LIGHT SCATTERING TECHNIQUES AS A KEY IN PROVIDING INSIGHTS INTO THE INTERACTIONS AND STABILITY OF ALKALI-ACTIVATED MATERIALS BASED ON BLAST FURNACE SLAG

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Abstract

Light scattering techniques represent a group of methods providing the absolute information on the molecular weight, particle size, conformation, polydispersity and the stability of analyzed dispersion systems. These techniques are primarily used for the characterization of biopolymers, synthetic polymers and nanoparticles. The utilization in the area of alkali-activated materials based on blast furnace slag is more challenging, mainly due to their highly alkaline nature and also due to the generally used high content of solid fractions dispersed in liquid media. This contribution was focused either on the optimization of sample preparation as well as on the definition of the optimal setting of measuring parameters to be able to properly use the electrophoretic light scattering (Zetasizer Nano ZS; Malvern Panalytical Ltd.) for the description of the stability of these complex samples. For these purposes, we studied dispersion systems of blast furnace slag in activating solutions (sodium hydroxide, sodium carbonate and sodium silicate). The obtained zeta potential provided crucial insight into the individual sample stability. The results are indicating that the proper technique of sample dispersion and the maintenance of the precise content and ratios of individual components represent important parameters managing the stability of alkali-activated materials based on blast furnace slag.

Keywords: Alkali-activated materials, blast furnace slag, conductivity, stability, zeta potential

1.   INTRODUCTION

The development of modern building materials is nowadays closely connected to government restriction as well as by the environmental issues such as tendencies to reduce CO_2 emissions and the efforts to utilize the waste materials and by-products from other industries to protect nature and natural raw materials [1]. Alkali-activated materials (AAM) represent the non-traditional cementitious materials, which fulfil these ideas and currently are studied as materials that could serve as the potential substitute to the ordinary Portland cement in some applications [2]. The typical example of AAM is alkali-activated blast furnace slag (AAS) [3]. Generally, these materials show interesting chemical [4,5] and temperature resistance [6] and high early strength [7] of the material but on the other hand the high autogenous and drying shrinkage must be mentioned as the main disadvantage of the broader practical application of AAM [8]. The published research also indicates the necessity to design a specific admixture exclusively for the individually used AAM to overcome this issue [9], otherwise, AAMs will never fulfil their potential and will never be competitive to Portland cement [10].

At this point, the need for a technique allowing the simple description of interactions among blast furnace slag (BFS) and other components in the systems (activation solutions, admixtures) seems to be crucial. One of the methods how to determine these characteristics is the method of electrophoretic light scattering allowing to determine the zeta potential of the electrokinetic potential in the interfacial double layer of BFS grains [11]. As can be found in the literature [12] this important parameter characterizing the surface chemistry of BFS is dependent on pH, the nature of the used alkaline activator and also on the addition of admixture used for further processing of BFS dispersions. Moreover, the values of zeta potential determined for AAS are also

influenced by the concentration of analysed particles. Kashani et al. [12] highlighted that the values of zeta potential of AAS have a direct connection to the rheological properties of slag-based suspensions containing sodium or potassium hydroxides and sodium silicate. The lowest yield stress was observed for slag suspension containing sodium silicate, followed by slag in water without activator, while it markedly increased for sodium hydroxide. Higher yield stress values are in accordance with the structure-making/structure-breaking theory of structural forces as well as with the determined values of zeta potential that were usually negative for slag in water, which was induced by the partial deprotonation of silanol groups on the slag surfaces. Contrary to alkali hydroxide activators, increasing dose of sodium silicate induced a shift to the more negative values of zeta potential and thus contribution of the repulsive electric double layer forces increased.

The zeta potential in cementitious suspensions can be determined using the electroacoustic method [13], enabling the measurement of concentrated suspensions [14], but an issue of too high alkalinity can still arise. In addition, often only the electrophoretic light scattering is available. However, it inherently requires a diluted sample, which may affect the results obtained. Therefore, our experimental work focused on optimizing the electrophoretic light scattering method for the investigation of the interactions and stabilization of BFS in various used AAS. For these purposes, we have used the dilution approach, where we studied the direct relation of BFS to Na^+ concentration and the total content of these components in the system to be able to predict the behaviour of original non-diluted samples.

2.   EXPERIMENTAL

2.1.   Materials

The individual samples of alkali-activated pastes were prepared using a blast furnace slag (BFS) with Blaine fineness of 400 $m^2 \cdot kg^{-1}$ and density of 2.88 $g \cdot cm^{-3}$. The chemical composition of BFS as was obtained by X-ray fluorescence analysis (XRF) is given in **Table 1**. The individual studied samples of alkali-activated slag (AAS) were prepared using the activation solutions of sodium hydroxide (Lach-Ner s.r.o), sodium carbonate (Lach-Ner, s.r.o) and sodium silicate having the molar ratio of SiO_2/Na_2O (Ms = 1.50) (Vodní sklo, a.s.).

Table 1 Chemical composition of blast furnace slag obtained by XRF analyses

material	Chemical composition (wt.%)									
	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3
blast furnace slag	34.7	9.1	41.1	10.5	1.4	0.4	0.9	1.0	0.6	0.3

2.2.   Sample preparation

Concentration series of all activating solutions were prepared in advance prior to their mixing with slag. The specific range of concentrations was given by their achievability with respect to the original composition of the activators: 0–5 mol $Na^+ \cdot dm^{-3}$ for sodium carbonate solution, 0–9.93 mol $Na^+ \cdot dm^{-3}$ for sodium silicate solution and 0–15 mol $Na^+ \cdot dm^{-3}$ for sodium hydroxide solution. Then each activating solution was mixed with slag (1:1 by volume) to obtain 10 cm^3 of the whole suspension (paste) and homogenized with a spatula for 3 minutes. After another two minutes of rest, the paste was diluted by demineralized water in the range 1:10, 1:50, 1:100, 1:250, 1:500 and 1:1000 and immediately characterized by electrophoretic light scattering (section 2.4).

2.3.   Physico-chemical characterization of activation solutions

The individual alkali-activated solutions were characterized through potentiometric pH determination using the Titrando 888 module equipped with a combined Unitrode electrode for a highly alkaline pH region with an integrated Pt1000 temperature sensor (Metrohm AG, Switzerland). The data shown further in the text represent the mean values of five repeated measurements (results in the form of mean values ± SD, n = 5). The data processing was performed using Tiamo software (version 2.5; Metrohm AG, Switzerland).

Dynamic viscosity of all the used alkali-activated solutions was measured employing Höppler falling ball viscometer AMVn (Anton Paar GmbH, Austria). The data shown further in the text represent mean values of three repeated measurements (results in the form of mean values ± SD, $n = 3$).

2.4. Zeta potential measurement

The effect of the type of alkaline activation (sodium hydroxide, sodium carbonate, sodium silicate with Ms = 1.5), their concentration in the sample (range from 0 to 15 mol·dm^{-3} concentration of Na$^+$) and the dilution ratio (dilution by volume with distilled water in the range of 1:10, 1:50, 1:100, 1:250, 1:500 and 1:1000) of the individual alkali-activated BFS dispersions was investigated by the method of electrophoretic light scattering using Zetasizer Nano ZS (Malvern Panalytical Ltd., UK). Simultaneously the average scattered light intensity, conductivity and the zeta potential of the suspensions were measured in three repeated measurements of three individually taken samples (results are presented in the form of mean values ± SD, $n = 9$). The obtained data from ELS analysis were processed by the Zetasizer software (version 7.11; Malvern Panalytical Ltd., UK).

3. RESULTS AND DISCUSSION

The principal task of this work was the investigation of the effect of the type of used alkali-activated solution and their concentration in the sample on the interactions with BFS. For these purposes, the measurement of zeta potential using the method of electrophoretic light scattering was selected. This method is used for investigation of the surface chemistry of colloidal dispersions, description of their surface charge with the corresponding stability of particles against mutual aggregation and for investigation of the interactions among particles in the system [5]. Due to the experimental limitations (mainly the limits for the pH, conductivity and concentration), it was not possible to study the sample directly, but we had to perform a dilution with distilled water to be able to subsequently extrapolate the zeta potential to the original samples. For these purposes, the dilution ratios between 1:50 and 1:1000 (by volume) were used.

3.1. Physico-chemical characterization

The physico-chemical characterization of all the used activation solutions by measurement of their pH, conductivity and dynamic viscosity was realized as the initial experiments necessary for subsequent discussion of zeta potential results obtained on AAS in a broader context in Section 3.2. The results of the measured pH and dynamic viscosity for all the used activation solutions are shown in **Figure 1**.
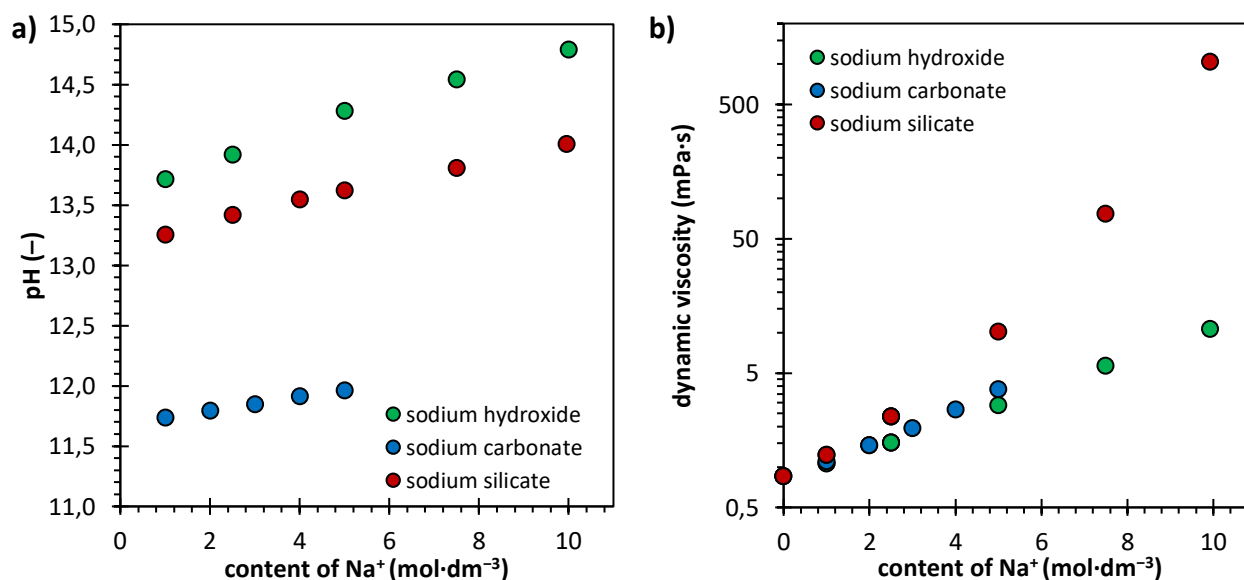

Figure 1 a) pH and b) dynamic viscosity of activation solutions recalculated on the real content of Na$^+$ ions

The determined pH values are indicating expected dependences on the real content of Na$^+$ ions. Especially for sodium hydroxide solutions, the data need further corrections on activity coefficients. The highest pH values were measured for sodium hydroxide solutions and on the other hand in agreement with our expectation, the lowest pH values were measured for sodium carbonate solutions. The data from the measurement of dynamic viscosity of the individual activating solutions (**Figure 1b**) are indicating similar trends of sodium hydroxide and sodium carbonate (logarithm of dynamic viscosity has almost linear dependence on the concentration of Na$^+$ in the solution). The different behaviour was observed in the sodium silicate activation solution, where the dependence of logarithm of dynamic viscosity on the concentration of Na$^+$ was much higher and indicated an almost polynomial trend in the data. These results are in good correlation with published literature [15].

3.2. Zeta potential measurement

The zeta potential measurement by using the method of ELS was used as the principal experimental approach for the investigation of the interactions and stability of dispersions of BFS in alkali-activated solutions (sodium hydroxide, sodium silicate and sodium carbonate). Due to the experimental limitations of ELS (pH and conductivity and concentration limits) the measurement was performed under the broad range of used dilution ratios (diluted by volume with distilled water 1:50, 1:100, 1:250, 1:500 and 1:1000). For this reason, the lowest used dilution (1:10) was not reliably measured and thus the results are not shown.
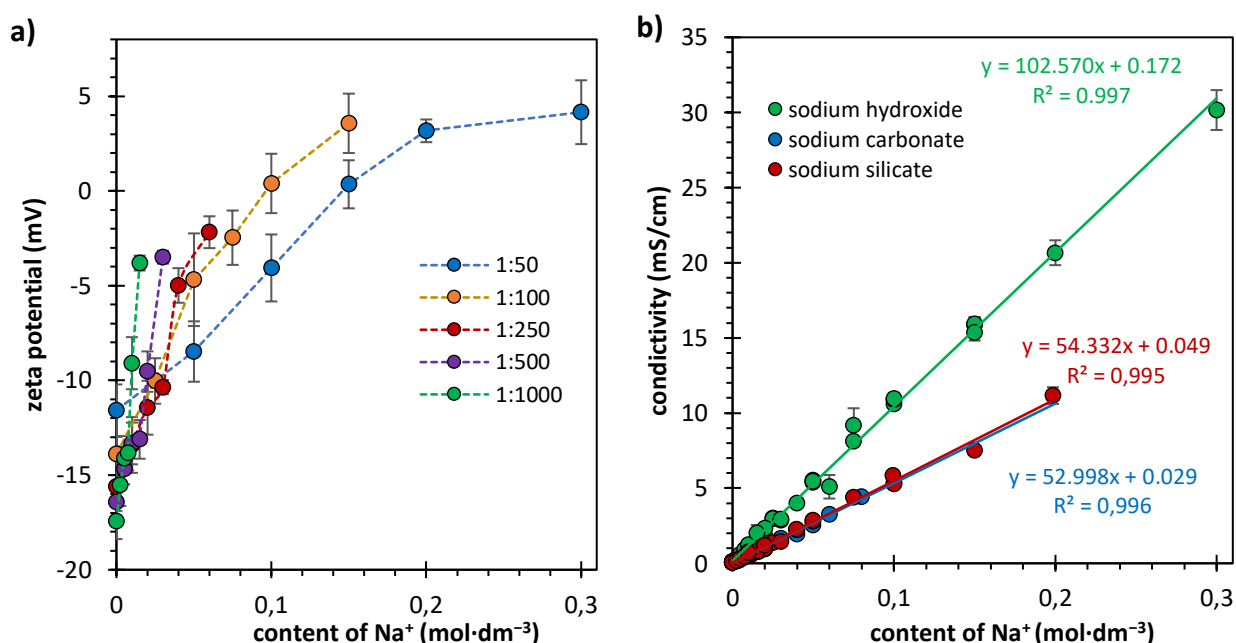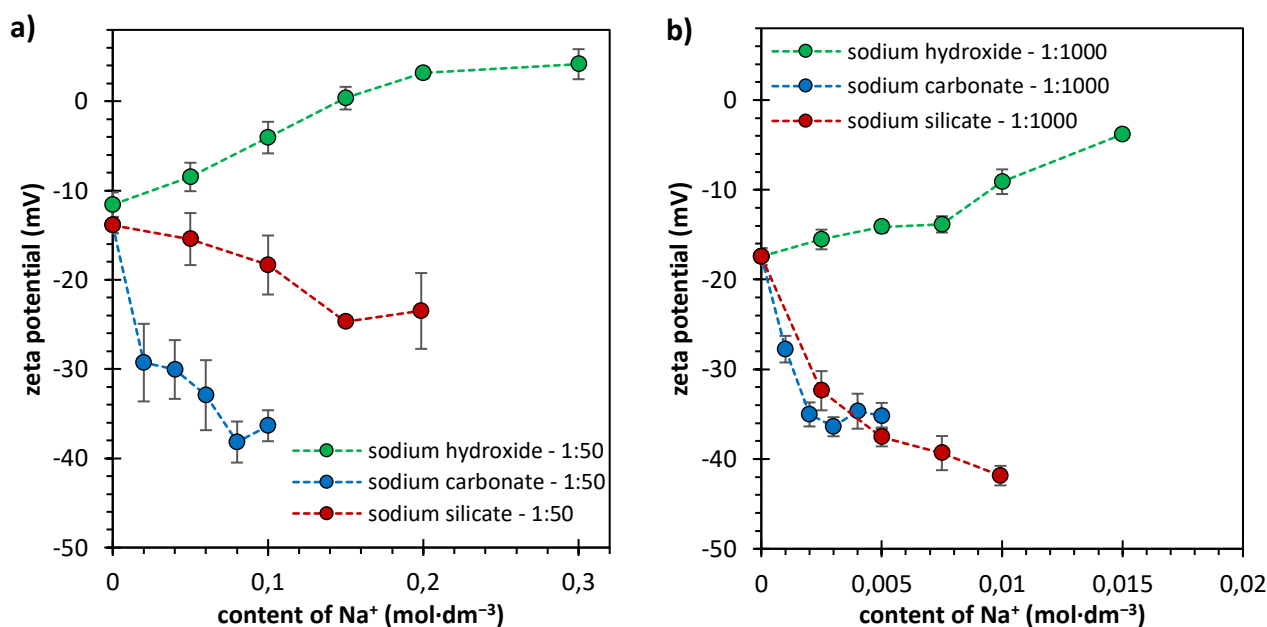

Figure 2 a) Development of zeta potential of various used dilution ratios of BFS dispersions in sodium hydroxide recalculated on the real content of Na+ ion in the samples, b) Measured conductivities of BFS dispersions in all used alkaline activators recalculated on the real content of Na+ ion in the samples.

The main task in this part of the experiments was the utilization of the dilution approach as the possibility to get an overview of the trend in zeta potential for individual samples in respect to the used dilution ratio, helping to predict and extrapolate the behaviour of original undiluted samples. The example of obtained zeta potential dependencies on the concentration of Na$^+$ ions in the samples as were obtained for sodium hydroxide alkaline activation for the individual used ranges of dilution are shown in **Figure 2a**. The results are indicating that the dilution has a minimal effect on the zeta potentials of BFS in distilled water without the addition of activators, where the average zeta potential (-15.7±2.2) mV was determined. With the increasing concentration of Na$^+$ ions in the samples the difference from the original dispersions of BFS in the water started to be more pronounced. The trends in our data are also indicating that from the concentration of Na$^+$ ions 0.05 mol·dm^{-3},

sample high conductivity and pH are starting to be the key features tailoring and affecting the final value of measured zeta potential of BFS dispersion. **Figure 2b** experimentally confirmed the direct relation of the concentration of Na^+ ions in BFS dispersions and its measured conductivity. Our dilution approach also indicated that at the concentration of Na^+ ions 0.1 $mol \cdot dm^{-3}$, BFS dispersions reached zero zeta potential, which is indicating their low electrostatic stabilization against aggregation. Further addition of Na^+ ions gradually shifted zeta potentials into the positive region of the scale. These results are in good agreement with published literature [12].

The comparison of two selected dilution ranges (1:50 and 1:1000 by volume) for the other two studied alkaline activators is shown in **Figure 3**. The presented data are indicating an opposite effect observed for the activation with sodium carbonate and sodium silicate in comparison to sodium hydroxide alkaline activation of BFS. In all studied dilution ranges, we have observed a significant shift to the more negative values of BFS dispersions zeta potential in comparison with original BFS dispersion in water. Again, this finding is in good correlation with published data [12]. This is indicating a more pronounced negative charge of individual particles in these samples with further addition of both these activating solutions and also an increase in their colloidal stability. These results are really interesting, especially considering the observed dependences of conductivities of BFS dispersions on Na^+ ion concentration showed in **Figure 2b**.

Figure 3 Development of zeta potential of BFS in used alkaline activators recalculated on the real content of Na+ in the samples – a) 1:50 dilution (by volume) with water; b) 1:1000 dilution (by volume) with water

The conductivities of sodium silicate and sodium carbonate dispersions are showing similar trends as the data for sodium hydroxide. These experimental data are indicating a completely different mode of operation of sodium carbonate and sodium silicate compared to the classical BFS activation using sodium hydroxide. The literature [9,12] explain this behaviour by the adsorption of carbonate or silicate anions onto the BFS grains.

The comparison of the dilution of sodium carbonate and sodium silicate is indicating an almost negligible effect in the case of sodium carbonate. This AAS showed the lowest pH in comparison with sodium silicate and sodium hydroxide solutions and due to this fact, the further dilution of these BFS dispersions has an almost negligible effect on the measured zeta potential and corresponding stability of these samples. On the other hand, sodium silicate solutions showed more alkaline pH and also significantly higher dynamic viscosity in comparison to sodium carbonate, which are probably the main reasons for the observed more significant role of dilution on the measured zeta potentials of BFS dispersions.

Although the trend seems similar for both dilutions presented in **Figure 3**, lower dilution gives values closer to zero (for NaOH even to positive values) and it is thus questionable, what situation is in the highly concentrated suspensions prior to their dilution with higher ionic strength etc. Therefore, the results illustrate that the dilution extent together with the nature of the alkaline activator are crucial parameters for the obtained absolute values of zeta potential and one should be cautious when trying to predict the behaviour of the real concentrated suspension. The comparison of the values with those of concentrated suspensions could be very interesting but unfortunately has not been done due to the unavailability of the electroacoustic method able to measure concentrated suspensions [11,13,14] at our department.

4.   CONCLUSION

The main task of our work was the investigation of the effect of the type and the concentration of used alkaline activators on the stability and interactions between colloidal particles of BFS. For these purposes, we have used zeta potential as a crucial feature of analyzed samples together with the sample-dilution approach allowing us to predict further behaviour of these systems in a more concentrated state. These experiments were also supplemented by the physicochemical characterization of activation solutions as well as prepared BFS dispersions. The outcomes of our experiments are straightforward. The dilution approach was successful for modelling and extrapolation of possible behaviour and stability of BFS dispersions in all used alkali-activated solutions (sodium hydroxide, sodium silicate and sodium carbonate). We have also observed a different mode of action in the case of sodium hydroxide, where the addition of activation solution increased the zeta potentials from negative values (for zeta potential of slag in water observed average value (-15.7±2.2) mV) to 0 mV and further to positive values. Contrary to this, in the case of sodium silicate and sodium carbonated the addition of AAS into the BFS slag dispersions caused a gradual shift toward more negative values of measured zeta potentials, which is indicating more significant colloidal stabilization of BFS particles in these systems. The results of our work are indicating that the proper technique of sample dispersion and the maintenance of the precise content and ratios of individual components represent crucial parameters managing the stability of alkali-activated materials based on blast furnace slag.

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