

Characterization of a novel geopolymer based on acid-activated fayalite slag from local copper industry

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In the present study the copper smelter slag from the Aurubis enterprise (Pirdop, Bulgaria) was used as geopolymer precursor. The X-ray fluorescence and powder diffraction analysis showed that the slag contains significant amount of iron, presented by the minerals fayalite and magnetite. The slag was activated with phosphoric acid solution to prepare fresh geopolymer paste. Rapid exothermic reaction took place and the material hardened in minutes. The obtained inorganic polymer material was characterized by XRD, FTIR, DSC and Mössbauer spectroscopy. In conclusion, our study shows that the waste slag from local copper industry could be used as a potential geopolymer precursor to produce building materials. This novel method could reduce the huge amounts of fayalite slag generated during the last decades.

Keywords: geopolymer, copper slag, fayalite, acid-activated, inorganic polymer, iron silicate fines.

INTRODUCTION

The global copper industry produced 22,286 thousands of tons of copper during 2016 [1]. Apart from copper concentrate and fuel, smelter inputs include silica (800 kg/t of copper concentrate) and limestone (250 kg/t). These materials subsequently form the slag, which amounts to about 1.55 t/t, assuming concentrate with a grade of 25%. [2]. Apart from silicates and copper, the slag typically contains 100% of the iron, 70% of the zinc, 30% of selenium and tellurium, 25% of tin and nickel, 20% of cadmium, cobalt and antimony, and 10% of the silver, gold, platinum, and lead that was originally present in the concentrate [2]. Due to technological reasons, the slag from the flash furnace and the converters contains residual copper which is extracted through grinding and flotation [3]. Two products are obtained at the slag flotation plant: flotation copper concentrate and flotation tailings, called fayalite slag or iron-silicate fines. Fayalite slag is powdery material with a high content of iron and silicon dioxide in the form of minerals, mainly fayalite, magnetite, quartz, etc. The specific density of the material is about 3.6 g/cm³ (bulk density 2.4 g/cm³) [3].

The slag is hardly reusable, because of its specific fineness and composition. It is not economically viable to extract the iron at this level of technology. However, fayalite slag is marketable as a road surface, Portland cement production and concrete additive. Still huge amount of the produced slag remains unutilized. With this in mind, geopolymer technology is focused exactly at industrial waste utilization.

Geopolymers are a class of inorganic polymer materials with amorphous or semi-crystalline three-dimensional silico-aluminate structure [4]. The geopolymer materials possess high compressive strength, chemical resistance, thermal stability, low CO₂ footprint, possibility of utilizing industrial waste materials, etc. There are discussions in the scientific community about the term ‘geopolymer’ and there are other names describing the same or similar materials, including the terms: “alkali-activated material”, “alkali-bounded-ceramics”, “hydroceramics”, “inorganic polymer concrete”, “aluminosilicate inorganic polymer”, etc. [5, 6]. However, these materials seem promising and they are potential alternative of conventional Portland cement and ceramics. In the present study the term geopolymer will be used to describe the prepared material through acid activation of fayalite slag.

According to Joseph Davidovits, the “father” of the term “geopolymer”, there are two routes of geopolymer synthesis: in alkaline medium using

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alkali hydroxides and silicates; and acidic medium with phosphoric acid [4]. Depending on the composition and synthesis route the geopolymers comprise the following molecular units (or chemical groups):

- Si-O-Si-O- siloxo, poly(siloxo)
- Si-O-Al-O- sialate, poly(sialate)
- Si-O-Al-O-Si-O- sialate-siloxo, poly(sialate-siloxo)
- Si-O-Al-O-Si-O-Si-O- sialate-disiloxo, poly(sialate-disiloxo)
- P-O-P-O- phosphate, poly(phosphate)
- P-O-Si-O-P-O- phospho-siloxo, poly(phospho-siloxo)
- P-O-Si-O-Al-O-P-O- phospho-sialate, poly(phospho-sialate)
- (R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone
- Al-O-P-O- alumino-phospho, poly(alumino-phospho)
- Fe-O-Si-O-Al-O-Si-O- ferro-sialate, poly(ferro-sialate) [7].

The ferro-sialate geopolymer has a molecular structure in which part of the Fe atoms are found in tetrahedral structural position within the ferro-sialate geopolymeric sequence [8].

Limited studies are attempted on acidic activation of iron rich slags so far. To the best of authors' knowledge, only one such study [9] was reported for Belgian fayalite slag, used to prepare geopolymer with compressive strength of up to 19 MPa. Alkali activation of similar slags were studied by: Komnitsas et al. [10–12] and Maragkos et al. [13] using Greek ferronickel slag; Onisei et al. [14–15] and Peys et al. [16] using Belgian fayalite slag. Other studies on iron rich geopolymers, synthesised from bauxite residue [17], iron rich fly ash [18] and lead smelter slag [15] are known too.

In terms of the activator, in the present study ortho-phosphoric acid was used to prepare geopolymers. Usually phosphoric acid is a part of acid-base reaction with a metal oxide to form inorganic polymer. Phosphate inorganic polymers (or phosphate-bonded ceramics/cement) are synthesized at room temperature and they set rapidly like conventional polymers. These materials find a wide range of applications such as dental cements, construction materials, oil well cements and hazardous and radioactive stabilizers [4]. Phosphate geopolymers may be formed by using virtually any divalent or trivalent metal oxide that is sparingly soluble. In dental cements Ca and Zn is used to form hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), respectively [19]. The magnesium oxide also react quickly to form products similar to those found in zinc phosphate ceramics. Magnesium phosphate-based ceramics were developed for uses in structural materials, repair cements [20], solidification of low-

level radioactive and hazardous wastes [21]. When a partially neutralized phosphoric acid solution is reacted with a metal oxide, a ceramic-like material is formed with a reaction product $\text{M}_x\text{B}_y(\text{PO}_4)_{(x+y)/3}$, where M stands for a metal and B can be hydrogen (H) or another metal such as aluminium (Al) [19].

In the present study geopolymer was formed by acid-base reaction with phosphoric acid solution and fayalite slag. The purpose of the study is to use industrial waste products to obtain new iron phosphate geopolymer for waste stabilization and use in construction and building material. The precursors react rapidly and the geopolymer hardens in minutes. There are economic, environmental and social benefits to develop technology utilizing fayalite slag. The scientific and technical knowledge in the field of geopolymers and phosphate cements could be the key to solving the problem with utilizing the ecologically hazardous fayalite slag.

EXPERIMENTAL

Methods of analysis

The powder XRD patterns of the precursors and the geopolymer samples were performed with Philips PW1830 and Cu $K\alpha$ radiation.

The chemical composition of the raw fayalite slag was determined by XRF using apparatus Panalytical Axios Max WD.

FT-IR spectra were collected using a Tensor 37 spectrometer (Bruker) with a 4 cm^{-1} resolution after averaging 72 scans on standard KBr pellets in the spectral region $400\text{--}4000\text{ cm}^{-1}$ at room temperature. Micro-IR spectra were performed using Hyperion 2000 IR microscope after averaging 126 scans, collected from $50\text{ }\mu\text{m}$ areas.

The Mössbauer spectra were obtained at room temperature by a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}\text{Co/Rh}$ (activity $\cong 20\text{ mCi}$) source and a-Fe standard were used. The experimentally obtained spectra were fitted using CONFIT2000 software [22]. The parameters of hyperfine interaction such as isomer shift (δ), quadrupole splitting (ΔE_q), effective internal magnetic field (B), line widths (Γ_{exp}), and relative weight (G) of the partial components in the spectra were determined.

The differential scanning calorimetry and the thermogravimetry (DSC–TG) were carried out on the DSC–TG analyzer SETSYS2400, SETARAM at the following conditions: temperature range from 20 to $1200\text{ }^\circ\text{C}$, in a static air atmosphere, with a heating rate of $10\text{ }^\circ\text{C min}$, and 10–15 mg sample mass.

Table 1. Chemical composition of the fayalite slag determined by XRF, (%)

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	ZnO	MgO	K ₂ O	Na ₂ O	CuO	PbO	TiO ₂	MoO ₃	SO ₃
58.42	29.34	4.40	2.66	1.32	0.89	0.71	0.58	0.49	0.37	0.30	0.27	0.26

Materials

The smelting process of the copper industry produces vast amounts of waste slag. The geopolymer precursor in the present study was the copper smelter fayalite slag from Aurubis (Pirdop, Bulgaria). Its chemical composition is presented in Table 1. The fayalite slag was dried in oven at 105 °C to constant mass. The measured moisture content was about 10%. The raw material was well characterized in previous studies [23].

Analytical grade ortho-phosphoric acid (85%) was used to prepare the activator solution. The phosphoric acid was diluted with tap water to obtain hardener solution with desired concentration.

Specimen preparation

The geopolymer mixtures were prepared by mixing dried fayalite slag with tempered hardener solution. Rapid exothermic reaction takes place after mixing. The fresh geopolymer mixture was homogenized with mechanical stirrer for 30 seconds and poured into cylindrical moulds (50×30 mm). Seconds after pouring the material hardens. The samples were demoulded after 4 hours and held in laboratory conditions until compressive strength test at the 28th day.

Preliminary studies showed optimal dosage of the activating solution, in respect of pourable mixture and strength: 15.5 g ortho-phosphoric acid

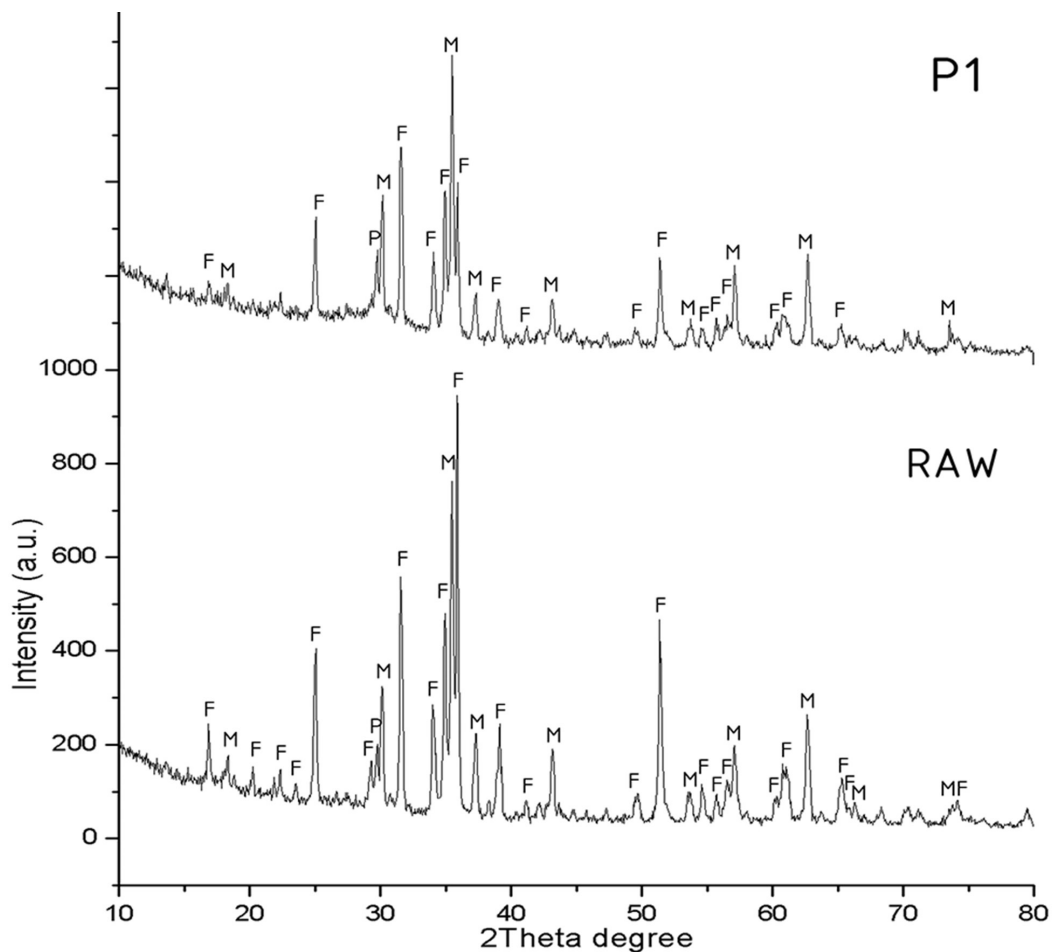


Fig. 1. Powder XRD results from fayalite slag (raw) and the prepared geopolymer (P1). F – fayalite, M – magnetite, P – pyroxene.

(85%), 15.5 g H₂O, per 100 grams of dried fayalite, giving the composition of the obtained geopolymer specimens (series P1): Fe₂O₃/P₂O₅ = 3.76; H₂O/P₂O₅ = 1.71 (molar ratios). The water to solid weight ratio was 0.196. Increase in the concentration of phosphoric acid boosted the reaction and there was no time to make homogenous and pourable mixture. The research team found a retarder of the reaction and the result will be subject of future papers.

RESULTS AND DISCUSSION

Compressive strength

The compressive strength of three cylindrical specimens (50×30 mm) from series P1 was measured at 28-th day at rate of load increase of 2400 N/s. The measured compressive strength was 16.1 MPa. The compressive strength is similar to the results of Katsiki et. al study [9].

Powder XRD

The results from the powder X-ray diffraction analysis of the raw fayalite slag and the prepared geopolymer are presented in Figure 1. The raw fayalite slag consists of fayalite, magnetite and small amount of pyroxene. Both diagrams look

similar, however, clearly visible decrease of the intensities, corresponding to fayalite as well as notable amorphous halo between 25–40° 2θ, indicating geopolymer formation are observed. The mineral phases magnetite and pyroxene look non-reacted.

FTIR

IR spectrum of raw sample (Fig. 2 bottom) reveals intensive absorption in the range 870–940 cm⁻¹ due to antisymmetric stretching (ν₃) of Si-O in olivine. The peak at 826 cm⁻¹ arises from the symmetric stretching (ν₁), while those at 562 cm⁻¹ from the symmetric bending of SiO₄ atomic groups in fayalite. Based on the chemical composition and the infrared peak positions, low Fo component in fayalite can be assumed. The second major phase defined by the X-ray data is a magnetite (Fe₂O₃), which can be detected by the peak of Fe-O stretching near 560 cm⁻¹ and may overlap Si-O bending vibrations. The peak observed at 474 cm⁻¹ in the range of Si-O bending (ν₄) together with broad band at 1100 cm⁻¹ indicate also the presence of amorphous SiO₂. Another band centered near 1052 cm⁻¹ may be due to a presence of pyroxenes because it falls in the range of Si-O-Si stretching bonds.

The IR spectrum of the activated sample reveals significant differences (Fig. 2). Peaks characteristic of fayalite are still presented in the range

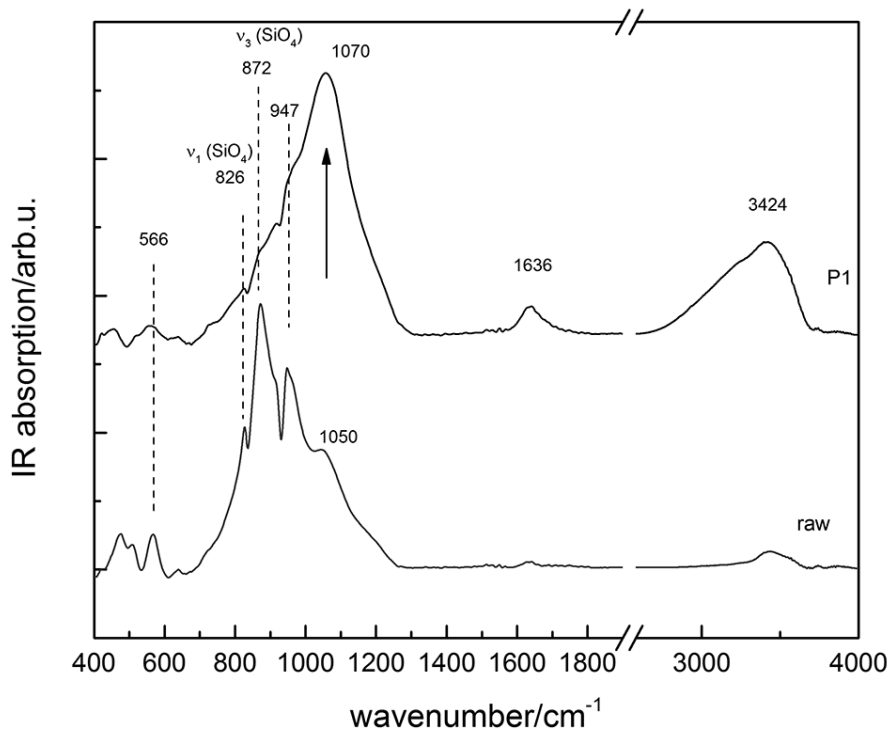


Fig. 2. Infrared spectrum of the raw fayalite slag (bottom) and the prepared geopolymer (top).

820–950 cm^{-1} , while the intensity of the absorption near 1070 cm^{-1} increases significantly as a result of chemical reaction with phosphoric acid. Because the structure of olivine contains isolated SiO_4 tetrahedra, peaks at frequencies higher than 1000 cm^{-1} are not expected and the occurrence of intensive absorption in this spectral range is an indication of a new mineral phase formation. The position of its maximum is in the range of P-O stretching vibrations of phosphates and also of silicate-phosphate glasses [24, 25]. At the same time the amount of water molecules increases as seen from the bending and stretching vibrations at 1640 and 3400 cm^{-1} , respectively. In order to clarify possible phase we also performed micro-infrared measurements in micrometer-sized areas. It is seen from Figure 3 that the fayalite grains are not completely reacted and the remaining large-sized crystals are intersected by veins containing the amorphous new phase with strong infrared peaks near 1060 cm^{-1} .

Mössbauer spectroscopy

The Mössbauer spectrum of RAW sample is composed of sextet and doublet components (Fig. 4).

A model with 3 sextets and 3 doublets is used for spectrum fitting, and results for calculated component parameters are presented in Table 2. The parameters of the sextet components correspond to the mineral magnetite: Sx1 – tetrahedrally coordinated Fe^{3+} ; Sx2 – octahedrally coordinated $\text{Fe}^{2.5+}$ (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 $\text{Fe}^{2.5+}$ ions, which have non-iron cationic neighbors in the spinel structure (e.g., Al, Mg, 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_2SiO_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 (X-ray diffraction data), it can be assumed that Db3 is due to Fe^{2+} ions in the amorphous phase (glass, melt). The Mössbauer spectrum of P1 sample (Fig. 5) contains the components contained and described in the RAW spectrum and an additional doublet named Db4 in Table 2. Calculated param-

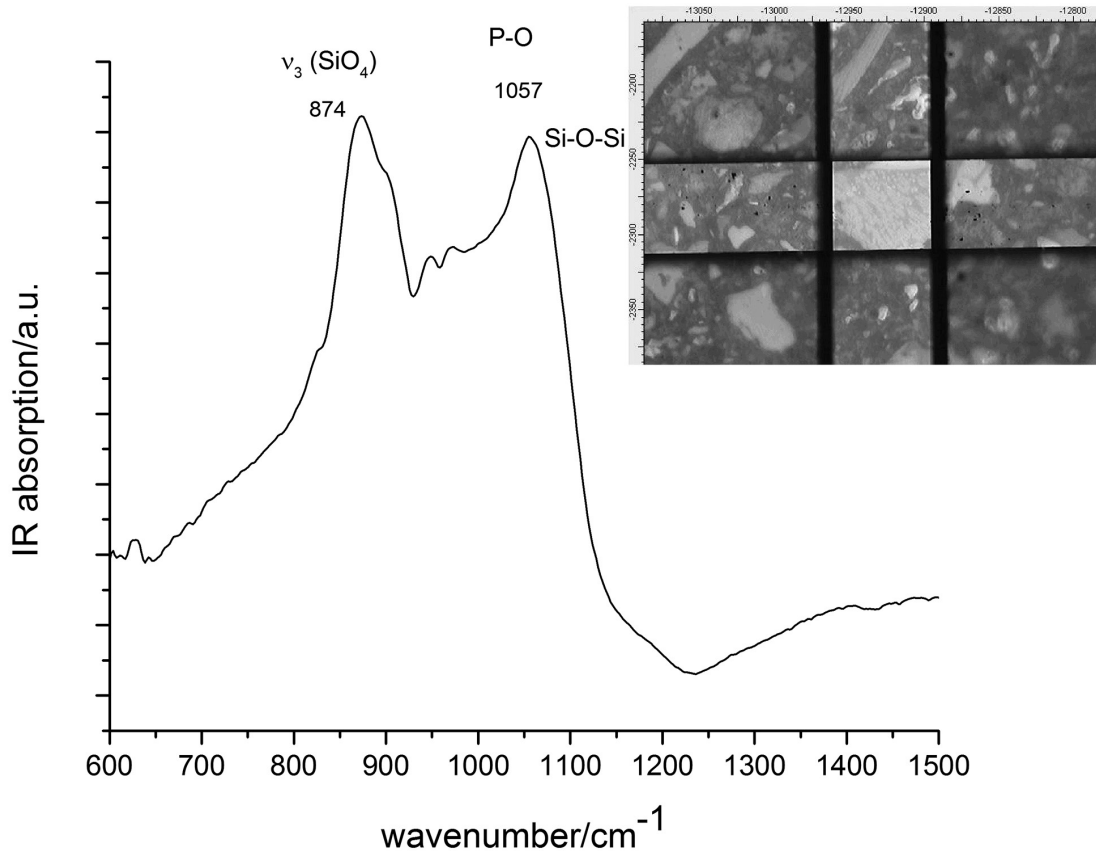


Fig. 3. μIR spectrum collected from fayalite grain with area $50 \times 50 \mu\text{m}$.

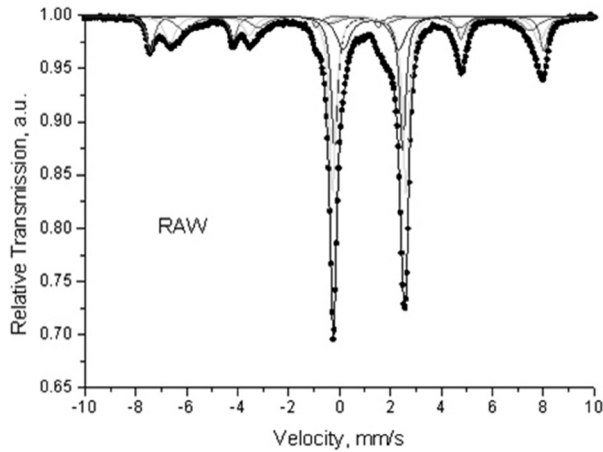


Fig. 4. Mössbauer spectrum of RAW sample.

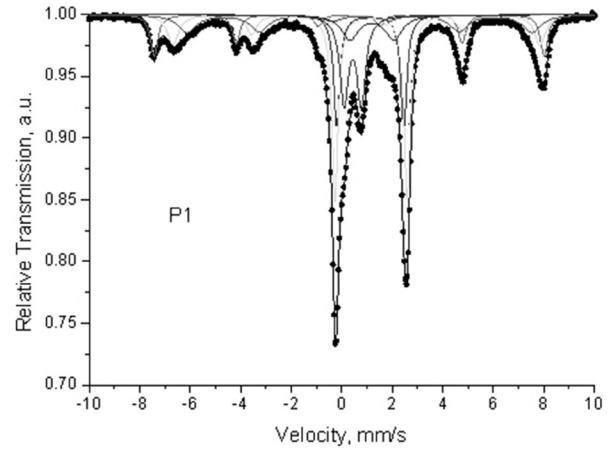


Fig. 5. Mössbauer spectrum of P1 sample.

eters of Db4 correspond to Fe^{3+} ions in octahedral coordination. In the absence of diffraction reflexes from additional crystalline phase containing Fe^{3+} , this is probably the second amorphous phase, which could be a result of geopolymerization. The relative weight of Db4 is 15% and it is at the expense of the doublets of the fayalite phase (Db1, Db2, Db3) comparing with the RAW sample spectrum.

STA (DSC–TG)

The thermal behaviour of samples Raw and P1 was investigated. Two processes were observed on DSC–TG(DTG) curves of these samples: (i) dehydration and (ii) oxidation Figure 6. Both samples at first sight showed similar thermal behaviour, but

some differences were also observed. The dehydration of sample RAW was minimal and marked by endo – effects 1 and 2, as the first stage is more distinct than the second. The dehydration of sample P1 in comparison with RAW, showed two well distinguishable stages (endo effects 1, 2) and a small one 3 (Fig. 6 – right). The weight losses during the sample dehydration show significant differences: in sample Raw, the mass loss was 0.63% while in sample P1 = 7.53%. The dehydration continues until 300 °C in sample Raw, while up to 420 °C in sample P1. Both samples showed gradual exothermic reactions after the end of dehydration processes probably due to oxidation of the iron minerals. The weight increased with 4.04% in sample Raw, while in sample P1 the weight increased with 2.08%.

Table 2. Mössbauer parameters of investigated samples

Sample	Components	δ , mm/s	ΔE_q , mm/s	B, T	Γ_{exp} , mm/s	G, %
RAW	Sx1- Fe_3O_4 , $\text{Fe}^{3+}_{\text{tetra}}$	0.30	0.00	48.0	0.36	13
	Sx2- Fe_3O_4 , $\text{Fe}^{2.5+}_{\text{octa}}$	0.62	-0.05	45.1	0.54	15
	Sx3- Fe_3O_4 , $\text{Fe}^{2.5+}_{\text{octa}}$	0.72	-0.05	42.3	0.78	13
	Db1- Fe_2SiO_4 , Fe^{2+} – M1	1.14	2.68	–	0.30	21
	Db2- Fe_2SiO_4 , Fe^{2+} – M2	1.17	2.88	–	0.30	27
	Db3- Fe^{2+}	1.24	2.19	–	0.65	11
PG1	Sx1- Fe_3O_4 , $\text{Fe}^{3+}_{\text{tetra}}$	0.30	0.00	48.0	0.35	12
	Sx2- Fe_3O_4 , $\text{Fe}^{2.5+}_{\text{octa}}$	0.61	-0.05	45.2	0.52	13
	Sx3- Fe_3O_4 , $\text{Fe}^{2.5+}_{\text{octa}}$	0.70	0.01	42.4	0.86	14
	Db1- Fe_2SiO_4 , Fe^{2+} – M1	1.13	2.65	–	0.30	14
	Db2- Fe_2SiO_4 , Fe^{2+} – M2	1.17	2.87	–	0.30	24
	Db3- Fe^{2+}	1.20	1.74	–	0.81	8
	Db4- Fe^{3+}	0.44	0.68	–	0.40	15

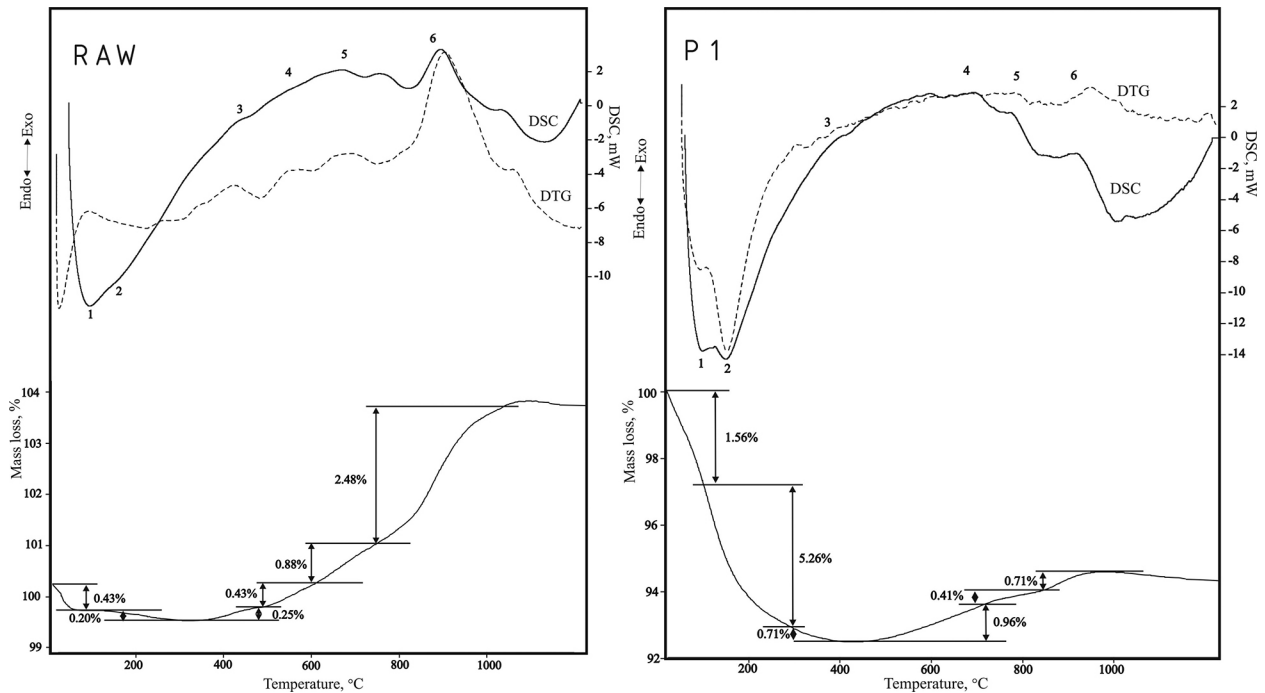


Fig. 6. DSC–TG(DTG) curves of the raw fayalite slag (left) and prepared geopolymer material (right).

CONCLUSIONS

Mixing fayalite slag (iron silicate fines) with ortho-phosphoric acid leads to rapid reaction and hardening. The resulting geopolymer material possesses sufficient compressive strength (16 MPa). Powder XRD showed newly formed amorphous phase after geopolymerization at the expense of fayalite. This is supported by Mössbauer spectroscopy, which reveals that 15% of the iron (mainly from the mineral fayalite) oxidizes from Fe^{2+} to Fe^{3+} after geopolymerization. The bigger particles of the precursor reacted only at the surface and amorphous phase was formed into the cracks.

More detailed studies and analysis are needed to reveal this rapid reaction and characterize the obtained hard material. This novel method could lead to technology capable to reduce the huge amounts of fayalite slag generated for the last decades as a result of copper production.

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