



## Synthesis of Hydroxy-sodalite from Fine Fractions of Sandy Clay Loam Soil (Natural Aluminosilicate)

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**Abstract :** Hydroxy-sodalite zeolites of different morphologies were synthesized using fine fractions of sandy clay loam soil (Natural aluminosilicate) by alkaline fusion method prior to conventional alkaline hydrothermal reaction (90°C for 24 hours). Mineralogical, textural properties and elemental analysis of the products were probed by employing x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), BET surface area and the cation exchange capacity (CEC). XRD and FTIR analysis confirmed the formation of Hydroxy-sodalite particles under all the experimental conditions. The BET surface area and total pore volume of the Hydroxy-sodalite formed varied from (31 – 51) m<sup>2</sup> / g and (0.17 – 0.21) cm<sup>3</sup> / g respectively. Cation exchange capacity as high as 203.06 meq / 100 g (low Si/Al ratio ≈ 1.02) was obtained at an optimum condition of NaOH / raw material ratio of 1.2 and a fusion temperature of 600°C.

**Keywords :** Sandy clay loam soil, Hydroxy-sodalite, synthesis, alkaline fusion.

### 1. Introduction

In recent years, the interests in the use of zeolites in environmental protection, agriculture and other industrial applications have increased as a result of their unique properties as ion exchangers, molecular sieves, adsorbents and catalysts. Zeolites are crystalline microporous aluminosilicates of alkali and alkaline earth metals with well-defined pores structures. They are built up of 3-dimensional frameworks of [SiO<sub>4</sub>]<sup>4-</sup> and [AlO<sub>4</sub>]<sup>5-</sup> tetrahedral, linked at their corners to form different channels and cages<sup>1</sup>. The negative charge on the lattice is neutralized by the positive charge of cations, typically, alkali or alkaline earth metal ions located within the pores of the material.

Hydroxy-sodalite (HS) is a type of zeolite that belongs to clathrasils group which is made of cubic array of β-cages and exhibits similar structure of sodalite (Na<sub>8</sub>[Al(SiO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>]) where framework charges are balanced with hydroxide anions<sup>2</sup>. These β-cages or sodalite cages (secondary building units) are formed from the arrangement of Si and Al tetrahedral units (primary building) through the association of simple 4-rings (S4R)

and simple 6-rings (S6R)<sup>1</sup>. Because of small pore size (2.8 Å) and high ion exchange capacity, hydroxy-sodalite has been considered a good candidate material for a wide range of applications such as hydrogen storage, optical materials, adsorbent and base catalyst. Furthermore, this product with a high cation exchange capacity (CEC) could be used for waste water treatment as an inorganic ion-exchanger or an ion-adsorbent capable of removing cations such as NH<sub>4</sub><sup>+</sup> and toxic heavy metal ions from water and sewage and as soil amendment material<sup>3</sup>.

Zeolites may be found in natural deposits or synthesized. The continuous increase in the consumption of zeolites calls for further work seeking cheaper raw materials for their synthesis. Generally, zeolites are synthesized from sodium aluminosilicate gel, from various silica and alumina sources by hydrothermal treatment. However, the preparation of synthetic zeolites from chemical sources of silica and alumina is expensive. Therefore to reduce costs, zeolite researchers are seeking cheaper raw materials for zeolite synthesis<sup>4</sup>. Different clay minerals have been used as a starting material for zeolite synthesis: kaolinite<sup>5</sup>, Smectite<sup>6</sup>, bentonite<sup>7</sup>, halloysite<sup>8</sup> and interstratified illite-smectite<sup>9</sup>. However, these clay minerals with high purity are widely utilized in many facets of our society thus may limit their availability for zeolite synthesis. Use of processed clay materials may also increase cost.

In this study we report the synthesis of hydroxy-sodalite from fine fractions of sandy clay loam soil with low organic matter content (Natural aluminosilicate) by alkaline fusion followed by hydrothermal synthesis method. X-ray diffraction (XRD), scanning electron microscopy (SEM) / energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and N<sub>2</sub>-BET surface area determination and cation exchange capacity (CEC) were used to characterize the products. We had previously reported the adsorption potential of fine fractions of sandy clay loam soil on ammonium ion from aqueous solution<sup>10</sup>.

## 2. Experimental

### 2.1. Raw Materials

The sandy clay loam soil samples used in this study were collected from Ikasa village, Ndian Division, South West Region of Cameroon (N04° 58.321' E008° 47.970')<sup>10</sup> with the area dominated by Cretaceous and Mio-Pliocene sediments<sup>11</sup>. The particle size distribution was as follows: clay (25.47%), silt (19.64%) and sand (54.89%). Fractions of the sandy clay loam soil less than 100 µm were then taken by wet sieving after which they were air dried. To increase the surface area, the soil was further ground into fine powder using a mortar and was then passed through an 80 µm mesh opening size sieve. This sample was denoted as SCL and has been previously studied by *Nanganoa et al*, 2013<sup>10</sup>.

Chemical analysis of SCL was carried out by ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectrometry) and the content of the major elements are listed in Table 1. Chemical composition has an important influence on the potential application of the raw material. Table 1 shows the chemical composition of SCL. The main constituents of SCL are silica (60.08%), alumina (23.02%) and the other oxides are present in trace amounts. However, potassium oxide (6.61%) is relatively high which might be attributed to the illite and feldspar present in the material. The loss on ignition is 7.75% indicating a low organic matter content of SCL. The material has little oxides of iron (1.29%) and calcium (0.03%), which is good for obtaining zeolites as Fe-bearing minerals can show an inert behaviour and Ca-bearing phases, can act as inhibitors to zeolite synthesis through the formation of calcium silicate hydrate phases<sup>12</sup>. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is an important parameter for synthesis of zeolites. The ratio for SCL = 2.6. Thus it is a good candidate for the synthesis of low-Si zeolitic materials such as hydroxy-sodalite with high cation exchange capacity.

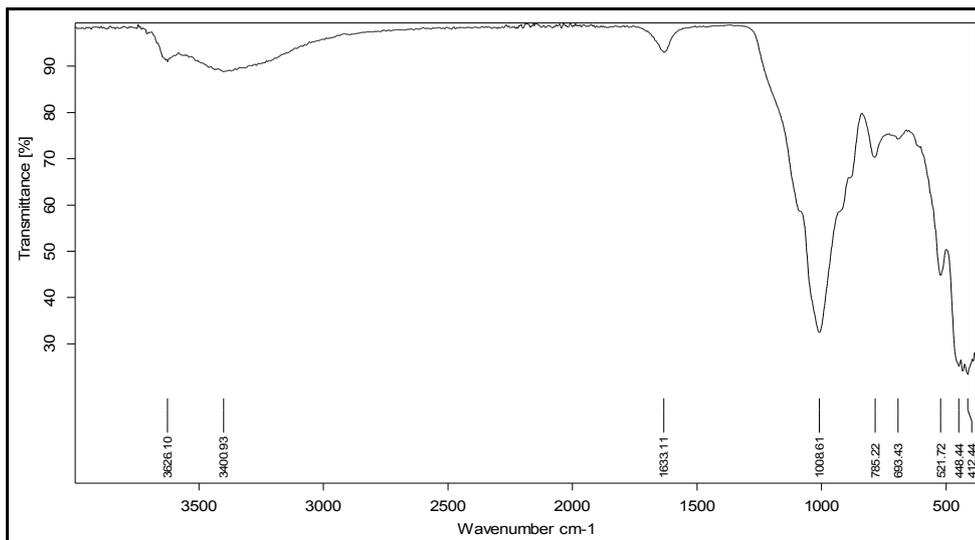
The mineralogical composition of SCL was obtained using a Bruker D8 advanced diffractometer, operating on the Co- $\alpha$  radiation and 2 $\theta$  scanning ranging from 3° to 64° with a scanning step of 0.035°. The X-ray diffraction analysis showed that the major crystalline phase found in SCL is quartz as identified by the sharp peak at 3.34. Other phases present were illite, smectite, kaolinite and K-feldspar<sup>10</sup>.

The Fourier transform infrared spectroscopy (FTIR) spectrum of SCL was recorded on a Bruker alpha P FTIR spectrometer in the 4000-400 cm<sup>-1</sup> range. The FTIR spectrum of SCL is shown in Figure 1 indicating the presence of a variety of aluminosilicate bands. The vibration bands at 1008 and 448 cm<sup>-1</sup> are attributed to Si-O bending mode. The bands at 1633 and 3400 cm<sup>-1</sup> are assigned to bending and stretching vibrations of O-H of

water respectively<sup>13</sup>. The band at 3626 cm<sup>-1</sup> corresponds to O-H stretching vibration and the bands 785 and 693 cm<sup>-1</sup> correspond to Si-O and Si-O-Al vibrations respectively<sup>14</sup>. The CEC of SCL was determined by the ammonium acetate method (1 M NH<sub>4</sub>OAc at pH =7). The CEC of SCL was estimated to be 28.6 meq /100 g. SEM image of SCL is discussed below. The specific surface area of SCL was determined by the Brunauer-Emmett-Teller (BET) method through nitrogen adsorption and was 27.6 m<sup>2</sup> / g<sup>10</sup>. Sodium hydroxide powder was used as source of sodium and to dissolve aluminum. Al(OH)<sub>3</sub> was used to adjust the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. Both reagents were purchased from Sigma.

**Table 1: Chemical composition of SCL**

Constituent	Value (%)
SiO <sub>2</sub>	60.08
Al <sub>2</sub> O <sub>3</sub>	23.02
Fe <sub>2</sub> O <sub>3</sub>	1.29
MgO	0.77
CaO	0.03
Na <sub>2</sub> O	0.13
K <sub>2</sub> O	6.61
TiO <sub>2</sub>	0.38
P <sub>2</sub> O <sub>5</sub>	0.04
LOI	7.75



**Figure 1: FTIR Spectrum of SCL**

## 2.2. Synthesis of hydroxy-sodalite

The alkaline fusion method prior to hydrothermal reactions was used in the synthesis of hydroxy-sodalite. 10 g of SCL raw material was mixed with 10g, 12 g and 14 g of NaOH powder. These mixtures were heated in ceramic crucibles in a muffle furnace at 600 °C for 1 hour. The resultant materials were cooled in a desiccator and ground again to obtain fused materials. 93.6 mL distilled water was added to fused materials with or without 0.93 g Al(OH)<sub>3</sub> in Teflon bottles. This was followed by a 24 hours aging process which involves agitation on a reciprocal shaker at room temperature to obtain the aged materials. The aged materials were then heated in an air oven at 90 °C for 24 hours to obtain the products. The products were filtered, washed several times with distilled water until the filtrates had pH ≤ 10. They were then dried in an oven at 105 °C overnight. The experimental conditions are summarized in Table 2.

**Table 2: Experimental conditions for alkaline activation of SCL by using a fusion step prior to hydrothermal reaction**

Test	Raw material	Reagents		Alkaline fusion		Water (g)	Ageing t (hrs)	Hydrothermal reaction		Zeolitic product
		NaOH(g)	Al(OH) <sub>3</sub> (g)	T(°C)	t (hr)			T (°C)	t (hrs)	
1	10	10	/	600	1	93.6	24	90	24	HS
2	10	12	0.93	600	1	93.6	24	90	24	HS
3	10	14	0.93	600	1	93.6	24	90	24	HS

## 2.3. Characterization of products

### 2.3.1 XRD analysis

The zeolitic phase(s) in the solid products were identified by X-ray diffraction using a Rigaku D/Max-2500 instrument, operating on the Cu- $\alpha$  radiation and  $2\theta$  scanning ranging from  $5^\circ$  to  $80^\circ$  with a scanning step of  $0.02^\circ$ .

### 2.3.2 FTIR analysis

The Fourier transform infrared spectroscopy (FTIR) spectra of the zeolitic materials were recorded in the range  $4000-400\text{ cm}^{-1}$  on a Bruker alpha P FTIR spectrometer in transmission mode, used in conjunction with a diamond attenuated total reflectance (ATR) accessory. A force was applied to the sample for spectrum collection.

### 2.3.3 SEM-EDS analysis

Morphology of the end products was examined by scanning electron microscope (SEM); An S-4700 (Hitachi) instrument was used coupled with energy-dispersive spectroscopy (EDS) analyzer. Samples were coated with gold prior to analysis. Elemental composition of hydroxy-sodalite was analyzed by energy dispersive spectroscopy (EDS) coupled to the Scanning Electron Microscope.

### 2.3.4 Surface area analysis of zeolitic materials

Surface area and porosimetry measurements were obtained on a Micrometrics Tri-Star surface area and porosity analyzer at 77 K by nitrogen isotherms according to BET method.

### 2.3.5 Cation exchange capacity analysis

Cation exchange capacity (CEC) was determined using sodium acetate procedure<sup>15</sup>. A mass of 4.0 g of zeolite was soaked with an excess amount of 1.0 M sodium acetate solution for 5 min, centrifuged and rinsed with isopropyl alcohol. Then a solution of ammonium acetate (1.0 M) was added to replace the amount of sodium adsorbed on the surface of the solid. The concentration of the displaced sodium was then determined using Flame photometry.

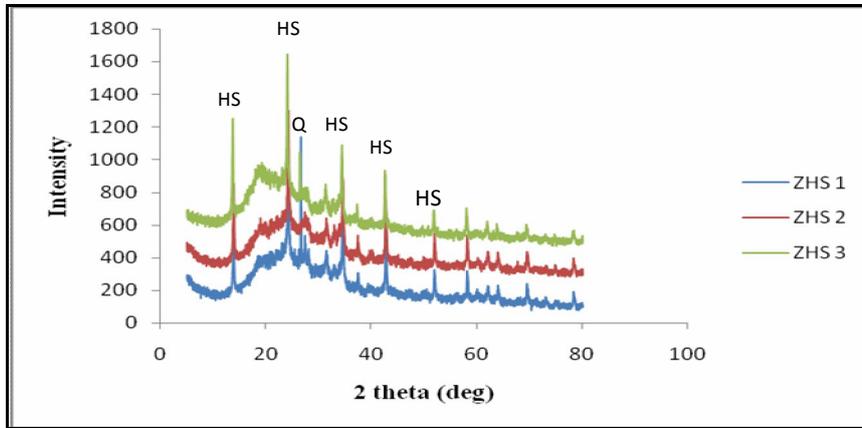
## 3. Results and discussion

### 3.1 XRD analysis of products

During alkaline fusion, the sodium hydroxide present in the mixture, acts as an activator to form soluble silicate salt. By employing this method on SCL larger amounts of aluminosilicates including quartz was dissolved. The zeolitic products formed were labeled as ZHS 1, ZHS 2 and ZHS 3 based on the mass of NaOH (10 g, 12 g and 14 g) respectively in experimental conditions.

The X-ray diffraction patterns of the as-synthesized zeolitic material are shown in Figure 2. The most noticeable changes in the X-ray diffractograms (Fig. 2) are the reduction in intensity of the quartz peaks and the appearance of peaks corresponding to hydroxy-sodalite (namely,  $6.38 - 6.46$ ,  $3.66 - 3.69$ ,  $2.59 - 2.61\text{ \AA}$ )<sup>16</sup>. As shown in Figure 2, the relative peak intensity of quartz decreased with increasing NaOH concentration. With

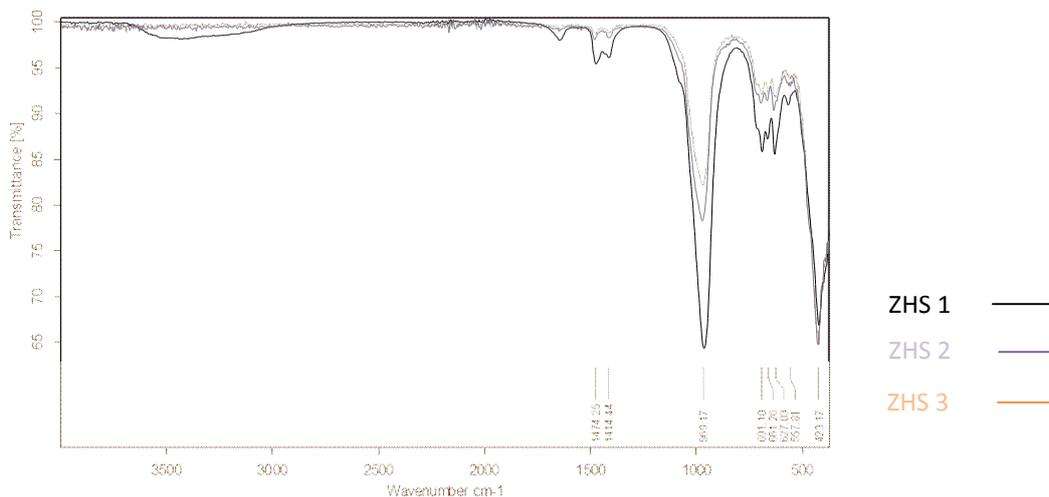
SCL: NaOH ratio of 1:1, the peak intensity of quartz was 1133 while for the ratio 1:1.2, the peak intensity was 433. This shows that NaOH affect the degree of zeolitization. Thus fusion of SCL with NaOH powder seems to be essential for dissolution of feldspars and quartz in the starting material. Berggaut et al, 1996 found that an intimate contact of NaOH with fly ash was crucial for complete decomposition of the fly ash<sup>17</sup>.



**Figure 2: X ray diffraction pattern of products(a) ZHS 1 (b) ZHS 2 (c) ZHS 3. HS = Hydroxy-Sodalite, Q = quartz**

### 3.2 FTIR spectroscopy analysis

FTIR spectra in Figure 3 show the characteristic zeolite bands observed in sodalite and cancrinite. The band around  $969\text{ cm}^{-1}$  was assigned to the asymmetric stretching vibration of T–O–T (T=Si, Al) while those that appeared around  $692$  and  $661\text{ cm}^{-1}$  were due to the symmetric stretching of T–O–T<sup>2, 18</sup>. The bands in the region of  $553\text{--}632\text{ cm}^{-1}$  are related to the presence of the double rings (D4R and D6R) in the framework structures of these feldspathoids. The band at  $423\text{ cm}^{-1}$  is related to internal tetrahedron vibrations of Si–O and Al–O of sodalite and cancrinite. The detailed FTIR assignments for sodalite and cancrinite have been summarized by Barnes et al. (1999a)<sup>19</sup> and later re-examined by Zhao et al. (2004)<sup>20</sup>.



**Figure 3: FTIR spectra of HS**

### 3.3 SEM-EDS analysis

The scanning electron micrograph of SCL is shown in Figure 4a and the three zeolite products (ZHS 1, ZHS 2 and ZHS 3) are shown in Figure 4(b – d). The SEM images of the synthesized zeolites showed different morphologies and were also different from the starting material thus confirming the transformation of SCL to hydroxy-sodalite. Synthesis of hydroxy-sodalite zeolite with different particle size and morphology can be

attributed to difference in preparation of synthesis solution<sup>21</sup>. The EDS measurement of ZHS 2 is presented in Figure 5. The Si/Al ratio is equal to 1.02.

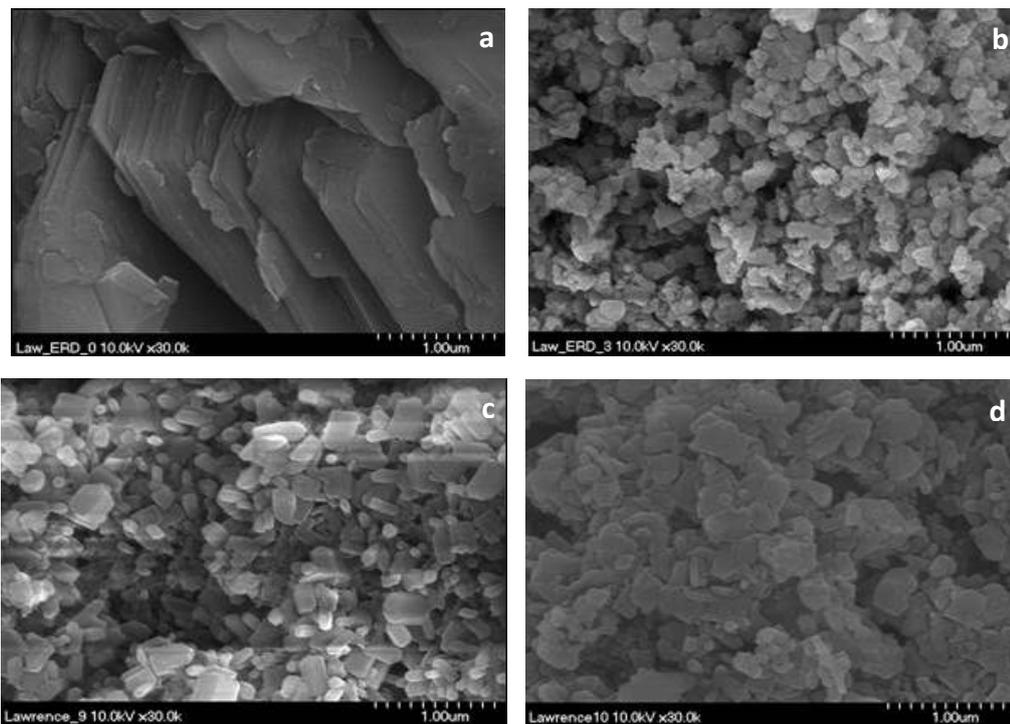


Figure 4: SEM images of the SCL (a) and synthesized products (b) ZHS 1 (c) ZHS 2 (d) ZHS 3

### 3.4 Surface area results

The BET surface area and pore volume of SCL and the zeolitic materials are given below in Table 3. The specific surface area values of the zeolitic materials were higher than that of the precursor material. The increasing order of the surface area analysis of the zeolites was ZHS 3 < ZHS 2 < ZHS 1.

### 3.5 Cation exchange capacity (CEC)

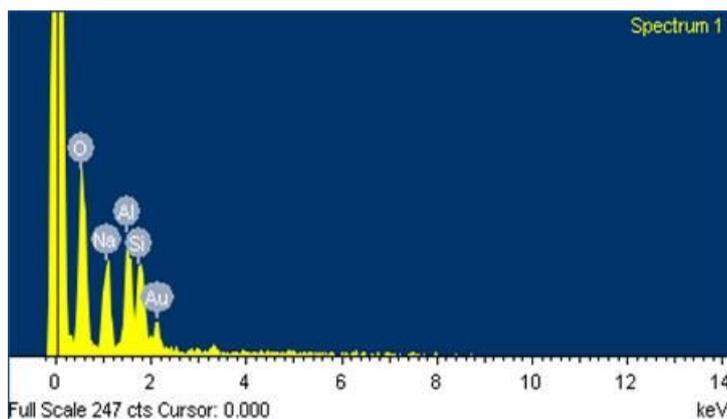
The CEC of the raw material (SCL) and zeolites are shown in Table 3. The CEC value of SCL is much lower as compared to those of ZHS 1, ZHS 2 and ZHS 3. The CEC was found to be high for product ZHS 2 (203.06 meq/100 g), while it was quite low for product ZHS 3 (91.98 meq/ 100 g) (Table 3). Variations in the CEC values with sodium hydroxide concentration may be attributed to factors such as the type and extent of zeolite formation<sup>22</sup>. From the point of view of potential application, the most interesting zeolitic product is ZHS 2, due to its high ion exchange capacity. The high CEC value of ZHS 2 is confirmed by the elemental analysis of EDS with low Si/Al ratio of 1.02 (Table 4 and Fig. 5). In general, if a zeolitic material has a low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, the cation exchange capacity will be high due to the substitution of Si (IV) by Al (III) in the zeolite framework that results in a negative charge<sup>23</sup>. The CEC values obtained for products ZHS 1 and ZHS 2 were very close or even higher than those obtained for natural commercial rich clinoptilolite products (150 – 200 meq / 100 g)<sup>24</sup>.

Table 3: Surface area and pore volumes derived from nitrogen adsorption data for the raw material, final products and CEC

Sample	BET surface area (m <sup>2</sup> / g)	Total pore volume (cm <sup>3</sup> / g)	CEC (meq / 100 g)
SCL	27.61	0.05	28.61
ZHS 1	50.62	0.19	154.01
ZHS 2	46.23	0.21	203.06
ZHS 3	31.71	0.17	91.78

**Table 4: EDS Elemental analysis of ZHS 2**

Element	Weight %	Atomic %
O K	47.53	61.85
Na K	13.45	12.18
Al K	16.28	12.56
Si K	17.31	12.83
Au M	5.42	0.57
Total	100	100

**Figure 5: EDS spectrum of ZHS 2**

## Conclusion

Fine fractions of sandy clay loam soil with quartz as the major crystalline phase was treated hydrothermally after fusion with NaOH either with or without  $\text{Al}(\text{OH})_3$  to obtain hydroxy-sodalite. Variation in the amount of reagents used in the syntheses of hydroxy-sodalite affected the properties such as morphology, BET surface area and CEC of the products formed. Alkaline fusion of SCL with NaOH powder at weight ratio (NaOH/SCL) of 1.2 at 600 °C for 1 h, dissolved quartz almost completely to form hydroxy-sodalite with Si/Al ratio of 1.02.

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