

# The influence of sulphur slime on the properties of alkali binding material from biomass bottom ashes

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**Abstract.** Alkali-activated materials are potential alternatives for Portland cement. Their use leads to reductions in CO<sub>2</sub> emissions and recycling of various industry by-products. These new alternative binders have a wide range of uses and high technological properties. In the research presented in this paper, the influence of additional sulphur slime powder (as accelerator) was investigated. The biomass bottom ash (BBA) was used as raw material and sodium hydroxide was used as the alkaline activator. The sulphur slime is a by-product in a fertilizer production plant. The samples were prepared with different amounts of sulphur slime; the levels of sulphur slime additive were 0%, 0.5%, 1.0%, 3.0% and 5.0% by weight in the raw material mixtures. Alkali-activated binders were mixed and conditioned at a temperature of 60 °C for 48 h, followed by curing at room temperature for 26 days. The microstructure of the material was analyzed through scanning electron microscopy (SEM) and the composition of the materials was analyzed using X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy. The compressive strength of hardened alkali activated paste was measured after 28 days. In all the cases investigated, the compressive strength of hardened cement paste samples increases with the presence of Sulphur slime powder. It was found that during the hardening process sulphur reacts with sodium hydroxide forming Na<sub>2</sub>SO<sub>4</sub>, which acts as an accelerator. According to some researchers, Na<sub>2</sub>SO<sub>4</sub> shows a significant accelerating influence in alkali-activated binder systems. The optimal amount of sulphur slime in raw materials mixtures was also evaluated.

**Keywords:** alkali-activated materials, Sulphur slime waste, biomass bottom ash

## 1. Introduction

The biomass bottom ash is a waste material generated by combustion as residue, and is collected in the bottom hopper of the burning furnace. There are various cases reported where bottom ash was used as a construction material. Carrasco et al. [1] investigated the addition of BBA in cement-based material. The results demonstrated that the addition of BBA increased the material's porosity, thereby decreasing its thermal conductivity and compressive strength. The best mechanical characteristics (compressive strength of 61.11 MPa) with an acceptable thermal conductivity value (0.773 W/(m·K)) were determined. Eliche-Quesada et al. [2] studied the feasibility of using fly or bottom biomass ash as a partial replacement in the production of eco-friendly fired bricks. The bricks do not present environmental problems according to the leaching study. Sklivaniti et al [3], reported on the



characterization of a bottom ash derived from the combustion of olive plants trimmings. The authors examined its suitability as a substitute in the production of composite cements. According to the results reported, the woody bottom ash could be used as a substitute for Portland cement, in the production of composite cements of the strength classes 42.5 and 32.5 of EN 197-1. Carrasco et al. [4] studied the effect of the addition of bottom ash from the combustion process of biomass plants to calcium-silicate samples, and its potential as a construction material. The calcium-silicate samples were manufactured by mixing bottom ash with different sources of lime and Portland cement. The amount of bottom ash added ranged from 10% to 90% of the dry weight of the mixtures. The compressive strength reported covered a range from 25.21 MPa (bottom ash / lime) to 61.11 MPa (bottom ash / Portland cement).

The application of BBA from thermal power plants as precursors for the production of alkali-activated binders has been reported in different studies. Matakah et al. [5] suggested the use of non-wood biomass combustion ash in the production of alkali-activated concrete and concluded that non-wood biomass ash could be an effective raw material in the production of alkali-activated concrete. Qiao et al. [6] investigated the fine fraction (<14 mm) of incinerator bottom ash. It was milled and thermally treated at 600, 700, 800 and 880 °C. The treated materials were activated with Ca(OH)<sub>2</sub> (10 wt%). Significant volumes of gas were generated during curing and this produced a macro-porous microstructure that limited the compressive strength to 2.8 MPa. The new materials may have potential for use as controlled low-strength materials.

In the geopolymer synthesis, a large variety of materials may be used as a source of aluminosilicate in amorphous or semi-crystalline state. Chen et al. [7] presented a study on geopolymer bricks manufactured using bottom ash from circulating fluidized bed combustion. The highest compressive strength of 21.9MPa was reached when the modulus was 1.5. Kalaw et al [8], reported that geopolymer samples were formed from the mixture of coal ash, using coal fly ash and coal bottom ash, and rice hull ash. Geopolymers were produced with a compressive strength of 18.5 MPa at 28-day of curing, when pre-cured at 80 °C for 24 h. Santa et al. [9] used pure bottom ash obtained after the mineral coal burning, as a source of aluminosilicate for geopolymer synthesis. The curing was performed at room temperature. The use of bottom ash for the geopolymer production exhibited good results, and the technology may be reproducible and environmentally viable for some samples analysed. Zhu et al. [10] used incineration bottom ash as the gas-forming agent, to replace costly aluminum powder, in the production of lightweight aerated metakaolin geopolymer. Results show that the gas generation capacity of incineration bottom ash is about 1/250 that of aluminum powder. Addition of incineration bottom ash remarkably increases the yield stress and viscosity of fresh pastes. Ul Haq et al [11] carried out research to develop geopolymer mortars and concrete from fly ash and bottom ash and compared the characteristics of the products obtained from either of these materials. Mechanical characterization indicated that geopolymer processed from fly ash reached a compressive strength of 61.4 MPa, whereas bottom ash geopolymer reached a compressive strength of 55.2 MPa. The mechanical characterization indicated that bottom ash geopolymers are almost equally viable as fly ash geopolymer.

In the present paper the application of sulphur slime as activation accelerator was studied. The Sulphur slime is a by-product of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) production waste from a fertilizer production plant. The slime occurs as a result of the cleaning operation of sulphur filters in the smelters, collectors, and sulphur repository. The amount of slime formed is calculated according to the norm (1t H<sub>2</sub>SO<sub>4</sub> – 0.45 t slime). The aim of this work is to determine the main properties of alkali activated biomass bottom ash binder containing dissolved sulphur slime.

## 2. Experimental techniques

It is known from previous work that the addition of crushed raw sulphur slime into alkali - activated material can cause formation of undesirable expansive materials, leading to rapid expansions and the destruction of samples within 24 hours [12]. To produce a strong and durable material the crushed

sulphur slime was crushed further using a ceramic ball mill to the fineness of cement. The specific surface area was determined using Blaine's method according to the EN 196-6: 2005 standard.

Five series of samples were formed with each material. The composition of alkali-activated biomass bottom ashes samples varied with varying content of sulphur slime powder as additional material: 0 %, 0.5 %, 1 %, 2 % and 5 % (Table 1).

**Table 1.** Mixture design and main oxide molar ratios of alkali-activated biomass bottom ashes

Sulphur slime powder, wt%	Mass parts, %				SiO <sub>2</sub> /Na <sub>2</sub> O, mol	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , mol
	Al(OH) <sub>3</sub>	Fly Ash	NaOH	H <sub>2</sub> O		
0	16.7	51.4	13.8	18.2	2.0	1.0
0.5	16.7	51.4	13.8	18.2	2.0	1.0
1	16.7	51.4	13.8	18.2	2.0	1.0
2	16.7	51.4	13.8	18.2	2.0	1.0
5	16.7	51.4	13.8	18.2	2.0	1.0

Fine sulphur powder was dissolved in the alkali solution prior to the mixing of the alkali-activated material. In the alkali solution, sulphur reacts with some NaOH and sodium sulphate is formed.



Then the alkali solution was added to the dry components - BBA and aluminum hydroxide. The components were mixed together until a homogenous paste was obtained. Then 20 × 20 × 20 mm cubes were formed in order to investigate the mechanical characteristics of the hardened samples. The moulds were filled and sealed to retain humidity for 24 hours. The samples were then placed in an oven at 60 °C, where they were kept for a period of 24 hours. After curing and drying, the bulk density and compressive strength of samples were evaluated. Elevated temperature was chosen because, according to various studies reported in the literature, this is more effective for alkali activation. The samples were kept sealed at ambient temperature for an additional 26 days. The cubes were tested for compression using an ELE AutoTest machine. The crushed samples were used for the XRD (powder samples) and SEM investigation.

SEM investigation was performed with a high-resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission gun (FEG).

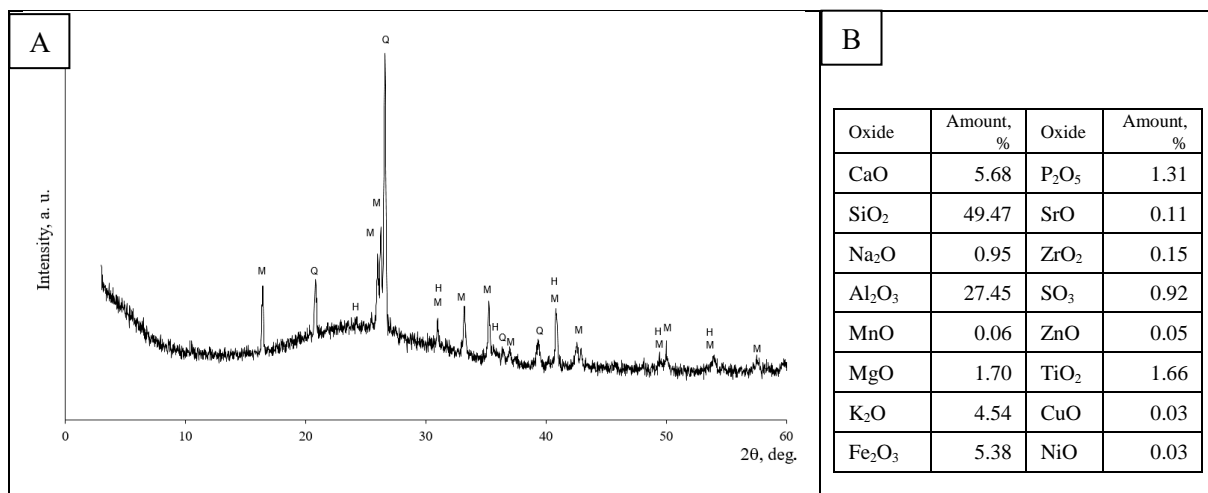
The X-ray diffraction analysis of the materials was performed using the X-ray diffractometer DRON-6, with CuK $\alpha$  radiation and Ni filter. The powder X-ray diffraction patterns were identified with references available in PDF-2 database (PDF – 2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA 19073-3273 USA). XRFA elemental analysis was used to determine the chemical composition of biomass bottom ash and sulphur slime. The elemental composition was recalculated to oxides (Fig. 1, B and Fig. 3, B).

### 3. Materials

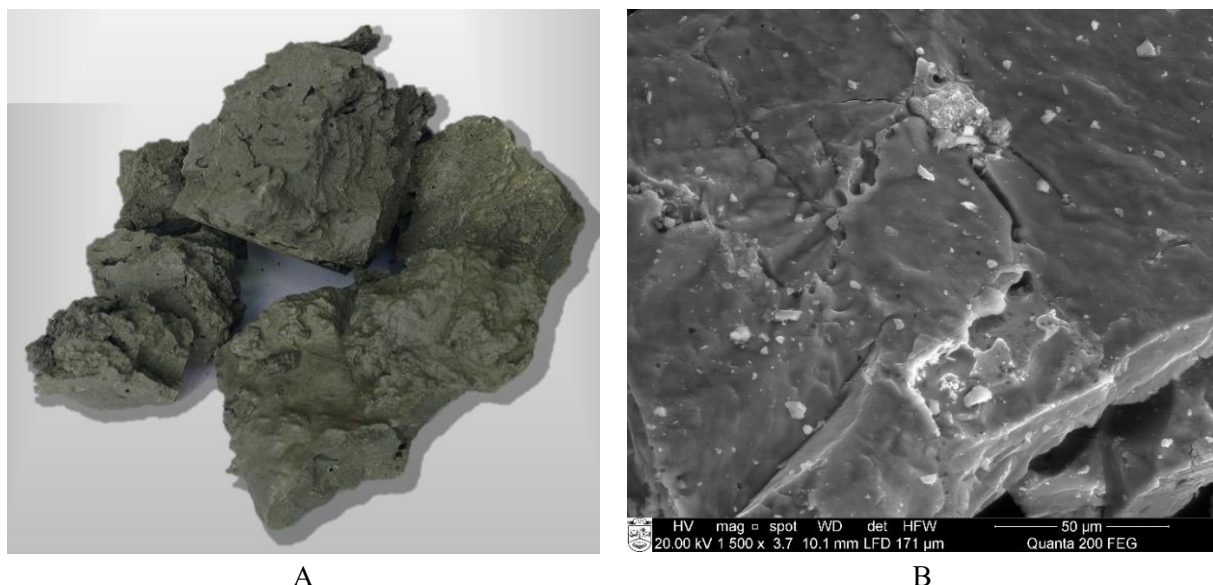
BBA from a Lithuanian combustion plant was used. The mineral composition of BBA was evaluated using XRD analysis (Fig. 1, A). It was concluded that the BBA contain significant amounts of: quartz, mullite and hematite. The bottom ashes consisted mainly of silicon, aluminum, potassium, calcium and iron (Fig. 1, B).

Sulphur slime is a grey solid material (Fig. 2, A). The SEM images indicate that sulphur slime has the compact and continuous structure, of a polymeric material. Furthermore, a small number of prisms, gypsum crystals are visible (Fig. 2, B).

The sulphur slime used in this research was obtained from the Lithuanian chemical industry plant SC “Lifosa”. On average the plant produces 45.3 t of sulphur slime every month and 544 t annually. Sulphur slime consists mainly of sulphur (50%), with a moisture content of 3% and a density of 1 500 kg/m<sup>3</sup>. According to the XRD analysis (Fig. 3) elemental sulphur and small amounts of CaSO<sub>4</sub>·0.5H<sub>2</sub>O and CaSO<sub>4</sub> are present in the mineral composition of this material. XRF analysis of chemical composition indicated that the major component of the material is sulphur (55.85%). The rest of the sulphur is contained in the CaSO<sub>4</sub>·0.5H<sub>2</sub>O and CaSO<sub>4</sub> composition. After recalculation to SO<sub>3</sub>, it makes up 26.97% of the composition.



**Figure 1.** XRD and XRF analysis of fly ashes (FA). Notes Q – quartz SiO<sub>2</sub> (83-539), M – mullite Al<sub>4.59</sub> Si<sub>1.41</sub> O<sub>9.7</sub> (83-1881), H – hematite Fe<sub>2</sub>O<sub>3</sub> (24-72).



**Figure 2.** Image of sulphur slime material (A) and SEM image of sulphur slime (B).

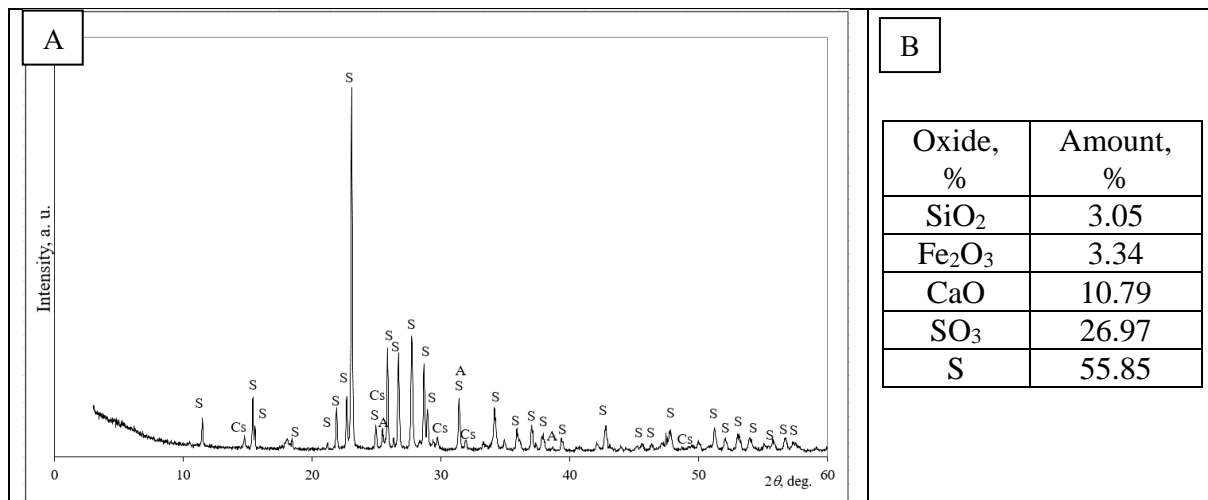
The main chemical element in sulphur slime is sulphur (55.85%). In addition, calcium oxide is identified at about 10.79% with small amounts of iron and silicon oxides (Fig. 3, B).

In alkali activation binding materials the most widely available and economical chemicals are the following: NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>O · nSiO<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>. In this research a strong acid salt, namely Na<sub>2</sub>SO<sub>4</sub> is used in addition to the NaOH.

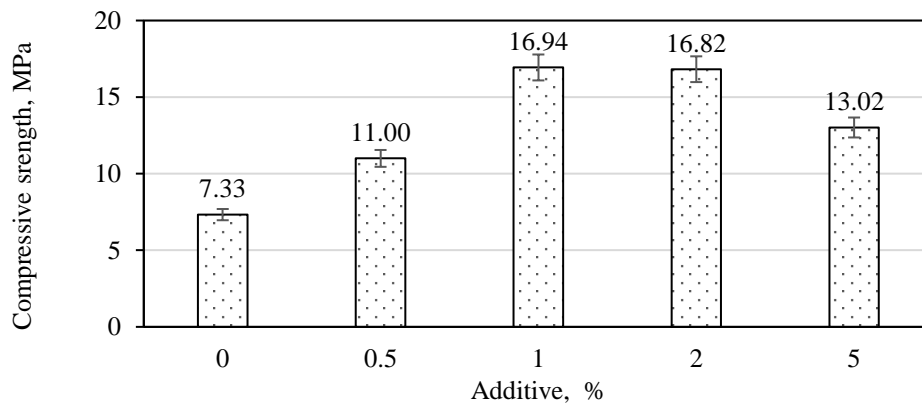
**4. Results and discussion**

The compressive strength was measured after 28 days of curing in ambient temperature. The sample bulk density was around 1250 kg/m<sup>3</sup>. In general, it does not appear that the sulphur slime had a significant influence on the sample density.

The compressive strength test results are presented in Fig. 4. As seen in figure 4 sulphur slime powder additive had positive effects on the compressive strength of samples within the additive range 0.5-2.0 %. The increasing amount of additive up to 1,0 % led to an increase in compressive strength reaching a peak of 16.94 MPa which is more than twice the compressive strength of the control samples (7.33 MPa). With 2.0 % additive, the compressive strength reached 16.82 Mpa, which is close to the compressive strength of samples with 1.0 % additive. Increasing the additive content up to 5.0 % has negative effects on the compressive strength (13.02 MPa). In general, it can be concluded that a small amount of additive can significantly increase the compressive strength of alkali activated biomass bottom ash. Therefore, the use of Na<sub>2</sub>SO<sub>4</sub> improves the strength development of biomass bottom ash materials.

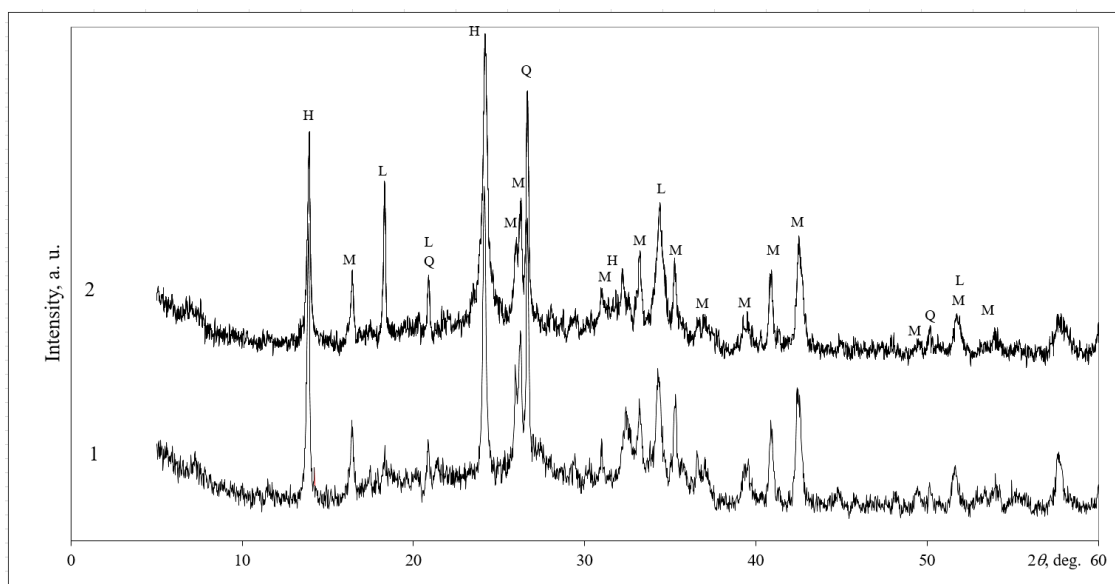


**Figure 3.** XRD and XRF analysis of sulphur slime. Notes Cs is semi-hydrate gypsum CaSO<sub>4</sub> · 0.5H<sub>2</sub>O (1-999), S is alfa elemental sulphur (24-733), A is anhydrite CaSO<sub>4</sub> (80-787).



**Figure 4.** Compressive strength of alkali-activated biomass bottom ashes: without (reference sample) and with 0.5%, 1%, 2% and 5% sulphur slime additive.

The main products of the alkali activation reaction were amorphous alkali aluminosilicate gel and a crystalline phase (Fig. 5 and Fig. 6). Figure 5 shows the XRD patterns of the products prepared after alkali activation of BBA. Hydrosodalite ( $\text{Na}_8\text{SiO}_{24}(\text{OH})_2(\text{H}_2\text{O})$ ) and calcium aluminium silicate hydroxide hydrate  $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})$  were produced. The height of the diffraction peaks for  $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})$  increased with the addition of  $\text{Na}_2\text{SO}_4$ . These correlate with the compressive strengths results. Qiao et al. [13] obtained similar results by using  $\text{Na}_2\text{SO}_4$ . Qian et al. [14] investigated the activation of fly ash in different blended cements. The addition of  $\text{Na}_2\text{SO}_4$  can significantly increase the strength of all these blended cements. Donatello et al. [15] stated that the  $\text{Na}_2\text{SO}_4$  salt acts as a safe and convenient in situ source of alkali to activate fly ash glassy phases.  $\text{Na}_2\text{SO}_4$  reduced setting times, shortened the induction period, and compressive strength development, but also restricted ettringite formation. In a recent study, Lee et al [16] compared the strength and microstructure of Portland fly ash cements, which contained 40% fly ash and which was activated with  $\text{Na}_2\text{SO}_4$ . The research results support the hypothesis that the addition of small amounts of activators is a viable solution for increasing the early-age compressive strength of fly ash concrete.



**Figure 5.** X-Ray diffraction pattern of alkali-activated biomass bottom ashes: without (reference sample) and with 5% sulphur slime. Notes: Q – quartz  $\text{SiO}_2$  (83-539), M – mullite  $\text{Al}_{4.59}\text{Si}_{1.41}\text{O}_{9.7}$  (83-1881), H – hydrosodalite  $\text{Na}_8\text{SiO}_{24}(\text{OH})_2(\text{H}_2\text{O})$  (72-2329), L – calcium aluminium silicate hydroxide hydrate  $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})$ .

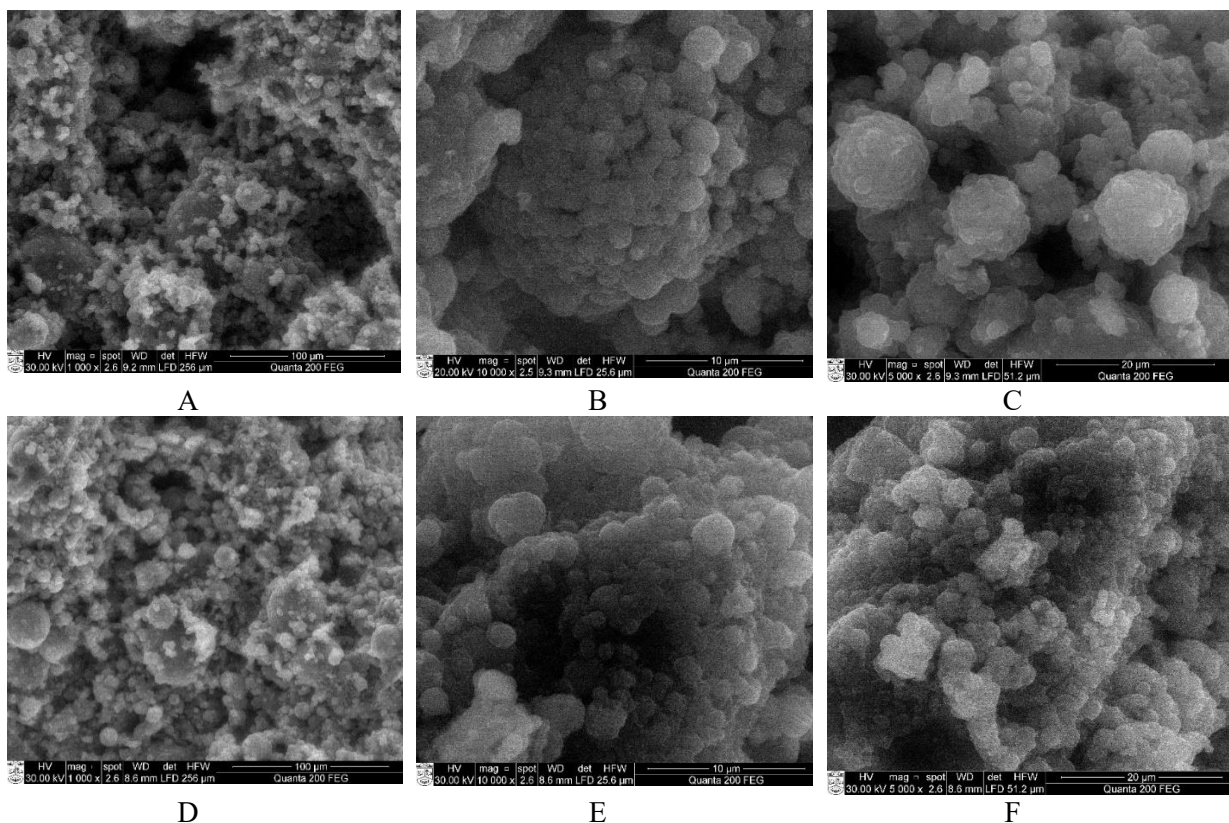


Activation with a combination of  $\text{Na}_2\text{SO}_4$  and  $\text{NaOH}$  yields the double amount of hydration products. In this case hydrosodalite and calcium aluminium silicate hydroxide hydrate formed (Fig 5, curve 2).

The activation of ash has been studied widely and the addition of  $\text{Na}_2\text{SO}_4$  has been proved to be a successful method. In the research reported by Naik et al [17] the optimized blended cements consisted of 2 to 4% sodium sulfate anhydrite as a chemical activator. X-ray diffraction (XRD) and scanning electronic microscopy (SEM) analyses indicate that the addition of sodium sulfate accelerates the formation of CSH gel. Many studies have been conducted on accelerating the pozzolanic properties of fly ash in the blended cement systems.

The microscopic analysis, shown in Fig. 6, d, also confirmed the results as samples with 2% Sulphur slime were found to have greater transformation of the amorphous compound to the crystalline compound making its microstructure even denser than the other mixture without Sulphur slime powder, presented in Fig. 6a. Hydrosodalite prevailed in all investigated samples without and with sulphur slime additive [18].

Therefore, the higher strength of the alkali sulphate-activated pastes is attributed to acceleration of the pozzolanic reactions and the additional hydration products.



**Figure 6.** SEM pictures of alkali-activated biomass bottom ashes: without (A, B, C) and with 2% sulphur slime (D, E, F).

## 5. Conclusions

Based on the results obtained in this research, the following conclusions were made:

- The additive of sulphur slime is effective in increasing the compressive strength of alkali activated biomass bottom ash. Small amounts of the additive (up to 2%) can double the value of compressive strength. The addition of sulphur slime ( $\text{Na}_2\text{SO}_4$ ) has beneficial effects on the compressive strength development of the samples.
- The application of  $\text{Na}_2\text{SO}_4$  changes the chemical composition of alkali-activated material - calcium aluminium silicate hydroxide hydrate occurs in the binder's system, which can be attributed to the increase in the compressive strength.

The resulting Alkali Activated Material (AAM) microstructure was denser, consisting of amorphous gel-like structures.

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