Aspects of application of industrial aluminosilicate wastes in production of zero-cement construction composites

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Abstract. Utilization of industrial wastes in great volume is one of the basic strategies of industrialized countries [1]. Such by-products of metallurgical industry as blast furnace slag are widely used in construction when production of cement-based materials. The studies related to synthesis of free-of-cement binders, using a blast furnace slag as a basic binding component are also carried out. However, significant variability in composition and properties as well as insufficient knowledge explains a limited application of blast furnace slag as independent binding component. That is also relevant to alkali activated free-of-cement binders. In framework of this study the aspects of strength characteristics formation in alkali-activated binders based on blast furnace slag taking into account the parameters of alkaline activation and curing conditions. The concentration of alkaline agent was determined to be effects differently in the studied slags. Positive effect on structure and strength formation in the binder during thermal curing was observed.

1. Introduction

In terms of current crisis in the industry, the problems of rational use of natural resources, including the different types of industrial wastes are very meaningful, particularly, in construction field. It can be associated with partial and complete replacement of expensive and nonrenewable natural resources by more chip natural and industrial analogues. That will lead to the following:

– reduction in expenses for cement, natural aggregates, energy recourses etc.;

– utilization of great volume of industrial wastes, stored in discharges, and occupying the huge effective areas;

– production of construction composites with high-performance characteristics vs. the composites based on traditional raw materials;

In the most of developed countries the industrial wastes are used as mineral component, reactive aggregates and fillers when production of advanced construction materials. the blast furnace slag from steel production are among the most popular large-tonnage industrial wastes, those should be utilized in great volume.

Taking into account the differences in characteristics of blast furnace slag the reactivity degree of them and methods of reactivity improving are important to study [8, 9]. It will allow extension of application area for the slag as nonreactive aggregate, supplementary pozzolan and as high-reactive binding component [10, 11].
In this work the parameters of synthesis of cement free alkali-activated binders based on blast furnace slag from different plants were investigated taking into account differences in alkali component and curing conditions.

2. Materials and equipment
This paragraph follows a section title so it should not be indented. In this paper blast furnace slags from two different metallurgical plants (S1 and S2) were used. For alkali activation of the applied slags the following alkaline components were used: NaOH, KOH, Na₂SiO₃. Chemical and phase analysis of the slags was realized with diffractometer ARL 9900 (Thermo Fisher Scientific (Bremen) GmbH, Germany) using Co-anode irradiation as well as Ni- and Fe-filters to attenuate the β-irradiation). The step angle was 0.03°. Measuring time in the scan point was 1 sec. The Soller slits with aperture of 1.5° were brought into the X-ray optics of goniometer to reduce the angular asymmetry of X-ray line profiles initiated by a beam vertical divergence. The quantitative Full profile XRD-analysis to study the raw materials and relevant alkali-activated binders was carried out with the DDM program where the Rietveld algorithm and Derivative Difference Minimization algorithm were realized. Microstructure of the binders was studied with scanning electron microscope TESCAN MIRA 3 LMU (Czech Republic).

3. Experimental part
3.1. XRD and XRF analysis
The slags S1 and S2 were characterized by low hydraulic activity as well as differences in chemical and mineral composition due to variation in raw materials and parameters of production (Table 1, 2).

| Slag | Oxides content, wt.% |
|------|----------------------|
|      | LOI | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | TiO₂ | K₂O | Na₂O | MgO | MnO |
| S1   | 2.42 | 1.6 |
|      | 38.1 | 5.6 | 0.5  | 41.6 | 0.2 | 0.5 | 0.5 | 12   | 0.05 |
|      | 0.6  | 0.6 | 0.7  | 0.6  | 0.9 | 0.07 |
|      | 92.8 |
| S2   | 38.1 | 6.1 | 0.5  | 43.4 | 0.1 |
|      | 0.7  | 0.6 | 0.9  | 0.01 |
|      | 99.3 |

Results of XRF-analysis demonstrated that content of alkali oxides in S1 was up to 45 %, and in S2 was by up 55 %. Total content of SiO₂ and Al₂O₃ oxides was by up 45 %.
According to data from Table 1, as well as taking into account the knowledge about correlation between chemical composition and hydraulic activity of blast furnace slag [13, 14] the studied slags are classified as materials with low hydraulic activity.
XRD-analysis demonstrated the prevailing two followings silicate phases: merwinite (Ca₃Mg(SiO₄)₂) and akermanite (Ca(MgSi₂O₅)) in the both slag presented (Table 2). Meanwhile, the wide halo in Figure 1 gave evidence of the presence of X-ray amorphous phase of 90 % at least.
So, results of XRF and XRD analysis demonstrated the potential suitability of the S1 and S2 for alkali-activated binder synthesis.

### Table 2. Mineral composition of the slags

| Slag | Merwinite, wt.% | Calcite, wt.% | Quartz, wt.% | Akermanite, wt.% |
|------|----------------|--------------|--------------|-----------------|
| S2   | 78.7           | 15.6         | 5.8          | –               |
| S1   | 31.8           | –            | –            | 68.2            |

3.2. **Strength characteristics**

One of the basic parameter of suitability of blast furnace slag in alkali-activated system is reactivity under high basicity. So, in this work the reactivity degree of the studied slags was determined using the followings alkaline components: NaOH, KOH, Na$_2$SiO$_3$.

### Table 3. Experimental composition of the alkali-activated binders

| №  | Composition based on | Type of alkaline component | Concentration of alkaline component, wt.% |
|----|----------------------|---------------------------|------------------------------------------|
| 1  | 1N$_{S1}$           | NaOH                      | 10                                       |
| 2  | 2N$_{S1}$           | NaOH                      | 20                                       |
| 3  | 3N$_{S1}$           | NaOH                      | 30                                       |
| 4  | 1K$_{S1}$           | KOH                       | 10                                       |
| 5  | 2K$_{S1}$           | KOH                       | 20                                       |
| 6  | 3K$_{S1}$           | KOH                       | 30                                       |
| 7  | 1N$_{S2}$           | Na$_2$SiO$_3$             | 10                                       |
| 8  | 2N$_{S2}$           | Na$_2$SiO$_3$             | 20                                       |
| 9  | 3N$_{S2}$           | Na$_2$SiO$_3$             | 30                                       |
Initially, the slags were grinded in ball mill up to specific surface area of 400 cm²/g. The compositions of alkali-activated binders were prepared according to Table 3 followed by casting in metal cubic forms of 7×7×7 cm. The metal forms with the binder were cured in steam chamber under the following regime: buildup of temperature up to 60 °C during 1 hour. The curing process was performed at constant 60°C for 24 hours followed by temperature release during 2 hours. After the steam curing the samples of the binder were demoulded and hardened in ambient conditions (t=23±°C, humidity was up to 52 %) during 2 and 7 days before a strength test (Figure 2).

![Figure 2](image_url)

**Figure 2.** Effect of different alkaline components and concentration of them on strength characteristics in the alkali-activated binders, based on: a) S1; b) S2

The slags S1 and S2 activated with KOH of 20 % had the highest compressive strength. The higher content of KOH led to inhibition of the binder consolidation and decreasing of strength value.

For any binding system the choice of raw materials and ratio of them as well as curing conditions are extremely effect on formation of structure and strength characteristics in a final material.

In this study the two type of curing conditions were used: ambient conditions (t=22±3 °C, relative humidity = 52 %) and steam curing with the following regime: buildup of temperature up to 60 °C during 1 hour. The steam curing process was performed at constant 60°C and relative humidity of 100 % for 24 hours followed by temperature release during 2 hours. After the steam curing the samples of the binder were demoulded and hardened in ambient conditions (t=23±°C, humidity was up to 52 %). The results of the experiment are presented in Table 4.
Table 4. Effect of curing conditions on strength characteristics of the alkali-activated binders

| Alkaline component | NaOH | KOH | Na₂SiO₃ | NaOH | KOH | Na₂SiO₃ |
|--------------------|------|-----|---------|------|-----|---------|
| Slag               | S2   |     | S1      |      |     |         |
| Compressive strength, MPa |
| **Ambient conditions** | | | | | | |
| 2 days             | 1.18 | 4.59| 11.45   | 7.85 | 5.53| 27.32   |
| 7 days             | 7.93 | 22.78| 28.23  | 13.12| 11.67| 31.41   |
| **Steam curing**   | | | | | | |
| 2 days             | 13.99| 12.08| 27.22 | 20.12| 11.07| 16.38   |
| 7 days             | 17.12| 19.05| 17.22 | 18.23| 18.24| 15.26   |

Data from Table 4 demonstrated that steam curing effected positively on compressive strength formation at early setting time, especially, in the binding systems with NaOH and KOH. The binding compositions after steam treatment demonstrated enhancement in strength values more than three times vs. binding compositions cured in ambient conditions. However, the steam curing of the binder based on S1 and Na₂SiO₃ led to double reducing in compressive strength.

3.3. SEM-analysis

Structure skeleton of the alkali-activated binders demonstrated morphological differences in the newly formed phases depending on type of alkaline component and curing conditions (Figure 3).
Figure 3. Microstructure of alkali activated binder based on S1 at different curing conditions

Contact zone between grains of slag and alkaline component as well as friable structure were clearly observed in the binding systems cured in ambient conditions. This indicates on slow chemical interaction between the components. More compact structure was typical for the binder after steam curing providing higher strength characteristic (Table 4).

Conclusion. In this work the effect of characteristics and concentration of alkaline component as well as characteristics of the slag on formation of structure and strength parameters in the alkali-activated binder. For S1 was determined the most effective alkaline component to be NaOH. Increasing of concentration of NaOH in this system led to reducing of compressive strength. The binders based on S2 had the best strength parameters with Na$_2$SiO$_3$. In this case, increasing of Na$_2$SiO$_3$ content in the binder provided reducing in strength. Positive effect of thermal treatment (steam curing) on structure compacting and growing of strength characteristics was determined.
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