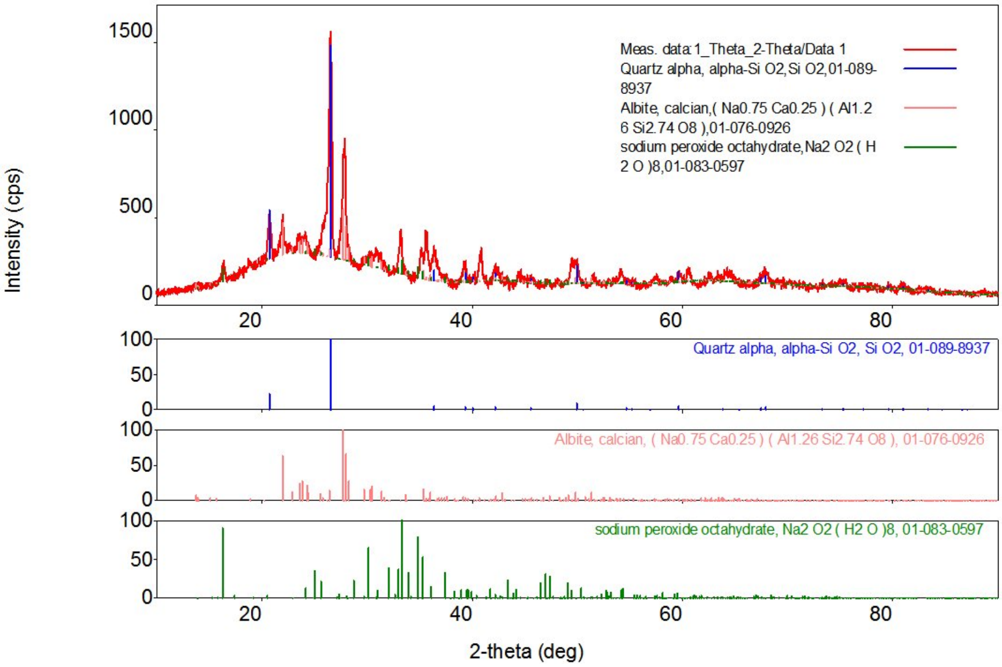

Figure 5. X-ray diffraction analysis of sample roasted at 950ºC.

XRD analysis of ash samples after heat treatment (see Figures 5 and 6) shows that at 950°C albite and sodium peroxide octahydrate are formed, the latter is the most stable crystalline hydrate of sodium peroxide. At 1100°C formation of mullite, which is stronger then albite, is observable. Formation of mullite is also confirmed by the differential thermal analysis described above.

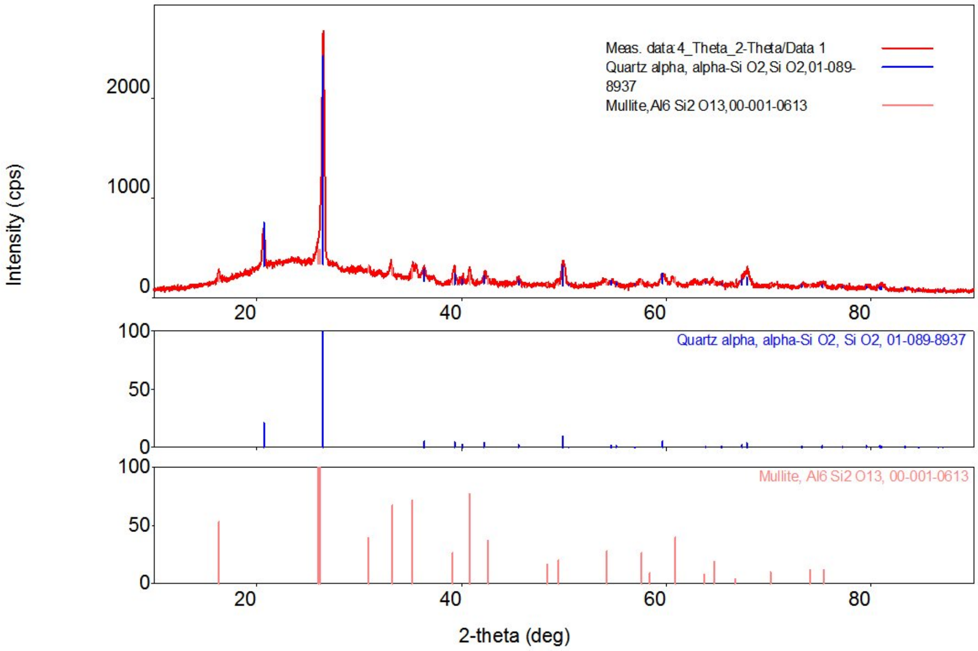

Figure 6. X-ray analysis of sample roasted at 1100°C.

Measured activity of radionuclides showed the following results: ^{40}К – 526 Bq/kg, ^{232}Th – 72 Bq/kg, ^{226}Ra – 37 Bq/kg. Calculation of the specific activity was made according to the formula:

$$A_{эфф} = A_{Ra} + 1.31A_{Th} + 0.085A_{K} \qquad (1)$$

where A_{Ra} ,A_{Th} , A_{K}- - Specific activities of radium, thorium, potassium, respectively, Bq/kg.

Calculated ash waste activity is 175 Bq/kg; that does not exceed, requirements of building regulations, according to which bottom-ash can be ranged in the first grade of construction materials, and can be used for all types of construction.

To determine capability of ash and slag further use it is necessary to define basic classification features: indexes of acidity and basicity, silica ratio and quality factor.

To determine acidity index of M_k we calculate ratio of the sum of acidic oxides to the sum of basic ones:

$$M_k = \frac{SiO_2 + Al_2O_3}{Fe_2O_3 + CaO + MgO} \qquad (2)$$

Acidity index of samples, taken from the precipitator, is equal to 2.9, samples from the ash disposal - 4.7.

To determine basicity index M_o we calculate ratio of the sum of basic oxides to the sum of acidic ones:

$$M_0 = \frac{CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3} \qquad (3)$$

Basicity index of samples, taken from the precipitator, is equal to 0.2, samples from the ash disposal – 0.16.

Silica ratio M_c is calculated as ratio of silica to the sum of aluminum and iron oxides:

$$M_c = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} \qquad (4)$$

Silica ratio of samples, taken from the precipitator, is equal 1.7, samples from the ash disposal – 1.9.

Quality factor K is the ratio of oxides, increasing hydraulic activity, to the oxides, reducing it:

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

Quality factor of samples, taken from the precipitator, is equal to 0.7, samples from the ash disposal – 0.54.

Findings show that the bottom-ash wastes are acidic ashes. Acidic ashes have unstable chemical composition, a low content of free calcium oxide and a high content of silica. These ashes do not have cementing properties, but after addition of intensifiers become cementitious.

4. Conclusions

Ash-and-slag wastes were examined for their recycling and usability as a secondary resource to reduce the anthropogenic impact on the environment.

Physical-chemical characteristics of waste behavior during thermal processing have been specified. Chemical analysis has revealed that oxides of silicon (56.25%) and aluminum (21.84%) are the principal components of BAM. Analysis of the particle size distribution has shown that 60% of particles have dimensional characters from 10 to 70 microns. Both X-ray diffraction analysis and differential thermal analysis have shown formation of mullite at temperatures above 1100°C. Effective specific activity of radionuclides in BAM, calculated by isotope activities of radium (^{226}Ra), thorium (^{232}Th) and potassium (^{40}K), is 175 Bq/kg.

Thus, the examinations have demonstrated possibility of BAM utilization as a secondary resource for reducing the anthropogenic impact on the environment.

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