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Physico-chemical and Mineralogical Properties of Fly Ash from Thermal Power Stations in Northern Vietnam

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Abstract: Fly ash is produced as a result of coal combusion at high temperatures in thermal power stations and discharged in ash ponds which absorb huge amount of water, energy, and land area. As the demand for power increases, the amount of fly ash from thermal power stations in Northern Vietnam is increasing year by year. Therefore, the environmental friendly fly ash management would remain a great concern. In this paper, physico-chemical and mineralogical properties of fly ash from Pha Lai, Mong Duong and Ninh Binh thermal power stations were studied for ultilization to improve soil properties. Results shows that the properties of fly ash depend on the nature of parent coal, conditions of combustion, type of emission control devices, and storage and handling methods. The fly ash samples occur 1-8 μm in particle size and rounded to angular in shape. They are alkaline (pH_{KCl} >9) and CEC considerably ranged from 8.44 meq/100 g to 8.68 meq/100 g. All samples comprised of Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb and Pb with the highest contents of Al and Si. Of which, the highest content of Al and Si presents in fly ash sample from Pha Lai and Ninh Binh, respectively. High contents of K, P, Ca, Mg, S and some micro-nutrients are also found in fly ash samples. However, they have very low contents of radioactive elements (^{226}Ra, ^{238}U, ^{232}Th, ^{40}K) and heavy metals. Besides, fly ash contains minerals such as quartz (SiO_2) and mullite ($Al_2Si_2O_{13}$).

Keywords: Fly ash, thermal power station, fly ash properties, improving soil properties.

1. Introduction

Fly ash is produced as a result of coal combusion at high temperatures in thermal power stations. As the demand for power increases, the amount of fly ash produced from thermal power stations in Vietnam is increasing year by year. The thermal power plants estimate to consume 2,172 million tons of coal and discharge from 651 to 760 million tons of fly ash for a production capacity of 7,240 million Wh in 2020 [1]. In fact, the coal ash byproduct has been classified as a Green List waste under the Organization for Economic Cooperation and Development (OECD). However, this industrial byproduct has not been properly utilized rather it has been neglected like a waste substance in Vietnam. Given in this circumstance, interest in the use of fly ash as a soil amendment derived from (i) the need of develop sustainable uses of this by-product and (ii) reports revealing improved soil quality and crop growth following addition of fly ash to some soils due

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to an increased soil water holding, capacity surface area, capillary action, nutrient-holding capacity compared with sands, and improved soil nutritional status of soils via increases in cation exchange capacity (CEC) and by provision of some essential nutrients [2, 3, 4, 5]. However, since almost all naturally existing elements are present in fly ash [4], the potential release of trace elements may also be an issue determining the suitability of some sources for use as a soil amendment. As far as you concern, the physico-chemical and mineralogical properties of a particular fly ash are dependent on the composition of the parent coal, conditions during coal combustion, efficiency of emission control devices, and practices used during storage and handling [6]. Knowledge on these properties of fly ash is essential for understanding and in the future predicting the behavior of fly ashe in agricultural ecosystems. Therefore, the present study evaluated some physico-chemical and mineralogical properties, of relevance to sand soil quality improvement, for fly ashes from three thermal power stations namely Pha Lai, Mong Duong and Ninh Binh in Northern Vietnam.

2. Materials and methods

2.1. Sample collection

Fly ash samples captured by highly efficient electrostatic precipitators were collected from dumping sites of three thermal power stations, namely Pha Lai, Mong Duong and Ninh Binh, in 2015 for characterization. After collection, the fly ash was thoroughly mixed and stored in plastic-lined containers at room temperature before use.

2.2. Nano Scanning Electron Microscope (NanoSEM)

The FEI Nova NanoSEM 450 scanning electron microscope which delivers best in class imaging and analytical performance was used to study the morphology of the fly ash particles.

2.3. pH and cation exchange capacity (CEC)

The pH of 1 M KCl after being mixed with fly ash (1:2.5 w/v) was potentiometrically measured with a pH meter. The CEC of fly ash was determined by ammonium acetate method (IS:2720).

2.4. Particle Induce X-ray Emission (PIXE)

PIXE is a unique technique for performing non-destructive analysis, which is based on the measurements of characteristic X-rays induced by the energetic proton beam directed onto the surface of a specimen. This technique has been used for a variety of analytical applications with an MeV accelerator. In present study, the Model 5SDH-2 Pelletron Accelerator (NEC, USA) was used to determine the elemental composition of fly ash.

2.5. X-ray fluorescence (XRF) and X-ray diffraction (XRD)

The chemical composition of fly ash samples were analyzed using X-ray fluorescence spectrometry (Shimazu 1800, Japan). This is an X-ray instrument used for routine, relatively non-destructive chemical analyses of major and trace elements in rocks and minerals.

The fly ash sample were also evaluated for their mineralogical composition by the SIEMENS D5005 X-ray diffractometer (Bruker, Germany). X-ray diffraction is the most powerful technique used for analysis of minerals identification and quantification. The analysis provides information about the minerals present in a sample and also the abundance.

2.6. Gamma Spectroscopy System

Gamma spectroscopy is the science of identification and/or quantification of radionuclides by analysis of the gamma-ray energy spectrum produced in a gamma-ray spectrometer. In this study, the ORTEC GEM - 30 Gamma Spectroscopy (USA) was used to identify and quantify radioactive elements in fly ash samples.

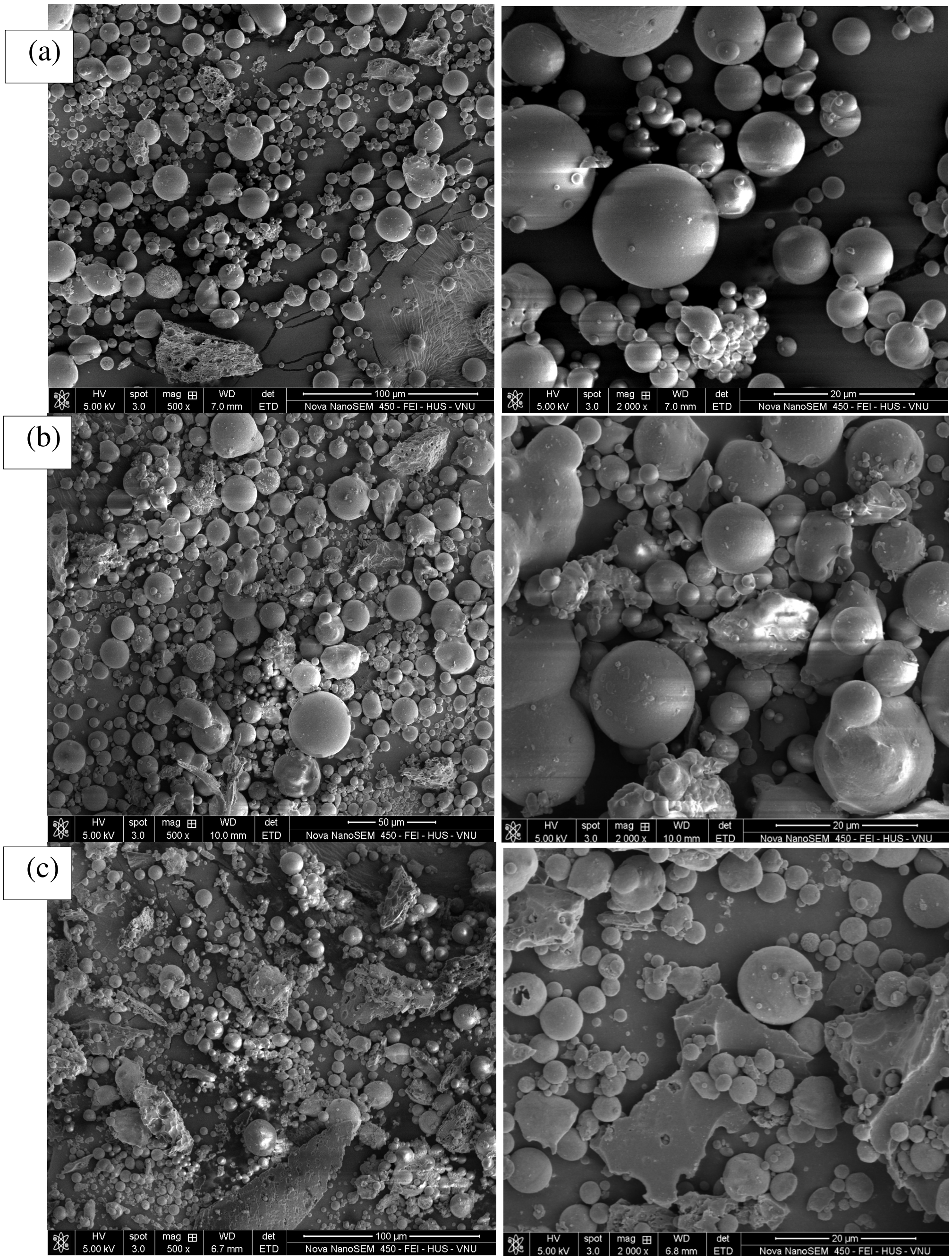

Figure 1. SEM micrographs of fly ash samples (a) Pha Lai, (b) Mong Duong, (c) Ninh Binh (X 500 and X 2000).

3. Results and discussion

3.1. Morphology of fly ash particles

The typical SEM photomicrographs of the fly ash samples were shown in Figure 1. The samples consists of almost regular spherical (cenospheres) particles ranging 1 μm to 8 μm in diameter. Pha Lai fly ash is finer than the others. Usually, fly ash composed of mostly small and spherical particles [7].

Table 1. Elemental composition of fly ash samples taken from thermal power stations.

Element	Pha Lai			Mong Duong			Ninh Binh		
	Conc. (ppm)	% Stat.	LOD* (ppm)	Conc. (ppm)	% Stat.	LOD* (ppm)	Conc. (ppm)	% Stat.	LOD* (ppm)
Mg	6414.6	2.04	137.3	5999.1	2.07	137.1	11143.9	1.44	117.5
Al	114238.6	0.24	87.3	98171.2	0.25	117.7	123879.5	0.23	81.2
Si	239005.7	0.15	96.3	204369.7	0.16	20.2	210781.3	0.16	72.9
P	404.2	12.91	65.4	474.5	9.66	58.5	426.9	12.08	69.5
S	909.1	3.03	20.9	2445.6	1.61	16.4	14035.5	0.67	14.4
Cl	-	-	-	160.1	11.00	24.6	828.5	4.19	34.0
K	35327.7	0.16	22.9	31118.0	0.60	48.4	33094.3	0.59	86.0
Ca	5152.9	1.15	79.4	7326.2	2.33	210.2	19564.2	1.20	241.3
Ti	4285.7	0.43	18.5	3586.3	2.94	51.8	3828.6	2.61	62.1
V	-	-	-	152.5	9.81	40.1	-	-	-
Cr	154.1	3.37	9.0	137.7	3.60	8.6	113.9	4.77	10.0
Mn	275.0	2.24	9.5	265.7	2.26	8.6	290.6	2.22	9.9
Fe	31119.2	0.15	15.0	30122.4	0.15	9.4	36901.2	0.13	7.2
Ni	69.6	4.77	3.6	67.9	4.72	3.7	81.7	4.48	4.4
Cu	57.8	6.34	3.6	53.0	6.83	3.8	63.1	6.11	3.7
Zn	112.7	4.15	3.3	123.1	3.94	3.5	134.7	3.92	3.0
Rb	254.4	8.48	17.6	260.9	8.61	29.4	267.2	9.00	33.1
Sr	135.3	14.28	19.8	-	-	-	129.3	14.81	27.1
Pb	134.3	11.25	16.2	-	-	-	129.3	14.10	23.0

*LOD: Limit of Detection

Fly ash is comprised primarily of fine particles, therefore if applied at sufficient rates it can be used to change soil texture increasing soil water holding capacity [5]. The physical structure of fly ash often consists of "hollow spheres" and these particles show an increased surface area, capillary action, and nutrient-holding capacity compared with sands [2].

3.2. pH and cation exchange capacity (CEC) of fly ash

The pH of fly ash depends largely on the sulphur content of the parent coal [8] and the type of coal used for combustion affects the sulphur content of fly ash [9]. In this study, all fly ash samples were alkaline (pH_{KCl} >9). The pH_{KCl} ranged from 9.4 in Ninh Binh to 9.7 in Pha Lai and to 9.9 in Mong Duong fly ash. It may be due to low sulfur content of parent coal and presence of hydroxides and carbonates of Ca and Mg. Thus, they can be used as soil amendment to decrease soil acidity. The CEC of fly ash samples from Pha Lai, Mong Duong and Ninh Binh were 8.44, 8.46 and 8.68 (meq/100g), respectively. High CEC in fly ash could be expected to aid the retention and availability of cationic plant nutrients in soils when amended with fly ash [4].

3.3. Elemental composition of fly ash

Almost all naturally existing elements are present in fly ash [4]. Elemental composition of fly ash samples from Pha Lai, Mong Duong and Ninh Binh was determined using the Model 5SDH-2 Pelletron Accelerator (NEC, USA) and shown in Table 1. Their PIXE spectra of fly ash samples were also presented in Figure 2, 3 and 4. All fly ash samples are comprised of Mg, Al, Si, P, S, Cl, K, Ca, V, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Pb with the highest contents of Al and Si. Of which, the highest content of Al (123,879.5 ppm) and Si (239,005.7 ppm) were consisted in fly ash sample from Pha Lai and Ninh Binh thermal power stations, respectively. Al in fly ash is mostly bound in insoluble aluminosilicate structure, which considerably limits its biological toxicity [9]. Whereas, the contents of Cl and V in Pha Lai, V in Ninh Binh and Sr and Pb in Mong Duong fly ash sample were below the limit of detection. The rather high contents of K, Fe, Ca and Mg are found in fly ash samples. Therefore, the amendment with fly ash can improve the nutritional status of soils by provision of these essential nutrients.

3.4. Chemical Composition

The chemical compositions of fly ash samples are given in Table 2. It can be noticed that the major matrix elements in fly ashes were oxides of Si and Al and together with significant percentages of K, Fe, Mg, Ca, Ti, Na and P. There was not considerable variation in the ratios of these and other elements among the different samples of fly ash.

Table 2. Chemical composition of fly ash samples taken from thermal power stations.

Chemical composition	Pha Lai		Mong Duong		Ninh Binh	
	Content (%)	Standard deviation	Content (%)	Standard deviation	Content (%)	Standard deviation
SiO_2	57.02	0.17	54.27	0.13	37.41	0.06
Al_2O_3	23.82	0.13	25.02	0.02	17.39	0.21
Fe_2O_3	4.69	0.15	4.71	0.11	5.61	0.13
P_2O_5	0.13	0.00	0.16	0.00	0.16	0.00
K_2O	6.56	0.05	6.76	0.01	5.16	0.05
CaO	0.81	0.01	0.91	0.00	1.21	0.01
MgO	1.16	0.00	1.22	0.01	1.11	0.01
TiO_2	0.78	0.02	0.78	0.02	0.63	0.01
Na_2O	0.09	0.00	0.16	0.00	0.17	0.00
MnO	0.04	0.00	0.04	0.00	0.06	0.00
H_2O-	0.35		0.58		14.02	
LOI (H_2O+)*	4.36		5.24		16.91	

* Loss on ignition

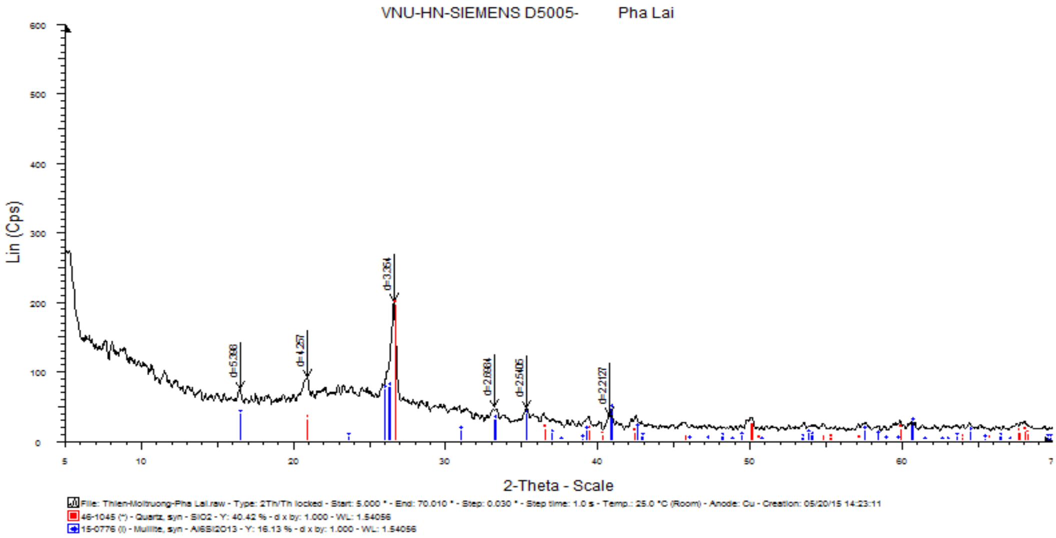

Figure 2. XRD pattern of Pha Lai fly ash.

3.5. Mineralogical composition

The XRD patterns of fly ash samples were presented in Figure 5, 6 and 7. Results obtained by XRD showed that quartz is the most predominant mineral present in all fly ash sample. The major mineralogical constituents of Pha Lai fly ash are quartz (SiO_2) (40,42%) and mullite ($Al_6Si_2O_{13}$) (16,13%), Mong Duong fly ash are quartz (SiO_2) (70,89%) and mullite ($Al_6Si_2O_{13}$) (23,15%), whereas Ninh Binh fly ash are quartz (SiO_2) (61,51%), mullite ($Al_6Si_2O_{13}$) (26,10%) and calcite ($CaCO_3$) (11,98%).

3.6. Radioactive elements

The experimental results of analysis for radioactive elements on fly ash samples using ORTEC GEM -30 Gamma Spectroscopy (USA), as shown in Table 3, the contents of ^{226}Ra, ^{238}U, ^{232}Th, ^{40}K are very low and acceptable for agricultural soils. Therefore, the potential release of radioactive elements was not an issue when use these fly ash samples as a soil amendment.

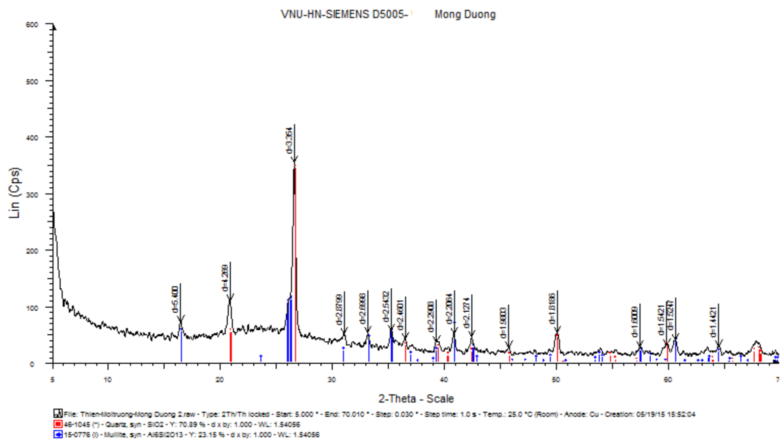

Figure 3. XRD pattern of Mong Duong fly ash.

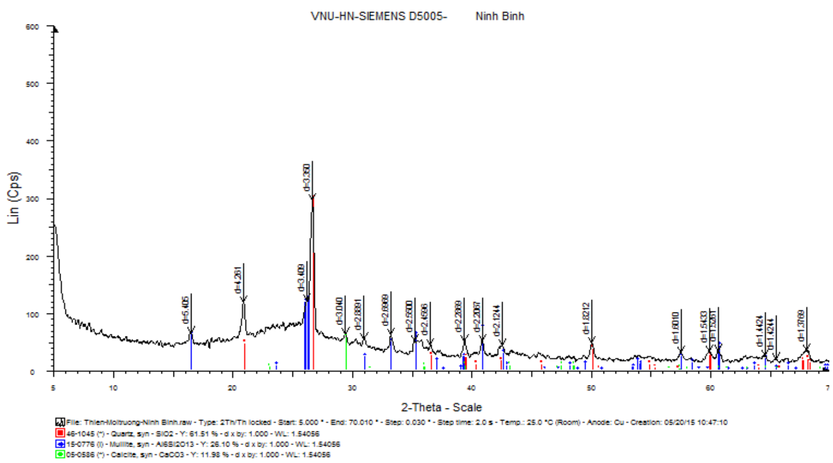

Figure 4. XRD pattern of Ninh Binh fly ash.

Table 3. Radioactive elements in fly ash samples taken from thermal power stations.

Samples	Radioactive elements (Bq/kg)			
	^{226}Ra	^{238}U	^{232}Th	^{40}K
Pha Lai	50.41	58.69	130.36	1043.5
Mong Duong	41.09	51.66	92.50	1104.7
Ninh Binh	43.33	53.51	101.15	1193.20

4. Conclusions

Some physico-chemical and mineralogical properties of fly ash samples from three thermal power stations namely Pha Lai, Mong Duong and Ninh Binh were evaluated. Regardless of inconsiderabe differences in properties of fly ash due to parent coal source, combustion, storage and handling conditions, all samples are alkaline and have high CEC, almost cenospheres particles, high contents of K, Fe, Ca and Mg, low contents of heavy metal and radioactive elements, and main constituents of quartz (SiO_2) and mullit ($Al_6Si_2O_{13}$). Therefore, the amendment of sandy soil with sufficient rates of these fly ash materials may improve sandy soil quality and thereby increase crop production.

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Một số tính chất lý, hóa và khoáng học của tro bay từ các nhà máy nhiệt điện ở miền Bắc Việt Nam

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Tóm tắt: Tro bay được tạo ra từ việc đốt than tại các nhà máy nhiệt điện và thải ra hồ chứa gây lấn chiếm diện tích đất và ô nhiễm môi trường. Do nhu cầu tiêu thụ điện năng ngày càng cao, lượng tro bay thải ra từ các nhà máy nhiệt điện ở miền Bắc Việt Nam ngày càng nhiều. Vì vậy, việc quản lý tro bay theo hướng tiếp cận thân thiện với môi trường vẫn là một mối quan tâm lớn. Trong bài báo này, một số tính chất lý, hóa và khoáng học của tro bay từ các nhà máy nhiệt điện Phả Lại, Mông Dương và Ninh Bình đã được nghiên cứu nhằm ứng dụng chúng trong cải tạo đất. Kết quả cho thấy, tính chất của tro bay phụ thuộc vào bản chất của than đá, phương pháp đốt, công nghệ kiểm soát và thu gom. Tro bay có kích thước hạt khoảng 1-8 µm, chủ yếu ở dạng hình cầu, có tính kiềm và CEC biến động từ 8,44 meq/100g đến 8,68 meq/100g tro bay. Tro bay đều chứa các nguyên tố Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb và Pb. Trong đó, Al và Si là hai nguyên tố có hàm lượng cao nhất. Hàm lượng cao nhất của Al và Si được phát hiện lần lượt trong mẫu tro bay từ nhà máy nhiệt điện Phả Lại và Ninh Bình. Các nguyên tố dinh dưỡng (K, P, Ca, Mg và S) trong tro bay có hàm lượng khá cao và chứa hầu hết các nguyên tố dinh dưỡng vi lượng như Fe, Zn, Cu, Mn, Cr, Ni... Ngoài ra, trong tro bay còn chứa các nguyên tố phóng xạ (^{226}Ra, ^{238}U, ^{232}Th, ^{40}K), các nguyên tố vết và kim loại nặng, tuy nhiên hàm lượng của chúng khá thấp. Thành phần khoáng của tro bay chứa chủ yếu các khoáng quartz (SiO_2) và mullite ($Al_2Si_2O_{13}$).

Từ khóa: Tro bay, nhà máy nhiệt điện Phả Lại, tính chất tro bay, cải tạo tính chất đất.