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# THE STRENGTH OF GEOPOLYMERS BASED ON RED MUD AND FLY ASH

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**Abstract**

Alkali activated materials (geopolymers) are relatively new materials, thanks to their good mechanical, physical, thermal properties and at the same time environmental friendliness, they could be widely adopted in different fields. The experiments, described in this article, are focused on the investigation of compressive strength of alkali activated materials based on fly ash and red mud. For the following experiments were prepared five series of samples with different ratio of red mud to fly ash. All the samples had the form of cubes with dimensions 30mmx30mmx30mm. The tests on compressive strength were conducted in 7, 28 and 56 days after final heat treatment. The test showed that the highest strength had the samples with the smallest amount of red mud (5%). In 56 days it was 29 MPa. Meanwhile the samples with the biggest amount of red mud (50%) were not even tested because of samples cracking during heat treatment.

**Keywords**

Alkali activated materials; fly ash; red mud; water glass; compressive strength

## 1 INTRODUCTION

The wide study of alkali activated materials was started in the first part of the last century. From that time were made a lot of experiments in order to find new alternative materials to concrete and other silicates with good properties and lower price [1 – 5, 7-8].

Nowadays, there are not only the aspects of price and quality important but also of ecology. Utilization of production waste materials or decreasing of $CO_2$ emission are the next very important tasks which scientists have to solve. Cement production is the biggest emitter of $CO_2$ among all building materials. With each year consumption of cement grows and these days its production reaches 1.7 billion tons per year [9]. If we take into consideration that during production of 1 ton of clinker it is emitted 0.8 – 1.3 ton of $CO_2$ to the atmosphere, it becomes obvious, that production of cement plays not the last role in pollution of environment. For that reason in many countries pays special attention to the study of clinker free cements. [10,11,13 – 15].

The other advantage of alkali activated materials is they could be made on the base of waste materials (fly ash, slag) [3,5-8,11,12,14]. Each year on the planet it is produced hundred million tons of industrial wastes. Only a little amount of them finds further usage in different fields, the most part of wastes is stored, which requires huge areas, financial costs, and of course have a negative impact on the environment.

For the experiments, described in this paper, were used two types of waste materials. The first was fly ash – the industrial by-product, generated during combustion of coal. The annual world production of this waste material varies around 500 million tons [16]. And the second was red mud

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– the by-product of the aluminum production from bauxite (the Bayer process). The world production of this waste is 120 million tons per year [17]. It was prepared five series of samples with different proportion of red mud to fly ash in order to find the optimal composition of the substance. The amount of red mud varied from 50% till 5 % and amount of fly ash varied from 50% to 95%, all samples were tested on compressive strength.

## 2 MATERIALS

For this experiment were used two types of waste materials: fly ash – produced during combustion of coal at electric power station and red mud – the by-product of the manufacture of alumina from bauxite by the Bayer process.

The fly ash was taken from Opatovice electric power station (Czech Republic). Its chemical composition and particle size distribution are shown in the Table 1 and Figure 1.

**Tab.1** Chemical composition of fly-ash, wt.%

| | $SiO_2$ | $Al_2O_3$ | NaO | K2O | CaO | MgO | $Fe_2O_3$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|
| **Fly-ash, Opatovice** | 61.4 | 31.1 | 0 | 2.2 | 0.2 | 1.6 | 2.6 | 0.9 |

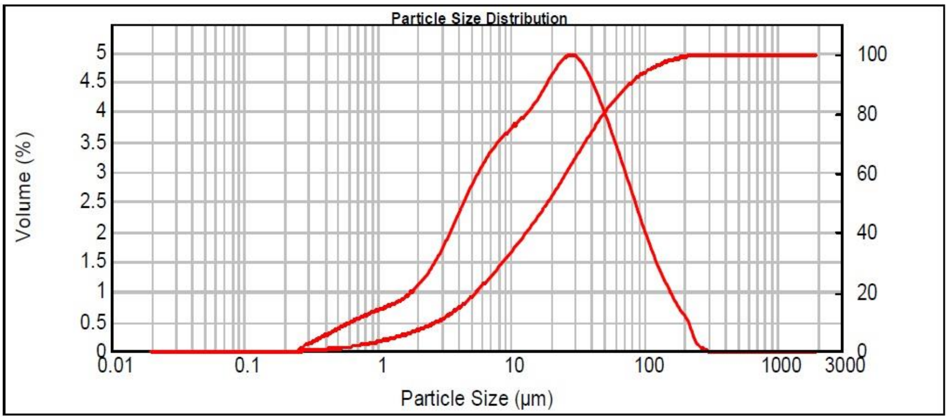


**Fig. 1** Particle size distribution of fly-ash

Red mud was taken from Ajka alumina plant (Hungary). Red mud is an alkaline residue (pH about 10) derived from alumina extraction by Bayer process from bauxite ore. Its chemical composition is shown in the Table 2. Red mud contains a significant quantity of entrapped NaOH. During experiments the red mud was used in wet state as it was taken from the alumina plant. Amount of water in red mud was about 14 wt.%.

**Tab. 2** Chemical composition of red mud, wt.%

| | $Fe_2O_3$ | $Al_2O_3$ | $Si0_2$ | $Na_2O$ | $TiO_2$ | CaO | MgO | $K_2O$ | $Cr_2O_3$ | NiO |
|---|---|---|---|---|---|---|---|---|---|---|
| **Red mud, Ajka** | 33.1 | 14.8 | 13.2 | 9.1 | 5.4 | 6.5 | 0.3 | 8.8 | 3.3 | 5.5 |

## 2.1 Samples preparation

We were prepared five groups of samples in a form of cubes with different ration of fly ash and red mud. The compositions of the samples are shown in the Table 3. The fly ash/red mud ratio in solid powder was the next:

- set of samples B50 consisted 50% of fly ash and 50% of red mud,
- B25 – 75% of fly ash and 25% of red mud,
- B15 – 85%of fly ash and 15% of red mud,
- B10 – 90% of fly ash and 10% of red mud,
- B5 – 95 of fly ash and 5% of red mud.

To the mixture of fly ash and red mud was added water glass. Than the mixture was well mixed, formed and put on high frequency vibration table for 30 minutes. In order to make samples were used silicon molds, which had a square form and were suitable for preparing of 16 samples with dimensions 30mmx30mmx30mm. The heat treatment of the samples was provided in two steps. Firstly, the formed pieces were put into the stove for 16 hours under the temperature 65°C. Than the next day, the samples were unmolded and put again into the stove for 24 hours under the temperature 65 °C.

After the heat treatment till testing the samples were left in normal laboratory conditions.

**Tab. 3** Composition of the samples (where M is Na or K)

| Component / Sample No. | **Fly ash (wt.%)** | **Red mud (wt.%)** | **Water glass (wt.%)** | **$SiO_2/Al_2O_3$** | **$M_2O/SiO_2$** |
|---|---|---|---|---|---|
| **B50** | 45.9 | 45.9 | 8.2 | 3.04 | 0.20 |
| **B25** | 59.6 | 19.9 | 20.5 | 3.60 | 0.11 |
| **B15** | 63.8 | 11.3 | 25 | 3.78 | 0.09 |
| **B10** | 66.3 | 7.4 | 26.3 | 3.85 | 0.08 |
| **B5** | 65.8 | 3.5 | 30.8 | 4.00 | 0.08 |

## 2.2 Strength measurement

The tests of strength of cured samples were conducting on testing machine ZD 10/90. The strength of samples was tested on compressive strength in 7, 28 and 56 days after final heat treatment.

The cubes were stressed in one direction by smoothly increasing strength till the appearing of cracks. Than the load was reduced, so that’s why the full crush of samples didn’t take place (Fig.2). Strength was calculated from maximum force during test. Strain rate was 5 mm per minute.

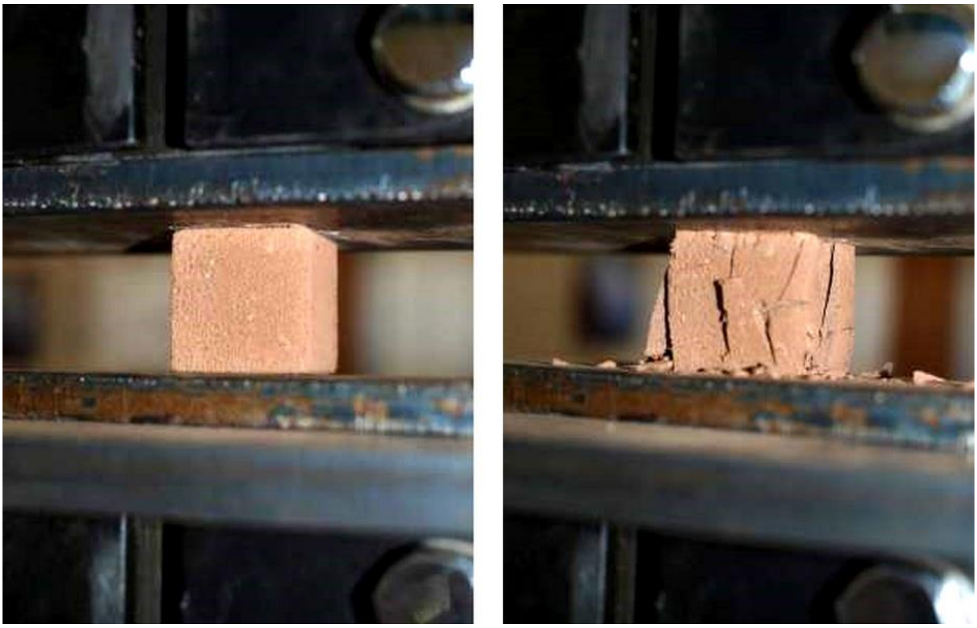

**Fig. 2** Compressive strength testing of the samples

### 2.3 Composition measurement and microstructure

Microstructure of samples after compressive strength tests was observed by SEM (Scanning Electron Microscope) TESCAN VEGA 3 Easy Probe. The chemical compositions were determined by EDS BRUKER probe (SEM component). SEM observation and determination of chemical composition was performing in high vacuum mode with uncoated samples.

## 3 RESULTS AND DISCUSSION

During the heat treatment of samples B50 all pieces were cracked (Fig.3), so that’s why testing of these samples wasn’t carried out.

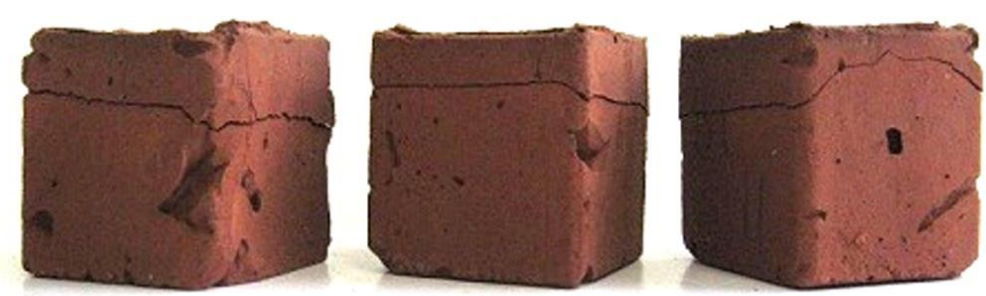

**Fig. 3** Samples B50 after final heat treatment

All the rest samples B25, B15, B10, B5 were tested on compressive strength in 7, 28 and 56 days after final heat treatment. All tested samples do not show any visible damage.

The results of the compressive strength tests are shown in the Figure 4.

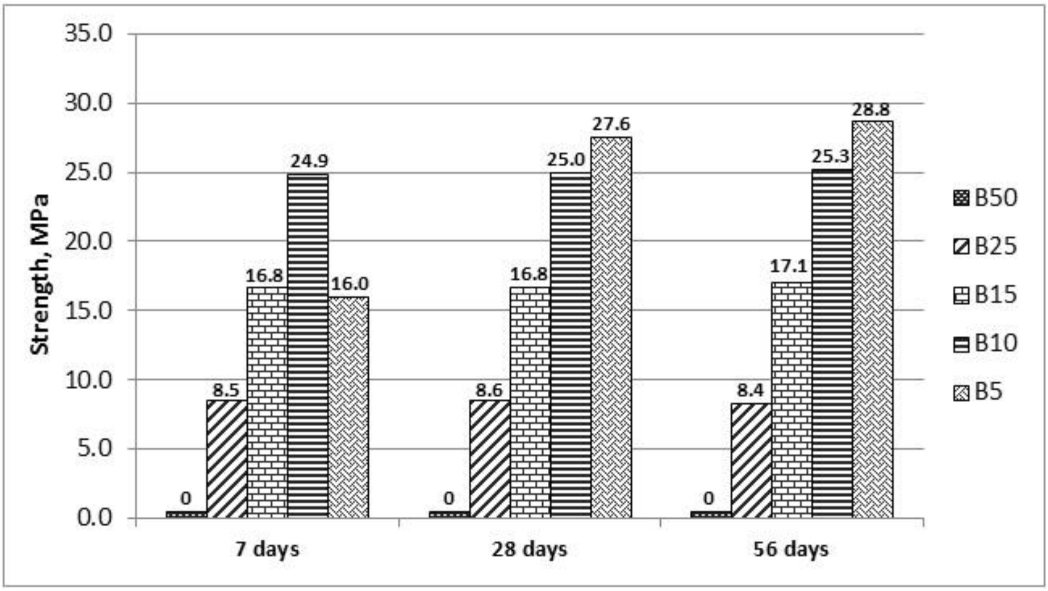


**Fig. 4** Compressive strength test results

The smallest strength among the all tested samples had the samples B25, which consisted the biggest amount of red mud – 25%. In 7 days after final heat treatment the average strength of these samples was 8.5 MPa and it remained the same in 28 and 56 days. The samples B15 with 15% of red mud had the strength two times higher than samples B25. Its average was around 17 MPa, it also remained the same in 28 and 56 days. The average strength of the samples B10 (with 10% of red mud) was around 25 MPa and it almost didn't change in one and two month. The highest strength had the samples B5 with the smallest amount of red mud (5%). It varied from 16 MPa in 7 days after final heat treatment till 29 MPa in 56 days.

The relatively small increasing of strength (slow curing) of B5 samples was probably connected with low amount of alkali metals oxide (ratio $M2O/SiO2$ was 0,08; see Tab. 3). Low amount of alkali metals oxide react very slow with silica/alumina for curing. For this reason the strength increases for about 2 month for full chemical reaction.

Chemical compositions and microstructure of selected samples after compressive strength tests were tested using SEM. Chemical compositions of selected samples is summarize on Table 4. From chemical composition is possible to see the increasing amount of sodium with increasing amount of red mud. Red mud is main source of alkali metals ions – amount of Na increase though the amounts of water glass decrease (see Table 3).

**Tab. 4** Chemical composition of selected samples, wt.%

| | O | Na | Mg | Al | Si | K | Ca | Ti | Fe |
|---|---|---|---|---|---|---|---|---|---|
| **B5** | 52.0 | 4.7 | 0.7 | 13.9 | 22.5 | 1.6 | 0.7 | 1.0 | 2.9 |
| **B25** | 54.4 | 5.8 | 0.6 | 11.2 | 20.9 | 1.2 | 0.9 | 1.1 | 3.9 |
| **B50** | 56.1 | 8.6 | 0.5 | 8.3 | 16.8 | 1.0 | 1.3 | 1.2 | 6.2 |

Relatively low strength of samples with high amount of red mud is probably due to very high concentration of alkali metals oxides. These oxides of alkali metals may hydrate during weathering of samples. Product of hydrating weakens the structure of geopolymer – products of hydrolysis of alkali metals salts is show at Fig. 5. The needle shape crystals (visible on Fig. 5) contain lots of sodium.

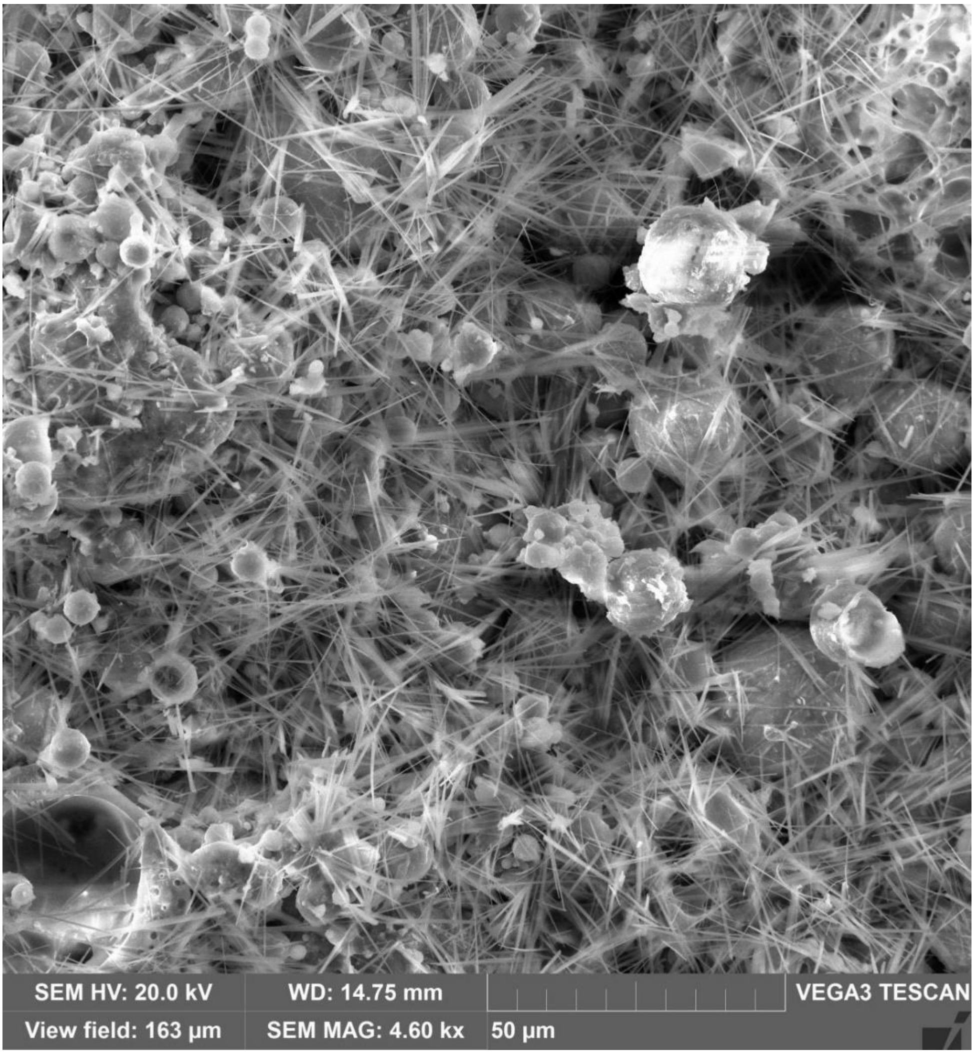


**Fig. 5** SEM structure of B25 sample. Products of weathering of alkali metal salts

### 3.1 Other materials based on red mud/fly ash – comparing

Materials based on red mud and/or fly ash was prepared early with different properties. Our samples based on red mud and fly ash was prepared from waste materials and water glass. For this reason our material is relatively cheap and for sample preparation is produce very low amount of $CO_2$. Our samples have compressive strength about 25 MPa that is comparable with samples of based on similar materials.

The alkali activated materials based on fly ash and red mud studied Jian He et al. In their paper they compared two types of geopolymers, one based on metakaolin and the second on red mud and class C fly ash. To the metakaolin was added sodium silicate solution and sodium hydroxide and to the red mud-fly ash mixture – sodium trisilicate powder. The results of the tests showed that metakaolin based samples had the higher compressive strength and at the same time shorter period of complete curing than red mud-fly ash samples. Metakaolin based samples achieved the strength of 31 MPa and were cured completely as less as 9 days, while red mud-fly ash samples had the strength 13 MPa and complete curing took more than 21 days. [22]

Gordon et.al. investigated composites formed by the addition of various amounts of hydrated lime, condensed silica fume and limestone to the red mud. The strongest composite had the compressive strength 15-18 MPa in 28 days and 18-22 MPa in 122 days correspondingly. These samples contained equal quantities of red mud and limestone, blended with a 2:1 mix of hydrated lime and condensed silica fume. [19]

Jiakuan Yang and Bo Xiao studied composites based on red mud, fly ash and sand with addition of lime, gypsum and/or Portland cement. Depending on the proportion of the components the strength of the samples varied from 8.7 till 26.7MPa in 7 days and from 11.7 till 29.5 MPa in 28 days. According to their suggestion the optimal composition of the material is 25 – 40% of red mud, 18 – 28% of fly ash, 30 – 35% of sand, 8 – 10% of lime, 1 – 3% of gypsum, and about 1% of Portland cement. [20]

Much higher strength can be reached in case of slag usage instead of fly ash. Zhihua et al. studied alkali-slag-red mud cement (ASRC) and got very good results. ASRC based on slag (70%) and red mud (30%) with addition of alkali activator – solid water glass with modulus 1.2 and sodium aluminate clinker. ASRC cement had high early and ultimate strength and a good strength development, in 1 day the strength was 20 MPa, in 28 days – 56 MPa and in 180 days – 66.5 MPa. [21,22]. Similar results of strength after 28 days reach the Zhou et al. They used the red mud, slag and lime in diverse ratios.

Ke et al. investigated the compressive strength of blend based on thermally treated red mud and blend. They used one-part thermal preactivated red mud/sodium hydroxide powder and water for preparing of paste. Their samples reach the strength up to about 10 MPa after 7 days. After 7 days the samples was a significant strength loss [5].

## 4 CONCLUSIONS

We were prepared five groups of samples. As basic materials were used fly ash and red mud, as an alkali activator sodium silicate with silicate modulus 3.35. The fly ash/red mud ratio was the next: set of samples B50 consisted 50% of fly ash and 50% of red mud, B25 – 75% of fly ash and 25% of red mud, B15 – 85%of fly ash and 15% of red mud, B10 – 90% of fly ash and 10% of red mud, B5 – 95 of fly ash and 5% of red mud. During heat treatment all the samples of the set B50 were cracked, therefore the further investigation didn’t take place. The rest samples were tested on compressive strength in 7, 28 and 56 days after final heat treatment. The test results showed that with proportional increasing of fly ash and decreasing of red mud in the substance the strength of the samples was increasing. The highest strength had the samples B10 and B5. It was 25 and 29 MPa correspondingly in 56 days after final heat treatment. So, according to results of this investigation it can be told that optimal ratio of the basic components in the substance is 90 – 95% of fly ash to 10 – 5% of red mud.

The investigated materials show strength that is comparable with early prepared similar materials. For our samples is not necessary any heat treatment of base materials. Main advantage of prepared material is utilization of waste materials, low production of $CO_2$ and low energy consumption for preparation in comparison of classics cement materials.

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