CHAPTER- IV

CHEMICAL ANALYSIS RESULTS AND DISCUSSION

4.1 INTRODUCTION

The chemical analysis characterizes the chemical components of the geomaterials in addition to identifying its major and minor elements as well as any unknown trace elements. It is necessary to identify the chemical components of soil since they have a significant influence on the strength characteristics of the soil. The elemental and mineralogical components of the stabilizing agents contribute to the evaluation of its pozzolanic, self-hardening, or chemical reactivity. A detailed understanding of the underlying mechanism of the strength enhancement is necessary to assess the material's potential as a stabilizing agent. Therefore, the microstructure of both the treated and untreated clayey soil has been analysed using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-Ray fluorescence (XRF), and Fourier transform infrared (FTIR) spectroscopy. The purpose of these tests is to determine the phases and morphological alterations brought about by cementitious development of the composite combination of fly ash and nano-silica in the clay soil. The chemical composition of the fly ash, nano-silica, and soil was determined by performing the analysis given in the following sections.

a) Scanning Electron Microscopy (SEM) Analysis

b) Energy Dispersive X-Ray Spectroscopy (EDS) Analysis

c) X-Ray Diffraction (XRD) Analysis

d) X-Ray Fluorescence (XRF) Analysis

(e) Fourier Transform Infrared (FTIR) Spectroscopy Analysis

4.2 SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

The SEM analysis of soil, fly ash and nano silica was conducted using the ultra-high magnification (Field Emission Scanning Electron Microscopy) instrument manufactured by CARL ZEISS. The micro-level morphology of the fly ash was evaluated by utilizing a size range of 10 μm to 1 μm at different magnifications ranging from 1000x to 20000x. The nano silica was examined using a size range of 10 μm to 200 nm under various magnifications between 1000x and 1000000x in order to assess the micro level morphology. The micro level morphology of the soil was conducted with a size range of 20 μm to 200 nm at different magnifications between 500x and 100000x. Fig. 4.1. to Fig. 4.3. illustrate the SEM images of fly ash, nano - silica and soil at different magnifications. As observed in Fig. 4.1, the fly ash exhibits a promising composition of glassy, spherical-sized particles along with a few coarse particles with irregular shapes. The appearance of these irregular shapes may have resulted from partial combustion that happened during the production process (Nath et al. 2016). The light weight of fly ash is attributed due to the spherical particles, which are commonly referred to as cenospheres and plerospheres. Cenospheres are hollow spherical particles with smooth surfaces and thin walls, while plerospheres are spheres with a small sphere inside of them (Chepaitis et al. 2011; Kumar et al. 2016). The total amount of minerals in the feed coal and the combustion procedure both affect the development of cenospheres during combustion (Ghosal and Self 1995; Goodarzi and

Hower 2008). The chemical and phase composition of the cenosphere, as well as physical characteristics including particle size, particle size distribution, and shell thickness, all have a significant impact on the cenosphere's performance in lightweight composites. As thicker shell particles offer greater strength than thinner ones, the thickness of cenosphere particles is crucial when the strength of the cenosphere-composites is necessary for the final application (Blanco et al. 2000).

The two most noticeable morphological features in fly ashes with low calcium content were plerospheres and cenospheres. The high calcium fly ash was found to contain iron particles, spherical particles with a calcium coating on their surface, and irregularly shaped clusters (Das and Yudhbir 2005). The fly ash of cenospheres type have excellent properties such as low bulk density, great workability, high heat resistance, and high strength, which make them suitable for a wide range of applications (Ranjbar and Kuenzel 2017).

From Fig. 4.2, it can be observed that nano silica exhibits a micro-sized cauliflower like porous structure. SEM allows for a wide range of magnification to reveal the characteristics of the soil microstructure. From Fig. 4.3, it can be observed that the soil consists of large number of pore spaces within the particles. It can be concluded that the soil does not include spherical particles like fly ash, but rather flaky, angular, and thin chipped particles. Better interlocking behaviour from these particle shapes aids in increasing the apparent cohesiveness and the angle of internal friction.

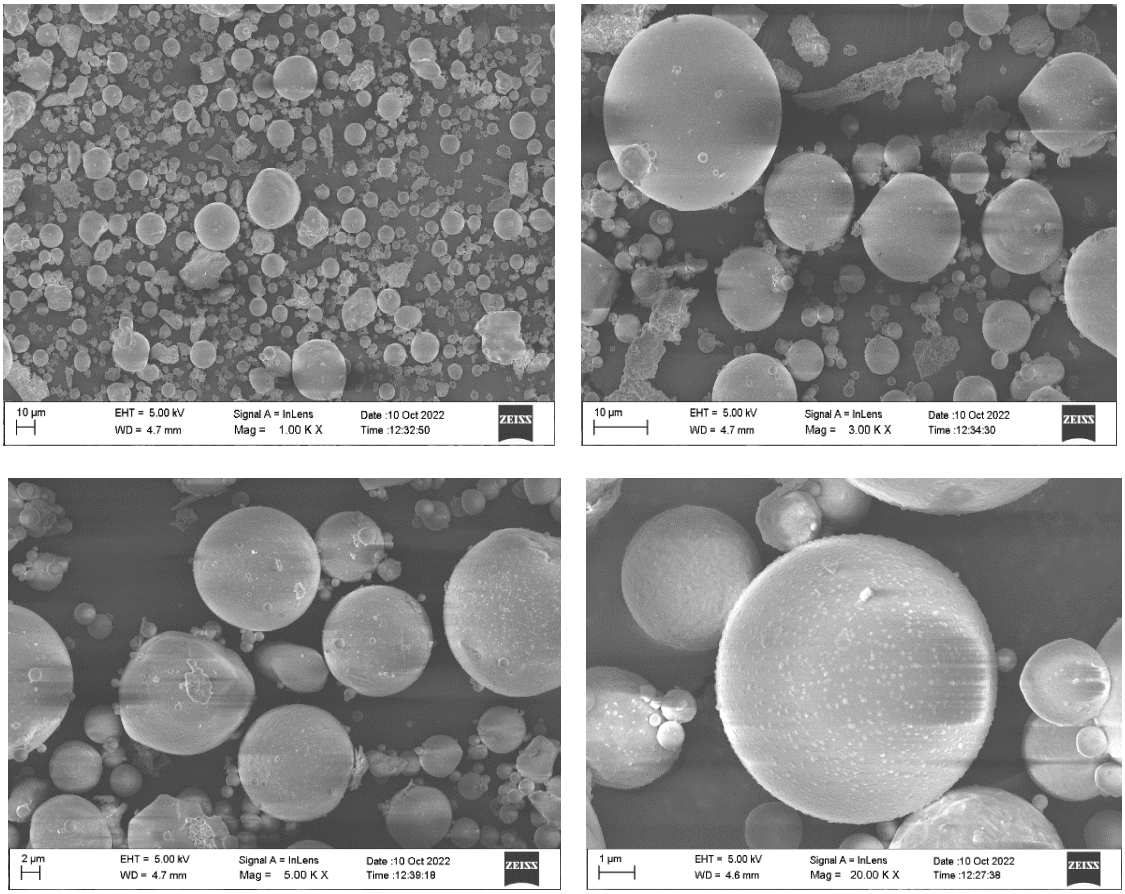


Fig. 4.1. SEM image of fly ash sample under different magnification.

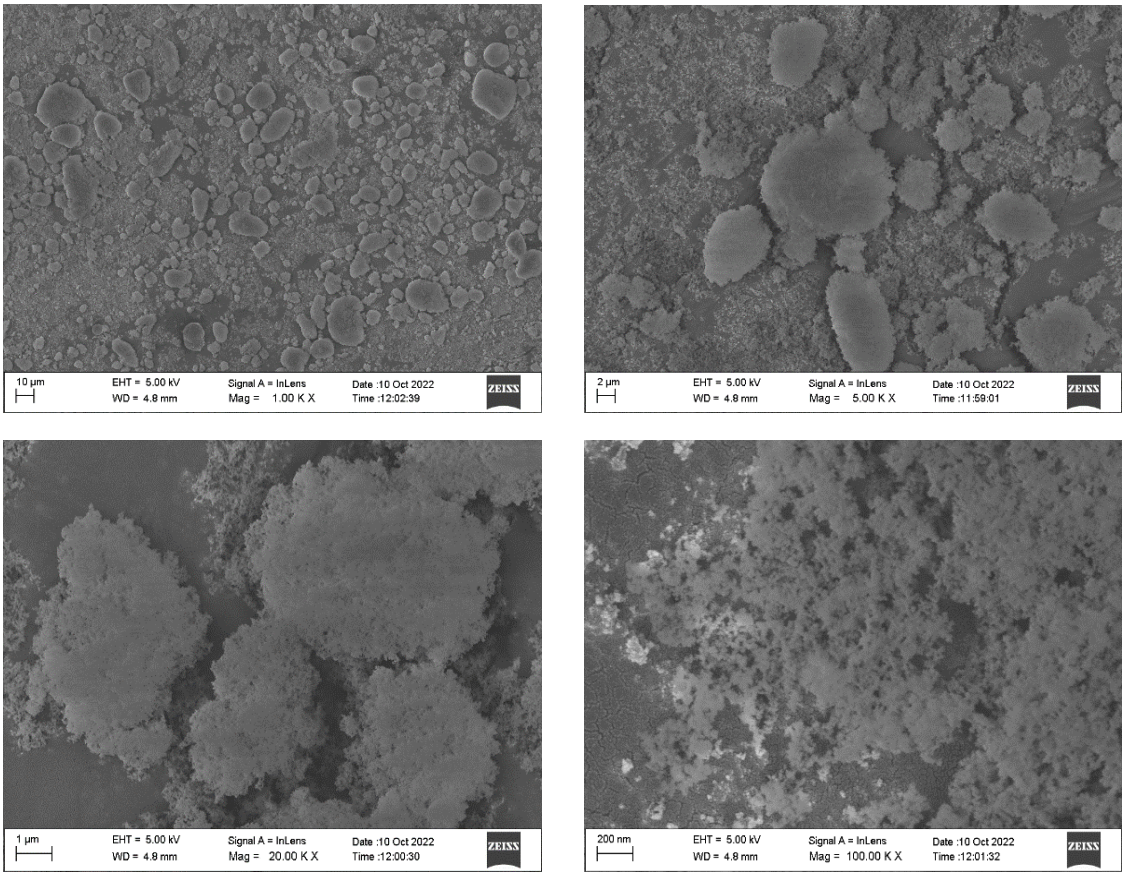


Fig. 4.2. SEM image of Nano Silica sample under different magnification.

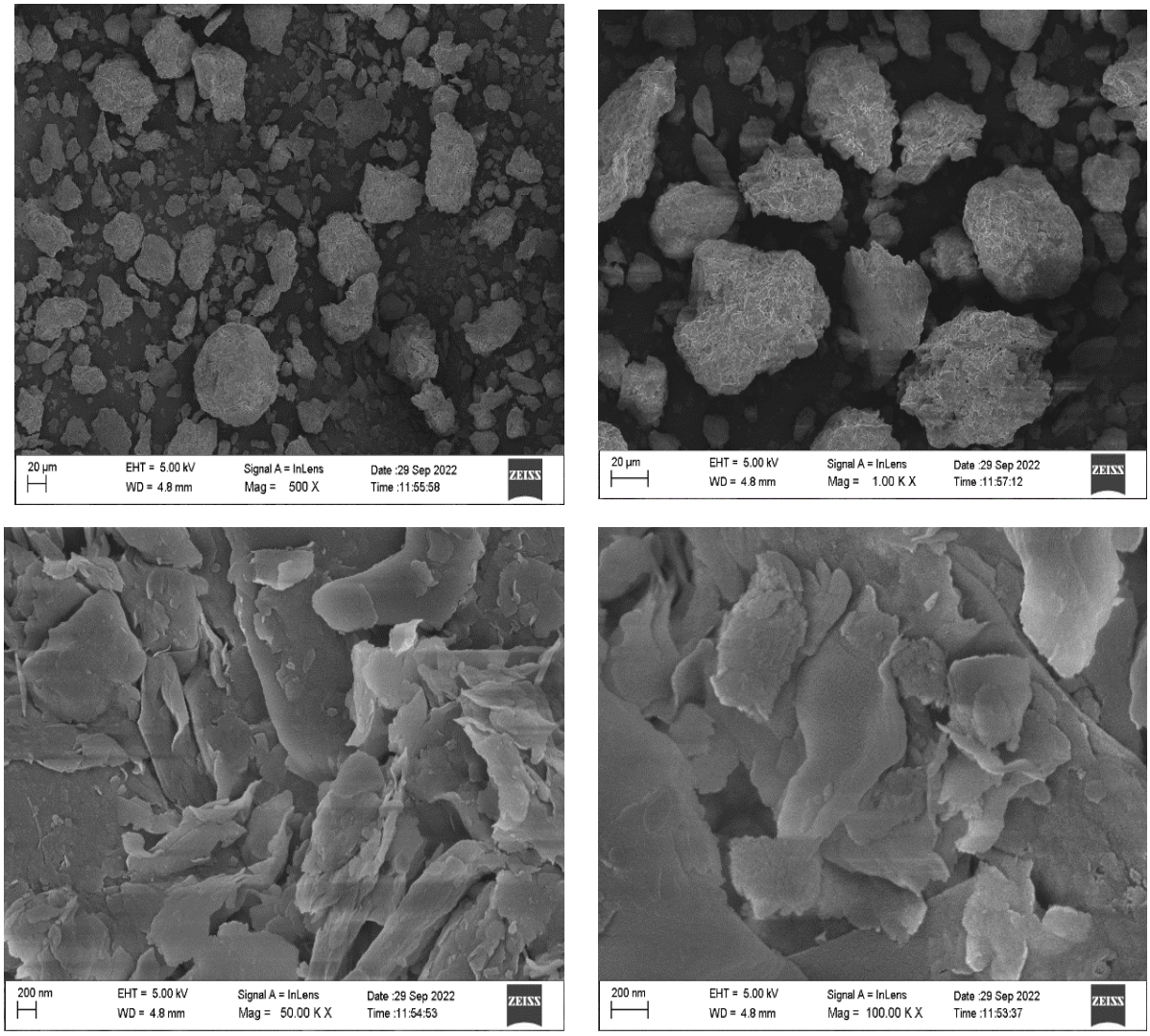


Fig. 4.3. SEM image of soil sample under different magnification.

The SEM micrograph analysis was also used to examine the microstructure of the specimen stabilized with 1% Nano-SiO_2, and the specimen stabilized with 1% Nano-SiO_2 and 20% fly ash. It was discovered that the parent soil consisted of some porous structure within the particles (Fig. 4.3). Fig. 4.4(a) depicts that cementitious (C-S-H) gel filled the void spaces between the particles significantly, resulting a stronger soil matrix. Fig. 4.4(b) demonstrates the microstructure of a specimen treated with the optimum amount of Nano-SiO_2 (1%) and fly ash content (20%). As the void spaces were filled with the calcium silicate hydrate (C-S-H) and calcium aluminate

silicate hydrate (C-A-S-H) gel formed by the cementitious and pozzolanic reactions between the particles and binding agents in the presence of water, resulting a denser soil matrix (Tastan et al. 2011). These cementitious and pozzolanic reactions result in the evolution of cementitious gel, which strengthens the weak soil.

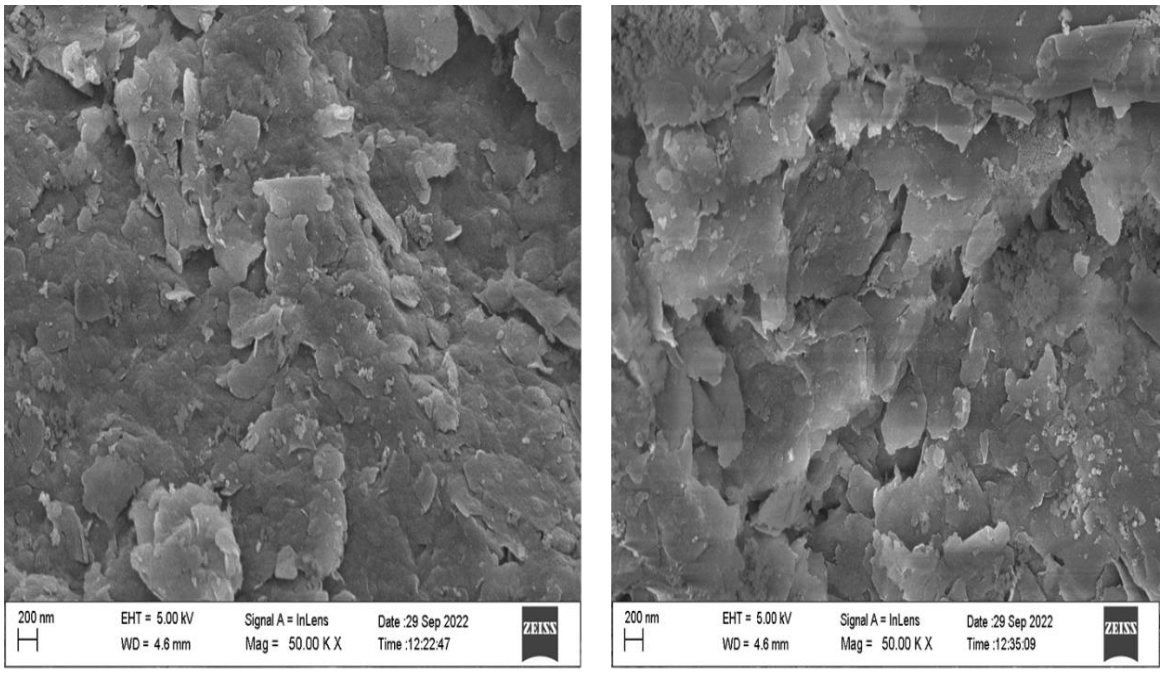


Fig. 4.4. SEM image of (a) Soil+1% NS and (b) Soil+1% NS+20% FA.

4.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDX) ANALYSIS

The EDX investigation was conducted in conjunction with the same equipment, i.e., field emission scanning electron microscope. The elemental details of the near-surface elements of a sample are provided, together with the overall spatial mapping inside the sample. Here, an energy dispersive spectrometer is used to collect the X-rays that the sample emits after it is exposed to a high energy electron beam. The X-ray energy that is produced gives information on the elemental features of the sample because it is a property of the atomic structure of the element from which it is emitted (Gupta et

al. 2020). The elemental analysis was conducted at several points of the sample in order to confirm the repeatability of different elements within the sample. The EDX graphs for fly ash (FA), Nano-SiO_2 (NS), source soil, soil+1% NS, and soil+1% NS+20% FA are displayed in Fig. 4.5 to Fig. 4.9 respectively. The EDX analysis identifies the chemical element in the specimen that is responsible for the strength improvement. The EDX results show that the fly ash had a variety of elemental compositions, including Si, Al, Fe, K, Mg, Na, and Ca when the data from various points were examined. The primary chemical elements of the fly ash are Si, Al, and Fe (Fig. 4.5). Similarly, the EDX results of the Nano-SiO_2 revealed the presence of the elemental compositions such as Si, Ca, Na, Ti, and Fe, with Si as the major constituents of the element (Fig. 4.6). Again, the EDX results for the soil showed the presence of various elemental compositions including O, Na, Mg, Al, Si, S, K, Ca, and Fe, with O, Si, Al, and Fe being the primary constituents (Fig. 4.7).

The EDX results of the soil stabilized with Nano-SiO2 revealed the presence of Si, Ca, Na, and Fe minerals, and the major component is Si (Fig. 4.8). According to the EDX results, the fly ash-treated soil contained Si, Al, Fe, Mg, and Ca minerals. The major chemical component present in the fly ash-treated soil are Si, Al, and Fe (Fig. 4.9). The EDX results of parent soil indicated the existence of O, Na, Mg, Al, Si, S, K, Ca, and Fe minerals, and the major compounds are O, Si, Al, and Fe (Fig. 4.7). As the chemical compound, CaO reacts with water, it will form Ca (OH)2 compound, and then Ca2+ and 2(OH)- ions are formed (dissociated from Ca (OH)2). Further, when Ca2+ and 2(OH)- ions react with SiO2 and Al2O3, (C-S-H) and (C-A-S-H) gels are formed. These cementitious gels manage to bind the soil particles together and create a denser soil matrix.

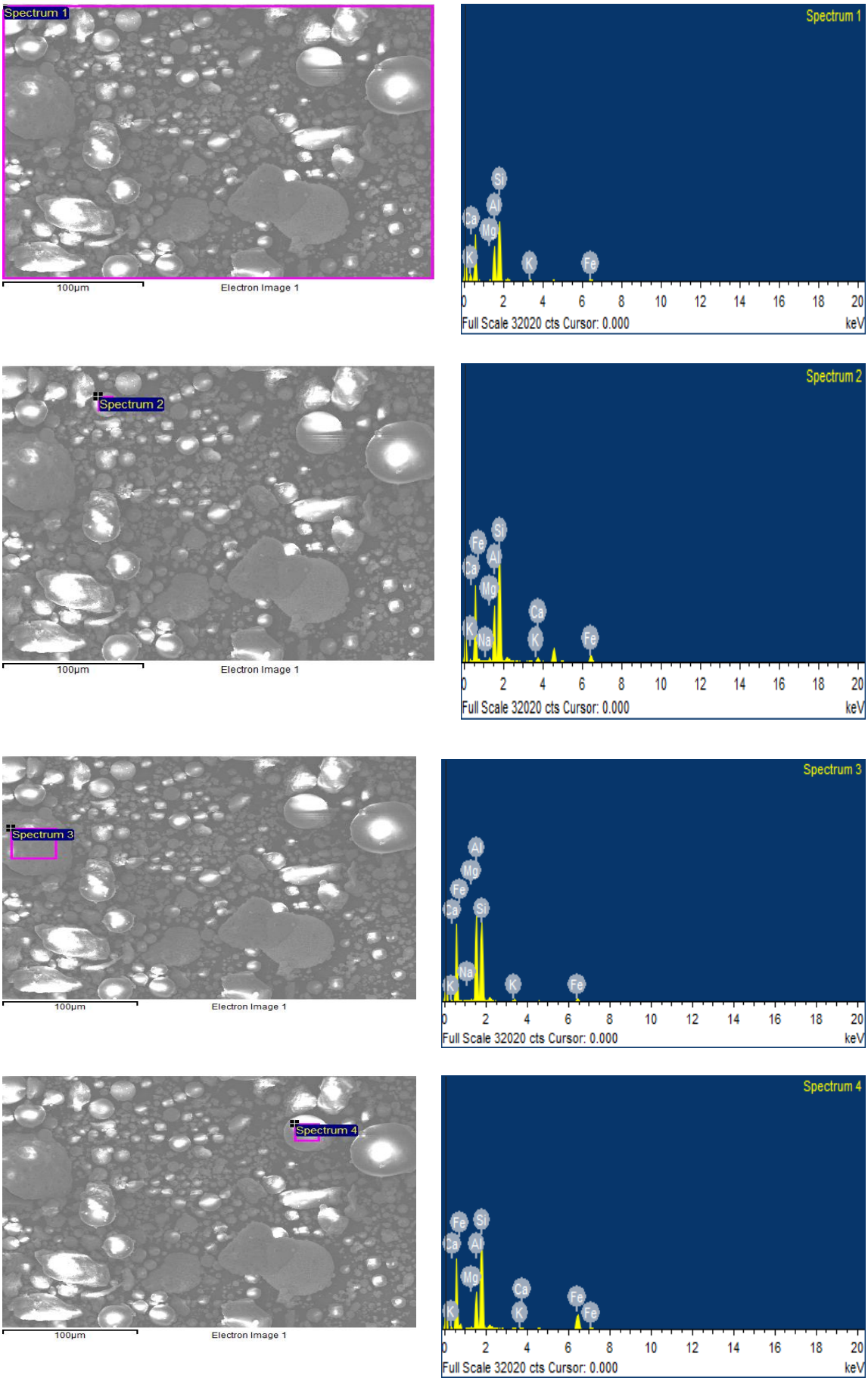


Fig. 4.5. EDX image of fly ash at four locations.

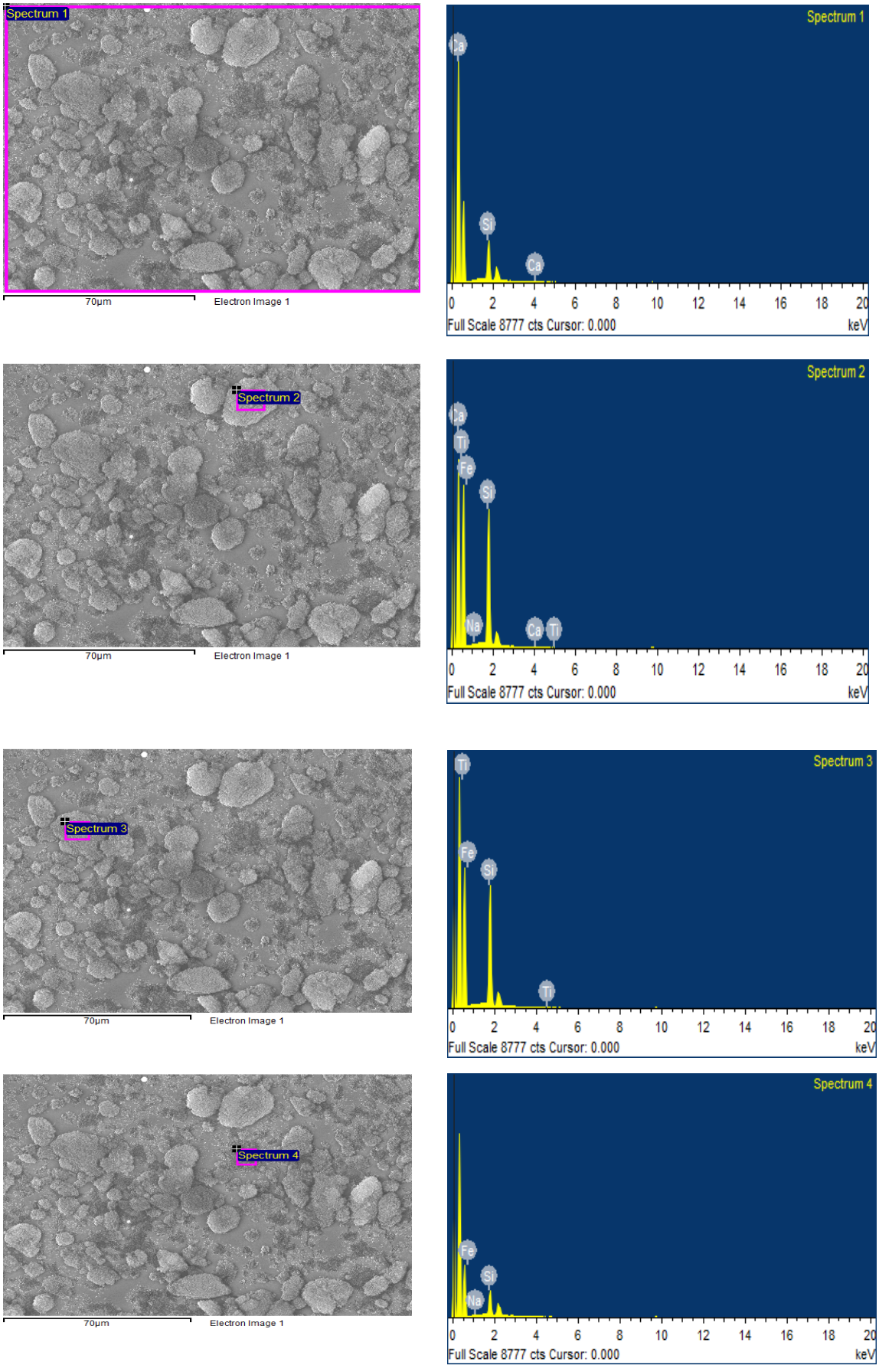


Fig. 4.6. EDX image of Nano-SiO_2 at four locations.

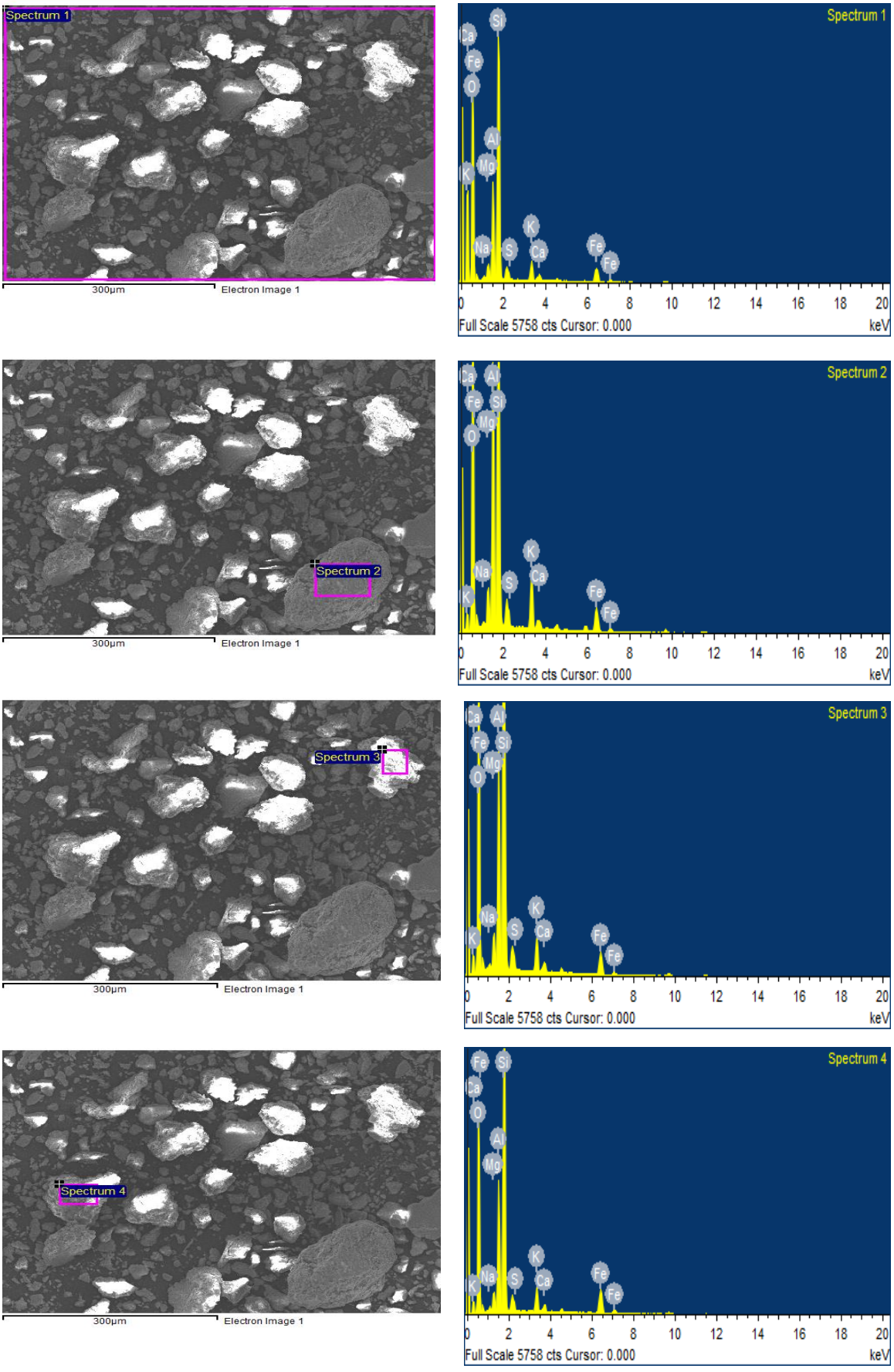


Fig. 4.7. EDX image of soil at four locations.

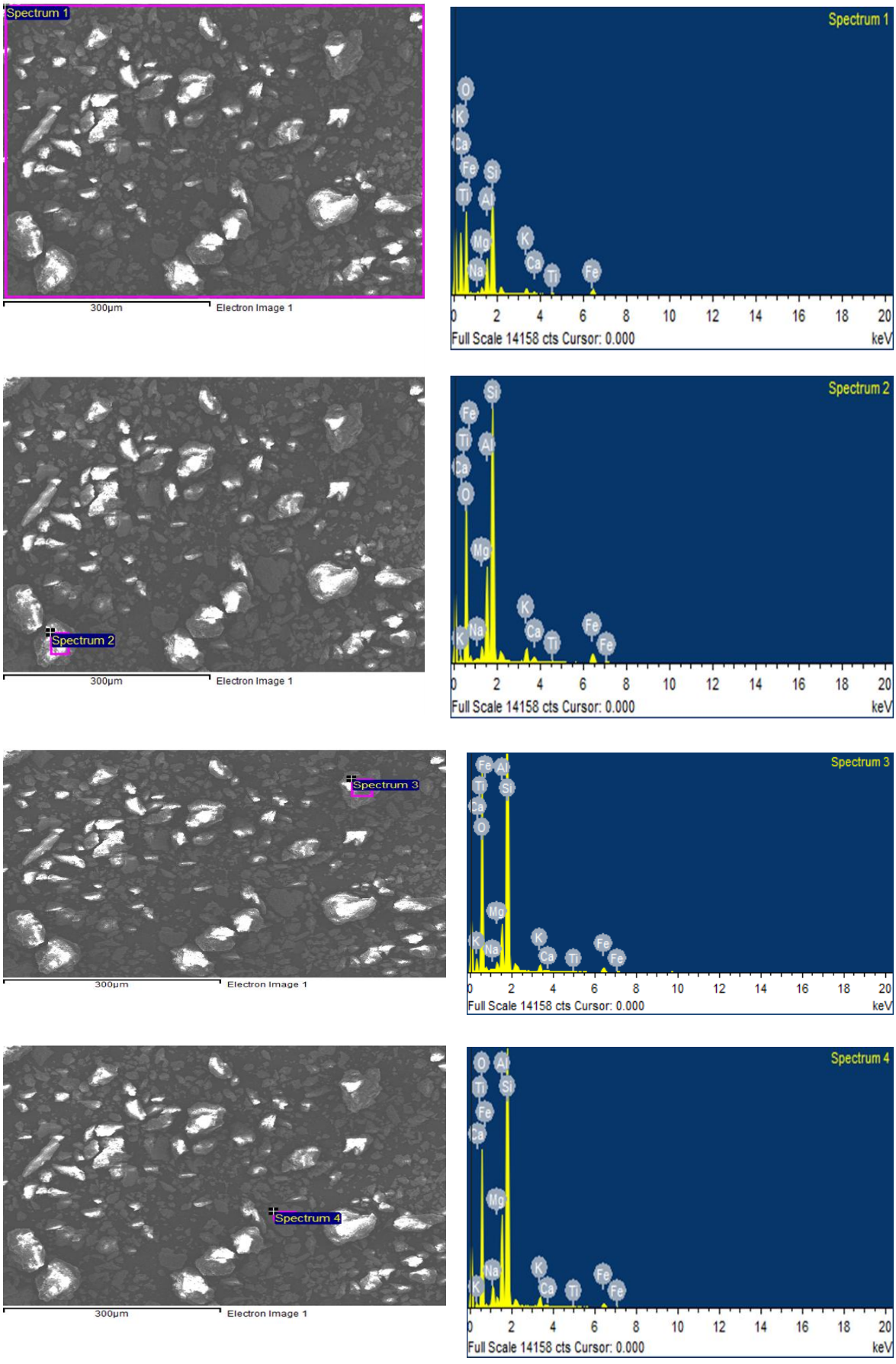


Fig. 4.8. EDX image of soil+ 1% NS at four locations.

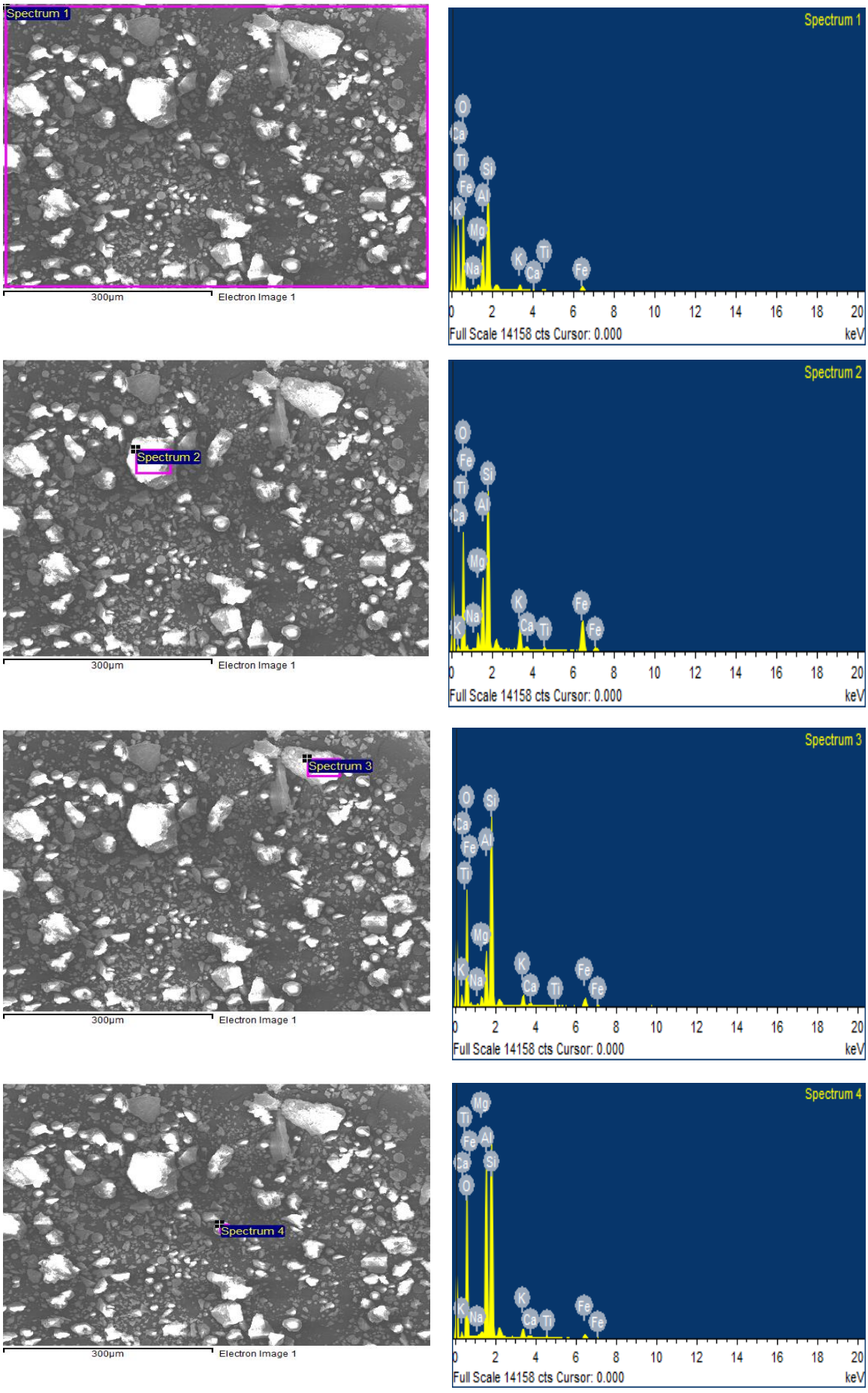
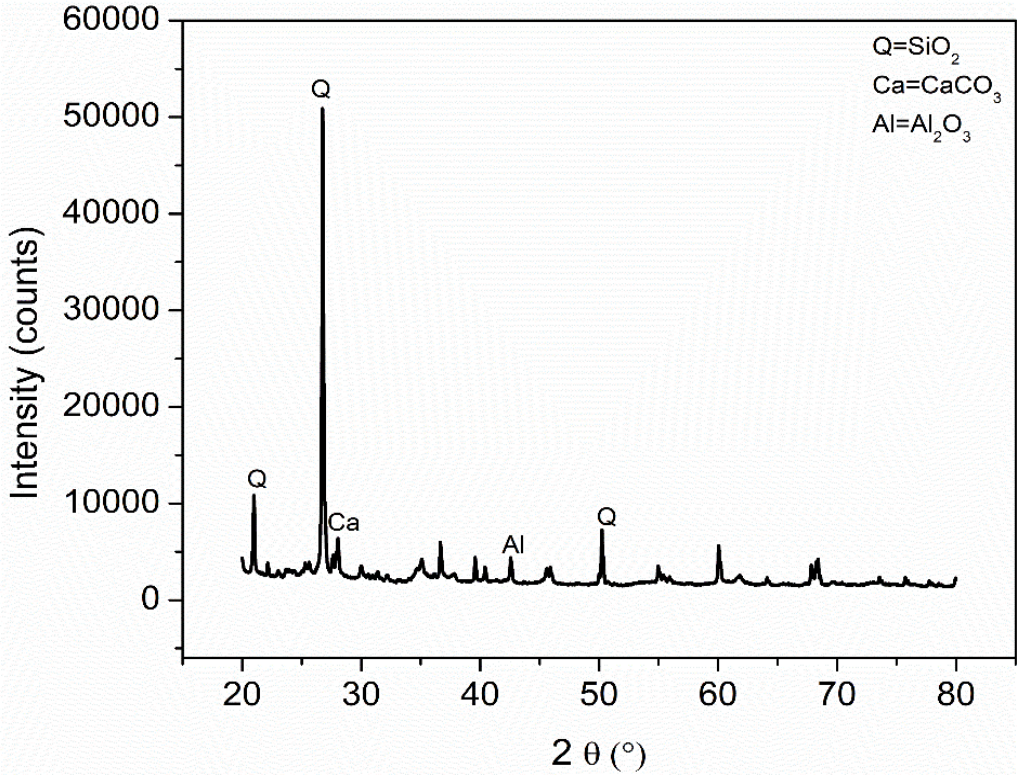


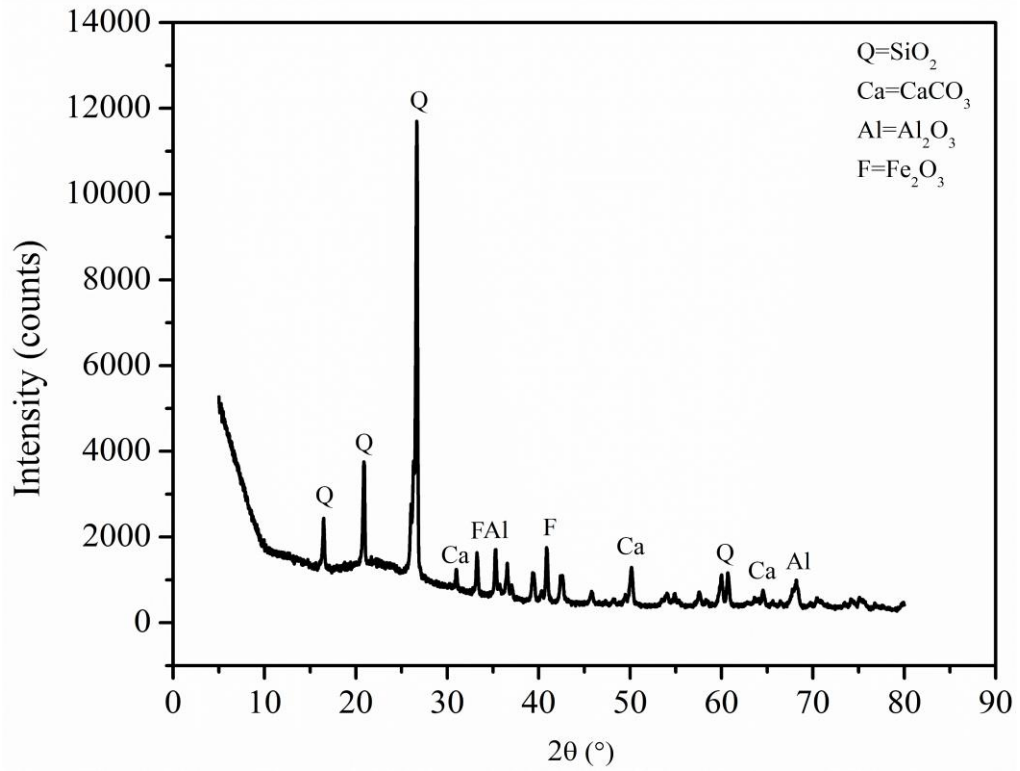
Fig. 4.9. EDX image of soil+ 1% NS +20% FA at four locations.

4.4 X-RAY DIFFRACTION (XRD) ANALYSIS

The chemical compounds present in the treated and untreated soil sample was determined by performing the XRD test. The XRD analysis was performed with a 2θ value ranging from 5° to 80°. Fig. 4.10 (a) and (b) depicts the XRD profile of parent of soil, fly ash and respectively. Fig. 4.11 (c) depicts the XRD profile of Nano silica. The XRD profile of soil showed the Quartz (Q), Calcium carbonate ($CaCO_3$) and Aluminium Oxide (Al_2O_3) as main crystalline phase. The XRD profile of fly ash showed the Quartz, Calcium carbonate, Iron oxide (Fe_2O_3) and Aluminium oxide (Al_2O_3) as main crystalline phase. The XRD profile of Nano Silica showed the Quartz as main crystalline phase. Fig. 4.11 (d) and Fig. 4.12 (e) depicts the XRD pattern of Soil+1%NS and Soil+1%NS+20%FA. The XRD profile of Soil+1%NS showed the formation of CSH gel at various 2θ range of 34.9° and 38°. The XRD profile of Soil+1%NS+20%FA showed the formation of C-A-S-H gel at various 2θ range of 22°, 28°, 35° and 62°. The pozzolanic reaction, a time-dependent process that develops between calcium and silica and aluminium, results in cementitious compounds such as C-S-H and C-A-S-H gel. The stabilized soil's increased strength is owing to the cementitious compounds that develop in the soil-binder matrix. However, the strength of the treated soil decreased when the fly ash amount exceeded beyond 20%. For stabilized soils with fly ash content up to 20%, cementation of the particles takes place due to development of pozzolanic reaction. However, in stabilized soils with higher fly ash levels, the pozzolanic reaction does not take place, and the additional fly ash binder particles act as unbonded particles, decreasing the material's overall strength. Similar observation was noticed by past researchers (Sharma et al. 2012; Sharma et al. 2016).

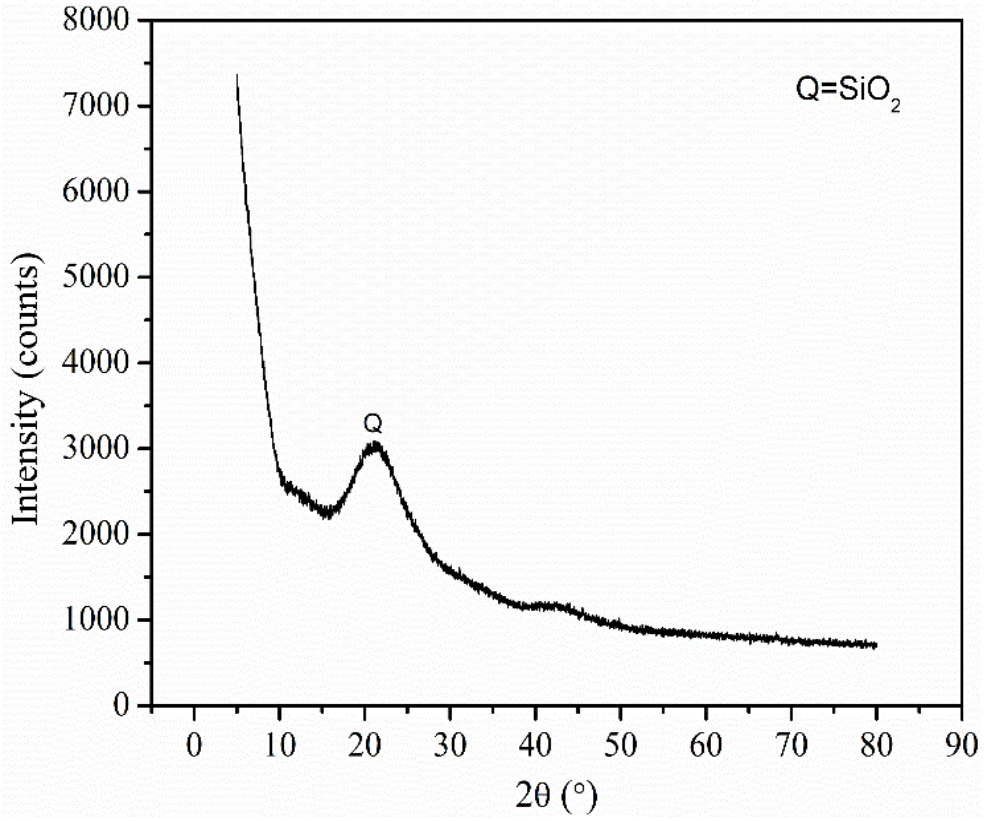


(a)

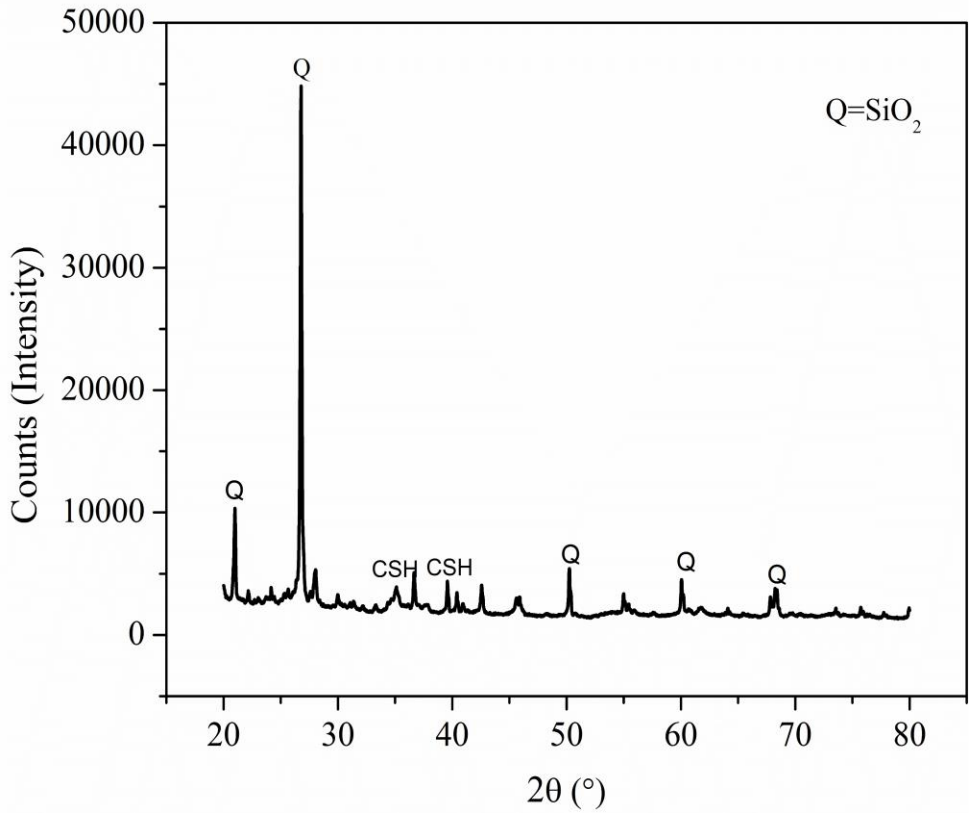


(b)

Fig. 4.10. XRD pattern of (a) Soil and (b) Fly ash.

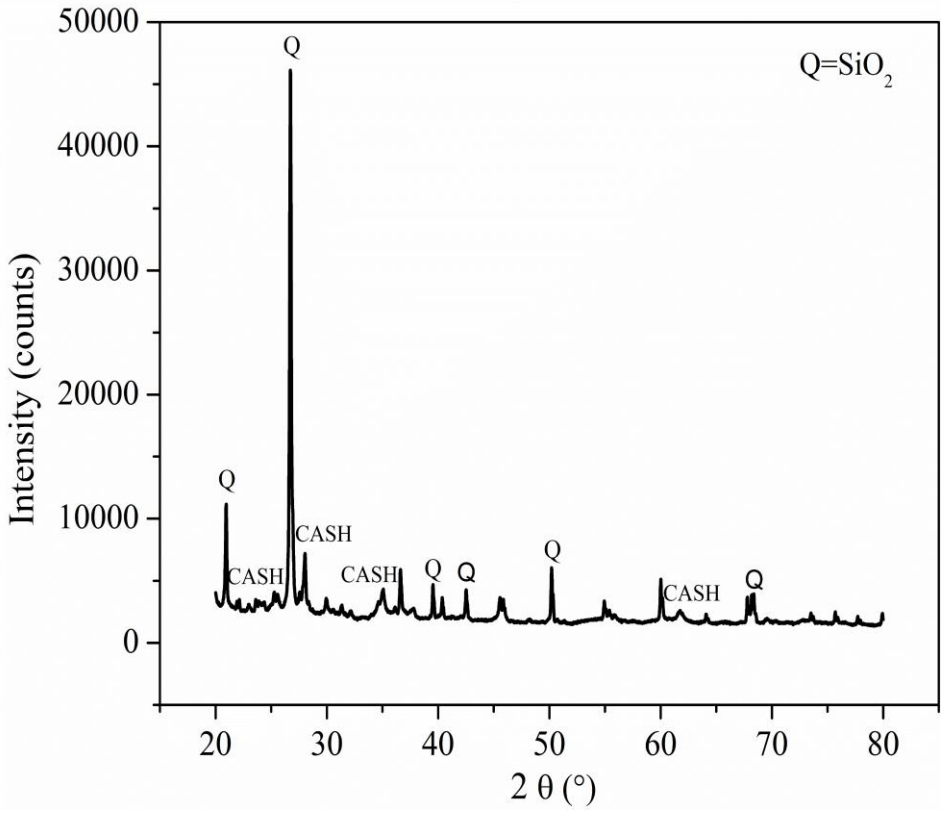


(c)



(d)

Fig. 4.11. XRD pattern of (c) Nano SiO_2 and (d) Soil+1% NS.



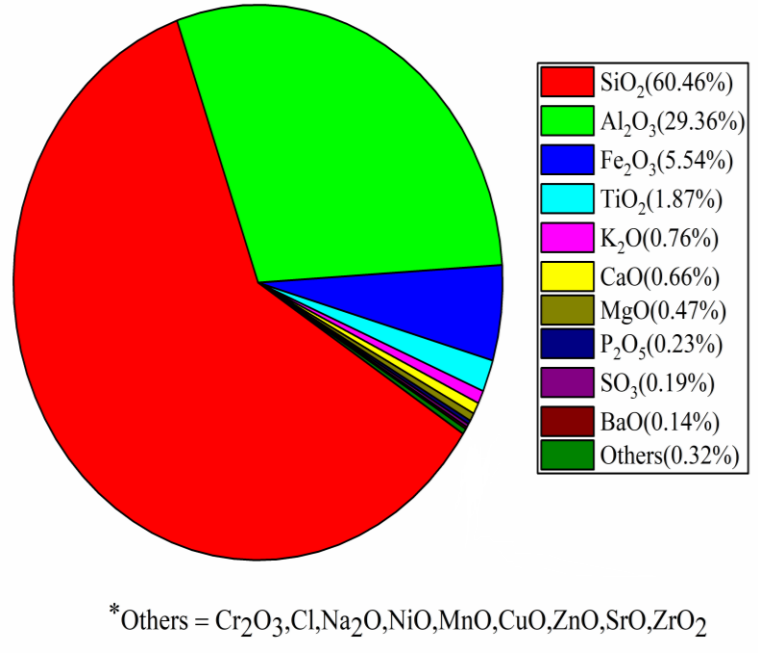
(e)

Fig. 4.12. XRD pattern of (e) Soil+1%NS+20%FA.

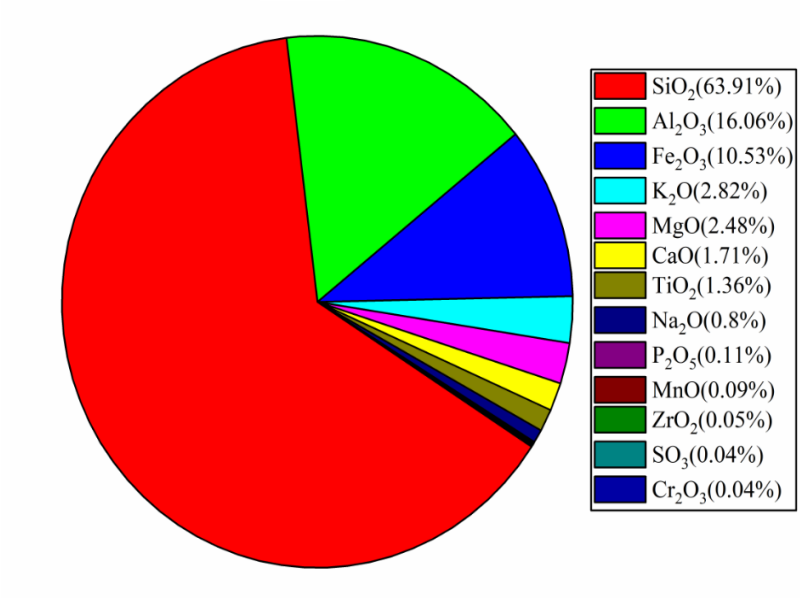
4.5 X-RAY FLUORESCENCE (XRF) ANALYSIS

The X-ray fluorescence (XRF) spectrometry, a non-destructive experimental technique, analyses the intensities of the X-ray spectral lines that the elements emit as a result of secondary excitation, allowing for the qualitative and quantitative examination of chemical elements. The XRF results of fly ash (FA), soil+1% NS, and soil+1% NS+20% FA are illustrated in Fig. 4.13 (a) and (b) and Fig. 4.14 (c) respectively. According to ASTM C618-15 (ASTM 2015a), there are two main categories of fly ashes based on the type of coal burned and its chemical composition. They are referred to as classes C and F. Class-C fly ashes are produced by incinerating sub-bituminous coal or raw lignite. They have self-cementing properties and are pozzolanic by nature. Over time, these ashes become stronger and more durable when exposed to water. They are often rich in alkali and sulphate (SO_4), contain more than 20% lime (CaO), and don't generally need an activator. ASTM C618-15 (ASTM 2015a) states that the total Al_2O_3 + SiO_2 + Fe_2O_3 for a Class-C fly ash should be between 50 and 70 percent. Class-F fly ashes are produced by burning bituminous and anthracite coals that are older and harder. They are pozzolanic by nature and contain less than 10% lime (CaO). ASTM C618-15 (ASTM 2015a) states that the total Al_2O_3+SiO_2+Fe_2O_3 for a Class-F fly ash should be more than 70%. It is evident from Fig. 4.12 that the sum of SiO_2 (60.46%), Fe_2O_3 (5.54%), and Al_2O_3 (29.36%) of present fly ash contributes more than 70% of the chemical elements. As a result, the fly ash used in the current investigation was classified as class F type. Approximately 90% of the primary components of fly ash are oxidized compounds of Si, Al, Fe, and Ca. The minor chemical constituents such as Mg, K, Na, Cl, Ni, Ti, P, Ba, Zn, Cu, and S are other elements that contribute a minor fraction of the bulk composition. The main constituents of soil+1% NS and soil+1% NS+20% FA treated specimens are

silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), and iron oxide (Fe_2O_3), as shown in Fig. 4.13 (a) and (b). The treated soil also contains minor amounts of CaO, Na_2O, K_2O, TiO_2, MgO, MnO, P_2O_5, SO_3, and Cr_2O_3 minerals. A series of reactions take place when binders such as fly ash and Nano-SiO_2 are mixed with soil in the presence of water. These reactions cause the chemical element of CaO in the binders to dissociate, forming cementitious and pozzolanic gels such as calcium silicate hydrate gel (CSH) and calcium aluminate silicate hydrate gel (CASH). The soil or the binding agent is the source of the pozzolans due to the presence of siliceous or aluminous materials. There are two ways in which these reactions aid in soil stabilization. Firstly, the interchange of calcium ions in the pore water with monovalent cations on clay surfaces and the compression of the adsorbed layer due to the high ionic strength of the pore water diminish the plasticity of the soil (Rogers and Glendinning 2000). Second, a stronger soil matrix is produced by the solid particles being bound together by the CSH or CASH gels that are generated by cementitious and pozzolanic processes (Thomas and Rangaswamya 2020; Renjith et al. 2021). The chemical composition of the Indian coal fly ash along with present fly ash is presented in Table 4.1.

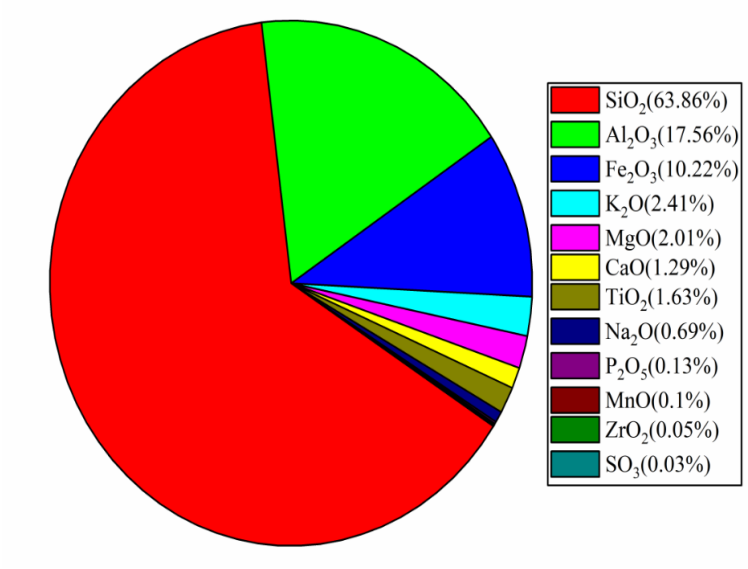


(a)



(b)

Fig. 4.13. XRF results of (a) fly ash (b) Soil+1% NS.



(c)

Fig. 4.14. XRF results of (c) Soil+1% NS+20% FA.

Table 4.1. Summary of the chemical composition of the Indian coal fly ash along with present fly ash.

Thermal power station	% of Chemical composition												References
	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	SO_3	TiO_2	Na_2O	P_2O_5	MnO	LOI	
Parichha (UP)	59.9	17.9	7.8	1.4	NA	NA	0.4	NA	NA	NA	NA	8.2	Das and Yudhbir 2004
Panki (UP)	63.6	27.2	4.4	2.4	NA	NA	0.3	NA	NA	NA	NA	2.6	Das and Yudhbir 2004
Neyveli (TN)	26.4	25.8	25.8	16.8	NA	NA	1.0	NA	NA	NA	NA	1.4	Das and Yudhbir 2004
Raichur (Karnataka)	54.4	28.6	3.2	1.6	1.7	1.4	NA	1.8	0.3	NA	NA	5	Sharma and Sivapullaiah 2016
Rajghat (UP)	61.21	30.07	4.17	0.10	0.02	0.40	< 0.01	2.60	< 0.01	NA	NA	1.4	Kaniraj and Havanagi 1999
Badarpur (UP)	57.5	33.0	4.8	0.5	0.4	0.2	NA	1.4	0.2	NA	NA	1.5	Mir and Sridharan 2013
Dadri (New Delhi)	60.12	30.16	6.36	1.00	NA	0.53	0.01	NA	0.06	0.007	NA	0.40	Kaniraj and Gayathri 2004
Ranges for Indian fly ash	38–63	27–44	3.3–6.4	0.2–8	0.04–0.9	0.01–0.5	NA	0.4–1.8	0.07–0.43	NA	0–0.5	0.2–3.4	Pandian 2004
Present fly ash	60.46	29.36	5.54	0.66	0.76	0.47	0.19	1.87	NA	0.23	NA	NA	Present study
Present soil+1% NS	63.91	16.06	10.53	1.71	2.82	2.48	0.04	1.36	0.8	0.11	0.09	NA	Present study
Present soil+1% NS+20% FA	63.86	17.56	10.22	1.29	2.41	2.01	0.03	1.63	0.69	0.13	0.1	NA	Present study

4.6 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY ANALYSIS

The FTIR spectrum response of infrared (IR) spectroscopy typically observed the stretching and bending vibrations of the OH and Si–O groups in the range of 400 and 4000 cm^{-1}. FTIR is based on the principle that most molecules absorb light in the IR region of the electromagnetic spectrum, and that this absorption exactly corresponds to the intrinsic vibrational frequency of the bonds that comprise the molecules. Fig. 4.15 indicates the FTIR spectra of Si–O–Si band in soil, soil+1% NS, and soil+1% NS+20% FA treated soil. It is significant to note that a large number of bands occurred in the low frequency range (500–1000 cm^{-1}), which is a characteristic region of amorphous Si-Al bonds. Similar observation was noticed by **(**Abed et al. 2024). The FTIR spectrum of the treated soil was observed a broad group of Si–O–Si band in the wide ranging of 600–1500 cm^{-1}. This band possibly associated with the complex spectra of C-S-H (Thomas and Rangaswamy 2020; Bahmani et al. 2014). Additionally, there are some bands in the wavenumbers of 1650cm^{-1} and 3500cm^{-1} that are attributed to the stretching and bending vibrations of OH groups (Kani et al. 2022). The aforementioned results demonstrate that SiO_2 nanoparticles readily formed C–S-H gel by reacting with fly ash in the clayey soil. The C-S-H gel may improve the microstructure and reduce the porosity of the soil by filling in the capillary pores, potentially increasing its strength.

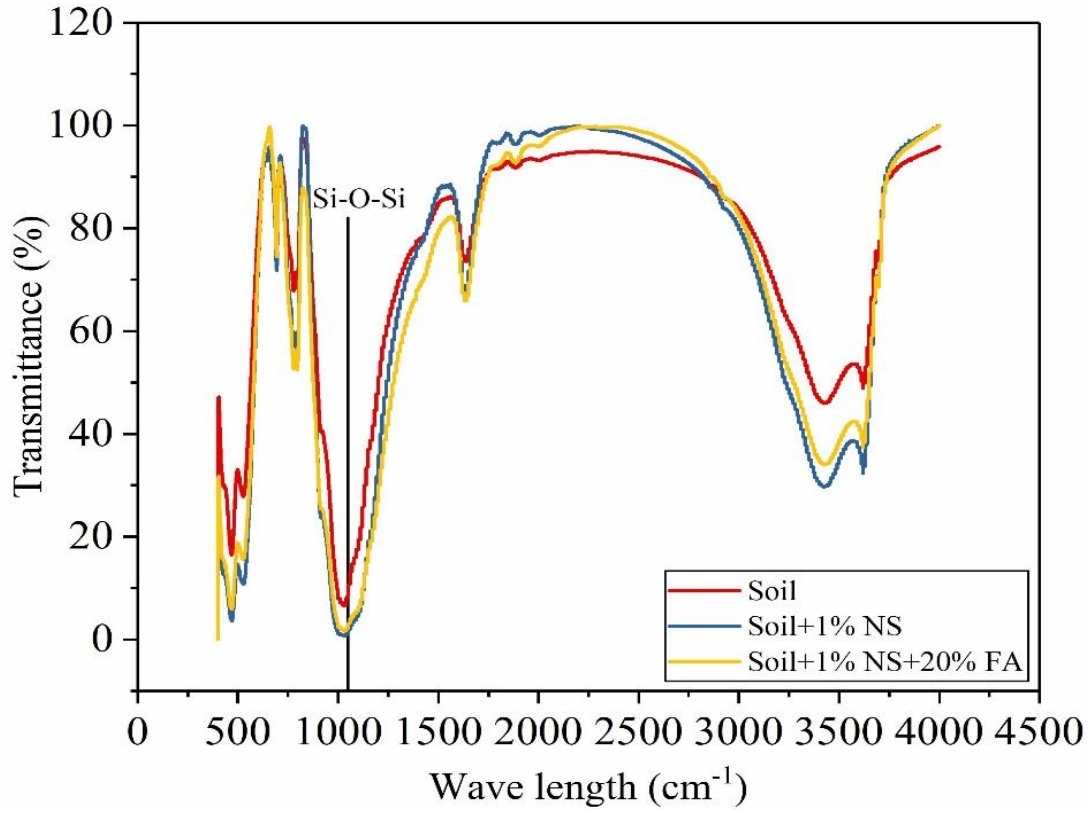


Fig. 4.15. FTIR pattern of Soil, Soil+1% NS and Soil+1%NS+20%FA.

4.7 SUMMARY

Here, the chemical analysis of the source soil, fly ash, Nano-SiO_2, soil+1% NS and soil+1% NS+20% FA has been briefly summarized. The SEM images revealed that the fly ash consists of spherical-sized particles and a few coarse particles with irregular shapes, which are known as cenospheres and plerospheres, respectively. The microporous structure of Nano-SiO_2 resembles a micro-sized cauliflower. The soil has thin, chipped, angular, and flaky particles instead of spherical ones like fly ash. The untreated soil has a large number of visible pores, and as it stabilizes, the size of the pores gets smaller. The reduction in pore size is brought about by the pozzolanic reaction that occurs after the formation of CSH and CAH gel in the treated soil. The EDS results showed a range of elemental compositions, including Si, Al, Fe, K, Mg, Na, and Ca, when the data from various locations were examined. From XRF test results, it can be concluded that several reactions occur when binders such as fly ash and Nano-SiO_2 are blended with soil in the presence of water. The cementitious and pozzolanic gels known as CSH and CASH are produced when these reactions lead to the dissociation of the chemical element CaO in the binders. These cementitious gels can create a stronger soil matrix by binding soil particles together.