Physical chemical studies of dispersed aluminosilicate wastes for obtaining the burned building materials

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Abstract. This paper presents results of the studies that determined that grinding can be one of the ways to modify aluminosilicate wastes. The optimal grinding modes were defined in laboratory conditions. Physical and chemical studies of modified ashes were carried out by means of X-ray phase analysis, differential thermal analysis and microscopy. The results have shown that modified ashes of thermal power stations when being applied in production of ceramic brick influence positively the processing properties of raw materials and the ready products.

1. Introduction
High development rates of industrial and civil engineering both at domestic and international markets are followed by the increase in production output of building materials as well as products of different kinds and different application. Ceramic industry takes one of the leading positions at the market of building materials. From the one hand, the field of ceramic building materials faces a problem of untimely delivery of high-quality raw materials. From the other hand, the increase in energy consumption leads to increase in the amount of wastes from coal burning – bottom ashes. Therefore one of the objectives of modern science is studying the possibility of their recycling into different industries. The problem arises in different processing characteristics of ashes (physical, chemical and mineral properties). The widest application of thermal power station wastes are in production of different kinds of building materials: cement, concrete, wall materials, slag wool [1-3]. The most relevant is the application of ashes in production of ceramic brick [4].

2. Materials and methods
It is known that chemical and granulometric composition of ashes obtained from burning of black coal sufficiently differs from each other, even within the limits of one ash disposal area [5]. Moreover, applications of ashes without the preliminary treatment for instance in production of ceramic brick increases the risk of obtaining products with unstable properties [6]. This is one of the key reasons of rare cases of application of thermal power station wastes in production of building materials, especially at the Russian market.

In this regard a relevant issue is studying the modification methods of aluminosilicate ashes wastes to improve their processing characteristics that enable obtaining ceramic building materials with good and stable properties.
The goal of the presented research was to study the structure and phase composition of the preliminary-treated aluminosilicate wastes and their influence on brick properties.

2.1. Physical-chemical studies of aluminosilicate and clay brick

The raw materials under study are ashes from burning the black coals at the electric station in the city of Tomsk (Russia) and clay of Verkhovoe field in Tomsk region. Chemical composition of raw materials is given in Table 1.

| Item  | Oxides content, m% |
|-------|-------------------|
|       | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | R₂O  | TiO₂ | Loi  |
| Clay  | 64,80 | 12,10 | 4,53  | 5,90 | 3,08 | 2,97 | 0,70 | 5,92 |
| Ash   | 61,80 | 22,40 | 3,95  | 3,00 | 1,81 | 1,34 | 1,25 | 4,45 |

Table 1 shows that content of aluminum oxide 12,1% in clay makes it acid (Al₂O₃ < 14%). CaO and MgO in clay in the amount of 5,9% and 3,0% are most likely found as carbonate compounds. At the indicated quantitative combination of aluminum oxide characterizing the raw materials with its fire resistance and fluxing agents - magnesium oxide, calcium oxide and ferrous oxide the raw materials can be classified as low-melting.

High content of Al₂O₃ (22,4 %) and SiO₂ (61,8 %) in ash can be the reason of mullite-like compounds crystallization. Loss of less than 5% while calcination shows low amount of residual fuel thus minimizing the shrinkage processes while burning.

The earlier obtained results [7] showed that one of the ways to improve aluminosilicate ashes is dispersion.

Plastic deformation while grinding leads to the change in crystal structure of quartz. At the same time its reaction capacity grows sharply and the temperature of thermal dissociation decreases. That can lead to the reduction of temperature of formation the principal minerals specific to ceramic products.

Use of mills where mechanical impulse from grinding media is brought by the simultaneous combination of impact, pressure and shear is the most effective [8]. Planetary mill refers to such kinds of mills. The optimum grinding modes were defined in the laboratory conditions (Table 2).

| No. | Time of grinding, hours | <3 | 3-5 | 5-7 | 7-10 | 10-14 | >14 |
|-----|------------------------|----|-----|-----|------|-------|-----|
| 1   | 1                      | 84,1| 6,9 | 3,0 | 2,2  | 1,5   | 2,3 |
| 2   | 2                      | 86,3| 7,2 | 2,5 | 1,9  | 1,0   | 1,1 |
| 3   | 4                      | 92,1| 3,4 | 1,9 | 1,5  | 0,8   | 0,3 |
| 4   | 6                      | 93,1| 2,7 | 2,0 | 1,3  | 0,7   | 0,2 |
| 5   | 8                      | 93,2| 2,6 | 2,0 | 1,3  | 0,7   | 0,2 |
| 6   | 10                     | 93,4| 2,5 | 1,9 | 1,3  | 0,7   | 0,2 |

It should be noted that the optimum grinding time is 4 hours as further grinding shows almost no difference in grain size composition. This can be explained by the inverse process of conglomeration – aggregation of particles under action of adhesive forces and also high strength of mono-crystal particles of small sizes [9].
The obtained ash powder was studied by scanning electron microscope TM3000 at the zooming of x200 and x1000. Ashes microstructure is shown in Figure 1.

![Microphotographs of ashes; (a) ashes before grinding, (b) ashes after grinding.](image)

**Figure 1.** Microphotographs of ashes; (a) ashes before grinding, (b) ashes after grinding.

Microphotographs as shown in Figure 1 demonstrate the structure and the nature of particles of aluminosilicate raw materials before and after the grinding. Ashes in the city of Tomsk are peculiar with domination of spherical particles of the regular shape with close and open porosity of less than 10 μm in size and also small content of large porous inclusions of irregular shape. After grinding (Figure 1b) mainly occurs the fragmental destruction of large inclusions with the formation of flour particles. Spherical particles of the regular shape that are quartz-containing compounds do not change their size due to high hardness. The structure becomes more homogenous and dense thus contributing to the increased reaction capacity while ceramics sintering.

Thermal studies of raw materials were held using thermal analyzer SDT Q600 at the speed of temperature increase of 20 degrees per minute, with interval 20–1100 °C. The results of thermal analysis are presented graphically in Figure 2.

Figure 2 shows that clay of Verkhovoe field is characterized by 4 endo-effects and 2 exo-effects. Endo-effect at the temperature interval 30–150 °C is connected with the removal of adsorbed moisture and interpacket water from the structure of clay minerals. Effect 500°C – dehydration of
hydrous micas. At the temperature 575 °C polymorphic transformation of quartz occurs. The interval 620–750 °C is characterized with loss of hydroxyl groups by crystal lattice of montmorillonite and its destruction and the decay of carbonate inclusions. Exothermic effect at the temperature of 355 °C is connected with oxidation of organic substances. 910 °C – recrystallization of amorphous decomposition products and formation of new minerals.

At thermal treatment of ashes in interval 40–200 °C the loss of water adsorbed by the developed surface of particles occurs. Carbonate dissolution is observed at the temperature of 697 °C. Burning out of the residual fuel – 500–700 °C. The nature of intensiveness and weight loss indicates the amount of non-burned residues representing the coal particles as well as carbon residues and half-carbon residues. The relatively small exothermic effect with maximum 933,9 °C reflects crystallisation of mullite-like compounds in aluminosilicate phase.

Figure 2. DTA curves and TG of raw materials; (a) clay, (b) thermal power station ashes.

X-ray structure analysis of ashes after grinding and clay was held using X-ray diffraction meter Rigaku MiniFlex. The results of X-ray phase analysis is given in Figure 3.

Figure 3. X-ray patterns of raw materials; (a) clay, (b) thermal power station ashes. Q – quartz, B – biotite, Ca – calcite, il – illite, M – mullite.
X-ray phase analysis showed that clay from the city of Tomsk is presented by quartz, illite, biotite and calcite phases. This raw material can be referred to the group of hydromicaceous-montmorillonite clays. The ash except for quartz is defined by the clearly observed mullite phase. It can further serve while clinkering of ceramic fragment as the center of initiating crystallization of mullite-like compounds providing strength properties to the ready products.

2.2. Obtaining laboratory samples of ceramic brick
To define the influence of dispersed ash on the properties of clay brick and ceramic products a number of experiments have been held. Laboratory samples of ceramic brick were prepared by semi-dry compaction method adding ashes into furnace charge in the amount of 50%. The samples were moulded and burned in the muffle furnace at the temperature of 950–1000 °C. The experiment has shown that when using minced ashes the strength of clay brick increases by 30 % in comparison with the samples from unmilled raw materials. Air shrinkage decreases by 30 %, fire shrinkage - by 50 %. Water absorption of ready ceramic samples reduces by 20 %. As the burning temperature increases up to 1000 °C the properties of products undergo almost no changes thus allowing pointing out the completeness of the basic phase formation processes at the temperature of 950 °C.

2.3. Physical-chemical studies
The carried out research enables to conclude that the main phase changes while burning out the ceramic brick samples made from reasonable compositions with dispersed ash in furnace charge are as follows: the formation of initial melt from clay matter and several low-melting ashes grains; occurring mullite- and anortite-like compounds being the strengthening phases.

The main strengthening structural changes are: healing of pores with the formed glass phase and contraction of non-melted raw materials particles at the same time forming the solid product.

**Figure 4.** Microphotographs of ceramic samples structure of the reasonable composition (ashes content 50 %) with the use of dispersed ashes of thermal power station.

Generally while sintering of compositions when mixing thermal power stations ashes and clay matter the strengthening phases occur (mullite and anortite) that can be explained by existence of these phases in the initial ashes. When burning out the compositions with Tomsk ashes solid-phase sintering prevail while when obtaining the ceramic products with ashes from the city of Seversk – liquid-phase sintering prevails. Presence of clay in furnace charge and the amount of clay matter that can provide the defined raw materials is crucial when forming the ready product while burning process as it is the envelop for non-plastic inactive particles of ashes.
3. Conclusions
The carried out analysis of bottom ash wastes of thermal power stations has shown that one of the methods to enhance the quality of raw materials is dispersion using grinding in mills which are peculiar with the combined action of impact forces, pressure and shear forces influencing the grinding material.

Resulting from the physical-chemical analysis of ashes in the city of Tomsk it can be concluded that modified ash powder can contribute to the intensive formation of mullite-like compounds while combined burning with clay. It should be noted that the temperature of mullite crystallization according to differential thermal analysis is 933 °C, i.e. to obtain the regular ceramic brick the burning temperature no more than 950–960 °C is enough and that was proved experimentally.

Low content of combustible residues in ash and large amount of micro-dispersed particles less than 3 um contributes to obtaining of products with decreased porosity and that in its turn influence positively on water permeability and frost resistance of ready products.

Introduction of modified ashes into furnace charge, those ashes serving as leaner, leads to the reduction of shrinking deformation of ceramic product and broadens the sintering range.

Therefore dispersion of bottom ash wastes of thermal power stations by means of grinding is an advanced way of enhancing the quality of raw materials of poor quality for its further application in production of ceramic brick. Its introduction in different ratio enables to adjust processing properties both of raw materials and of ready ceramic product as well. Mass use of thermal power stations ashes can reduce the environmental impact and reduce total costs for ashes disposal.

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