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Dielectric properties of coal ash

Laura González Valdés, Aage Valentin Friis, Dorota Nowak-Woźny

Politechnika Wrocławska, Wydział Mechaniczno-Energetyczny
Katedra Technologii Energetycznych, Turbin i Modelowania Procesów Cieplno-Przepływowych
E-mail: laura.gonzalez-valdes@pwr.edu.pl

ABSTRACT

Mineral matter of coal causes serious operational problems related to ash deposition in coal fired power plants such slagging and fouling, and so it has become the main subject of study in terms of current utilization. Moreover, the standardized tests currently used as the preferred predictive tools for slagging properties of coal sources have been lately reproved in the literature and uncertainties arrive due to the poor repeatability and reproducibility. That is why, methods for determining the sintering temperatures are being extensively investigated across the industry. This study focuses on the electrical properties of coal ash and its relation to the ash sintering process, where physical and chemical processes take part inside the material. The following methodology is based upon the continuous registration of the changes of resistance measured as an AC and DC property. The proposed laboratory stand allows measuring 'in situ' a coal ash sample being heated to analyse its electrical properties. It was found that the values measured are temperature dependant and could reflect the chemico-physycal changes in the material, which may directly suggest the transformation of the intrinsic properties, giving insight into the sintering process.

KEYWORDS: *coal, mineral matter transformation, ash sintering, dielectrical properties*

1. INTRODUCTION

Coal is generally considered for many purposes as consisting of two kinds of materials: on the one hand, the organic components or macerals and, on the other, a range of minerals and other inorganic constituents, widely referred to as mineral "matter" [1]. While the organic components are fundamental to define the nature of the coal (type and range) and all the benefits derived from coal come essentially from the maceral components, it is precisely the mineral matter that is the main subject of study in terms of current utilization [2, 3, 4].

The non-combustible component leaves a residue of ash when the coal is burned, giving rise to depositional problems on furnace walls such as slagging-ash deposits in the high temperature areas of furnaces directly exposed to flame radiation- and fouling–ash deposits in the convection section of the boiler [5]. Serious operational hazards such as channel burning, pressure drop problems or unstable operation may result in cut backs, causing direct loss in power production [6]. The mineral matter can also be a source of other operational challenges such unwanted abrasion, stickiness, corrosion or contamination associated with the handling and use of coal. That is why, the knowledge and understanding of the mineral matter transformation has a direct impact on handling ash-related problems and so increasing plant performance [7].

To date a number of techniques are available to characterize the mineral matter present in coal; however, a universal method for a complete qualitative and quantitative characterization does not exist due to the complex character of these constituents [8]. Given that each method has different advantages and limitations, it is generally concluded that the best approach is to use a combination of them depending on the purpose of study, degree of detail desired, and availability of techniques [9].

Coal ash fusion characterization and the ash fusion temperatures (AFTs) are important parameters for the coal industry [2]. Although this standardized AFT test is currently used as the preferred predictive tool for slagging properties of coal sources various authors have described uncertainties due to the poor repeatability and reproducibility [10, 11]. This leads to the search for a new approach and new techniques to analyze the mineral matter transformations under thermal treatment.

The proposed methodology is based on a series of non-standar electrical measuremets, namely ESR measurements (Equivalent Serial Resistance), on a coal ash sample placed as a dielectric between two electrodes [12]. Figure 1 shows a graphical representation of a capacitor. This way to evaluate the ash fusion characteristics may be taken from the ceramic industry as coal ash is the combination of silica and metal oxides, which in turn, is very similar to the raw materials of the conventional silicate ceramics industry [13]. The electrical conductivity method may be used to interpret phase changes during powder sintering as the electrical conductivity is related to the concentration of metal ions and it depends on the temperature increase [14]. That is why, the dielectric properties of the selected coal ash sample were measured as a function of temperature and frequency.

Though very few in number, investigations and experiments on the electrical properties of ashes have been conducted during the second half of the 20th century for various reasons. Early studies conducted on refuse ashes in the UK were done with focus on the ash behavior in electrostatic precipitators and thus with focus on the resistivity of the fly ashes. The resistivity was shown to peak around 100°C and decline with the increase of temperature afterwards with high similarity to the characteristic of a semiconductor [15].

Measurement of electrical properties to determine ash sintering temperatures and thereby improve the common ash fusion tests were proposed in the 80's and early 90's both as a supplement to the ash fusion test and as a separate methods for determining the onset of fusion in ashes. The lack of repeatability of the results obtained by these

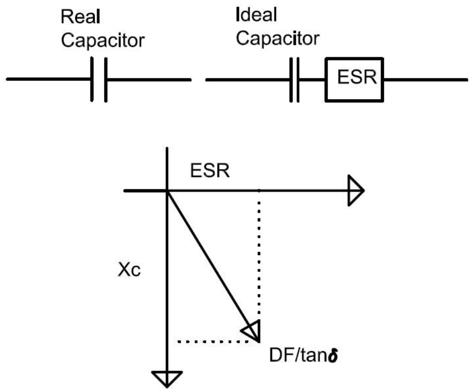

Fig. 1: Capacitor graphical representation

experiments was however problematic and critics regarded the inaccuracy too high for the method to provide a significant improvement to the already well-known methods. Other problems, such as the variations in contact between the electrodes and the ash samples under oxidizing conditions were assumed to be too problematic for developing a standardized test based on electrical properties [16].

A literature review on the subject shows, that none of the aforementioned scientific research has been continued extensively and the very fact that no such methods have achieved commercial success by a widespread adaptation in the industry suggests, that further research on the subject is needed. Moreover, any of the above have tried to relate the sintering transformation on the ash sample cause by temperature changes with its dielectrical properties in spite that the electric method may provide valuable information about the phase changes and the transformation of the microstructure of the sample during the heating process [17].

2. Materials and methods

A typical brown coal from a Polish mine was selected for this study. The raw fuel was placed in a muffle furnace in order to prepare an ash sample by slow combustion (about 48 hours) at low temperature (500°C). In order to obtain a homogeneous sample, only the portion passing through a 0.5 mm sieve mesh was used in this study. An ash sample of 1.5 g was formed into a cylindrical pellet with a diameter of 20 mm using a steel matrix. In order to create a compact powder, the pellet was pressed into shape with a pressure of 20 MPa for a few seconds in a hydraulic press. To avoid the rather delicate and porous pellet sticking to the sides of the matrix and thus cracking while being removed for the experiment, a cylindrical plastic liner was inserted prior to the compressing.

The sample pellet was then placed between two copper electrodes, with contact surfaces corresponding to those of the pellet. The connection to the electrodes was made by isolated 1.5 mm copper wires, which were further isolated by a heat resistant Silica Yarn sleeve. Figure 2 shows the electrodes used in the study and their specific dimensions.

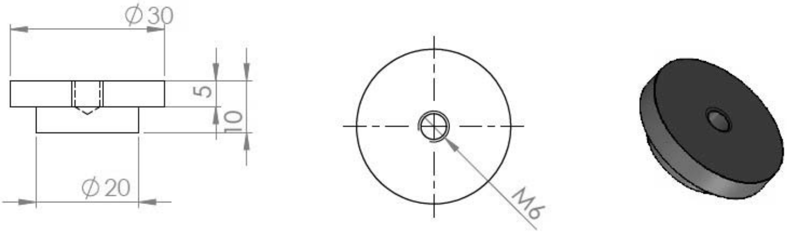

Fig. 2: The copper electrodes. All dimensions in mm

AC measurements were done using a Quadtech 7600 Plus Precision LCR meter, which was directly connected to a computer, where all data were registered and stored on site. For each temperature a series of measurements were taken at various frequencies ranging from 0.5 kHz to 2 MHz. Different variables might be chosen for measurements such as dissipation factor (DF), Equivalent Serial Resistance (ESR) and Capacitance in both parallel and serial (Cp, Cs). The measured values displayed by the apparatus and so presented in this study are all averaged values based on three measurements at the same frequency.

DC measurements were done using a Keithley 6517B Electrometer/ high resistance meter. This apparatus reads out a single ohmic resistance value (R) based on an applied DC voltage and a measurement of the current. To avoid measuring outside the ranges of accuracy given by the supplier of the apparatus a 10MΩ resistance was parallelly inserted into the circuit.

The furnace used for the experiment, is a Czylok SM2002 electrical furnace. The sample was heated at ambient air from room temperature to 900°C at a heat rate of 50°C pr. minute. In the interval 400-500°C measurements were done at every 50°C and in the interval 500°C to 900°C at every 25°C. These temperature ranges were chosen, as the initial sintering processes of ashes are assumed to take place here resulting in changes in the electrical properties of the sample. In order to avoid EMI, the furnace was put in standby whilst doing the measurements at each temperature.

The experimental setup is depicted in Fig. 3, showing the direct connection to the Quadtech 7600 Plus Precision LCR meter [18] used for AC measurements and above, the Keithley 6517B Electrometer/ high resistance meter employed for the DC measurements [19].

3. Results and discussion

The coal ash resistance measured in both AC and DC circuits was the parameter chosen to be analyzed in the following section.

As it can be seen in Fig. 4, the AC experiment shows changes in ESR as a function of temperature. For all frequencies, the ESR measurements show similar patterns with no distinct systematic deviations. Although it is important to notice that the ESR values descrease as the frecuency increases, going flat in the high frequency region. The values measured are generally peaking between 525 and 575°C with an overall peak at 575°C. Given that ESR is related to intrinsic properties of the material pertaining to physical

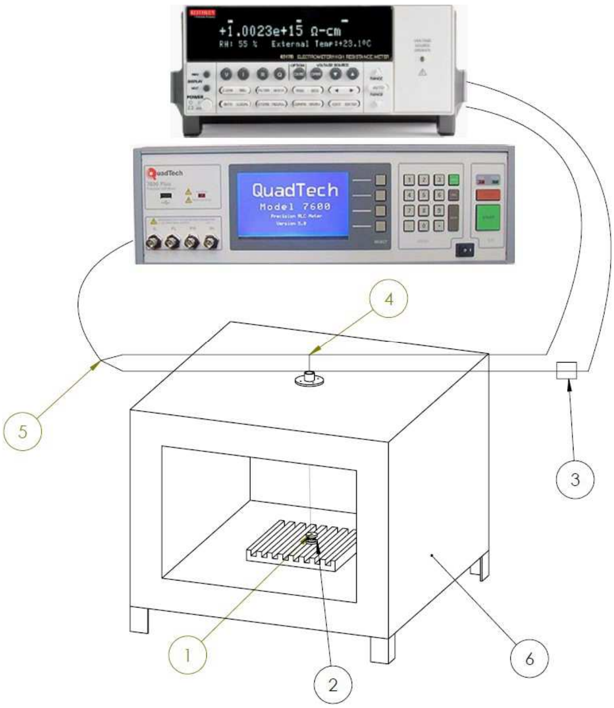

Fig. 3: The experimental setup: (1) ash sample, (2) electrodes, (3) 10 Mohm resistance, (4) isolated copper wires, (5) triax cable, (6) furnace

and chemical transformations, this peaking behaviour could indicate some chemical transformation or a phase change in the material. This is however difficult to verify, as there are not many available data in the literature about interpretation of electrical properties of ashes and probably none about the ESR properties.

The ESR rating of a capacitor is a rating of quality. A theoretically perfect capacitor would be lossless and have an ESR of zero. It would have no in-phase AC resistance. Although in ceramic capacitors, the equivalent series resistance is one of the most important parameters considered for an electronic circuit, generally selecting those with low ESR as this parameter represents the losses occurring within the metallic elements and the dielectric material. In such capacitors, the dielectric losses mainly depend on microstructural factors, dielectric formulation, and concentration of impurities. Porosity, morphology, and grain size are the main microstructural factors that determine the equivalent series resistance. K. Prompa et al. [20] studied the effect of the sintering conditions (sintering time/ temperature) on the dielectric properties of ceramic capacitors, founding a direct influence of sintering on dielectric properties such as dielectric loss, increasing values as the microstructural evolution of the sample evolve according with the sintering rate.

The ESR values versus temperature for the 1 kHz band graph represented in Fig. 4 are of especial interest as this particular frequency is the one widely used in literature. As it can be observed, temperature itself does have an affect on ESR. The above mentioned peak at 575°C is more explicit in this frequency and the declining trend hereafter

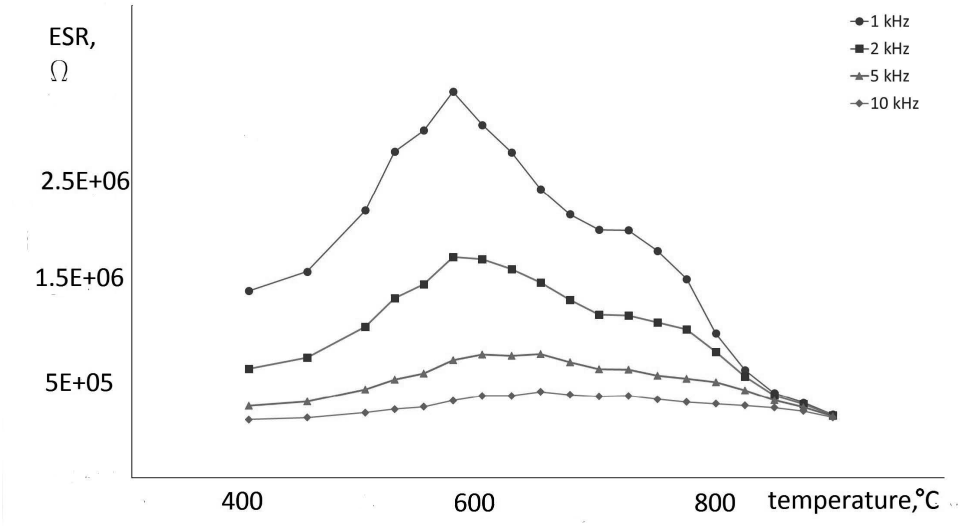

Fig. 4: ESR versus temperature for selected frequencies

likewise. The somewhat higher values from 725°C to 800°C may indicate another process regarding phase changes of chemical species at this temperature range, as more than one value breaks the trend and thus cannot be rejected as a measuring error.

Paritosh S. et al. [21] also found a connection between the temperature treatment of inorganics fillers for ceramic capacitors and their electro-mechanical properties. The dielectric parameters measured were temperature dependent and so related to the structure, morphology, and distribution of inorganic fillers.

The results of the DC experiments are shown in Fig. 5. As it can be seen, the decrease in resistance between temperatures in the lower part of the range is quite significant, and the similarity between the values for a typical semiconductor and the obtained resistance values is clearly seen in the range displayed, 550°C to 900°C.

The ohmic resistance measured in the DC experiments and the ESR values result in graphs, the shape of which are nowhere near similar. This dissimilarity is assumed to be due to the fact that ESR and ohmic resistance measured in DC describe two different phenomena and thus cannot be compared directly as such.
The experimental results were further analyzed and plotted on a natural logarithm-scale ordinate (Fig. 6 and Fig. 7), where the horizontal ordinate is the inverse temperature.

The DC resistivity plot fits a straight line with little approximation, thus further indicating semiconductor properties. According with Jinjin X. [22], the variation of fly ash resistivity with the increase of temperature could be described by Arrhenius equation. The linear fit seems to be more accurate at high temperatures, being consistent with the idea that the increase of temperature plays a key role on main charge carriers encountered in the sample.

On the other hand, the ESR versus inverse temperature curves depicted in Fig. 7 showed a nonlinear relationship. As previously mentioned, the close relationship between this parameter and the intrinsic changes of the sample may be the reason, indicating that the transformations of the sample due to the temperature increase are of different nature (different chemico-physycal processes).

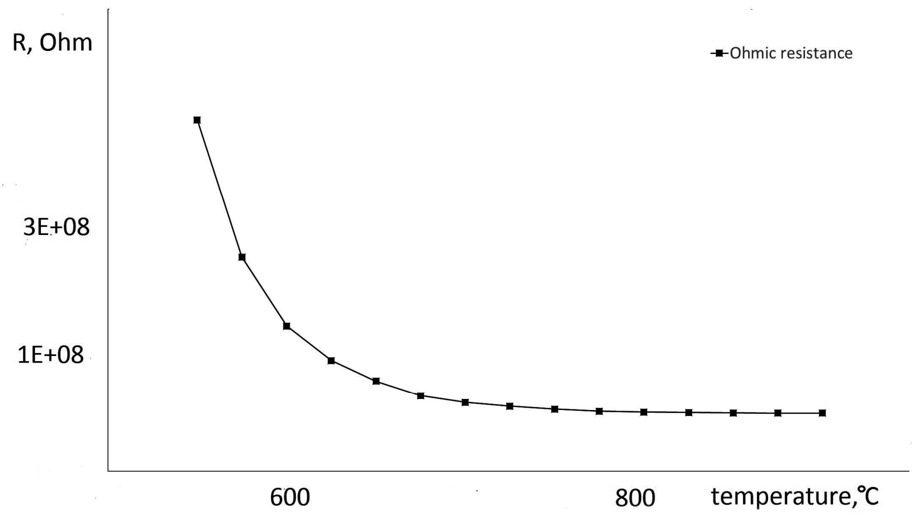

Fig. 5: DC resistance by temperature

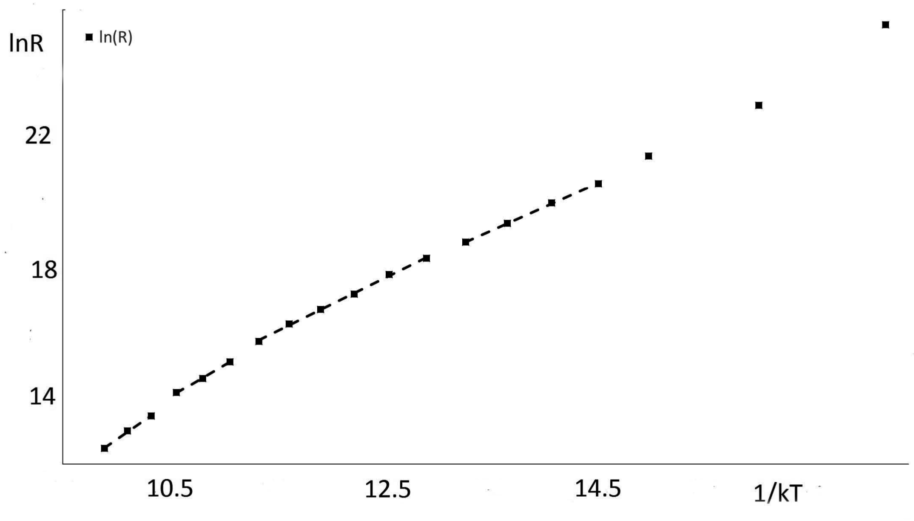

Fig. 6: DC resistance by inverse temperature

4. CONCLUSIONS

The resistance was the property chosen to analyse the changes in electrical properties studied on a laboratory prepared coal ash sample. The equivalent series resistance (ESR) was measured as an AC property while the ohmic resistance was measured as a DC property in the circuit. Despite their somewhat similar decreasing trend, they describe two different phenomena and thus cannot be compared directly as such. Both methods are temperature dependent, indicating the changes happening in the ash sample

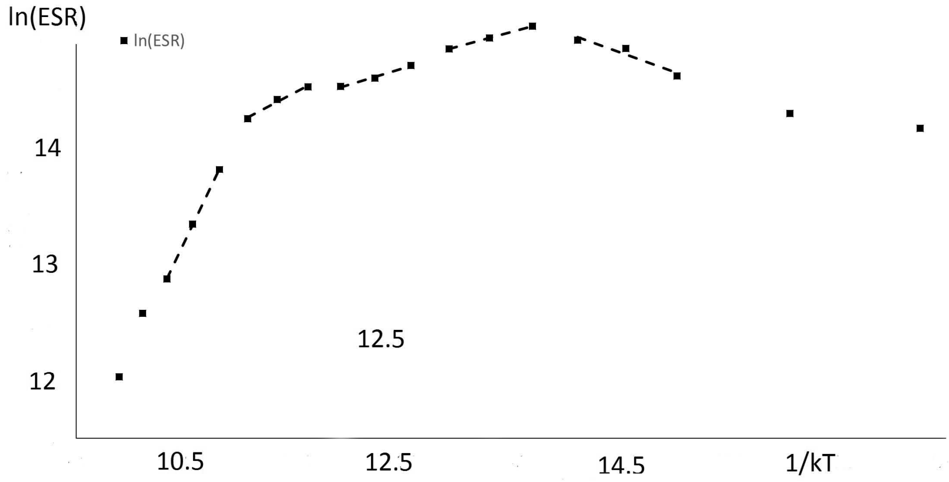

Fig. 7: Natural logarithm of ESR vs inverse temperature for frequency 1kHz

under thermal treatment, although the interpretation of the results obtained differ from each other.

The results obtained for the ESR show characteristic peaks at certain temperatures which in turn, could suggest that the method may be used directly as a way of determining specific temperatures where chemico-physical processes take place in the sample.

On the other hand, the ohmic resistance measured as a DC property in the circuit does not show distinctive regions where the parameter changes could directly suggest the transformation of the intrinsic properties of the material.

In spite of the feasibility of this method, it cannot stand alone as a way of assessing the properties of the solid residue. The complex chemical composition of the ashes, their structure, microstructure, and numerous heterogeneities may be reflected by the measurement. The understanding of the main physical and chemical transformations occurring inside the sample would be a key factor in assessing properly the results of the electrical test. Therefore a combination with microscopic studies such as SEM or CCSEM coupled with XRD would be very supportive to fulfil the studies.

It is also important to mention that, even thought the presented results are based on a coal ash sample, the method could be also applied to any kind of solid fuel ashes. Newer and alternative energy sources as biomass or sewage sludge, which are being thermally utilized in order to reduce environmental hazards are not exempt of these operational problems [23, 24]. In spite of their energy and environmental advantages, important ash related problems also arise when those renewable fuels are subjected to thermal conversion.

Nevertheless, the knowledge of the sintering process on solid fuels is still scarce and therefore this method may be appropriate and useful in practice, even though further work and more detailed analysis are needed for a comprehensive interpretation.

LITERATURA

[1] Ward C. R., *Analysis and significance of mineral matter in coal seams*, Int Coal Geol **50**, 135–168, 2002.

[2] Bo Liu, Qihui He, Zihao Jiang, Renfu Xu, Baixing Hu, *Relationship between coal ash composition and ash fusion temperatures*, Fuel **105**, 293–300, 2013.

[3] Jianbo L., Mingming Z., Zhezi Z. et al.., *Effect of coal blending and ashing temperature on ash sintering and fusion characteristics during combustion of Zhundong lignite*, Fuel **195**, 131–142, 2017.

[4] Jianbo L., Mingming Z., Zhezi Z. et al., *The mineralogy, morphology and sintering characteristics of ash deposits on a probe at different temperatures during combustion of blends of Zhundong lignite and a bituminous coal in a drop tube furnace*, Fuel Process Technol. **149**, 176–186, 2016.

[5] Liu Y., Gupta R., Elliott L. et al., *Thermomechanical analysis of laboratory ash, combustion ash and deposits from coal combustion*, Fuel Process Technol. **88**, 1099–1107, 2007.

[6] Van Dyk J.C., Melzer S., Sobiecki A., *Mineral matter transformation during Sasol-Lurgi fixed bed dry bottom gasification – utilization of HT-XRD and FactSage modelling*, Minerals Engineering **19**, 1126–1135, 2006.

[7] Van Dyk J.C., Benson S.A., Laumb M.L., Waanders B. *Coal and coal ash characteristics to understand mineral transformations and slag formation*, Fuel **88**, 1057–1063, 2009.

[8] Vassilev S. V., Tascon J. M. D., *Methods for Characterization of Inorganic and Mineral Matter in Coal: A Critical Overview*, Energy and Fuels **17**, 271–281, 2003.

[9] Huggins F. E., *Overview of analytical methods for inorganic constituents in coal*, Int. J. Coal Geol. **50**, 169–214, 2002.

[10] Jak E., *Prediction of coal ash fusion temperature with the FACT thermodynamic computer package*, Fuel **81**, 1655–1668, 2002.

[11] Gupta S. K., Wall T. F., Creelman R. A. and Gupta R. P., *Ash fusion temperatures and the transformations of coal ash particles to slag*, Fuel Process Technol. **56**, 33–43, 1998.

[12] Nowak-Wozny D., Wozny L., González Valdés L., *Dielectric loss factor of sintered coal ash*, E3S Web Conf. – Energy and Fuels 2016 **14**, 1–8, 2017.

[13] Du S., Yang H., Qian K., et al., *Fusion and transformation properties of the inorganic components in biomass ash*, Fuel **117**, 1281–1287, 2014.

[14] Zhang G. and Chou K., *Correlation Between Viscosity and Electrical Conductivity of Aluminosilicate Melts*, Metallurgical and materials transactions **43B**, 849–855, 2012.

[15] White H.J., *Electrical resistivity of Fly Ash*, Air Repair **3**(2),79–86, 1953.

[16] Charles D.A. Coin et. al., *An improved Ash Fusion Test*, Application of Advanced Technology to Ash-Related Problems in Boilers – Edited by L. Baxter and R. DeSollar, Plenum Press, New York, 188–200, 1996.

[17] Gonzalez Valdes L., Nowak-Wozny D., *Mineral phase transformation of wood and cereal pellets – electrical test and FactSage calculations*, Technical Issues **3**, 126–134, 2016.

[18] IET LABS, INC., *https://www.ietlabs.com/7600-lcr-meter.html*, accessed May 2018.

[19] Tektronix for Europe, *https://www.tek.com/datasheet/high-resistance-low-current-electrometers-series-6500-6430/model-6517b-electrometer-high-r*, accessed May 2018.

[20] Prompa K., Swatsitang E., Saiyasombat C, Putjuso T., *Very high performance dielectric and non-ohmics properties of CaCu3Ti4.2O12 ceramics for X8R capacitors*. Ceramics International – accepted for publication on 16 April 2018.

[21] Paritosh S., Hitesh B., Singh B.P. et al., *Electro-mechanical properties of free standing micro- and nano-scale polymer-ceramic composites for energy density capacitors*, J. of Alloys Compounds **648**, 698–705, 2015.

[22] Jinjin X., Zhongzhu G., Jun Z., *Experimental study on fly ash resistivity at temperatures above 673 K*, Fuel **116**, 650–654, 2014

[23] Fernandez R.G., Garcia C.P., Lavin A.G. et al., *Study of main combustion characteristics for biomass fuels used in boilers*, Fuel Process. Technol. **103**, 16–26, 2012.

[24] Magdziarz A., Wilk M., Gajek M. et al., *Properties of ash generated during sewage sludge combustion: A multifaceted analysis*, Energy **113**, 85–94, 2016.