

Synthesis and evaluation of basic oxygen furnace slag based geopolymers for removal of metals and sulphates from acidic industrial effluent-column study



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ABSTRACT

Basic Oxygen furnace slag (BOFS) based geopolymers with open porosity ranging from 21%–57 % and density between 1255 kg/m³–2432 kg/m³ were synthesized. The synthesized geopolymers potential; to be used as attenuators for metal removal and neutralization of Acid Mine Drainage (AMD); were assessed and evaluated through column test studies conducted over a period of 133 days. The results show that BOFS based geopolymer composites can be used as attenuators as over 99 % metals were removed during the first 50 days. The results also revealed that higher porosity promoted greater neutralizing ability by dissolution of soluble salts from the BOFS based geopolymer; which improves the removal efficiencies of sulphates, metals and neutralization of AMD. Characterization of the composites after contact with AMD revealed that gypsum was the main mineral phase in the geopolymers indicating that precipitation was the major mechanism that enhanced metal and sulphates removal. BOFS based geopolymers can be used to replace armoring neutralizing agents such as limestone. The research contributes to sustainable development by addressing the environmental pollution posed by AMD and utilization of BOFS as a medium for remediation of AMD. The utilization of BOFS for remediation of AMD mitigates and responds to the environmental problems and demands associated with such waste

1. Introduction

The closure and scaling down of mine activities in South Africa since the late 1970s has led to voids being left and rain water filling up these voids leading to Acid mine drainage (AMD). The AMD starts to build up inside these voids and results in discharge of highly acidic effluent; that seriously pollutes the surface and ground water. Water polluted by AMD often has high concentrations of metals, sulphates and acidity which are toxic to human beings and aquatic life, leaving receiving streams devoid of most living creatures, causing chronic and acute illnesses in human beings and also damaging the infrastructure and building foundations due to its corrosive nature [1]. Therefore, the removal of toxic contaminants in AMD is of paramount importance. There are number of technologies that are used for treating AMD nationally and internationally. These technologies include precipitation, ion-exchange, adsorption, coagulation and bio-sorption. These technologies are reliable and effective however, they have their limitations as they generate large quantities of voluminous sludge that contain

radioactive elements, high operational costs particularly high energy consumption, selective adsorption and maintenance requirements make them impractical for most remote, abandoned mines [2]. Based on the aforementioned reasons, there is a global need to develop a low cost, effective and efficient method that can neutralize and remove toxic contaminants from AMD. Recently, there has been an increase of interest in developing low cost neutralizing agents or adsorbents from industrial wastes and it has become a very significant issue [3]. However, the application of geopolymers to remove metals from wastewater is a developing concept that has been scarcely investigated. Although it was reported and highlighted by several researchers as discussed below; that geopolymerisation significantly increases the sorption capacity of the silica and alumina sources, however, the research in this area still remains limited. Limited research has been reported on the use of geopolymer composites compared to geopolymer powders. Li et al. [4] developed a methylene blue adsorptive FA based geopolymer that achieved a maximum adsorption capacity of 0.12 mmol/g. Wang et al. [5] developed FA based geopolymer that can be used to adsorb Cu²⁺

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from synthetic wastewater and a adsorption capacity of 92 mg/g was reported. [6] developed a powdered kaolin/zeolite to study its potential to adsorb Cu (II), Ni (II), Zn (II), Cd (II) and Pb (II) from wastewater. They reported that maximum adsorption capacity was attained at a ratio 150 g: 50 g (zeolite:kaolin). Furthermore the same author [7] conducted a similar study using different metals namely; Cd, Cu and Cr [8]. The metals were successfully removed from a synthetic Cd-Pb-Cu-Cr mixed wastewater system. In this study BOFS based geopolymers with varied pore sizes were developed, assessed and evaluated as a neutralizing agent and adsorbent for removal of Fe, Al, Ni, Cu, Zn and SO_4^{2-} , using a continuous process for a period of 133 days. BOFS was chosen in this study because is composed of hydrated amorphous silica magnesium oxide and high content of CaO that classifies BOFS as basic/alkaline by-product [9]. The aforementioned characteristics reveal that BOFS has potential to be transformed into geofilters through alkaline activation; that can be used as a long term solution to curbing low pH values, high iron and sulphates concentrations in AMD. To the authors knowledge there's no reports in literature that explored or investigated the feasibility of using BOFS based geopolymer as an adsorbent to remediate AMD. Furthermore the use of BOFS based geopolymers both as powder or composite in column studies to remediate AMD has not been explored. Therefore geopolymers that were developed in this present study in a form of composites were used in packed beds, making it easier collect and recycle them when exhausted [10]. This is a key practical and beneficial approach in the real world compared to the use of powdered geopolymers.

2. Materials and methods

2.1. Materials

Geopolymers were prepared using BOFS supplied by ArcelorMittal (South Africa). NaOH supplied by Rochelle chemicals was used as an activator. Hydrogen peroxide (H_2O_2) supplied by Sigma Aldrich was used as a blowing agent to increase the porosity of geopolymers. AMD was collected from a local coal mine in Witbank. 1000 ppm standards of Fe, Cu, Zn, Al, Mn and Ni supplied by Rochelle chemicals were used for the preparation of elemental calibration standards for AAS analysis. Ethanol, glycerol and NaCl were used to prepare the conditioning reagent for sulphate analysis. Sulphates precipitation for UV-vis analysis was achieved through the use of BaCl_2 . Na_2SO_4 was used to prepare SO_4^- ion calibration standards. HCl and HNO_3 were used for sample digestion.

2.2. Geopolymer paste preparation

283 g of BOFS, 56.6 mL of NaOH solution and H_2O_2 solution were mixed until a homogeneous paste was formed. The H_2O_2 content to add in the paste was varied to evaluate its effect on the geopolymers' pore structure and removal efficiency. In these compositions, the 56.6 mL of NaOH was substituted by 0, 0.5, 1 and 1.5 wt. % of H_2O_2 to make up 20 % S/L ratio. After forming a workable paste, the paste was poured into $50 \times 50 \times 50 \text{ mm}^3$ moulds. The cast sample was allowed to set and was removed from the mould when it was stiff enough for demoulding. The hardened samples were then cured at 80°C until they were borne dry.

2.3. Characterization of the raw AMD

Table 1 shows the AMD constituents that were present in the raw AMD. Raw AMD is characterized as highly acidic ($\text{pH} < 3$) with high conductivity and turbidity that is way above the stipulated range by the Department of Water Affairs and Sanitation (DWAS) in South Africa. This was attributed to high levels of Fe, Mn, Ni, Al, Cu, Zn and SO_4^{2-} . Traces of Cr, Pb, B, Ca, Mg and Na were also present. The highly concentrated AMD constituents (Fe, Mn, Ni, Al, Cu, Zn and SO_4^{2-}) were

Table 1
Raw AMD characteristics.

Parameters	Raw AMD	DWAS Guidelines
pH	2.5	> 6
Turbidity (NTU)	547	0–5
EC (Mv)	240	0–700
Na (mg/L)	49	0–50
Mg (mg/L)	27	0–27
Ca (mg/L)	30	0–32
Fe (mg/L)	546	0–0.1
Mn (mg/L)	542	0–0.05
Ni (mg/L)	390	0–0.07
Al (mg/L)	344	0–0.9
Cu (mg/L)	432	0–1
Zn (mg/L)	364	0–0.5
Cr (mg/L)	0.054	0–0.01
Pb (mg/L)	0.9	0–0.01
B (mg/L)	0.2	0.01
SO_4^{2-} (mg/L)	3400	0–500

chosen as species of concern that were addressed in this research project. Parameters such as turbidity, pH and conductivity were also monitored during the experiments as they were above the range of acceptable limits stipulated by DWAS.

2.4. Column based tests

Four fixed bed columns were constructed out of Perspex sheets as shown in Fig. 1. The AMD was pumped from the bottom of the column to the top where treated AMD was collected. AMD was allowed to percolate through the geopolymer continuously for 24 h a day for a period of 133 days. After 133 days there was no significant difference in the water quality between the influent AMD and treated effluent i.e. indicating the bed was saturated. Samples of the effluent from the column were initially collected at intervals of 1 h. Thereafter, samples were taken after 6 h and increased to a day and a week as sequential changes in metal concentrations became insignificantly different. Samples were taken at a flowrate of 6 mL/min, preserved and kept for metal and sulphates ion analysis. Atomic Absorption Spectrometer (Thermo scientific ICE 3000 Series) was used to analyze the concentration of metals in the raw and treated AMD. The sulphates content of raw and treated AMD was determined using UV-vis spectrophotometer (PG Instruments T60). The turbidity, pH and conductivity were measured using a Metler Toledo dual meter (InLab738 ISM conductivity probe Turbidity meter AL250T-IR in kit).

2.5. Characterization of BOF slag based geopolymer before and after column studies

The characterization of the geopolymers were conducted before and after the column tests. The chemical and mineralogical phases were identified using XRD (Siemens D 501 diffractometer). Fourier-transform infrared spectroscopy (FTIR) (Thermo scientific ISIO) was used for

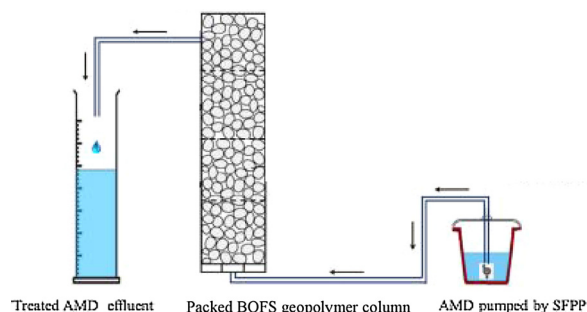


Fig. 1. A schematic diagram of the constructed column [13].

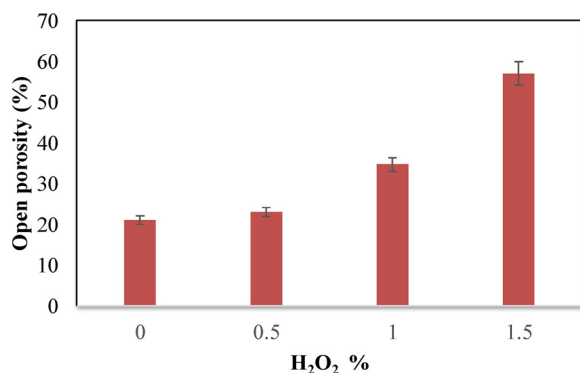


Fig. 2. The effect of H₂O₂ content on open porosity of the geopolymer.

structural analysis. The microstructural analysis was carried out using Scanning Electron Spectroscopy (SEM, Tescan Vega 3 XMU).

3. Results and discussions

3.1. The effect of H₂O₂ on the open porosity of BOF slag based geopolymer

Fig. 2. shows that hydrogen peroxide can be used as a blowing agent to increase the porosity of the BOFS based geopolymers. As the H₂O₂ content was increased, the geopolymers became more porous. The open porosity of the geopolymers increased in the following order 0% < 0.5% < 1% < 1.5% with corresponding % of open porosities as follows 21%, 22%, 35% and 57% respectively. Fig. 3 shows the geopolymer images at different H₂O₂ content.

Fig. 3. shows the micrographs before (a) and after addition of H₂O₂ (image b, c and d). The b, c and d micrographs represent the addition of 0.5%, 1% and 1.5% H₂O₂ content respectively. The increase in H₂O₂ content resulted in an increase in the number and pores size of the geopolymers.

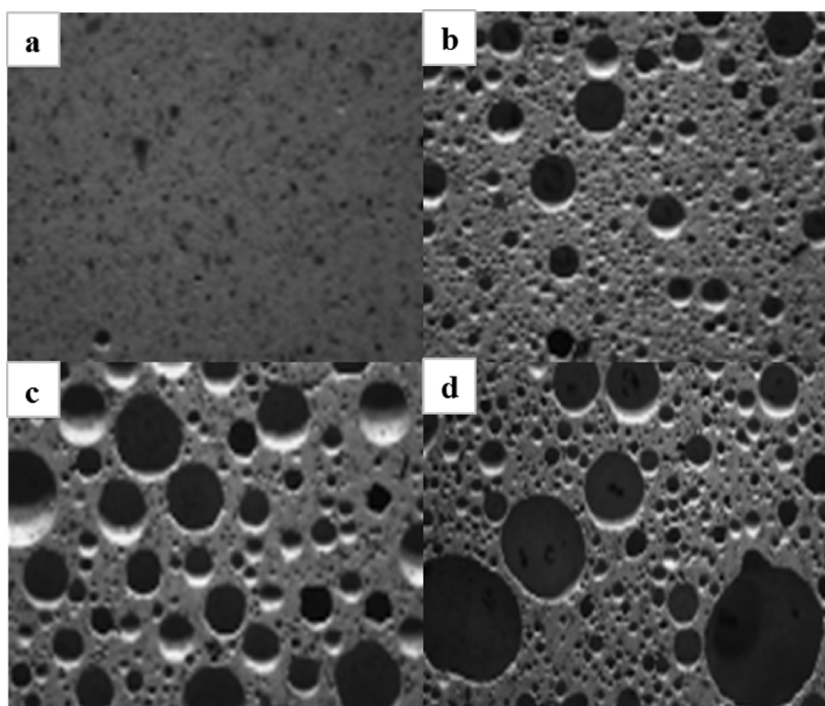


Fig. 3. The effect of H₂O₂ on the BOFS geopolymer composites.

3.2. The effect of H₂O₂ content on the density and water absorption

Fig. 4. shows that as the geopolymers becomes more porous they absorb more the water while their density decreases. Similar results have been report by [10]. Low bulk density is associated with high water uptake due to high porosity associated with such composites [11]. Low porosity is also associated with high contacts between particles hence less water can be absorbed.

3.3. Effect of variation of flowrate on metal removal efficiency

Four columns were ran using different flowrates as shown in Fig. 5. in order to find out the optimum residence time. As the volumetric flowrate was increased beyond 6 mL/min the removal efficiencies decreased. At 15 mL/min a removal efficiency of 44% was obtained. Above 6 mL/min it was observed that the flowrate was higher which resulted in the precipitates coming out with the supernatant solution and also the residual concentrations obtained in all columns were beyond the range for acceptable discharge into sewers and rivers as depicted in Table 1. Thus 6 mL/min was found to be the optimum flowrate. Below the optimum flowrate the removal efficiency was not statistically significant as shown in Table 2.

Table 2 shows that an *F* value of 1.8 against an *F* critical value of 18.5. Therefore there was no statistically significance in removal efficiency between 6 mL/min and 4 mL/min. Hence 6 mL/min was chosen as the optimum flowrate to conduct the column tests Fig. 5.

3.4. Effect of porosity on the metals removal efficiencies

Fig. 6. shows the % removal of different metals from AMD at different H₂O₂ concentrations over a period of 133 days of column tests. It can be seen that the higher the concentration of H₂O₂, the longer it takes for % metal removal to decrease with an increase in number of days. All the graphs of geopolymers prepared with 1.5% H₂O₂ gave the highest % metal removals with increase in number of days as compared to the geopolymers prepared with 0%, 0.5% and 1% H₂O₂. This is attributed to the fact that the pore size and number increases with the increase in H₂O₂ content, which enhances the number of available sites

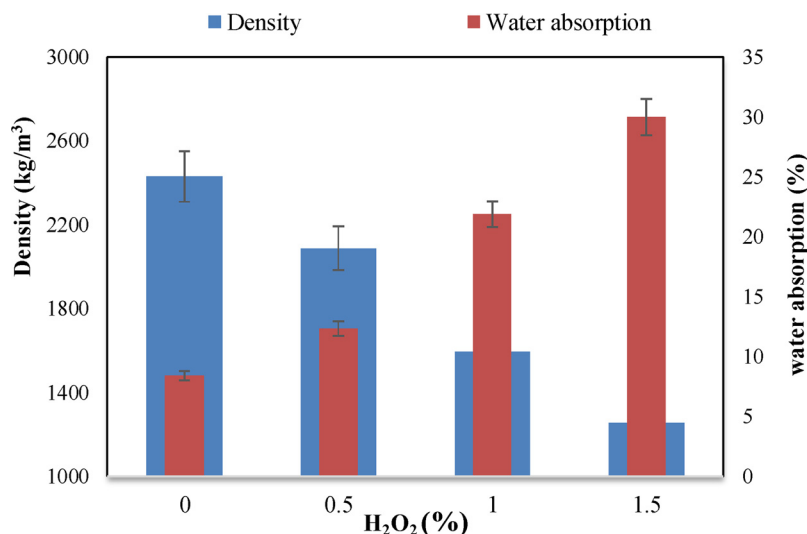


Fig. 4. The effect of H₂O₂ content on the density and water absorption.

Table 2
Statistical Anova analysis.

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.09	1	0.09	1.8	0.311753	18.51282
Within Groups	0.1	2	0.05	-	-	-
Total	0.19	3	-	-	-	-

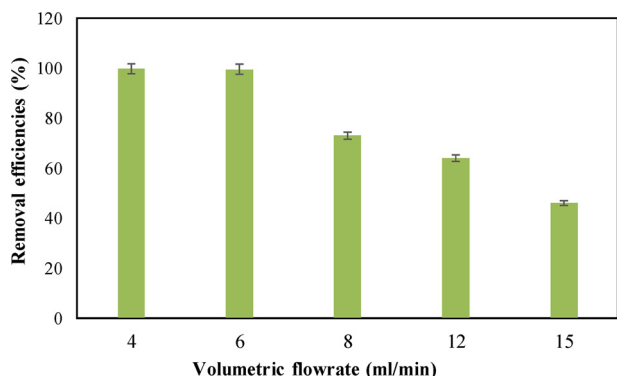


Fig. 5. The effect of variation of flowrate on the Fe removal efficiency.

for metal sorption [10]. 100 % metal removal was achieved for all the metals at different porosities in the early days of column tests however; as the number of days increased depending on the % H₂O₂ of the geopolymer; the % metal removal tends to decrease accordingly. The Fe³⁺ graph revealed that 100 % removal of Fe was achieved in all the geopolymers prepared at different H₂O₂ content though, as the number of days increased; the metal removal % starts to decrease in the following order 0% < 0.5 % < 1% < 1.5 %. The column with geopolymers prepared with 1.5 % H₂O₂ content maintained 100 % Fe removal until the 93rd day followed by column with geopolymers prepared with 1% H₂O₂ at 39th day; the column with geopolymers prepared with 0.5 % H₂O₂ followed after 16 days and the column with 0% H₂O₂ geopolymers had the least number of days to maintain 100 % Fe removal for only 7 days. Thereafter, there was a steady decrease in % removal of Fe where the 1.5 % H₂O₂ column displayed a decrease in the % Fe removal to 85 % on the 100th day and 55 % on the 133rd day; compared to a sharp decrease in the column with 1% H₂O₂ geopolymers where on the 100th day only 59 % Fe removal was achieved and 43 % on the 133rd day. There was also a significant decrease in % removal with lower

contents of H₂O₂ where the columns with 0.5 % and 0% H₂O₂ geopolymers achieved 47 % and 27 % Fe removal respectively on the 100th day thereafter the % removal declined to 35 % and 24 % respectively. Al³⁺, Mn²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ decreased from 100 % to 43 %, 58 %, 48 %, 41 % and 46 % respectively in the column with 1.5 % H₂O₂ geopolymers, followed by a column with 1% H₂O₂ geopolymers where Al³⁺, Mn²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ decreased from 100 % to 45 %, 38 %, 46 %, 52 % and 50 % on the last day of column tests. The decrease in % removal with an increase in number of days might be due to the increased competition of ions for the sorption sites. Mn had the lowest % removal as compared to Fe, Al, Ni, Cu and Zn with number of days hence they are easily sorbed onto the pores of geopolymers matrix and are preferred over Mn [12]. The ionic radius of the metals used change in the order of Mn > Al > Ni > Zn > Fe Low Spin > Cu (II). pK_h values for Fe, Al, Mn, Ni, Cu = Zn are 9.5, 5.1, 10.7, 9.6 and 7.5 respectively whilst the K_{sp} values of their metal hydroxides are 4.57 × 10⁻¹⁷, 3 × 10⁻²⁴, 2 × 10⁻¹³, 1.6 × 10⁻¹⁶, 1.6 × 10⁻¹⁹ and 3 × 10⁻¹⁷ respectively. Fe, Al, Cu, Ni and Zn have the least values meaning that they have less affinity for the solvent hence they are easily sorbed by the geopolymer matrix and they are not affected by competition from Mn in the initial stages of column testing. However, as the geopolymer matrix is reused continuously over a period of 133 days the competition of metal ions greatly affects the removal efficiency (%) due to the sorption sites being saturated. Fig. 7. shows % sulphates removals over a period of 133rd day.

Fig. 7. shows that BOF slag based geopolymers could significantly reduce sulphates content as over 99 % sulphates removal was achieved on the 1st day and decreased as the geopolymers are reused continuously for 133 days. The removal efficiency of sulphates decreased from 99 % on the 1st day to 21 %, 12 %, 9% and 4% on the last day for columns with geopolymers prepared with 1.5 %, 1%, 0.5 % and 0% of H₂O₂ respectively. The efficient removal of sulphates in the early days of column tests was perhaps caused by the dissolution of Ca (OH)₂ that was formed by the reaction of CaO and AMD. The Ca(OH)₂ releases Ca ion that reacts with SO₄²⁻ in AMD forming gypsum (CaSO₄.2H₂O) (To be confirmed by XRD and SEM) [13]. The gypsum then starts to precipitate out of AMD at pH above 3.8, resulting in the removal of sulphates from the acidic mineral effluent [13]. In this case there was a drastic removal of sulphates from the onset of column tests which was due to high pH values as shown in Fig. 8 which accumulates alkalinity. SO₄²⁻ was preferentially removed by the column loaded with 1.5 % H₂O₂ geopolymers which outperformed the columns loaded with 0%, 0.5 % and 1% H₂O₂ geopolymers. This could be attributed to the fact

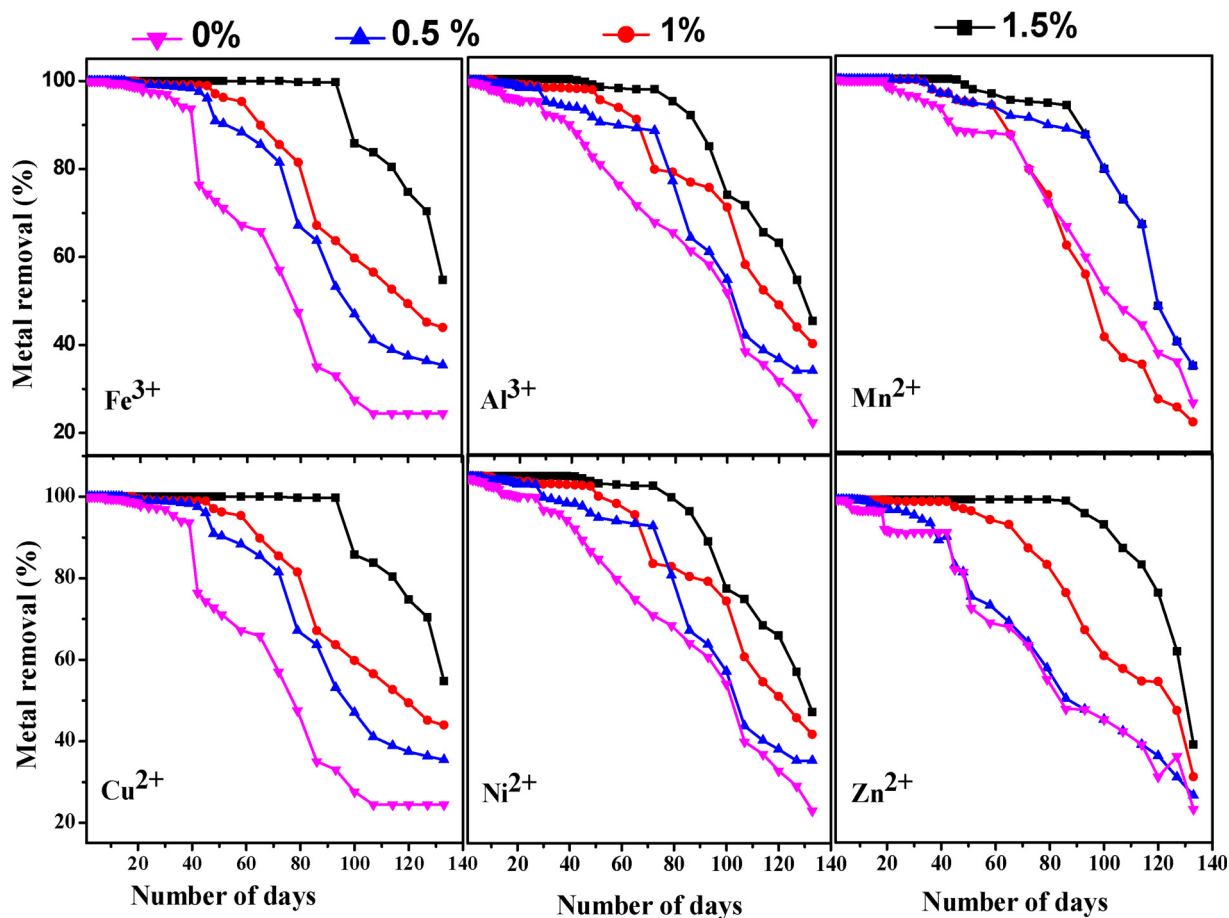


Fig. 6. The effect of different H₂O₂ concentrations on metals removal efficiencies.

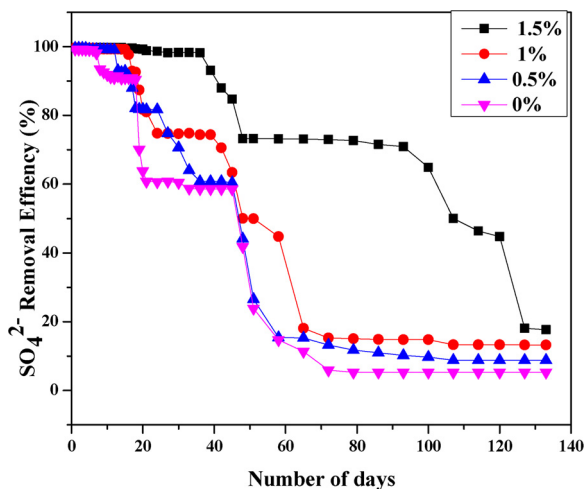
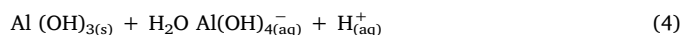
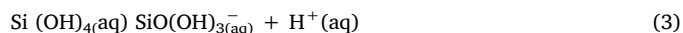
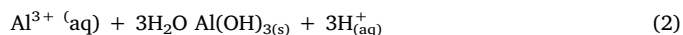


Fig. 7. The effect of variation of porosity on sulphates removal efficiency.

that the column with 1.5 % H₂O₂ geopolymers had higher number of pores compared to the columns with 0%, 0.5 % and 1% H₂O₂ geopolymers; when the H₂O₂ content rises, it enhances the number of accessible sites for sulphates removal. Over 99 % sulphates removal was achieved by all the columns with different H₂O₂ content in the geopolymers. However, as the days progressed with the columns being continuously reused there was a decline in % sulphates removal in the following order 0% > 0.5 % > 1% > 1.5 %. The column with 1.5 % geopolymers maintained 99 % sulphates removal over a period of 27 days thereafter there was a gradual decrease until the 93rd days where

over 75 % removal was achieved then a sharp decrease was observed and 21 % removal of sulphates was achieved on the last day of column tests. However, this was not the case with the column with 1% H₂O₂ geopolymers, 99 % sulphates removal was achieved for a period of 15 days, then a steady decrease was observed until the 42nd day where 70 % removal was achieved thereafter a gradual decrease in sulphates removal was observed with only 13.2 % sulphates were removed. The column with the least H₂O₂ content 0.5 % and the column with 0% H₂O₂ had the lowest removal of % sulphates where over 99 % sulphates were removed for 12 days and 7 days respectively. Thereafter there was a steady decrease in sulphates removal until the 30th day, 70 % removal was obtained; then a sharp decline was observed where just 8 % sulphates removal was achieved in both these columns. These results suggest that indeed H₂O₂ can be used to liberate the neutralizing agents in the geopolymer matrix to enhance the removal of sulphates, but as the columns are reused the neutralizing agents in the geopolymer matrix deplete which results in a decrease in sulphates removal. In addition the decrease in sulphates removal might also be due to the dissolution of silica and precipitation of aluminium hydroxide which generates acidity as illustrated in the Eq. 1 to 4. [14]



The silica released from the geopolymer matrix reacts with AMD according to Eqn. (1), while aluminium at pH > 10 precipitates as hydroxide according to Eqn. (2). Thereafter the dissolution of silica

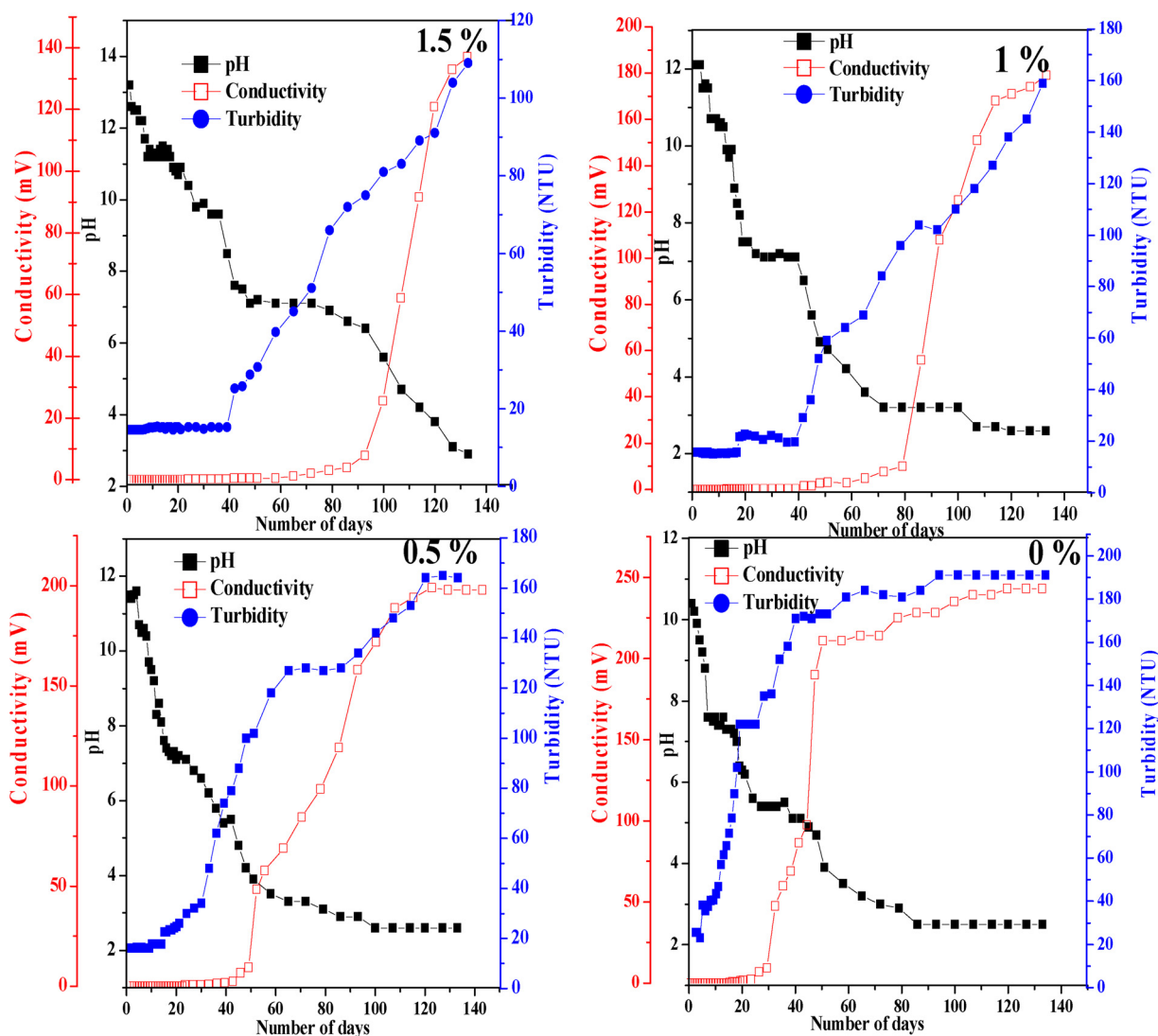


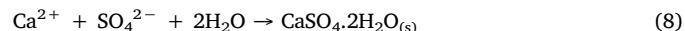
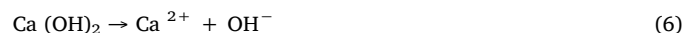
Fig. 8. pH, conductivity and turbidity profiles of geopolymers prepared with different H₂O₂ content over a period of 133 days.

hydroxide and aluminium hydroxide release H⁺ ions which generates more acidity [15]. This affects the removal of sulphates which depend on the pH of the solution.

3.5. pH, conductivity and turbidity

Fig. 8. shows the trends of conductivity, pH and turbidity with time at different porosities over a period of 133 days as the AMD is percolated through the different columns. It can be seen that as the H₂O₂ content increases there was a significant increase in the pH of the supernatant solutions compared to AMD before treatment. The pH of AMD was 2.5 but after contact with geopolymer matrix content increased to 13, 12.2, 11.7 and 10.5 for columns with 1.5%, 1%, 0.5% and 0% H₂O₂ geopolymer content respectively whilst; the conductivity and turbidity was at its lowest in the initial stages of column tests. This can be attributed to the fact that porosity increases the contact between effluent and geopolymer matrix, enabling more dissolution of alkaline neutralizing agents from the geopolymer. In addition at higher porosities there was dissolution of soluble salts on the surface of geopolymer matrix and dissolution of unreacted CaO and NaOH, which contributed to the increase in concentration of OH⁻ ions [16]. Furthermore the trends reveal that the geopolymer constituent mainly CaO removes metals from the acidic mineral effluent (AMD) by dissolving the aforementioned constituent into the solution hence increasing the pH of

the treated AMD. CaO reacts with water to form Ca(OH)₂ which dissociates and releases the Ca²⁺ and OH⁻ ions [17] (Eqs. (5) – (6)). The OH⁻ reacts with metals to form metal hydroxide (Eqs. (7) Cheng et al. [18]).



The reaction of AMD with geopolymers in the columns resulted in an increase in pH which caused the removal of the metal ions mainly by precipitation, co-precipitation and sorption [19]. Moreover, it can be seen that 100% metal removals reported in Fig. 6 corresponds with a pH range of 10.5–13 suggesting that most of the metals were removed mainly by precipitation and co-precipitation. This was attributed to an increase in the pH of the solution, resulting in Fe precipitating at pH > 3, Al at pH > 4, Mn at pH > 8.5, Cu at pH > 5, Ni at pH > 5 and Zn at pH > 7 ([20], Pozo-Antonio et al., 2014; [21]). In addition the Na⁺ ions from the NaOH used to alkali activate the aluminosilicate in the raw BOFS are present on the surface of geopolymers which; also contributed to the removing of metal ions through ion exchange in accordance with the studies reported by [8]. The pH of the treated AMD decreases with an increase in number of days, whilst the conductivity

and turbidity increases. The pH decreasing trend with number of days was also seen in Fig. 8 which suggest that pH is the main parameter which affects the removal of metals. The increase in conductivity, is linked to the fact that once saturation is reached there is no more release of ions from the geopolymer and no removal of ions from AMD. Thus conductivity gradually rises as the geopolymer neutralization capacity is exhausted. Initially, due to rapid precipitation which removes the ions from solution, the conductivity drops. Also at the beginning of the column tests it is notable that the conductivity and the turbidity are at their lowest point, which might be an indicator that the cation and sulphates have been removed in the treated AMD hence, 100 % metal and 99 % sulphates removals were achieved initially. In addition the treated AMD was less turbid in the initial stages of column tests however; as the geopolymers in the columns are reused the turbidity increases. The increase may be due to precipitated ions. Initially these may be trapped in the pores of the geopolymer matrix but may later be washed out of the column increasing turbidity. Therefore it can be concluded that the metal removal efficiency is depended on the pH of the geopolymers to neutralize and remove sulphates and metals from AMD. The decreasing trend of pH and increasing trend of turbidity and conductivity of columns with geopolymers prepared with different H_2O_2 content as depicted in Fig. 8 was the same; the only difference was that the column with 0% H_2O_2 geopolymers had the lowest pH as compared to the 0.5 %, 1% and 1.5 %. This might be due to the soluble species in the column with 0% H_2O_2 were minimal because they were trapped in the geopolymer matrix and were not fully available to react and neutralize the AMD as compared to the columns with 0.5 %, 1% and 1.5 % H_2O_2 geopolymers. The column with 1.5 % H_2O_2 geopolymers outperformed the columns with 0%, 0.5 % and 1% H_2O_2 geopolymers in terms of neutralization, metal removal and reusability.

According to [22]; removal of sulphates is poor at lower pH values hence; when Fig. 8 is correlated with Fig. 7 it can be seen that at higher pH over 99 % sulphates removals were attained, however, as the pH gradually decreases, it affects the removal of sulphates and increases the conductivity and turbidity of the supernatant solution. The increase in conductivity suggests that ions such as OH^- and Ca are dissolved in solution from the geopolymers. This is attributed by the fact that the CaO in geopolymer matrix has the ability to increase the pH of AMD and accumulates alkalinity where CaO undergoes a reaction as depicted in Eqn 5–7.

Eqn 7.8 shows that sulphates are removed from AMD mainly as gypsum as supported by Fig. 8 (To be confirmed by XRD and SEM). Although there might be other precipitates which could possibly form. Therefore it can be concluded that BOF slag based geopolymers can be used multiple times to remove metals, acidity and sulphates. Unlike the traditional method of neutralizing AMD where lime and other neutralizing agents are added to the AMD and are consumed and cannot be reused, this technology can be used to replace the traditional method of neutralizing AMD. Most of the water quality parameters of the treated water are within stipulated Water Quality Guidelines for irrigation and agriculture by the South African Department of Water and Sanitation (DWS) [19].

3.6. XRD analysis of geopolymers before and after AMD treatment

The XRD results shown in Fig. 9, reveal that the reference sample contained dicalcium silicate, tricalcium silicate, portlandite and a zeolite called hirschite. The reference sample denotes a synthesized geopolymer before AMD treatment. The treatment of AMD by geopolymers at different H_2O_2 content led to development of new peaks and disappearance of some peaks especially portlandite as compared to the reference sample. The disappearance of portlandite and tricalcium silicates peaks might be due to dissolution of these mineral phases from the geopolymer matrix to the AMD during the AMD treatment process. The dissolution of CaO resulted in the formation of portlandite which reacted to form peaks of gypsum, gibbsite, goethite, manganite and

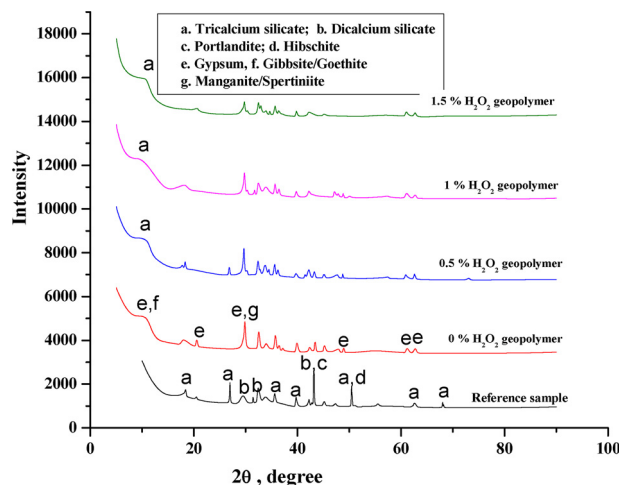


Fig. 9. XRD diffractogram of geopolymers at different H_2O_2 content before and after AMD treatment.

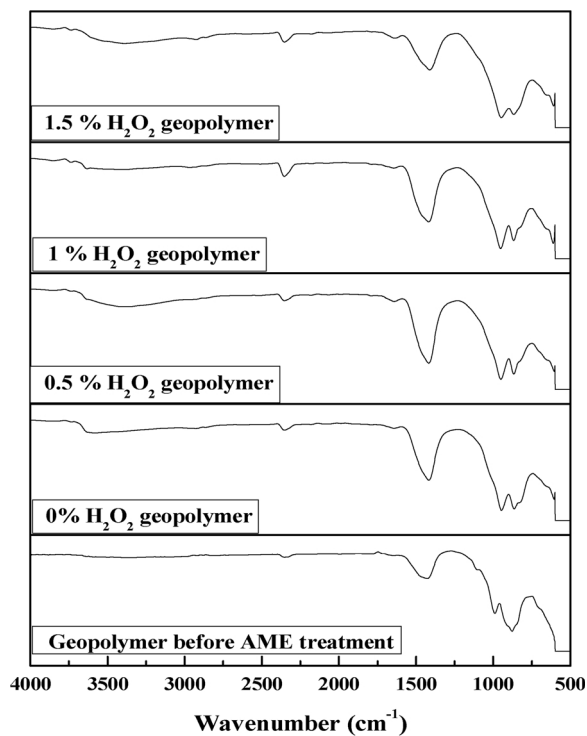


Fig. 10. The IR spectra of BOFS based geopolymer before and after AMD treatment.

spertiniite at 10.7° , 29° and 62.4° respectively ([21]). The aforementioned mineral phases reveal that Ca reacted with sulphates to form gypsum, Al precipitated as gibbsite, Fe as goethite, Mn as manganite and Cu as spertiniite. These phases were detected as major based on the intensity of the peaks. The absence of significant peak broadening (indicator of large content of amorphous phase) shows that the amount of such precipitates was low. Amorphous phases like metal hydroxides are not be detected by XRD. It can be concluded that gypsum was the main mineral phase in the geopolymers which reveal that precipitation was the major mechanism that enhanced metal removal. However, the crystallinity structure of the diffractogram suggests sorption mechanism might have also played a role in the removal of metal ions and sulphates. There was no major difference observed in the structure of the geopolymers before and after AMD treatment. The XRD diffractogram substantiates the explanation given in Section 3.3 and Fig. 8. There was

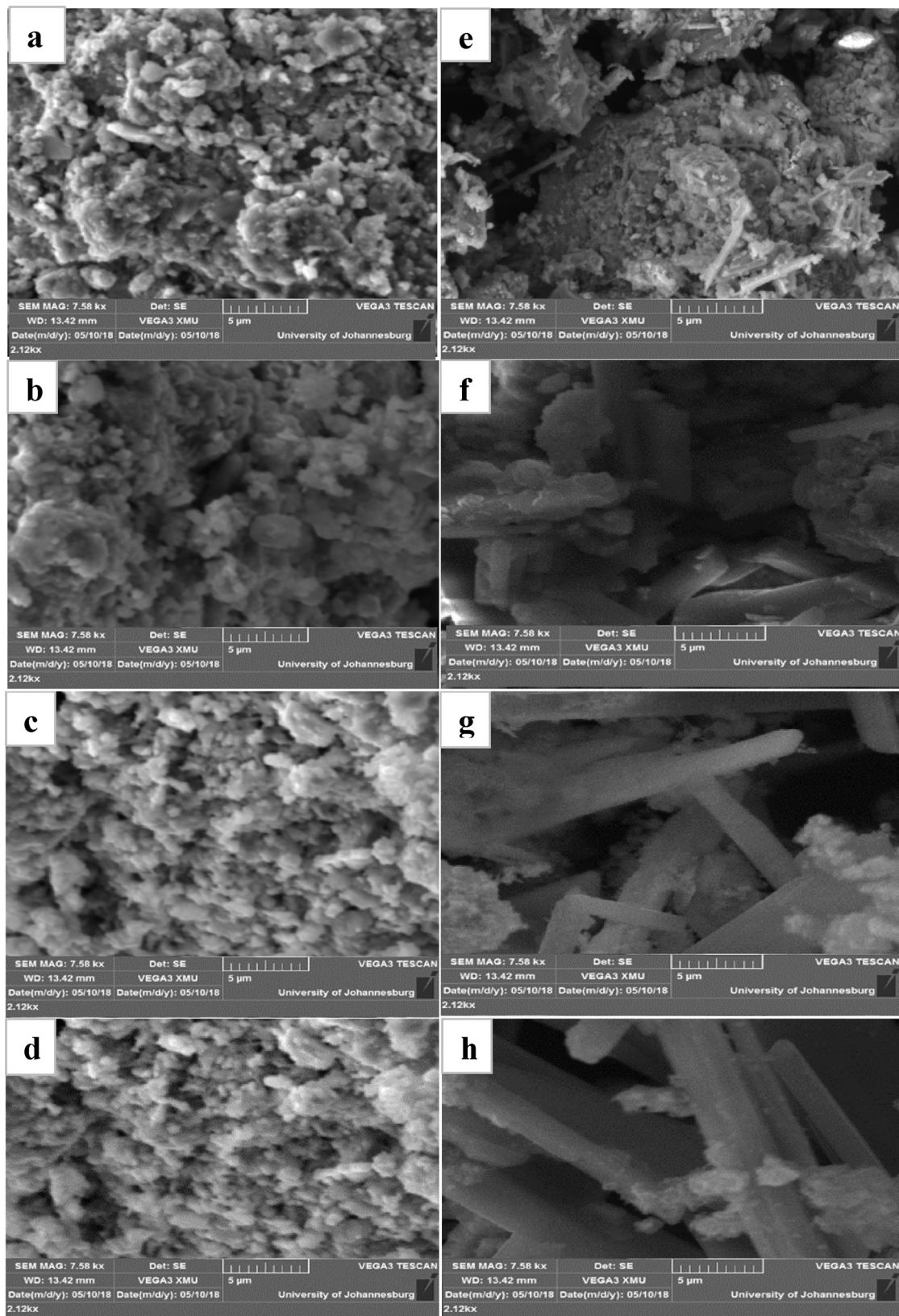


Fig. 11. SEM micrographs of BOFS geopolymers before AMD treatment (a, b, c and d) and BOFS geopolymers after AMD treatment (e, f, g and h).

no difference in the diffractogram with variation of H₂O₂ content before and after treatment.

3.7. FTIR analysis of geopolymer before and after AMD treatment

The FTIR spectra of the BOFS based geopolymer before and after AMD treatment at various H₂O₂ content is shown in Fig. 10. A broad band covered 3800 cm⁻¹ to 2800 cm⁻¹ after AMD treatment is due to stretching vibrations of O–H groups [23,12]. This band also indicates the presence of hydroxides in the geopolymer matrix after AMD treatment. The wide and an increased intensity of the band at 1418 cm⁻¹ and 3500 cm⁻¹ suggests precipitation of Cu–OH and AlO–H respectively [24]. The AMD treatment resulted in a shift to the right at 981 cm⁻¹ to 867 cm⁻¹ and a slight increase in intensity which suggests metal sorption mechanism and ion exchange to a lower extent. The aforementioned supports the mechanisms of removal that were suggested and discussed in Fig. 8. The shift of CaSiO₃ band at 1500 cm⁻¹ to the right as compared to the reference sample (geopolymer before AMD treatment) also suggests metal sorption. The precipitation and ion exchange might be due to the CaO and NaOH reacting with water to form Ca(OH)₂ which dissociates releasing OH⁻ ions which reacts with metal cations to form metal hydroxides and Ca reacting with SO₄ to form gypsum as shown in Eq. 5 to 8 [25]. Therefore the obtained IR structure after AMD treatment validates the results and discussions in Section 3.3.

3.8. Morphology of the BOFS/FA geopolymers before and after AMD treatment

Fig. 11 shows the SEM micrographs of BOFS geopolymers at different H₂O₂ content; 0%, 0.5 %, 1% and 1.5 % represented by a, b, c and d respectively. The BOFS geopolymers after contact with AMD for 133 days is shown in micrographs e, f, g and h, where e, f, g and h represent different H₂O₂ content; 0.5 %, 1% and 1.5 % respectively. Before AMD treatment the geopolymers at different H₂O₂ content appeared sub rounded, spherical, porous and closely packed. After contact with AMD the particles appeared rod-like or cylindrical mixed with spherical structures forming. This change in morphology indicates formation of new mineral phases/precipitates coating on the surfaces of the BOFS geopolymers or dissolution of soluble salts that covered the BOFS geopolymer surface [21]. It is noticed that the rod-like, needle and spherical structures formation becomes more pronounced as the H₂O₂ content rises; indicating that the increase in H₂O₂ accelerates the dissolution rate of soluble salts which in turn increases the pH of the solution; resulting in substantial precipitation of metal and formation of gypsum and other new mineral phases as shown in Fig. 9.

4. Conclusion

The study intended to evaluate and assess the developed BOFS based geopolymer composites treated with distinct concentrations (0 %, 0.5 %, 1 % and 1.5 %) of H₂O₂ as attenuators to remediate AMD. The results show that BOFS geopolymer composites can be used to remediate AMD. The percolation of AMD through the packed geopolymers resulted in a significant increase in pH. The significant increase in pH led to a complete removal of metals and sulphates from AMD in the initial stages of columns. The removal of metals and sulphates decreased with an increase in number of days indicating that the packed geopolymers are reaching their saturation/ exhaustion point. H₂O₂ can be used to increase the porosity of the BOFS geopolymer matrix. The column with geopolymers treated with 1.5 % H₂O₂ outperformed the columns with geopolymers prepared with 0%, 0.5 % and 1% H₂O₂. Higher porosity promoted greater neutralizing ability by dissolution of soluble salts from the BOFS geopolymer which improves removal efficiencies of sulphates and metals. The increase in conductivity during column test reveals that the AMD constituents namely metals and

sulphates remained in solution which in turn affects the turbidity of the treated AMD. BOFS geopolymer can be reused for more than 50 days to neutralize and remove AMD species in solution. Characterization revealed that gypsum was the main mineral phase in the geopolymers indicating that precipitation was the major mechanism that enhanced metal and sulphates removal. The crystallinity structure of the diffractogram suggests sorption mechanism also played a role in the removal of metal and sulphates. The FTIR confirms that sorption, co-precipitation, ion-exchange mechanisms were contributed to the removal of metal and sulphates with precipitation as the main mechanism of removal.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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