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Mineralogical, Microstructural and Thermal Characterization of Coal Fly Ash Produced from Kazakhstani Power Plants

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Abstract. Coal fly ash (CFA) is a waste by-product of coal combustion. Kazakhstan has vast coal deposits and is major consumer of coal and hence produces huge amounts of CFA annually. The government aims to recycle and effectively utilize this waste by-product. Thus, a detailed study of the physical and chemical properties of material is required as the data available in literature is either outdated or not applicable for recently produced CFA samples. The full mineralogical, microstructural and thermal characterization of three types of coal fly ash (CFA) produced in two large Kazakhstani power plants is reported in this work. The properties of CFAs were compared between samples as well as with published values.

1. Introduction

Coal fly ash (CFA) is a waste by-product from coal combustion in power plants all over the world. Kazakhstan produces around 19 million tons of CFA annually and has accumulated more than 300 million tons of CFA in ash disposal areas across the country [1-2]. According to statistics, the utilization rate of CFA in Kazakhstan is under 10%, which is considerably lower as compared to EU states (over 90%), India (60%), China (67%) and the USA (nearly 50%) [1, 3]. Characterization of this material is of utmost importance as it determines how and in which sectors of industry it could be utilized.

To this aim, in this work a full-scale mineralogical, microstructural, thermal characterization is provided and analytical methods of spectroscopy/chromatography are utilized. Three types of Kazakhstani CFAs, namely Ekibastuz (E-CFA), Karazhyra (K-CFA) and Maikuben (M-CFA) from Astana and Oskemen city power plants (Central and East Kazakhstan, respectively) were analysed. In order to obtain a full data on chemical and physical properties all samples underwent characterization using advanced instruments as X-Ray diffraction (XRD) analysis to retrieve mineralogical phases present in CFAs, X-Ray Fluorescence (XRF) analysis to obtain elemental composition of CFAs and FTIR for specific functional groups identification. In addition to this, thermogravimetric and differential calorimetric analysis (TGA/DSC) were applied to acquire information regarding thermal properties of CFAs, while Total Carbon (TC) analysis to quantify the residual carbon. The Particle Size Analyzer (PSA) and Porosimetric analysis were used to estimate the particle size groups present in crude CFAs, their respective specific surface area, average pore size and total pore volume.


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2. Materials and methods

2.1. Materials

A representative CFA sample with a composition typical of the average CFA output was collected under maximum electricity load from the electrostatic precipitators of Astana city coal-fired power plant (E-CFA) and coal-fired power plant of Oskemen city (K-CFA and M-CFA). All CFA samples were used as received without preliminary washing and sieving. Prior to experiment CFA samples were homogenized and dried in oven at 70 ℃ for 12 h.

2.2. Methods

2.2.1. Mineralogical characterization of fly ash

XRD was used to obtain information on mineralogical phases present in CFA. The samples were analyzed as received without prior purification and sieving. The XRD pattern was recorded on a SmartLab X-ray diffraction instrument (Cu, K-β filter, 40 kV and 30 mA) with a diffraction angle of 2θ and a scanning range of 5–100◦ (Rigaku). Phase identification was made by searching the Auto-search option of powder diffraction file library. All analysis are duplicated and the average values are presented in this study.

XRF (PANalytical Axios) was used to get the elemental composition of each CFAs. The CFA sample was analyzed as received without prior purification and sieving. The ratio of CFA sample with commercial borate flux was set at 10 g to 3 g (total mass of 13 g) with a diameter of pellet at 5 cm and thickness of pellet at 0.5 cm. The analyses were conducted under inert atmosphere.

2.2.2. Microstructural characterization of fly ash

PSA (Malvern Mastersizer 3000) instrument was used to obtain the information on volumetric percentage of each particle size and their distribution across the range of 0.01 μm to 10 000 μm. Distilled water was used as a dispersant for all samples of CFA in Hydro-MV mode.

A Nitrogen Porosimeter (Quantachrome, Autosorb-1) was applied to obtain data on specific surface area (SSA) and porosity of the particles of fly ash. The dry sample of fly ash was first degassed for 2-3 hours prior to analysis at stepwise heating from 50 ℃ to 200 ℃. A 9 mm glass cell without rod was used for all porosimetric analysis.

2.2.3. Thermal properties characterization of fly ash

TGA-DSC was used to determine the thermal properties of CFA. The temperature range applied was 50 ℃ to 950 ℃ with heating rate of 10 ℃/min under inert atmosphere. The isothermal heating was hold at 50 ℃ for 1 minute with minimum initial mass of 10 mg.

2.2.4. FTIR characterization of fly ash

In order to determine specific functional groups present on the surface of CFA samples, they were analyzed on FTIR spectroscopy (ThermoFisher Scientific, Nicolet iS5) with attenuated total reflection (ATR) unit. This analysis required approximately 0.1 g of sample with each measurement being duplicated.

2.2.5. Chemical analysis of fly ash

Total carbon analysis of each CFA sample was conducted applying Multianalyzer N/C 3100 instrument (Analytik Jena) using 100 mg of CFA sample for analysis at furnace temperature of 950 ℃ under pure oxygen atmosphere. All measurements were triplicated and the average values are presented in this study.

3. Results and discussion

3.1. Mineralogical characterization of fly ash

Mineralogical analysis of E-CFA, K-CFA and M-CFA on XRD give information on phase content with estimated percentage of each containing mineral. According to figures 1-3, the main minerals containing in all CFA samples are quartz, mullite and magnetite/hematite.

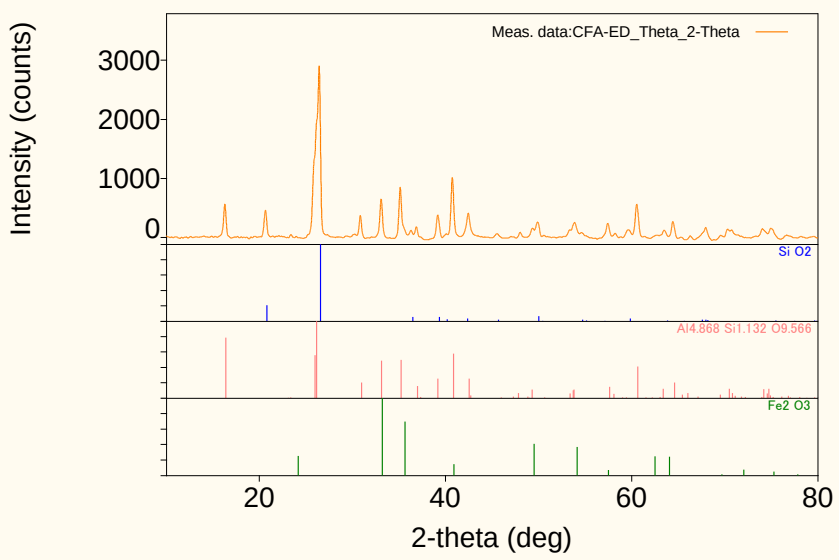


Figure 1. XRD spectrum of E-CFA.

The additional semi-quantitative tool of software allows assuming the crystalline phases in percentage. According to that calculation, the content of crystalline mullite and quartz in E-CFA are 67% and 33%, respectively. K-CFA demonstrated more even distribution of mullite and quartz: 56% and 44%, accordingly; whereas M-CFA showed 11% iron oxide (magnetite), 56% quartz and 33% mullite. It should be noted that the amount of magnetite/hematite present in CFAs was not detected on this instrument because it is mostly amorphous and only crystalline particles of this phase was used in percentile calculation of software.

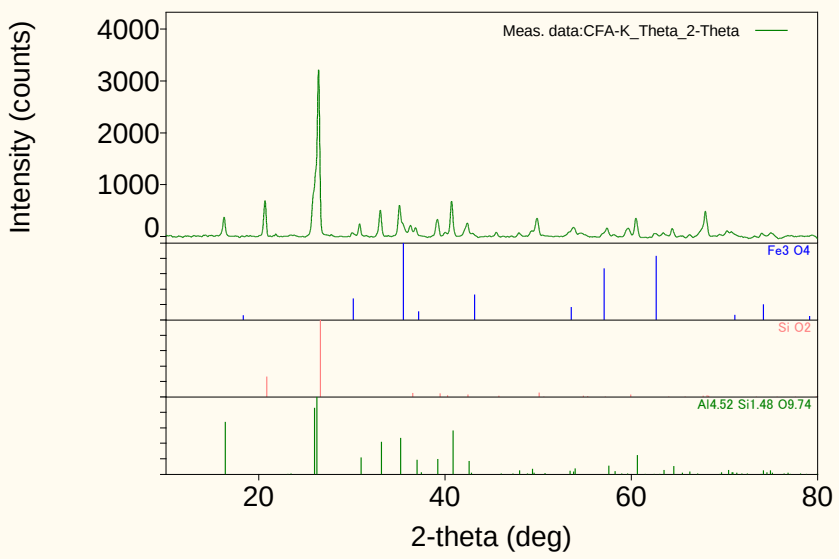


Figure 2. XRD spectrum of K-CFA.

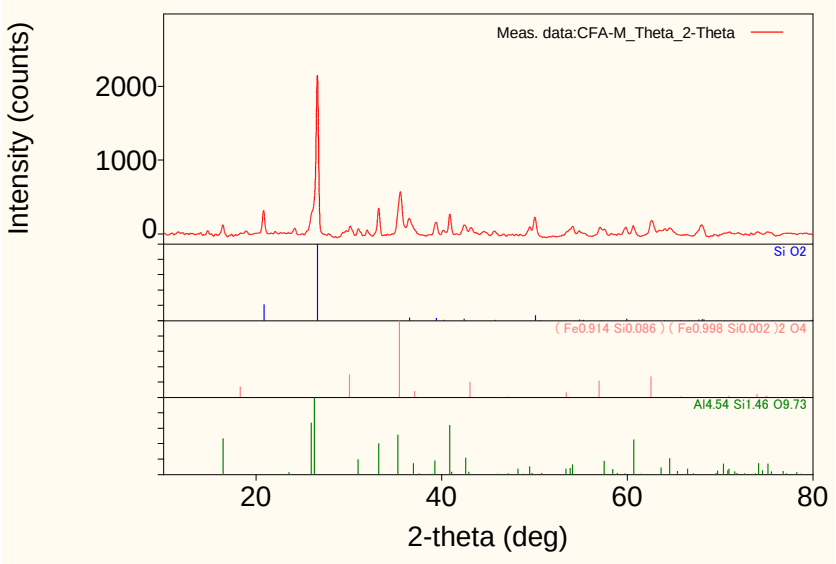


Figure 3. XRD spectrum of M-CFA.

The detailed elemental composition of E-CFA, K-CFA and M-CFA obtained on XRF are shown in table 1. According to data the main elements containing in raw CFA are Al, Si, Fe and Ca, which was expected. However, it is apparent that the content of iron oxide is comparatively higher in E-CFA in contrast with K-CFA (16.076%) and M-CFA (18.138%) samples and significantly higher than in CFA from other regions in the world [4-10], which could be of benefit for practical applications.

Table 1. Elemental composition of Kazakhstani CFAs in wt.%.

Compound	E-CFA	K-CFA	M-CFA
Na_2O	0.187	0.678	0.763
MgO	0.628	0.716	1.423
Al_2O_3	18.071	25.761	21.750
SiO_2	44.128	49.802	44.425
SO_3	0.204	0.237	2.248
Cl	0.138	0.026	0.021
K_2O	0.514	1.324	1.857
CaO	6.077	2.798	6.775
TiO_2	1.353	1.636	1.169
Cr_2O_3	0.035	0.033	0.024
MnO	0.608	0.216	0.432
Fe_2O_3	27.786	16.076	18.138
CuO	0.032	0.042	0.035
ZnO	0.013	0.052	0.024
Ga_2O_3	0.008	-	0.008
SrO	0.059	0.195	0.342
Y_2O_3	0.008	0.012	0.008
ZrO_2	0.048	0.060	-
BaO	0.103	0.143	0.369

It is interesting to note that M-CFA and E-CFA contain similar amount of Ca (6.775 and 6.077wt.%) that is more than 2 times higher as in Karazhyra CFA (2.798 wt.%). The total amount of alkaline metals are relatively higher M-CFA (11.187wt.%). All CFA samples contain some trace amount of heavy metals with concentrations below 1wt.% (Cr, Cu, Zn, Ga, Sr, Y and Zr). The Si/Al ratio of E-

CFA, K-CFA and M-CFA are 2.15, 1.70 and 1.80, respectively. These results are comparable with data obtained elsewhere [6-7,11].

3.2. Microstructural characterization of fly ash

The characteristic property of all coal derived materials are their porosity, which is important to investigate because they demonstrate a high adsorption or separation potential. The general porosimetric analysis using inert gas (argon or nitrogen) could give the following valuable data as porosity type, the SSA, total volume of pores, average pore size.

Table 2 summarizes the experimental results obtained for all CFAs samples by applying three different methods, namely BET, BJH and DFT. It should be noted that the BET method is mainly used for comparison with literature values, since this approach is generally applied for porosimetric analysis of porous materials.

It is clearly seen from the results obtained that the most porous is K-CFA, where it shows the average pore diameter of 8.457 nm with the SSA value at 32.873 m^2/g. The total pore volume for pores less than 3091 nm is 0.069 cm^3/g. This is followed by M-CFA that demonstrate very close pore size at 7.573 nm and SSA at 29.319 m^2/g. The total pore volume is lower for 0.011 cm^3/g than in K-CFA. On the other hand, E-CFA show the lowest values in all characteristics. The literature values of average micro-pores size using BET, DFT and BJH methods show that it could be as small as 0.7 nm [10] and reach up to 15.3- 27.2 nm [12, 13] and 570-780 nm for macro-pores [11, 14]. The SSA values by BET method could range from 1.1 to 15.6 m2/g depending on phase content and porosity [12-16]; while total volume could vary from 0.004 to 0.022 cm3/g [13,15].

Table 2. Porosimetric analysis of Kazakhstani CFAs.

CFA type	Average pore diameter [nm]	Specific surface area [m^2/g]	Total pore volume [cm^3/g]
K-CFA	8.457 (BET)	32.873 (BET)	0.069 (BET)
	7.573 (DFT)	19.203 (DFT)	0.044 (DFT)
	3.362 (BJH)	31.440 (BJH)	0.053 (BJH)
M-CFA	7.938 (BET)	29.319 (BET)	0.058 (BET)
	4.520 (DFT)	21.392 (DFT)	0.046 (DFT)
	4.223 (BJH)	34.073 (BJH)	0.056 (BJH)
E-CFA	5.525 (BET)	23.018 (BET)	0.032 (BET)
	6.160 (DFT)	12.935 (DFT)	0.027 (DFT)
	3.413 (BJH)	17.734 (BJH)	0.028 (BJH)

According to the results of particle size analysis shown in table 3, K-CFA and E-CFA demonstrate similar distribution with 90% of particles being less than 229 μm and 260 μm, respectively. In terms of average particle size for these two CFAs it ranges between 94-109 μm. As for M-CFA, it reveals much lower particle size being of 8.6 μm (10%) and at the same time wider distribution with 90% of particle size being under 419 μm.

Table 3. Particle size analysis of CFAs.

CFA type	Uniformity	Dv(10), μm	Dv(50), μm	Dv(90), μm
E-CFA	0.702	15.2	109	260
K-CFA	0.675	29.4	94.1	229
M-CFA	1.921	8.6	60.6	419

3.3. Thermal properties characterization of fly ash

Thermal behavior of CFAs was determined using TGA-DSC. According to results shown in figure 4, E-CFA lost 4.58% of its weight in total upon heating to 950 ℃, which means that the main content of CFA is inorganic compounds. The derivative weight demonstrates the highest peak of loss at 641.67 ℃

(-0.012 mg), and two more noticeable losses at 73.51 ℃ (-0.006 mg) and 337.96 ℃ (-0.003 mg). The rest of the curve shows a steady loss throughout the temperature range. A heat flow change, on the other hand, reveals a minor endothermic peak at around 790 ℃ that might be due to reactions (decomposition and oxidation) or other types of transformations occurring while heating.

On the other hand, a distinct two-step mass loss curse for M-CFA could be observed in figure 5. According to analysis data, the first batch of loss was at 123.1 ℃ (-0.199 mg), then the mass of sample decreased smoothly until it reached the region of temperature between at 565.8-667.25 ℃ (-0.071 mg). The results reveal that in total the sample loss was 0.85 mg or 2.4wt.% that is almost 2 times lower than in E-CFA, which in turn means that M-CFA coal absorbed less water phase and contains less volatile organic matters in its structure. In figure 6 we can see the results for K-CFA, where the total mass loss showed the lowest value at approximately 0.28 mg or 0.57wt.%. The shape of the curve is similar to E-CFA with steady decrease by time.

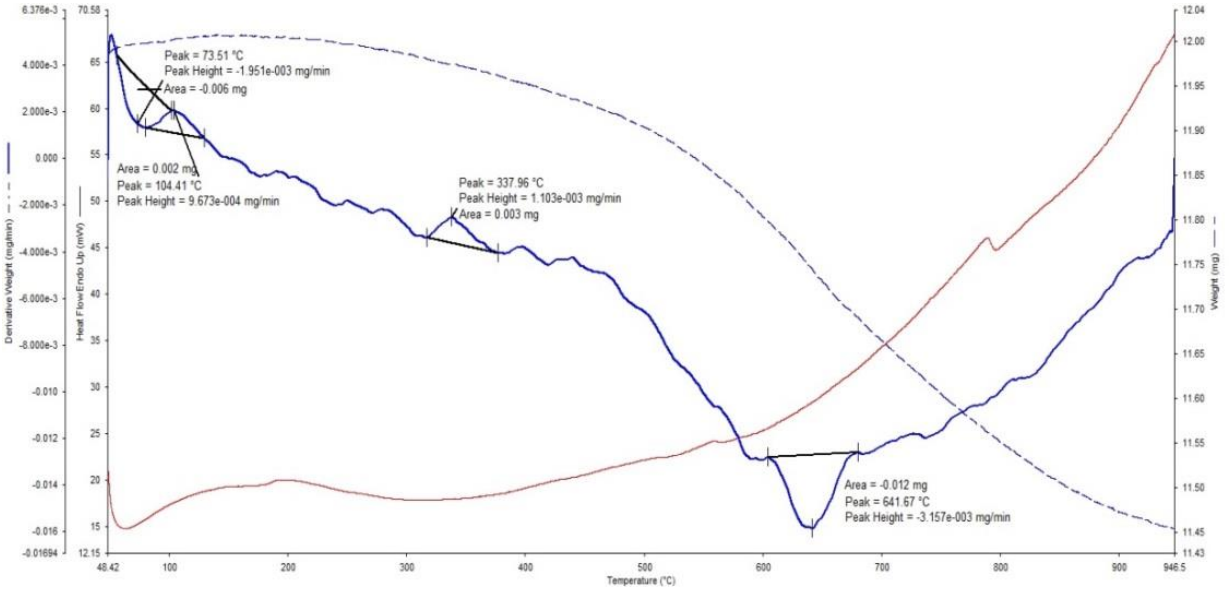


Figure 4. Thermal properties of E-CFA from Astana Power Plant.

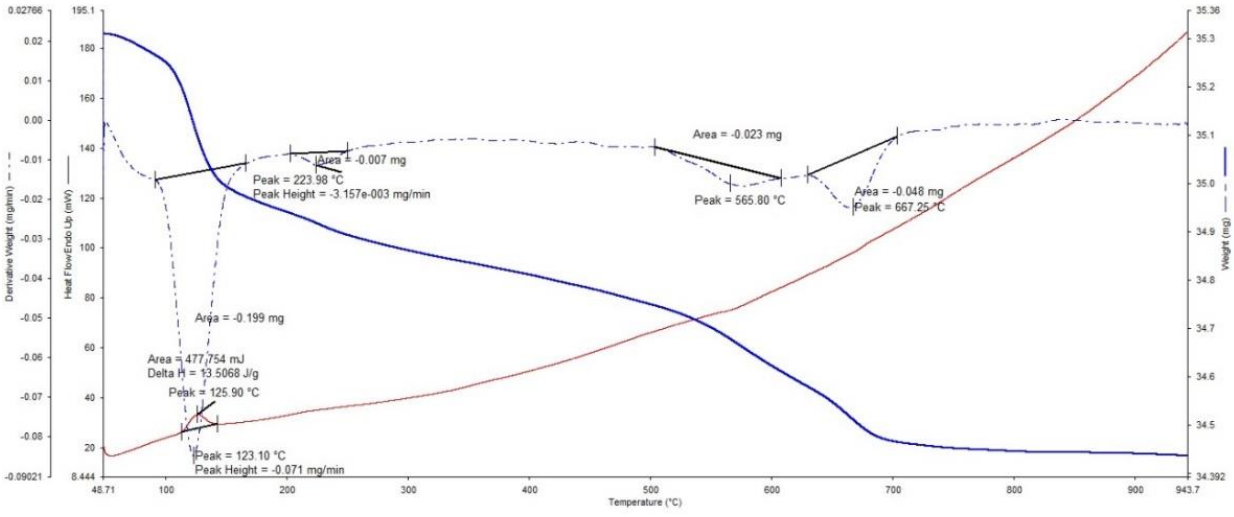


Figure 5. Thermal properties of M-CFA from Oskemen Power Plant.

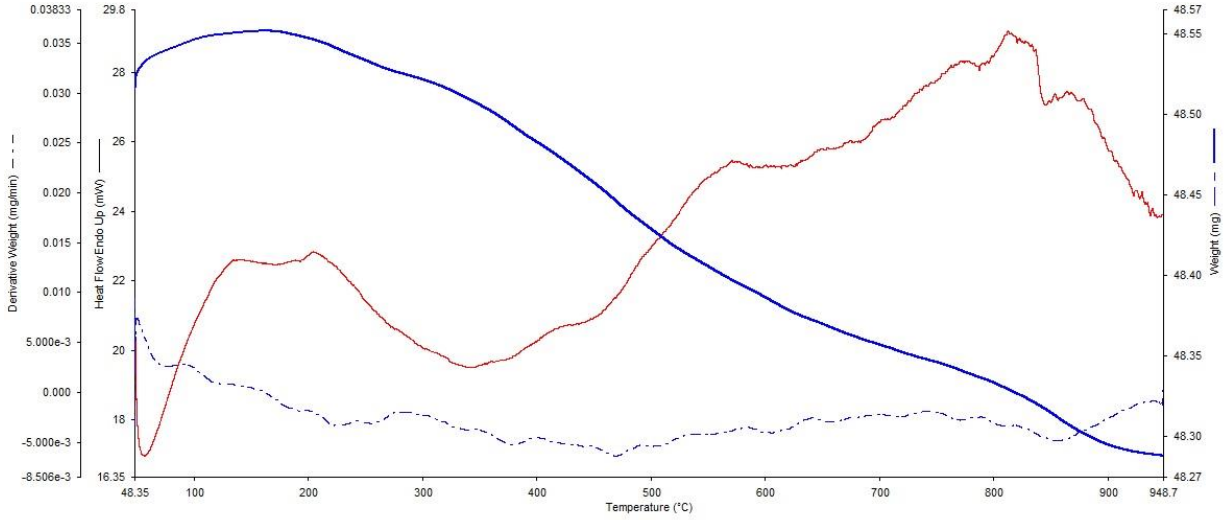


Figure 6. Thermal properties of K-CFA from Oskemen Power Plant.

3.4. FTIR characterization of fly ash

All CFA samples were characterized on FTIR spectroscopy to determine specific functional groups. Figure 7 shows the comparative spectrum of E-CFA, K-CFA and M-CFA. According to spectrums all of them have similar functional groups. For example, a characteristic peak at 1020-1050 cm-1 demonstrate the presence of Si-O- and Al-O-, while peaks at 795-775 cm^{-1} are the symmetric stretches. Similarly, there is a minor peak at 660-670 cm^{-1}, which might correspond to Al-O-, Si-O-, Fe-O-. There are also two peaks at 2160 cm^{-1} and 2025 cm^{-1} that also correspond to aluminosilicate functional groups.

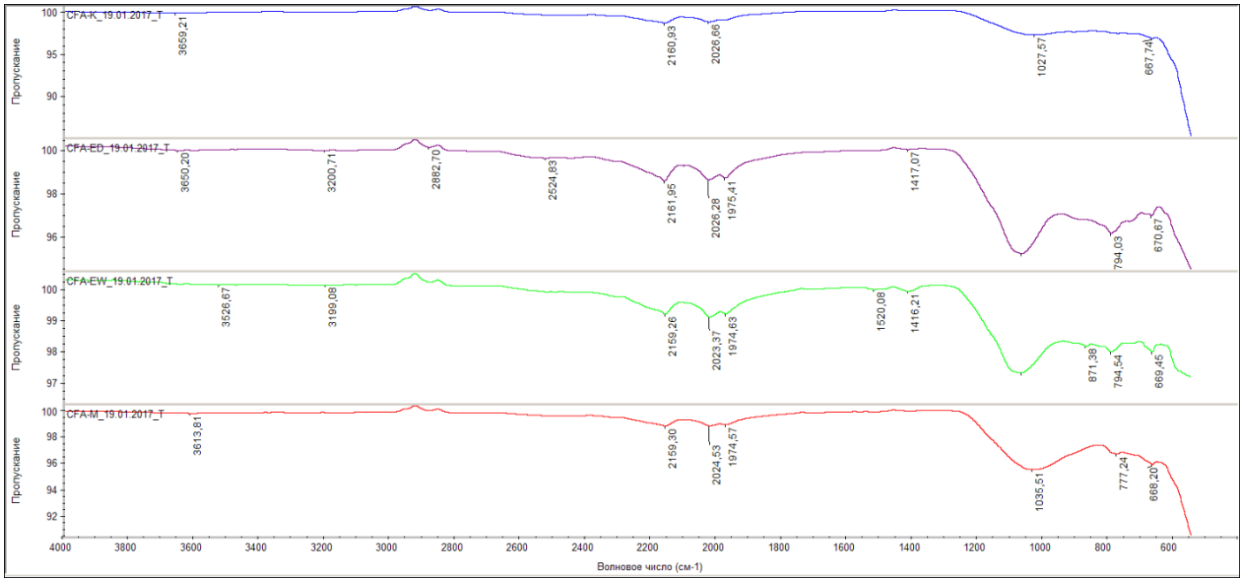


Figure 7. FTIR spectrum of all CFAs (note CFA ED and CFA EW are wet and dry E-CFAs).

3.5. Chemical analysis of fly ash

Total carbon content of all 3 CFAs was determined using HT-300 instrument. According to the results that amount of total carbon in Ekibastuz, Karazhyra and Maikube CFAs are 2.15wt.%, 0.58wt.% and 0.82wt.%. These values correspond to mass loss results in TGA/DSC analysis, where the highest and lowest loss were recoded for Ekibastuz and Karazhyra CFAs, respectively.

4. Conclusion

The E-CFA, K-CFA and M-CFA were fully characterized for mineralogy, microstructure and thermal properties. The advanced instruments such as XRD, XRF, Nitrogen Porosimeter, PSA, TGA-DSC, FTIR and TC were successfully applied to obtain valuable data on these Kazakhstani CFA, which helps to update the database. It was identified that the main phases in all three CFAs are mullite, quartz and magnetite/hematite, while the major elements containing in raw fly ash being Si, Al, Fe and alkaline metals. Porosimetric analysis revealed that the BET surface area of CFAs range between 23-32 m^2/g with mesoporous structure. The results of particle size analysis showed that 90% of particles are less than 419 μm. In addition to that the thermal analysis showed a curve of steady decrease upon heating till 950C with TC amount ranging between 0.82-2.15wt.%.

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