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Characterization of the fly ashes from the lignite burning power plants of northern Greece based on their quantitative mineralogical composition

G. Kostakis*

Technical University of Crete, Department of Mineral Resources Engineering, GR 73100 Chania, Greece

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ABSTRACT

In the present work, mineralogical analysis of fly ashes produced from the brown coal burning power plants of Agios Dimitrios, Kardia, Ptolemais, LIPTOL, Amynteon, and Achlada-Meliti (Western Macedonia, Greece) was performed, with the aim of characterizing the ashes on the basis of their quantitative mineral phase composition and asses their variability at different time periods. The fly ashes from the Agios Dimitrios, Kardia, and Ptolemais power plants were found to have nearly the same mineralogical composition, consisting mainly of feldspars, lime, anhydrite, quartz, calcium silicates, and high amounts of amorphous phases. The fly ashes from Amynteon were slightly different, having lower content of lime and higher content of feldspars, whilst those from LIPTOL had a relative variable quantitative composition. The fly ashes from the Meliti-Achlada power plant consisted mainly of amorphous phases (very high amounts), mullite, feldspars, and quartz. The mineralogical composition of the ashes produced in all the power plants, except from these of LIPTOL, did not fluctuate significantly over time. An assessment of the hydraulic (cementitious) or pozzolanic character of the ashes is proposed, introducing the use of triangle diagrams A–B–C, which represent the total fraction of the phases with hydraulic or pozzolanic (A), inert (B) character, and the amorphous phases (C).

1. Introduction

The power plants of Agios Dimitrios (1595 MW), Kardia (1200 MW), Ptolemais (620 MW), LIPTOL (smaller Ptolemais power plant, 43 MW), and Amynteon (600 MW), situated in the Ptolemais–Amynteon coal basin, and of Achlada-Meliti (330 MW), situated in the Florina coal basin (Western Macedonia, Greece, Fig. 1) produce about 65% of the electric power consumed in Greece. The coals of these basins are low-rank brown coal of lignite or lignite–xylite type, respectively [1]. After crushing, drying, and pulverizing, they are combusted in tangential swirl burners of the power plants. In all power plants about 55 Mt/a coal is burned. The mineral matter content of the feed coals is depending upon the power plant and time, and the ash production reaches up to 10 Mt/a. Although the chemical composition of the feed coal ashes produced from these power plants, as well as their variation with time is well known, reliable published data about the mineralogical composition of the fly ashes or the lignite fuel are sporadic and qualitative or semi-quantitative [2–5]. The fly ash from the power plants of the Ptolemais–Amynteon district typically contains apart from the amorphous at least 13 crystalline phases [5,6]. Accurate knowledge of the mineralogical composition of the fly ashes is useful for optimizing the utilization or disposal of the ashes and for interpreting the mechanisms causing the slagging and fouling of the boilers, as well as the abrasion of the boiler tubes and other parts of the power plants. The aim of this work is (i) to give a complete, as much as possible, view of the phase composition of the fly ashes produced in the aforementioned power plants; (ii) to study the variation of the ash composition over a long time interval (of the order of few months); and (iii) to estimate the reactive character of the fly ashes.

2. Materials and methods

2.1. Sampling

A large number of fly ash samples were taken in a time covering the ash production of about 3 months. The sampling was performed directly from the loading band at the outlets of the bins (silos) of the power plants. Ash samples of about 1 kg each were collected and sealed in plastic bags immediately after the arrival of the ash from the electrostatic precipitator. Two types of samples were taken: (a)

* Tel.: +30 28210 37605; fax: +30 28210 37840.
E-mail address: kostakis@mred.tuc.gr.

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Fig. 1. Power plants of Agios Dimitrios (1), Kardia (2), Ptolemais (3), LIPTOL (4), Amynteon (5), and Achlada-Meliti (6).

Samples representing the daily fly ash production for a time period of 7 days, which were obtained by mixing and homogenizing of three samples taken every 8 h during the day, and (b) samples representing the weekly production, each resulting by mixing seven daily samples. In the Agios Dimitrios, Kardia, LIPTOL, Amyntaeon, and Achlada-Meliti power plants, samples were taken from one power unit of each one power plant. In the Ptolemais power plant, samples were taken from three power units (I, II, and IV) at the same times.

2.2. Mineralogical and chemical analysis

Twelve fly ash samples were analysed from the Agios Dimitrios power plant (7 daily and 5 weekly samples), 11 samples from the Kardia power plant (7 daily and 4 weekly samples), 40 from the Ptolemais power plant (19 daily and 21 weekly samples), 14 from the LIPTOL power plant (7 daily and 7 weekly samples), 7 daily and 4 weekly samples taken from the Amynteon power plant, and 7 from the Meliti-Achlada power plant. The samples from the Ptolemais power plant were taken simultaneously from three different power units (units I, II and IV, 130 MW each one), burning the same feed coal, to enable the detection of possible differences in mineralogical composition of the ash, possibly due to different burning conditions of the lignite in the boilers of each unit within the same power plant.

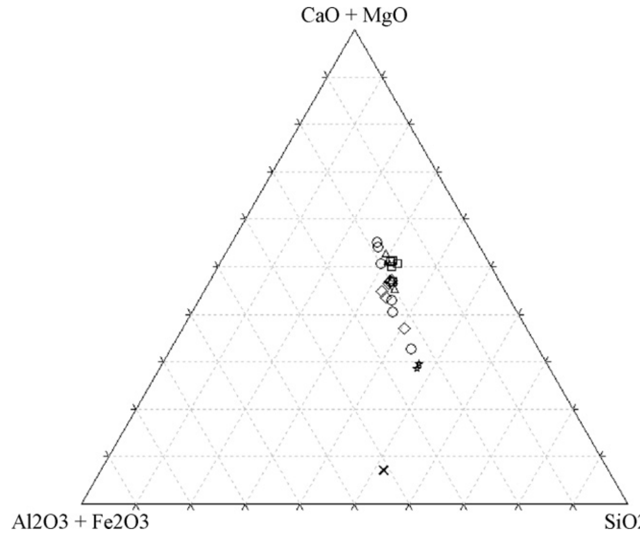

Fig. 2. The chemical composition of the fly ashes from the power plants of Agios Dimitrios (□), Kardia (△), LIPTOL (○), Ptolemais, unit IV (◊), Amynteon (☆) (weekly samples) and Meliti-Achlada (×, 7 almost identical values of daily samples).

All ash samples were subjected to mineralogical analysis, and a part of them, representing the ashes of each power plant, to chemical analysis as well. For the mineralogical analysis an X-ray diffractometer was used. For the chemical analysis an XRF spectrometer was used for some of the samples (laboratories of the Department of Mineral Resources Engineering, Techn. Univ. of Crete) and an ICP Spectrometer (laboratories of the Public Power corporation of Greece) for the rest of them (for the latter the samples were prepared according to ASTM D 6349-00). For the collection of the X-ray data, the diffractometer was operated with a copper X-ray tube at 40 kV/35 mA, scintillation detector, graphite monochromator, Soller slits, and divergence slits. The data were collected over a range from 7° to 70° 2θ using a step size of 0.03° 2θ and a counting time up to 15 s/step. The X-ray powder data collected for the quantitative estimation of the crystalline phases were refined by the Rietveld method [7–10] using the Rayflex Autoquan program [11]. Since an amorphous component is present in the ashes, a crystalline internal standard (corundum) was added to the specimens, in order to allow quantitative phase analysis.

When multi-component materials as complex as some fly ashes are analysed by means of the Rietveld method, various factors lead

Table 1
The chemical composition (minimum–maximum values, %wt.) of 25 weekly ash samples from the power plants of Agios Dimitrios, Kardia, Ptolemais, LIPTOL, Amyntaeon and 7 daily samples from the Meliti-Achlada power plant (in %wt.).

	Ag. Dimitrios	Kardia	Ptolemais, unit I	LIPTOL	Amyntaeon	Meliti-Achlada
Samples	5	4	7	7	2	7
SiO_2	27.06–29.72	25.35–30.59	27.38–35.30	22.98–38.27	42.50–41.85	47.27–47.86
Al_2O_3	10.00–12.05	9.22–11.72	11.09–13.51	10.22–14.45	13.53–14.30	30.29–30.76
Fe_2O_3	4.98–5.42	6.00–6.35	5.15–5.88	5.68–6.82	7.15–7.33	7.33–7.55
CaO	37.78–40.30	35.54–41.00	29.10–36.66	24.07–41.84	21.97–22.67	3.93–4.17
MgO	4.05–4.74	4.24–4.76	2.85–3.37	4.51–6.00	3.58–3.63	2.42–2.49
Na_2O	0.42–0.53	0.35–0.46	0.42–0.62	0.26–0.50	1.11–1.20	0.98–1.43
K_2O	0.96–1.17	0.92–1.04	1.04–1.49	0.98–1.42	1.67–1.72	1.57–1.66
TiO_2	0.47–0.52	0.47–0.57	0.62–0.77	0.48–0.68	0.73–0.77	1.05–1.16
MnO	–	–	–	–	–	0.13
SO_3	3.55–5.04	3.72–4.63	4.52–6.92	4.92–7.82	4.22–4.89	1.83–1.86
P_2O_5	0.23–0.27	0.25	0.19–0.20	0.27–0.32	0.20	0.10
C	0.90–1.58	1.19–1.58	1.52–2.09	1.05–1.28	0.92–0.93	n.a.
I.L.	3.38–4.69	4.39–6.12	4.62–6.17	3.01–4.30	2.08–2.28	n.a.

Table 2
Ash composition (average values, standard deviations, wt.%) of 54 daily samples of the Ag. Dimitrios, Kardia, Ptolemais (unit I, II and IV), LIPTOL, Amynteon and Meliti-Achlada power plants.

	Ag. Dimitr.	Kardia	Ptolemais (3 units)	LIPTOL	Amynteon	Meliti-Achl.
Samples.	7	7	19	7	7	7
Anhydrite	4.8 ± 0.7	6.5 ± 0.3	8.3 ± 1.7	7.4 ± 2.9	6.4 ± 0.5	–
Lime	12.8 ± 1.7	12.9 ± 0.5	7.6 ± 2.0	6.2 ± 2.8	6.9 ± 1.2	–
Periclase	2.1 ± 0.2	2.3 ± 0.2	1.1 ± 0.1	1.8 ± 0.5	1.1 ± 0.1	–
Hematite	0.9 ± 0.3	0.9 ± 0.1	1.0 ± 0.1	1.3 ± 0.2	1.9 ± 0.3	0.5 ± 0.1
Gehlenite	8.8 ± 1.0	6.8 ± 0.6	4.9 ± 1.3	2.5 ± 1.2	8.4 ± 0.6	–
Magnetite	–	–	–	–	–	1.1 ± 0.2
Hercynite	–	–	–	–	–	2.6 ± 0.3
Ca_2SiO_4	4.3 ± 0.4	5.2 ± 0.7	2.1 ± 0.6	2.2 ± 2.0	3.2 ± 0.8	–
Brownmillerite	6.4 ± 1.0	11.1 ± 0.6	4.4 ± 0.7	4.2 ± 1.8	3.5 ± 0.8	–
Merwinite and (or) Mayenite	1.4 ± 0.7	1.8 ± 0.3	0.9 ± 0.2	1.6 ± 0.2	1.1 ± 0.5	–
Mullite	–	–	–	–	–	8.5 ± 0.4
Calcite	3.1 ± 1.0	3.4 ± 0.8	6.8 ± 3.3	4.5 ± 1.2	1.4 ± 0.6	–
Quartz	5.6 ± 0.5	3.7 ± 0.3	6.9 ± 0.7	11.8 ± 3.2	5.5 ± 0.9	5.8 ± 0.6
Feldspars	12.7 ± 2.7	6.8 ± 0.9	8.9 ± 2.6	10.7 ± 3.8	13.9 ± 1.7	5.5 ± 0.8
Muscovite/illite	2.9 ± 0.5	1.2 ± 0.6	3.1 ± 0.7	2.9 ± 1.5	–	–
Pyroxenes	–	–	–	–	4.8 ± 0.9	–
Amorphous	34.0 ± 6.5	37.5 ± 1.4	43.9 ± 3.9	44.2 ± 7.5	41.2 ± 2.9	74.8 ± 1.5

to uncertainty and errors [12–15]. One of the most important of these factors, which in practice it is impossible to avoid by the routine analysis, is the uncertain knowledge of the chemical composition of the solid solution phases contained in a sample. In the fly ashes investigated in this work, feldspars, gehlenite (melilithe), brownmillerite, and other solid solution phases were identified. For each of these phases obtained from the qualitative analysis, a crystalline phase of approximately similar (but not necessarily identical) chemical composition was chosen for the Rietveld refinement. Because of this a corresponding uncertainty in the results of the quantitative phase analysis is inevitable, and it is very difficult to estimate precisely its impact.

Windburn et al. [13] have used fly ash Standard Reference Materials of relatively similar composition to the ashes investigated in the present work, using standard samples obtained from the National Institute of Standards and Technologies (USA), to estimate the errors related to the application of the Rietveld method on the phase analysis of fly ashes. They recommend estimating standard errors based on phase abundance. More specifically, for a crystalline phase of <1% per weight, the expected error is about 30%; for weight fraction between 1 and 5%, the error is up to 25%; and for weight fractions >5%, the respective error is up 15%. In the present work, higher standard errors than the above are expected, considering the higher number of the solid-solution and other crystalline phases contained in the ashes investigated, in comparison to the fly ash standard samples mentioned.

3. Results and discussion

3.1. Chemical composition of the ashes

The chemical composition of a part of the ash samples investigated is shown in Table 1. In Table 1, the range of the component oxides concentration determined from the weekly ash samples from all power plants, are shown. According to these results, the ashes of the Agios Dimitrios, Kardia, and Ptolemais power plants have a relatively high or very high CaO content. The CaO content in the LIPTOL ashes varies widely from moderate to very high, in the Amyntaeon ashes it is moderate, while in the ashes from the Meliti-Achlada power plant it is very low. The SiO_2 content is relatively moderate in the ashes from of the Agios Dimitrios, Kardia and Ptolemais plants, as well as most of the ash samples from the LIPTOL power plant, while it is high in the ashes from the Amyntaeon and Meliti-Achlada power plants. The content in Al_2O_3 and the rest of the oxides is limited, except for the ashes from the Meliti-Achlada power plant, where the Al_2O_3 content is extremely high. In the triangle diagram SiO_2–(CaO + MgO)–(Al_2O_3 + Fe_2O_3) (Fig. 2), it is obvious that the chemical composition of the ashes varies between three different marginal types: (a) CaO + MgO rich (CaO + MgO > 40%, the ashes of Agios Dimitrios and Kardia and the most samples of Ptolemais and LIPTOL); (b) SiO_2 rich (SiO_2 >40%), the ashes of Amynteon and one sample of Ptolemais and LIPTOL); and (c) Al_2O_3 + Fe_2O_3 very rich, with high SiO_2,

Table 3
The ash composition (average values, standard deviations, wt.%) of 42 weekly samples of the Ag. Dimitrios, Kardia, Ptolemais (unit I, II and IV), LIPTOL and Amynteon power plants.

Power Plant	Ag. Dimit.	Kardia	Ptolemais (3 units)	LIPTOL	Amynteon
Samples	5	5	21	7	4
Anhydrite	5.0	6.4 ± 0.6	8.6 ± 1.0	11.0 ± 2.4	5.8 ± 0.6
Lime	12.8 ± 1.7	12.6 ± 2.1	7.8 ± 1.5	8.6 ± 2.2	5.3 ± 1.3
Periclase	2.0 ± 0.2	2.1 ± 0.2	1.2 ± 0.2	3.0 ± 0.4	1.2 ± 0.1
Hematite	0.7 ± 0.1	1.1 ± 0.3	0.9 ± 0.1	1.0 ± 0.4	1.0 ± 0.1
Gehlenite	7.7 ± 0.9	7.9 ± 0.7	5.3 ± 1.1	6.2 ± 2.4	7.4 ± 1.1
Ca_2SiO_4	3.9 ± 0.5	3.2 ± 0.9	2.3 ± 0.8	4.1 ± 0.7	4.5 ± 1.1
Brownmillerite	7.3 ± 1.1	9.3 ± 1.5	5.3 ± 1.0	9.0 ± 3.3	4.5 ± 0.9
Merwinite or/and Mayenite	1.2 ± 0.4	1.5 ± 0.5	0.9 ± 0.3	1.3 ± 0.7	0.9 ± 0.2
Calcite	3.3 ± 0.3	2.7 ± 0.9	8.4 ± 2.6	4.7 ± 2.0	1.1 ± 0.3
Quartz	4.7 ± 0.8	3.9 ± 0.4	6.0 ± 0.8	6.2 ± 2.6	5.9 ± 0.5
Feldspars	9.8 ± 1.8	6.6 ± 1.2	7.5 ± 1.6	7.6 ± 1.4	12.9 ± 3.5
Muscovite/illite	2.6 ± 0.3	1.1 ± 0.1	2.9 ± 0.7	1.4 ± 0.4	0.7
Pyroxenes	–	–	–	–	5.8 ± 1.3
Amorphous	40.0 ± 2.7	41.9 ± 4.2	42.8 ± 3.1	36.3 ± 7.3	43.2 ± 5.5

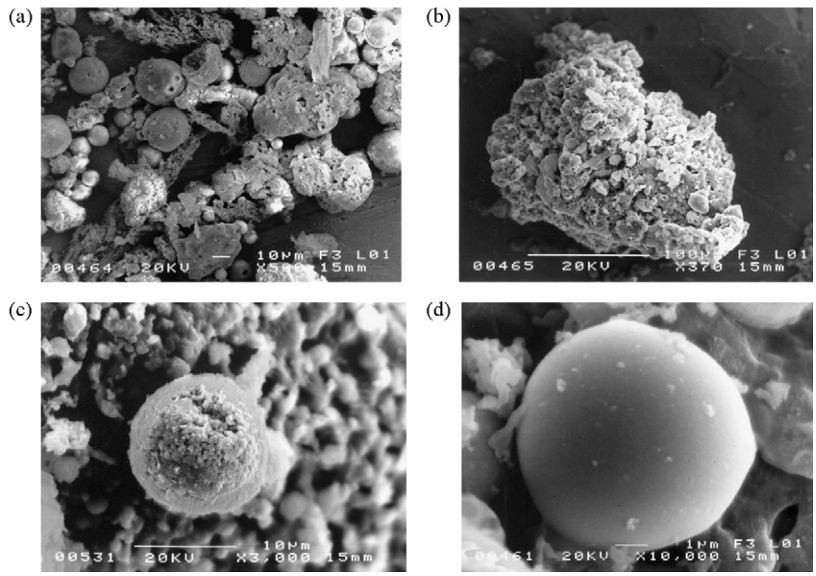

Fig. 3. Fly ash particles of the Agios Dimitrios power plant (REM). Loose, irregularly shaped particles (a), particle agglomerate (b), spheroidally shaped agglomerate of very small particles (c) and glass spheroid (d).

and extremely low CaO content (all 7 samples of Meliti-Achlada). Between types (a) and (b) a continuum in the composition of the ashes is observed.

3.2. Mineralogical composition of the ashes

The results of the mineralogical analysis of the daily samples from the above power plants are shown in Table 2 and these of the weekly samples in Table 3, with the following results:

(a) The ashes of the Agios Dimitrios, Kardia, Ptolemais and LIPTOL power plants consist, in general, mainly of amorphous phases; anhydrite ($CaSO_4$); lime (CaO); gehlenite ($Ca_2Al\ [AlSiO_7]$); feldspars $\{(Ca,Na)[(Si,Al)_4O_8]–(K,Na)[(Si,Al)_4O_8]\}$; quartz ($SiO_2$); small amounts of calcite ($CaCO_3$); brownmillerite $\{Ca_2(Al,Fe)_2O_5\}$; Ca_2SiO_4; and very low amounts or traces of periclase (MgO); hematite (Fe_2O_3); muscovite $\{KAl_2[(OH)_2/AlSi_3O_{10}]\}$/illite $\{(K,H_3O)Al_2[(OH,F)_2/(Si,Al)_4O_{10}]\}$; and merwinite $\{Ca_3Mg[SiO_4]_2\}$ or/and mayenite ($Ca_{12}Al_{14}O_{33}$).

The mean constituents of the Amynteon power plant ashes are the amorphous phase, anhydrite, lime, feldspars, gehlenite, and quartz. Pyroxenes, brownmillerite, and Ca_2SiO_4 are present in lower amounts; while calcite, hematite, periclase, and muscovite/illite appear in very low amounts or in traces.

The fly ashes of the Achlada-Meliti power plant have a significantly different composition from the ashes mentioned above, containing mullite, feldspars, quartz, hercynite, hematite, magnetite and very high amounts of amorphous phases.

(b) The qualitative mineralogical composition of the samples, representing the daily ash productions from the power plants during time intervals of 1 week (in each power plant) is found to be constant (Table 2). In addition, the differences observed regarding the percentages of the different mineral species, were, in general, limited. Also from the samples representing weekly ash productions during a time interval of about 3 months (Table 3), the qualitative mineralogical composition of the ashes of each power plant was be found to fluctuate only in a limited extent.

In the ashes of the LIPTOL power plant, the variation of the quantitative mineralogical composition in time, both daily and weekly, was the most pronounced among all of the power plants.

The differences between the quantitative phase composition of the ashes produced during different time periods in three different units of the Ptolemais power plant were limited (Fig. 5). The widest variations were detected in the contents of lime (unit IV), calcite (all three units), feldspars (units I and IV), and quartz (unit IV).

The investigation of the ash samples from the Agios Dimitrios power plant using a Raster Electron Microscope (REM) shows that a large part of the ash consists of glass in the form of spheroids or irregularly shaped particles, rich in Ca, Fe, Si, and Al, as well as sintered agglomerates and spheroids (Fig. 3). Similar pictures can be seen for ashes of lignite burning power plants from other regions [16,17]. A smaller part of the amorphous phases is expected to consist of dehydrated minerals of the kaolinite group, since in the feed coals of the power plants of the Ptolemais–Amynteon non-negligible amounts of minerals of the kaolinite group have been found [2,3] and char and or/unburned lignite particles, as indicated by the carbon content and the loss of ignition of the fly ashes (Table 1).

In the discrete lignite layers, the interbedded sediments from the open pits of Notio Pedio, Kardia, Komanos, and Amynteon, where lignite is mined, and in the fuel feedstocks of the Ptolemais, Kardia, and Amynteon power plants investigated in the past [2,18] the most common minerals found are quartz, calcite, minerals of the kaolinite group, gypsum, feldspars, muscovite/illite, chlorite, dolomite, and pyrite. Talc, aragonite, and amphiboles seldom occurred. The concentrations of the minerals and the presence of the minor minerals usually varies widely, in each mine between the discrete lignite layers [19] and between discrete layer packages as well. The comparison of the mineralogical composition of the fly ashes with the composition of the lignite from the open pits and fuel feedstocks mentioned above leads to the conclusion that the biggest part of the crystalline phases of the ashes determined consists of phases formed by the burning process. These phases are gehlenite, Ca_2SiO_4, brownmillerite, hematite, magnetite, mullite, pyroxene, hercynite, merwinite, mayenite, and probably anorthite; another part consists of dehydration, decomposition or oxidation products, namely anhydrite, lime, periclase, and hematite; while the smaller part consists of unaltered primary lignite minerals namely quartz, calcite, feldspars, and muscovite/illite. The calcite content of the lignite is the factor that mainly affects the formation of the fly ash phases at the Agios Dimitrios-, Kardia-, Ptolemais-, LIPTPL-, and Amynteon power plants. The lime produced by the decomposition of calcite reacting with SO_2 (produced from the oxidation mainly of pyrite and from organic sulphur present in lignite) forms anhydrite (additionally to the anhydrite produced from the dehydration of gypsum contained in the lignite). When lime reacts with quartz and silicates or/and oxides, gehlenite Ca_2SiO_4, brownmillerite, merwinite or (and), mayenite, probably pyroxenes, and anorthite (additional to the feldspars containing in the lignite) are formed, and only in a few cases pyroxene. The formation of hematite and magnetite is mainly due to the oxidation of pyrite. Since the lignite of the Florina basin contains, among others, very high percentage of quartz, and high percentage of kaolinite, meta-aluminate, pyrite, and siderite [20], the formation of mullite and hercynite in the fly ash of the Meliti-Achlada power plant is anticipated as a result of the reaction of minerals of the kaolinite group and the meta-aluminate with quartz or iron oxide (mainly produced from the oxidation of pyrite and the decomposition of siderite), respectively.

3.3. Characterization of the fly ashes based on the mineralogical composition

On the basis of the chemical analysis carried out during the last decades [21,22] the fly ashes of the Agios Dimitrios, Kardia, and Ptolemais power plants are classified as CaO-rich. The Amynteon power plant ashes are moderate regarding the CaO content and rich in SiO_2, while the Meliti-Achlada ashes are very poor in CaO, very rich in SiO_2 and extremely rich in Al_2O_3. It is in general assumed that the CaO-rich fly ashes have hydraulic while the SiO_2-rich pozzolanic properties. However the chemical analyses do not provide information of the percentage of CaO present as free lime or bonded in other phases, or the percentage of SiO_2 present as an amorphous phase, or seen in crystalline form or bonded in silicates. Given that each phase contained in the fly ash has a hydraulic (cementitious), pozzolanic, or inert behaviour [23,24], it appears promising to attempt to present a concise view of the reactive character of the fly ash using its quantitative mineralogical composition. For this purpose, the content of the minerals, grouped in three different groups according to their reactive character are projected in triangle diagrams (e.g., Figs. 4 and 5). The first group (A) contains the sum of the amounts of the minerals having hydraulic properties, namely anhydrite, lime, periclase, brownmillerite, Ca_2SiO_4, and merwinite (mayenite). The second group (B) involves the sum of the amounts of the inert minerals, namely quartz, calcite, hematite, feldspars, and muscovite/illite. Finally, the third group (C) involves the amounts of the amorphous phases (mainly glass and remains of clay minerals of the lignite decomposed by burning). Some of the amorphous components may exhibit pozzolanic or latent hydraulic reactivity. Triangle diagrams of this kind, especially in connection with grain distribution data, are believed to be more appropriate than the chemical composition given in tables or diagrams, to indicate the reactive character of the ash.

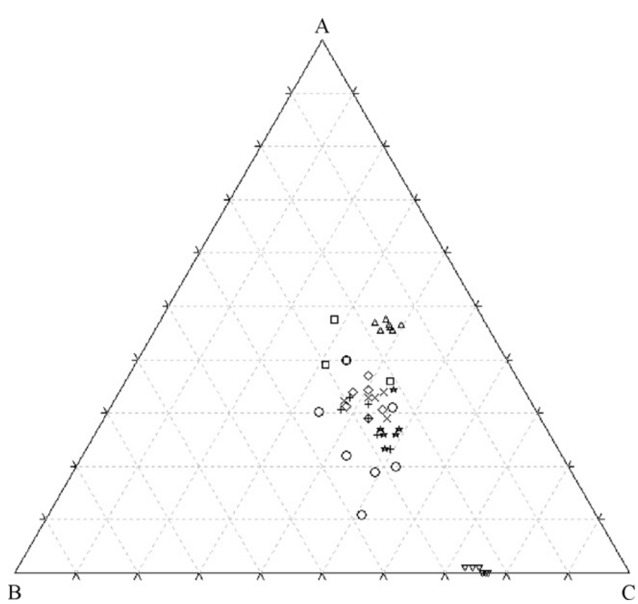

Fig. 4. Mineralogical composition of the daily-samples of the fly ashes from the power plants of Agios Dimitrios (□), Kardia (△), Ptolemais (units I (+), II (×) and IV (⋆)), LIPTOL (◯), Amynteon (◊) and Meliti-Achlada (▽) A = anhydrite + lime(+portlandite) + periclase + gehlenite + Ca_2SiO_4 + brownmillerite + merwinite/mayenite. B = quartz + calcite + mullite + hematite + feldspares + magnetite + hercynite + muscovite/illite + pyroxene. C = amorphous phases.

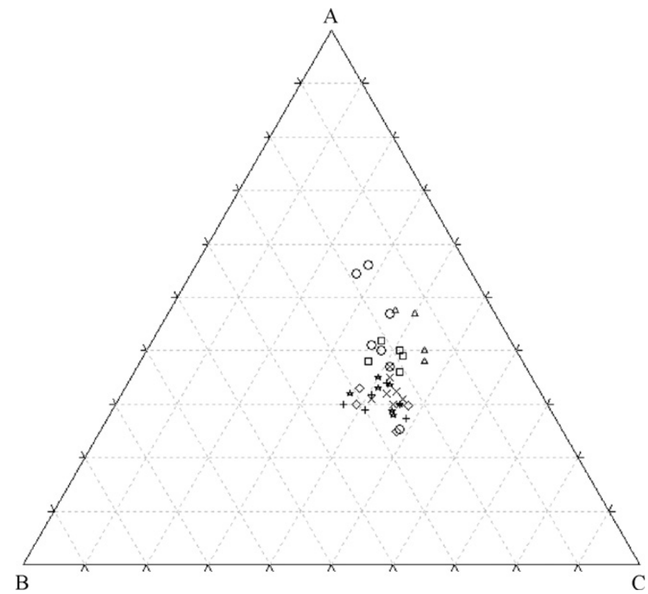

Fig. 5. Mineralogical composition of the weekly samples of the fly ashes from the power plants of Agios Dimitrios (□), Kardia (△), Ptolemais (units I (+), II (×) and IV (⋆)), LIPTOL (◯) and Amynteon (◊). A = anhydrite + lime (+portlandite) + periclase + gehlenite + Ca_2SiO_4 + brownmillerite + merwinite/mayenite. B = quartz + calcite + hematite + feldspares + muscovite/illite + pyroxene. C = amorphous phases.

Based on Figs. 4 and 5, it is obvious that the high percentage of lime and the other hydraulic reacting minerals present in the fly ashes of the power plants of Agios Dimitrios, Kardia, Ptolemais, LIPTOL, and Amynteon, suggests the hydraulic character of these ashes. This conclusion is confirmed by the experiences gained in Greece using fly ashes of Ptolemais power plant [21]. The presence of very high amounts of amorphous phases in the Meliti-Achlada fly ash indicates a pozzolanic character, since the glass phase as well as the likely present "metakaolin" in the amorphous phases are considered to be of pozzolanic character [23]. Although it is not possible to detect "metakaolin" by the XRD method used, its presence is assumed based on the presence of kaolinite in the mineral matter of the lignite from the Florina basin and the very high Al_2O_3 content of the fly ashes from the Meliti-Achlada power plant determined in this work (Table 1).

4. Conclusions

The fly ashes of the Agios Dimitrios, Kardia, and Ptolemais power plants have been found to contain anhydrite, lime, feldspars, quartz, gehlenite, Ca_2SiO_4, brownmillerite, muscovite/illite, calcite, merwinite or (and) mayenite, periclase, hematite, and amorphous phases. The quantitative mineral composition of the ashes of these power plants was relatively similar. The quantitative composition of the LIPTOL ashes fluctuates, but mostly differs only slightly from the fly ashes of Agios Dimitrios, Kardia and Ptolemais. In the fly ashes of the Amynteon power plant pyroxenes were detected in addition to the phases mentioned above, whereas, mostly, higher amounts of feldspars and lower amounts of lime have been found compared to the former power plants. The fly ashes of the Achlada-Meliti power plant have a significantly different composition from the ashes mentioned above, since they contain mullite, feldspars, quartz, hercynite, hematite, magnetite, and very high amounts of amorphous phases.

The variations in the quantitative mineralogical composition of the ashes produced in all power plants during a period of about 2 months were limited, whilst the ashes produced by three different units (boilers) of the same power plant (Ptolemais) did not show essential differences.

The fly ashes investigated varied between three different types with reference to the chemical composition: (a) CaO rich with moderate Al_2O_3 content (Agios Dimitrios, Kardia, and most Ptolemais and LIPTOL power plant ashes), (b) SiO_2 rich with moderate CaO and Al_2O_3 contents (mainly the Amyntaeon power plant ashes) and (c) Al_2O_3 very rich, with high SiO_2 and very low CaO content (Achlada-Meliti power plant ashes).

The use of triangle diagrams A–B–C, based on the mineralogical constituents of hydraulic character (A), inert character (B), and the amorphous phases content (C) of the ashes is introduced. Based on these diagrams, the following qualitative character of the fly ashes is assessed: (1) hydraulic or intensive hydraulic character for the ashes of Agios Dimitrios, Kardia and Ptolemais, (2) moderate hydraulic character of the Amynteon, (3) hydraulic of fluctuating intensity of the LIPTOL and (3) a pozzolanic character for ashes of the Meliti-Achlada power plant.

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