MINERAL MATTER TRANSFORMATION IN OXY-FUEL COAL COMBUSTION

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The paper presents the results of the mechanical, electrical, CCSEM and XRD measurements of hard coal, conducted in simulated conditions of sintering in atmospheres of O_2/CO_2. The changes of the coal ash resistivity are correlated with the content of the oxides and with the sintering temperature determined by the mechanical test and Leitz method. The SEM-EDS analysis was conducted for deposits on the probe. The changes of the measured ash samples, observed during sintering process in O_2/CO_2 atmosphere, were discussed in the ash microstructure point of view.

Keywords: coal combustion, ash, slagging, sintering

1. INTRODUCTION

Coal will remain fossil-fuel energy source and then two problems have to be solved: reduction of greenhouse gas and slagging and fouling prediction. The formation of sintered ash and slag deposits on heat exchange surfaces in coal, biomass or sewage sludge co-firing, is a very important problem, because massive built-up of ash deposits forces to interrupt energy conversion for cleaning boiler elements. The formation of sintered deposits is usually explained by the presence of a liquid phase or molten surface layer on ash particles. Such parameters as viscosity and surface tension (both temperature dependent) of ash particles, govern the rate of sintering according to the model proposed by Frenkel and Raask (Frenkel et al., 1945; Raask, 1979). When all ash fusion temperatures are low, the risk of slagging is very high and readily inferred. Similarly, when all ash fusibility temperatures are high, it is easy to predict that the risk of slagging is very low. Currently carbon capture and storage technologies are the focus of research centers and industry. Carbon capture includes oxy-fuel combustion. During oxy-fuel combustion a combination of O_2 and recycled CO_2 is used for combusting fuel. A dfferent gas atmosphere resulting from oxy-fuel combustion gives rise to questions related to the properties of ash and its deposits (slagging and fouling) (Wang et al., 2008; Werther et al., 1999; Zhang et al., 2004). Slagging and fouling are the results of chemical reactions and physical transformations occurring mainly under in fuel and combustion products. Natural fuels contain many mineral components constituting primary plant or rock material (contemporaneous) and also gathered in later periods (epigenetic). Outer mineral matter which occurs in the form of sand, loam, granite, gypsum or clay can be removed mechanically and does not interfere with the process of fuel burning. The inner substance, however, occurring mainly in the form of heavy metals bounded with the fuel organic substance, is not possible to be removed mechanically, and is the main hazard related to ash formation during the combustion process. Currently, in power stations hazard extent is being reduced by selection of fuel, sieving of mineral matter, adjusting boiler's work parameters in order to avoid temperature leaps, and applying additions (calcium sorbent). Additions cause transformation of

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physical or chemical properties of fuel, for example kaolin clay, containing mainly kaolinite that captures ferrous alkali. Fly ash particles encountering on their way obstacles in the form of, for example, heaters' tubes, collide with them. This occurs mainly in corner parts exposed directly to dust (windward part). On the elements not directly exposed to dust (leeward part) collisions of particles with surfaces are of non-resilient nature. What can be observed as the result of that process is condensation of hot particles of dust on cooler elements, and, consequently, also diffusion process and chemical reactions between dust particles and surface material on which dust condenses. Properties of deposits formed depend on the combusted fuel composition and on firing conditions. The standard ash fusion test (AFT) - the predictive tool for plant performance - has poor accuracy. It is a subjective, wholly empirical test, based on observations rather than measurements, which gives no direct indication of the propensity of heated ash to become sticky and cause furnace slagging.

The paper presents the results of mechanical (Moroń et al., 2002), thermal and electrical measurements of ash samples prepared from bituminous coal, sewage sludge and biomass. The sintering tendency of the ashes was based on the chemical analysis, Ash Fusion Test data, and Equilibrium Phase Diagrams. Correlations were drown between the ashes sintering temperature and electrical resistivity of the samples (Ahn et al., 2002; Raask, 1979). The resistivity changes were correlated with the equilibrium phases formed during heating process. Ash fusion standard temperature (AFT) systems, using digital imaging techniques, can mitigate some of the problems associated with the standard AFT test (Moroń et al., 2002; Płaza et al., 2006). The ash fusion test (AFT) is still widely used to assess the deposit characteristics of coal in combustion systems and initial deformation temperature (IDT) is accepted as the temperature where ash softens and becomes sticky.

2. EXPERIMENTAL PART

To find answers about the impact of O_2/CO_2 atmosphere on the process of mineral matter transformation, measurements were conducted during ash sintering process in the temperature range 500 °C - 1200 °C (resistivity, breaking stress, computer control scanning electron microscopy - CCSEM, X-ray diffraction). The measurement procedure is presented in Figure 1.
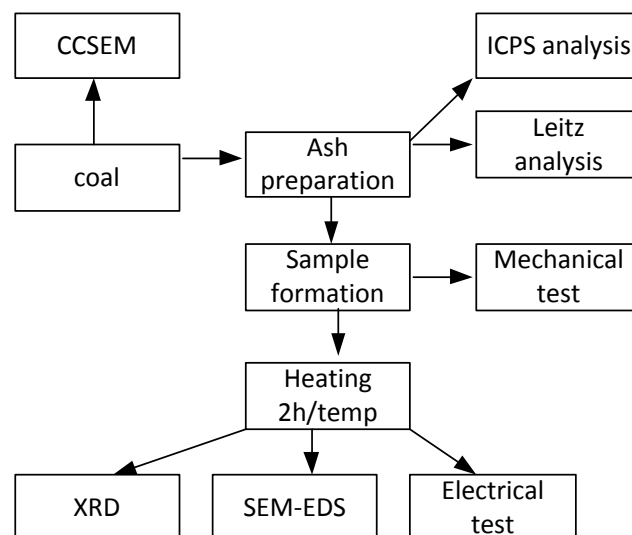

Fig. 1. Measurement procedure

XRD, CCSEM, SEM-EDS and electrical experiments were conducted. The samples for electrical and mechanical experiments were prepared with ash pressed to form a cylinder with a diameter equal to $3.2 \cdot 10^{-4}$ m^2 and thickness of about a half centimeter. The samples were isochronally heated, for two

hours at every 100 °C in temperatures from 500 °C to 1100 °C, and, after heating process, cooled to room temperature (RT) in a dry atmosphere. Right after such thermal processing, the thickness of samples and the electric parameters were measured at room temperature. The heating procedure was performed in CARBOLITE CFW 1200 furnace with 3216P1 temperature program selector. The electrical experiment was conducted by placing a sample on an isolated (grounded) base in Faraday cage, and connecting in (in two electrode system) to Keithley meter. Coal samples were prepared for CCSEM and morphological analysis by first grinding to 80% passing 200 mesh to match the size of the coal fired in a pulverized coal combustion system. These ground samples were dried, mixed with molten carnauba wax, placed in a mold, and allowed to harden. The coal mounted in carnauba wax was cross-sectioned and polished to a fine (1 μm) finish. The samples were coated with carbon to provide a conductive surface for imaging. The polished cross-sections were placed in the electron microscope equipped with an x-ray microanalysis and image analysis system for analysis. The SEM was operated at 15 kV. Backscattered electron imaging was used for morphological analysis. In backscattered electron imaging, higher-atomic-number materials appear brighter than lower-atomic-number materials – regions containing iron (atomic number 26) appear brighter than those containing silicon (atomic umber 14).The fouling in oxy-fuel combustion technology was measured in 3-meter flow reactor with probes (Fig. 2).
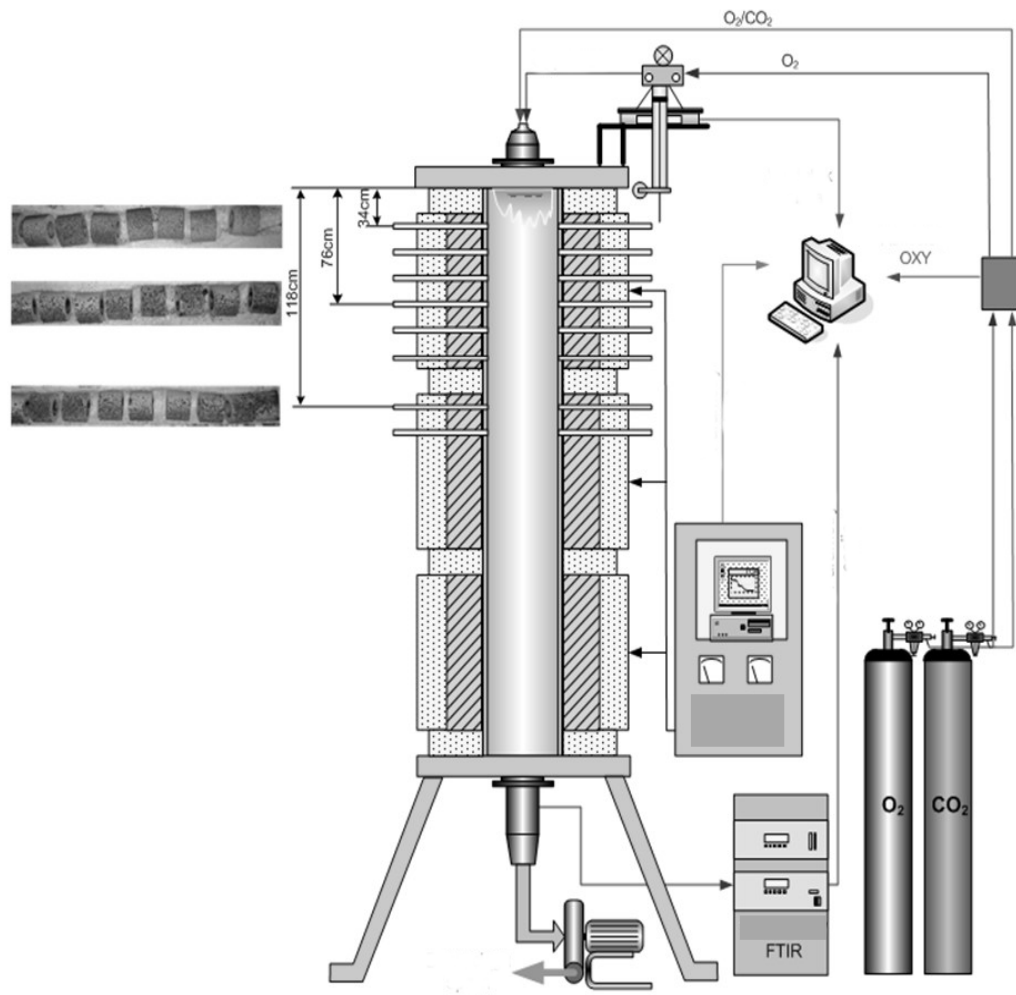

Fig. 2. Measurement system for fouling process (flow reactor with probes)

3. RESULTS

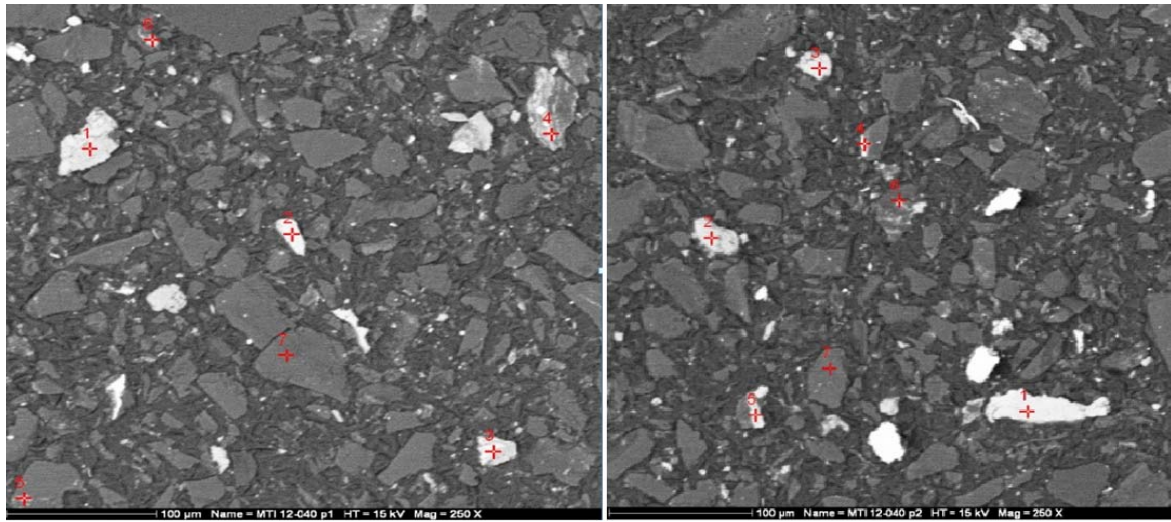The analysis of coal Janina (backscattered electron images) are shown in Fig. 3.

Fig. 3. Backscattered electron images of coal sample

The presented backscattered electron images reveal large, excluded particles which can be rich in silicon, aluminum, and potassium, (points 1 and 2 in Figures 3a and b), calcium and magnesium (point 3, Figure 3a), or quartz (point 3, Figure 3a). Particles present in the coal structure are also rich in these elements and can also contain pyritic minerals as found in point 4 of Figure 3a and point 4 of Figure 3b. An analysis of the coal matrix found appreciable levels of silicon, aluminum, phosphorus, sulphur, potassium, calcium, and iron. Phosphorus appears to be mostly associated with the organic matrix as does sulphur with the exception of pyritic minerals found in the included particles. The results of elementary analysis are shown in Table 1.

Table 1. The results of elementary analysis of excluded and included particles of mineral matter and coal matrix

		Na [wt%]	Mg [wt%]	Al [wt%]	Si [wt%]	P [wt%]	S [wt%]	K [wt%]	Ca [wt%]	Fe [wt%]	O [wt%]
						particle (a)						
1	excluded	0.2	0.2	23.1	32.3	0.4	0.5	2.7	0.2	0.7	39.9
2	excluded	0.2	0	25	35.8	0.4	0.3	14.5	0.2	0.9	22.6
3	excluded	0.5	16	1	0.8	0.2	0.6	0.2	26.4	5.3	49
4	included	0.4	0.3	4.9	9.8	1.2	38	0.7	0.3	38.6	5.9
5	included	0.3	0.3	18.4	41.8	1.1	1.2	3.5	0.4	1	32
6	included	0.2	0	31.1	53.3	1.5	1	0.3	0.3	0.8	11.4
7	Coal matrix	0	0	4.5	16	14.8	9.7	3.7	3.5	5.3	42.6
						particle (b)						
1	excluded	0.2	0.2	24.1	33.6	0.3	0.4	11.4	0.6	0.9	28.4
2	excluded	0.2	0.3	25.8	38.7	0.7	0.8	2.2	0.2	1.5	29.6
3	excluded	0.2	0.1	0.7	54.4	0.3	0.2	0.1	0.1	0.4	43.3
4	included	0.6	0.3	3.2	6.6	1.2	41.9	1	1.5	43.9	0
5	included	0.2	0.7	19.2	33.3	0.7	3.1	3.1	0.2	3	36.6
6	included	0.2	0.2	0.4	93.2	0.8	0.5	0.6	0.6	1.2	2.2
7	coal matrix	0	0.3	13.4	29.6	7.1	13	1.4	4.1	1.6	29.5

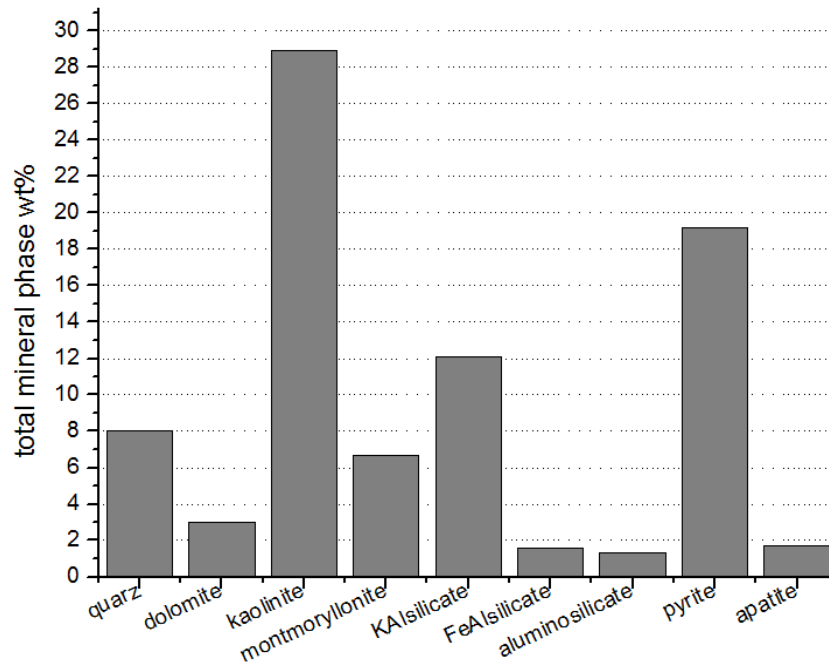Analysis of mineral matter in Janina coal was conducted. The results are shown in Figure 4.

Fig. 4. Major mineral matter in Janina coal

The major mineral matter in Janina coal occurs in the form of kaolinite (28.9 wt. % of mineral matter), pyrite (19.2 wt. %) and A-Al-silicate (12.1 wt. %) and quartz (8%). Other minerals (dolomite, montmorillonite, Fe-Al-silicate, aluminosilicate, apatite) are characterised by the contents of a row of single percentage. Particle size distribution of major and minor mineral matter in particles with size from 1 μm to 100μm is shown in Fig.5.
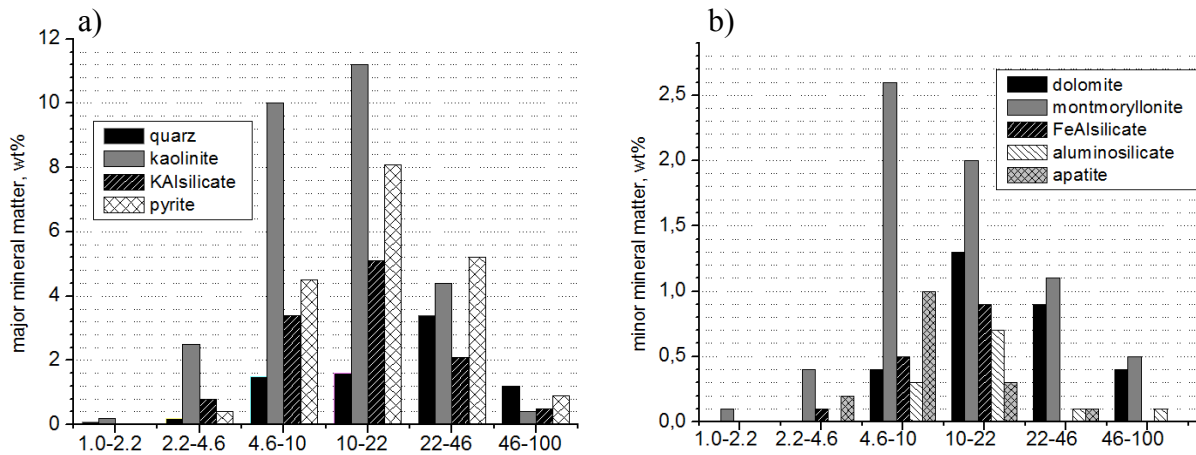

Fig. 5. Particle size distribution of Janina coal mineral matter major (a) and minor (b)

The analysis reveals that the majority of the minerals (37.8 %) are 10 to 22 microns in size, followed by minerals 4.6 to 10 microns (29.6 %), 22 to 46 microns (20.2 %), and the large particles accounted for 4.8 %. The smallest bin size, 1.0 to 2.2 microns contained the least (0.9 %) of the minerals found. The major minerals identified were kaolinite (28.9 %), followed by pyrite (19.2 %), potassium aluminum silicates (12.1 %), quartz (8.0 %), montmorillonite (6.7 %), and dolomite (3.0 %). The sum of the mixed layered clay minerals was 52.5 %. The unclassified minerals accounted for 11.2 % of the total.

When ash fusion temperatures are low, the risk of slagging is very high and readily inferred. Similarly, when all ash fusibility temperatures are high, it is easy to predict that the risk of slagging is very low. The ash fusion test (AFT) is still widely used to assess the deposit charactersctics of coal in combustion systems and initial deformation temperature (IDT) is accepted as the temperature where ash softens and becomes sticky, allowing further slag formation.. However, there are uncertainties in its use as a predictive tool for plant performance that is poor repeatability and reproducibility of ash fusion measurements. The ash fusion test has poor accuracy. It is a subjective, wholly empirical test, based on observations rather than measurements, which gives no direct indication of the propensity of heated ash to become sticky and cause furnace slagging. Because of these problems our group is working on new methods, inter alia mechanical and electrical ones. The ash sintering process was studied by measuring changes of tensile stress, electrical resistivity and apparent density during ash sintering process. The results are shown in Fig. 6. On the basis on the results presented in Figure 6, the following observations were made: two characteristic ranges of the resistivity, tensile strength and apparent density changes, a good accordance with the characteristic temperature ranges for resistivity, tensile strength and apparent density changes and a good accordance with the characteristic points defined as the intersection of linear approximation of the presented results. On the basis of the nonstandard methods for Janina coal ash the characteristic sintering temperature was determined as a value 760 ºC ± 10ºC.

Energy production from coal combustion results in the emission of carbon dioxide that is the dominant contributor of greenhouse gases. The policy and regulation of reduction of CO_2 emission in well-developed countries is regulated by international initiatives (Kyoto protocol and Intergovernmental Panel on Climate Change).
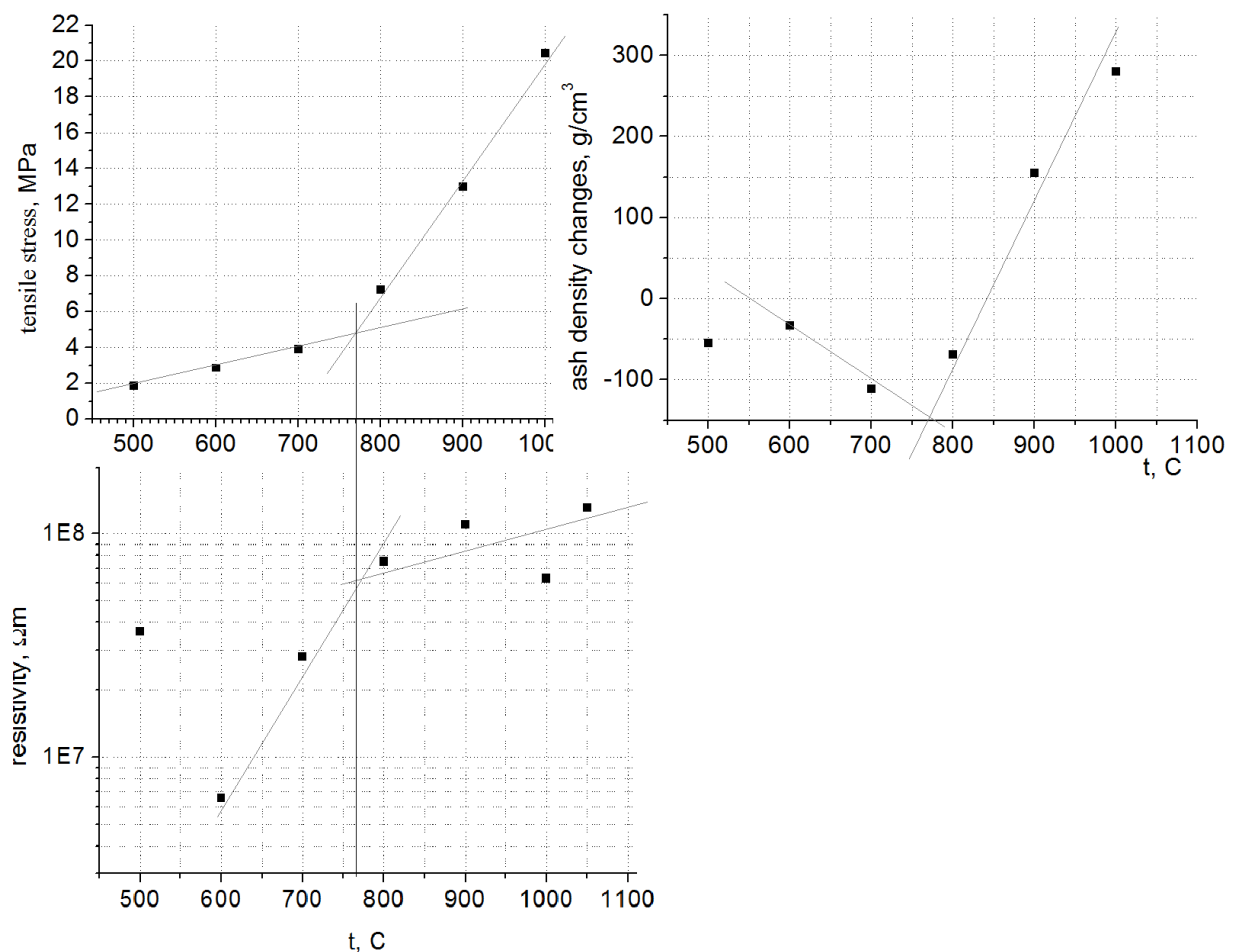

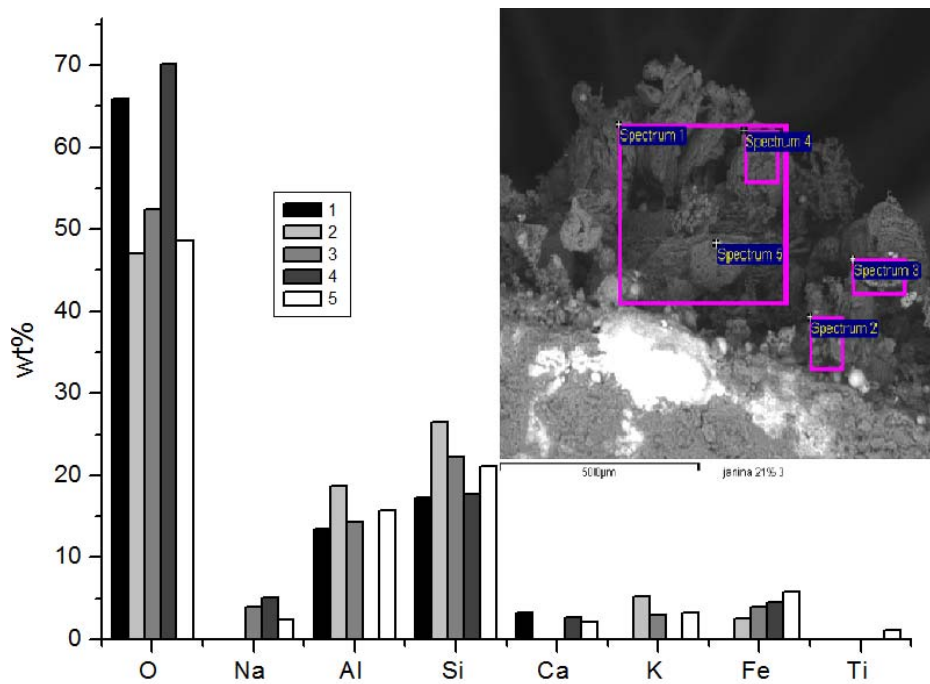Fig. 6. Janina Coal ash resistivity, tensile strength and density changes during sintering process

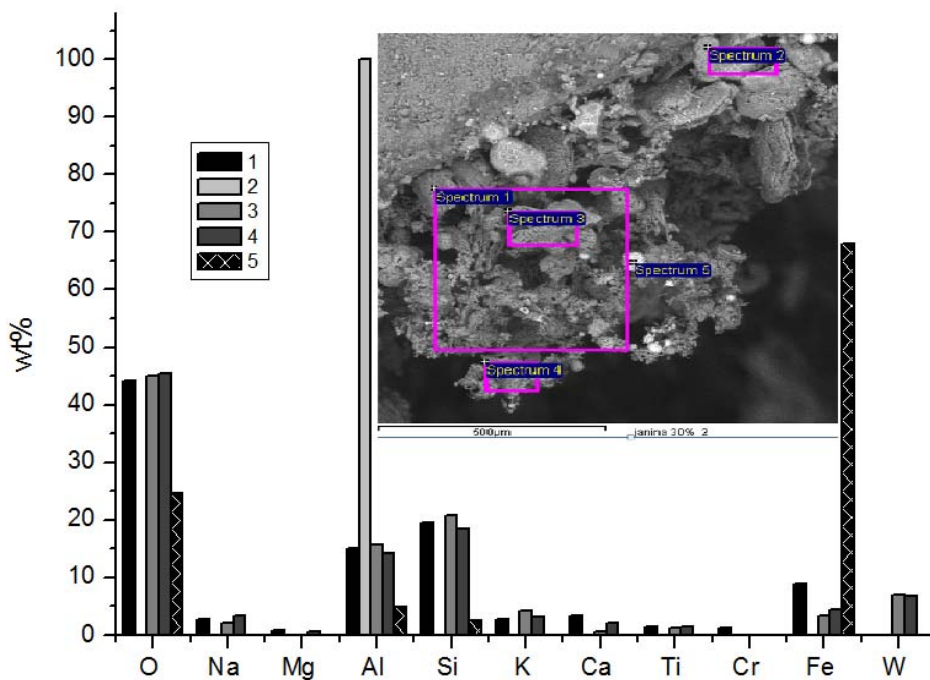Fig. 7. Janina Coal ash deposits during combustion process in 21%O_2+79%N_2 atmosphere

Fig. 8. Janina Coal ash deposits during combustion process in 30%O_2+70%N_2 atmosphere

One of the options for capture and storage of CO_2 from coal combustion and gasification is oxy-fuel combustion in oxygen rather than in air, with recycled flue gas. This technology requires extensive research in the light of a tendency to slagging and fouling because gas temperature and the amount of excess air determine evaporation of mineral matter species – particle temperature strongly depends on oxygen concentration. Combustion atmosphere influences the fragmentation of coal particles and excluded minerals and coalescence of included particles (Wall et al., 2009; Gupta et al., 1998). The presented experiment (measuring system shown in Figure 2) was conducted to examine the rate the Janina coal ash deposit formation on the probe, during combustion process in two atmospheres: 21 % O_2 and 79 % N_2 and 30 % O_2 and 70 % CO_2. While comparing the thickness of deposits on the probes

it was found that the rate of deposit formation during combustion in 30 % O_2+70 % CO_2 atmosphere was higher than that in 21 % O_2 + 79 % N_2 atmosphere. The deposits on probes placed at a distance of 116 cm from the base of the flame, were examined by SEM-EDS. The results are shown in Figs 7-8.

On the basis of SEM-EDS results for Janina coal deposits during combustion in 21 % O_2+79 % N_2 atmosphere, it was determined that: the inner layer is rich in Si, Al and K elements; the middle layer is rich in Na elements; the outer layer is rich in Fe and Ca elements; the middle part contains regular particles (size about 100 µm) rich in Si, Al, Fe, K and Na elements and on average, the layer contains relatively large amount of Si, Al and Ca elements.

The SEM-EDS results for Janina coal deposits during combustion in oxy-atmosphere (30 % O_2 + 79 % N_2) suggest that: the inner layer contains a relatively high level of Al elements; the middle part of deposit layer contains a relatively high concentration of K, Fe, Si and Al elements; in the outer part of deposit layer the concentration of Na, Ca, Ti and Fe is higher than that in the middle part, but the concentration of K, Al and Si is slightly smaller; The entire volume of the layer contains relatively small (<50 µm) particles rich in Fe elements (about 70 %) and a relatively large amount of Si, Al, Fe K Na and Ti elements. The comparison of SEM-EDS results for deposit layers obtained during Janina coal combustion in 21 % O_2 + 79 % N_2 atmosphere and in 30 % O_2 + 70 % CO_2 suggests that the distribution of elements in these layers depends on the atmosphere (Figure 9).
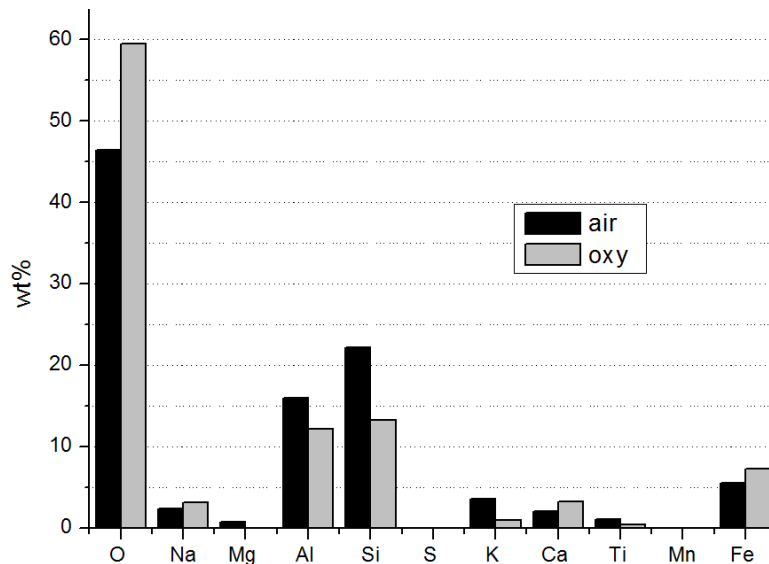

Fig. 9. Janina Coal ash deposits during combustion process in air and oxy atmosphere, comparison

In general, the deposit layer produced during combustion of Janina coal in 30 % O_2 + 70 % CO_2 atmosphere contained slightly lower content of Al, Si, Ti and K elements and the higher content of Na, Ca and Fe. Probably this effect is associated with the effect of particle dimensions and deference in composition of ash associated with different temperatures during combustion in tested atmospheres (Wall et al., 2009; Gupta et al., 1998). In deposits produced during combustion of Janina coal, no sulphur was found.

4. CONCLUSIONS

- New measurements in a laboratory scale comparing changes of ash properties such as resistivity, tensile strength and apparent density were made.

- The procedure of the determination of coal ash fusion temperature, based on resistivity, tensile strength and apparent density changes, has been specified.

- The Janina coal morphology has been determined – major mineral matter in Janina coal occurs in the form of kaolinite (28.9 wt. % of mineral matter), pyrite (19.2 wt. %), K-Al-silicate (12.1 wt. %) and quartz (8%). Minor mineral matter occurs in the form of dolomite, montmorillonite, Fe-Al-silicate, aluminosilicate and apatite.

- The mineral matter particle size distribution in Janina coal has been determined - the majority of the minerals (37.8 %) are 10 to 22 microns in size, followed by minerals 4.6 to 10 microns (29.6 %), 22 to 46 microns (20.2 %), and the large particles accounted for 4.8 %; the smallest bin size, 1.0 to 2.2 microns contained the least (0.9 %) of the minerals found.

- Oxy atmosphere promotes the formation of deposits, the deposit layer produced during combustion of Janina coal in 30 % O_2 + 70 % CO_2 atmosphere contained slightly low content of Al, Si, Ti and K elements and the low content of Na, Ca and Fe. Probably this effect is associated with the effect of ash particles size – the ash particles were finer when produced in oxyfuel conditions due to reduced gas flow and increased temperature. The combustion conditions affect the ash particle size distribution of elements. In deposits produced during combustion of Janina coal, no sulphur was found.

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