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DETERMINATION OF ALKALINE REACTIVITY OF GEOPOLYMER'S RAW MATERIALS: PRACTICAL ASPECTS

Alkaline reactivity characterizes the dissolution and reactive capacity of a solid material in alkaline media. The results are of significance in the development of technology for geopolymers obtaining based on the studied raw materials. However, no validated analytical procedure for estimation of alkaline reactivity of coal combustion by-products and mine tailing exists. It imposed the development of specific procedure for analysis and its verification. This report presents a procedure based on ICP-OES measurement of the concentration of Al, Si and Ca in alkali solution. Some problems of the analysis were successfully addressed, as a high salt content of leachates, and the procedure was verified applying a reference laboratory approach. The alkaline reactivity was studied as a function of time at 6.5 M NaOH during 48 h. Additionally, to reactive silica determination, the study was extended to reactive alumina and calcium, as these components contribute to the development of geopolymer matrix. To estimate the percentage of dissolved Al, Si and Ca detailed precise data about chemical composition of raw materials were required. To achieve it, samples components were determined by ICP-OES after digestion in acid oxidizing medium, combined with alkali fusion for silica determination, as well as loss of ignition and humidity determination. In contrast to the approach, usually reported in the literature, presenting the alkaline reactivity as a concentration of dissolved ions in the alkaline solution, in this study we proposed a new procedure. Alkaline reactivity was estimated: by a percentage of dissolved component in mg per kg dry sample. This approach allowed comparability of the data between various laboratories, procedures or raw materials. Moreover, the approach allowed the relative ratio between reactive components to be calculated.

Keywords: Geopolymers; mine tailing; alkaline reactivity

1. Introduction

Mining activity generates enormous amount of waste materials often collected in tailing dumps. The last decades a line of research projects was aimed at recycling, reusing and valorization of the generated waste materials [1-4]. Geopolymerization appears to address some of the important environmental issues opening the possibility to apply low CO_2 footprint technology and valorization of waste materials. Geopolymers are alkali-activated materials produced by alkali activation of aluminosilicate raw materials containing relatively high concentrations of silica and alumina. Mine tailings are proved suitable geopolymer precursors due to relatively high content of sources of Si and Al species for the gel formation. However, the reactivity in alkaline media strongly depends on the phase composition of mine tailings [1-7]. The characterization of alkaline reactivity of raw materials is a requirement for adequate assessment of the potential for waste valorization throughout geopolymer technology [1,8-10]. However, a widely approved analytical procedure for testing alkaline reactivity is not available. Although the intensive research on this direction [7-15], the particularities and analytical characteristics of the applied analytical methods are scarcely reported. Moreover, different solid to liquid ratio, concentration of alkali or reaction time could be found in the literature [7-13] that limit the comparability of the results. Usually, atomic emission spectroscopy or mass spectrometry with inductively coupled plasma (ICP-OES or ICP-MS) were used for determination of the concentration of dissolved Si and Al [14-17]. Despite the advantage of ICP-OES for fast, reliable and multicomponent analysis, some important problems should be addressed: as matrix interference, high salt content of samples or relatively high concentrations of the target chemical species, choice of appropriate calibration method [16-19]. Therefore, a verification of analytical method should be performed in order to ensure reliability of the obtained results [20].

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Hence, this research is focused on a verification of protocol for testing of alkaline reactivity of mine tailings, as well as investigating the potential of mine tailings to be applied as raw material for geopolymer obtaining.

2. Methods

2.1. Samples description

A mine tailing from an inactive tailing dump situated near by the city of Burgas, Bulgaria was studied. The sample was sampled following the internal laboratory procedure of the company, which provided the samples. The sample was studied after air-drying without additional grinding. The fraction below 200 µm was used in the present study.

2.2. Determination of chemical composition

The chemical composition of studied samples was determined by XRF analysis and ICP-OES after aqua regia digestion, Si content was determined gravimetrically, and loss of ignition was determined at 1000°C. A previously validated ICP-OES procedure was applied [21].

2.3. Determination of alkaline reactivity

One gram (±0.0002 g) of a studied sample was transferred into a plastic beaker. A volume of 20 mL of NaOH at concentration 6.5 mol/L was added to each sample. The samples were agitated on reciprocal shaker at 100 min^{-1}. Different reaction times were studied: 30 min; 60 min; 4 h; 14 h; 24 h and 48 h. For each studied period, individual samples were prepared. The samples were centrifuged for 5 min at 6000 min^{-1} and 15.0 mL of the obtained supernatant was transferred in a volumetric flask. The samples were filtered through filter paper directly into the flask containing 25 mL of diluted HNO_3 (1:1.5). The solutions were diluted upto 50.00 mL with distill. H_2O. The concentrations of Al, Si and Ca were determined by ICP-OES measurement.

2.4. ICP-OES measurement

The analytical function of the ICP-OES measurement (I = k*C) was calibrated by an external standard method. Reference materials: individual standard solutions of Al and Si, were appropriately diluted to achieve suitable working range. The tested samples were appropriately diluted in order to adjust the sample concentration to the linear range, as well as to minimize the effect of high salt content of the samples. Analytical wavelengths free from interference were selected for measurements. Each sample was measured in duplicate and the mean values were calculated.

2.5. Calculation of content of dissolved components

The ICP-OES measurement provided data about concentration of elements in the sample in mg/L. The dilution factor was taken into account. The content of dissolved in alkaline media components was calculated by the equation.

$$C\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{V_{al} * C_{sol}}{m_{sample}}$$

where: C (mg/kg) is the content of dissolved component in mg per kg dry material; V_{al} – volume of the aliquot of the supernatant taken for analysis in L; C_{sol} – concentration of the component in the solution in mg/L; m_{sample} – the weight of the dry material in kg.

3. Results and discussion

3.1. Chemical composition of the studied mine tailing

The chemical composition of the studied mine tailing is presented in TABLE 1. The results were calculated as corresponding oxides when appropriate. The results showed relatively high content of silica (80.10%) and alumina (16.90%) which made the studied mine tailing suitable precursor for geopolymer obtaining. However, it should be pointed out that the phase composition will highly determine the alkaline reactivity of the sample.

TABLE 1

Chemical composition of the studied mine tailing

Component	Content, %
SiO_2	60.1
Fe_2O_3	19.8
Al_2O_3	10.5
CaO	3.94
Na_2O	0.07
MnO	0.15
MgO	4.85
other	0.05
P*	0.23
S*	0.03
LOI	10.08

* determined by XRF

The previous study showed the mineralogical composition of the mine tailing [22]. The silicon could be found as quartz, clinochlore, orthoclase, albite and coesite. The aluminum could be found in alumosilicate minerals: orthoclase, clinochlore and albite. The solubility in alkaline media depends on the mineralogical composition of the mine tailing material.

3.2. Verification of the method for determination of alkaline reactivity of the mine tailings

To assure the reliability of the obtained results the analytical procedure should be validated or verified [20]. However, a standard reference procedure or certified reference material appropriate for determination of alkaline reactivity of mine tailings do not exist. Thus, in order to verify the procedure and to validate the interpretation of the experimental data and conclusion derived, the reference laboratory approach was adopted in this study. The step of analysis the most problematic in this study was ICP-OES measurements. It was expected a pronounced effect of high salt content of the tested samples due to the high concentration of alkali used. Although the obtained data in both laboratories, using different types of ICP-OES instruments and modes of measurements, differed in confidential interval, the observed trend in concentration changes as a function of reaction time were the same. The results are illustrated on Fig. 1.

3.3. Alkaline reactivity of the studied mine tailing

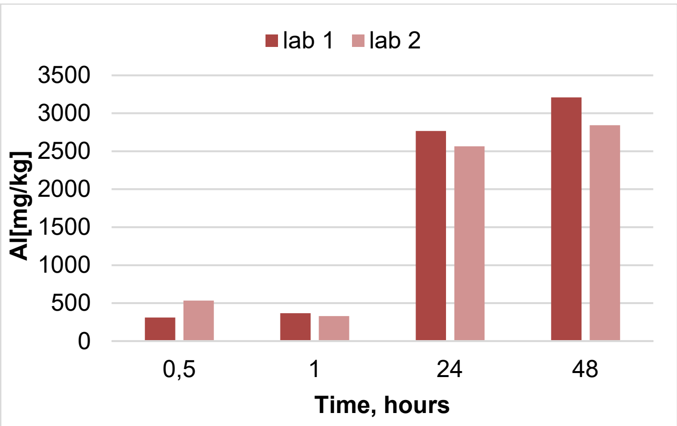
The alkaline reactivity of mine tailing is presented in TABLE 2. The concentrations of dissolved components into 6.5 M sodium hydroxide are presented. In order to estimate the alkaline reactivity of the studied raw material the results were additionally presented as mg dissolved component per kg dry raw material.

TABLE 2

Concentration of dissolved component of the studied mine tailing in 6.5 M NaOH

Time	m, g	V mL	Ca, mg/L	Al, mg/L	Si, mg/L	Ca, mg/kg	Al, mg/kg	Si, mg/kg
30 min	1.02	20.0	15.1	2.43	3.18	295	47.7	62.3
60 min	1.03	20.0	14.9	2.33	3.44	289	45.2	66.8
4 h	1.03	20.0	15.1	3.83	7.62	293	74.4	148
14 h	1.02	20.0	13.3	5.98	14.2	261	117	278
48 h	1.04	20.0	12.5	6.93	17.9	241	133	344

The dissolution of Al, Si and Ca was followed for 48 h. The results are presented on Fig. 2. As can be seen from the Fig. 2, the highest concentrations in the liquid phase were observed for Ca. Calcium was dissolved at the early stage of the contact and at 30 min it reached its maximal value. Concentrations of Si and Al constantly increased with time. Steady value was observed after 14 h of contact between mine tailing and NaOH solution. In contrast, no steady value was observed of Si concentration during the studied period. The quantity of dissolved Si increased faster after 4 h contact time, the slope of the curve become steeper. The ratio between quantities of dissolved Si to Al changed from 1.3 (at 30 min) to 2.6 (at 48 h).



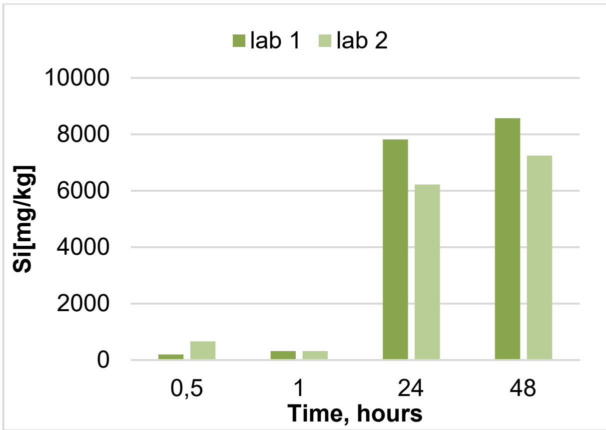


Fig. 1. Comparison between results of ICP-OES using different instruments and mode of measurement. The concentration of NaOH was 6.5 M, a pooled mine tailing sample was tested. The content of dissolved Al and Si in mg/kg dry mine tailing material is presented

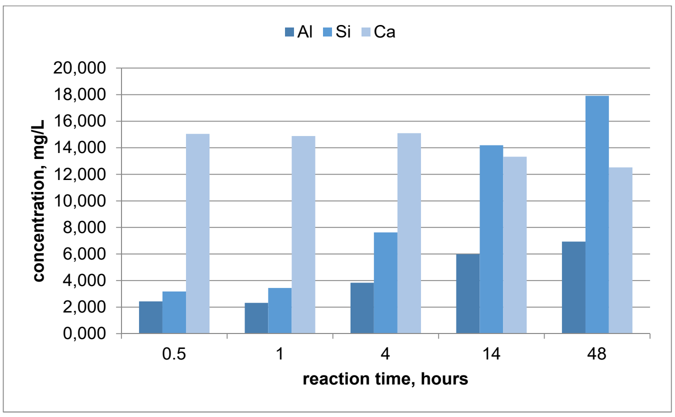


Fig. 2. Concentration of dissolved components of mine tailing in 6.5 M NaOH as a function of time

4. Conclusion

A procedure for determination of mine tailing alkaline reactivity is described. A protocol for verification of the testing procedure is demonstrated. A mine tailing from a closed concentrator plant and recultivated tailing dump located in the region of East Bulgaria is studied. The obtained results showed that the studied sample contained relatively high concentrations of Si (80% as SiO_2) and Al (17% as Al_2O_3), as well as low content of S, hence the tailing material showed potential to be used as raw material for geopolymer obtaining. Study of alkaline reactivity demonstrated that the highest rate of dissolution in NaOH medium showed calcium, followed by silicon and aluminum. The ratio between dissolved Si and Al was between 1.3 and 2.6

depending on the reaction time. The obtained results showed that the mine tailing could be used as precursor for geopolymer obtaining, however an appropriate mixture of raw materials should be designed.

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