

## ORIGINAL ARTICLE

# Low temperature minerals growth and heavy metals (Cd, Cr and Pb) trapping on the geopolymer surfaces of gold mine tailings

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### ABSTRACT

*This paper aimed to verify the initial cement minerals in mine tailings, chemical activators, and low temperature minerals growth effects on heavy metals (Cd, Cr and Pb) stabilization in the geopolymers. Leaching of heavy metals from the geopolymers into water was studied by measuring the content of heavy metals and pH of leachates. Previous characterization was carried on mine tailings and fly ashes. The microstructures and structures of geopolymers were investigated through FESEM, XRD and FTIR. The results indicated that heavy metals could be effectively immobilized in the low temperature minerals based geopolymers. It was observed 67 and 5 times of Cd and Pb were respectively stabilized above the permissible emission limit values in surface water. However, the geopolymers could be left on soil surfaces eco-friendly. It provides a clarification of initial cement minerals in mine tailings, chemical activators and low temperature minerals growth effects on heavy metals (Cd, Cr and Pb) stabilization in the geopolymers. According to the nucleation and growth of calcium silicate hydrate gel, portlandite, calcite and dolomite fill up the spaces and cavities between the grains then decreases heavy metals mobility. The immobilization of heavy metals in geopolymer may be due to diffusion, adsorption and equilibrium thermodynamic of heavy metal cations in the frameworks of unreacted initial cement minerals and low temperature minerals growth of geopolymer phases.*

**Keywords:** gold mine tailings, heavy metals, geopolymers, mineral growth, diffusion and adsorption

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### INTRODUCTION

Geopolymer contains a large variety of binder minerals at low-temperature. Minerals and other solids play a vital role in determining partitioning and speciation of heavy metals and compounds. Use of binder minerals is very useful to trap heavy metals pollutants. Geopolymerization is a synthetic aluminosilicates process derived from mineral growth has advantages in heavy metals stabilization. Minerals growth is also natural phenomenon that occurs in soil during weathering of rocks. It is a process referred to as mineral precipitation or neof ormation. In other cases, minerals form via transformation from pre-existing minerals and incorporate parts of crystallographic structures inherited from the parent mineral, a process referred to as transformation. Geopolymerization includes cement hydration, a combination of chemical activators, interfacial phenomena and solid-wastes reactions. Nevertheless, numerous external factors influence mineral growth such as: temperature, redox conditions, time-mineral growth, biological factors, physical factors-the porosity and permeability of sediment, soil or rock[26].

Mineral growth is controlled by conditions at the interface of mineral surface and aqueous solution. Crystal growth can be viewed as a three-step mechanisms involving: (1) movement of reactants (ions) to surface of crystal growth by advection or diffusion; (2) reaction on the mineral surface, involving, sequentially, attachment/adsorption of ions to surface, diffusion or ions to bonding sites, and formation of chemical bonds with reaction surface; and (3) desorption and diffusion or advection of reaction products away from reaction surface[26]. Advection is the movement of matter by physical flow in response to a force. Contrary to the advection, diffusion is the migration of ions or particles from areas of high

concentration to areas of low concentration. It is a spontaneous process in response to the tendency of systems to progress from ordered to more disordered, i.e. in the direction of greater entropy [26]. In recent years, geopolymerization, derived from mineral growth has been identified as the best attractive technology for heavy metal ions and radioactive elements trapping in wastes. [1] gives a comprehensive and critical review on the utilization (i.e., kaolinite, fly ash, and blast furnace slag as the aluminosilicate as sources of source raw material binders in geopolymerization. Mainly alkali activator geopolymers are used for soil stabilization and solidification. They can be used in mixtures or with additives and/or salts to the raw materials. These agents would be most effective in promoting the growth of minerals on the geopolymer surfaces at low temperature through decreasing interfacial tension and heavy metals trapping. However, alkali-activated slag binders have been studied for the immobilization of  $\text{Cr}^{6+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ . It has been reported that the microstructure and phase composition of hydrated slag play an essential role in the immobilization of heavy metals [12]. Similar study was carried on the immobilization efficiency of  $\text{Cr}^{6+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  ions in alkali-activated fly ash binders [34], it was found the immobilization of heavy metal ions in geopolymer binders depends on the chemical form in which the contaminants are associated. Others studies [15] were performed on the nano- $\text{SiO}_2$  and nano- $\text{Y-Al}_2\text{O}_3$  - modified composite geopolymers from municipal solid waste incineration fly ash (MSWIFA) and class C fly ash (CFA) to study the effect of microstructure and self-solidification /stabilization (S/S) of heavy metals. It has been reported that, nano- $\text{SiO}_2$  has a better performance than nano- $\text{Y-Al}_2\text{O}_3$  due to improve structure, and immovability of heavy metals from the geopolymer. Some studies were carried out on the mixture of inorganic geopolymers: volcanic glass, calcined halloysite-rich clay and mine tailings in the aim to investigate the strength, microstructure and composition of the geopolymer binders on the leaching behavior of heavy metals [7]. However, many researchers working in related field have pointed out that the immobilization of heavy metals depends on strength, microstructures, composition phase, chemical forms, particle sizes, surface area and mechanical properties of the geopolymers. No researchers have been carried to verify the initial cement minerals in mine tailings, chemical activators, and low temperature minerals growth effects on heavy metals (Cd, Cr and Pb) stabilization in the geopolymers. This paper aims to verify the initial cement minerals in mine tailings, chemical activators, and low temperature minerals growth effects on heavy metals (Cd, Cr and Pb) stabilization in the geopolymers. Different characterizations such as leaching of heavy metals, microstructures and structures of geopolymers were investigated.

## **MATERIAL AND METHODS**

### **Mine tailings of Mari valley, Betare Oya**

Mari valley located in the North-East of Bétaré Oya, belongs to the Lom Series, one of the volcano-sedimentary Neoproterozoic basins of Cameroon; is an old mine site. The gold mine tailing samples were collected from Artisanal Gold Mine of Betare Oya, East-Cameroon.

### **Fly ashes of Kaniha, Odisha**

In the present research work, dry fly ash samples (class- F) were collected from National Thermal Power Corporation, Kaniha, Odisha, and were used as the binder to make the geopolymers. Fly ashes were used as binder because mine tailings are not more reactive.

### **Mineralogical, physical and chemical characterization of mine tailings and fly ashes**

The studies were carried out in laboratories of Environment & Sustainability Department, Bhubaneswar, India. After sample collection, the mine tailings were ground in ball mill to obtain very fine particles. Then the mine tailings and fly ash were kept for two days at  $80^\circ\text{C}$  in an air oven to remove the moisture. Before initiation of this research work, as-received fly ashes and mine tailings, chemical, physical, mineralogical and morphological characterization of fly ashes and mine tailings were determined by XRF, leaching test, XRD, FESEM and FTIR analysis to get some information about the raw materials if the materials are good for geopolymerization.

### **Chemical composition of mine tailings and fly ashes**

#### **X- Ray fluorescence**

The X- ray fluorescence, Minipal-4, EDXRF PAN analytical using press powder was used to determine the percentage in oxides of mine tailings and fly ashes. The percentage of oxides of mine tailings and fly ashes are shown in Table 1a&b.

The major elements associated in these samples are alumina, silica, iron and titanium oxides. Silica content in both samples are found to be above 60%, while the alumina in mine tailings and fly ash sample were 12.8 and 32.3% respectively. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in mine tailings is 2.80 that are good for geopolymerization.

### Leaching test (NF X 31-147)

A standard method of leaching was followed during the course of the investigations. The leaching test based on standard [25] was used to determine total concentration of heavy metals in the leachates of mine tailings and fly ashes. As given in Table 2a&b, the total concentrations of heavy metals were found above permissible limit.

Fly ash used in this research work is classified as class F fly ash according to the specification of ASTM C618-08 as given in Table 3. The percentage of carbon in this fly ash is low as indicated by the lower loss on ignition (LOI), and therefore, it has a higher pozzolanic activity and lower water demand. The  $\text{SO}_3$  is less than 1% which will ensure high volume stability and also good for durability.

### Microstructures of mine tailings and fly ashes

#### Field Emission Scanning Electron Microscopy (FESEM)

The Field Emission Scanning Electron Microscopy (FESEM) with Carl Zeiss SUPRA 55VP was used to determine the microstructures with impurities of mine tailings and fly ash and change in shape of geopolymers. The FESEM photographs of gold mine tailing and fly ash powders are given in Figures 1&2 respectively. FESEM pictures of mine tailing samples (Figure 1) show that the crystalline phases with high intensities of major elements O, Al, Si, K and low intensities of heavy metals. FESEM pictures of fly ashes contain semi-crystalline to amorphous phases as observed in Figure 2. The high intensities of Si, O, and Al in both samples show that the materials are good for geopolymerization.

### Structural properties of mine tailings and fly ashes

#### X-ray diffraction analysis (XRD)

The X-ray diffraction analysis (XRD), PAN-analytical X'Pert Pro diffractometer equipped with a diffracted-beam monochromator was used to identify the structures and main mineralogical composition of mine tailings, fly ashes and geopolymers. The analysis was performed using a diffractometer with Co, Mo and Cu  $\text{K}\alpha$  radiation (40kv and 30mA). The diffractogram interpretation was made with the assistance of the X'Pert Quantify search match High score software (PANalytical). The XRD patterns of the mine tailings and fly ashes are shown in Figures 3&4 respectively. The XRD pattern of the mine tailings (Figure 3) indicates that the main crystalline minerals are silica or quartz ( $\text{SiO}_2$ ) in association with staurolite, ilmenite, sillimanite, kyanite, andradite, kaolinite, rutile and feldspar. As detected by XRD, andradite, is a tricalcium silicate cement mineral present in mine tailings. The hydration of tricalcium silicate leads to a possible calcium silicate, portlandite and calcite formation and deposit between grains then decreases heavy metals mobility. The XRD pattern of the fly ash powder shows that the main crystalline components are mullite and quartz in association with sillimanite, hematite and magnetite. The peak positions are well matched with the JCPDS files and X'Pert Quantify search match.

#### Fourier- Transform Infrared (FTIR)

Fourier- Transform Infrared (FTIR) using IR Prestige FTIR-84005, SHIMADZU Corporation (Kyoto, Japan) was used to provide information about the vibrational transitions and rigidity of chemical bonds in mine tailings, fly ashes and geopolymer materials. FTIR spectra of mine tailings and fly ashes are given in Figures 5&6 respectively. It was observed that the peak at  $462\text{ cm}^{-1}$  is ascribed to the Si-O plane bending (Figures 5 &6) [15]. The bands  $793\text{ cm}^{-1}$  was assigned to Si-O-Si asymmetric stretching (Figure 5) [30]. The bands at 800-1200 were attributed to Si-O stretching vibrations of  $\text{SiO}_4$  (Figures 5 &6) [8, 3,21, 23and 34]. The peaks  $1036\text{ cm}^{-1}$  was attributed to T-O-Si (T= Si or Al) [30] (Figure 5). The high vibration was observed and centered on the peak  $1102\text{ cm}^{-1}$  in Figures 5 &6. The peak at 1102 was attributed to Si-O stretching vibration [1]. The peak at 2350 corresponds to C-O vibrations in  $\text{CO}_2$  constrained in amorphous phase (Figures 5 &6) [27,28]. The vibrations bands at approximately  $3680\text{ cm}^{-1}$ ,  $3436\text{ cm}^{-1}$  and  $1636\text{ cm}^{-1}$  correspond to OH groups (Figures 5 &6) [21, 22]. These different vibrational transitions and rigidity of chemical bonds reveal that mine tailings and fly ashes contain Si-O-Si and Si-O/Al-O-Si precursors responsible for geopolymerization,  $\text{CO}_2$  and OH mean a possible carbonatization and hydration of minerals.

### Components of geopolymer mixtures

Table 4 shows the chemical activators used in experimentation, along with their acronyms. The geopolymer reactions are alkali synthesis of aluminosilicate materials which happen at a high rate when the alkaline activator contains soluble silicate, either sodium or potassium silicate. It is well known that the addition of sodium silicate solution to sodium hydroxide, sodium carbonates and water solution enhances the hydration and precipitation then decrease the mobility of heavy metals.

The stabilization test was carried out using the chemical activators sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium hydroxide (NaOH) at different concentrations.

### Preparation of chemical activator solution

The chemicals used to manufacture geopolymer materials are water soluble, sodium hydroxide in flakes or pellets form with 97 to 98% purity, bulk quantity of sodium silicate solution ( $\text{SiO}_2/\text{Na}_2\text{O}=2$ ,  $\text{Na}_2\text{O} = 14.7\%$ ;  $\text{SiO}_2 = 29.4\%$ ;  $\text{pH}=12.8$ , water = 55.9% by mass and viscosity centipoises=400) were purchased from a local supplier. The alkaline chemical activator solution, sodium hydroxide, along with sodium silicate solution (commercial grade) was prepared in 1:1 ratio, by dissolving 500 g of sodium hydroxide in 0.5 liter of water at different concentration 5M, 10M and 15M of sodium hydroxide and a pink of  $\text{Na}_2\text{CO}_3$  are added to the deionized water - sodium silicate- water solution to prepare the chemical activator solution. The pH of the chemical activator solution is above 11.5. The  $\text{CO}_3^{2-}$  will act as reactant to precipitate with heavy metals. The solution was used for different types of test runs.

### Experimentation

#### Formulation of geopolymers

The experiments were carried out by adding different proportions of below-mentioned binder without or in combination to the mine tailings. The geopolymer pastes were prepared based on the ratio of alkali activators  $\text{Na}_2\text{O}/\text{SiO}_2=0.2$ ,  $\text{Na}_2\text{SiO}_3/\text{NaOH}=1$ , the ratio of raw materials  $\text{SiO}_2/\text{Al}_2\text{O}_3=2.11$  for fly ashes,  $\text{SiO}_2/\text{Al}_2\text{O}_3= 2.80$  for mine tailings. The preparation of the geopolymer pastes was performed in a 1000 ml beaker by mixing 10 ml of chemical activators with 50g of mine tailings and with different percentage of fly ashes(0, 25, 50 and 75%) and at different concentration of NaOH (5 M, 10 M, and 15 M). The pastes were prepared manually until the total hydration of raw materials was achieved. It was prepared at room temperature and at 80°C in an air oven during 48 hours to allow geopolymerization setting. After 48 hours, the geopolymer pastes were removed from oven for different analysis.

The Tables 5a&b above give the different formulation of geopolymers.

Stabilization using NaOH (5M) + $\text{Na}_2\text{SiO}_3$ +  $\text{Na}_2\text{CO}_3$  at the atmospheric conditions.

Stabilization using NaOH (5 M, 10M and 15M) + $\text{Na}_2\text{SiO}_3$ +  $\text{Na}_2\text{CO}_3$  at 80°C.

The total number of required experimental runs was 16.

#### EN 12457-2 leaching test

It is mandatory that all hazardous materials need to be characterized before disposal into the landfill site. Standard [13] is a one-step leaching procedure, which is applied to assess if a waste material can be accepted for disposal in a landfill site. The experimental concentrations obtained in the test can be compared with the limit threshold values issued by the Legal limits Limit I: maximum permissible limits in groundwater; Limit II: emission limit values in surface water. Testing of heavy metals leaching from geopolymers (aged 28 days) was performed according to a standard procedure EN 12457-2. The speed of rotation was 60 rpm. Deionized water was used as the leachates at a liquid to solid of 10 L/kg for the materials with particle size of below 4 mm, for 24 h. During the experiments 20 g of geopolymers (dry mass) was mixed with 200 ml of deionized water. After 24 h of leaching the samples were vacuum filtered through a membrane filter of 0.45  $\mu\text{m}$ . The eluates were acidified with nitric acid to the value of  $\text{pH} \sim 2$  and analyzed by Atomic adsorption spectrophotometer (AAS) and ICP-OES PerkinElmer and Optima 2100 DV were used to analyze total concentration of heavy metals of mine tailings, fly ash and geopolymer materials.

The Table 6 indicates the Legal limits [14]. Limit I: maximum permissible limits in groundwater; Limit II: emission limits values in surface water.

## RESULTS AND DISCUSSION

### Stabilization through geopolymerization technology

#### Leaching behavior of geopolymer materials

The results of stabilization test of heavy metals are given in Tables 7-9. The stabilization of heavy metals was evaluated at different percentages of fly ashes (0%, 25%, 50% and 75%), different temperatures (room temperature and 80°C), different concentrations of alkali activator NaOH (5M, 10M and 15M) and constant concentration of alkali activators.

#### Effect of raw materials

The mixture of different proportions of fly ashes and mine tailings did not affect more the result of heavy metals stabilization but it was observed pH decreases with the percentage of fly ashes. The decreasing of pH in the geopolymers may be due to heavy metals hydrolysis.

#### Effect of temperature

At room temperature as indicated in Tables 7-9, it was observed that Cd is not completely stabilized at 5 M NaOH. The complete stabilization of Cd at this temperature could be attributed to different phase formation at low temperature and a possible calcium silicate hydrate (C-S-H gel) which is a structure very far from equilibrium and is thermodynamically unstable at ambient temperature. Contrary at

80°C, but at same concentration, Cd is completely stabilized and the others heavy metals increase in stabilization in the geopolymers. Heavy metals increasing stabilization in the geopolymers suggests the interaction of heavy metals and mineral growth can take place at the room temperature but it needs some temperature to establish chemical binding of heavy metals and to grow minerals.

#### **Effect of chemical activators**

It was also observed the effect of chemical activators such as sodium hydroxide on geopolymers. At 5 M NaOH, the hydration of geopolymers by sodium hydroxide is not sufficient to stimulate the reaction surfaces of silicates then to form calcium silicate hydrate and portlandite or to precipitate as carbonate, oxides and hydroxides on geopolymer surfaces. However, at 10M NaOH, the hydration was achieved with increasing of all heavy metals in stabilization. The increasing of heavy metals stabilization is related to large surface areas of calcium silicate hydrate and portlandite to sorb heavy metals. But at 15 M NaOH, the stabilization of heavy metals decreases, this suggests the hydration of geopolymer is limited with the concentration of sodium hydroxide.

#### **Stabilization of geopolymer materials.**

Tables 7-9 give the results of heavy metals (Cd, Cr and Pb) stabilization in the geopolymers.

#### **Effect of pH**

As shown in Table 7, Cd stabilization in geopolymers followed this order 99.45% at (5M) NaOH at the atmospheric conditions <100% at (5M) NaOH at 80°C temperature > 99.48% at (10M) NaOH at 80°C temperature > 97.78% at (15M) NaOH at 80°C temperature.

In Table 8, Pb stabilization followed this order 79.68% at (5M) NaOH at the atmospheric conditions <96.40% at (5M) NaOH at 80°C temperature < 97.24% at (10M) NaOH at 80°C temperature > 96.45% at (15M) at 80°C temperature.

It is noted Cr stabilization followed this order 86.64% at (5M) NaOH at the atmospheric conditions <92.32% at (5M) NaOH at 80°C temperature < 99.08% at (10M) NaOH at 80°C temperature > 99.00% at (15M) NaOH at 80°C temperature.

As observed in Table 7, at 5M NaOH concentration, 100% Cd is stabilized at 80°C temperature, this could be attributed to pH 8-10.30 corresponding to carbonate minerals  $\text{CdCO}_3$  very less soluble form of Cd.

However, at 10M NaOH, the stabilization of Cd is not completed because the pH ranging 10.30 - 12 corresponding to hydroxide form of Cd  $(\text{OH})_2$ , a soluble form of Cd. This solid phase is considered unstable, soluble and amphoteric. This finding is in agreement with the previous studies of [4,20], carbonate precipitation sometimes has an advantage over hydroxide precipitation when metal carbonates are less soluble than corresponding hydroxides.

However, in Tables 8 & 9, it was observed the difficulties of Pb and Cr to complete stabilization.

According to pe/pH Pourbaix diagram, the pH 8-12 corresponds to dominant solid phase of Pb, a hydroxide forms  $\text{Pb}(\text{OH})_2$  unstable domain of stability, soluble and amphoteric. and pH 8-12 the dominant solid phases of Cr correspond to oxide  $\text{Cr}_2\text{O}_3$  and oxyanion form  $\text{CrO}_4^{2-}$ , but  $\text{CrO}_4^{2-}$ , corresponds to very soluble form of lead and chromium.

This solid phase is considered unstable, soluble and amphoteric. Several studies have demonstrated the difficulty to stabilize heavy metals Pb and Cr in hydroxide form [4,20].

In the given Tables 7, 8 & 9, at 15 M NaOH, Cd, Cr and Pb stabilization decreases again. The dissolution of Cd, Cr and Pb means that their optimum pH was reached. Hydroxide, oxide and carbonate precipitation occurs when the pH of a solution of dissolved metal ions is raised to some optimum level for a specific metal. The optimum pH is different for each metal and for different valence states of a single metal.

Mineral growth in geopolymers is purely thermodynamic equilibrium controls; each metal has its domain of stability according to pH of solution, potential redox and concentration of metal in solution. According to pe/pH Pourbaix diagram, the domains of stability of low temperature minerals in solid phases are oxides, hydroxides and carbonates. The concentration of heavy metals depends on the speciation.

As given in Table 10 Stabilization compared to legal limits [14], geopolymer is a hazardous material. All hazardous materials should be characterized before disposal into the landfill site.

In the given table above, many geopolymers were formulated but the best stabilization was found at 10M NaOH) with 97.24% Pb and 99.08% Cr but 100% Cd was stabilized at 5M NaOH. Cd is 67 times and Pb is 5 times stabilized above the permissible emission limit values in surface water legal limits (G.U.R.I, 2006), however, geopolymers could be left on soil surfaces eco-friendly.

#### **Microstructures of polymeric materials**

Various characterizations were carried out to study the microstructures of the best stabilization of heavy metals.

### Field Emission Scanning Electron Microscopy (FESEM)

The FESEM photograph of the best geopolymers stabilized at 10 M NaOH compared to mine tailing is given in **Figures 7a&b**.

The results of the elementary chemical composition of mine tailings compared to geopolymers are given in the **Table 11**

As given in the present research work, the geopolymer material surfaces (**Figures 5a&b**) contains the major elements C, O, Na, Al, Si, Ca and some minor elements Cr, Cd and Pb. The structure of the mine tailings changed from crystalline structure to the amorphous structure in geopolymers.

As mentioned in **Table 11 a** the intensities of major elements were 54.42% Si, 4.06% Al, 24.24% O and 0% C in mine tailings. However, in **Table 11 b**, their intensities decrease up to 0.38% Si, 0.18% Al, and increase up to 31.84% O and 9.80% C in geopolymer surfaces. The decreasing of Si and Al mean that they are formatives or trainers of network crystalline structures of silicate minerals. Low concentrations of minor elements were observed 0.63% Pb, 0.20% Cd, 9.48% Cr in mine tailings but increase up to 1.1% Pb, 0.83% Cd, 15.80% Cr on geopolymer surfaces; this suggests that they are trapped on mineral surfaces or act as balancing charges in geopolymers. Heavy metal compounds precipitate on the surface of a solid more readily than from bulk solution[19]. It is reported that minor components can modify the crystal growth by substitution in the lattice of the calcium silicate hydrates[11]. In **Table 11 b**, it was observed the presence of C and Ca in geopolymers. C and Ca enter in mineralogical composition of many minerals such as carbonates, hydroxides and silicates. This suggests a possible calcite, portlandite and calcium silicate minerals. It has reported that calcium oxide is certainly one of the most important factors determining the thermodynamics and kinetics of C-S-H formation[11]. It also influences the morphological and structural features of C-S-H[11]. If the amount of heavy metal is sufficient, precipitation and co-precipitation of heavy metal and calcium can occur, forming amorphous structures of hydroxides. Heavy metal hydroxides could substitute for  $\text{Ca}(\text{OH})_2$  in C-S-H gel[11].

### Structural properties of geopolymeric materials.

#### X-ray diffraction (XRD)

X-ray diffraction (XRD) was carried out to detect low temperature non silicate minerals growth and unreacted minerals found in the best geopolymers stabilized at 10 M NaOH. The peak positions are well matched with the JCPDS files and X'Pert Quantify search match. XRD pattern of geopolymer material is given in Figure 8 and Table 12.

The XRD pattern of geopolymer material showed that the crystalline phases are 65% quartz, 29% calcite, 8% dolomite, 17% cassiterite, 7% sillimanite, 6% grossular, 6% biotite 2M1, 4% brucite and 4% karrooite as given above.

As given in Table 12, it was observed a variety of minerals growth on geopolymer surfaces have detected by XRD as mineral precipitation or neoformation or minerals form via transformation from pre-existing minerals and incorporate parts of crystallographic structures inherited from the parent mineral. In Table 12, XRD patterns of geopolymer material showed the disappearance of feldspar, staurolite, ilmenite, kyanite, andradite, kaolinite and rutile, the neoformation or precipitation of calcite, dolomite, cassiterite, brucite and karrooite, transformation of andradite ( $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{Si}_3$ ) in grossular  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ , staurolite ( $\text{H}_3\text{Al}_{17.89}\text{Fe}_{3.39}\text{Li}_{0.112}\text{Mg}_{0.766}\text{O}_{48}\text{Si}_{7.576}\text{Zn}_{0.092}$ ) in biotite ( $\text{H}_{2.95}\text{Al}_{3.32}\text{Ba}_{0.23}\text{Fe}_{2.01}\text{K}_{1.77}\text{Mg}_{3.16}\text{O}_{24}\text{Si}_{5.17}\text{Ti}_{0.34}$ ) and the pre-existing minerals of quartz and sillimanite in geopolymer materials. As shown in Table 12, low-temperature non silicate minerals growth developed on the geopolymer surfaces are mostly carbonate minerals such as calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMgCO}_3$ ) associated with some oxides such as karrooite ( $\text{MgO}_5\text{Ti}_2$ ), cassiterite  $\text{SnO}_2$  and hydroxides  $\text{Mg}(\text{OH})_2$ . Calcite and dolomite represent the second and third abundant minerals in geopolymers. However, it was also detected by XRD a little presence of calcium silicate phases, grossular  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  in geopolymers, this might be present in mine tailings due to incongruous calcium silicate minerals, andradite ( $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{Si}_3$ ) remained in geopolymers.

#### FTIR

FTIR spectra were conducted to detect chemical bonds of low temperature non silicate mineral growth in the best geopolymers stabilized at 10 M NaOH. Chemical bonds of minerals growth on geopolymer material prepared at 10 M NaOH compared to mine tailings is given in Table 13.

As seen in Table 13, FTIR analysis showed that during setting of geopolymers, there is disappearance, neoformation and pre-existing of chemical bonds formation. The chemical bonds in the mine tailings were shifted in higher wave numbers (Figure 9). FTIR revealed the presence of polymers Si-O-Si, Si-O-Al, Si-Al-Ca in geopolymers, these are polymers responsible for geopolymerization. This finding is in agreement with our previous XRD results. It was observed that the peaks at  $462\text{ cm}^{-1}$  and  $727\text{ cm}^{-1}$  are ascribed to the Si-O in plane bending and Si-O/Al-O-Si bending vibrations[15] in the mine

tailings. However, it was observed the new chemical bonds at the peaks 870, and 740  $\text{cm}^{-1}$  in the geopolymers. This is due to vibrations caused by the presence of  $\text{Na}_2\text{CO}_3$  [29], these bands are common in ring silicates and provide an indication of the degree of amorphisation of the material [15]. It was observed that the intensities of mine tailings and fly ash have decreased due to dissolution of Si and Al (Figures 3 & 4). The high vibration observed at 1102  $\text{cm}^{-1}$  previously in the mine tailings and fly ashes shifted at 1332  $\text{cm}^{-1}$  in low intensities due to carbonation. The peak at 2920  $\text{cm}^{-1}$  is attributed to C-O vibration in  $\text{CO}_2$  constrained in amorphous phase [27, 28]. The vibrations bands at approximately 1636  $\text{cm}^{-1}$ , 3436  $\text{cm}^{-1}$  and 3680  $\text{cm}^{-1}$  correspond to OH [15]. Geopolymers contain a relatively large amount of water in large pores available for evaporation, which would not result in capillary strain. This fact may be attributed for the low temperature [6, 5].

#### Immobilisation mechanisms of heavy metals

According to chemical mechanism, the possible immobilization mechanisms of heavy metals could be diffusion, sorption, chemical incorporation (surface complexation, precipitation, co-precipitation, diadochy), and micro- or macro-encapsulation [11].

The most important factor governing mineral growth is diffusion of ions because charge balance must be maintained, either by exchange of ions of the same charge (i.e. cation for another cation, or one anion for another anion), or by paired migration of charge-balanced cation-anion pairs [11]. As seen in Table above, the structure of biotite ( $\text{H}_{2.95}\text{Al}_{3.32}\text{Ba}_{0.23}\text{Fe}_{2.01}\text{K}_{1.77}\text{Mg}_{3.16}\text{O}_{24}\text{Si}_{5.17}\text{Ti}_{0.34}$ ) contains Fe. Many heavy metals can substitute iron in crystallographic structure due to charge balance must be maintained. It described calcite and dolomite have amorphous crystallographic structure. The precipitation or neof ormation minerals, heavy metals could be adsorbed in pore and then decrease heavy metals mobilities. In the precipitation of cement hydration products, heavy metal ions may be adsorbed on their surfaces and then enter the lattice to form a solid solution, altering their structures (crystallinity, particle size) and solubility [17]. As detected by XRD, grossular  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  a cement remained in geopolymers suggests incongruous of andratite ( $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{Si}_3$ ) a calcium silicate in mine tailings. There is a possible calcium silicate hydrate and portlandite in geopolymers. These calcium silicate hydrate and portlandite surfaces contain many sites of heavy metal deposits. [16] confirmed that C-S-H gel has a strong capacity of binding metals. Some heavy metals, for example,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , form hydroxides and deposit on calcium silicate minerals [18]. Chromium can be chemically incorporated into all of the cement hydration products, primarily substituting for both calcium and silicon in C-S-H.  $\text{Cr}^{3+}$  could be also bound into the silica matrix itself as  $\text{Cr}(\text{OH})_3 \cdot x\text{SiO}_2$  [11]. However, it is explained, when calcium silicate phases  $\text{C}_3\text{S}$  is in contact with water, a membrane of C-S-H gel and portlandite ( $\text{CH}$ ,  $\text{Ca}(\text{OH})_2$ ) are formed and deposited on the surface of  $\text{C}_3\text{S}$  grains as proposed by [11]. The carbonation of  $\text{C}_3\text{S}$  results in an increasing capacity of retaining heavy metal cations and heavy metal hydroxyl ions, because of the large surface area and meta-stability of decalcified C-S-H gel and calcium carbonate [10]. These metals may, therefore, substitute for  $\text{Ca}^{2+}$  at the C-S-H surface. Almost all calcium in natural crystalline phases of calcium silicate hydrate can be replaced with heavy metals. Like the structure of glass, heavy metals may act as network modifiers or network intermediates [9]. Calcium silicate hydrate gel, portlandite, dolomite and calcite are cement minerals. The nucleation and growth of calcium silicate hydrate gel, portlandite, calcite and dolomite fill up the spaces and cavities between the grains.

Various studies [31, 33] have found that calcium has a positive effect on geopolymeric binders. the presence of CaO in mine tailings and the addition of sodium carbonate  $\text{Na}_2\text{CO}_3$  play an important role in heavy metals precipitation. When the CaO content is high, CaO reacts with OH<sup>-</sup> in the alkaline aqueous system to form calcium silicate hydrate gel C-S-H and portlandite ( $\text{CH}$ ,  $\text{Ca}(\text{OH})_2$ ) which then reacts with  $\text{CO}_2$  in the atmosphere forming calcite ( $\text{CaCO}_3$ ) [19] and dolomite ( $\text{CaMgCO}_3$ ) by eliminating water on the geopolymer surfaces. The microstructural porosity decreases, resulting in the formation of amorphous Ca-Al-Si gel which strengthens the final product. It is opined that the presence of many carbonate minerals at low temperature are responsible for heavy metals immobilization [32].

**Table 1a:** Chemical composition of gold mine tailing and fly ash in (%) of oxides.

Oxides (%)	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{TiO}_2$	$\text{V}_2\text{O}_5$	$\text{Cr}_2\text{O}_3$	$\text{MnO}$
Mine tailing	12.8	63.9	0.40	0.030	0.12	5.88	0.05	0.037	0.30
Fly ash	32.3	62.4		0.898	0.766	1.29	0.034	0.021	

**Table 1b:** Chemical composition of gold mine tailing and fly ash in (%) of oxides.

Oxides (%)	Fe <sub>2</sub> O <sub>3</sub>	CuO	ZnO	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	RuO <sub>2</sub>	Eu <sub>2</sub> O <sub>3</sub>	Re <sub>2</sub> O <sub>7</sub>	PdO
Mine Tailing	14.7	0.050	0.14	0.050	0.32	0.93	0.32	0.03	
Fly Ash	2.057	0.0209			0.015	0.253	0.045		0.073

**Table 2a:** Chemical composition of mine tailing in (mg/kg).

Metals	Fe	Ti	Al	Ga	Mn	Zr	Ca	Mg	Zn
Mine tailings	16620	14370	5713	1554	1071.51	617.4	474.2	246.5	124.17
	<b>Y</b>	<b>Ba</b>	<b>Co</b>	<b>As</b>	<b>V</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Ta</b>
	50.1	37.7	31.6	24.8	21.3	139	22.12	16.54	6.1
	<b>Sr</b>	<b>Ag</b>	<b>Cd</b>	<b>Mo</b>	<b>Pb</b>	<b>Hg</b>	<b>Au</b>	<b>Ru</b>	
	4.9	4.7	2.4	1.8	57.7	1.3	15.8	166	

**Table 2b:** Chemical composition of fly ash in (mg/kg)

Metal	Fe	Mn	Cd	Zn	Cr	Pb	Ni	Cu	Co
Fly ashes	7671.5	183.1	16.3	88.7	392.8	199.8	55.8	81.8	39.0

**Table 3:** Classification of NTPC fly ash as Class F.

Component	SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> (%)	SO <sub>3</sub> (%)	Na <sub>2</sub> O(%)	LOI (%)
ASTM C618	≥70.0	≤5.0	≤1.5	≤6.0
NTPC Fly ash	90.75	0.22	0.06	1.17

**Table 4:** Components of geopolymers mixtures.

Typology	Denomination	Acronym
Binder	Fly ashes	FA
Chemical activators	Sodium silicate	Na <sub>2</sub> SiO <sub>3</sub>
	Sodium hydroxide	NaOH
	Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>

**Table 5a:** Formulation of geopolymers

	%Fly ashes	NaOH(M)	V/V=1 aOH/Na <sub>2</sub> SiO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> =0.25 g	T°C
1	0	5	1	0.25	25
2	25	5	1	0.25	25
3	50	5	1	0.25	25
4	75	5	1	0.25	25
5	0	5	1	0.25	80
6	25	5	1	0.25	80
7	50	5	1	0.25	80
8	75	5	1	0.25	80

**Table 5b:** Formulation of geopolymers

	%Fly ashes	NaOH(M)	V/V =1 NaOH/Na <sub>2</sub> SiO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> =0.25 g	T°C
9	0	10	1	0.25	80
10	25	10	1	0.25	80
11	50	10	1	0.25	80
12	75	10	1	0.25	80
13	0	15	1	0.25	80
14	25	15	1	0.25	80
15	50	15	1	0.25	80
16	75	15	1	0.25	80

**Table 6:** Legal limits (G.U.R.I, 2006). Limit I: maximum permissible limits in groundwater (G.U.R.I, 2006); Limit II: emission limit values in surface water (G.U.R.I, 2006) in (mg/l).

	pH	Fe	Mn	Cd	Zn	Cr	Pb	Ni	Cu	Co
Limit I		-	-	0.005	3	-	0.01	0.02	1	-
Limit II		2	-	0.02	0.5	-	0.2	2	0.1	-

**Table 7:** Stabilization of Cd using NaOH (5, 10 and 15M) +Na<sub>2</sub>SiO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> from atmospheric temperature to 80°C.

	%FA	NaOH (M)	T°C	pH	% Cd Stabilization		% FA	NaOH(M)	T°C	pH	% Cd Stabilization
1	0	5	25	10.49	99.45	9	0	10	80	10.09	99.48
2	25	5	25	10.61		10	25	10	80	10.09	
3	50	5	25	10.62		11	50	10	80	10.00	
4	75	5	25	10.62		12	75	10	80	9.97	
5	0	5	80	10.58	100	13	0	15	80	10.65	97.78
6	25	5	80	9.61		14	25	15	80	10.49	
7	50	5	80	9.12		15	50	15	80	10.08	
8	75	5	80	8.87		16	75	15	80	9.95	

**Table 8:** Stabilization of Pb using NAOH (5, 10 and 15M) +Na<sub>2</sub>SiO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> from atmospheric temperature to 80°C.

	% FA	NaOH (M)	T°C	pH	%Pb Stabilization		% FA	NaOH(M)	T°C	pH	% Pb Stabilization
1	0	5	25	10.49	79.68	9	0	10	80	10.09	97.24
2	25	5	25	10.61		10	25	10	80	10.09	
3	50	5	25	10.62		11	50	10	80	10.00	
4	75	5	25	10.62		12	75	10	80	9.97	
5	0	5	80	10.58	96.40	13	0	15	80	10.65	96.45
6	25	5	80	9.61		14	25	15	80	10.49	
7	50	5	80	9.12		15	50	15	80	10.08	
8	75	5	80	8.87		16	75	15	80	9.95	

**Table 9:** Stabilization of Cr using NAOH (5, 10 and 15M) +Na<sub>2</sub>SiO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> from atmospheric temperature to 80°C.

	% FA	NaOH(M)	T°C	pH	%Cr Stabilization		% FA	NaOH(M)	T°C	pH	% Cr Stabilization
1	0	5	25	10.49	86.64	9	0	10	80	10.09	99.08
2	25	5	25	10.61		10	25	10	80	10.09	
3	50	5	25	10.62		11	50	10	80	10.00	
4	75	5	25	10.62		12	75	10	80	9.97	
5	0	5	80	10.58	92.32	13	0	15	80	10.65	99.00
6	25	5	80	9.61		14	25	15	80	10.49	
7	50	5	80	9.12		15	50	15	80	10.08	
8	75	5	80	8.87		16	75	15	80	9.95	

**Table 10:** Stabilization using NaOH (10 M) +Na<sub>2</sub>SiO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> at 80°C compared to legal limits (G.U.R.I, 2006).

	%flyash	Cd	Pb	Cr
Geopolymer	25	0.0003	0.0374	0.0228
Limit II		0.005	0.01	
Ratio Limit II/geopolymer lixiviat		67.00	5.00	

**Table 11:** Elementary chemical composition of the mine tailings (a) compared to the geopolymers prepared at 10 M NaOH (b) under the Field emission microscope equipped with EDS.

a) Mine tailings		b) Geopolymers	
Spectrum 1, 2, 3....4	% average	Spectrum 1, 2, 3....16	% average
O	24.24	C	9.80
Al	4.06	O	31.84
Si	54.42	Na	33.13
K	1.73	Al	0.18
Mg	0.67	Si	0.38
V	0.50	Ca	0.94
Cr	9.48	Cr	15.80
Ni	0.63	Ni	4.74
Cu	0.77	Cu	5.09
Zn	0.82	Zn	3.35
Pb	0.63	Pb	1.11
Co	1.26	Co	2.40
Cd	0.20	Cd	0.83

**Table 12:** Comparison between mineralogical compositions of mine tailings with geopolymer materials prepared at 10 M NaOH.

Minerals	Mine tailings	geopolymers
Quartz (SiO <sub>2</sub> )	✓	✓
feldspar Al <sub>1</sub> Na <sub>1</sub> O <sub>8</sub> Si <sub>3</sub>	✓	
staurolite (H <sub>3</sub> Al <sub>17.89</sub> Fe <sub>3.39</sub> Li <sub>0.112</sub> Mg <sub>0.766</sub> O <sub>48</sub> Si <sub>7.576</sub> Zn <sub>0.092</sub> )	✓	
Ilmenite (FeO <sub>3</sub> Ti)	✓	
Sillimanite (Al <sub>2</sub> O <sub>5</sub> Si)	✓	✓
kyanite, Al <sub>2</sub> O <sub>5</sub> Si	✓	
kaolinite (H <sub>8</sub> Al <sub>4</sub> O <sub>18</sub> Si <sub>4</sub> )	✓	
Cassiterite SnO <sub>2</sub>		✓
rutile (TiO <sub>2</sub> )	✓	
biotite (H <sub>2.95</sub> Al <sub>3.32</sub> Ba <sub>0.23</sub> Fe <sub>2.01</sub> K <sub>1.77</sub> Mg <sub>3.16</sub> O <sub>24</sub> Si <sub>5.17</sub> Ti <sub>0.34</sub> )		✓
Calcite CaCO <sub>3</sub>		✓
Dolomite CaMgCO <sub>3</sub>		✓
Karooite (MgO <sub>5</sub> Ti <sub>2</sub> )		✓
Grossular Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	✓	✓
Brucite Mg(OH) <sub>2</sub>		✓

**Table 13:** Chemical bonds of minerals of the mine tailings compared to the geopolymers stabilized at (10 M) NaOH analyzed by FTIR

Residual chemical bonds of minerals of the mine tailings		
λ (cm <sup>-1</sup> )	Characteristic bonds	References
462	Plane blending of Si-O	Guo <i>et al.</i> , 2014
793	Asymmetric stretching of Si-O-Si	Waijareanet <i>et al.</i> , 2014
800-1200	Si-O Stretching vibrations of SiO <sub>4</sub>	Mingyuet <i>et al.</i> , 2009
1036	T-O-Si (T= Si ou Al)	Waijareanet <i>et al.</i> , 2014
1102	Vibrations d'extension Si-O	Ahmariet <i>et al.</i> , 2012
New chemical bonds of minerals of the geopolymers		
870, 740	Vibrations of Na <sub>2</sub> CO <sub>3</sub>	Villa <i>et al.</i> , 2010
2350	Vibrations of C-O en CO <sub>2</sub>	Ahmariet <i>et al.</i> , 2012
2920	Vibrations of C-O en CO <sub>2</sub> constrained in amorphe phase	Sakulich, 2009
3680, 3436 and 1636	Grouping OH	MacKenzie <i>et al.</i> , 2007

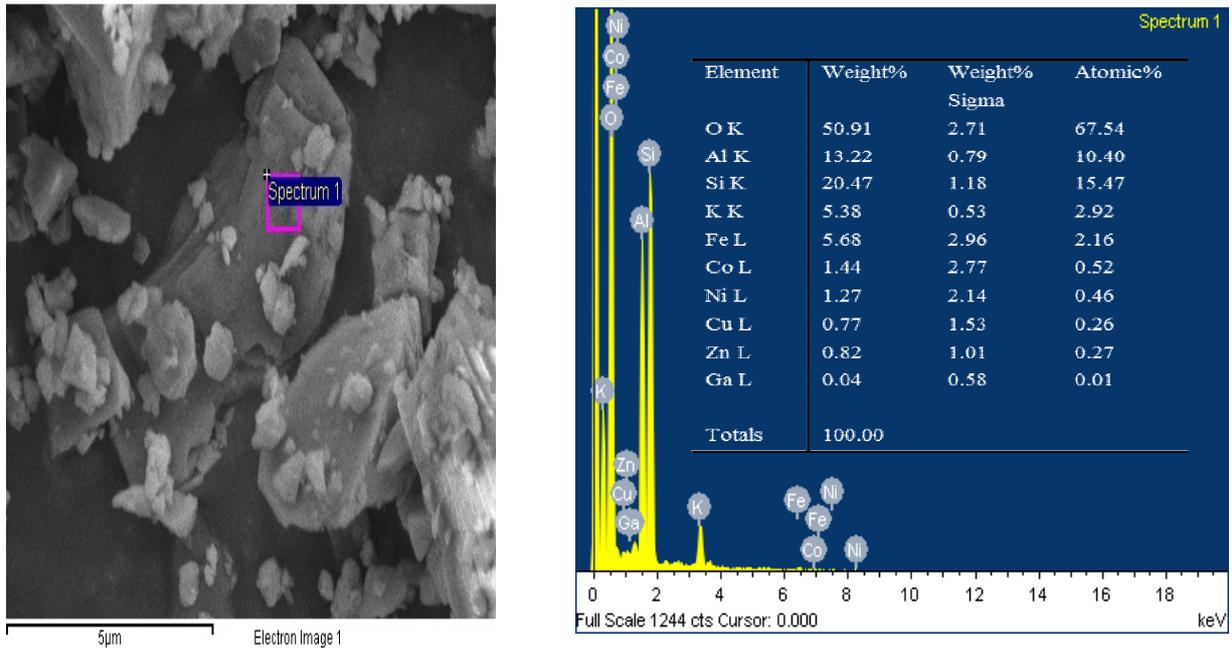


Figure 1:FE-SEM pictures and elemental composition of gold mine tailings.

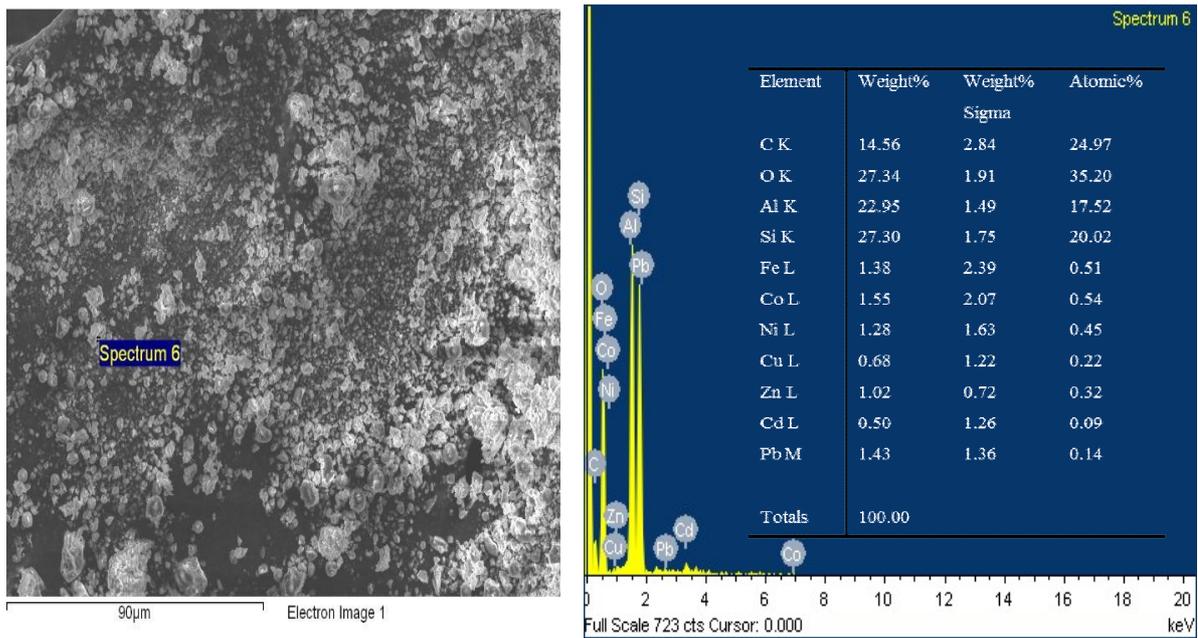
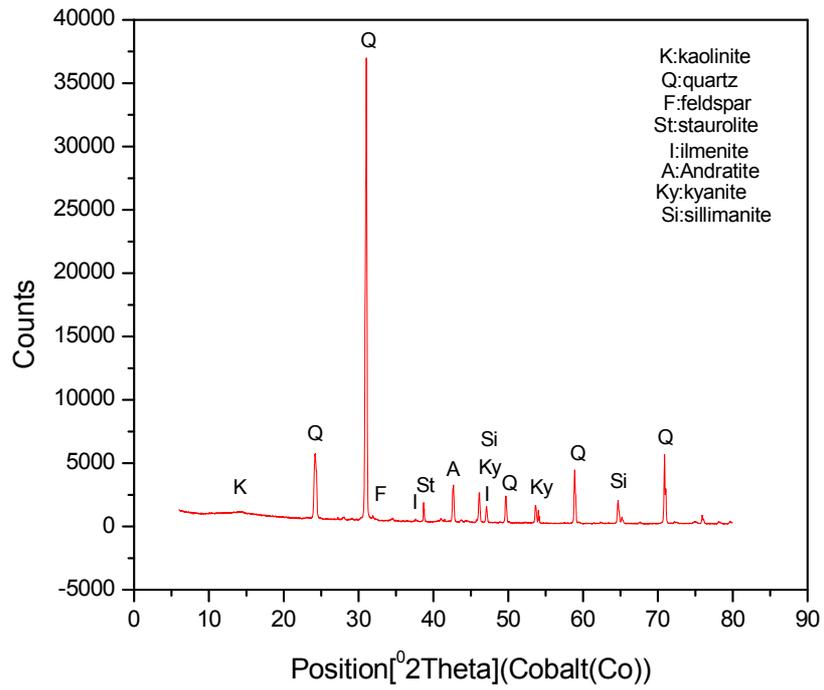
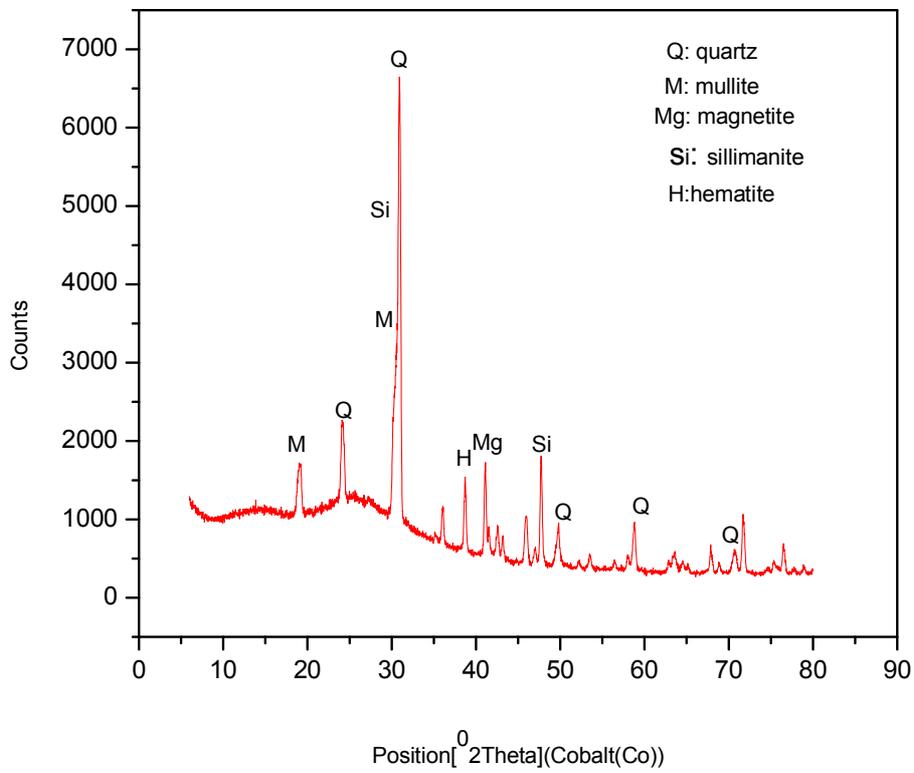


Figure 2:FE-SEM pictures and elemental composition of fly ashes



**Figure 3:** X-ray powder diffraction pattern of gold mine tailings.



**Figure 4:** X-ray powder diffraction pattern of fly ash.

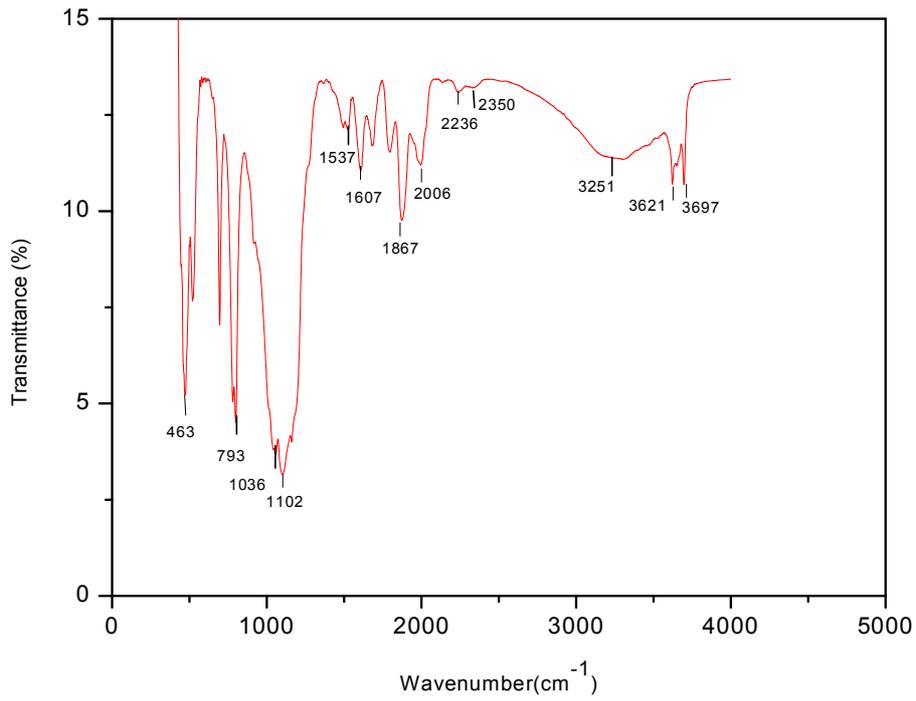


Figure 5:F-TIR spectra of mine tailings.

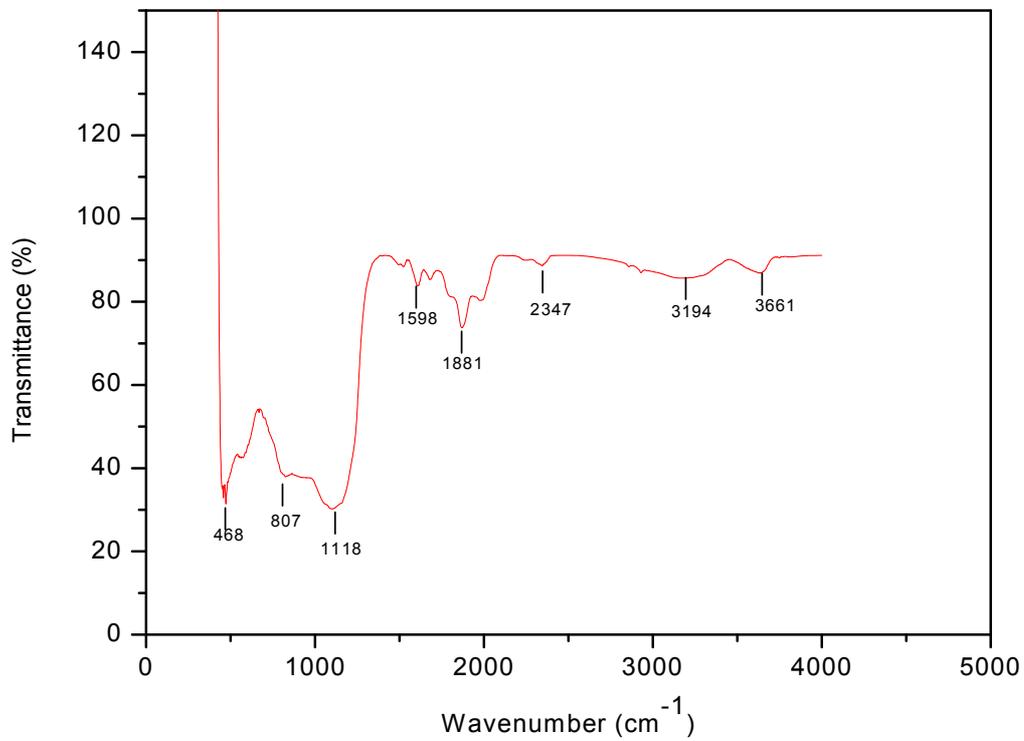
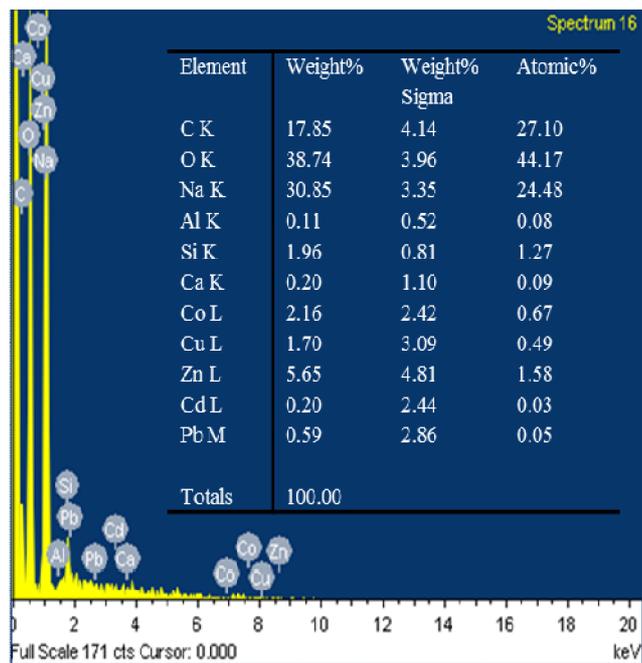
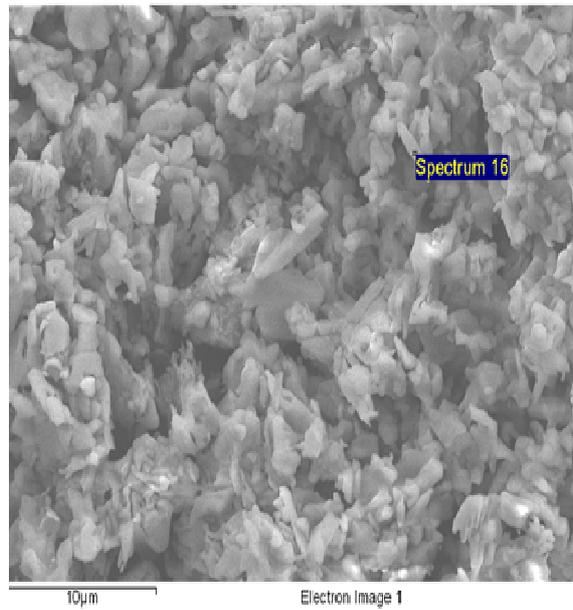
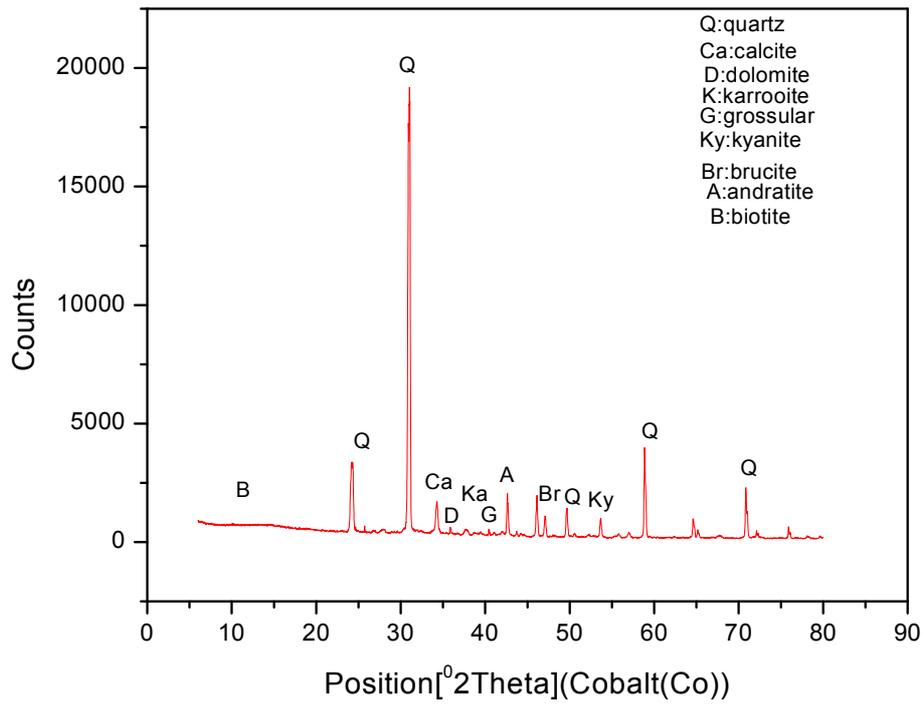


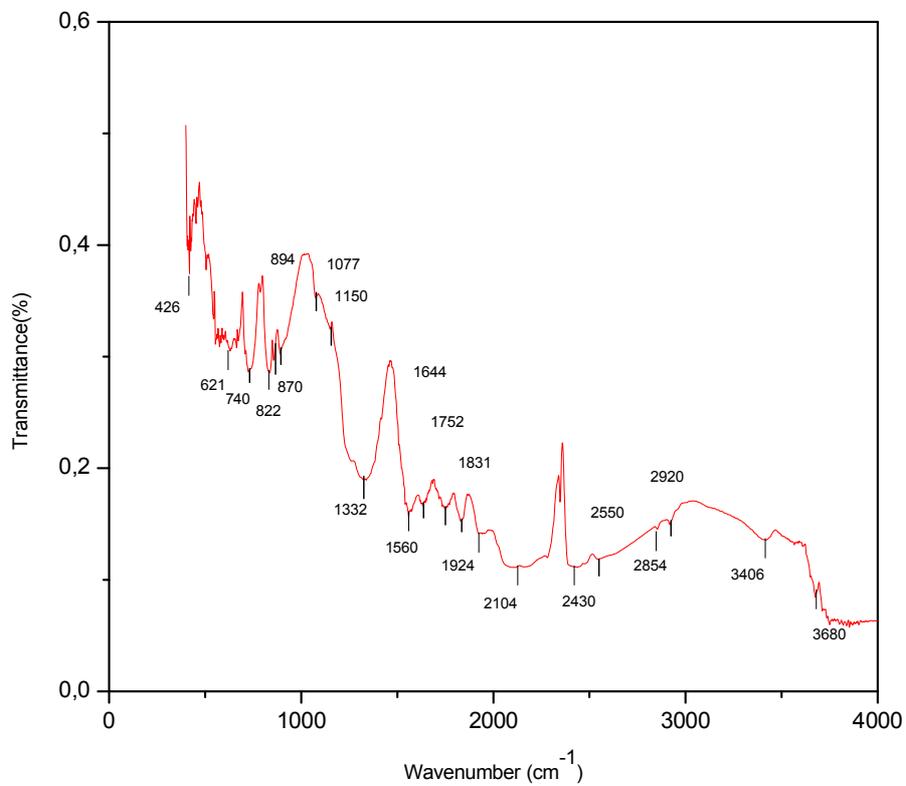
Figure 6:F-TIR spectra of fly ash.



**Figure 7:**FESEM photograph of the best geopolymers stabilized at 10 M NaOH compared to mine tailing.



**Figure 8:** X-ray powder diffraction pattern of geopolymer



**Figure 9:** F-TIR spectra of geopolymer materials.

## CONCLUSIONS

Heavy metals were successfully stabilized in low temperature minerals based geopolymers when both samples contain high metal concentrations. Depending on the FESEM studies, heavy metals play a role of balancing charge of tetrahedral Al in unreacted minerals and geopolymer frameworks. The more heavy metals immobilized in the geopolymer is due to the adsorption, substitution, diffusion of calcium hydroxide to form calcium silicate hydrate gel, portlandite, dolomite and calcite as cement in pores where heavy metals could be sorbed in the networks then decreases their mobility. The formation of metal oxides, hydroxides, carbonates and silicates are probable mechanisms for immobilization of metals based geopolymers. Chemical activators enhance heavy metals immobilization by helping mineral growth and balancing charges. The immobilization process developed in the present article has an advantage in heavy metals speciation in geopolymer. However, geopolymers could be left on soil surfaces eco-friendly. For future research is needed for thermodynamic of solid phases in geopolymers.

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