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# Reaction Products of Lime Zeolite Stabilized Kaolin Humic Acid

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**Abstract.**
Lime, a traditional calcium based stabilizer, had been widely used in chemical stabilization to improve the strength of soil. Past researches had shown that the major reaction product of lime and soil such as Calcium Silicate Hydrate (CSH) was formed abundantly under the observation of microscopic studies. However, sometimes it will be quite difficult to confirm the existence of CSH phase if solely based on its needle like structures, especially when other rod like structures will also exist. Practically, the recognition of the CSH phase by using XRD spectrum through matching with published data had speed up the process of identification. If the method is viable, then theoretically, the molecular weight ratio of silica and calcium, S/C of CSH gel is specific and can be determined based on its possible chemical compound. Hence, this study was carried out in an attempt to examine the possibility use of its S/C ratio as a quick method to confirm the existence of CSH gel. Two types of artificial organic soils were formed by admixing kaolin (inorganic matter) and humic acid (organic matter) with the ratio of 7:3 and 5:5. Four types of admixtures with different percentages ratio of lime and zeolite (a kind of pozzolan) were used to stabilize the soils. The specimens were cured at elevated temperature of 50°c in order to accelerate the development of reaction products. Field Emission Scanning Electron Microscope with attached Energy Dispersive Analyzer (FESEM-EDX) was utilized to observe and determine the existence of reaction products and its bulk chemical composition. The S/C ratio of needle like structures were determined and it is found that the S/C ratio fluctuates and varies significantly from one specimen to another. It is believed that due to the limitations of the experimental setup, the EDX analysis can only serve as semi-quantitative and act as a reference guide on the existence of element. Despite of its limitations, the EDX analysis is useful in distinguish the CSH from other structure which is physically un-identical.

## Introduction

Chemical stabilization of soil by using lime or other types of calcium based stabilizer, such as cement had been widely studied by researchers [1]. It is believed that the reaction products are the main contributor for the enhancement of strength. CSH is found to be the most important reaction products because of its ability to form a continuous layer that binds together the original binder particles into a cohesive whole. In comparison, other hydration products are form as discrete crystals that are intrinsically strong but do not form strong connections to the solid phases that are in contact with and thus cannot contribute much to the overall strength. [2]. Recognize the importance of the CSH gel in the chemical stabilization, it is of great interest to identify the formation of CSH gel as a mark of the good soil-lime stabilization. The formation of CSH gel is a time-dependent process and sometimes it can be continuous for years. Even though it is recognized that the process of polymerization occurs slowly at ambient temperatures, the process can be greatly accelerated by elevated temperature curing and is also encouraged by drying process [3]. Based on the microscopic analysis using Scanning Electron Microscope (SEM), major reaction products namely Calcium Silicate Hydrate and ettringite were found abundantly formed on clay fabrics for cement stabilized soil. Growing and binding of the reaction products with the clay fabrics had resulted in the reduced pore spaces which correspond well with the increased strength and reduced permeability [4]. However, most often high organic content in the soil reduces the effectiveness of lime or cement stabilization [5]. Soils with high organic contents normally experiencing lower strength increment after stabilization, if compared with inorganic soils that stabilized with the same types and same amounts of stabilizer [6].

The possible chemical reaction between silica and lime (calcium hydroxide) in the presence of water can be explained as follow:-

$$2SiO_2 + 3Ca(OH)_2 + H_2O \rightarrow 2Ca_{1.5}SiO_{3.5}\cdot 2H_2O \quad (1)$$

in which:-

2*(28+16*2)= 120gm

3*{40+2*(16+1)}= 222gm

By referring to the equation (1), the molar ratio of SiO2 over Ca(OH)2 (S/C ratio) to form the secondary CSH gel is 0.54054. Researcher [12] suggested that from the theoretical approach and based on its chemical reaction, the molecular weight ratio of SiO2 and Ca(OH)2 (S/C) in CSH gel is specific and can be defined as "Optimum S/C ratio".

## Materials and Methods

The main aim of this study is to establish the use of microscopic technique to identify and recognize the reaction products of soil-lime stabilization. In order to study the effect of organic matter on soil lime stabilization, two types of artificial organic soil with different organic contents were admixed with blended lime-zeolite. Zeolite is a kind of natural pozzolan that originated from areas that volcanic activiy is active. It contains large quantity of reactive or soluble silicon oxide and aluminium oxide which able to react with Ca(OH)2 forming C-S-H gel and aluminates, resulting in the improvement of microstructure of hardened cement concrete and making the concrete more impervious [7, 8].

Artificial organic soils with different organic contents were produced by adding different percentages of inorganic soil (kaolin) with organic matter (humic acid) manually based on its dry weight without taking into consideration on its differences in density. Kaolin clay is chemically known as hydrated aluminum silicate, which is platy in structure, hydrophilic and readily water dispersible. Kaolin grade S300 distributed by Kaolin (M) Sdn. Bhd. is reported to be fine grained with less than 10% residue on No. 100 mesh [9] and well graded with uniformity coefficient of 6.234 and coefficient of curvature as 1.42 [10]. Humic acid utilized in this study was originally imported from China which normally used in agriculture to improve the soil which is rich in alkali-salt. The humic acid is extracted from Leonardite- a naturally occurring, oxidized form of lignite coal, which sometimes described as the salts of humic acids admixed with mineral matter such as gypsum, silica, and clay. Its loss on ignition is reported to be as high as 60% at 440°c and more than 99% of its total carbon is organic carbon [11], which indicated that the humic acid is highly organic. Blended lime-zeolite were produced by replacing certain percentage of lime with zeolite. The coding of the material refers the contents of the respective materials. As an example, 8L2ZT is refer to blended lime-zeolite with 80% of lime content and 20% of zeolite content. Similarly, artificial soil K7HA3 means the soil is consists of 70% kaolin and 30% humic acid.

The specimens are cured in an oven with elevated temperature of 50°c for a period of 7 days, 28 days and 56 days, with the aim to speed up the pozzolanic reaction. Upon the maturity of the curing period desired, the specimen was crushed with an uniaxial compression machine for its strength. However, the strength analysis is excluded when preparing this paper. The specimen after tested for its strength was crushed into small pieces with small hammer and further dried in the oven for 3 days to remove the moisture content. Small portion of the dried specimen was randomly chosen for microscopic analysis using Field Emission Scanning Electron Microscope for its morphology and bulk chemical composition with the attached X-ray Energy Dispersive Analyzer. Each sample was sputtered with gold for 90s at 30mA under high vacuum conditions until they will completely coated to reduce the potential charging due to non-conductivity behaviour of the specimen.

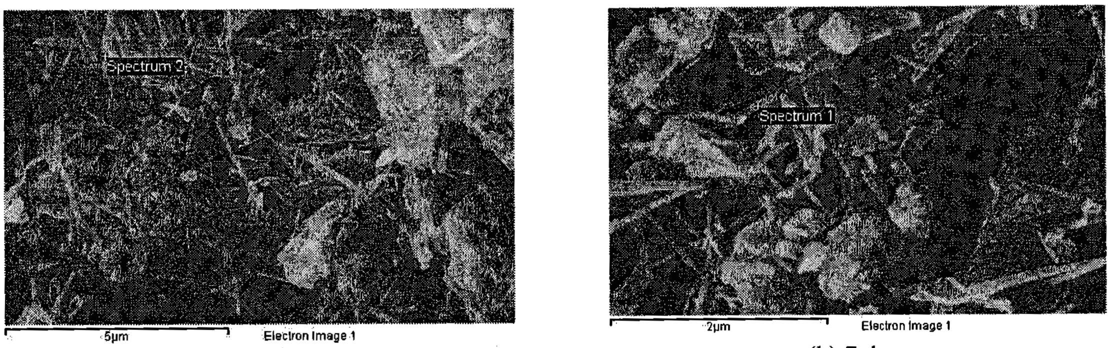
**Results and Discussion**

The SEM micrograph of the stabilized artificial organic soils with various types of additive were shown in Figure 1 to Figure 8, whereas the original structure of unstabilized materials of kaolin and humic acid were shown in Figure 9. As can be seen from the figures illustrated, needle like structures were abundantly found in the specimens with lower organic contents (artificial organic soil K7HA3) comparative to the soil with higher organic contents (artificial organic soil K5HA5). Hence, it is evidently shown that higher organic contents have negative effect on the stabilization by retarding the formation of new reaction products.

In terms of the types of additive, low replacement of lime with zeolite seems to have no significant effect on the formation of new reaction products. The findings is corresponding well with the study on its strength development which also found that by introducing small quantities of zeolite with lime may increase the strength of the stabilized materials and the strength will not be affected by the reduction of the lime content [13]. However, it should be noted that the specimens with no lime added are actually act as control specimen which found that no new reaction product is formed. Hence, it is clearly explained that existence of needle like structure is evident that CSH structure was formed by pozzolanic activity and the process required lime as suggested theoretically in equation 1.

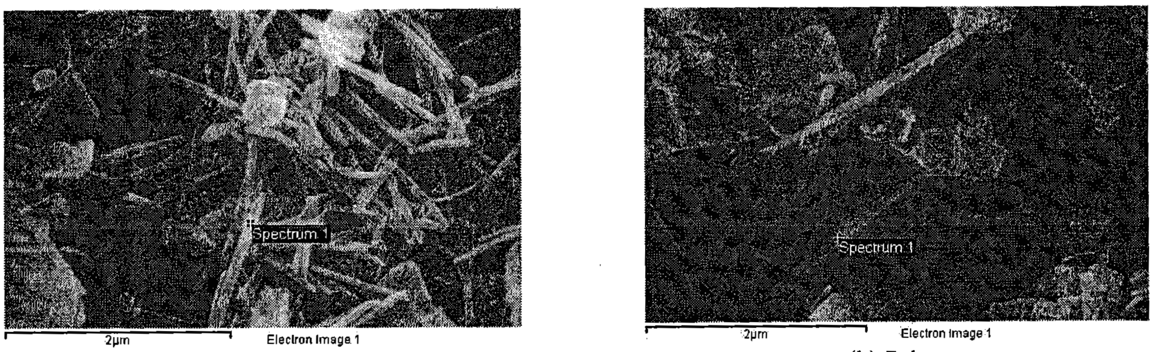
Based on the quantitative analysis of EDX, the ratio of Silicon versus Calcium varies widely from 0.115 to 21.082. The rod like structures noticed in the sample K7HA3-0L10ZT (7 days) and K5HA5-0L0ZT (7 days) which having ratio of Si/Ca of zero were clearly explained the structures were not CSH but the originally available structure that exist in kaolin as shown in Figure 9(a). As for specimens cured for 56 days with 0L10ZT, small amount of calcium contents were found on the rod like structure. It is believed that long curing periods have resulted some chemical reaction to be taken place in between the kaolin and zeolite, in which the zeolite naturally contains small amount of calcium as shown in Table 4.

In order to compromising the problem of charging due to the non-conductivity behaviour of the specimens, the 5kV voltage were used in this study. It is realizing that higher voltage is supposing required especially when quantitative analysis of bulk chemical composition is needed. However, higher voltage was resulted in drifting of the images which made the user impossible to specifically choose interest areas or points for EDX analysis. The set back of having low voltage is evident when low intensity of $K\alpha$ peaks of Calcium was noticed for all the specimens. Besides it, the EDX analysis also having the limitation to detect light materials, namely hydrogen, helium and lithium. Hence, it is important to clearly state that the quantification of the chemical composition in Table 1,Table 2, Table 3 and Table 4 are semi-quantitative and only serve as relative reference.



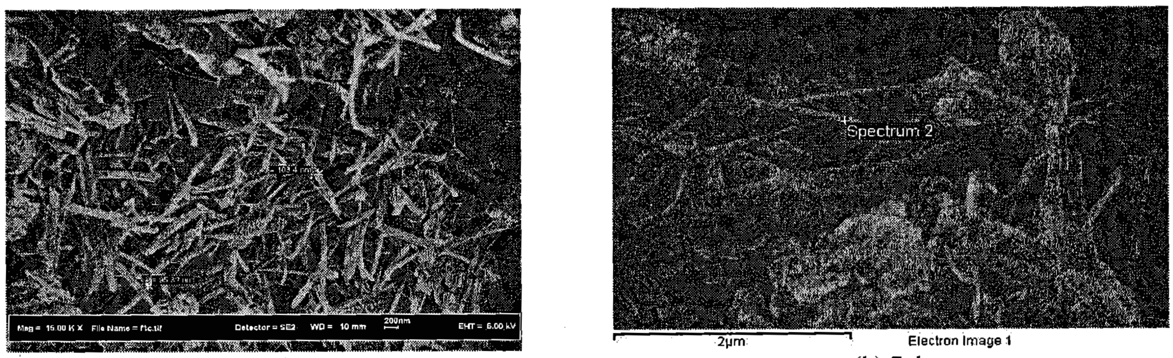

(a) 56 days (b) 7 days

Figure 1 SEM micrograph of needle like structure for sample K7HA3-10L0Z



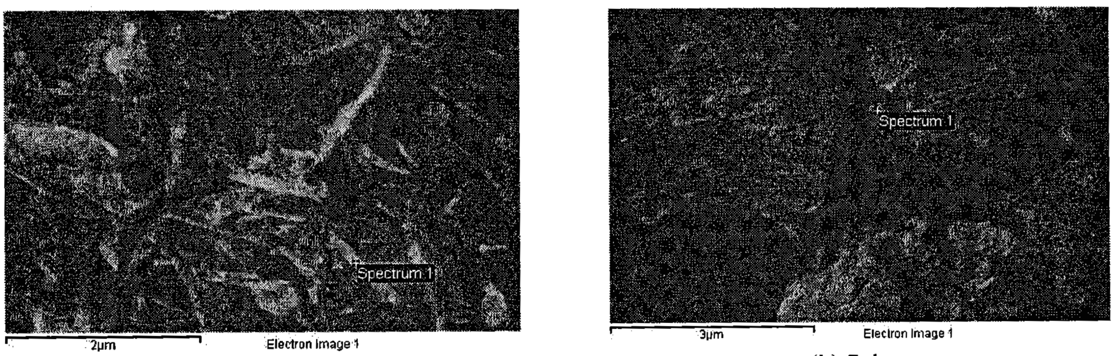

(a) 56 days (b) 7 days

Figure 2 SEM micrograph of needle like structure for sample K5HA5-10L0ZT




(a) 56 days (b) 7 days

Figure 3 SEM micrograph of needle like structure for sample K7HA3-8L2ZT




(a) 56 days (b) 7 days

Figure 4 SEM micrograph of needle like structure for sample K5HA5-8L2ZT

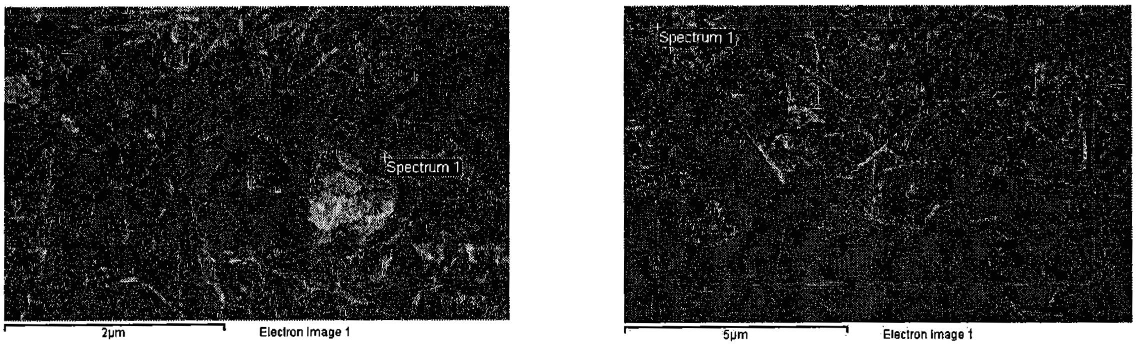



Figure 5 SEM micrograph of needle like structure for sample K7HA3-5L5ZT

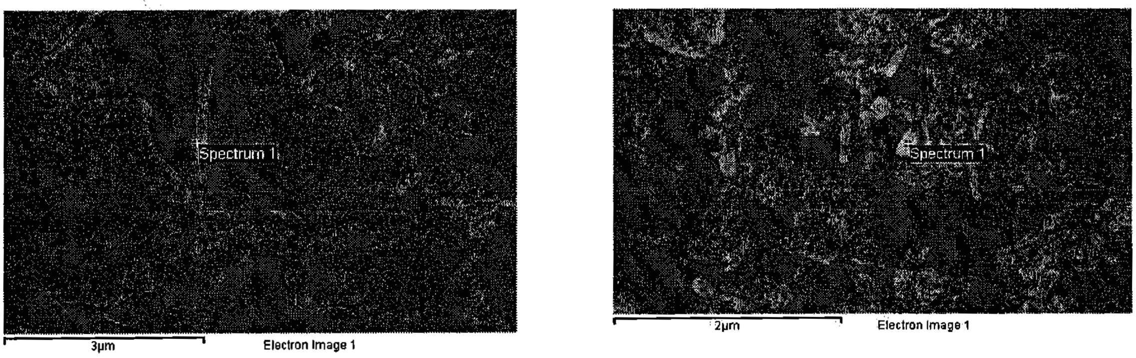
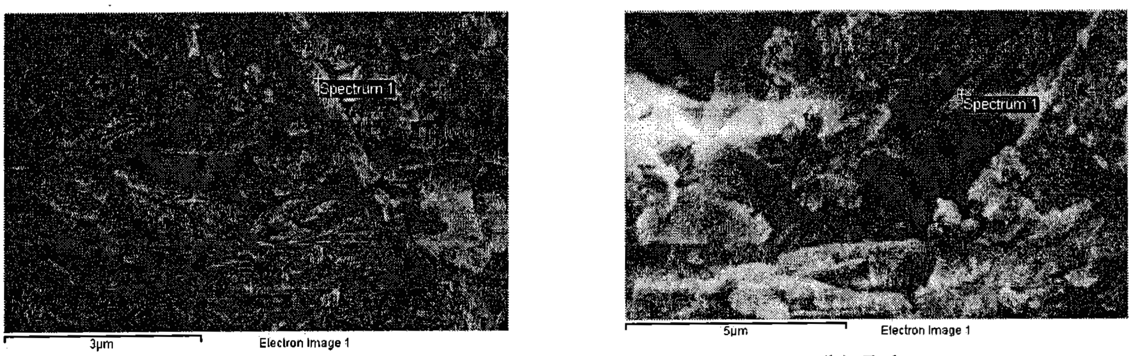
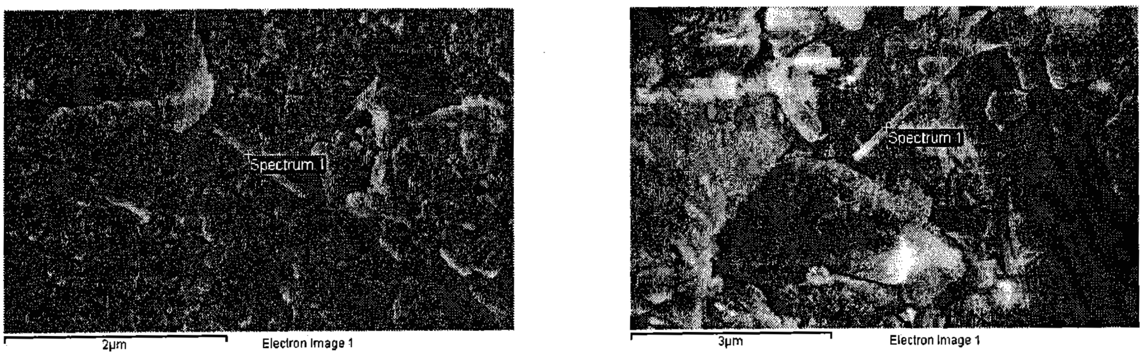



Figure 6 SEM micrograph of needle like structure for sample K5HA5-5L5ZT



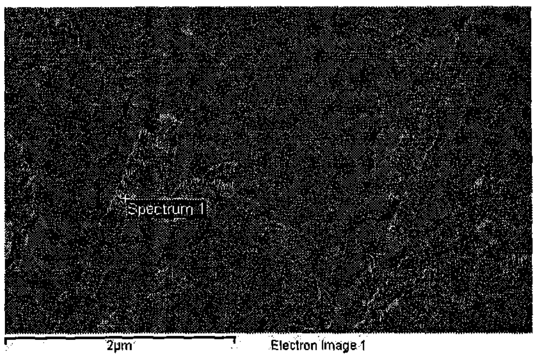

(a) 56 days (b) 7 days

Figure 7 SEM micrograph of needle like structure for sample K7HA3-0L10Z

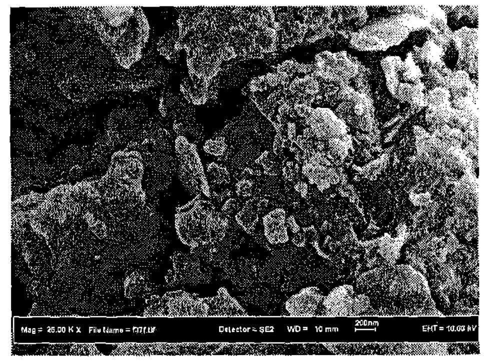



(a) 56 days (b) 7 days

Figure 8 SEM micrograph of needle like structure for sample K5HA5-0L10ZT




(a) Kaolin



(b) Humic acid

Figure 9 SEM micrograph of kaolin & humic acid

Table 1. Approximate chemical composition of needle like structure for soil type K7HA3. (EDX- FESEM)(All values are in % and normalized in order to sum 100%)

| Sample ID | K7HA3-10L0ZT | | K7HA3-8L2ZT | | K7HA3-5L5ZT | | K7HA3-0L10ZT | |
|---|---|---|---|---|---|---|---|---|
| Element | 56 days | 7 days | 56 days | 7 days | 56 days | 7 days | 56 days | 7 days |
| C K | 8.28 | 18.28 | 5.18 | 19.96 | 11.78 | 3.11 | 11.29 | 3.65 |
| O K | 51.52 | 40.6 | 64.34 | 51.4 | 34.26 | 50.19 | 81.07 | 38.03 |
| Na K | - | - | - | - | 0.09 | 0.39 | 0.13 | 0.3 |
| Mg K | 0.86 | 0.82 | 1.59 | - | 0.24 | 0.2 | 0.35 | 0.56 |
| Al K | 7.5 | 12.05 | 8.6 | 10.35 | 2.15 | 13.19 | - | 9.73 |
| Si K | 3.01 | 14.41 | 12.47 | 16 | 48.7 | 19.53 | 1.44 | 34.8 |
| S K | 2.25 | - | 1.05 | - | - | - | - | - |
| K K | 0.42 | 2.09 | 3.96 | 0.14 | 0.48 | - | 1.09 | 9.28 |
| Ca K | 26.14 | 11.74 | 2.81 | 2.16 | 2.31 | 13.38 | 4.63 | - |
| Fe L | - | - | - | - | - | - | - | 3.65 |
| Totals | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Ratio Si/Ca | 0.115 | 1.227 | 4.438 | 7.407 | 21.082 | 1.460 | 0.311 | 0.000 |

Table 2. Approximate chemical composition of needle like structure for soil type K5HA5. (EDX- FESEM)(All values are in % and normalized in order to sum 100%)

| Sample ID | K5HA5-10L0ZT | | K5HA5-8L2ZT | | K5HA5-5L5ZT | | K5HA5-0L10ZT | |
|---|---|---|---|---|---|---|---|---|
| Element | 56 days | 7 days | 56 days | 7 days | 56 days | 7 days | 56 days | 7 days |
| C K | 5.94 | 6.23 | 9.08 | 8.69 | 6.71 | 36.15 | 29.08 | 0.89 |
| O K | 16.43 | 19.49 | 49.34 | 41.96 | 50.7 | 35.8 | 33.14 | 45.98 |
| Na K | - | - | - | - | 0.28 | 0.38 | 0.3 | 0.05 |
| Mg K | 0.97 | 0.44 | 1.1 | 0.46 | 0.63 | 1.35 | 0.43 | 0.28 |
| Al K | 15.66 | 6.3 | 10.64 | 19.5 | 10.01 | 5.22 | 12.13 | 9.82 |
| Si K | 14.71 | 29.14 | 10.98 | 20.18 | 28.78 | 7.51 | 20.77 | 31.68 |
| S K | - | - | 2.69 | - | - | 0.21 | - | - |
| K K | 18.18 | 2.02 | 0.77 | 0.17 | 0.01 | 0.82 | 1.31 | 11.3 |
| Ca K | 28.1 | 36.38 | 15.39 | 9.05 | 2.88 | 12.55 | 2.84 | - |
| Fe L | - | - | - | - | - | - | - | - |
| Totals | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Ratio Si/Ca | 0.523 | 0.801 | 0.713 | 2.230 | 9.993 | 0.598 | 7.313 | 0.000 |

Table 3. Approximate chemical composition of kaolin and humic acid.
(EDX- FESEM)(All values are in % and normalized in order to sum 100%)

| Sample ID | Kaolin S300 | | Humic acid | K7HA3 | K5HA5 |
|---|---|---|---|---|---|
| Element | Plain area | Rod like structure | | | |
| C K | 6.70 | 6.46 | 44.54 | 30.40 | 45.31 |
| O K | 52.78 | 55.25 | 37.82 | 44.54 | 32.95 |
| Na K | 0.07 | - | 0.24 | 0.07 | 0.09 |
| Mg K | 0.92 | 0.52 | 0.54 | 0.26 | 0.44 |
| Al K | 14.20 | 15.36 | 6.80 | 10.82 | 4.76 |
| Si K | 20.26 | 20.04 | 5.91 | 12.43 | 4.85 |
| S K | - | - | - | - | 0.16 |
| K K | 3.48 | 1.53 | 0.14 | 0.23 | 0.15 |
| Ca K | 1.59 | 0.23 | 2.67 | 1.26 | 2.75 |
| Fe L | - | 0.61 | 1.33 | - | 8.54 |
| Totals | 100 | 100 | 100 | 100 | 100 |
| Ratio Si/Ca | 12.74 | 88.00 | 2.213 | 9.865 | 1.764 |

Table 4. Approximate chemical composition of additives.
(EDX- FESEM)(All values are in % and normalized in order to sum 100%)

| Sample ID | 10L2ZT | 8L2ZT | 5L5ZT | 0L10ZT |
|---|---|---|---|---|
| Element | | | | |
| C K | 6.48 | 9.53 | 12.81 | 13.21 |
| O K | 48.68 | 52.19 | 45.78 | 48.24 |
| Na K | - | 0.08 | - | - |
| Mg K | - | 0.66 | 0.29 | 0.52 |
| Al K | - | - | - | 4.94 |
| Si K | - | - | - | 28.26 |
| S K | - | - | - | - |
| K K | - | - | - | 4.00 |
| Ca K | 44.84 | 37.54 | 41.13 | 0.83 |
| Fe L | - | - | - | - |
| Totals | 100 | 100 | 100 | 100 |
| Ratio Si/Ca | - | - | - | 34.048 |

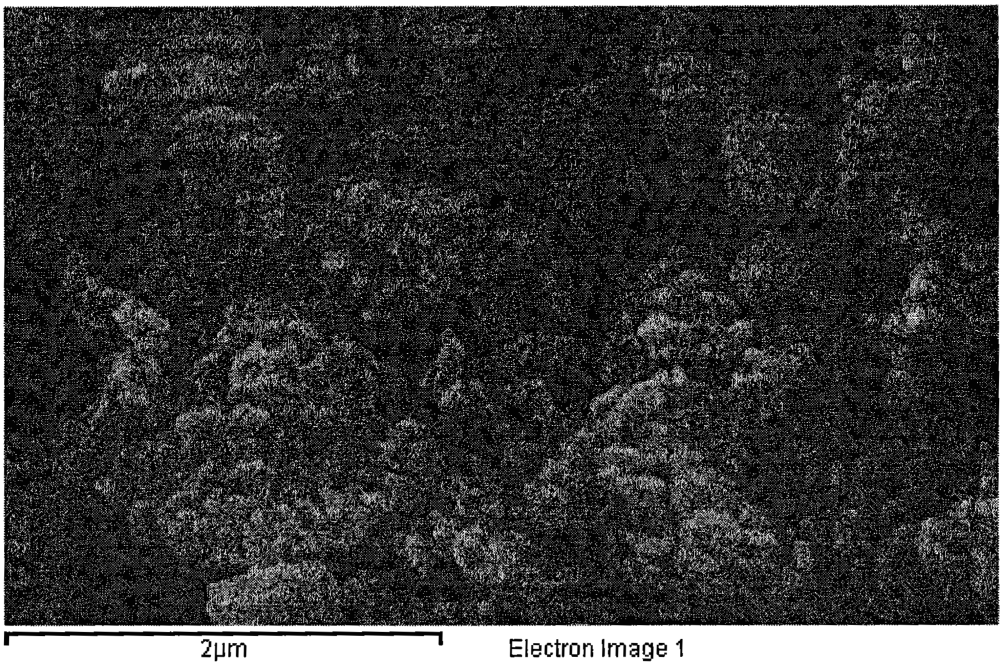



Figure 10: Lime (calcium hydroxide)

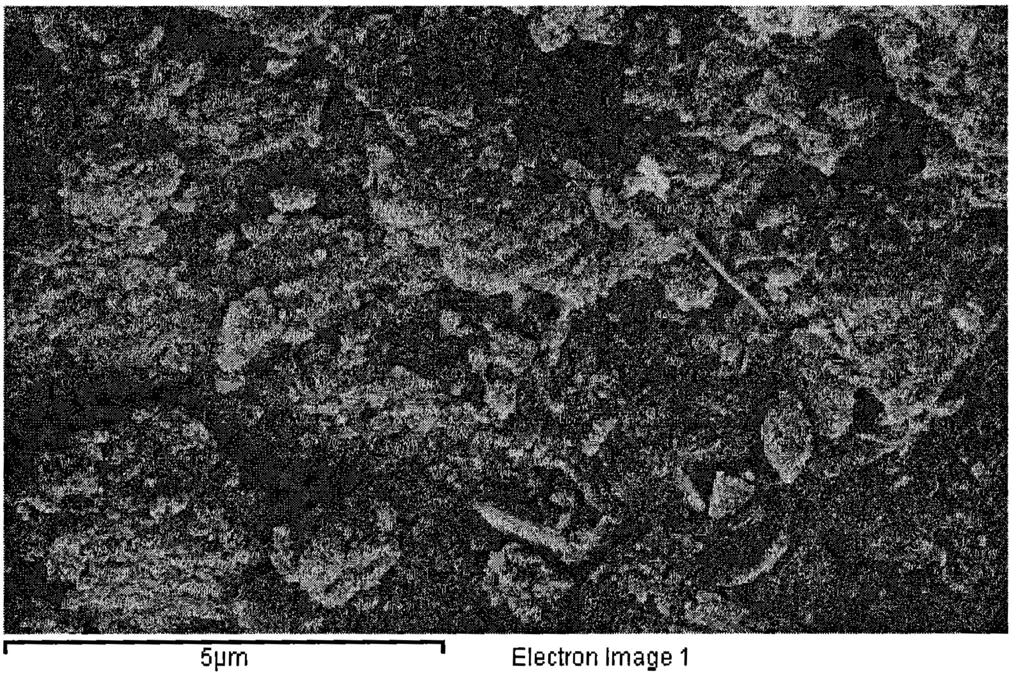



Figure 11: Zeolite (natural)

**Conclusion**

Microscopic technique is effective in recognizing the reaction product of pozzolanic activity, whereas EDX analysis is essential in complimenting the morphology study especially when the physical appearance of the material is un-identical.

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