CHAPTER- IV

CHEMICAL ANALYSIS RESULTS AND DISCUSSION

4.1 INTRODUCTION

The chemical constituents of soil have significant influence on its physical property hence it is essential to identify the chemical constituents of the fly ash and local soil. In the same way, morphology of soil particles governs the shear strength behaviour of the soil especially the angle of internal friction. However, elemental and mineralogical constituents help in the determination of pozzolanic or self-hardening or chemical reactivity of the soil. Therefore, in order to investigate the morphology, mineralogy, and chemical constituents of the considered materials, the scanning electron microscope (SEM), the energy dispersive X-ray (EDX), the X-ray diffraction (XRD), and the X-ray fluorescence (XRF) tests have been conducted. The chemical constituents of the fly ash and local soil were described in the subsequent sections by performing the following analysis.

a) Scanning Electron Microscope (SEM) Analysis
b) Energy Dispersive X-Ray (EDX) Analysis
c) X-Ray Diffraction (XRD) Analysis
d) X-Ray Fluorescence (XRF) Analysis
e) Potential of Hydrogen (pH)

4.2 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

The Scanning Electron Microscope (SEM) analysis of the fly ash and local soil was conducted in the Central Instrumentation Facility (CIF) available at IIT(BHU), Varanasi. The experiment was performed using HR-SEM instrument manufactured by the FEI (Thermo Fisher). In order to view the micro level morphology, the fly ash was analyzed considering size range of 20 μm to 1 μm under different magnification between 3500x to 50000x. Similarly, the local soil was investigated 5 μm to 500 nm with varying magnification 10000x to 120000x. The morphological illustration of the fly ash and local soil has been shown in Fig. 4.1 & 4.2. From Fig. 4.1, it can be seen that the fly ash has promising content of glassy spherical size particles followed by irregular particles. These spherical particles are generally called as cenospheres and plerospheres which are responsible of the light weight nature of fly ash. Spherical hollow fly ash particle having thin walled & smooth surface is termed as cenospheres, whereas plerospheres are spheres that consist of a small size sphere inside it (Paulson and Ramsen 1970; Page et al. 1979; Dudas and Warren 1987). Both of these spheres are very common in the low calcium fly ash than that of the high calcium fly ash (Das and Yudhbir 2005). The concentrations of cenospheres/plerospheres are depend on the carbon and iron content (Kolay and Singh 2001). The fundamental time required for the development of 50 micron plerospheres and cenospheres is 1 ms (Fisher and Natusch 1979) & 0.3 ms (Raask 1968) respectively. About 1%–2% of cenospheres are generally present in fly ash and it is very light in weight (Wolfe and Gjinolli 1999; Siddique 2010). The cenospheres consist of alumina- silica, iron, and alkali at its outmost shell (Sarkar et al. 2007) and their size varies from 1 to 300 μm (Torey 1978). The segregation of cenospheres from the fly ash can be done by the wet separation technique (Manocha et al. 2011) and the dry separation technique (Hirajima et al. 2010).

The cenospheres have beneficial properties like low density, chemically inert, light weight, and excellent thermal resistance (Raask 1968; Fisher et al. 1976; Bhatt et al. 2019), which enhances the application of fly ash in light weight filler and aggregate (Hanif et al. 2017).

In the same way, the detailed surface morphology of the local soil has been demonstrated in Fig. 4.2. From this figure, it can be concluded that the local soil contains particles of shape flaky, angular, and thin chipped form instead of spherical shape as like in fly ash. These shapes of particles provide better interlocking behaviour that helps in the enhancement of the angle of internal friction and the apparent cohesion. These particles form a flocculant soil structure that has a higher tendency of disturbance upon the saturation. The local soil particles have higher surface area than that of the fly ash because of the dominance of spherical particles. The HR SEM instrument has well equipped with energy dispersive X-ray detector which has been used for the elemental composition analysis and can be performed simultaneously at different locations. The elemental analysis of both local soil and fly ash has been discussed in the next sections in details.

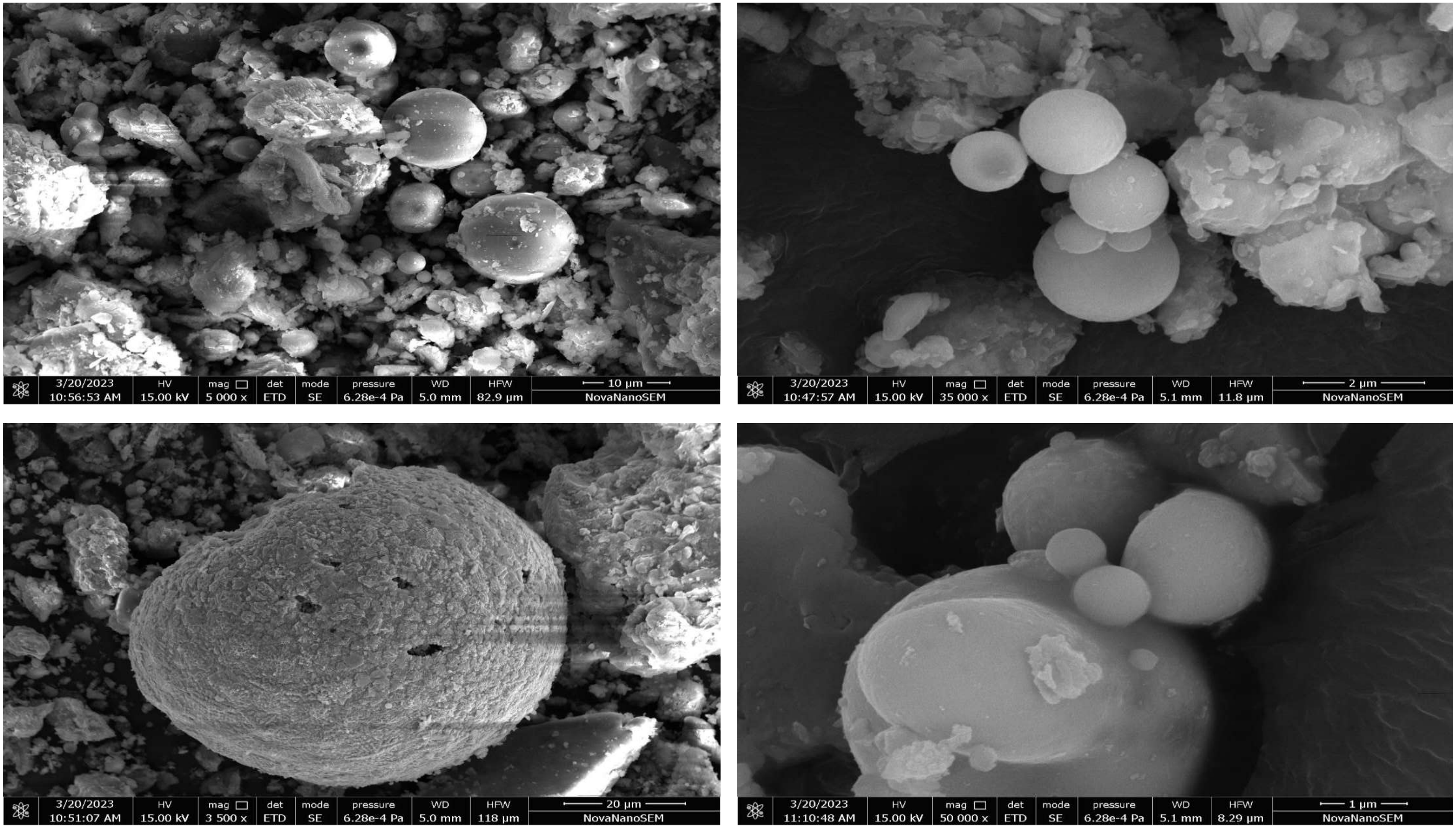


Fig. 4.1. Scanning electron microscope analysis of fly ash sample under different magnification.

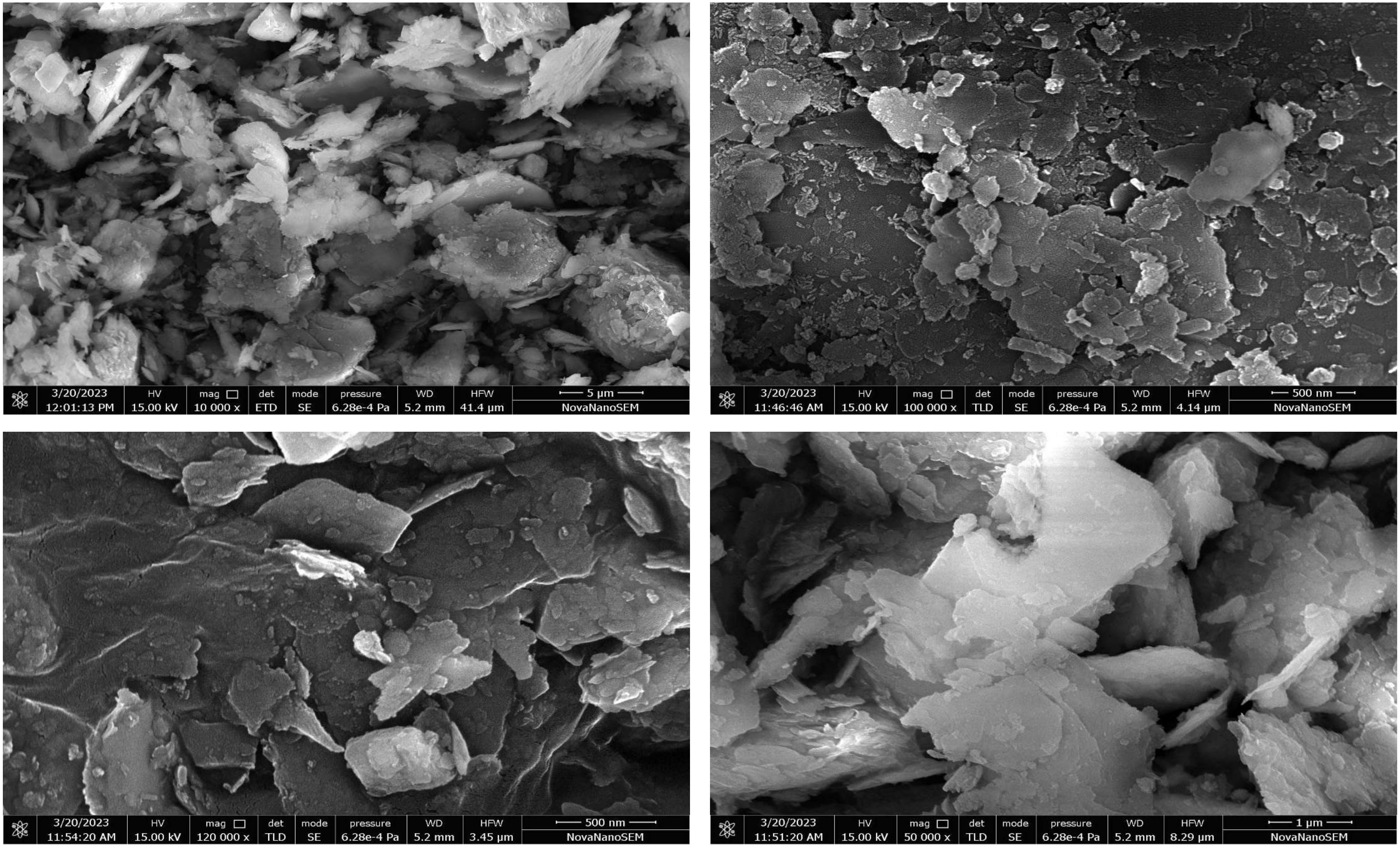


Fig. 4.2. Scanning electron microscope analysis of local soil sample under different magnification.

4.3 ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS

The Energy Dispersive X-ray (EDX) analysis was performed in the same instrument, i.e., high resolution scanning electron microscope. This elemental analysis was done at different locations of the specimen in order to verify the repeatability of various elements inside the specimen (Fig. 4.3 & 4.5). Subsequently, the EDX outcomes of the fly ash and local soil has been presented in Fig. 4.4 and 4.6 respectively. The results of multiple location were examined and found that the fly ash has variety of elemental composition such as Aluminium (Al), Silicon (Si), Iron (Fe), Oxygen (O), Potassium (K), Titanium (Ti), Strontium (Sr), Magnesium (Mg). Similar type of elemental composition has been found in local soil except Ti. The fly ash exhibits maximum peaks of Al, Si, and O whereas local soil shows maximum peaks of Al, Si, O, Mg, and K. Also, most of the researchers observed these elements in fly ash and normal soils (Kutchko and Kim 2006; Kumar et al. 2020; Keykha et al. 2014; Taha et al. 2021). Normally, the elements that are more prevalent in coal is also more

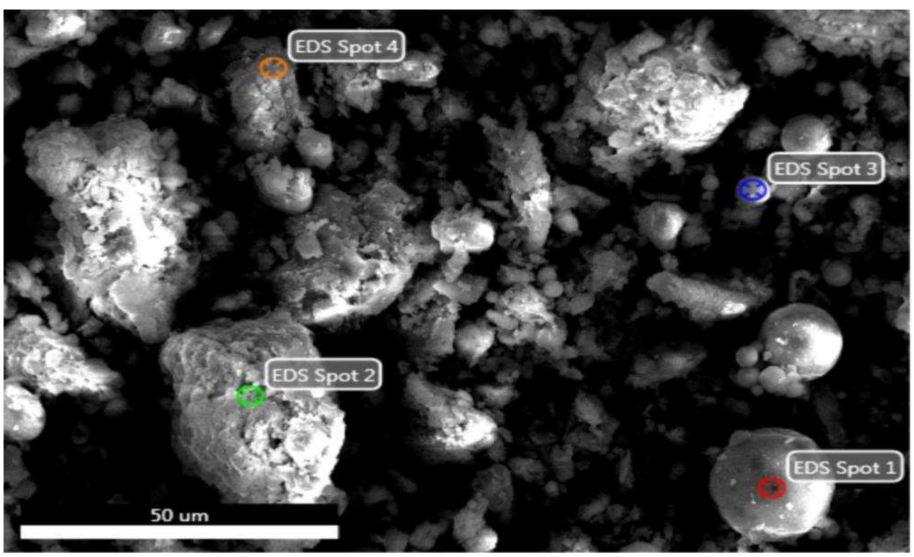
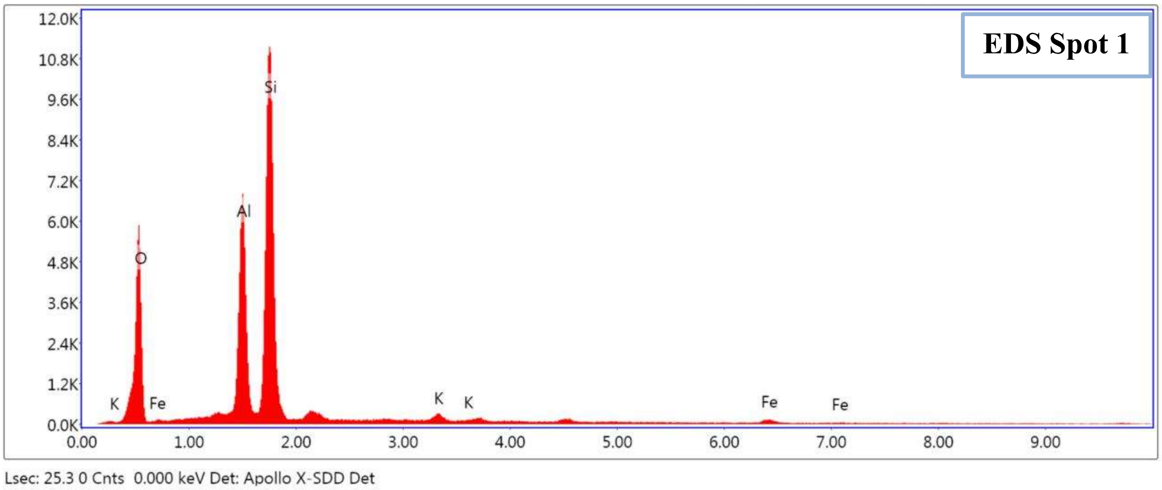
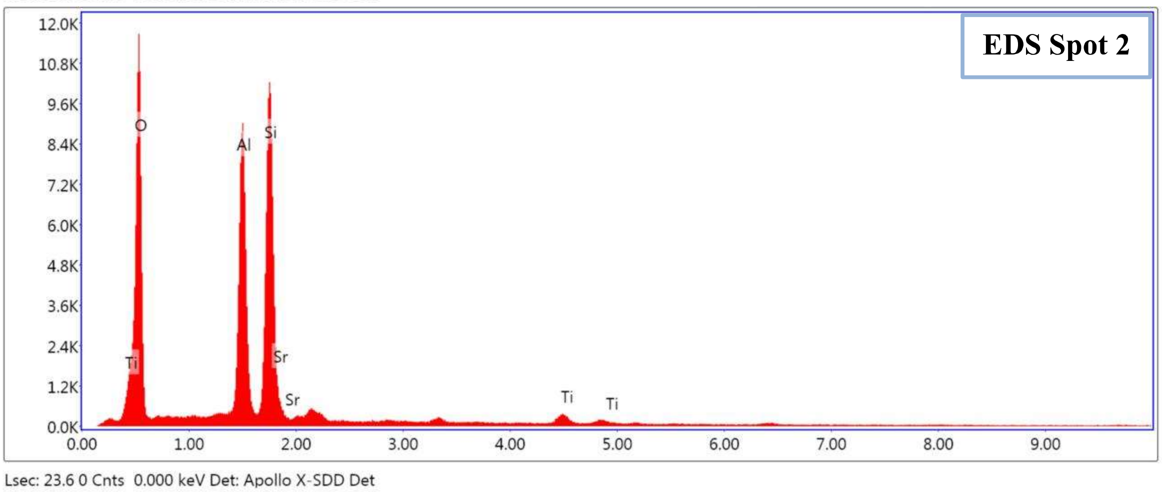
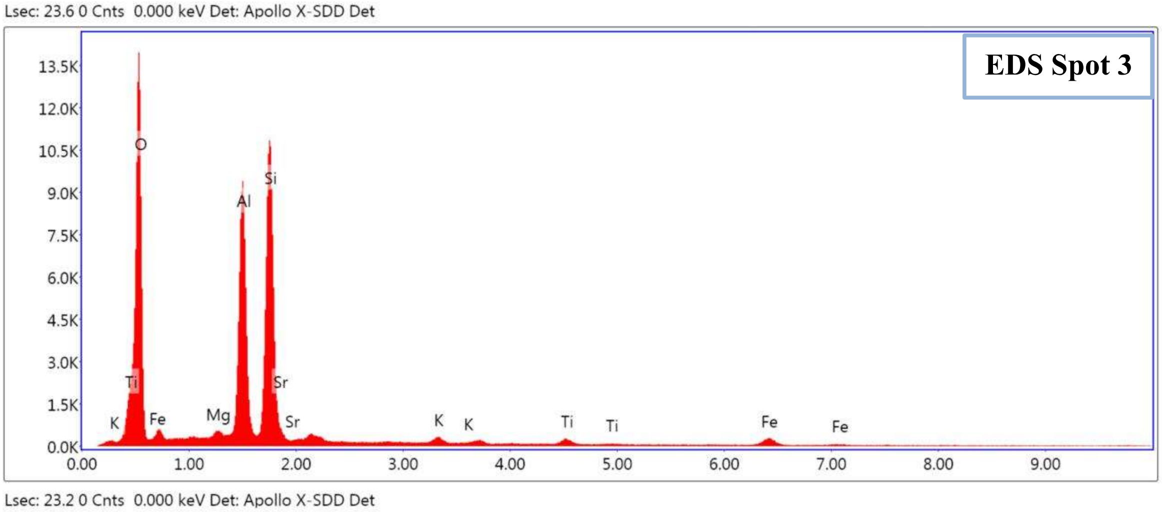


Fig. 4.3. Selected location of fly ash specimen for the EDX analysis.

prevalent in ash (Lichtman and Mroczkowski 1985).


EDS Spot 1
O
Al
Si
K
Fe
K
K
Fe
Fe
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00
0.0K 1.2K 2.4K 3.6K 4.8K 6.0K 7.2K 8.4K 9.6K 10.8K 12.0K
Lsec: 25.3 0 Cnts 0.000 keV Det: Apollo X-SDD Det


EDS Spot 2
O
Al
Si
Ti
Sr
Sr
Ti
Ti
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00
0.0K 1.2K 2.4K 3.6K 4.8K 6.0K 7.2K 8.4K 9.6K 10.8K 12.0K
Lsec: 23.6 0 Cnts 0.000 keV Det: Apollo X-SDD Det


EDS Spot 3
O
Al
Si
Ti
Sr
K
Fe
Mg
Sr
K
K
Ti
Ti
Fe
Fe
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00
0.0K 1.5K 3.0K 4.5K 6.0K 7.5K 9.0K 10.5K 12.0K 13.5K
Lsec: 23.2 0 Cnts 0.000 keV Det: Apollo X-SDD Det

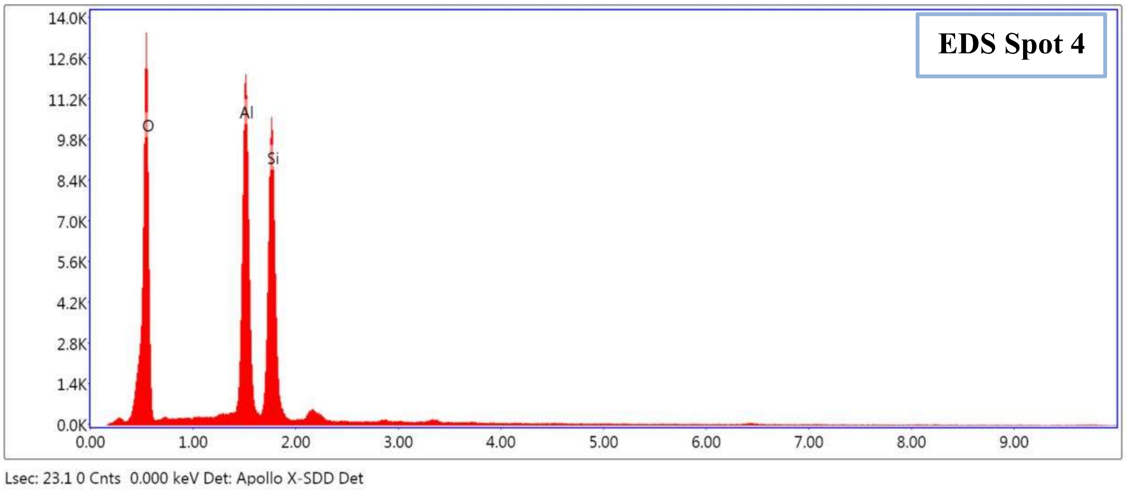


Fig. 4.4. Graphical representation of the elemental composition of fly ash at four locations.

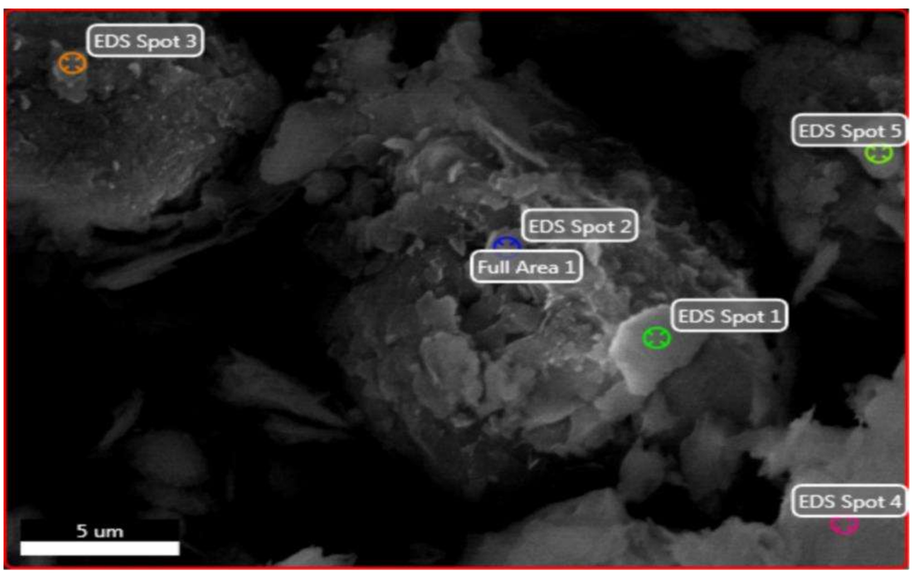
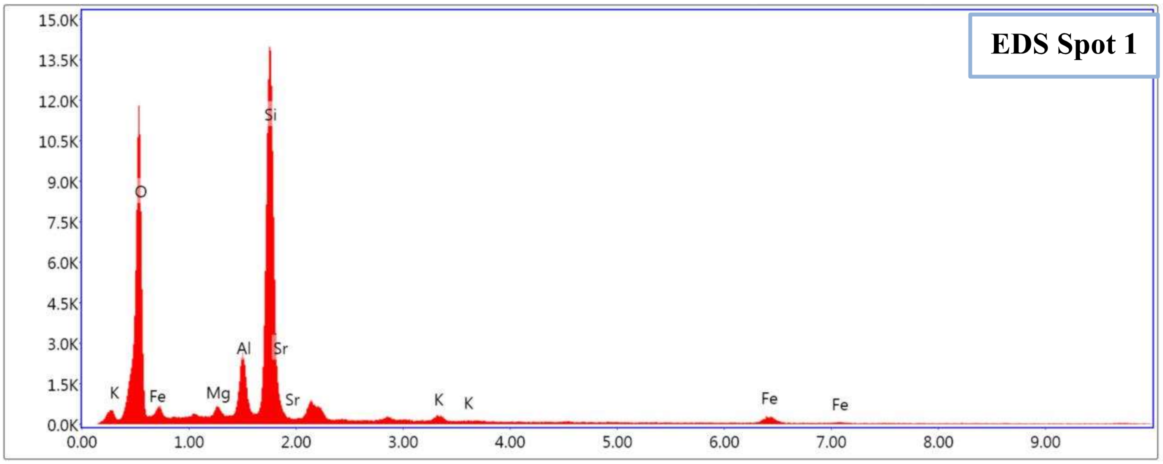
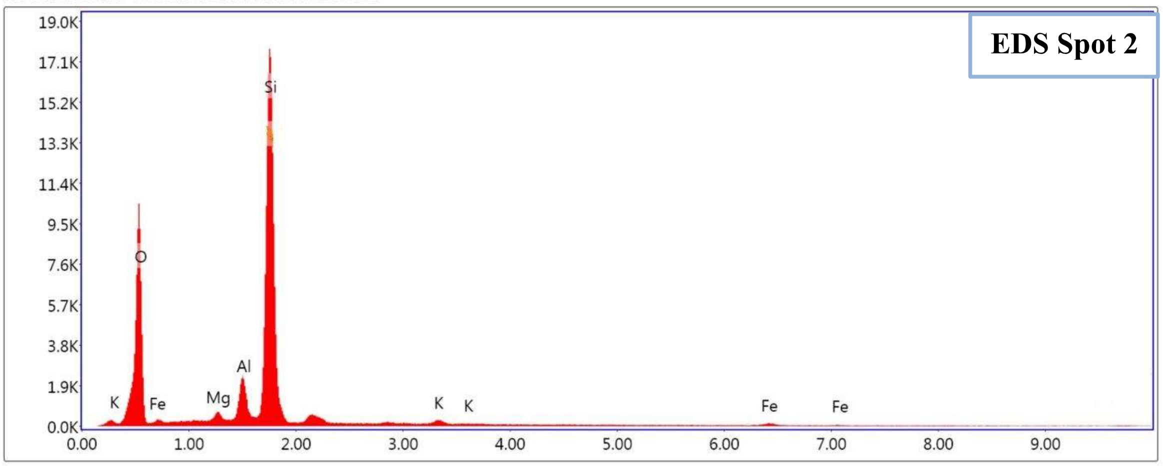


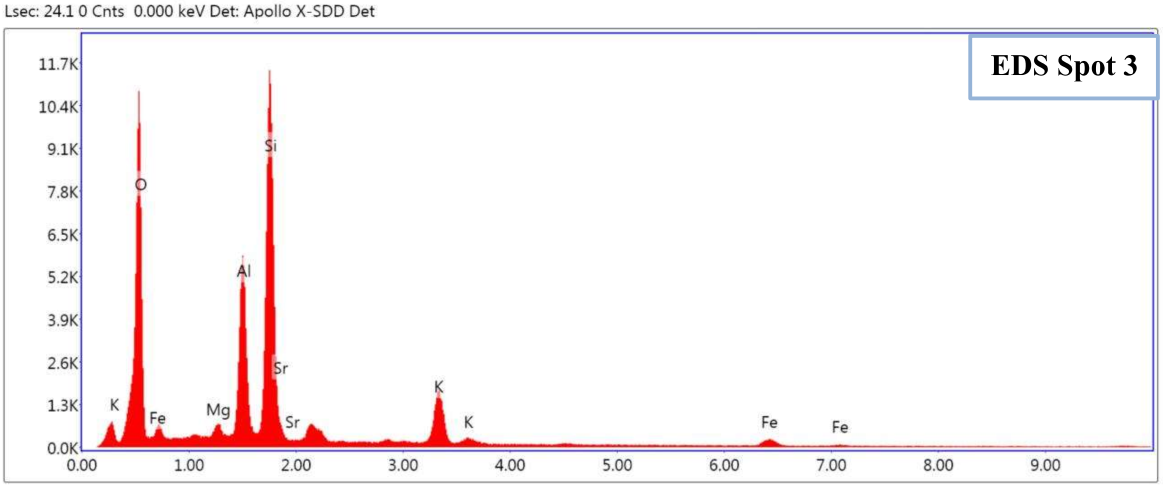
Fig. 4.5. Selected location of local soil specimen for the EDX analysis.



Lsec: 23.9 0 Cnts 0.000 keV Det: Apollo X-SDD Det



Lsec: 24.1 0 Cnts 0.000 keV Det: Apollo X-SDD Det



Lsec: 23.5 0 Cnts 0.000 keV Det: Apollo X-SDD Det

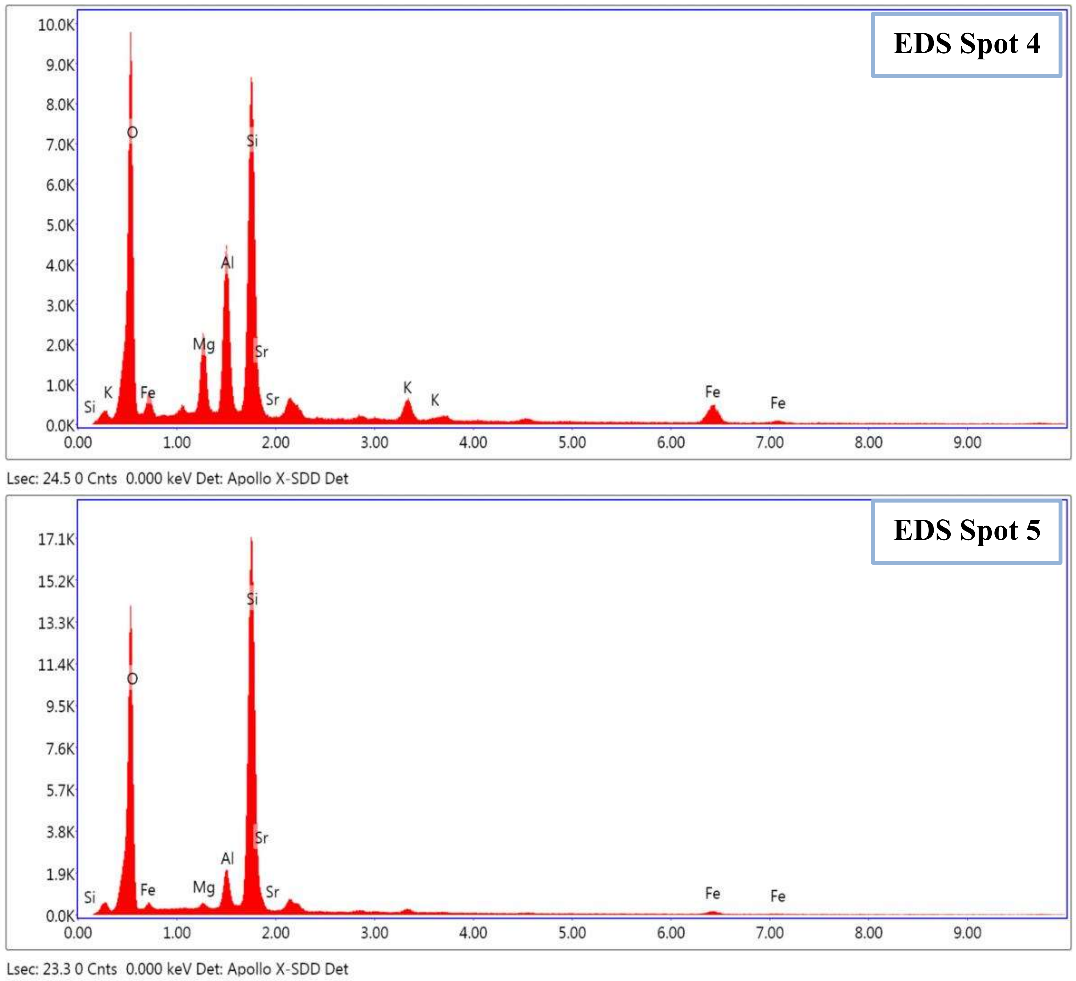


Fig. 4.6. Energy dispersive X-ray analysis of local soil at five locations.

4.4 X-RAY DIFFRACTION (XRD) ANALYSIS

The X-Ray Diffraction (XRD) pattern of the fly ash and local soil powder was obtained using a cobalt target with wavelength (λ) of 1.79 Armstrong. The test was performed at a 2-theta range between 5°-85° with a scan rate of 0.05°/minute. The obtaining peaks are indicating their crystalline nature. With the help of JCPDS database, the peaks were identified to be that of the Quartz (SiO_2), Alumina (Al_2O_3), Hematite (Fe_2O_3), and Titanium dioxide (TiO_2) in the case of fly ash (Fig. 4.7). However, the local soil shows peaks of Quartz (SiO_2), Stilpnomelane ($K(Fe^{2+},Mg,Fe^{3+})_8(Si,Al)_{12}(O,OH)_{27}\cdot n(H_2O)$), Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$), Leucite ($KAlSi_2O_6$), Gupeiite ($Fe_3Si$), and Biotite

($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) which has been shown in Fig. 4.8. The obtained compounds were also confirmed by X-Ray fluorescence (XRF) test. Whereas, the compound with less than 10 weight percentage in XRF are not detected in XRD test. Therefore, due to the high percentage contribution of Quartz in both the sample, the clear peaks can be noticed in the XRD plot. The Quartz, Alumina, Hematite, and Titanium dioxide has a crystal structure of tetrahedrons, hexagonal, rhombohedral, tetragonal respectively. In the same way, the Stilpnomelane, Muscovite, Leucite, Gupeiite, and Biotite has a crystal structure of Triclinic, Monoclinic, Tetragonal, Isometric, Monoclinic respectively.

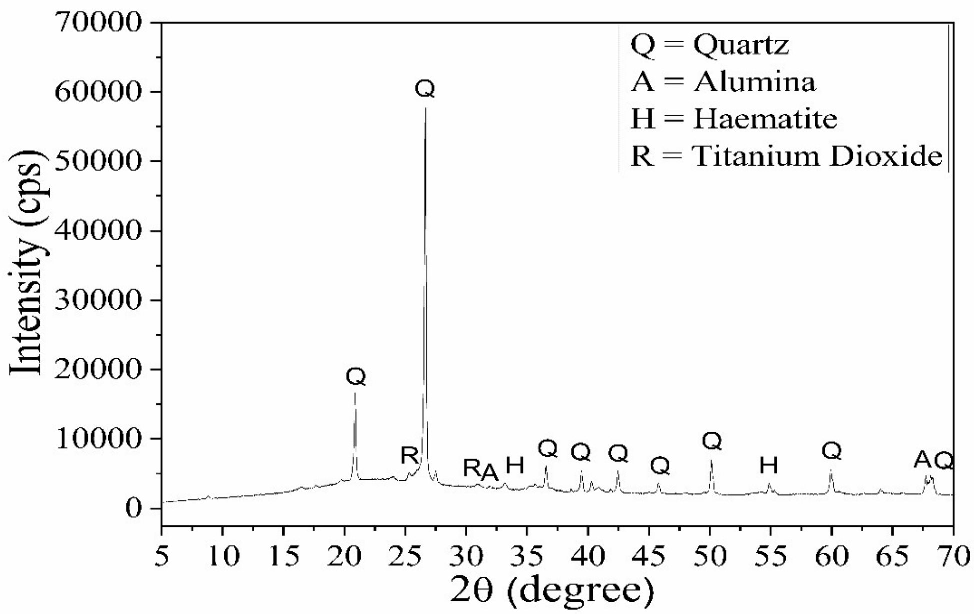


Fig. 4.7. Mineralogical analysis of fly ash using the XRD analysis.

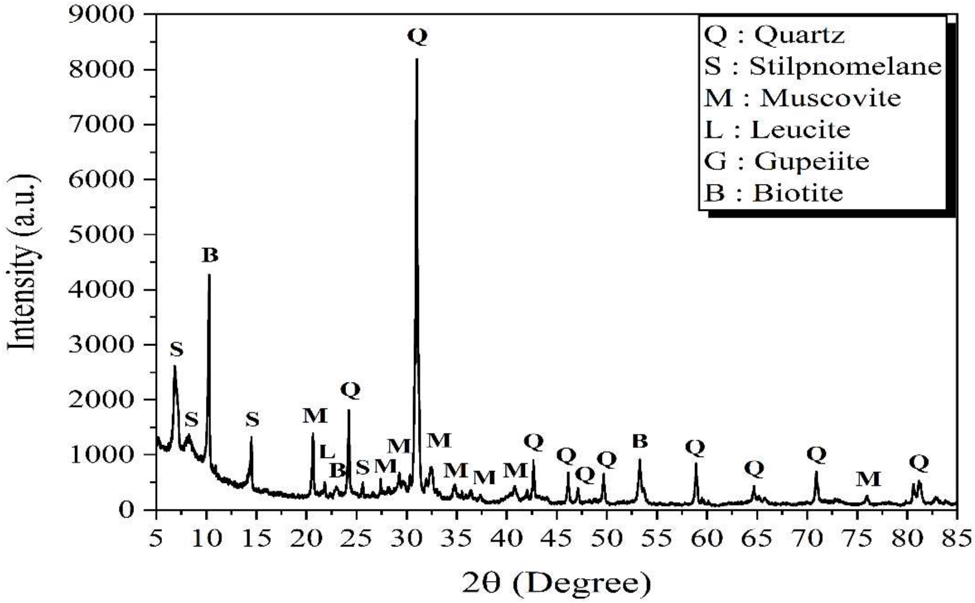


Fig. 4.8. Mineralogical analysis of local soil using the XRD analysis.

4.5 X-RAY FLUORESCENCE (XRF) ANALYSIS

The outcome of the XRF analysis of fly ash has been presented graphically in Fig. 4.9, and also tabulated with an exact concentration of different compounds in Table 4.1. From the above characterization of soil, it has been found that the soil is free from any harmful chemical constituents. Also, the formation of soil is through natural phenomena, hence it can be treated as non-hazardous. Considering all these factors into account only the fundamental characterization of soil has been done (excluding XRF). From the Fig. 4.9, this can be seen that the combination of Al_2O_3, SiO_2, and Fe_2O_3 contributes around more than 95% of the chemical constituents. The Al_2O_3, SiO_2, and CaO are responsible for the pozzolanic and hardening nature of the fly ash in geopolymer concrete. The classification of fly ash (Class C or F) is usually carried out by knowing the concentration of alumina, silica, and iron oxides. Class C defines the class of fly ash having more than 50% of the sum of silica, alumina, and iron oxides whereas this sum amount is greater than 70% in the case of class F fly ash (Mehta 1989;

ASTM C618-03 2003). Hence, from the XRF analysis, the present fly ash is classified under class F category. The burning of high quality coal (anthracite and bituminous coal) results in the generation of low calcium fly ash; on the contrary, the combustion of low quality coal produces high calcium fly ash (Zahedi and Rajabipour 2019). The concentration of various compounds in the fly ash collected from all over India has been described in the Table 4.2. The concentration of these compounds of the present fly ash are found to be within the range of Indian fly ash (Table 4.2). Also, the combined concentration of heavy metals is observed to be less than 0.3% of the total concentration. Therefore, this fly ash can also be used in the place where contamination of ground water is prominent.

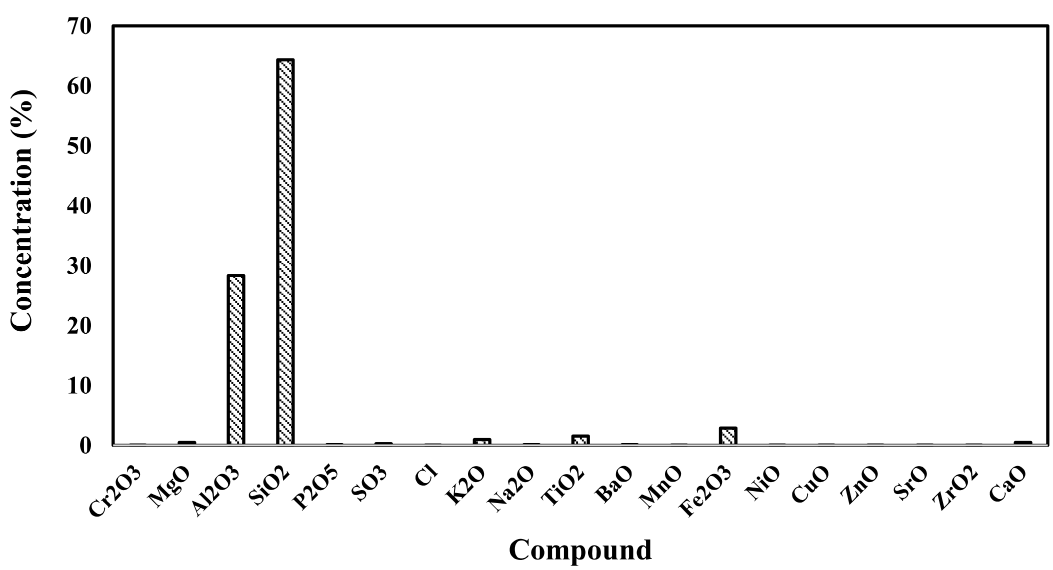


Fig. 4.9. Graphical representation of percentage of compound present in fly ash.

Table 4.1 Percentage contribution of various compound present in fly ash.

Compounds	**Concentration** (%)
Cr_2O_3	0.026
MgO	0.512
Al_2O_3	28.359
SiO_2	64.335
P_2O_5	0.141
SO_3	0.327
Cl	0.034
K_2O	0.952
Na_2O	0.114
TiO_2	1.542
BaO	0.13
MnO	0.0035
Fe_2O_3	2.919
NiO	0.011
CuO	0.013
ZnO	0.011
SrO	0.014
ZrO_2	0.053
CaO	0.499
Total	100

Table 4.2 Chemical alteration of fly ash tested from different states in India

States	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	MgO	P_2O_5	SO_3	Mn_3O_4	Na_2O	Na_2O_3	LOI	References
Telangana	55.45	27.13	7.28	2.74	1.90	2.55	1.20	0.54	0.55	NA	1.75	NA	0.92	Singh and Subramaniam 2018
Andhra Pradesh	48.81	31.40	7.85	3.80	2.93	1.52	0.70	1.27	0.91	NA	1.04	NA	3.01	
Jharkhand	61.54	26.94	3.21	1.64	2.03	1.78	0.56	0.44	0.00	0.05	0.12	NA	1.45	Shreya et al. 2015
Odisha	60.23	31.15	4.29	0.76	2.42	0.96	0.10	0.09	NA	NA	NA	NA	0.52	Mishra and Das 2010
Assam	37.57	14.72	5.56	0.57	0.86	1.27	0.47	0.059	0.27	0.018	0.36	NA	35.43	Saikia et al. 2015
Karnataka	51.06	20.29	10.82	7.11	0.26	0.25	2.32	NA	NA	NA	0.25	NA	7.19	Prashant et al. 2001
Tamil Nadu	50.40	18.81	16.61	9.00	0.28	0.23	1.41	NA	NA	NA	0.18	NA	2.60	
Uttar Pradesh	62.89	27.08	6.12	0.80	1.10	0.27	0.10	NA	NA	NA	NA	0.10	1.50	Chandra 2009
New Delhi	57.36	31.78	4.62	0.62	1.65	0.59	0.23	NA	NA	NA	NA	0.23	2.66	
Bihar	60.35	30.12	5.62	0.80	1.81	0.56	0.40	NA	NA	NA	NA	0.12	0.20	
West Bengal	60.30	30.90	5.02	0.90	1.30	0.50	0.60	NA	NA	NA	NA	0.15	0.30	
Chhattisgarh	62.09	31.30	3.33	0.03	1.82	0.04	0.01	NA	NA	NA	NA	0.09	1.21	
Maharashtra	60.02	34.25	1.19	1.05	1.62	0.82	1.30	0.48	0.36	NA	0.26	NA	2.17	Joshi and Kodu 2012
Haryana	54.2	33.6	4.59	1.35	2.43	1.88	0.453	1.09	0.2	NA	NA	NA	NA	Chand et al. 2009
Madhya Pradesh	62.57	23.75	5.25	1.75	NA	0.82	1.36	NA	NA	NA	0.14	NA	NA	Tiwari et al. 2014
Punjab	45.18	26.57	4.98	1.96	1.95	1.53	NA	NA	NA	NA	NA	NA	NA	Kumar et al. 2014
Rajasthan	53.36	26.49	10.86	1.34	1.47	0.80	0.77	1.43	1.70	NA	0.37	NA	1.39	Das 2018
Fly ash range	38-63	27-44	3.3-6.4	0.2-8	0.4-1.8	0.04-0.9	0.01-0.5	NA	NA	NA	0.07-0.43	NA	0.2-5.0	C-Farm
Pond ash range	37.7-75.4	11.7-53.3	3.5-34.6	0.2-0.6	0.2-1.4	0.1-0.7	0.1-0.8	NA	NA	NA	0.05-0.31	NA	0.01-20.0	
Fly Ash (Uttar Pradesh)	64.34	28.36	2.92	0.5	1.54	0.95	0.51	0.14	0.33	NA	0.11	NA	NA	Present study

NA: Not available

4.6 POTENTIAL OF HYDROGEN (pH)

The pH value of the fly ash is generally more than the other classes of coal ash and depicts the alkaline behavior (FAM 2001). The classification of fly ash based on pH is explained in Table 4.3. Fly ash produced in India falls in the pH range of acidic ash. The pH of the present fly ash was coming in the acidic range, i.e., pH is equal to 6.42. The more elevated magnitude of pH of class C fly ash and fly ash with alkaline oxides have been observed by Pandian (2013). As per the XRF results, the present fly ash is falling under class F category. Similarly, the average pH of the present local soil has been found to be 7.37. However, the pH of natural soil varied in the range of 5–8, which has increased to 12.8 when it got mixed with lime and fly ash (Dermatas and Meng 2003). Similarly, the application of fly ash (8%) to the calcareous soil and acidic soil results in an increment of pH from 8 to 10.8 and 5.4 to 9.9 respectively (Page et al. 1979). This increase in pH of the soil is due to the accelerated production of Ca, Na, Al and OH ions in the fly ash (Wong and Wong 1990). Plank and Martens (1974) and Page et al. (1977) have found fly ash characteristics from acidic to basic range (pH 4.5 to 12). The prominent content of sulfur leads to the generation of low pH ashes. In addition, leachate produced from the fine fly ash is composed of high trace elements because of the low pH in comparison to the coarser particles (Tan and Xiao 2012). The use of a significant amount of fly ash introduces changes in the pH of the soil and increases the salinity of the soil (Sharma et al. 1997).

Table 4.3 Typical range of pH of fly ash for the acidic and basic classification. (Kolbe et al. 2011)

Fly Ash	pH value
Acidic ash	1.2 – 7
Mildly Alkaline ash	8 – 9
Strong Alkaline ash	11 - 23

4.7 SUMMARY

The summary of the chemical analysis of fly ash and local soil has been briefly emphasized. Fly ash displays distinct characteristics as compared to the local soil. The fly ash particles are spherical and have a glassy texture, commonly referred to as cenospheres and plerospheres. On the other hand, the local soil particles are flaky, angular, and thin-chipped in shape. When it comes to elemental composition, fly ash contains high levels of aluminum (Al), silicon (Si), and oxygen (O) as its primary constituents. In contrast, the local soil has elevated levels of Al, Si, O, magnesium (Mg), and potassium (K). In terms of mineral composition, fly ash exhibits major peaks of Quartz, Alumina, Hematite, and Titanium dioxide. However, the local soil showcases the presence of Quartz as well as additional minerals such as Stilpnomelane, Muscovite, Leucite, Gupeiite, and Biotite. Chemically, fly ash is primarily composed of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), and iron oxide (Fe_2O_3), which collectively make up more than 95% of its chemical constituents. This composition classifies the fly ash as class F fly ash. Furthermore, there is a notable difference in the behavior of fly ash and local soil. Fly ash exhibits acidic behavior, while the local soil demonstrates a basic nature.