Analysis of the alkali-activated fly ashes from electrostatic precipitators by impedance measurements

J Walter¹, D Mierzwiński¹ and K Kosiba¹
¹ Institute of Materials Engineering, Faculty of Materials Science and Physics, Cracow University of Technology, al. Jana Pawła II 37, 31-864 Cracow, Poland

E-mail: jwalter@mech.pk.edu.pl

Abstract. Curing the fly ash materials with addition of sand activated by 8 M sodium hydroxide (NaOH) was analysed by impedance spectroscopy. The measurements were carried out for 6 hours from the moment the samples were put into the oven at 75 °C. It was found characteristic similar shape of impedance curves recorded versus time of solidification process. Starting from the curve obtained after 52 min to longer times impedance curve crossed at about 30 Hz. The first lower than 30 Hz frequencies range showed continues decreasing of impedance values with increasing the time. Changes in impedance curve versus time looks different for second frequencies higher than 30 Hz. Temperature of the material increases slightly over temperature of the oven as a result of exothermic reactions which can be seen at impedance vs. time curve as a bulge. The starting of these reactions can be seen more precisely in the second range of the frequency as a continuous increase of impedance value preceded by its initial fast decline. The main purpose of the article is the possibility of using the described method, it can be particularly useful for assessing the starting point of an exothermic reaction and its progress in the case of different masses of heated material.

1. Introduction
Geopolymers are modern materials which can be used in building construction. This term is used to describe a group of materials which can be synthesised from aluminosilicate and high concentrated alkali solution at a temperature range of from ambient temperature to about 100°C [1]. Geopolymers production attracted the interest of scientist because it can be applied parallelly or instead of concrete in many applications.

Another group of materials which can be obtained on a similar way are materials based on fly ash (FA) containing oxides SiO₂, TiO₂, Fe₂O₃, MgO, Na₂O, CaO, K₂O and Al₂O₃ and others [2, 3, 4]. The largest amount of FA is generally a product of burning coal in coal-fired power plants and combined heat and power plants. Burning of coal exceeds temperature of 1300°C. During this process, mineral components that cannot be burned are partly or completely melted. These are usually parts of the rock contained in the coal. The molten particles are largely melted particles pass in the flue gas stream and trapped in the filter as FA. Fly ash can be alkali-activated using high concentrate alkaline in strong water solution. Major advantages of alkali-activated materials are good mechanical performance, low shrinkage with enhanced chemical resistance and thermal stability [5, 6, 7]. Moreover, technology of alkali-activated materials has a reduced environmental impact due to lower CO₂ emission and energy
consumption, compare to concretes. FA utilisation is also a significant result of fabrication this kind of materials. Some researchers reported that the electrical conductivity of fly ash based materials depends on the NaOH concentration in activator solution and liquid activator/ash ratio as well as on frequency spectrum [8, 9], others presented dielectrical and electrical study of FA composite [10]. Nowadays impedance spectroscopy (EIS), one of non-destructive methods is more frequently applied for investigations of the materials with capacitive properties [11, 12, 13, 14]. Depending on the capabilities of the device, the tested material, different frequency ranges are used. Our research was carry out to analyse process of curing the FA — sand composite. The frequency range has been chosen that way to be able to carry out a quick measurement because the materials electrical properties are constantly changing while curing. The measurement results were saved as an impedance module in the frequency function.

2. Experimental
The fly ash from Skawina Power Plant (Poland) has been used for production of alcali-activated material. The starting composition consisted by weight 50% of the fly ash and 50% of the building sand. Materials were carefully mixed by 15 minutes using mechanical low speed mixer to obtain evenly distribute particles of powders. The next step was to apply alkaline activator. For this purpose sodium hydroxide (NaOH — Sigma-Aldrich) in concentration of 8 M in distilled water was used. The amount of activator was calculated on the basis of a weight ratio of fly ash to the activator equal to 0.4. Powders with addition of the activator were then mixed by next 15 minutes. Prepared this way material with a slightly liquid consistency was used immediately for filling specially prepared cylindrical mould with two stainless steel electrodes. Vibrator was applied in the next step to remove bubbles of an air from the mould filled with the material.

The mould with total mass equals to 475 g contained 381 g of material was placed in an oven at 75°C. The temperature of the oven was precisely stabilised. Using short electrical cables stainless steel electrodes were connected to the Zahner IM6e workstation to record changing in very low electrical signals generating by the device. The workstation was set in two electrodes mode without any polarisation of the electrodes. The alternating current with amplitude of 50 mV has been applied between electrodes. Frequency of the current were changed during the measurement in the range of 1 Hz to 10 kHz. Each measurement result in impedance curve versus current frequency took 90 seconds. It was taken four measurements per hour for 6 hours during the process of the material curing. The temperature of the material was measured by the calibrated NTC thermistor.

3. Results and discussion
Temperature measurement showed rapid heating of the material after insertion into the oven — Figure 1. The temperature of material reaches the furnace temperature after about 90 minutes and then exceeds it and next slowly decreases keeping oven temperature at the end of recording.
Figure 2. Temperature of material versus time of process.

Figure 3 shows changing of the impedance measured in the range of frequency starting from 1 Hz up to 10 kHz while time of the process increases. All curves crossing themselves at the frequency about 30 Hz. Below this frequency starting from 1 Hz as the time of the solidification process increases, the lower impedance modulus values were always observed in this frequency range. For frequencies higher than 30 Hz the curve shifts are more complicated. The dashed lines showed in Figure 3 describes the curves going down in the graph as the temperature increases. The lowest dashed line (the red one) was recorded after 52 minutes at the temperature equal to 67.4 °C. This is a result of the material heating up, and a beginning of slow solidification. The measurements taken after more than 52 minutes have shown the shift of the impedance curves towards larger values. The highest temperature of 76.2 °C was registered after 135 and 150 minutes of the process. A steady decrease in temperature is observed for times longer than 150 min. The temperature of the material is slowly approaching the oven temperature. Figure 4 shows the impedance changes at the frequency of 1 Hz. It can be seen in the temperature range of 67.4 °C to 76.2 °C the characteristic course of the curve (Figure 4) corresponding to the increase in temperature caused by the rise of the temperature of heated material and chemical reactions going in it. It was found that the solidification process of a 381 g of the material placed in an oven with a temperature of 75 °C begins at a temperature of about 65 °C and the influence of exothermic reactions decreases after about 150 min.
Figure 3. Impedance change versus frequency – time and temperature dependence.
Figure 4. Impedance and temperature changes at 1 Hz versus the time of solidification process.

Figure 5. Impedance and temperature changes at 1 kHz versus the time of solidification process.

These processes can be also observed at the higher frequencies. Figure 5 summarises the measurements recorded at the frequency of 1 kHz. Initially the fast decrease in impedance values up to about 52 min. (64.7 °C) was observed with increasing temperature. Next the value of impedance slowly increasing. The same tendency was found for higher frequencies up to 10 kHz as well as for lower than 1kHz but higher than about 30Hz as it was shown in Figure 3. The beginning of exothermic reactions on time axis is easier to recognise in this frequency range because of bigger visible changes on impedance curve.
4. Conclusions

Proposed method of analysing alkali-activated process of the fly ash solidification with addition of sand can be very useful for examining the progress of the process. The measurement which takes 90 seconds is short enough to influence on solidification processes and applied current which is a result of very small voltage amplitude equals to 50 mV cannot also cause any changes in material. Research showed measurable changes in impedance curves versus frequency taken during solidification process of investigated material. The characteristic shape of these curves can be used to check progress of reaction. Heating of mould with semi-liquid material can be observed in lower frequencies as dropping down the impedance values while time increases.

The analysis of impedance curves recorded while process is in progress showed two characteristic ranges of frequencies. The first range from 1 Hz to about 30 Hz (Figure 3) showed a continuous decrease in the impedance value during the process while the changes are getting smaller with increasing frequency. More accurate analysis depicted in Figure 4 for one frequency equals to 1 Hz showed the characteristic curve bulge in the range of material temperature from 64.7ºC to about 76 ºC. Shape of the curve and its bulge can be useful for estimation of the time of main exothermic solidification processes. The second range beginning from about 30 Hz and ending in the end of recorded frequency seems to be more convenient to find beginning of the exothermic reactions what can be useful especially in case of different mass of heated material.

References

[1] Suwan T and Fan M 2017 *Materials and Manufacturing Processes* **32** 5 461
[2] Saravanan G, Jeyasehar C A, Kandasamy S 2013 *Journal of Engineering Science and Technology Review* **6** 25
[3] Duan W, Lopez M, Juenger M C G, Aughenbaugh K L and Stutzman P 2016 *Front. Mater.* **3** 1
[4] Fernández-Jiménez A and Palomo A 2003 *Fuel* **82** 2259
[5] L. Provis, J.S.J. Van Deventer *Alkali Activated Materials* (Springer, 2014)
[6] Canfield G M, Eichler J, Griffith K *Journal of Materials Science* 2014 **49** (17) 5922
[7] Gunasekara C, Setunge S and Law D W 2017 *ACI Structural Journal*, **114** S60 743
[8] Hanjitsuwan S, Hunpratub S, Thongbai P, Maensiri S, Sata V and Chindaprasirt P 2014 *Cement and Concrete Composites* **45** 9
[9] Hanjitsuwan S, Chindaprasirt P and Pimraksa K 2011 *International Journal of Minerals, Metallurgy, and Materials* **18** 94
[10] Singh P, Bhattacharya B and Singh P K 2017 *Phase Transitions* **90** 3 236
[11] Suryanto B, McCarter W J, Starrs G and Chrisp T M 2017 *Procedia Engineering* **171** 705
[12] Dong B, Qiu Q, Gu Z, Xiang J, Huang C, Fang Y, Xing F and Liu W 2016 *Cement and Concrete Composites* **65** 118
[13] Dong B, Wu Y, Teng X, Zhuang Za , Gu Z, Zhang J, Xing F and Hong S 2019 *Construction and Building Materials* **211** 261
[14] Malkawi A B, Al-Mattarneh H, Achara B E, Mohammed B S and Nuruddin M F 2018 *Construction and Building Materials* **189** 19