CHAPTER 4

X – RAY AND SCANNING ELECTRON MICROSCOPE CHARACTERIZATION OF LEONARDITE

4.1 Introduction

Leonardite originated on the surface of lignite deposits by post sedimentary oxidation. A significant difference between lignite and leonardite is the oxygen content; leonardite usually contains about 28 - 29%, while lignite contains about 19 –20 % (Hoffman *et al.,* 1993). In the past, leonardite was dumped as mine waste in the mines. because of its low heating value. Generally, minerals in leonardite vary widely; the amount present is the shale group (muscovite, illite) the clay group, the sulfide group, carbonate group and the salt group (Ozbayoglu, 2006).

Silicate minerals may constitute up to 60 weight percent of the mineral matter part of the coal. Quartz is usually the second most abundant mineral, with up 20 weight percent being common. The carbonate minerals (calcite, siderite and to a lesser extent, dolomite and ankerite) and the iron disulfide minerals (pyrite and marcasite) make up, on the average, about 10 weight percent each group.

Coal consists of primary macromolecules of poly aromatic polynuclear structure with some heteroatom groups and their secondary network. X-ray diffraction analysis (XRD) analysis is a fundamental method for studying the carbon stacking structure in coal. and the organic matter in coals contains significant amounts of oxygen, sulfur and nitrogen heteroatoms incorporated in various functionalities (e.g. carboxylic, phenolic groups), which vary in abundance depending on the specific conditions of the coal beds.

Instrumental techniques like TEM4,5, FT–IR6, Raman spectroscopy7 and NMR8 have been used for coal molecular structure determination. The role of X-ray diffraction (XRD) study in coal science is enormous. It was initially directed towards measuring the minerals and/or the low- and high-temperature ash in coal. XRD analysis is a fundamental method for evaluating carbon-stacking structure. The degree of ordering, interlayer spacing (d002) and crystallite size (La,Lc) have been established as the structural parameters for evaluating the stacking structure of highly crystalline carbon materials.

The powder X-ray diffraction (XRD) is probably the most utilized method both for qualitative and quantitative determination of minerals in coal (e.g.Querol *et al.,* 1993, Acharya, 1992, Mandile and Hutton, 1995, Ward and Taylor, 1996, Wertz and Collins 1998, Ward *et al.,* 1999, 2001). For quantitative mineral determination the methods of internal standard or spike (e.g. Gaigher, 1983, Ward, 1989) and/or Rietveld´s method (Rietveld, 1969, Weiss *et al.,* 1983, O'Connor and Raven, 1988, Taylor, 1991, Bish and Post, 1993) are widely used.

Analytical methods must be selected to suit the material to be analyzed in order to obtain the most accurate analysis. In this study, leonardite from various locations was examined for mineral crystallography by X-ray diffraction (X- ray Diffraction; XRD) (Buncha, 2544). The chemical composition of leonardite was analyzed by X-ray fluorescence spectrometery (XRF). The crystal morphology of Leonardite samples was examined using a scanning electron microscope (SEM). We believe that the information from this study can be used to evaluate the potential use of leonardite in agriculture, i.e. soil and crop yield improvement.

4.2 Materials and Methods

4.2.1. Samples Selection

Base on chemical properties obtained from the previous experiments (chapter 3, Table 3.7) and the availability of the samples, only five leonardite samples were selected for further investigation.

4.2.2. Analysis of Cation Exchange Capacity (CEC) and Ash

Determination of CEC was perform as described by Chapman (1965). Briefly, ammonium acetate (pH 7) was used as extracting solution. The amount of 25.0 g of each leonardite sample was thoroughly mixed with 125 mL of the 1 M NH_4OAc, shake thoroughly and allow to stand 16 hours (or overnight). Then, gently wash the samples four times with 25 mL of the NH_4OAc. Discard the leachate and clean the receiving flask. Extract the adsorbed NH_4^+ by leaching the leonardite again with eight separate 25 mL additions of 1 M KCl. Discard the leonardite and transfer the leachate to a 250 mL volumetric. Dilute to volume with additional KCl. Determine the concentration of NH_4-N in the KCl extract.

Calculations:

Where NH_4-N is reported in mg N/L:

CEC (cmolc/kg) = (NH_4-N in extract - NH_4-N in blank) / 14

Where NH_4-N is reported in mg NH_4/L:

CEC (cmolc/kg) = (NH_4-N in extract - NH_4-N in blank) / 18

Ash (% Ash)

Ash content of leonardite samples were analyzed. All the samples were heated to 700 °C for 3 h. The ash (residue) was calculated on an oven dry basis.

4.2.3. Mineral Crystallography by X-ray diffraction spectrometery (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

The leonardite samples were finely ground, homogenized, and average bulk composition were determined. Leonardite powder less than ~10 µm (or 200-mesh) in size was preferred. Only a few tenths of a gram (or more) of each leonardite sample, as pure as possible, was used for XRD analysis. Each leonardite sample was placed on to a glass slide, then the following steps was performed;

- smeared uniformly onto a glass slide, assuring a flat upper surface
- packed into a sample container
- sprinkle on double sticky tape

Care was also taken to create a flat upper surface and to achieve a random distribution of lattice orientations unless creating an oriented smear. Leonardite sample were also examined for mineral crystallography by X-ray diffraction spectrometery (XRD, Bruker D 8-Advance diffractometer).

4.2.4. Analysis of Chemical Compositions by X-ray fluorescence spectrometery (XRF)

X-ray diffraction analysis was carried out on a Bruker D 8-Advance diffractometer in order to identify the crystalline phases of the selected leonardite samples (4.2.3). The major chemical compositions of leonardite were analyzed by X-ray fluorescence spectrometer (XRF).

Each leonardite sample was crushed and ground to a find powder. The powder was fine enough to pass through a 200 mesh screen (74 mm opening size). Leonardite powder was prepared as folowings;

1) The accompanying plastic ring Sample Holder and mylar sheets were used as a container specimen.

2) A spoon was used to scoop samples crushed and packed into such a container. The thickness of the sample was approximately 0.5 cm.

Then the sample was placed on energy X-rays, MESA 500 w (X - ray tube vol. Select Auto (15 keV and 50 keV) Preset time selected 200 sec Select Formular choose Fomular 1 (Oxide).

4.2.5. Analysis of Crystal Morphology by Scanning Electron Microscope (SEM)

The leonardite samples were dried, crushed and sieved to size 0.05 mm. Then the samples were placed on a sheet of carbon and were then gold coated by a Cressing Sputter Coater 108 before analysis by Scanning Electron Microscope (SEM). Analysis was carried out using a Camscam SEM (JEOL model JSM-5910LV) and recording characteristics of the leonardite.

4.3 Results and Discussion

4.3.1. The selected leonardite samples from preliminary chemical analysis

The five selected samples of leonardite were LD 2-3 (Mae Moh 2), LD3-2 (Mae Moh 3), LD4-2 (Chiang Muan2), LD8-1 (Lee 2) and LD8-3 (Lee 2) (Table 4.1). The pH values of leonardite samples from Mae Moh (2.38–2.44) and Lee mines (1.84–1.99) were very low. These pH values were typical range for leonardite. In contrast, the pH value of leonardite sample from Chiang Muan (5.63) was quite high compared with those from other locations (Table 4.1). This might due to the fact that leonardite piles at the sampling site was contaminated with soils. Leonardite from Lee; LD8-3 and LD8-1 gave the highest humic acid content with values of 85.05 and 72.44, respectively. The OM and C/N ratio of these two samples were also very high compared to the rest of selected samples. On the average, the results showed that the pH, humic acid and organic matter (OM) varied according to locations. However, there seemed to be little differences in chemical properties within the same location. Therefore, two samples from Mae Moh, one sample from Chiang Muan and two samples from Lee were selected for further investigations.

Table 4.1 Chemical properties of five selected leonardite samples

Sample code	Location	properties of leonardite			
		pH	Humic acid (%)	OM (%)	C/N ratio
LD2-3	Mae Moh 2	2.38	44.32	22.45	26.13
LD3-2	Mae Moh 3	2.44	61.58	27.84	29.17
LD4-2	Chiang Muan 2	5.63	31.97	25.16	40.71
LD8-1	Lee2	1.99	72.44	53.96	69.66
LD8-3	Lee2	1.84	85.05	61.02	62.32

4.3.2. Cation Exchange Capacity (CEC) and Ash in Selected Leonardite Samples

Cation exchange capacity (CEC) of selected leonardite samples ranged from 44.18 -94.16 cmol/kg. The highest total CEC was found in LD8-3 (94.16 cmol/kg) followed LD8-1 (89.63 cmol/kg) (Table 4.3). The lowest CEC was found in LD 2-3 (44.18 cmol/kg). The results indicated high levels of all the leonadite samples particularly those from Lee mines. These high CEC leonardite have a high potential to raise CEC in soils with low CEC. The higher CEC the better nutrients absorption and soil fertility. In addition, soils with high CEC can reduce runoff or leaching of positive charge nutrients into the water. The amount of ash ranged from 73.50 to 35.76 %. It was found that LD8-3 contained the highest ash (73.50 %) followed by LD8-1, LD 2-3 and LD3-2 (64.79, 41.34 and 41.36 %, respectively). The lowest ash value was found in LD4-2 (35.76%) (Table 4.2).

Table 4.2 Total cation exchange (CEC) and ash (% Ash) of selected leonardite samples

Sample code	Location	Total cation exchange ($cmol^{(+)}/kg$)	Ash (%)
LD2-3	Mae Moh 2	44.18	41.36
LD3-2	Mae Moh 3	44.27	41.34
LD4-2	Chiang Muan 2	52.84	35.76
LD8-1	Lee2	89.63	64.79
LD8-3	Lee2	94.16	73.50

4.3.3. Elemental analysis of minerals by X-ray diffraction (XRD)

The mineral compositition analysis by X-ray diffraction (XRD) showed that all the samples mainly consisted of Silica (Si) group (quartz), Feldspar group (albite and brushite) and also clay minerals (kaolinite, illite, niter and montmorillonite). (Table 4.3, Fig. 4.1). Our results were consistent with those of Chammui who found that the XRD pattern of leonardite indicated the presence of clay minerals (e.g. montmorillonite), and other minerals, i.e. gypsum, pyrite and quartz.

The results showed that LD2-3 contained Quartz, albite, brushite, kaolinite and illite (Table 4.3, Fig. 4.1) . The chemical composition of these minerals are as follows;

Quartz = SiO_2
Albite = $Na(AlSi_3O_8)$
Brushite = $CaPO_3(OH) \cdot 2H_2O$
Kaolinite = $Al_4(OH)_8(Si_4O_{10})$
Illite = $K(AlFe)_2AlSi_3O_{10}(OH)_2 \cdot H_2O)$

The results showed that LD3-2 contained the element of the mineral Quartz, brushite, kaolinite and illite (Table 4.3, Fig. 4.2). The chemical formulas of these mineral are as followings;

Quartz = SiO_2
Brushite = $CaPO_3(OH) \bullet 2H_2O$
Kaolinite = $Al_4(OH)_8(Si_4O_{10})$
Illite = $K(AlFe)_2AlSi_3O_{10}(OH)_2 \bullet H_2O)$

The results showed that LD4-2 contained the element of the mineral Quartz, brushite, kaolinite, illite and montmrillonite (Table 4.3, Fig. 4.3). The chemical formulas of these mineral are as followings;

Quartz = SiO_2
Brushite = $CaPO_3(OH) \bullet 2H_2O$
Kaolinite = $Al_4(OH)_8(Si_4O_{10})$
Illite = $K(AlFe)_2AlSi_3O_{10}(OH)_2 \bullet H2O)$
Montmrillonite = $3MgO \bullet 4SiO_2 \bullet H_2O$

The results showed that LD8-1 contained the element of the mineral Quartz, brushite and niter (Table 4.3, Fig. 4.4). The chemical formulas of these mineral are as followings;

Quartz = SiO_2
Brushite = $CaPO_3(OH) \bullet 2H_2O$
Niter = KNO_3

The results showed that LD8-3 contained the element of the mineral Quartz, brushite, illite and niter (Table 4.3, Fig. 4.5). The chemical formulas of these mineral are as followings;

Quartz = SiO_2
Brushite = $CaPO_3(OH) \bullet 2H_2O$
Illite = $K(AlFe)_2AlSi_3O_{10}(OH)_2 \bullet H2O)$
Niter = KNO_3

Table 4.3 Mineral composition of leonardite examined by XRD analysis

Sample code	Location	Mineral composition [1]
LD 2-3	Mae Moh 2	Quartz, albite, brushite, kaolinite and illite
LD3-2	Mae Moh 3	Quartz, brushite, kaolinite and illite
LD4-2	Chiang Muan 2	Quartz, brushite, kaolinite, illite and montmrillonite
LD8-1	Lee2	Quartz, brushite and niter
LD8-3	Lee2	Quartz, brushite, illite and niter

[1] Quartz = SiO_2, albite = $Na(AlSi_3O_8)$, brushite=$CaPO_3(OH)\bullet 2H_2O$, kaolinite =$Al_4(OH)_8(Si_4O_{10})$, illite = $K(AlFe)2AlSi_3O_{10}(OH)_2\bullet H_2O)$, montmrillonite = $3MgO \bullet 4SiO_2\bullet H_2O$ and niter = KNO_3

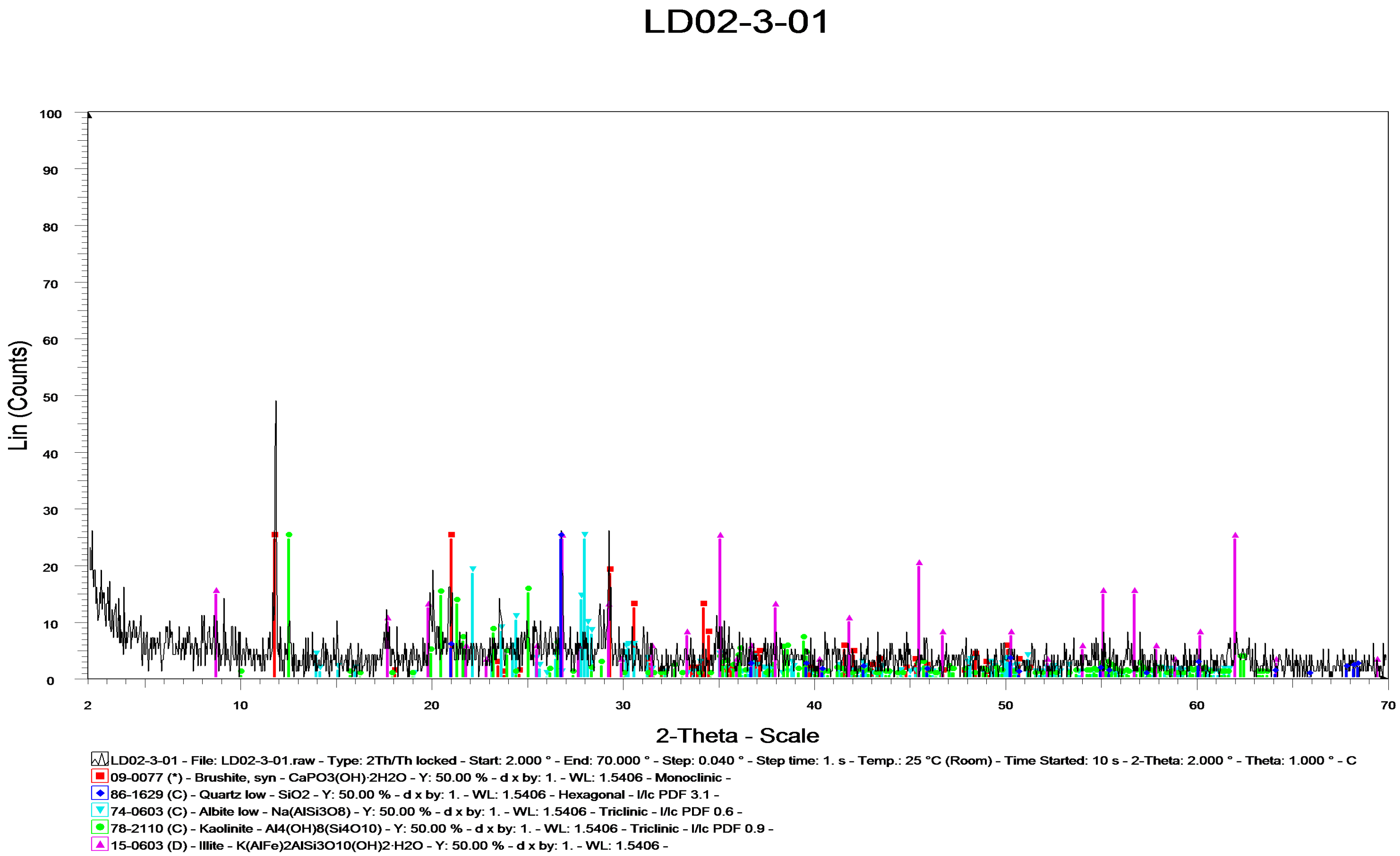

Figure 4.1 X-Ray diffraction patterns of leonardite samples: LD 2-3 (Mae Moh 2)

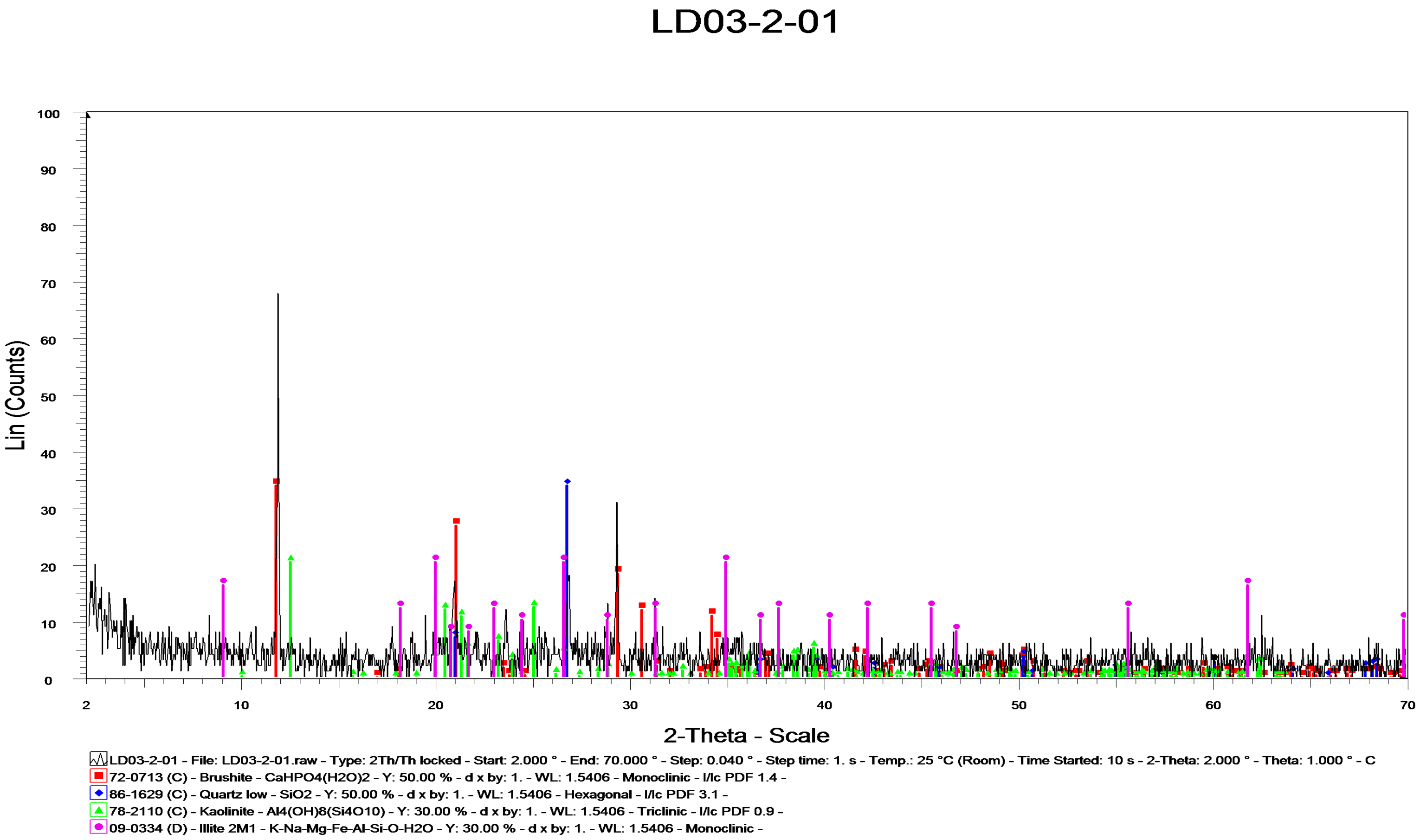

Figure 4.2 X-Ray diffraction patterns of leonardite samples: LD3-2 (Mae Moh 3)

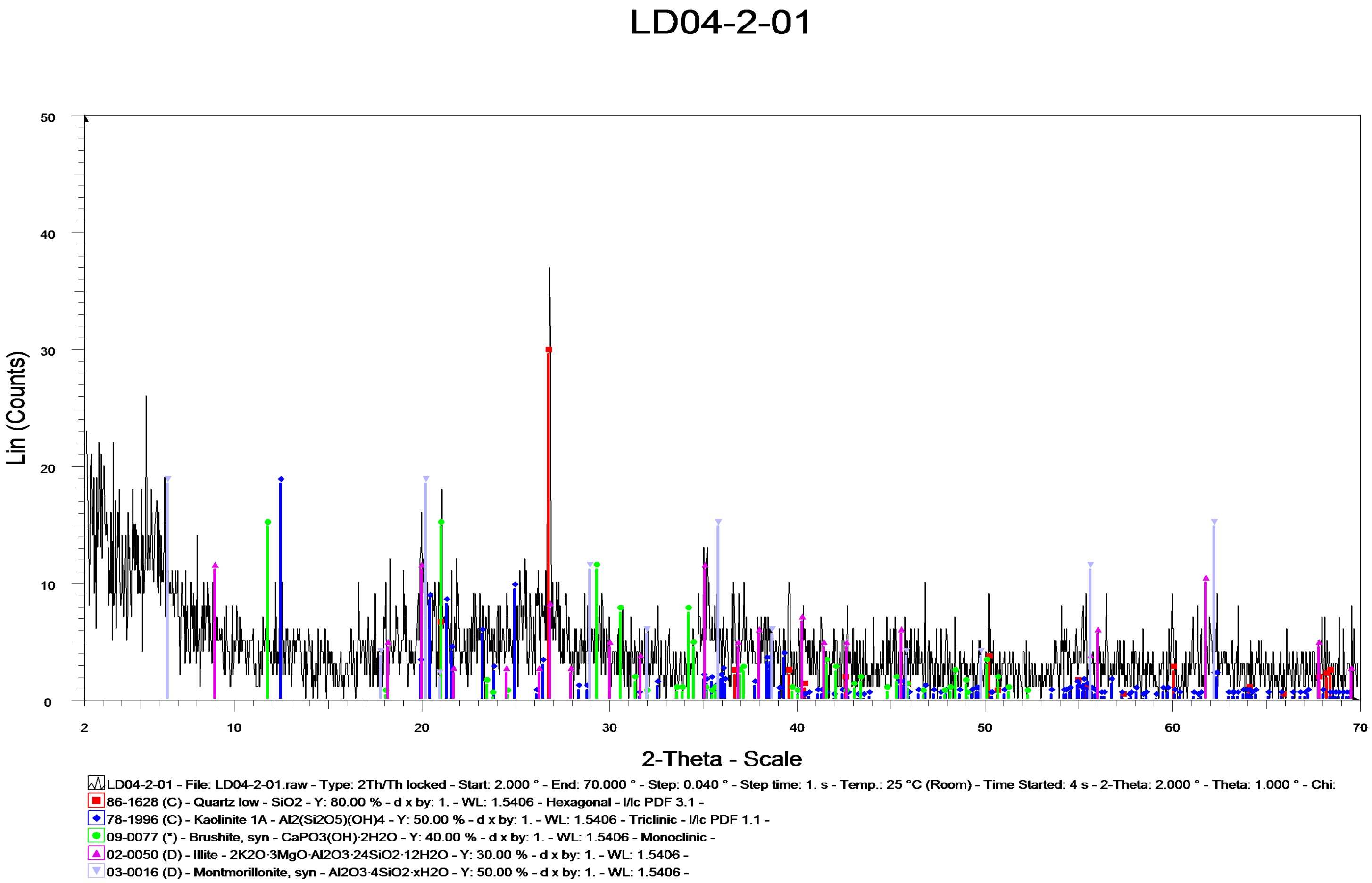

Figure 4.3 X-Ray diffraction patterns of leonardite samples:LD4-2 (Chiang Muan2)

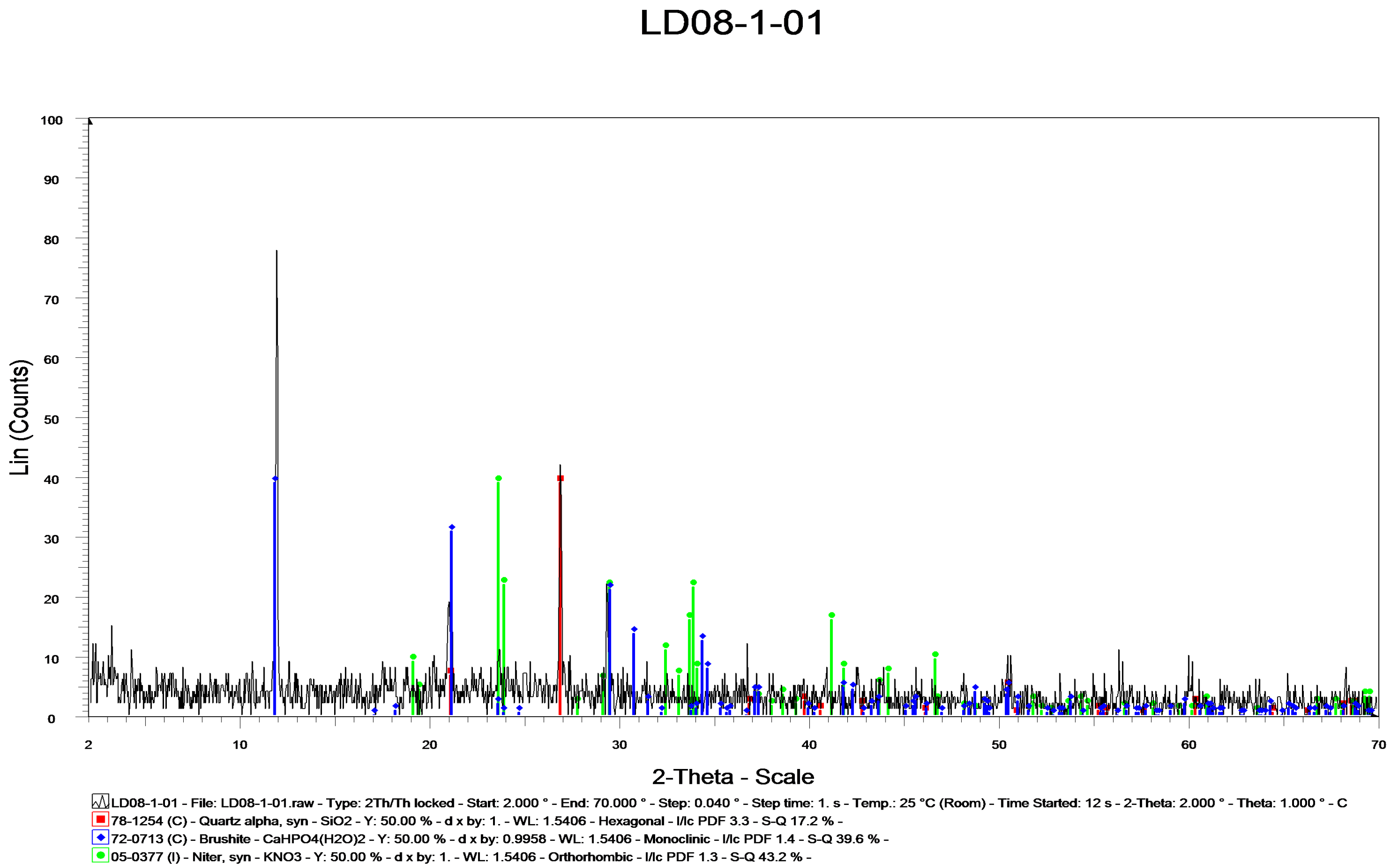

Figure 4.4 X-Ray diffraction patterns of leonardite samples:LD8-1 (Lee 1)

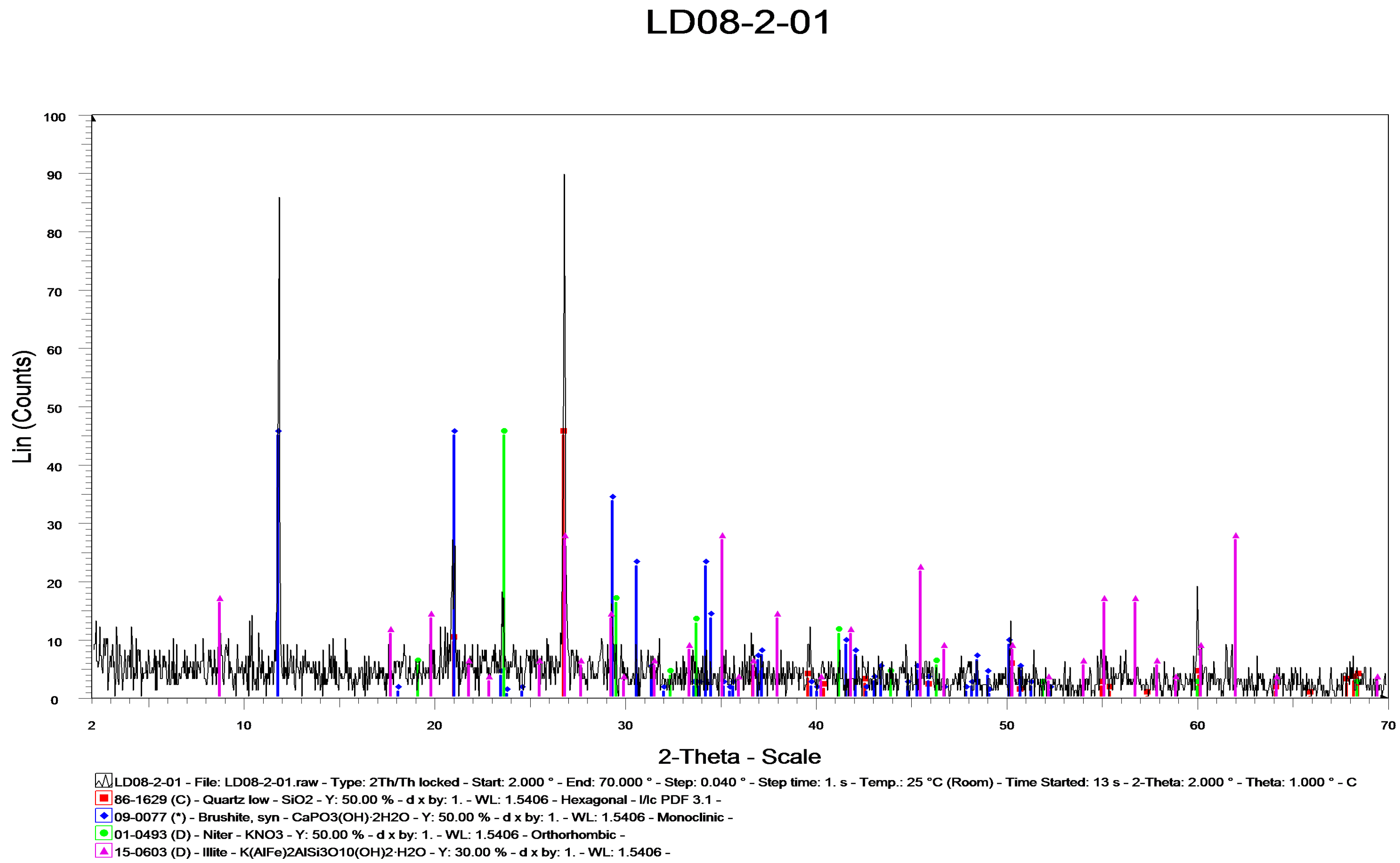

Figure 4.5 X-Ray diffraction patterns of leonardite samples:LD8-3 (Lee 2)

4.3.4. The analysis of the elemental content of leonardite by X-ray fluorescence spectrometry (XRF)

The analysis of the elemental content by X-ray fluorescence spectrometry (XRF) indicated that the leonardite samples consisted of various elements: Al, Fe, K, Mg, Mn, Na ,P, Si, Ti, Ca, Ba, Pb and Rb. The results showed that LD 2-3 contained Al_2O_3, total iron (Fe_2O_3), K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2 and CaO; and the values were 12.836, 4.741, 2.915, 1.111, 0.01, 1.233 1.182, 35.241, 0.505 and 3.717 %wt., respectively (Table 4.4).

Leonardite sample LD 3-2 contained Al_2O_3, total iron (Fe_2O_3), K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2, CaO and PbO; and the values were 8.785, 9.261,3.644 , 0.733, 0.015,0.402 , 2.872,35.146 ,0.418 , 5.829, 0.721 %wt., respectively. LD 4-2 contained of Al_2O_3, total Iron (Fe_2O_3), K_2O, MgO, Na_2O, P_2O_5, SiO_2, TiO_2 and CaO; and the values were 14.612 ,2.861 , 2.260, 1.684, 0.215, 1.111, 48.300, 0.589 and 2.308%wt., respectively (Table 4.4).

LD 8-1 contained Al_2O_3, Total Iron (Fe_2O_3), K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2 and CaO; and the values were 3.720, 4.802,1.232, 0.200, 0.013, 1.718, 0.591, 16.420, 0.342 and 4.169 %wt., respectively.

LD 8-1 contained Al_2O_3, Total Iron (Fe_2O_3), K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2, CaO and PbO; and the values were 4.939, 6.556, 2.033,0.312 , 0.011, 0.207,0.652 , 23.413,0.382 ,4.348 , %wt., respectively.

Table 4.4 Elemental analysis of leonardite samples by X-ray fluorescence spectrometry

Compound	Sample code				
(wt%)	LD2-3	LD3-2	LD4-2	LD8-1	LD8-3
Al_2O_3	12.836	8.785	14.612	3.720	4.939
Fe_2O_3	4.741	9.261	2.861	4.802	6.556
K_2O	2.915	3.644	2.260	1.232	2.033
MgO	1.111	0.733	1.684	0.200	0.312
MnO	<0.01	0.015	<0.01	0.013	0.011
Na_2O	1.233	0.402	0.215	1.718	0.207
P_2O_5	1.182	2.872	1.111	0.591	0.652
SiO_2	35.241	35.146	48.300	16.420	23.413
TiO_2	0.505	0.418	0.589	0.342	0.382
CaO	3.717	5.829	2.308	4.169	4.348
PbO	nd	0.721	nd	nd	nd
Rb_2O	nd	nd	nd	nd	nd
BaO	<0.01	<0.01	<0.01	nd	nd
SO_3+Loss on Ignition (LOI)	36.56	32.56	26.41	66.79	57.10
Total	100.04	100.39	100.35	99.99	99.95

nd = Not Detectable

In general, the element Si was the most abundant element, 16.42-48.30% by weight (Table 4.4). This was consistent with XRD analysis (Table 4.3) that showed that quartz (SiO_2) was the most abundant mineral in leonardite.

On average, the elements Al and Fe seemed to be the next highest after Si. Their values ranged from 3.720 to 14.612 and 2.861 to 9.261 %wt., respectively. As a result, when the dissolution of leonardite takes place, the pH of the material was extremely acidic. This was due to the release of hydrogen ions (H^+) by Al, which is the most important acid cation in acid soil (Paiboon, 2546). The reaction is as follows:

$$Al^{3+}\,(aq) + H_2O(l) \longleftrightarrow Al(OH)^{2+}\,(aq) + H^+(aq)$$

The content of potassium (K_2O) ranged from 1.232 to 3.644 %wt. The results were in accordance with Alfredo *et al.*, (2005) and Halil *et al.*, (2011) They reported the concentration of K in leonardite to be 0.51 and 3.97 (%K), respectively. The potassium (K) content in leonardite was higher than the standard values of organic fertilizer (DOA, 2005). The total P values of all our leonardite samples were 0.591-2.872%. The results were in accordance with all the previous reports of P concentration in leonardite (Arif *et al.,* 2013; Halil *et al.* 2011; Ali *et al.,* 2007; Alfredo *et al.,* 2005 and John *et al.,*1998).

The pH values of the soil mixed with leonardite should be measured prior to crop cultivation since the Fe content in leonardite was quite high and might be toxic to the plant at a low pH due to high solubility of all trace elements.

The values of Ca and Mg were also at good levels to be used as soil amendments although the Mg content in LD8-1 and LD8-3 was the lowest among selected leonardite samples. It was interesting to note that the Lead (Pb) content in all the samples could not be detected, thus making it possible to introduce leonardite application in agriculture without toxicity from the heavy metal lead.

4.3.5. Structural Characterization of leonardite by SEM (Scanning Electron Microscope).

An examination of the structural characteristics of leonardite was performed by SEM. The surface appearance, size and shape of leonardite powder is shown in Fig. 4.6 to 4.10.

The SEM shows the surface characteristics of the material, size and shape of the powder particles.

The structural characteristics of leonardite by SEM (scanning electron microscope). The images showed that the surface leonardite consisted of a thin, flat sheet of splice overlaps as shown in Fig. 4.6 to 4.10.

The leonardite sample, LD4-2 was assumed to be contaminated by soil. Thus, as shown in Fig 4.8, the overlay of the flat sheet seemed to be tighter than leonardite from other sources. However, the overall appearances of leonardite from the various sources are very similar. It would be of interest to study in depth by higher magnification of electron microscopy SEM or other equipment which allow us to figure out more details of leonardite specimens.

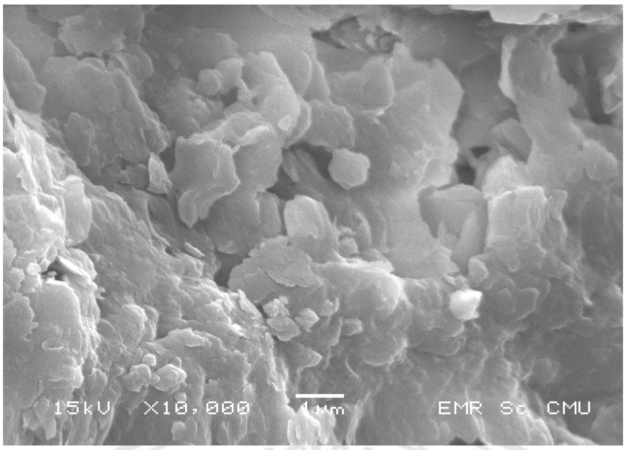

Figure 4.6 SEM images of leonardite samples: LD 2-3: Mae Moh 2

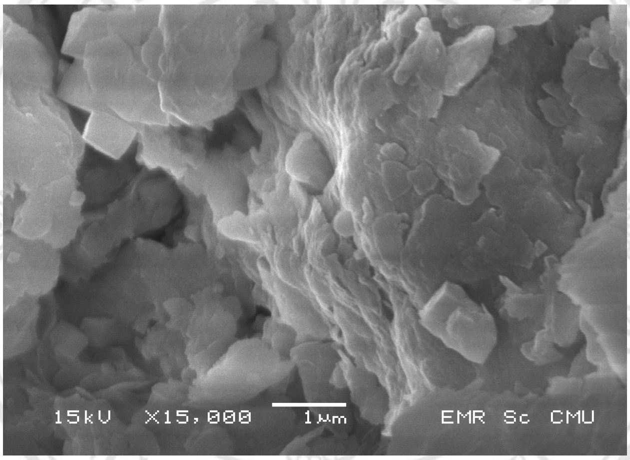

Figure 4.7 SEM images of leonardite samples: LD3-2: Mae Moh 3

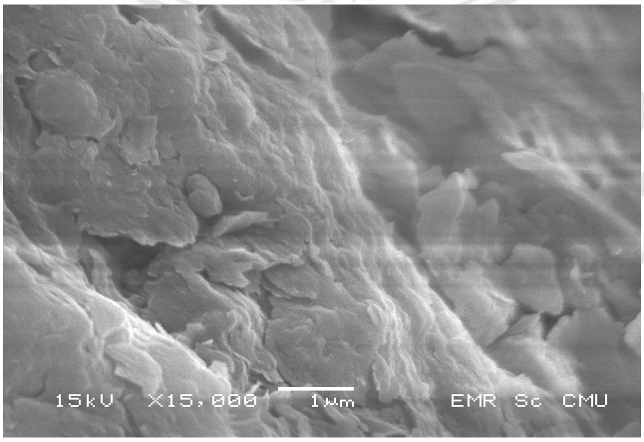

Figure 4.8 SEM images of leonardite samples: LD4-2: Chiang Muan2

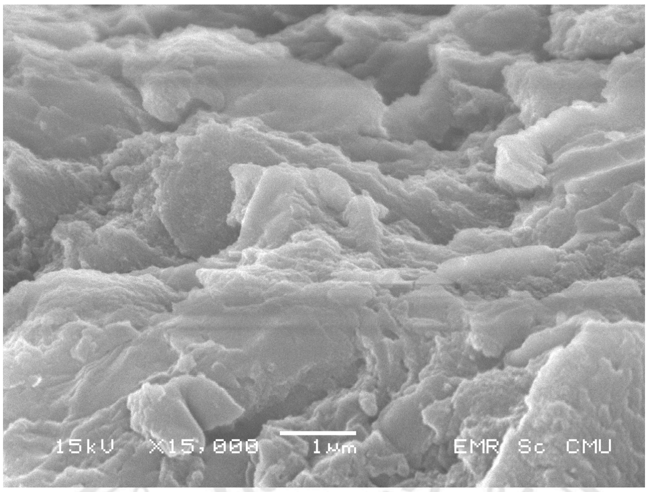

Figure 4.9 SEM images of leonardite samples: LD8-1: Lee 2

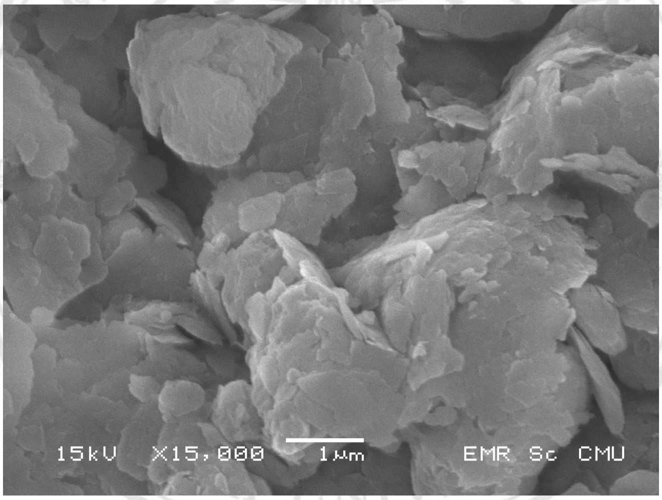

Figure 4.10 SEM images of leonardite samples: LD8-3: Lee 2

Elemental analysis of leonardite samples by SEM (Fig. 4.11 to 4.15) were in accordance with experimental studies of chemical elementary, the elements Al and Fe values ranged from 1.27 to 13.70 and 0.34 to 13.70%wt., respectively (Table 4.6). The elements Al and Fe seemed to be the next highest after Si. As a result, when the dissolution of leonardite takes place, the pH of the material was extremely acidic. The values of Ca and Mg were quite low which confirm the acidic properties of loenardite. The heavy metals found in leonardite were As and Cd and the value ranged from -0.04 to 0.28 and -0.82 to 0.38 %wt., respectively. When applied, leonardite might be not toxic to the environment.

Table 4.5 Elemental analysis of leonardite samples by SEM (Scanning Electron Microscope)

Element	LD2-3		LD3-2		LD4-2		LD8-1		LD8-3	
	Weight %	Atomic %	Weigh t%	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
B K	12.47	17.37	6.45	11.02	34.73	46.27	24.36	33.32	27.05	37.95
C K	20.93	26.24	-5.21	-8.01	0.93	1.11	14.32	17.64	12.90	16.28
N K	8.66	9.30	9.73	12.81	7.23	7.43	6.99	7.38	6.53	7.07
O K	40.64	38.25	54.29	62.62	39.19	35.28	35.55	32.86	33.04	31.32
Mg K	0.49	0.30	0.95	0.72	0.50	0.30	-0.01	-0.01	0.05	0.03
Al K	5.04	2.81	8.98	6.14	7.45	3.97	0.57	0.31	0.34	0.19
Si K	6.60	3.54	13.89	9.13	10.92	5.60	1.28	0.68	0.35	0.19
P K	-0.69	-0.34	-1.39	-0.83	-0.92	-0.43	-1.35	-0.64	-0.50	-0.25
S K	2.92	1.37	5.19	2.98	0.18	0.08	9.96	4.59	7.57	3.58
K K	0.78	0.30	1.49	0.71	0.61	0.23	0.08	0.03	0.07	0.03
Ca K	0.20	0.08	4.04	1.86	0.47	0.17	10.49	3.87	0.11	0.04
Mn K	0.00	0.00	0.02	0.01	-0.15	-0.04	-0.10	-0.03	0.05	0.01
Fe K	2.75	0.74	3.34	1.10	1.83	0.47	1.27	0.34	13.70	3.72
Ni K	-0.16	-0.04	0.03	0.01	-0.07	-0.02	0.47	0.12	-0.26	-0.07
Cu K	1.24	0.29	0.54	0.16	0.22	0.05	2.03	0.47	1.03	0.25
Zn L	1.02	0.23	0.47	0.13	0.06	0.01	-0.40	-0.09	-0.25	-0.06
As L	0.19	0.04	-0.74	-0.18	-0.04	-0.01	0.28	0.06	-0.06	-0.01
Mo L	-3.44	-0.54	-1.26	-0.24	-3.51	-0.53	-5.63	-0.87	-1.81	-0.29
Cd L	0.38	0.05	-0.82	-0.13	0.38	0.05	-0.17	-0.02	0.09	0.01
Totals	100		100		100		100		100	

Standard; B: B, C: CaCO3, N: Not defined, O: SiO2, Mg: MgO, Al: Al2O3, Si : SiO2, P: GaP, S: FeS2, K: MAD, Ca: Wollastonite, Mn: Mn, Fe: Fe, Ni : Ni, Cu: Cu, Zn : Zn, As : InAs, Mo : Mo and Cd: Cd (1-Jun-1999 12:00 AM)

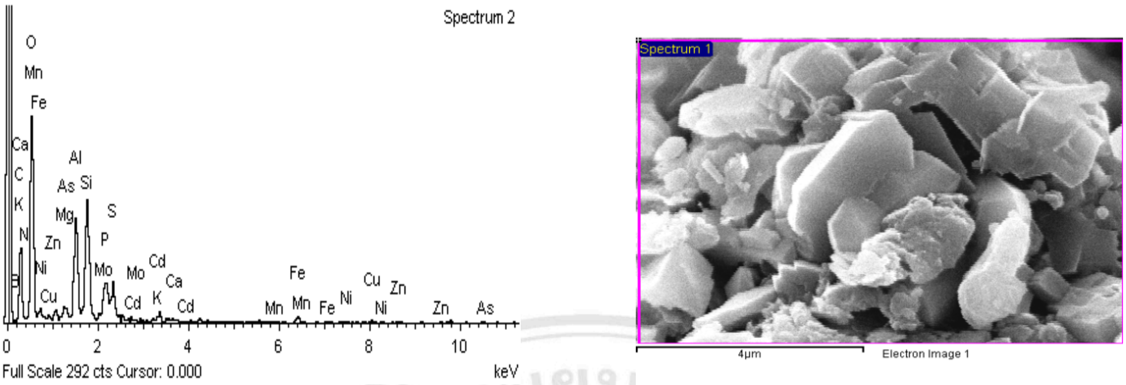

Figure 4.11: Elemental analysis of leonardite samples : LD2-3 (Mae Moh 2) by SEM

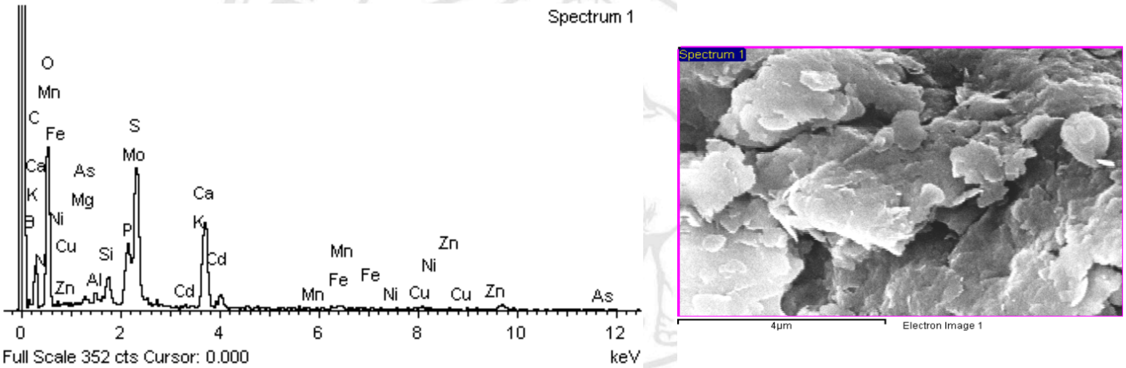

Figure 4.12: Elemental analysis of leonardite samples : LD3-2 (Mae Moh 3) by SEM

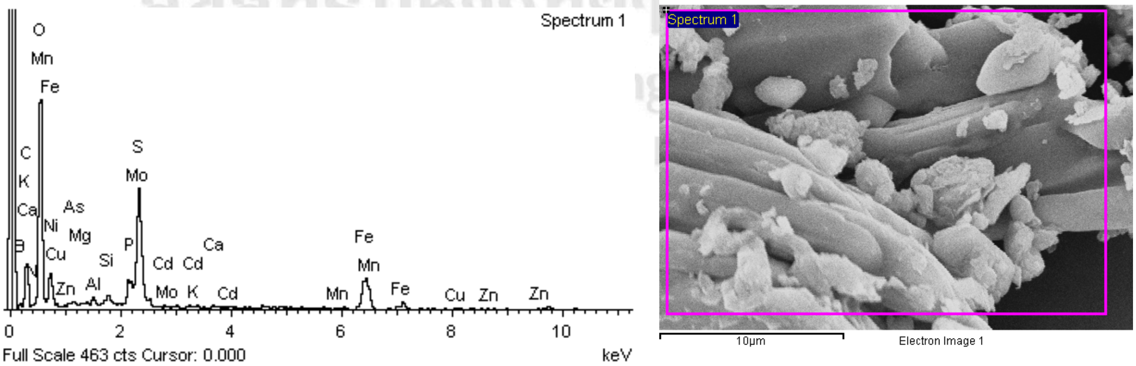

Figure 4.13: Elemental analysis of leonardite samples: LD4-2 (Chiang Muan 2) by SEM

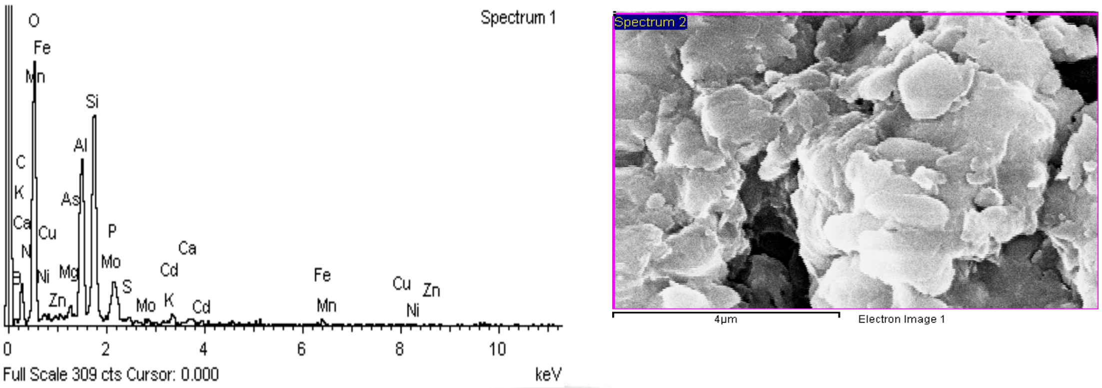

Figure 4.14: Elemental analysis of leonardite samples : LD8-1 (Lee 2) by SEM

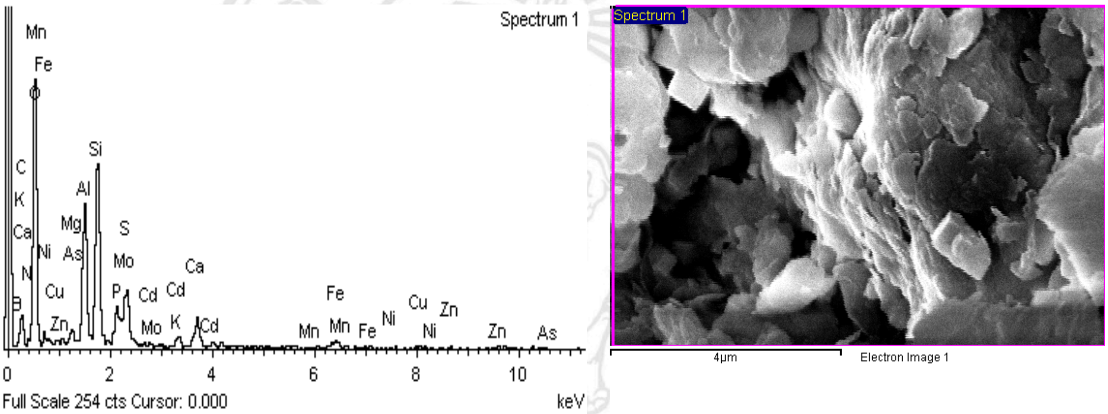

Figure 4.15: Elemental analysis of leonardite samples : LD8-3 (Lee 2) by SEM

4.4 Conclusion

The pH values of all leonardite samples were very low (1.84–2.44) except for that of LD4-2 (5.63). Leonardite from Lee; LD8-3 and LD8-1 gave the highest humic acid content with the value of 85.05 and 72.44%, respectively. The OM and of these two samples was also very high compared to the rest of the selected samples (61.02 and 53.96%, respectively).

In the present study, characterization of leonardite samples from various deposits in northern Thailand was performed using X-ray and SEM techniques. Leonardite from Lee; LD8-3 and LD8-1 gave the highest humic acid content with values of 85.05 and 72.44%, respectively. The OM and C/N ratio of these two samples were also very high compared to the rest of the selected samples. X-ray diffraction (XRD) analysis showed that all the samples mainly consist of Quartz. The analysis of leonardite mineral composition by X-ray diffraction (XRD) showed that all the samples mainly consist of Silica group (quartz), Feldspar group (albite and brushite) and also clay minerals of (kaolinite, illite and montmorillinite). The samples also contained niter which is a source of nitrogen.

The elemental analysis by XRF indicated that the leonardite samples consisted of various elements: Si, Al, K, Fe, Mg, Mn, P, Na, Ca and Ti. The element Si is the most abundant element (16.42-48.30%). This was consistent with XRD analysis which showed that the quartz (SiO_2) was the mineral in greatest amount in leonardite. On average, the elements Al and Fe seemed to be the next highest after Si. The value of potassium (%K_2O) ranged from 1.232 to 3.644 % wt. The pH values of the soil mixed with leonardite should be measured prior to crop cultivation since the Fe content in leonardite was quite high and might be toxic to the plant at a low pH due to high solubility of all trace elements. The levels of Ca and Mg were also high enough for use as soil amendment, although the Mg content in LD8-1 and LD8-3 was the lowest among the selected leonardite samples. It was interesting to note that lead (Pb) could not be detected in any of the samples. Thus making it possible to introduce leonardite application in agriculture without toxicity.