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DETERMINING THE ROLE OF INDIVIDUAL FLY ASH PARTICLES IN INFLUENCING THE VARIATION IN THE OVERALL PHYSICAL, MORPHOLOGICAL, AND CHEMICAL PROPERTIES OF FLY ASH

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Abstract. The properties of fly ashes vary because of the differences in the properties of their individual particles, and the determination of variation in these properties is of interest to the industries which use pulverized raw fly ash in applications, such as in cementitious materials and in the recovery of certain rare elements from raw fly ash. To investigate the differences in individual particles, four pulverized raw fly ashes from thermal power plants of the Czech Republic were used in this research. It was observed from FE-SEM that all four fly ashes consist of glassy hollow spherical, solid spherical, porous spherical, bright spherical, porous slaggy and compact slaggy particles. Box and whisker diagrams were plotted from the data of EDX individual particle analyses, which showed that the data of percentages for the Si, Al, and Fe elements is more scattered as compared to other elements. It was further observed from ternary phase diagrams and pseudo coloured images, that nature of fly ash particles changes from alumino silicate glassy to alumino silicate calcite metallic to pure ferro-metallic, where glassy particles showed high percentages and pure calcite particles were absent in fly ashes. Furthermore, a comparison between the XRF, the EDX total area analyses, showed that the EDX individual particle analysis gives more realistic and reliable data with median, mean, and the standard deviation for percentages of each element present in the fly ashes.

Keywords: fly ash; FE-SEM; EDX; analyses; glassy; metallic.

1. Introduction

Coal fly ash is a by-product of burning pulverized coal in coal-fired thermal power plants [1]. Around 750 million tonnes of fly ash are generated annually [2] but the global fly ash utilization is still 25 %, therefore a significant part of fly ash is being disposed into landfills [3]. Coal accounted for 39 % of the total world electricity generation in 2002, followed by gas 19 %, nuclear 17 %, hydro 16 %, oil 7 %, and renewables 2 %, while it is estimated that in 2030 the world's total electricity generation from coal will be 38 %, gas 30 %, hydro 13 %, nuclear 9 %, renewables 6 %, and oil 4 % [4]. Over 4 billion tonnes of coal are currently produced per year in the world, and the number is estimated to grow to 7 billion by 2030 [4, 5]. Estimates show that there are 869 billion tonnes of coal reserves in the world, half of which consist of brown coal. Based on current production rates, they would last around 115 years, which is significantly longer than the world's gas and oil reserves would last [6]. Forecasts have shown that in the next two decades coal will continue to be the primary source of energy as it has been in the last hundred years [7]. So fly ash will continue to be deposited in landfills for at least the next two decades if solutions for its re-utilization are not found.

The chemical composition of fly ashes is usually measured with the help of XRF analyses which give the average values of chemical composition and estimate that coal fly ash typically contains a high percentage of elements such as Si, Al, Ca, and Fe in it and relatively low percentages of heavy metals such as Cu, Zn, Pb, Hg with some rare earth elements [8, 9]. However, some elements in fly ash are more concentrated in certain particles than in the others and variation of chemical composition exists in fly ash particles. Therefore, the morphology of individual fly ash particles has a considerable effect on the overall chemical composition of the fly ash [10]. Morphologically, fly ash is composed of inorganics and incompletely combusted and/or non-combustible ingredients of spherical, hollow spherical, porous, angular, irregular or slaggy shapes [11, 12]. The high burnout temperatures achieved during the combustion process in conventional coal power stations strongly influence the morphology and chemical composition of fly ash [13]. In coal-fired boilers at furnace operating temperature, the coal particles may oxidize, fuse, decompose, agglomerate, or disintegrate depending on the melting point of the elements in them [14, 15]. However, elements with a high melting point remain unchanged during combustion, and sudden cooling after high temperatures results in the formation of spherical particles. Therefore, heating and cooling during the combustion process have a significant effect on the composition and morphology of fly ash particles [16]. The particle size of fly ash depends on factors such as the pre-combustion diameter of coal particles, or the distribution of mineral content in particles of coal [17].

The properties of fly ash depend significantly on the type and origin of the coal, and the factors affecting the properties of coal are connected to the formation factors of coal, which include the type of vegetation from which the coal was formed, the depths in which the coal was buried, the temperature and pressure at those depths, and the period of time for which the coal has been deposited at those depths [18, 19]. Victorian brown coal (lignite) from Australia was found to contain up to 70 % of water, which shows that brown coal can contain significant amounts of water, which is present in the pores of the coal particles, and when pulverized coal is spontaneously combusted, water escapes the particles of the coal. This process develops pores in the fly ash particles, which highly affects the morphology of fly ash [20, 21]. Therefore coal upgradation technologies are employed to remove a significant amount of water prior to the combustion of brown coal.

Usually, significant variations in the properties of fly ashes are observed because of different morphological shapes and varying chemical composition of their individual particles. The first objective of this research is to investigate different types of individual fly ash particles present in fly ashes and their influence in varying the overall physical and morphological properties of fly ashes. Then, by using FE-SEM EDX individual particle analyses, the nature of these individual particles is determined by plotting ternary phase diagrams and transforming grey scale FE-SEM images to pseudo-coloured images to calculate the percentages of the nature of different kinds of individual particles present in fly ashes. Furthermore, XRF analyses only give the average values of chemical composition, which lacks the details about the variation in chemical composition present in fly ashes due to their individual particles. Determining the variation in chemical composition is of interest to the industries which use pulverized raw fly ash in applications such as in cementitious materials in which silica containing particles are desired for pozzolanic reaction and calcium containing particles are desired for self-cementing properties. Moreover, the investigation of variation of chemical properties is desired by the industries which use fly ashes for recovery of rare earth elements such as mercury, which can be economically recovered from fly ashes if determined to be present in fly ashes in significant amounts. Moreover, the interest for the recovery of other elements from fly ashes, such as iron and aluminium, is growing, due to the low price of fly ash, which leads to economical recovery of these elements. The feasibility of recovery of elements can only be determined if the variation of chemical composition in fly ashes is known. Therefore, the second objective of this research is to use FE-SEM EDX individual particle analyses to develop statistical data for each element present in fly ashes. Then from statistical data to draw box and whisker plots for each element present in fly ashes to investigate the scattered nature of the data of percentages of elements present in fly ashes by which the spread of data around the median percentages of each individual element can be determined. The third objective of this research is to compare the data obtained by XRF, EDX total area, and EDX individual particle analyses to determine which method out of these three methods is more realistic and gives a detailed estimation of the chemical composition of fly ashes for the purpose of reliability.

2. Material and methods

2.1. Materials and physical properties

Pulverized brown coal fly ashes from the Ledvice thermal power plant, which is using coal deposits of Moravia, the Dětmarovice thermal power plant using coal deposits of Ostrava, the Počerady and Mělník thermal power plants using coal deposits of North and West Bohemia of the Czech Republic, and for comparison of physical properties, EN 197-1, CEM I 42.5 R cement were used in this research. Particle size analyses of fly ashes and cement were carried out on Fritsch Analysette 22, a laser particle size analyser, using its dry and wet dispersion unit. The density of fly ashes and cement were determined using a Helium Pycnometer, Pycnomatic ATC. For density measurements, 100 grams of powdered samples were oven dried at a temperature of 105 °C for 12 hours to ensure the removal of moisture from the samples, which could possibly affect the density measurements.

2.2. FE-SEM, EDX analyses

A field emission electron microscope (FE-SEM), Merlin Carl Zeiss (Germany), was used to capture the images of the specimens while operated at acceleration voltage of 30 kV, under high vacuum conditions. To determine the chemical composition AZtecEnergy EDX software from Oxford Instruments was used on the images of FE-SEM. The chemical composition of entire specimens was carried out using total area EDX analyses. On the other hand, in EDX individual particle analyses, fifty randomly selected points and small areas were chosen in each FE-SEM image of fly ash to determine the chemical composition of thirty one elements known to be present in the fly ash samples for which analyses were carried out in the AztecEnergy software. Microscopic samples were prepared with 1:3 solution of Araldite 2020/A epoxy resin

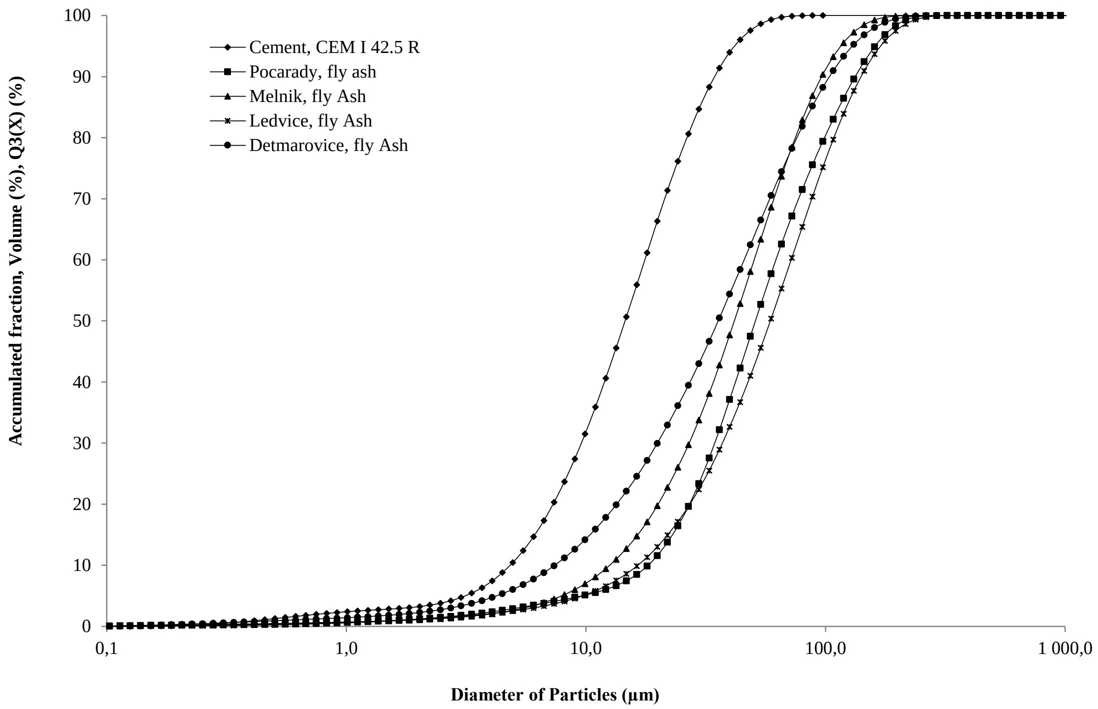

Figure 1. Comparison of cumulative particle size distribution of cement, and fly ashes from Počerady, Mělník, Ledvice, and Dětmarovice.

Physical properties	Cement	Počerady	Mělník	Detmarovice	Ledvice
Median diameter, d_{50} (µm)	14.57	51.07	41.69	35.67	58.86
97th percentile diameter, d_{97} (µm)	46.96	178.94	129.42	147.28	190.55
Span, $d_{90} - d_{10}$ (µm)	29.74	115.12	84.03	96.73	124.69
d_{90}/d_{10}	7.17	7.34	7.69	14.06	8.56
$C_u = D_{60}/D_{10}$	3.66	3.42	4.02	6.18	4.36
$C_c = D_{30}^2/(D_{60}D_{10})$	1.08	1.05	1.15	1.16	1.16
Density (g/cm^3)	3.15	2.21	2.05	2.29	2.17

Table 1. Physical properties comparison of cement, and Počerady, Mělník, Ledvice, and Dětmarovice fly ashes.

to Araldite 2020/B hardener with two drops of Xylen solution in a 50 ml solution of 1:3 epoxy to hardener ratio. The epoxy-hardener mixture added with the specimens of fly ashes was heated to 40 °C for 2 min to give the mixture a lower viscosity, thereby ensuring thorough penetration into the pores of the specimen. Then, to remove air bubbles from the samples, they were vacuum impregnated at 0.17 bar pressure for 2 hours in a Struers Citovac vacuum impregnation machine. Following impregnation, the specimens were left for hardening at a temperature of 40 °C for 24 hours. The specimens were then cut to the required size and were diamond polished on Struers, Tegramin-25. To avoid charging of the specimens under electron beam of field emission scanning electron microscope, the specimens were carbon coated to a thickness of 12.8nm with Quorum Q150R ES pumped sputter carbon coater. To distinguish the nature of individual fly ash particles, grey images obtained from field emission scanning electron microscope were transformed into pseudo-coloured images in five different colors by using the color difference observed on the original images in software developed using C++ computer language to calculate the percentages of particles with similar nature.

2.3. XRF analyses and LOI

An ARL 9400 XP sequential WD-XRF spectrometer was used to perform XRF analysis. It was equipped with Rh anode end-window X-ray tube type 4GN fitted with 50 µm Be window. All peak intensity data were collected by WinXRF software in vacuum. The generator settings-collimator-crystal-detector combinations were optimised for all 31 measured elements with analysis time of 6s per element. The obtained data were evaluated by standardless software Uniquant 4. The analysed powders were pressed into pellets of about 5mm thickness and with a diameter of 40 mm without any binding agent for the fly ashes from Ledvice, Dětmarovice, and Počerady power plants. The pellets of these fly ashes were covered with 4 µm supporting polypropylene (PP) film. However, the fly ash particles from Mělník did not stick together and therefore methacrylate was used as binding agent to bind the particles for analyses. The pellet for fly ash from Mělník was measured for XRF analyses without 4 µm supporting polypropylene (PP) film due to the use of binding agent. The time of measurement for each sample was kept at about 15 min to accurately determine the concentration of the elements and their oxides. The loss on ignition (LOI) method was used to estimate the content of un-burnt carbon in the samples. For trial purposes initially one fly ash sample was heated at 1000 °C for 1 h and the loss of weight was estimated. Subsequently the same sample was heated at 1200 °C for 1 h and very little change of mass was observed, therefore all measurements for LOI were carried out at 1200 °C for 1 h.

3. Results & discussion

3.1. Physical properties

Particle size influences the quality and efficiency of the materials considerably [22]. So, considering this aspect, particle size analysis was carried out on particle size analyser and the results are shown in Fig. 1. Measures of central tendency were calculated as shown in Tab. 1. It can be seen from Tab. 1 that the median diameter, d_{50}, for cement is considerably smaller than that of fly ashes, indicating smaller particle size of cement particles. Fly ashes from Ledvice and Počerady show a higher median diameter compared to fly ashes from Dětmarovice and Mělník, which shows that fly ashes from Ledvice and Počerady have a significantly large amount of coarse particles compared to that of fly ashes from Dětmarovice and Mělník. Ninety seventh diameter, d_{97} is a useful industrial measure to find the upper limit of particle sizes of fine powders [23]. It can be seen from Tab. 1 that d_{97} of cement is more than three times lower than that of fly ashes, and fly ashes from Ledvice and Počerady show a higher upper limit diameter compared to Dětmarovice and Mělník, indicating that even the upper limit diameter of these particles is more. Therefore, particles are coarser in Ledvice and Počerady fly ashes compared to Dětmarovice and Mělník fly ashes. Ledvice and Počerady fly ashes also show more values for the span $d_{90} - d_{10}$, which indicates that these two fly ashes have very fine micro size particles to large size particles of several hundred micrometres, whereas Dětmarovice and Mělník fly ashes have comparatively smaller spans, indicating that larger size particles are not present in them, while Portland cement particles show comparatively much less span compared to fly ashes. The differences in the particle size distribution of fly ashes can be attributed either to the differences in the coal source or the electrostatic precipitator at which they were captured. Usually there are three to four hoppers in an electrostatic precipitator for fly ash removal from particulate laden flue gas. When this flue gas is introduced from the inlet to the precipitator, firstly the larger sizes particles are collected at the first hopper which is close to the inlet while the smallest sizes particles are collected at the hopper which is away from the inlet. The end product of fly ash collected from the hoppers of the precipitator usually contains a mix of particles from each hopper. Because of this the particle size of the end product is significantly affected by the amount of particle sizes mixed from each hopper [24]. However, as the fly ashes used here are from different coal sources, if the fly ash capturing process is assumed to be the same for all the fly ashes, then the governing factor which influences the size of particles can be either attributed to the coal type or the combustion temperature inside the boiler. The percentile ratio d_{90}/d_{10} values shown in Tab. 1 are often used to characterize particles [25]. It can be seen here that cement and fly ashes have d_{90}/d_{10} values very close to each other, except for the Dětmarovice fly ash, which shows a very high value compared to the other fly ashes and cement. According to the classification of Merkus based on d_{90}/d_{10} [26], the cement and fly ashes from Počerady, Ledvice, and Mělník are broad ranged while the fly ash from Dětmarovice is very broad ranged. Coefficient of uniformity (C_u) and coefficient of curvature (C_c) were measured according to ASTM D-2487 [27], which shows that fly ash from Dětmarovice has $C_u > 6$, C_c between 1 and 3, therefore classified to be well graded, whereas cement and the other fly ashes don't satisfy this criterion and are classified as poorly graded. The density of fly ash particles varies significantly from particle to particle based on composition, porosity and entrapped gas bubbles within the particles [28]. It can be seen in Tab. 1 that fly ash from Mělník has the lowest value of density in the fly ashes and fly ash from Dětmarovice has the highest value of density in fly ashes, whereas cement in general has much higher density compared to that of fly ashes. There can be various reasons for the lower density of fly ash from Mělník, lower particle size compared to other fly ashes can be regarded as one of the reasons, and the large amount of entrapped gas bubbles forming more cenospheres can be another factor for the lower value of density. Vice versa is true for fly ash from Dětmarovice, which shows much higher value of density. On the other hand, the morphology of cement is different from fly ashes and has a higher particle density as compared to fly ashes, as also observed by [24].

3.2. Morphological properties

Measurements of particle sizes carried out by particle size analyser make the assumption that particles are spherical in shape and the diameters reported in the results are equivalent spherical particle diameters [29]. However, particles of fly ash can have several different shapes based on the combustion process and, type of coal [11, 12], therefore microscopic examination was carried out to determine the morphology of the fly ash particles. Field emission electron microscopic images at 75 × magnification were observed for the fly ashes from Počerady, Mělník, Dětmarovice, and Ledvice, as shown in Fig. 2. It is observed in Fig. 2 that all fly ashes consist of spherical, and slaggy particles. Moreover, some brighter particles were also observed. However, at 75 × magnification, the particle morphology cannot be clearly observed. Therefore, to observe the particle morphology clearly, FE-SEM images were captured at 500 × magnification, as shown in Fig. 3. It can be seen clearly in Fig. 3 that fly ashes consist of hollow spherical, solid spherical, porous spherical, bright particles, porous slaggy, and compact slaggy particles of micron, submicron and ultrafine size particles. It can further be observed that the particles of fly ashes from Počerady and Ledvice are porous, showing porosity in slaggy as well as spherical particles, whereas the particles of Mělník, and Dětmarovice are more compact, less porous, and more rounded compared to the particles of Počerady and Ledvice. The reason for differences in the particles of fly ashes is due to the rank of coal from which the fly ashes were combusted, or the differences in combustion temperature, or a combination of both. The finer the particles of fly ash, the higher the specific surface area, the better is the quality/rank of coal, which shows a larger amount of rounded particles and the higher the combustion temperature, the more rounded fly ash particles are formed [30]. Based on this, the fly ashes from Mělník; and Dětmarovice are classified as originating from a comparatively high-rank coal or burned at higher temperature, or either of these as compared to that of fly ashes from Počerady and Ledvice. The origin of porous particles in the fly ashes is influenced highly by the coalification process of coal. In this process, water is absorbed in plant remains and clay minerals to form coal. When the coal is spontaneously combusted in coal-fired thermal power-plant, this absorbed water is then immediately released, hence producing porous particles in fly ashes [31]. Hollow spherical particles seen in the fly ashes can be identified as cenospheres, which have been investigated by [32, 33]. The compact particles in fly ashes can be attributed to those particles of coal which contain very little absorbed water in them, which when combusted produced the compact fly ash particles. The slaggy fly ash particles are produced as a result of either low combustion temperature, or these particles were exposed to the combustion process for a short duration. In Fig. 3b for fly ash from Mělnik it can be seen that it contains a large diameter of bright sphere filled with more spherical particles in them. Such a type of sphere filled with spheres is called ferro-pleurospheres. It can also be seen here that both pleurospheres and a large number of cenospheres exist together in this specimen. The occurrence of both cenospheres and pleurospheres in the same sample of fly ash suggests that some cenospheres transform into secondary pleurospheres through a three-staged process described by [34]. This states that firstly stable cenospheres form due to the evolution of gas bubbles. Secondly, due to high temperature during combustion, collisions occur between particles which rupture the shell of the cenosphere, and finally the ruptured cenosphere is impregnated with microspheres to form secondary pleurospheres. However, from Fig. 3b it is seen that the shell of the ferrospheres is bright, which indicates that cenospheres also contains bright patches possibly rich in Fe. These cenospheres having Fe rich patches on them, when collide with other slaggy particles during secondary pleurospheres formation, this raptures the cenospheres, forming ferro-pleurospheres.

3.3. Chemical Properties using EDX total area and XRF analyses

The maximum area at lowest possible magnification was selected in FE-SEM images of Fig. 2, and EDX analysis was carried out for thirty one possible elements which are known to be present in fly ashes, for which the results are presented in Tab. 2. ASTM C 618 defines fly ash to be Class F if it contains at least 70 % of $SiO_2 + Al_2O_3 + Fe_2O_3$ [35] and according to this definition the fly ashes from Počerady, Mělník, Dětmarovice, and Ledvice are classified as Class F fly ashes. It can also be seen that all the fly ashes contain Si and Al in large amounts followed by Fe, Ca, K, Ti, Na, Mg, P, and Zr and various other trace elements like Bi, S, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, La, Ce, and Hg, as also determined by [36–38]. The fly ash from Počerady shows a high Si content and low Fe content compared to other fly ashes, which also indicates that Si is being replaced by Fe content in these fly ashes. The fly ash from Počerady is also rich in Na, Zr, Ni, and Zn. The fly ash from Dětmarovice contains a higher content of K, Ca, Fe, Mg, Ga, and Ge compared to the other fly ashes, and the fly ash from Mělník is rich in Ti, P, Ba, V, Mn, Co, Cu, As, Sr, La, and Ce compared to the other fly ashes. The differences in composition of elements in fly ashes can primarily only be attributed to the differences in the coal source. The elements oxygen and carbon are also known to be present in the tested specimens [15], but they have been excluded from the given EDX analyses because the preparation of samples usually absorbs the excessive amount of oxygen which if included in the analyses would lead to a wrong estimation of its content. During the preparation of the samples for electron microscope, the samples were coated with carbon, to avoid charging

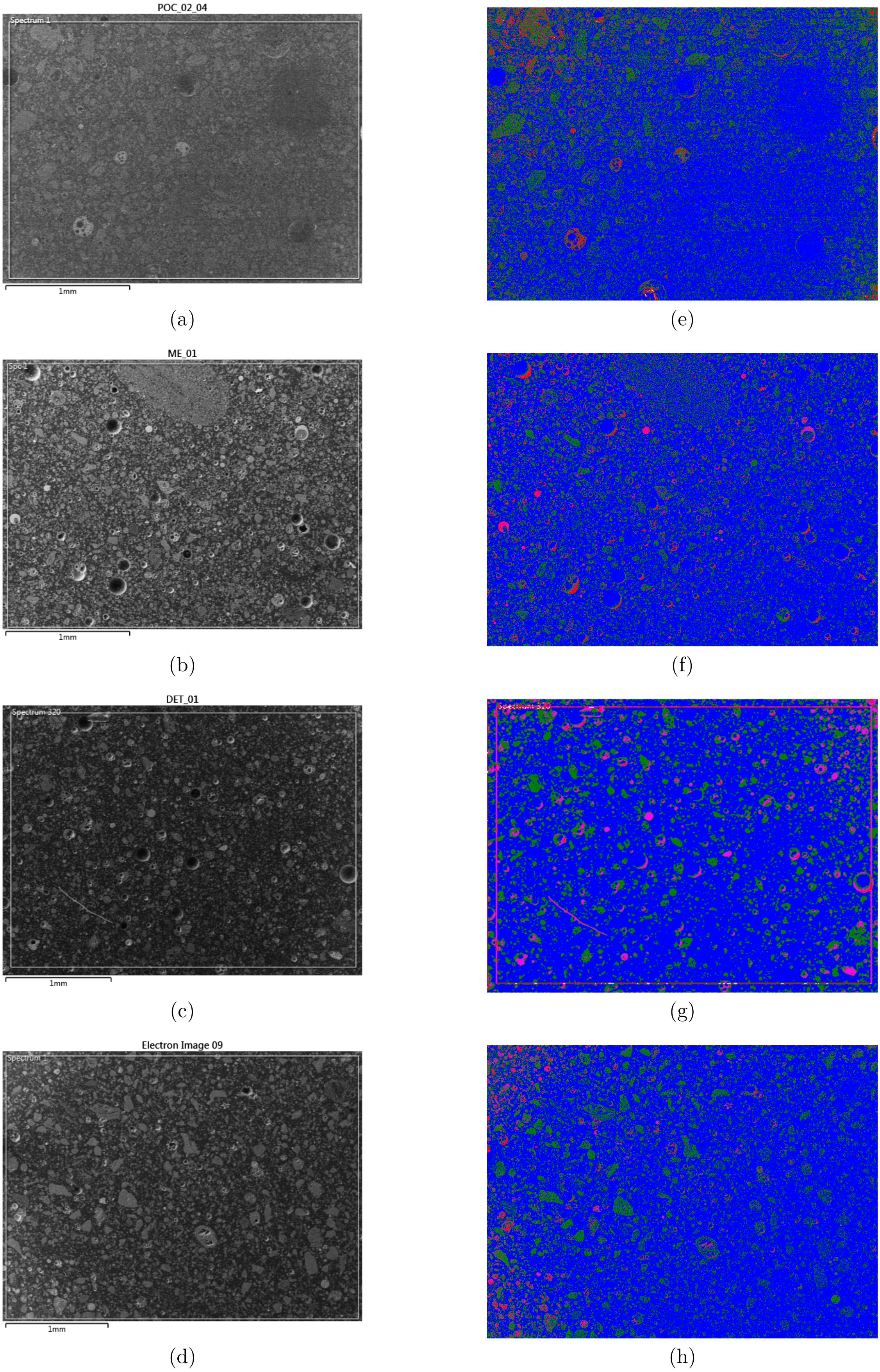

FIGURE 2. Field Emission Electron Microscopic images of fly ashes from (a) Počerady, (b) Mělník, (c) Dětmarovice, (d) Ledvice, at 75 X magnification, and transformed Pseudo-coloured images of fly ashes from (e) Počerady, (f) Mělník, (g) Dětmarovice, (h) Ledvice at 75 × magnification.

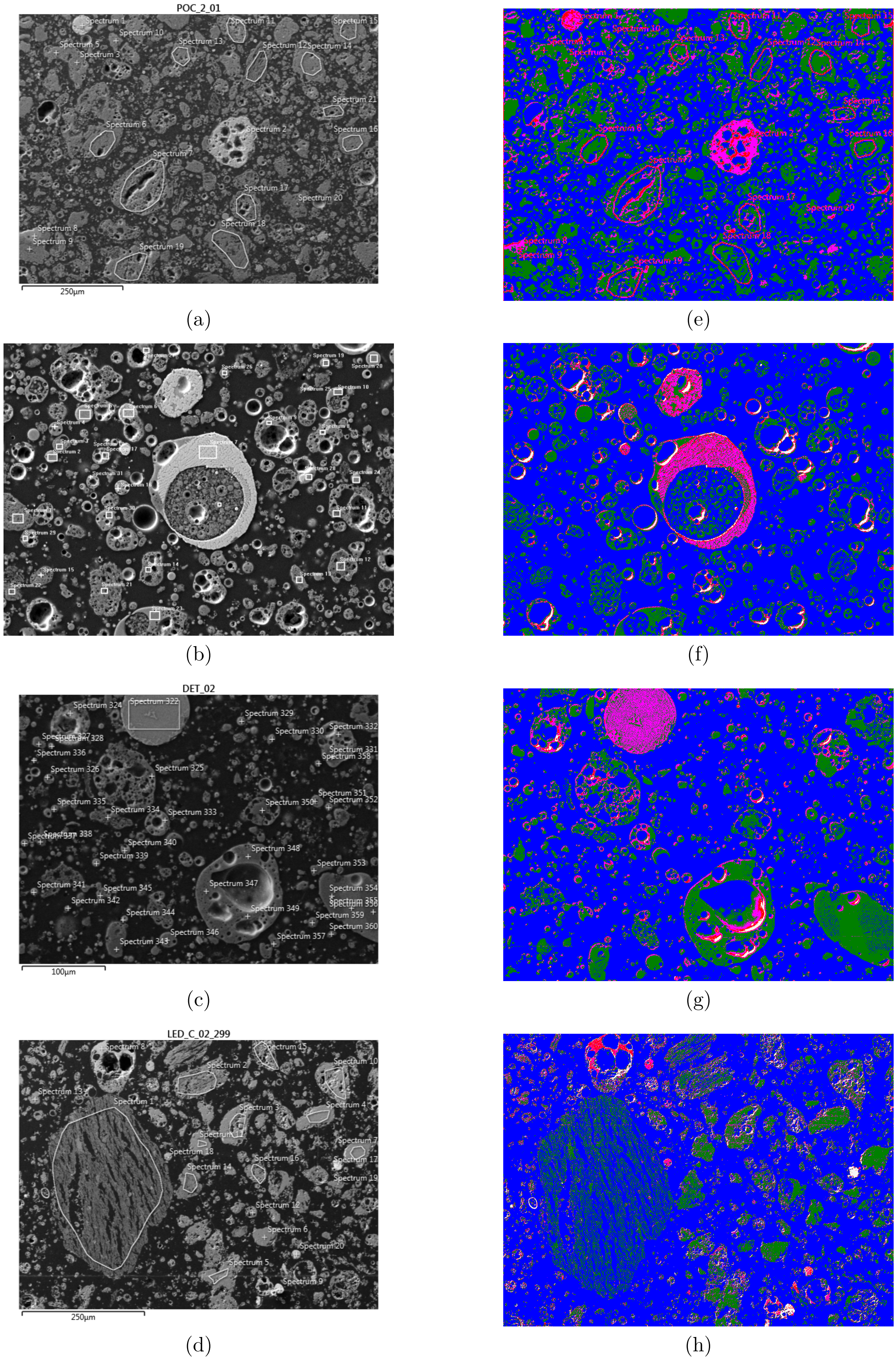

Figure 3. Field Emission Electron Microscopic images of fly ashes from (a) Počerady, (b) Mělník, (c) Dětmarovice, (d) Ledvice, at 500 X magnification, and transformed Pseudo-coloured images of fly ashes from (e) Počerady, (f) Mělník, (g) Dětmarovice, (h) Ledvice at 500 × magnification.

El. / oxide	Počerady					Mělník					Dětmarovice					Ledvice				
	(∗)	(†)	(‡)			(∗)	(†)	(‡)			(∗)	(†)	(‡)			(∗)	(†)	(‡)		
	Av.	Av.	Med.	Mean	St. d.	Av.	Av.	Med.	Mean	St. d.	Av.	Av.	Med.	Mean	St. d.	Av.	Av.	Med.	Mean	St. d.
Na / Na_2O	1.54	0.25	1.16	2.31	2.96	0.7	0.38	1.07	1.52	1.07	1.25	0.65	1.12	2.04	2.31	0.54	0.27	2.02	4.29	6.38
Mg / MgO	1.39	1.03	1.04	2.21	2.35	0.51	0.78	0.96	3.54	5.88	1.92	2.14	1.31	2.44	3.08	0.65	0.66	0.46	0.79	0.8
Al / Al_2O_3	26.18	33.93	25.37	23.08	10.1	25.58	35.83	22.78	19.51	10.5	20.71	29.26	16.81	16.28	8.52	27.86	37.55	29.68	26.45	8.42
Si / SiO_2	60.81	56.28	55.17	45.8	20.6	52.27	50.76	47.2	39.86	21.99	55.22	49.3	48.59	49.16	21.97	54.27	49.67	46.33	41.35	15.06
P / P_2O_5	0	0.17	0.46	0.74	1.15	0.83	0.2	0.51	0.59	0.4	0.71	0.34	0.62	1.09	1.25	0.69	0.15	0.23	0.35	0.42
S / SO_3	0	0.01	0.12	0.34	0.57	0	0	0.01	0.06	0.08	0	0.38	0	0.21	1.43	0.52	0	0.11	0.35	0.67
K / K_2O	2.09	1.81	2.4	2.46	1.52	2.4	1.13	1.36	1.63	1.48	5.85	3.28	5.02	4.63	3.19	1.79	0.85	0.31	0.5	0.55
Ca / CaO	1.34	1.92	1.33	1.66	1.31	2.45	3.68	1.52	5.11	8.89	4	3.44	1.58	6.98	11.86	1.63	1.17	0.26	1.38	2.43
Ti / TiO_2	0.89	1.87	0.76	0.82	0.51	3.71	3	1.75	3.05	6.3	1.37	1.13	0.78	1.41	2.14	3.14	2.89	0.54	1.02	1.2
V / V_2O_5	0	0.06	0.05	0.11	0.28	0.23	0.08	0.08	0.13	0.27	0	0.04	0	0.08	0.21	0	0.11	0.01	0.05	0.08
Cr / Cr_2O_3	0	0.03	0	0.07	0.2	0	0.03	0.01	0.07	0.13	0	0.03	0.03	0.42	1.26	0.07	0.04	0.03	0.03	0.03
Mn / MnO	0.03	0.03	0.06	0.31	0.58	0.17	0.05	0.09	0.37	0.72	0.15	0.11	0.06	0.24	0.43	0	0.02	0.01	0.07	0.11
Fe / Fe_2O_3	1.35	1.94	3.06	15.59	21.95	7.09	6.72	4.73	21.33	29.04	7.22	6.48	3.84	7.71	10.37	4.39	4.93	1.2	13.86	22.64
Co / Co_3O_4	0	0.01	0.05	0.24	0.57	0.04	0	0.1	0.14	0.16	0	0.01	0.07	0.18	0.42	0	0.01	0	0.06	0.1
Ni / NiO	0.06	0.01	0.03	0.11	0.32	0	0.01	0.03	0.12	0.38	0	0.01	0.03	0.17	0.37	0	0.02	0	0.05	0.1
Cu / CuO	0.07	0.01	0.06	0.09	0.12	0.19	0.02	0.04	0.06	0.07	0	0.01	0	0.07	0.14	0	0.02	0.01	0.04	0.07
Zn / ZnO	0.13	0.02	0.02	0.11	0.28	0	0.02	0.01	0.05	0.09	0.03	0.04	0.02	0.12	0.23	0	0.02	0	0.01	0.03
Ga / Ga_2O_3	0.11	0	0	0.12	0.36	0.02	0.01	0	0.11	0.43	0.14	0	0	0.19	0.67	0	0.01	0.01	0.06	0.1
Ge / GeO_2	0.03	0.01	0	0.15	0.38	0	0	0	0.09	0.33	0.28	0.02	0.03	0.15	0.29	0	0	0	0.13	0.48
As / As_2O_3	0	0	0.02	0.28	0.83	0.97	0.02	0.05	0.08	0.09	0.2	0	0	0.39	1.74	0.63	0	0.5	0.95	1.82
Se / SeO_2	0.05	0	0	0.14	0.36	0.36	0	0.01	0.1	0.16	0.47	0	0	0.18	0.44	0.64	0	1.48	1.39	1.72
Rb / Rb_2O	0.3	0.02	0.05	0.26	0.65	0	0	0.01	0.26	0.79	0	0.02	0.07	0.44	1.05	0.88	0.01	0	0.22	0.95
Sr / SrO	0	0.04	0.01	0.19	0.73	0.47	0.05	0.06	0.25	0.47	0.32	0.04	0.03	0.53	1.3	0.35	0.04	1.82	1.91	1.98
Y / Y_2O_3	0	0	0.02	0.33	1.09	0	0	0	0.14	0.25	0.16	0	0.07	0.67	2.04	0	0.01	1.64	2.16	2.45
Zr / ZrO_2	3.63	0.04	0.03	0.67	1.26	0	0.06	0.03	0.54	1.16	0	0.03	0.36	1.39	2.46	0	0.07	0.71	1.12	1.33
Ba / BaO	0	0.11	0	0.14	0.21	0.54	0.1	0.05	0.12	0.16	0	0.17	0	0.32	0.98	0.12	0.11	0	0.11	0.2
La / La_2O_3	0	0	0	0.3	0.81	0.8	0	0.01	0.23	0.81	0	0	0	0.24	0.74	0.05	0	0	0.06	0.19
Ce / CeO_2	0	0	0	0.43	1.74	0.18	0.01	0	0.24	0.62	0	0.01	0.05	0.48	1.26	0	0.01	0.06	0.12	0.22
Hg / HgO	0	0	0	0.14	0.32	0.49	0	0.07	0.17	0.3	0	0	0.01	0.58	1.58	0.84	0	0.09	0.37	0.66
Pb / PbO	0	0	0	0.31	0.55	0	0	0.02	0.3	0.62	0	0.25	0.02	0.94	2.11	0	0	0	0.52	1.4
Bi / Bi_2O_3	0.29	0	0.1	0.49	1.82	0	0	0.1	0.23	0.39	0	0	0	0.27	0.62	0.94	0	0	0.25	0.61
LOI	–	0.36		–	–	–	0.68		–	–	–	2.6		–	–	–	1.35		–	–

TABLE 2. Comparison of chemical compositions of fly ashes from Počerady, Mělník, Dětmarovice, and Ledvice using EDX total area analyses, XRF analyses, and individual particle EDX analyses. Legend: (∗) Total area EDX elemental analysis; (†) XRF oxides analysis; (‡) Individual particle EDX elemental analysis.

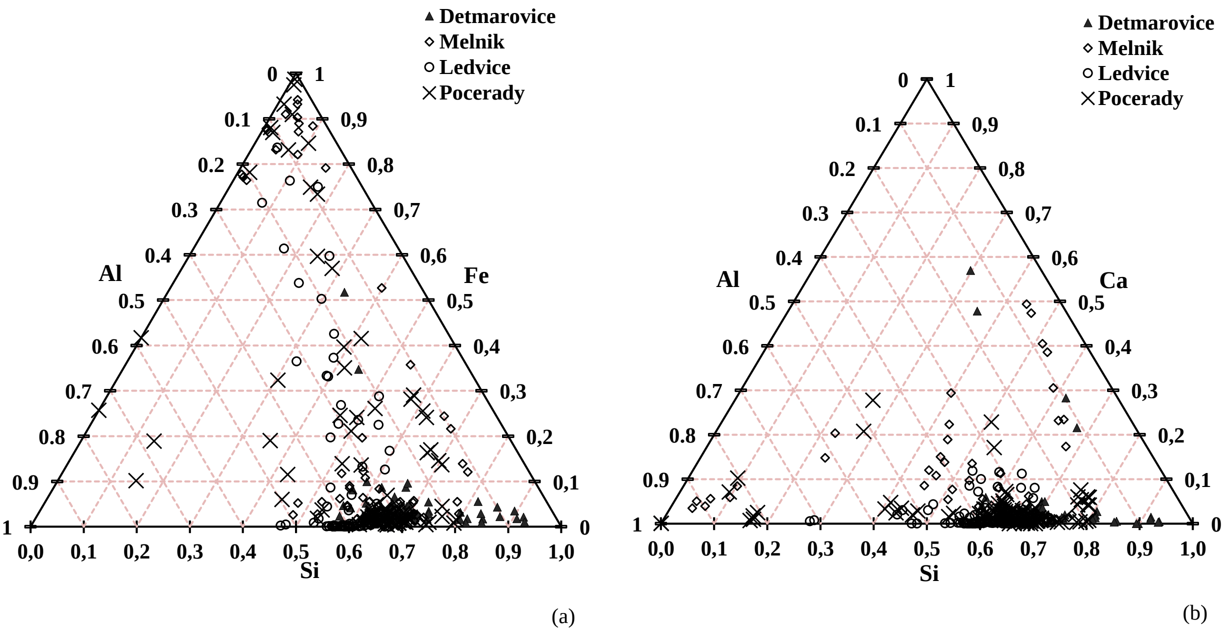

Figure 4. Ternary phase diagrams between (a) Si–Al–Fe and (b) Si–Al–Ca from EDX analyses of images of FE-SEM of Fig. 3.

under electron microscope. Because of the carbon coating of the specimens, carbon is excluded from the analyses as it would lead to inappropriate determination of its content if included in the analyses. A minor effect of some other elements might be present in the analyses because of the inorganic epoxy resin but as the same epoxy resin was used in all the specimens, for comparison purposes the results are accurate. From EDX analyses, the oxide composition of elements and un-carbon content of fly ashes were not determined, therefore XRF analyses were carried out for which the results are shown in Tab. 2. It can be seen here that all fly ashes have $SiO_2 + Al_2O_3 + Fe_2O_3$ more than 70 % which again according to ASTM C618 classifies them as Class F fly ashes. [35] The main difference observed from the comparison of total area EDX and XRF analyses in Tab. 2 is in the composition of Al and Al_2O_3 where it can be seen for all fly ashes that the percentage of Al_2O_3 from XRF analysis is about 10 % more as compared to the percentage of Al from total area EDX analysis, and more effect on the percentage of Si was observed, which was reduced in turn and the effect was distributed on other elements as well in small amounts. This shows that oxide of alumina (Al_2O_3) exists in high amount in fly ash as compared to oxides of other elements. It is further seen in XRF analyses in Tab. 2 that in fly ashes from Počerady and Ledvice the contents of CaO and Fe_2O_3 are low, because of which the particles of these fly ashes are more porous as compared to their contents in fly ashes from Mělník and Dětmarovice. As un-burnt carbon content was not determined using EDX analyses, to determine the percentage of un-burnt carbon in fly ash samples, the mass lost on ignition was determined as shown in Tab. 2. It can be seen here that LOI values for all fly ashes are very low, which shows that they originated from sub-bituminous coal [39] and it is unlikely that they would affect the properties of overall fly ash product. However, among all the fly ashes, fly ash from Dětmarovice shows a relatively high value of LOI, which means a higher amount of un-burnt carbon is present in it, which can affect its density slightly, but on the other hand it also has relatively high contents of Fe, and therefore it has more density as compared to other fly ashes.

3.4. EDX individual particle analyses

The individual particles of Fig. 3 were analysed by EDX analyses for the elements; Si, Al, Fe and Ca, as they are present in large percentages, as compared to other elements, as identified by the results of Tab. 2. Where necessary, small area analyses were used, and where particle detail was considerably small, point analyses were employed. The ternary Diagrams were plotted between the elements of Si–Al–Fe and Si–Al–Ca by calculating the ratios of percentages of three elements relative to each other from the results of the EDX analyses as shown in Fig. 4. In Fig. 4a,b Si was seen to vary from 0.5 to 0.95 for all the individual elements of the fly ashes, which showed that the majority of the fly ash particles are glassy in nature. However, in Fig. 4a it can also be seen that the bright particles seen in these images showed 0.1 to 0.98 ratio of Fe in them, and as the ratio of Fe increased in particles, the ratio of Si decreased, but simultaneously the ratio of Al decreased at a higher rate. As the ratio of Fe increased, the nature of the particles changed from glassy to glassy-metallic to metallic-glassy to pure metallic. On the other hand, Fig. 4b shows that the particles which are rich in Ca have a smaller ratio of

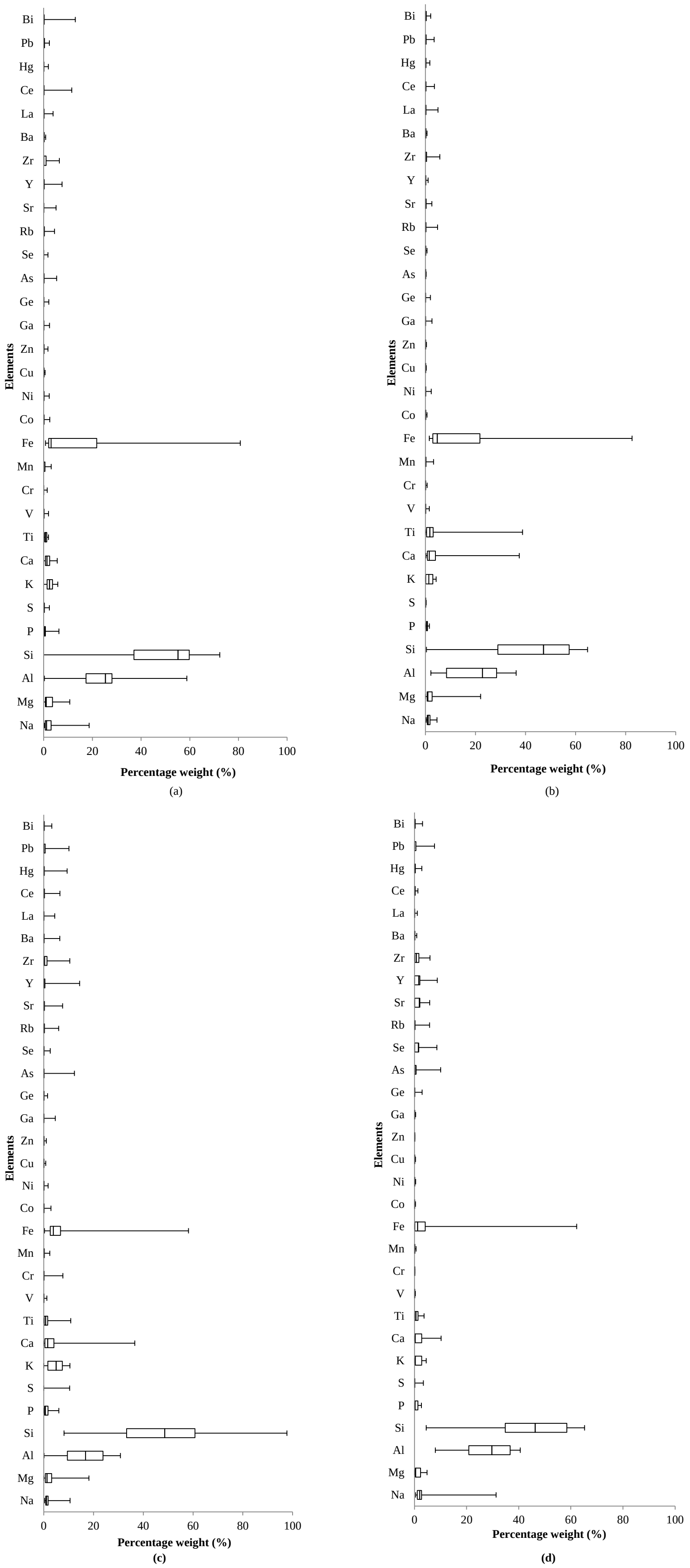

Figure 5. Box and whisker plots for chemical composition of fly ashes from (a) Počerady, (b) Mělník, (c) Dětmarovice, (d) Ledvice.

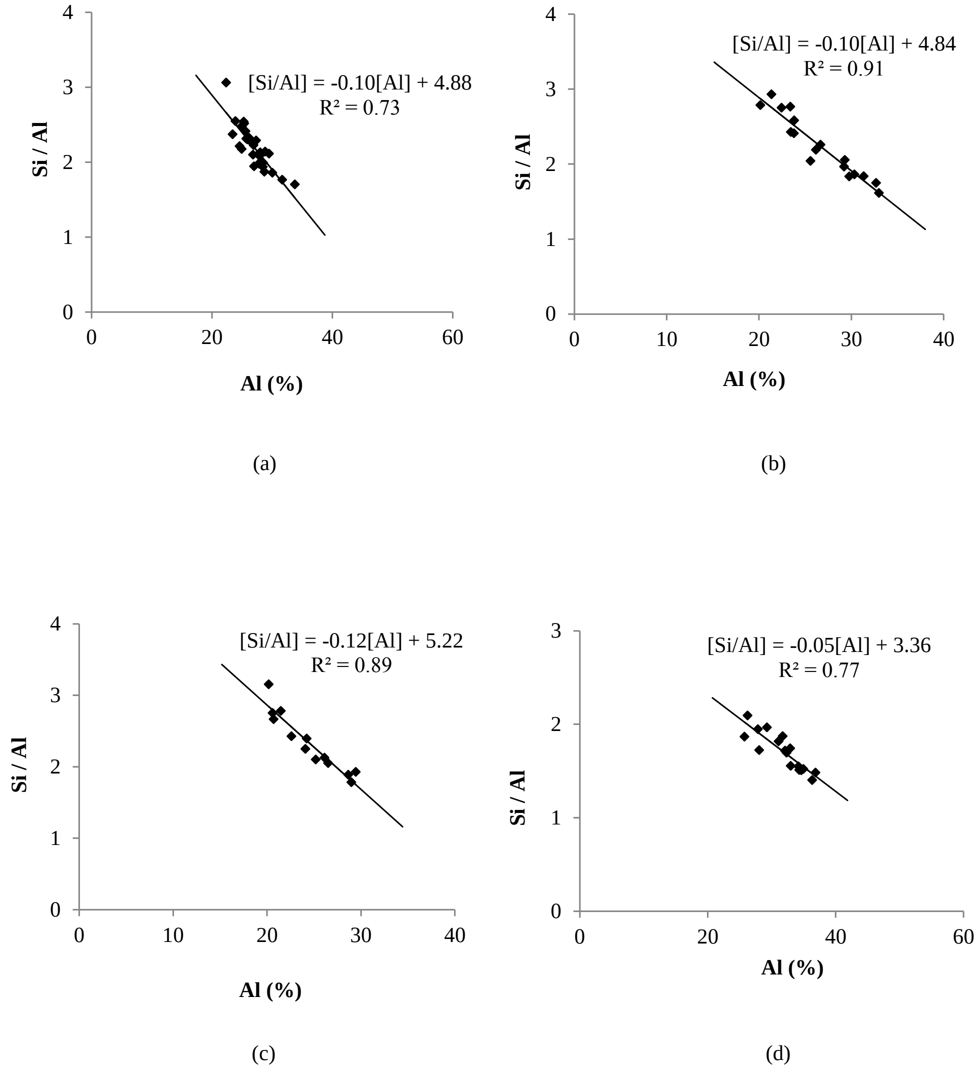

Figure 6. Si/Al vs Al for individual particles of Fig. 3 for fly ashes from (a) Počerady, (b) Mělník, (c) Dětmarovice, and (d) Ledvice.

Ca as compared to Fe-containing particles. Fig. 4a shows that as the Ca is increasing, particles change from glassy to glassy-calcite in nature, but pure calcite particles are not observed in the analyses.

Fig. 5a–d shows the box and whisker plots for percentages of each element present in the fly ashes from Počerady, Mělník, Dětmarovice, and Ledvice which show the minimum, lower quartile, median, upper quartile, and the maximum values of percentage of data of each element. It can be seen here clearly from box and whiskers plots that the percentages of elements in the fly ashes vary considerably, and the percentage of each element has a scattered set of data, which has a range of values in it. The range of percentages of Na is wider in the fly ashes from the Počerady and Ledvice fly ashes as compared to the Mělník and Dětmarovice fly ashes, and vice versa is observed for the percentages of Mg, in which it is seen that the Mělník and Dětmarovice fly ashes; show more range of percentages of Mg, while less range is observed for Počerady and Ledvice. The fly ash from Počerady shows a high variation in the values of Si, compared to the other fly ashes with high median value, which makes high Si containing particles of the fly ash from Počerady more active for pozzolanic reaction. However, the fly ashes from Mělník and Dětmarovice show a high range of values of Ca, which indicates that they possess particles with high Ca content in them with more median values as compared to fly ashes from Počerady and Ledvice. This again indicates that a lack of Ca in fly ash particles makes them more porous and less dense. Moreover, being rich in Ca, the fly ashes from Mělník and Dětmarovice, also possess better self-cementing properties as compared to the fly ashes from Počerady and Ledvice. High levels of titanium can be seen in the particles of the fly ashes from Mělník and Dětmarovice, which might also be responsible for the compactness of the particles. The fly ash from Dětmarovice also shows high levels of content of heavy metals, such as Ga, As, Rb, Sr, Y, Zr, Ba, La, Ce, Hg, and Pb, compared to the other fly ashes, which can primarily be attributed to the source of coal of the fly ash from Dětmarovice, which is known to be from a mix of black and brown coal deposits.

A comparison between the total area EDX elemental analysis, the XRF oxide analysis, and the individual particle EDX elemental analysis is shown in Tab. 2. Here EDX individual particle analyses show the values of the median, mean, and the standard deviation for percentage data of each element present in the fly ashes. The standard deviation usually presented in conjunction with the mean, determines how much a value in the data varies from the mean, and it is the most widely acceptable measure of dispersion, because it takes into consideration each variable in the data [40]. The value of the standard deviation is large, when values are spread apart from each other, and when values in a data set are tightly bound to each other, the value of the standard deviation is low [40]. It can also be seen in Tab. 2 that the values of the total area EDX analyses; and the XRF analyses are very close to the median values of the EDX individual particle analyses, except for the values of Al_2O_3 in the XRF analyses which are high as compared to Al in the EDX analyses because the oxide of alumina exists in high amount. It can be seen further here that the standard deviation of almost all the fly ash particles is quite large as compared to their mean percentages in which specifically the standard deviation percentages of Si, Al, and Fe are very high, because the mean percentages of these elements are also high. This means that the data of percentages of each element in each fly ash varies a lot, and the higher the mean percentage of elements in fly ash, the higher its standard deviation from the mean. This is because of the different nature of individual particles present in the fly ashes, in which some are glassy particles, having high Si and, Al contents and some are ferro-metallic particles rich in Fe, and very low in Si and Al.

Graphs were plotted for Si/Al versus Al, and the linear regression equations and their correlation coefficients were calculated, as can be seen in Fig. 6. From the results of individual analyses of fly ash particles it was seen that a majority of fly ash particles showed contents of Si > 50 %, and Al > 20 %, and the linear equations obtained for all fly ashes are nearly the same as those obtained by [41]. The brighter particles with a spherical shape were an exception to this, as they showed high contents of Fe. The fly ashes from Mělník and; Dětmarovice showed a high correlation coefficient which means that a stronger relationship between Si and Al exists between the particles of these fly ashes as compared to the Počerady and Ledvice fly ashes. The reason for the stronger relationship between Si and Al for Mělník and Dětmarovice fly ashes is that the particles of these fly ashes are compact as compared to the other two fly ashes. Moreover, the particles of the fly ashes from Počerady and Ledvice show a lower Fe content per particle compared to the fly ashes from Mělník and Dětmarovice, which is the cause of more porosity of the particles from the Počerady and Ledvice fly ashes.

3.5. EDX analyses of Magnetospheres

Magnetospheres or ferrospheres are known to be present in fly ashes from 0.5 to around 18 % [42]. It can be seen from Tab. 2 that fly ashes from Počerady, Mělník, Ledvice, and Dětmarovice show a Fe content from 1.35 % up to 7.22 % but the actual content of the magnetospheres can only be found by separating these particles from fly ashes as carried out by [43]. Magnetospheres found in fly ash are formed from iron minerals in boilers of power plants as a result of rapid heating with melting of constituents [44]. The bright particles seen in the fly ashes were closely focussed in FE-SEM at magnifications of 1500 × as shown in Fig. 7. Point analyses were carried out on FE-SEM images of Fig. 7, and only the results of two analyses of each fly ash for thirty elements are shown in Tab. 3. The phenomenon of higher porosity of particles of the Počerady and Ledvice fly ashes can also be seen in their magnetospheres. It can be seen from Fig. 7 that the magnetospheres of the Počerady and Ledvice fly ashes are porous, having hollow areas, while the magnetospheres of the fly ashes from Mělník and Dětmarovice are compact. For the Počerady fly ash, spectrum 1 shows a Fe content of around 80.78 %, and a Si and Al contents of 1.02 and 4.86 %. However, for spectrum 2, the Fe content is 27.78 %. Si, Al contents of 26.18, 31.94 % are found and a similar trend is seen for the other three fly ashes. Here EDX analyses reveal that magnetospheres have a glassy matrix rich in Fe on which metallic brighter regions of high Fe content can be found, which represent zones of very high Fe concentration, and these zones of high iron concentration vary in size for all four types of the fly ashes, as also determined by [43]. Moreover, it can also be seen that the zone of high Fe concentration has comparatively very high contents of Mg and slightly high contents of heavy metals compared to the inner glassy zone for all four fly ashes. It can further be seen from Tab. 3 that Spectrum 1 of Počerady is rich in Cr, Co, Ni, Ge, Sr, Y, Ba, La, Pb, Bi compared to Spectrum 2, which is also true for the other three fly ashes. On the other hand, the glassy zone of Mělník and Dětmarovice is comparatively very rich in Ca but slightly rich in Ca for the fly ashes of Počerady and Ledvice. This indicates that the magnetospheres from fly ashes of Počerady and Ledvice are porous due to having a lower Ca content, while Mělník and Dětmarovice fly ashes having very high Ca contents shows compact magnetospheres where no hollow areas are observed.

3.6. Transformed pseudo-coloured images

Pseudo-coloured images were transformed from the grey FE-SEM images as shown in Figs. 2, 3, and 7 using software based on C++ computer language, which

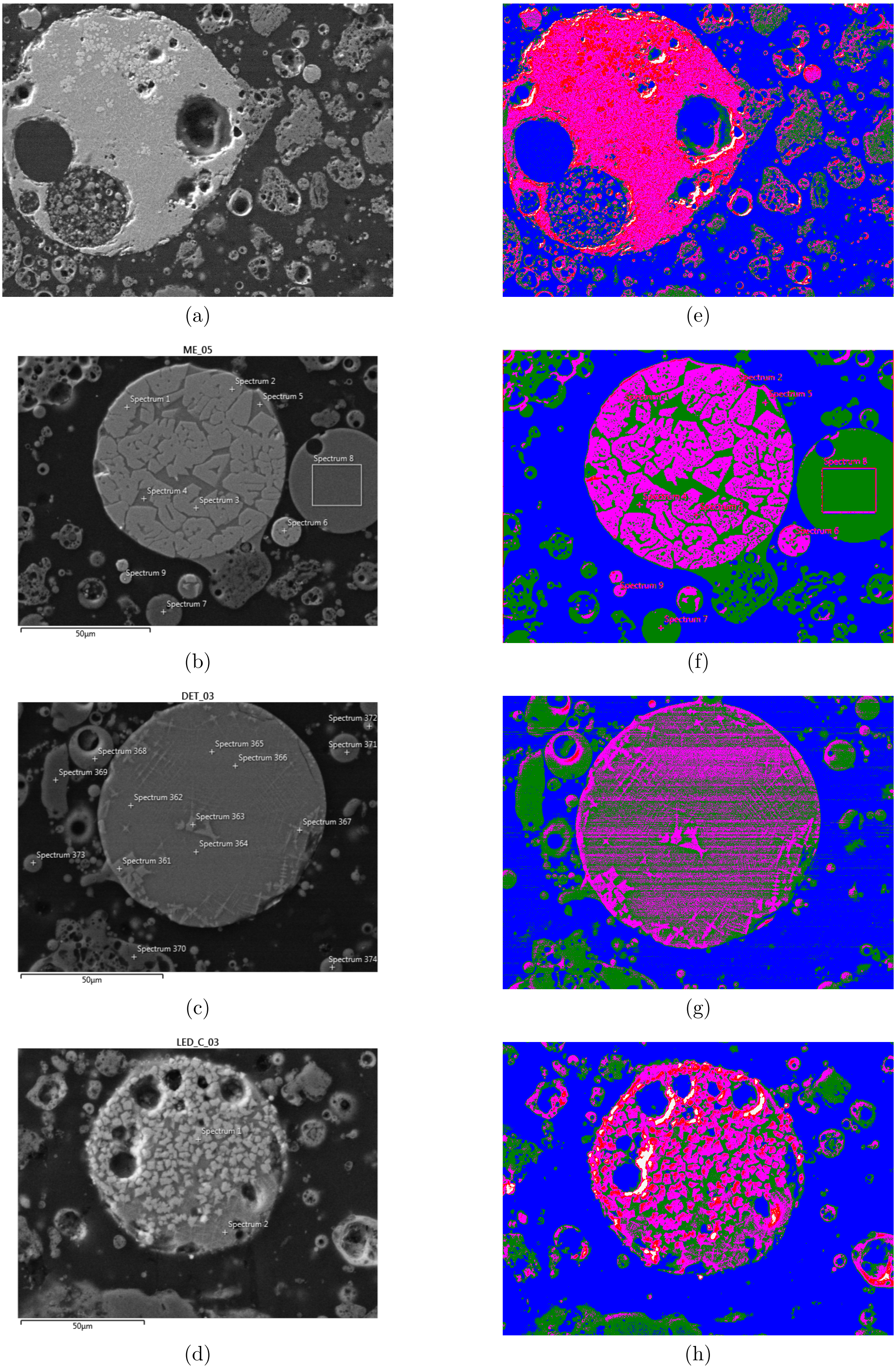

Figure 7. Original FE-SEM images for Magnetospheres observed in fly ashes from (a) Počerady, (b) Mělník, (c) Dětmarovice, (d) Ledvice at 1.50 KX magnifications, and transformed Pseudo-coloured images of fly ashes from (e) Počerady, (f) Mělník, (g) Dětmarovice, (h) Ledvice at 1500 × magnification.

Element	Počerady		Mělník		Dětmarovice		Ledvice	
	Sp. 1	Sp. 2	Sp. 361	Sp. 362	Sp. 1	Sp. 4	Sp. 1	Sp. 2
Na	5.51	3.53	1.78	1.14	2.95	0.96	1.27	1.14
Mg	4.32	3.64	18.14	3.16	21.38	7.66	3.47	2.58
Al	4.86	31.94	10.64	9.86	8.38	5.18	11.88	21.55
Si	1.02	26.18	3.13	20.76	1.04	35.57	9.82	34.23
P	0	1.02	0.02	1.88	0.08	0.8	0.2	0.38
S	0.09	0.55	0	0	0	0	0	0
K	0	0.83	0.02	0.12	0.1	0.11	0.11	0.79
Ca	0.15	2.11	4.77	36.47	0.87	36.7	0.67	2.05
Ti	0.43	0.92	0	0.37	0.04	0.32	1.03	1.67
V	0	0.07	0.16	0	0.11	0.11	0	0.09
Cr	0.04	0	0.03	0.03	0	0.08	0.06	0
Mn	0.5	0.58	1.45	0.54	0.28	0.06	0.33	0.34
Fe	80.78	27.78	58.15	24.91	62.99	11.24	70.02	33.13
Co	0.95	0	0.26	0.17	0.27	0	0.2	0
Ni	0.17	0.12	0.11	0.05	0.14	0.08	0.09	0.18
Cu	0	0	0	0	0.04	0.05	0.04	0.02
Zn	0	0.13	0.12	0.1	0.06	0.05	0	0
Ga	0	0	0	0	0	0	0.08	0
Ge	0.04	0	0.2	0	0	0	0	0
As	0	0	0	0.16	0.1	0	0.17	0
Se	0	0	0.16	0.09	0	0.07	0.3	0.04
Rb	0	0	0	0	0.18	0	0	0.01
Sr	0.06	0	0	0	0	0.18	0	0.04
Y	0.09	0.03	0	0	0	0.23	0	0.27
Zr	0	0	0.09	0.18	0.11	0.18	0	0.71
Ba	0.21	0.11	0.06	0	0.46	0.04	0	0.11
La	0.18	0.08	0.11	0	0.12	0	0	0
Ce	0.09	0.14	0.08	0.01	0	0.11	0	0
Hg	0	0.24	0	0	0	0	0.14	0
Pb	0.37	0	0.44	0	0.3	0.19	0	0.67
Bi	0.14	0	0.08	0	0	0.03	0.12	0

Table 3. Chemical analyses of magnetospheres from fly ashes of Počerady, Mělník, Dětmarovice, and Ledvice.

recognizes the changes in colour in grey images. It gives different colours to the different areas present in the images and calculates the respective percentage of abundance of a certain colour in the images. In these pseudo-coloured images, regions were differentiated into different categories and colours, based on the results of spectrums obtained from the EDX individual particle analyses. In these images, blue colour represents the solution of the hardener and epoxy resin that was used in preparing the samples, green colour represents the alumino-silicate glassy calcite ferro-metallic regions, purple colour represents the ferro-metallic alumino-silicate glassy regions, red colour represents the high ferro-metallic regions, and white colour represents the pure ferro metallic regions. The percentages of different coloured regions calculated from the images of Figs. 2, 3, and 7 are presented in Tab. 4a. This shows that the blue colour or the solution of hardener and epoxy resin represents around 75 % of the area of all samples of Fig. 2 and around 21 % of the area of samples is covered with glassy particles, whereas about 4 % of the remaining area is metallic. While the percentages from the pseudo coloured images of Fig. 3 show 56–76 % of solution of hardener and epoxy in blue colour, more glassy particles are observed for the Počerady fly ash, but it depends on the region that is magnified in the electron microscope to take the image. However, for Fig. 7, the percentage of the metallic part is very high, and a high percentage of red regions representing the high ferro-metallic regions is observed for the fly ashes from Počerady and Ledvice. It can also be seen also in pseudo coloured images of Fig. 7 that all the images that show red colour have high ferro-metallic regions on the circular boundary, and around the regions with hollow areas. Further, it is seen here that red and white regions of high and pure ferro-metals are present significantly more in particles having porosity in them, as also seen in the results of Tab. 3. Tab. 4b was prepared by taking the ratios of green, purple, red, and white areas among themselves by excluding the percentages of blue regions to exclude the effect of epoxy resin and hardener solution. It can be seen here that green regions representing the glassy alumino silicate particles are present up to

Colour	Počerady	Mělník	Dětmarovice	Ledvice
From Fig. 2 at 75 ×				
Blue	74.32	74.46	73.79	75.39
Green	21.45	21.5	21.42	21.64
Purple	3.63	2.65	3.64	2.37
Red	0.54	1.39	0.83	0.6
White	0.06	0	0.32	0
From Fig. 3 at 500 ×				
Blue	56.64	76.56	64.57	77.64
Green	33.37	15.18	26.87	13.66
Purple	7.4	6.07	8.14	5.7
Red	2.35	2.19	0.36	3
White	0.25	0	0.05	0
From Fig. 7 at 1500 ×				
Blue	46.52	44.28	42.08	58.32
Green	16.16	31.56	34.61	19.7
Purple	28.54	23	23.2	16.91
Red	7.8	0.91	0.11	3.95
White	0.97	0.25	0	1.12

(a)

Colour	Počerady	Mělník	Dětmarovice	Ledvice
From Fig. 2 at 75 ×				
Green	83.54	84.2	81.72	87.94
Purple	14.12	10.38	13.89	9.64
Red	2.11	5.43	3.18	2.42
White	0.23	0	1.2	0
From Fig. 3 at 500 ×				
Green	76.94	64.77	75.85	61.06
Purple	17.07	25.88	22.98	25.51
Red	5.41	9.35	1.02	13.43
White	0.58	0	0.15	0
From Fig. 7 at 1500 ×				
Green	30.23	56.65	59.75	47.27
Purple	53.37	41.27	40.05	40.56
Red	14.58	1.63	0.19	9.48
White	1.82	0.45	0	2.69

(b)

Table 4. Calculation of colour in pseudo-coloured images defining the nature of particles of fly ashes, (a) percentage of colours in transformed pseudo-coloured images, (b) ratios of percentage in-between colours excluding blue colour.

85 % in fly ashes and the metallic regions containing the alumino silicates and the pure metallic regions are about 15 % with little variations observed in the fly ashes. A similar observation can be made for the percentages of colours from Fig. 3, which again shows that the majority of the fly ash particles have a glassy alumino silicate nature. The percentages of colours for Fig. 7 show that a high amount of metallic content is present together with a glassy phase in the magnetospheres, and patches of higher ferro-metallic particles are present upon the magnetospheres which have porosity in them and are hollow. The amount of the glassy phase recorded from Fig. 7 in Tab. 4b also contains colour percentages of adjacent particles with the magnetospheres, which increases the percentage of the green regions representing the glassy phase.

4. Conclusions

Individual fly ash particles affect the properties of the fly ashes considerably, and to observe the variation in these properties, it is essential to use these fly ashes more efficiently to increase their utilization. Therefore, in this research physical and morphological properties of particles of the four fly ashes were analysed to determine the size and type of particles present in these fly ashes. Then, the nature of individual fly ash particles was determined using ternary phase diagrams and using pseudo coloured images, which were transformed from grey FE-SEM images. To determine the scattered nature of the data, the box and whisker diagrams were plotted from the results of the EDX individual particle analysis. Moreover, to find a more realistic method for determining the chemical composition of the fly ashes, a comparison was made between the XRF, the total area EDX, and the EDX individual particle analyses, which led to the following conclusions:

(1.) The fly ashes from Ledvice and Počerady showed high values of median diameter, which indicates a large number of coarse slaggy particles in them as compared to the other two fly ashes. The fly ash from Mělník showed low density in comparison to the other fly ashes, which is due to a high concentration of entrapped gas bubbles forming cenospheres in it, as compared to the other fly ashes. The fly ash from Mělnik can therefore be used for recovery of hollow spherical particles by wet or dry separation methods.

(2.) The FE-SEM images showed that the fly ashes from Počerady and Ledvice showed more porous particles in them, due to sudden escape of water from pores of coal during combustion, as compared to the fly ashes from Mělník, and Dětmarovice. From the EDX individual particle analyses, it was determined that lack of Ca in the particles makes them more porous.

(3.) The ternary phase diagrams of Si-Al-Fe showed that the nature of the fly ash individual particles changes from glassy to glassy-metallic to metallic-glassy to pure metallic, and the Si-Al-Ca ternary diagrams showed that the nature of the particles changes from glassy to glassy-calcite with an absence of pure calcite particles.

(4.) The transformed pseudo coloured images showed that the nature of the fly ash individual particles changed from the alumino-silicate glassy calcite ferro-metallic regions to the pure ferro metallic regions, and high percentages of the glassy regions were observed as compared to metallic regions. On the other hand, in the magnetospheres, high percentages of the ferro-metallic regions were observed, while the pure ferro-metallic regions were observed in porous particles.

(5.) Box and whisker plots showed the scattered nature of data from the median percentages of each element, which showed that in all the fly ashes percentages of Si, Al, and Fe are more scattered as compared to the other elements, and Ca percentage is more scattered in the fly ashes from Mělnik and Dětmarovice, which have compact particles. This shows that these two fly ashes possess self-cementing properties and are better to be used in cementitious applications.

(6.) Box and whisker plots developed for fly ashes in this research can be used by the industries desiring recovery of certain elements from fly ashes to determine possible economic considerations for the recovery of any element present in these four fly ashes. The concept of box and whisker plot diagram based on the EDX individual area analyses can be extended to any fly ash to determine the variation in chemical composition present in fly ashes, for rare elements recovery, or for other applications of the fly ashes.

(7.) It is established in this research that the XRF, and the EDX total area analyses only provide the average values of elements, or element oxides present in the fly ashes. On the other hand, the EDX individual particle analysis, is a more realistic chemical analysis method, which provides standard deviation values along with the mean percentages of each element present in the fly ashes, from which the variation present in the data can easily be identified.

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