Alkali-activated geopolymers based on iron-rich slag from copper industry

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Abstract. In the present study geopolymers were prepared using fayalite slag (iron-silicate fines) from copper producing plant (Aurubis Bulgaria AD). The influence of the different concentrations of alkali activator on properties and structure was examined. The prepared geopolymers were characterized by maximal compressive strength of about 27 MPa. The microstructural examination revealed that only small amount of the precursor reacted, but certain amount of ferric iron (Fe$^{3+}$) participate in the structure of newly formed geopolymer gel.

1. Introduction
Geopolymers, also referred as inorganic polymers or alkali activated materials, are alumino-silicate materials which possess superior physical and chemical properties and a wide range of potential applications. The synthesis of geopolymers involves reactions between powder precursor and concentrated solution yielding at ambient temperature tridimensional polymer structure [1]. There are two routes of synthesis: in alkaline media using alkali hydroxides and silicates; and second: in acid media – using phosphoric acid [2]. The raw material is homogenized with activator solution to initiate the geopolymerization process. Based on existing model for aluminosilicate weathering in aggressive media, the model of geopolymerization includes dissolution, reorientation and reprecipitation stages including an autocatalytic polycondensation step [3]. Initially kaolinite (and calcined version – metakaolin [2]) were used as geopolymer precursors but last decades wide range of natural [4] and industrial waste materials were intensively studies. Most of the studies are oriented to fly ash [5], [6] and blast furnace slag [7]. Both are utilized in concrete industry as mineral additive to Portland cement according EN 206-1. On other hand other important wastes, in terms of volume, are coal mine and floatation tailings, red mud from the production of alumina and several types of iron-rich slags from metallurgical plants [8]. Usually those industrial waste contain heavy metals as Cu, Zn, Cr, Pb, Mo, Cd, etc [9], thus are considered toxic and disposal without any proper management can cause serious environmental issues related to contamination of soil and water. Geopolymer technology has already been patented and used to immobilize and stabilize toxic or wastes materials [10]. One of the potential raw material is iron-rich slag from copper industry [11]. The role of iron in the geopolymerization process is not well studied and the results are often contradictory. Some of the authors report that iron could be part of the polymer structure partly replacing the aluminum in poly ferro-sialate framework [12].

The aim of the present study is to examine the influence of different concentration of the activator solution to the mechanical properties and to characterized prepared geopolymers based on fayalite slag (iron-silicate fines) from copper producing plant (Aurubis Bulgaria AD). The fayalite slag is hardly
marketable product due to its specific composition, fineness and presence of heavy metals. Huge amount remains unutilized and disposed in landfills in the territory of Bulgaria.

2. Materials and methods

2.1. Materials
The geopolymer precursor in the present study was copper by-product - fayalite slag from Aurubis (Pirdop, Bulgaria) with the following chemical composition (%): Fe$_2$O$_3$ – 58.42; SiO$_2$ – 29.34; Al$_2$O$_3$ – 4.40; CaO – 2.66; MgO – 0.89; K$_2$O – 0.71; Na$_2$O – 0.58; CuO – 0.49; PbO – 0.37; TiO$_2$ – 0.30; MoO$_3$ – 0.26, measured by XRF. The mineral composition of the slag was presented by fayalite, magnetite, minor quantity pyroxene, and absence of significant amorphous phase [13]. The chemical reagents used for the preparation of the activator solutions are: sodium silicate (water glass) derived from local industry with molar ratio of SiO$_2$/Na$_2$O=2.98 and density respectively – 1.49 g/cm$^3$; potassium hydroxide pellets and tap water.

2.2. Methods of analysis
The morphology and the chemical analysis of the prepared geopolymer was studied by scanning electron microscopy JEOL 6390 with energy dispersive spectrometer (SEM-EDS). Thin section of samples was prepared by polishing and covered with gold. The Mössbauer spectra were obtained at room temperature by a Wissel electromechanical spectrometer working in a constant acceleration mode. A 57 Co/Rh (activity @ 10 mCi) source and α-Fe standard were used. FTIR spectra were collected using a Tensor 37 spectrometer (Bruker) with a 4 cm$^{-1}$ resolution after averaging 72 scans on KBr pallets in the spectral region 400-4000 cm$^{-1}$ at room temperature.

2.3. Specimens preparation
The geopolymer mixtures were prepared by mixing oven dried fayalite slag with tempered hardener solution. The composition design is presented at Table 1. Series 15F1 and 15F2 share same Fe$_2$O$_3$/M$_2$O and Al$_2$O$_3$/M$_2$O ratio but former contains twice more sodium silicate solution. Series 15F5 was prepared only with potassium hydroxide solution. Each series have water to solid ration equal to 0.15 (w/w). The fresh geopolymer mixtures were homogenized with mechanical stirrer for 90 seconds and then poured into cylindrical moulds (50x30mm). The specimens were sealed in polyethylene and cured at laboratory conditions (23 °C, w=65%) for 14 days, then 7 days in 80 °C. On 21$^{th}$ day samples were demoulded and placed in laboratory conditions.

| Series | Activator solution per 100 g fayalite, (g) | Total molar ratios |
|--------|------------------------------------------|--------------------|
|        | Water glass | KOH | water | H$_2$O/M$_2$O | Fe$_2$O$_3$/M$_2$O | Al$_2$O$_3$/M$_2$O |
| 15F1   | 10          | 10.2 | 8.7   | 7.59     | 2.50     | 0.32 |
| 15F2   | 20          | 8.5  | 2.7   | 7.64     | 2.50     | 0.32 |
| 15F3   | 10          | 5    | 8.8   | 11.40    | 4.00     | 0.50 |
| 15F4   | 10          | 16.3 | 8.5   | 5.46     | 1.75     | 0.22 |
| 15F5   | -           | 17.9 | 14.4  | 5.36     | 1.75     | 0.22 |

3. Results and discussion

3.1. Compressive strength
The compressive strength was measured at 28$^{th}$ day and the results (with relative deviation) are presented in figure 1. The samples 15F2 and 15F3 showed the highest compressive strength of 27.96 MPa and 27.53 MPa, respectively. The compressive strength increased with the increase of Fe$_2$O$_3$/M$_2$O ratio. Increased alkalinity of the activator solution induces more dissolution and hinder the
polycondensation step which result in lower compressive strength. The results from previous study where geopolymers with natural zeolite were obtained, also precursor with low reactivity, it was observed that the increase of alkalinity lead to slower strength gain rate - the 28th day compressive strength was lower, but 180th higher [2]. The samples with higher concentration alkali in the activator showed bleeding during curing and were characterized by very low strength ~3 MPa.

However, sample 15F3 is of a greater practical and economical interest because it was prepared with less water glass and potassium hydroxide. Compared to other geopolymers based on similar waste materials the compressive strength was about 30 MPa for geopolymers based on Romanian lead slag, and more than twice less than geopolymer based on Greek ferronickel slag (56 MPa) [14], or 67 MPa – Polish ferronickel slag [15]. It should be noted that mentioned ferronickel slags contain significant amount amorphous phase and reactive minerals –like cristobalite, tridymite, which are not presented in the slag used in the present study.

### 3.2. Mössbauer spectroscopy

The Mössbauer spectra are presented in Figure 2. The parameters of hyperfine interaction such as isomer shift (δ), quadrupole splitting (ΔEq), effective internal magnetic field (B), line widths (Γexp), and relative weight (G) of the partial components in the spectra were determined (Table 2). The Mössbauer spectrum of RAW sample is composed of sextet and doublet components. The presented model comprises of 3 sextets and 3 doublets is used for spectrum fitting, as results for calculated component parameters. The parameters of the sextet components correspond to the mineral magnetite: Sx1 - tetrahedrally coordinated Fe$^{3+}$; Sx2 - octahedrally coordinated Fe$^{2.5+}$ (actually Fe$^{3+}$ and Fe$^{2+}$, but due to fast electron exchange between them, the spectral effect is one sextet component), Sx3 - also octahedrally coordinated Fe$^{2.5+}$ ions, which have non-iron cationic neighbors in the spinel structure (e.g., Mg, Mn, Cu, Al, etc.).

The calculated parameters of the doublet components (Db1 and Db2) correspond to the two different positions of the Fe$^{2+}$ ions in the structure of the mineral fayalite (Fe$_2$SiO$_4$). The doublet component Db3 cannot be related to the iron position in the crystalline phases of magnetite nor fayalite. Isomer shift values above 1.00 mm/s are typical for iron in second oxidation state. In the absence of a third crystalline phase in the sample (powder XRD data [13]), it can be assumed that Db3 is due to Fe$^{3+}$ ions in an amorphous phase.

The spectrum of sample 15F3 was identical with the raw material. Not much changes in the oxidation states or coordination of the iron were observed after geopolymerization, which means that both magnetite and fayalite stayed predominantly inert. Still, part of the doublet component Db3 related to amorphous phase decreased and new weak doublet named Db4 was observed. Calculated parameters of Db4 correspond to Fe$^{3+}$ ions in amorphous state. Similar doublet was reported by Pyes et. al. after
geopolymerization synthetic CaO-FeOx-SiO$_2$ slag. The observed doubled was significantly more distinct which could be explained by the superior reactivity of the laboratory prepared slag contained 97% amorphous phase [16]. It is believed that tetrahedral Fe$^{3+}$ shows a quadrupole doublet of room temperature Mössbauer spectrum with its high-energy line at ~0.4 mm/s [17]. On the contrary, Mysen stated that isomer shifts below 0.3 mm/s is typical for tetrahedral Fe$^{3+}$, whereas the isomer shifts of octahedral Fe$^{3+}$ occur above 0.4 mm/s. However, it could be stated that minor quantity of the iron during geopolymerization oxidizes to amorphous Fe$^{3+}$.

Figure 2. Mössbauer spectrums of geopolymer precursor (RAW) and prepared geopolymer (15F3)

Table 2. Mössbauer parameters of investigated samples: fayalite slag (RAW) and geopolymer (15F3)

| Sample | Components   | $\delta$, mm/s | $\Delta E_q$, mm/s | $B$, T | $\Gamma_{\text{exp}}$, mm/s | G, % |
|--------|--------------|----------------|-------------------|-------|-----------------------------|-----|
| RAW    | Sx1-Fe$_3$O$_4$, Fe$^{3+}$tetra | 0.3 | 0 | 48 | 0.36 | 13 |
|        | Sx2-Fe$_3$O$_4$, Fe$^{2.5+}$octa | 0.62 | -0.05 | 45.1 | 0.54 | 15 |
|        | Sx3-Fe$_3$O$_4$, Fe$^{2.5+}$octa | 0.72 | -0.05 | 42.3 | 0.78 | 13 |
|        | Db1-Fe$_2$SiO$_4$, Fe$^{2+}$ - M1 | 1.14 | 2.68 | - | 0.3 | 21 |
|        | Db1-Fe$_2$SiO$_4$, Fe$^{2+}$ - M2 | 1.17 | 2.88 | - | 0.3 | 27 |
|        | Db3- Fe$^{2+}$ | 1.24 | 2.19 | - | 0.65 | 11 |
| 15F3   | Sx1-Fe$_3$O$_4$, Fe$^{3+}$tetra | 0.31 | 0 | 48.1 | 0.4 | 14 |
|        | Sx2-Fe$_3$O$_4$, Fe$^{2.5+}$octa | 0.62 | -0.04 | 45.3 | 0.58 | 17 |
|        | Sx3-Fe$_3$O$_4$, Fe$^{2.5+}$octa | 0.74 | 0 | 42.4 | 0.83 | 13 |
|        | Db1-Fe$_2$SiO$_4$, Fe$^{2+}$ - M1 | 1.15 | 2.67 | - | 0.3 | 19 |
|        | Db2-Fe$_2$SiO$_4$, Fe$^{2+}$ - M2 | 1.17 | 2.91 | - | 0.3 | 28 |
|        | Db3- Fe$^{2+}$ | 1.31 | 2.16 | - | 0.64 | 8 |
|        | Db4- Fe$^{3+}$ | 0.45 | 0.83 | - | 0.3 | 1 |

3.3. FTIR

Figure 3 presents the FTIR spectra of the raw material and geopolymer series 15F3. The spectra of the slags (Raw) correspond to the in-depth study of another batch of the present slag [18]. Most of the observed bands are correlated with fayalite. The bands at 873 cm$^{-1}$ and 827 cm$^{-1}$ arises due to asymmetric stretching vibration of the $\nu_3$ mode of Si-O in olivine group. The band at 827 cm$^{-1}$ was due symmetric stretching ($\nu_1$), while features between 460-610 cm$^{-1}$ can be attributed to splitting of the degenerate $\nu_4$ asymmetric bending vibration. The peaks at 639 cm$^{-1}$ and 1047 cm$^{-1}$ was assigned to magnetite and pyroxene which showed overlapping peaks in this range [19].
The features of mineral phases presented in the precursor was still observed after geopolymerization. A significant peak appeared at about 1010 cm\(^{-1}\) associated with asymmetric stretching vibration T-O-Si (T – Si or Al). A strong band around 1000 cm\(^{-1}\) is a fingerprint of the inorganic polymer matrix [20]. Usually, this band is used for determination of the degree of geopolymerization. The band about 1642 cm\(^{-1}\) and 3431 cm\(^{-1}\) are bending (H-O-H) and stretching vibration (-OH) of water molecules, respectively. The band about 1456 cm\(^{-1}\) is related to C-O carbonate stretching vibration – a product of the efflorescence and contact of unreacted activation solution with atmospheric CO\(_2\).

![FTIR spectrums of raw fayalite (Raw) and the prepared geopolymers (15F3)](image-url)

**3.4. SEM-EDS**

The SEM images are presented in Figure 4. Individual fayalite and magnetite particles were observed on the cross section of geopolymer sample 15F3 (Figure 4 – a and b). The spectroscopic data above showed that those mineral phases did not react during geopolymerization. Thus, the non-reacted particles act as fillers bonded together by geopolymer gel. It was visible that the binder phase contains significant amount of capillary pores. The solid to binder ratio is relatively low (0.15 w/w), so probably the porous structure was due to insufficient binder phase to fill the volume between non-reacted particles. On higher magnification Figure 4-c) it was observed a particle embedded in geopolymer gel. The elemental analysis (EDS) in point 2 showed that the chemical composition corresponds to fayalite. The surrounding geopolymer binder phase was characterized by higher potassium, sodium and aluminum content, which is typical for geopolymer gel. Also, it contains iron. Based on elemental content we could calculate the molar ratio: \((Na^+K^+½Ca^2+) / (Fe^3+) = 0.95\). Theoretically the cations \((Na^+, K^+, Ca^{2+})\) should be equal to \(Al^{3+}\) and \(Fe^{3+}\) to balance their negative charge in the tetrahedral coordination [4]. The presence of Fe in the binder (~17% w.) and \((Na^+K^+½Ca^2+) / (Fe^3+)\) equal to about 1 could be a sign that part of the Fe is structurally integrated in the geopolymer binder.
4. Conclusion

The results from present study showed that the fayalite slag (iron-silicate fines) from copper producing plant (Aurubis Bulgaria AD) is low reactive geopolymer precursors. The first step of geopolymerization – dissolution could not provide sufficient binder phase to produce dense matrix. The concentration of the activating solution had great influence on properties of the prepared geopolymers. The optimal strength was obtained by preparing geopolymer with $\text{H}_2\text{O}/\text{M}_2\text{O}=11.40$, $\text{Fe}_2\text{O}_3/\text{M}_2\text{O}=4$; $\text{Al}_2\text{O}_3/\text{M}_2\text{O}=0.50$. With the increase of the alkali concentration - the compressive strength decrease, also bleeding of activator solution was observed on higher alkali dosages. The microstructural examination revealed that the main phases fayalite, magnetite and pyroxene stayed unreacted after geopolymerization. However, part of the amorphous phase presented in small amount react during geopolymerization and certain amount of ferric iron $\text{Fe}^{3+}$ was incorporated in the structure of the geopolymer binder phase.

Acknowledgments

The results in this work has been achieved in fulfillment of a project financed by the National Science Fund of Bulgaria under contract No. DM17/3 from 12.12.2017. The publication of the present article was financed the K2-2020 of IMC-BAS.
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