Alkaline Activator Impact on the Geopolymer Binders

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Abstract. Concrete structures are constantly moving in the direction of improving the durability. Durability depends on many factors, which are the composition of concrete mix, the usage of additives and admixtures and the place, where material will work and carry the load. The introduction of new geopolymer binders for geopolymer structures adds a new aspect that is type of used activator. This substance with strongly alkaline reaction is divided because of the physical state, the alkaline degree and above all the chemical composition. Taking into account, that at present the geopolymer binders are made essentially from waste materials or by-products from the combustion of coal or iron ore smelting, unambiguous determination of the effect of the activator on the properties of the geopolymer material requires a number of trials, researches and observation. This paper shows the influence of the most alkaline activators on the basic parameters of the durability of geopolymer binders. In this study there were used highly alkaline hydroxides, water glasses and granules, which are waste materials in a variety of processes taking place in chemical plants. As the substrate of geopolymer binders there were used fly ash which came from coal and high calcareous ash from the burning of lignite.

1. Introduction
Need of development in cement industry due to ecological aspect is very high. More and more stringent standards for the emission of carbon dioxide in the production of world's most popular binder, make the cement clinker in the light of the production amount and the degree of emission as a non-ecological material [1]. Every year market demand on cement binders is increasing. It tends to seek new solution to cement binders. Currently, the best solution is to replace the clinker cement by geopolymer one. Abstracting from ecological aspect, tests obtained on highly processed geopolymer cements and binders shows advantage due to durability tests [2, 3].

There is a similarity between the Portland cement and the geopolymer cement. Both of them when hardened give huge values of compressive strength and are resistant to high temperature and water after they hardened. They behave like hydraulic binders, they both are porous materials. In contrast to the Portland cement, the geopolymer contains only amorphous hydrates. In comparison to the crystalline ones, which occur in Portland cement. There is a present of calcium hydroxide in the pores of hardened Portland cement and because of the carbonate formation the surface is coated by a thin layer of calcium carbonate. The water in ordinary cement is used for the hydrate formation during the hardening process, whereas in geopolimerization process it plays role of transport for alkali activator.

The classical cements set owing to the special phenomenon of solvation, i.e. hydration. It is a compound process due to overlapping and a mutual influence of individual clinker phases that react with water. The total hydration process consists of three basic stages. The dissolution of soluble compounds in water, that is the proper hydration, which consists in the creation of the primary phase in a colloidal state (the formation of the plastic mass) and the crystallization of the hydration products (hardening of the plastic mass) [4]. The initial stage of the proper hydration of cement is connected first of all with the C3A phase [5]. As a result of a fast reaction of this phase, large crystals of hydrated calcium aluminates are produced (Figure. 1a). All the stages of hydration, as compared with the setting of the polymeric blend, are presented in Figure. 1.
The present state of knowledge gives the possibility to present that a geopolymer based on fly ash is characterized by following properties [6]:

- is built by structure similar to vitreous bodies [7],
- in structure of geopolymers there is presence of sodium and potassium cations ($\text{Na}^+$, $\text{K}^+$), which are not bonded so strong as it is in zeolites, it is a reason of potential efflorescence occurrence,
- structure of material is represented by a porous body,
- porous body of geopolymers contain water,
- the water is used in geopolymerization process as a transport of alkali activator,
- amorphous hydrates and crystalline can be noticed in structure only if material containing calcium are present (i.e. blast furnace slag, calcareous fly ash).

Last years of research under the process of geopolymerization brings much information. First of all, structure of hardened material was described. First model of geopolymer structure was given by Joseph Davidovits. He elaborated model, which could be designed for a poly-sialate-silox type (Figure. 2a) [8, 9]. Future progress in research obtained by Barbosa brings modified model, which in his structure was similar to vitreous bodies (Figure. 2b) [7].

**Figure 1.** Comparison of phases [4]: a) hydration of the Portland cement, b) polymerization
The problem in the introduction of new technology is in obtaining the substrate, which is also reflected in the difficulties in developing production technology. Currently the best material for geopolymer cement production are volcanic tuffs. The problem is the possibility of obtaining material and limited deposit. Other possibility is to use fly ash from the burning of coal and blast furnace slag from steel mills as substrates. In this case, it becomes troublesome to obtain homogeneity of material due to the process of their production.

Other problem is that alkali activation of alumino-silicate materials is complicated process, that has not been fully described yet. What is known by now, the reaction of alumino-silicate materials in a strong alkaline environment makes a disintegration of siliceous bonds. After that new phases, which start containing Al parts, in old siliceous structure are being formed. Alumino-silicate gels, which are widely called zeolite precursors, are mostly formed. This paper presents the effect of different alkaline activators on the strength of the hardened geopolymer binder produced from fly ash and blast furnace slag.

Geopolymeric concretes possess a high compressive strength, very small shrinkage and small creep, and they possess a high resistance to acid and sulphate corrosion [10, 11]. Some researchers also found that this concrete is also resistant to carbonate corrosion and possesses a very high fire resistance [12] and also a high resistance to UV radiation [13]. The widest and most interesting investigations concerning reinforced concrete elements (beams and pillars) from the geopolymeric concrete were carried out by the Curtin University of Technology in Australia in the year 2006 [14]. The results were obtained both for beams and pillars which were similar in behaviour to reinforced concrete elements from a concrete on the Portland cement (Figure. 3).

Figure 2. Model of geopolymer structure: a) proposed by Davidovits [8, 9], b) proposed by Barbosa [7]
Figure 3. Example of reinforced concrete beams from geopolymeric concrete damage [14]

2. Research base

In this study there were used three different alkaline activators obtained from chemical plants as materials, that are the direct product related to the activity and the by-product of other chemical processes (Table 1). Using alkaline compounds there were activated mixtures of two types of fly ash, the siliceous and the calcareous, and blast furnace slag (Table 2). The research material was obtained from domestic power plants and steel mills.

Table 1. Specification of alkaline substances used as activator

| Symbol | Name of alkaline            | SiO$_2$/Na$_2$O, molar module / molar mass* [g/mol] | Density [g/cm$^3$] | Viscosity cP (in temp. 20°C) |
|--------|-----------------------------|-----------------------------------------------------|--------------------|----------------------------|
| W1     | Sodium hydroxide            | 39.99*                                              | 2.13               | -                          |
| W2     | Potassium hydroxide         | 56.11*                                              | 2.12               | -                          |
| S1.1   | Sodium water glass          | 3.2-3.4                                             | 1.37-1.40          | 100                        |
| S1.2   | Sodium water glass          | 2.4-2.6                                             | 1.45-1.48          | 200                        |
| S1.3   | Sodium water glass          | 1.9-2.1                                             | 1.50-1.53          | 700                        |
| S2.1   | Potassium water glass       | 3.9-4.1                                             | 1.15-1.20          | 3                          |
| S2.2   | Potassium water glass       | 3.4-3.6                                             | 1.26-1.32          | 35                         |
| S2.3   | Potassium water glass       | 3.2-3.4                                             | 1.38-1.42          | 200                        |
| K1     | Dried sodium silica         | 1.9-2.1                                             | 0.75               | -                          |
| K2     | Dried potassium silica      | 3.2-3.4                                             | 0.35-0.50          | -                          |

Table 2. Chemical composition of fly ash and blast furnace slag used for research (mass %)

| Symbol | Type                                      | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | MgO | CaO | Na$_2$O | K$_2$O | P$_2$O$_5$ | Total  |
|--------|-------------------------------------------|--------|-------------|-------------|--------|-----|-----|--------|--------|-----------|--------|
| F1     | calcareous fly ash                        | 45.17  | 21.79       | 4.58        | 1.85   | 1.49| 21.06| 0.23   | 0.19   | -         | 96.36  |
| F2     | siliceous fly ash                         | 51.20  | 44.30       | 0.90        | 1.84   | -   | 0.25| 0.27   | 0.16   | 0.10      | 99.02  |
| G      | blast furnace slag                        | 41.50  | 9.92        | 0.95        | 0.63   | 6.49| 37.52| 0.22   | 0.36   | -         | 97.59  |

Fly ash were mixed with ground and screened blast furnace slag, and then mixed with powdered alkaline material. Prepared proportions of ash and blast furnace slag are given below (Table 3). Each of the mixtures was activated using a mixture of hydroxide and water glasses or dried silicates and water glasses (Table 4). In this manner there were obtained mixes for further studies.
Table 3. Proportion of used fly ash and grounded blast furnace slag

| Used fly ash and blast furnace slag | Prepared mass proportion of fly ash |
|-------------------------------------|-----------------------------------|
|                                     | M1  | M2  | M3  | M4  | M5  | M6  |
| F1 2                                | 2   | 3   | 4   | 0   | 0   | 0   |
| F2 0                                | 0   | 0   | 0   | 2   | 3   | 4   |
| G 1                                 | 1   | 1   | 1   | 1   | 1   | 1   |

Table 4. Proportion of alkaline agents used as alkaline activators.

| Used alkaline substances | Prepared mass proportion of alkaline substances |
|--------------------------|-----------------------------------------------|
|                          | A1   | A2   | A3   | A4   | A5   | A6   | A7   | A8   | A9   | A10  |
| W1 1                     | 1    | 1    | 1    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |
| W2 0                     | 0    | 0    | 0    | 0    | 0    | 1    | 1    | 1    | 0    | 0    |
| S1.1 2                   | 2    | 0    | 0    | 2    | 0    | 0    | 0    | 0    | 0    | 0    |
| S1.2 0                   | 0    | 2    | 0    | 0    | 2    | 0    | 0    | 0    | 0    | 0    |
| S1.2 0                   | 0    | 0    | 2    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |
| S2.1 0                   | 0    | 0    | 0    | 0    | 2    | 0    | 0    | 2    | 0    | 0    |
| S2.2 0                   | 0    | 0    | 0    | 0    | 0    | 2    | 0    | 0    | 2    | 0    |
| S1.2 0                   | 0    | 0    | 0    | 0    | 0    | 0    | 2    | 0    | 0    | 0    |
| K1 0                     | 0    | 0    | 1    | 1    | 0    | 0    | 0    | 0    | 0    | 0    |
| K2 0                     | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 1    | 1    | 0    |

Method of samples formation: A mechanical mixer firstly mixed fly ash, blast furnace slag and alkaline activator for 10 min. Sodium silicate solution mixed separately with water were then added. Following a further 5 min of mixing, the samples were cast in 40x40x160 mm forms and vibrated for 3 min in order to release bubbles. The forms were sealed and set at 85°C for 4 h in a sample-drying oven. After being removed from the forms, the samples were kept at room temperature for another 20 h, before the beginning of physical and mechanical property measurements. Table 5. summarizes the compositions of the geopolymers under discussion.

Table 5. Composition of prepared samples

| Type of substrate                        | Substrates proportion (% mass) | Water |
|------------------------------------------|--------------------------------|-------|
| Calcareaeous fly ash with sodium alkaline| Fly ash / blast furnace slag  | 1     | 0.080 | 0.160 | 0.35 |
| Calcareaeous fly ash with potassium alkaline| Dried sodium/potassium water glass | 0.192 | 0.30  |
| Siliceous fly ash with sodium alkaline   | Sodium/potassium water glass  | 1     | 0.080 | 0.160 | 0.35 |
| Siliceous fly ash with potassium alkaline| 0.096                         | 0.192 | 0.30  |
3. Results

The results of compressive strength for calcareous fly ash are shown in Table 6. The compressive strength was increased with an increase fly ash to grounded blast furnace slag concentration, as well as with alkaline increase of the activator (Figure 4, Figure 5, Figure 6, Figure 7). It happened because of alkaline concentration was high, the dissolution of Si4+ and Al3+ ions from fly ash increased and the formation of sodium and potassium alumino-silicate was enhanced leading to an increase in strength [15-17]. Same correlation was observed when siliceous fly ash samples were investigated. (Table 6, Figure 6, Figure 7). Change of alkaline from sodium to potassium based make also values of compressive strength higher.

Table 6. Compressive strength values of calcareous fly ash and blast furnace slag mixes [MPa]

| Time [d] | A1 | A2 | A3 | A4 | A5 | A6 | A7 | A8 | A9 | A10 |
|----------|----|----|----|----|----|----|----|----|----|-----|
| M1       |    |    |    |    |    |    |    |    |    |     |
| 1        | 7.45 | 6.02 | 5.25 | 6.71 | 4.99 | 10.05 | 8.14 | 7.09 | 8.54 | 5.82 |
| 7        | 12.85 | 10.39 | 9.06 | 10.92 | 7.25 | 16.06 | 12.88 | 11.32 | 14.13 | 10.08 |
| 28       | 14.14 | 11.44 | 9.96 | 12.44 | 8.76 | 16.26 | 13.28 | 13.64 | 14.72 | 11.87 |
| M2       |    |    |    |    |    |    |    |    |    |     |
| 1        | 7.08 | 5.61 | 4.62 | 6.372 | 4.38 | 9.55 | 7.3 | 7.15 | 8.01 | 4.97 |
| 7        | 11.82 | 10.01 | 9.04 | 10.756 | 7.23 | 14.77 | 12.55 | 10.55 | 12.18 | 8.62 |
| 28       | 13.99 | 11.3 | 9.16 | 10.912 | 8.42 | 15.02 | 13.42 | 12.23 | 12.98 | 10.11 |
| M3       |    |    |    |    |    |    |    |    |    |     |
| 1        | 4.3 | 4.27 | 4.02 | 5.79 | 5.13 | 8.52 | 8.4 | 6.8 | 7.05 | 6.04 |
| 7        | 7.33 | 6.87 | 6.94 | 9.88 | 9.45 | 11.58 | 10.48 | 8.45 | 12.04 | 10.85 |
| 28       | 8.47 | 8.12 | 7.63 | 10.98 | 9.49 | 14.15 | 13.42 | 13.55 | 13.01 | 10.52 |

Table 7. Compressive strength values of siliceous fly ash and blast furnace slag mixes [MPa]

| Time [d] | A1 | A2 | A3 | A4 | A5 | A6 | A7 | A8 | A9 | A10 |
|----------|----|----|----|----|----|----|----|----|----|-----|
| M4       |    |    |    |    |    |    |    |    |    |     |
| 1        | 21.55 | 19.41 | 20.22 | 20.85 | 18.12 | 24.15 | 21.78 | 22.27 | 21.95 | 20.13 |
| 7        | 26.75 | 24.28 | 24.15 | 25.51 | 24.70 | 28.18 | 25.27 | 26.00 | 24.11 | 22.19 |
| 28       | 32.85 | 30.21 | 27.88 | 29.12 | 25.45 | 39.94 | 36.75 | 31.15 | 31.11 | 28.30 |
| M5       |    |    |    |    |    |    |    |    |    |     |
| 1        | 19.17 | 17.39 | 19.02 | 18.17 | 17.82 | 22.18 | 20.11 | 21.74 | 20.01 | 18.62 |
| 7        | 21.87 | 20.11 | 21.14 | 22.90 | 23.11 | 30.11 | 27.38 | 30.93 | 28.26 | 25.44 |
| 28       | 27.15 | 24.98 | 24.43 | 28.36 | 27.23 | 32.28 | 29.60 | 31.02 | 30.10 | 27.07 |
| M6       |    |    |    |    |    |    |    |    |    |     |
| 1        | 18.3 | 17.98 | 18.02 | 17.18 | 16.12 | 21.19 | 20.82 | 20.11 | 19.35 | 18.00 |
| 7        | 21.22 | 21.05 | 22.12 | 24.50 | 22.02 | 28.10 | 27.87 | 26.22 | 26.29 | 25.13 |
| 28       | 24.20 | 22.11 | 23.87 | 26.10 | 25.10 | 30.02 | 27.99 | 27.15 | 28.23 | 26.76 |
Figure 4. Compressive strength of calcareous fly ash based geopolymer due to different molar ratio of used water glasses

Figure 5. Compressive strength of siliceous fly ash based geopolymer due to different molar ratio of used water glasses
Figure 6. Compressive strength of calcareous fly ash based geopolymer due to different ratio of blast furnace slag added

Figure 7. Compressive strength of siliceous fly ash based geopolymer due to different ratio of blast furnace slag added
4. Discussion
Mixes of silica and calcareous fly ash with blast furnace slag are suitable source materials for producing geopolymers. The strength results of hardened materials show, that siliceous fly ash is more reactive than calcium. They give higher values of compressive strength of the fly ash geopolymer mortar. It is reasonably high at 28 to even 39 MPa, and it is significantly higher than the 10 to 13 MPa of the calcareous fly ash geopolymer mortar. The strength of a geopolymer is also dependent on the type of used activator. Much higher values were obtained for potassium based than sodium based activators. What is more, hydroxides which are unfortunately user hostile give worse results due to strength than less inconvenience in use dried silicates. The same thing appears with siliceous glass. The one with lower SiO2 to K2O ratio gives better effect of geopolymerization. Increasing the strength of the material can be carried out by improving substrates. It can be performed in many ways. Firstly, the burning of coal at a higher temperature may cause a higher degree of glass transition in ash particles, which translates into an increase in mechanical properties of mixture. Such a treatment applies only to newly emerging ashes. In the case of defaulting on dumps waste materials, slag and ash treatment can be done by cleaning material particle effects and reduce the fractions in the process of grinding the material after it has been cleaned [18].

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