

# Molecular Characteristics of Cement-Lime Treated contaminated- Lateritic Clay Soil

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**Abstract.** The existence of contaminated land due to industrial and mining activities is an important apprehension in today's highly industrialized nations. However, the effect of these contaminants on the geotechnical properties of clayey soils can be modified by the chemical stabilization using traditional stabilizers like cement and lime, which result in achieving suitable material for construction purposes. Molecular characteristics of cement and lime stabilized contaminated- Lateritic clay soil presented in this research. This objective was applied by studying the induced alterations in molecular structure of cement-lime, and heavy metals stabilized lateritic soil using Fourier Transform Infrared (FTIR) spectroscopy. In current study, FTIR was performed to investigate the molecular amendments in the structure of treated samples before and after contamination. Based on the results, the major vibrational bands were attributed to the kaolinite minerals. Furthermore, other bands appeared due to the presence of quartz and hematite. A new band was detected at  $1462\text{cm}^{-1}$  with low intensity assigned to the carbonates, which was noticed increasing with time due to the producing of calcite. Also, it was detected a new sharp band at  $1384\text{cm}^{-1}$  related to zinc and copper nitrates due the presence of heavy metals.

**Key words:** Laterite, tropical soil, Portland cement, Hydrated lime ,physicochemical behavior, soil characterization, Contaminated soils.

## 1. Introduction

Raising public awareness regarding the harmful effects of environmental contamination (land, water and air) has grown considerably over the last two decades partly because of the active participation of environmental groups, due to the growth of industrial activities that produce materials and chemicals, in which they comprise large amounts of heavy metal-bearing wastes. Thus, the disposal of chemical contamination has become one of the major problems currently faced by developing countries. In cases of landfill design, to avoid heavy metals such as copper, zinc, lead and nickel contained in hazardous wastes from passing into the adjacent environment, the initial step is landfill location and design for containments should be removed as far as possible from groundwater tables and withdrawal wells [1]. The second step is to modify or stabilize the clay liners which increase the soil's capacity to adsorb and immobilize heavy metals. Hence, various techniques, in situ and ex situ, have been used which



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aimed to reduce the impact of these metals on the soil. Stabilization /solidification, as an alternative and convenient technique that is less environmentally hazardous, has been applied. Furthermore, the waste itself may also be stabilized with suitable chemicals like cement or lime in order to improve physical characteristics of the soil that subsequently increase its durability and strength and also reduce its compressibility [2]. Therefore, understanding and analysing physical characteristics, chemical properties, mineralogical and microstructure identification, as well molecular behaviour as studies of both soil and waste, were the main interest of recent studies.

However, to realize the potential effectiveness for the modification of specific engineering properties of the site's tropical soil, it is fundamental to study time-dependent of molecular and mechanical interconnection with soil- stabilizers as a function of heavy metals.

This study aims to identify and assess the various chemical reactions involved in the process of stabilizing contaminated tropical soils. To achieve this goal, it should examine the molecular structure in expression of functional groups and local bonding to assess the extent of penetration of stabilizers and the crystalline structure of heavy metals in the clay and its intermediate layers [1].

However, to study the molecular characteristics of contaminated lateritic clay soil, infrared spectroscopy technique is applied. This technique has effective history as integral method of X-ray diffraction (XRD) and other clay exploration methods as stated by [3]. For minerals characterization, an IR spectrum can be as an imprint. Furthermore, it can provide distinctive details about the structure of minerals, such as; sample specific to any family of minerals should it belongs the grade of uniformity in the structure, the nature of the isomorphous substituents, the uniqueness of the constitutional hydroxylated molecular water and the existence of both crystalline and non-crystalline impurities as stated by [4].

## **2. Transform infrared (FTIR) spectroscopy technique**

The infrared (IR) spectroscopy is a standard performance for spectrometry of data using respectable quality infrared absorption (i.e., in the range 400-4000  $\text{cm}^{-1}$ ) [5]. Investigation of the mid-IR absorption spectra and a description of the structural models of the minerals represent a foundation for considerate almost of essential elements of clay minerals. O-H stretching modes, which are located in the spectral region of 3400 to 3750 $\text{cm}^{-1}$  consider a common to most phyllosilicates. The metal-OH bending modes lie in the 600 - 950  $\text{cm}^{-1}$  region. Si-O and Al-O stretching modes are detected in the 700 - 1200  $\text{cm}^{-1}$  range. The Si-O and Al-O bending modes dictate the 150 to 600  $\text{cm}^{-1}$  region [5]. In this study, to realize the essential techniques which participated to the enhancement of lateritic soils stabilized with cement and lime, we studied the changes related to the temporal structure of the molecular structure of the treated soils

## **3. Experimental program and materials**

### *3.1. Materials*

The deposits of natural laterite clay soil was used which typically, has clay minerals constituents. In addition, they may also comprise specific kind of contaminations like salts and organic matters. In this study, contaminants were added to the deposits. As a result, to diminish intervention of these materials and the reactions of soil-stabilizer, and the additives unpolluted soil specimens were necessary. Table1 shows chemical and physical characteristics of the natural soil. It should be mentioned as seen in figure 1, the reddish brown colour for the Laterite clay soil is a result to the presence high quantities of free iron oxides within the soil compositions as stated by Mitchell and Soga, [6]. Furthermore, the topical laterite clay can be characterized by the following properties

- a) This type of soil is a little acidic in nature.
- b) The rate of specific surface area is high.
- d) Kaolinite is the prevailing clay mineral.

e) Quantities oxides of aluminium and silicon are almost comparable in this soil.



**Figure 1.** The image of natural laterite clay soil from its excavated site

**Table 1.** Physical properties and chemical compositions for laterite clay soil.

Engineering and Physical Properties (Laterite)	Values	Chemical Compositions Oxides	Values (%)
CEC (meq/100g)	22.7	SiO <sub>2</sub>	21.55
pH (L/S = 2.5)	4.86	Al <sub>2</sub> O <sub>3</sub>	24.31
Specific Gravity	2.75	Fe <sub>2</sub> O <sub>3</sub>	29.4
Liquid Limit, L.L(%)	72.8	Na <sub>2</sub> O <sub>3</sub>	0.07
Plastic Limit, PL (%)	35.6	K <sub>2</sub> O	0.11
Plasticity Index, PI	37.2	P <sub>2</sub> O <sub>5</sub>	16.71
(%) BS Classification	MH	SO <sub>3</sub>	3.98
ICL (%)2.00 Soluble	5	CO <sub>2</sub>	3.65
Maximum dry density (Mg/m <sup>3</sup> )	1.33		
Optimum moisture content (%)	34		
Unconfined compressive strength (kpa)	288		
Cc	0.24		

Note: ICL: Initial Consumption of Lime, Cc: Compression Index

A hydrated lime was used in this study. It works well with clayey soils, especially those with moderate to high plasticity index ( $PI > 15$ ). In addition, the Ordinary Portland Cement (OPC) was used as the second stabilizers in this work. The reagents added to simulate inorganic metal contamination were copper nitrate trihydrate ( $Cu(NO_3)_2 \times 3 H_2O$ , to provide the copper (II) ions ( $Cu^{+2}$ ), and zinc nitrate tetrahydrated ( $Zn(NO_3)_2 \times 4 H_2O$ , to provide zinc (II) ions ( $Zn^{+2}$ ). Both of them were from Merck KGaA-Germany. The two reagents were chosen due to their prevalence at many contaminated sites.

### 3.2. Samples preparation

The studies that applied previously on the laterite type of soils have been shown that the oven drying can noticeably alter the characteristics of soil plasticity and compaction as examined by Goswami and Mahanta in 2007 [7]. So, soil samples are equipped by cracked their particles into smaller sizes and then sieved through a 2mm sieve to confirm that the soil was of uniform grade. All that happens after

drying these samples through air-dried. Proportions of lime and cement mix were percentages by weight (0%, 5% and 10%) of dry soil. In accordance with BS 1377: Part 4: 1990 (section 3.3.4.1) [8], five sets of standard Proctor compaction tests are reported to determine the optimum moisture content of a number of lime and cement mixtures. It should be mentioned that the artificial soil samples contaminated with heavy metals were equipped by mixing zinc nitrate and copper nitrate as pollutant sources in natural laterite clay.

After the mixing process, the soils were compacted in 38 mm × 76 mm cylindrical moulds. The preparation process was concluded by making sure that the designed optimum water content and maximum dry density according to clause 4.1.5 of BS 1924: Part 2: 1990b were achieved. After that, the specimen was cured for two hours, removed from the mould, put in a thin-walled PVC tube, wrapped with thin plastic cover, and sealed with rubber tight lids. The samples were then stored to cure in a temperature controlled room ( $27 \pm 2$ oC) until experiments were done after 7, 14, 28, 100, and 200 days.

### 3.3 Program of testing

In this research, FTIR was conducted to examine the molecular alterations in the structure of treated samples before and after contamination. 2 mg of dried soil was mixed with 200 mg of potassium bromide (KBr) to create a homogeneous powder, which was then compressed into a solid pellet. The diaphanous KBr disk (pellet) was then inserted into a sample holder in which it was scanned using a Perkin Elmer Spectrum 2000 appliance to provide a beam pattern transmitted through the 400–4000  $\text{cm}^{-1}$  sample (figure 2).



**Figure 2.** Perkin elmer spectrum 2000 instrument (FTIR)-UTM-FS-Skudi-Johor-Malaysia

## 4. Results and Discussions

Typical FTIR spectra of naturally untreated Laterite clay soil at (400–4000  $\text{cm}^{-1}$ ) in the central infrared area is elucidated in figure 3 with major vibration bands tabulated in Table 2. It should be noted that the peak, 3695  $\text{cm}^{-1}$ , is representative of a kaolinite mineral, while 3620  $\text{cm}^{-1}$  is normally extant in many different phyllosilicate minerals [10]. It was suggested that 913  $\text{cm}^{-1}$  represented the existence of hematite [11] and that peak of 796  $\text{cm}^{-1}$  indicated quartz [12]. Other bands (Si–O vibrations) were detected at 697  $\text{cm}^{-1}$ , 538  $\text{cm}^{-1}$  and 470  $\text{cm}^{-1}$  and corroborated occurrence of kaolinite; a small band

appeared at  $1462\text{cm}^{-1}$  related to carbonates; and a peak vibration at  $1744\text{ cm}^{-1}$  was assigned to (C-O) groups.



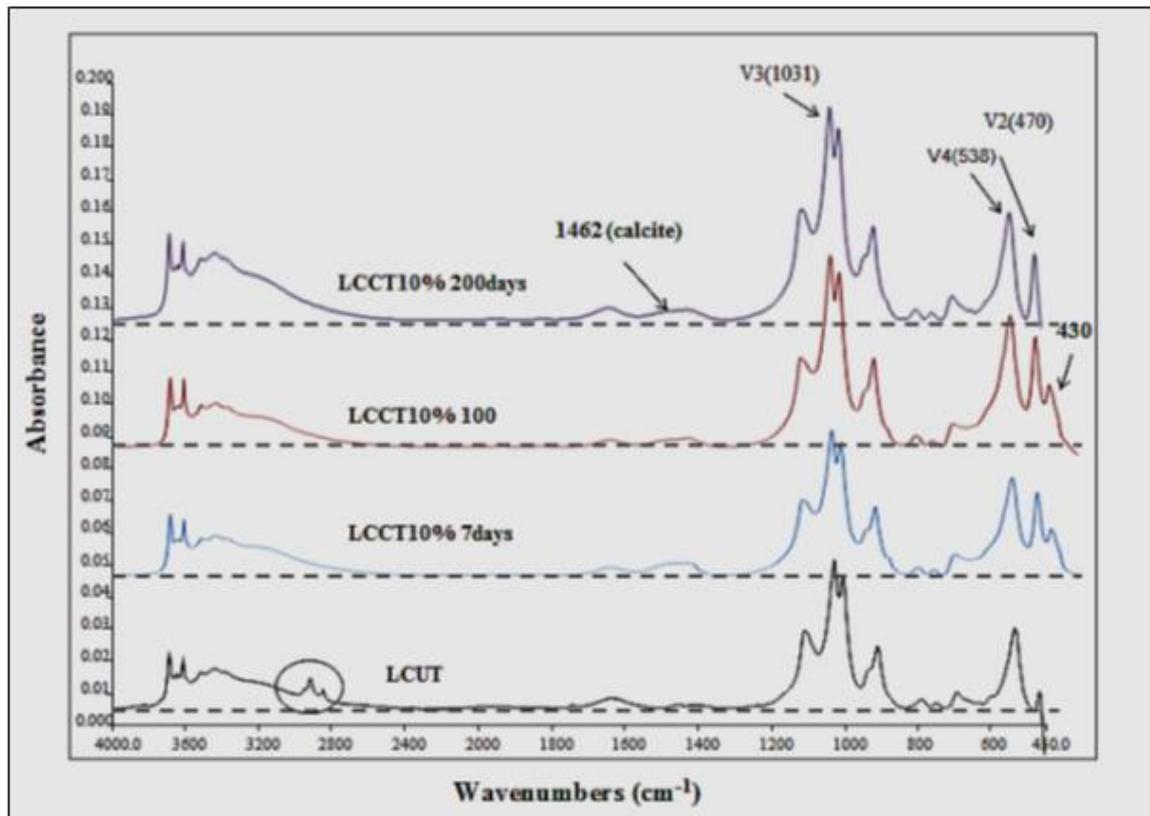
**Figure 3.** FTIR spectra for natural laterite clay soil

**Table 2.** The functional peaks in the FTIR spectra of Laterite clay soil

Vibrational bands $\text{cm}^{-1}$	Functional group
3620 and 3695	OH-stretching vibration of inner and inner hydroxyl group
3438	Symmetric stretching of water
2923 and 2846	Related to C-H groups
1008 and 1031	Corresponded to the perpendicular and in-plane Si-O stretching
1111	Si-O stretching
913	OH-deformation
796	Si-O
679	Si-O
538	Si-O out of plane bonding vibration
470	Si-O in plane bonding vibration
1638	Bonding mode vibration of interlayer water molecules H-O-H

Evaluation by FTIR spectrums for uncontaminated and copper/zinc contaminated cement treated Laterite clay specimens are revealed in figures 4 and 5, correspondingly. FTIR spectra of cured samples at 7, 100, and 200 days, shown in figure 4, demonstrate that handling of cement did not lead to significant modifications related to molecular structure of soil particles. However, when comparing the intensity of V3 at  $1031\text{cm}^{-1}$  it can detect a relative increase over time, indicating the polymerization of orthosilicate Si-O-Si units. This also indicated the progressive formation of pozzolanic compounds (C-S-H) during cement hydration over time. Furthermore, it was observed an increasing ratio of V4 to V2 over curing time, indicating increasing degrees of polymerization. Nevertheless, the increase was slight in concentration of assimilation at  $1462\text{ cm}^{-1}$  due to the creation of calcite after adding cement

to the samples [13]. Furthermore, it has been noted that a slight shift in the Si-O peak at  $1111\text{cm}^{-1}$  towards a higher wavelength. In addition, two peaks disappeared ( $2846$  and  $2924\text{cm}^{-1}$ ) as a result of hydrogen ion consumption during cement hydration [14].



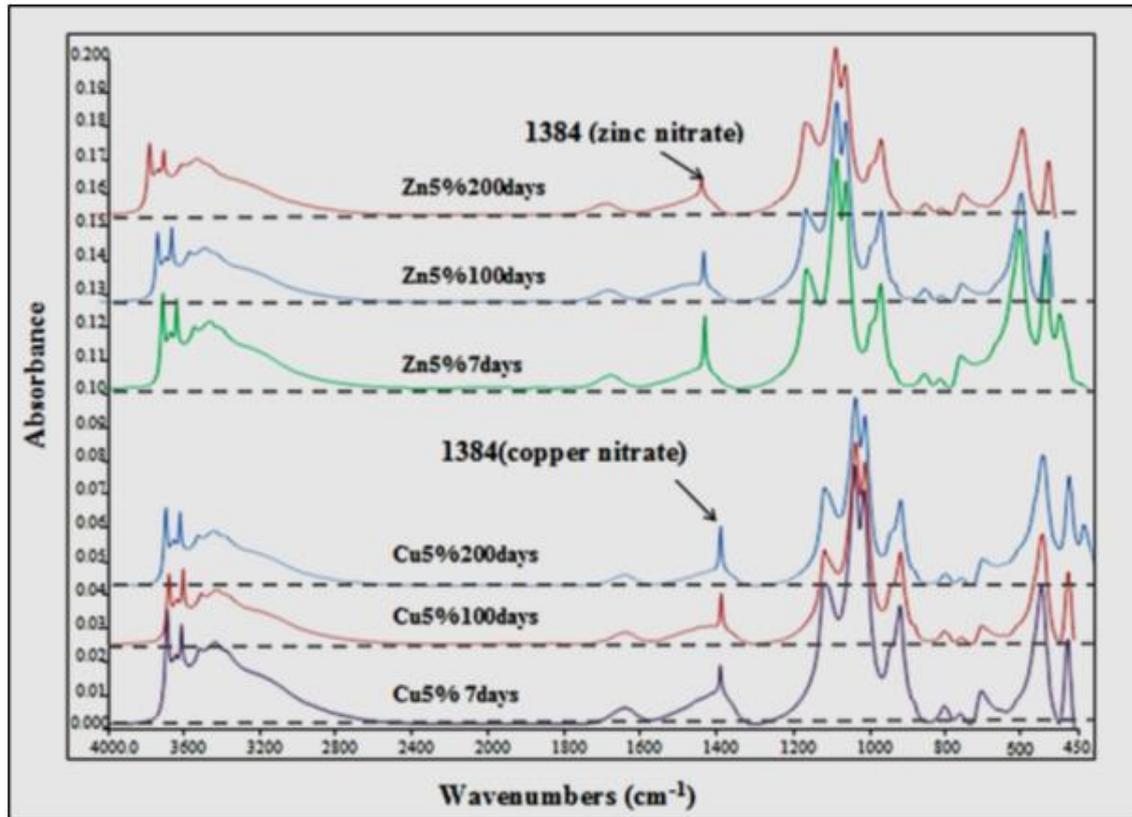
**Figure 4.** FTIR Spectrums of natural and cement treated Laterite clay soil at different time intervals

FTIR spectra for copper and zinc cement treated Laterite clay soil are presented in figure 5. The effect of copper nitrate on the cement soil matrix was noticeably reflected by the decreasing intensity in Si-O bands. This indicated effects from heavy metal nitrates on the molecular structure of treated clay soil. Another significant change was the appearance of a sharp band at  $1384\text{cm}^{-1}$ , attributed to nitrates from copper nitrate. In addition, there was an increase in the band for carbonates formed from copper carbonate [15].

FTIR spectra for zinc contaminated, cement treated Laterite clay were little different from copper, as shown in Figure 5. It was observed a sharp nitrate peak at  $1384\text{cm}^{-1}$ , assigned to zinc nitrate. Also, we noted a decrease in this absorption band over time that may be due to zinc's interference with the production of new compounds by cement and soil interactions as previously indicated by XRD. The presence of copper and zinc nitrate peaks within molecular structures of the soil matrix indicated heavy metal interference of functional groups that otherwise construct the soil [16].

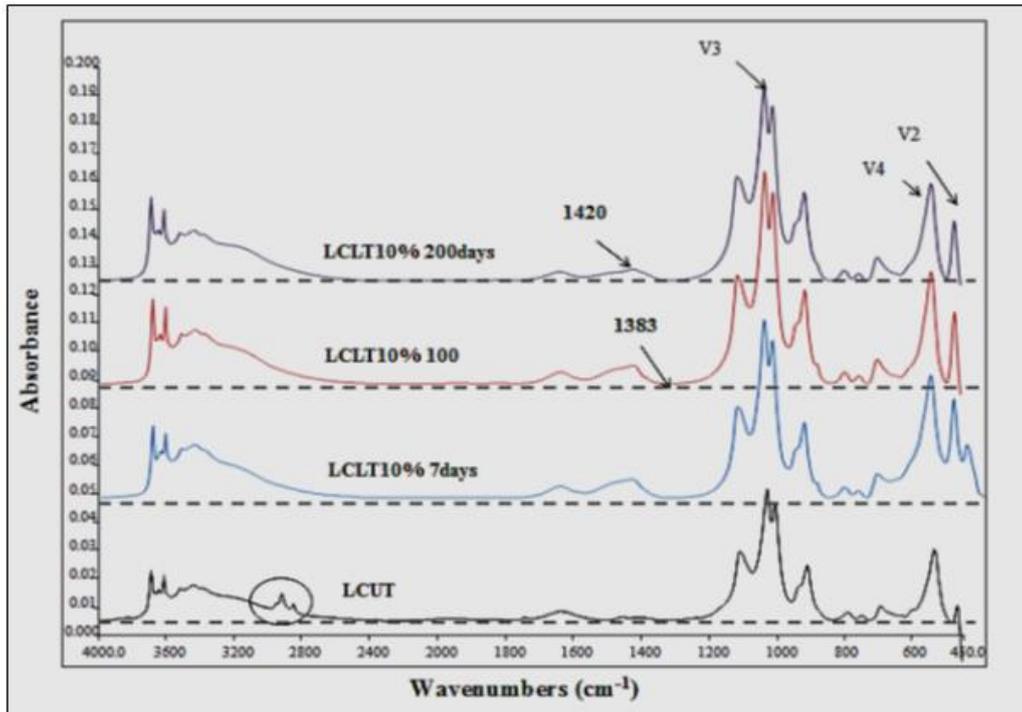
Figure (6) reveals FTIR spectra for lime stabilized laterite clay. As seen from the spectra of cured samples and in comparison to cement treated laterite clay samples (Figure 4), lime treatment also did not produce any significant alterations in the molecular characterization of particles of samples. Nevertheless, an absorption band at  $1420\text{cm}^{-1}$  was ascribed to Ca-OH due to the presence of lime. There was a slight reduction in this band at 200 days due to the consumption of lime over time. The intensity of V3 reveals a significant increase at 7 days compared to the untreated sample, but it then remained constant over time to 100 and 200 days. The ratio of V4 to V2 showed a minor increase over

time. Also, it was noticed disappeared the band at (2846 and 2924  $\text{cm}^{-1}$ ) as a result of hydrogen ion consumption during lime reactions.

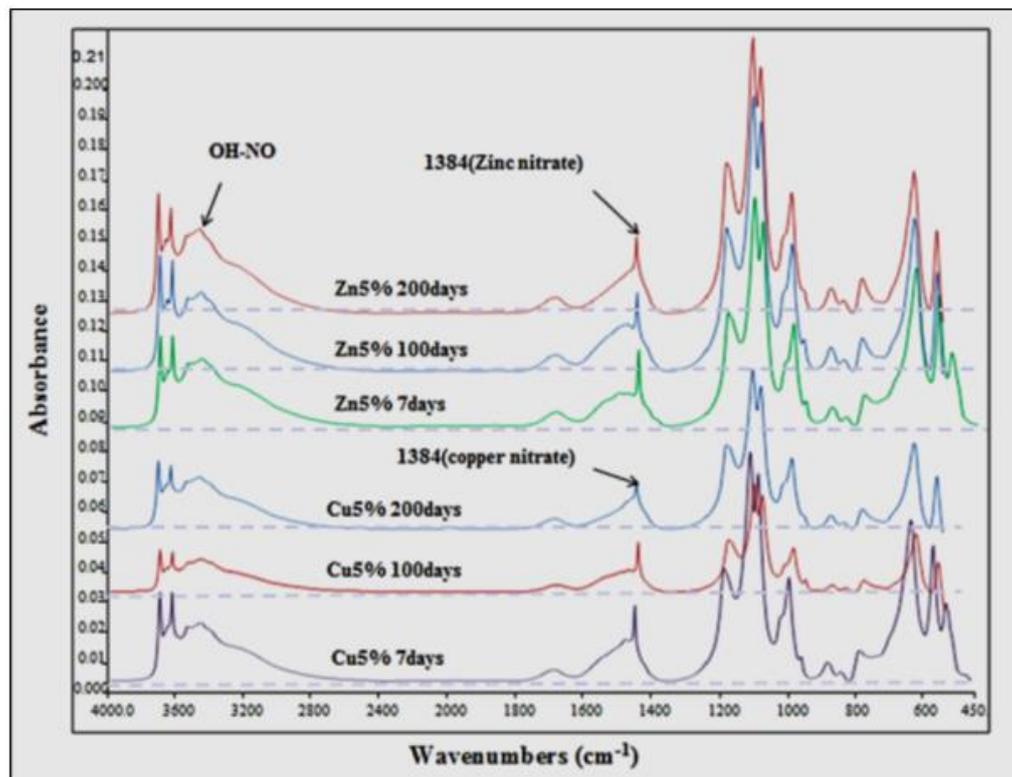


**Figure 5.** FTIR spectrums of copper and zinc doped with cement treated Laterite clay at different time intervals.

FTIR spectra from cured lime treated samples contaminated with copper and zinc are shown in figure 7. Effects from copper nitrate caused major changes in Si-O vibration intensity, especially by 100 days. This effect diminished, however, by 200 days due to progressive dissolution of lime and the pozzolanic cementitious formations that caused increased Si-O polymerization. Reduced intensity of Si-O units was less apparent with zinc contamination. Moreover, a new assimilation band appeared at 3445  $\text{cm}^{-1}$  assigned to OH-NO groups from nitrate additive [17]. Generally however, heavy metals did not appear to cause significant alteration in the efficient sets of soil treated particles.



**Figure 6:** FTIR spectrums of natural and lime treated Laterite clay soil at different time intervals



**Figure 7:** FTIR spectrums of copper and zinc doped with lime treated Laterite clay soil at different time intervals

## 5. Conclusions

The spectrums FTIR of treated samples recommended that the major vibrational bands were attributed to the kaolinite minerals. Also, it was noticed increasing the concentration of Si-O stretching as a result to improving in the grade of polymerization of orthosilicate Si-O-Si units as a result of stabilization process and formation the pozzolanic cementitious. While, a new absorption band was also observed at lime treated soil at 1420 cm<sup>-1</sup> attributed to Ca-OH, which is resulted from increasing the calcium ion after add the lime. Furthermore, a new sharp band was detected at 1384cm<sup>-1</sup> as a result to the presence of heavy metals related to nitrates of both zinc and copper.

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