

Short Communication

The Influence of High Temperature on the Properties of Solidified Suspension Made of Ash from Fluidized Combustion of Lignite

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Abstract

Our article shows the results of research on ash-water solidified suspensions heated at high temperatures. The ash-water suspensions are used in underground coal mines to fill the voids and cavings resulting from exploitation. The heating of the solidified samples has been conducted to simulate conditions of the process of self-heating of residual coal substances. Similar conditions may also occur on the surface, e.g. during fires, and knowledge of the influence of the high temperatures on these type of materials may be useful when such substances are used as components of the building materials.

For testing purposes we have used the ash from the fluidized bed combustion of lignite with and without the addition of the biomass. The conducted research covered the definition of the high temperature influence on the structure, leachability, phase composition, and mechanical properties of the suspension samples.

Keywords: fly ash, ash-water suspension, backfill, gob filling

Introduction

Among the most important directions of the management of the mineral wastes from power plants is to use them in the building industry, civil engineering, and mining [1]. The appliance range of different ash use varies and depends both on their properties resulting from their origin (the type of fuel), the type of installation, or the method of flue gas desulphurization, as well as the location of their production. This causes the big part of the solid by-products, especially from lignite combustion, to be landfilled in the neighborhood of the power plants [2]. Intense research on extending the possibilities of waste utilization are in progress.

The article describes the influence of heating high temperatures on the properties of solidified ash-water suspensions. The idea to start the subject came from the analysis

of the conditions of ash-water suspension usage in Polish hard coal mining, mainly for limiting the risk of endogenous fire occurrence [3, 4]. The suspensions are transported hydraulically from the surface, and rammed into the cavings appearing behind the front of exploitation (in longwall system). In such places the self heating of the residual coal substances occurs frequently, which may even lead to endogenous fires [3, 5]. The suspensions filling and caulking the voids among the rock crumbs limit oxygen access, cooling the rock and thereby limiting the self-heating process. In many cases the suspensions, just after initial or partial solidification, get into the zone of increased temperature that may reach even 1,000°C.

The analysis of the influence of high temperatures on binding material properties is a much broader issue and relates also to surface conditions. A good example can be researches on the resistance of building materials and thermal insulation materials to the high temperature caused by fires [6-11]. The tests have been conducted to determine the

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effect of temporary exposure of the solidified suspensions to high temperature.

The aim of the researches has been to define the properties of suspensions heated in different temperatures depending on the kind of ash used.

The Subject and Scope of Research

To prepare the suspension we used two types of fly ash taken from the combustion of lignite in the CFB boiler: TB2 – consisting of the addition of wood biomass (not more than 8%) and T2 – without any addition.

The research has been divided into two stages. During the first one the ash-water suspension has been prepared with different ratios of solids to water. The formulas were to fulfil the requirements for gob caulking according to the Polish standard PN-G-11011:1998. Each of the ashes was used to prepare the suspensions of the same fluidity. After the preliminary tests, the cylindrical samples of the height and diameter = 80 mm were prepared and then seasoned in dry conditions for 60 days. In the meantime the samples solidified. During the second stage of the research the solidified suspension samples were heated in a muffle furnace at 400, 600, 800, and 1,000°C. The samples were placed in the chilled furnace and within one hour the given temperature was reached and kept for the following hour. During the next step the furnace was switched off, and the samples stayed there till they reached the temperature of the surroundings, which took from 5 to 10 hours.

To define the influence of heating on the properties of ash-water suspensions prepared on the basis of two different ashes, the following tests were done: macroscopic rating of structure and state of the samples, mass changing, the chemical composition of ashes with use of spectroscopy (ICP-AES), and mass (ICP-MS) emission methods, the compression strength (Rc) of solidified and heated suspension samples, phase composition using X-ray diffraction, as well as leachability of chemical pollution – according to the PN-EN 12457-2.

The Results of Research

Despite similar origin the tested ashes differ in many aspects, inter alia, the chemical composition. For TB2 ash is it the following: SiO₂ 50.40%, CaO 22.49%, Al₂O₃ 13.72%, SO₃ 5.44%, Fe₂O₃ 3.95%, MgO 1.49%, Na₂O 1.18%, K₂O 0.75%, P₂O₅ 0.36%, and components for T2 ash: SiO₂ 53.50%, CaO 13.90%, Al₂O₃ 19.71%, SO₃ 3.80%, Fe₂O₃ 4.48%, MgO 2.07%, Na₂O 1.55%, K₂O 0.76%, and P₂O₅ 0.33%. This is particularly evident in the content of calcium oxide, which is bigger in the ash TB2 at the expense of Al₂O₃. Sulphate content is also slightly higher in the ash TB2. This may suggest that coal co-combusted with the biomass showed the bigger content of sulphur and the addition of biomass, just like the calcium oxide was to limit SO₂ emissions.

From the ashes we prepared ash-water suspensions of similar characteristics in fluidity – 180 mm, which is important for its safe of hydraulic transport and applications. The suspensions differ in the a/w proportion (ash to water), which means the total content of solid parts. The T2 suspensions contain 44.4% of ash T2, the suspensions TB2 – 53.5% ash TB2. This resulted in the lack of the supernatant water in the case of TB2 suspensions and for the suspensions T2 the amount reached 6.3%. The influence of the used type of ash was also visible during the setting time: the TB2 suspensions bond twice as fast (48 h) as the T2 suspensions.

The change in color and cracks on the same samples were observed after heating. It was especially visible in the case of TB2 suspensions heated at higher temperatures — the characteristic yellow tint was noticed as well as the cracks, whose number and size were the biggest for 1,000°C.

Sample heating caused a significant decrease in the mass of the samples: 8% for T2 suspensions and 16% for TB2 at 400°C and respectively, 13% and 25% at 1,000°C. The mass loss as a result of heating may be caused by water evaporation and, at the higher temperatures, burning of the residual coal substances and changes in the phase composition of the suspensions.

In the next step the heated suspension samples tested on compression strength – Rc, significant differences were found for reference samples (no heating). Samples suspensions of TB2 ash were characterized by the values of Rc at 1.2 MPa and ash T2 – only 0.1 MPa – over 20 times less. This may result from differences in the chemical composition of ash (bigger content of CaO in the TB2 ash) and bigger content of ash in suspension TB2.

Heating at ever higher temperatures caused the decrease in the value of Rc of the samples. In the case of the TB2 samples: heating the samples at 400°C caused the Rc decrease to 28% of the initial value, and in 1000°C – disintegration of the samples, and decrease of Rc in the other samples to 1% of the initial value. This value was close to the Rc of the T2 suspension samples heated at the same temperature. To compare, the Rc of the T2 suspension samples heated at 400°C reached ca. 58% of the initial value, and the ones heated at 1,000°C – about 34%.

Phase Composition

The phase compositions before and after heating are shown in the diffractograms (Figs. 1a and 1b). The main components of the suspensions T2 and TB2 were ettringite (hydrated calcium sulfide aluminate), calcium carbonate (in the form of calcite and vaterite), and quartz. What is more, gypsum hemihydrate and hematite were identified in the T2 suspension. The heating of the samples caused the disappearance of the ettringite crystals (at 400°C) and calcium carbonate (at above 800°C). Anhydrite appeared — in the samples heated to 400°C and higher, but in the samples heated to 1,000°C the feldspars and gehlenite appeared.

Leachability

Research on properties of the water eluate of the heated suspension samples and their composition have been conducted to define the influence of temperature on the leachability of chemical pollutions. The scope of the tests respected the requirements of the norm PN-G-11011, but covered the content of a greater number of metals and the indicators such as total and carbonate hardness and conductivity.

The heating of the suspension samples influenced the composition and property of water extras obtained from them. The observed changes have variable courses depending on the tested index, heating temperature, and the type of ash used to prepare the suspension.

Along with the heating temperature increase, for the both types of suspension we observed the decrease of total mineralization of the water extracts – both anions and cations. The total mass of the mineral compounds in the water eluate in the samples heated to 1,000°C decrease to about 70% for TB2 and about 75% for T2 in comparison to the water eluate of the reference sample (not heated). The biggest role in these changes was seen in the content of calcium cations and sulphate anion (Fig. 1c). The similarity in the courses is noticeable for the two types of the samples, despite the differences in absolute values.

The content of the sulfate for both types of suspension exceed the limit value according to the norm PN-G-11011, which does not disregard these suspensions as mixtures for

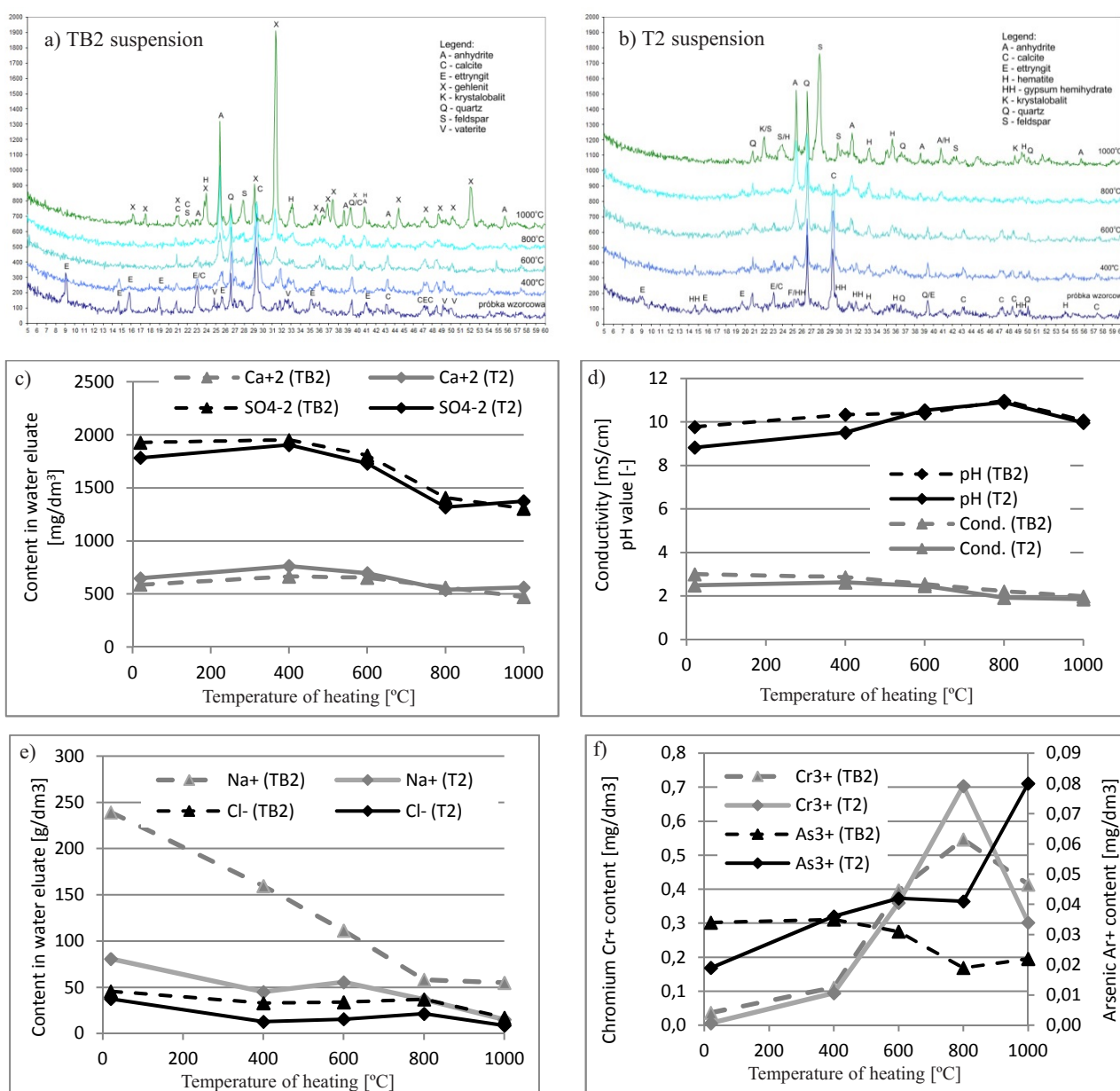


Fig. 1. Property changes in heated suspension samples: phase composition of suspension a) TB2, and b) T2; changes in the water eluate of suspension concerning: c) calcium and sulfates, d) pH value and conductivity, e) sodium and chlorides, and f) arsenic and chromium.

backfilling, as when allowing the tests the amount of underground water flowing to the mine area should be taken into consideration. What is more, in some mines the increased content of sulphates in eluate water is really needed because of the possibility of binding barium ions from mine water.

Along with decreasing mineralization of the samples the eluate conductivity falls, and at the same time pH index rises (Fig. 1d). What is characteristic is that the values of these indicators for two kinds of suspension differ significantly in the case of the reference samples, and the higher the temperature, the smaller the differences. The higher pH and the smaller content of calcium ions in the eluate of samples heated in the highest temperatures may testify to the thermal process of dissolution of the minerals containing calcium, and results in the occurrence of calcium oxide, which in the reaction with water changes into sparingly soluble calcium hydroxide.

The tendency of reducing the content of eluate components with the increasing heating temperature is also observed in the case of chlorides and sodium (Fig. 1e). For the unheated samples the content of sodium in TB2 (with biomass) reaches almost 240 mg/m³, and for T2 – three times smaller. In both cases these contents decrease with the increase of heating temperature and reach a level four times lower for the TB2 and over five times in the case of T2.

Different tendencies have been observed in the case of the change in the content of some metal ions. A good example can be barium, which shares in the eluate of both types of suspension rises for the higher heating temperature. This applies also to other heavy metals: molybdenum, chrome, and arsenic (the last one only for T2). Especially high content of chrome (above the limit of standard PN-G-11011) has been observed in the suspension of ash T2 heated to 800°C (Fig. 1f). The increasing amounts of metals in eluates may result from increasing solubility growing together with pH index [12, 13]. The content of other heavy metals such as zinc, lead, mercury, and cadmium reached the marginal low level.

Conclusions

This article presents the results of research on the properties of two different kinds of ash: from lignite combustion (T2) and co-combustion of lignite and biomass (TB2). Despite similar origins (the same type of CFB boiler, the same kind of lignite) the ashes differ in many aspects – mainly in chemical composition (the content of CaO) and water demand. The suspensions from both ashes were prepared in such a way as to have similar technological properties (consistency) that caused, however, differences in the total content of solid parts. Both kinds of suspensions fulfil the requirements of the norm PN-G-11011 for gob caulking (subject to sulphate content). The conducted research reveals the great influence of heating on the properties of the samples, which shows the decrease in the mass and uniaxial compression strength. This influence was, in many

cases, in accordance with the increase of temperature, and at the same time more distinctive for the suspensions made of the TB2 ash. The heating of the solidified suspension samples caused the decrease of mineralization of their eluates and the change in the content of components. In most cases the changes were similar for both kinds of suspensions. What attracts attention among the leachability tests is the content of such heavy metals as arsenic and chrome, which are higher for the heated samples.

The special role goes to the temperature of 800°C, which on the graphs of parameters changes and eluates components shown as a local extreme, especially obvious in the case of the suspension from co-combustion. This temperature refers approximately to the temperature of decomposition of some important components of suspension, among them calcium carbonate or gypsum. This may explain the bigger loss of mass, significant decrease of Rc, and visible cracks on the TB2 samples heated at 800°C and 1,000°C in comparison with suspension of ash T2.

The greater content of calcium carbonate and the products of flue gas desulphurization that contribute greatly to the increase of the resistance of TB2 at low temperatures may be responsible for higher susceptibility to the influence of high temperature. To prove these dependences and to define their strength, further research on suspensions of different recipes made of different kinds of ash is required. Such research is in progress now.

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