



Mineralogical composition of boiler fouling and slagging deposits and their relation to fly ashes: The case of Kardias power plant

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ABSTRACT

Slagging and fouling deposits from a pulverized lignite fired steam generating unit of the Kardias power plant (West Macedonia, Greece) were mineralogically investigated. The structure and cohesion of these deposits varied, usually depending on the level height of the boiler unit where they were formed. Some of the deposits had complex phase composition. The dominant components of the deposits of the burner zone and of the lower and intermediate boiler zones were the amorphous, anhydrite and hematite, while those of the highest levels contained amorphous, and anhydrite. Furthermore, in deposits formed in various other boiler areas gehlenite, anorthite, diopside, quartz, Ca_2SiO_4 , brownmillerite and other crystalline phases were also identified, usually in low amounts or in traces. The major part of the phases constituting the deposits were formed in the boiler, since only a minor part derived from the unreacted minerals present in lignite. Anhydrite was generated from the reaction of SO_2 with CaO formed mainly by the calcination of calcite as well as from dehydration of gypsum contained in lignite, while hematite was produced mainly from the oxidation of pyrite.

The calcium-containing silicates formed in the boiler were mainly the products of reactions between CaO and minerals contained in the lignite.

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1. Introduction

The slagging and fouling deposits in power plant boilers reduce significantly the heat conductivity of the tubes and consequently their heat exchange ability and for this reason they are studied by many scientists for a long period. The formation, composition and texture of slag and fouling deposits in pulverizing coal burners depends on the composition of the coal, their variation in time and their grain size, as well as on many parameters related to the construction details and the operation of the boilers. Such parameters are burning temperature, temperature gradient in the boiler system, air/coal ratio, gas velocity and others [1,2]. Gumz et al. [3] summed up investigations concerning structure, chemical and phase composition of slags of brown coal burning boilers; Pollmann [4] studied the chemical and mineralogical composition of deposits from several temperature zones of a coal burning power plant boiler; Watt [5] in a survey of thermal behaviour of coal minerals summarised several investigations; Beising et al. [6] and Hein [7] described slags formed in the furnace of brown coal burning boilers and presented their detailed mineralogical composition, while Reid [8] studied the relation of mineral composition to slagging, fouling and erosion during and after combustion. Sondreal et al. [9], Hein

[10], and Wall and Lindner [11] described the structure of typical deposits; Alfonso and Molino [12] described the physical nature of deposits; Walsh et al. [13] and Benson et al. [14] described processes contributing to the formation of ash deposits and increase of their thickness. Additional to these studies, Hatt [15], Pohl et al. [16], Gibb et al. [17], Couch [18], Bryers [19] and others reported on various structures and compositions of slag and fouling deposits of coal burning power plants. The complexity resulting from the effect of a great number of parameters, the differences of the local conditions in various power plants, especially the non avoidable fluctuation of the fuel quality, as well as a number of partially yet unknown effects on slag and fouling formation, do not usually enable adequate interpretation of results and reliable transfer from one power plant to another.

Because of the differences of local conditions in various power plants resulting from the complexity of effects of the great number of parameters mentioned above, it is important to investigate the slagging and fouling deposits in the power plant of Kardias, and extract useful conclusions in order to minimize deposits in similar power plants. The power plant of Kardias (West Macedonia, Greece) consists of four identical pulverized lignite fired steam generating units of a total installed capacity of 1.2 GW. The lignite fuel of this power plant is mined out in the Kardias mine of the Ptolemais-Basin (West Macedonia, Greece) and is combusted in tangential swirl burners. The lignite is of low heating value, very rich in mineral matter of varying quantity and composition [20]. The fly ash produced

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from the combustion of lignite in the Kardias power plant, consists mainly of Roentgen-amorphous phases (glass, amorphous mineral relicts, and char), crystalline phases formed in the boiler, derivatives of thermally decomposed minerals and non reacted minerals contained in lignite [21,22]. Since the boilers of all power plants of the Ptolemais territory, including those of Kardias power plant, are of the same type and combust lignite of the same wider area, the investigation of the fouling and slagging deposits in a boiler of the Kardias power plant is of regional interest. Using tests performed at a 1 MW semi industrial scale pulverized coal combustor and calculating slagging indices Agraniotis et al. [23] evaluated the ash deposition tendency of the lignite used in the Kardias power plant. The aim of the present work is to investigate the composition of fouling and slag deposits of the Kardias power plant, as well as to correlate them with the mineralogical composition of lignite and fly ash.

1.1. Experimental techniques

To ascertain a general view of the deposits, slag or fouling fragments were taken from various points at different heights of a boiler unit, namely from the superheater, the reheater, from a flue gas duct as well as from a heap of deposit fragments, which had fallen from various levels to the bottom of the boiler during maintenance works. The fly ash samples were collected directly from the loading band at the outlets of the bins of the power unit of the boiler in a time period of three months. For the mineralogical study of the samples X-ray diffraction (Bruker Advance D8 diffractometer system, Bragg-Brentano geometry) was used. 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 and graphite monochromator. 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 [22,24–27] using the Rayflex Autoquan program [28]. For the samples separation bottom loading technique was used. Since Roentgen-amorphous material was present, in order to perform quantitative phase analysis a crystalline internal standard (corundum, 15–20%) was added to the specimens. Their homogenisation was performed by hand in a mortar. The fly ash samples were kept in a drier immediately after preparation, to avoid the formation of portlandite. Some samples were also subjected to chemical analysis. For the chemical analysis XRF-spectrometer and molten specimens prepared by mixing of lithium-tetra-borate were used. For the analysis of SO_3 an analyser Leco 532-500 was used. The structure of slagging and fouling deposits was investigated using a polarizing as well as a scanning microscope.

Table 1

Chemical composition of slagging and fouling deposit fragments collected from various boiler heights (in m, B, Burner chamber; S, Superheater; R, Reheater).

	25 m (B)	42 m (S)	46 m (S)	54 m (S)	57 m (R)
CaO	21.48	23.91	26.05	32.85	26.58
SiO ₂	15.53	10.90	8.47	21.90	23.72
Fe ₂ O ₃	32.88	30.92	31.13	4.25	4.71
Al ₂ O ₃	6.33	5.37	4.50	9.77	11.07
MgO	2.34	1.61	2.00	5.51	5.37
K ₂ O	0.62	0.25	0.16	0.49	0.64
Na ₂ O	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01
TiO ₂	0.24	0.19	0.18	0.37	0.46
MnO	0.04	0.04	0.03	0.03	0.03
P ₂ O ₅	0.14	0.11	0.11	0.20	0.19
SO ₃	18.42	23.57	24.93	19.42	20.01
L.O.I.	0.93	1.77	1.37	5.07	5.34
Total	98.96	98.65	98.94	99.87	99.13

2. Results

2.1. Chemical composition of the deposits

The chemical composition of each sample representing the average composition of each deposit fragment (initial sample) is given in Table 1. The deposit fragments were taken from the burner zone (25 m height, B), the superheater (42, 46, 54 m height, S), the reheater (57 m height, R), and the flue gas duct (32 m height, F). As it is shown in Table 1, the dominant constituents in all samples were CaO and SO₃. The content of Fe₂O₃ was also high in samples taken from the lower and the middle heights of the boiler, while it decreased sharply in samples collected from the higher boiler sections. The contents of SiO₂ and Al₂O₃ were moderate and increased in the higher boiler zones, while the content of MgO was low and also increased in the higher zones. The contents of K₂O, Na₂O, TiO₂, MnO and P₂O₅ were very low in all samples.

The considerable ignition loss established in two samples is evidently due to the presence of non burned lignite (char) particles and calcite (is concluded considering the calcite content of the samples as shown from the results of the mineralogical analysis, seen in the following section).

2.2. Mineralogical composition

The specimens investigated with a X-ray diffractometer, were prepared from deposit fragments, which in some cases were up to 12 cm thick and 20 cm long (Fig. 1). In order to study the deposits in detail, and to ensure a certain identification of crystalline phases present in small amounts, having X-ray reflections overlapping with reflexes of other phases, two types of samples were pre-

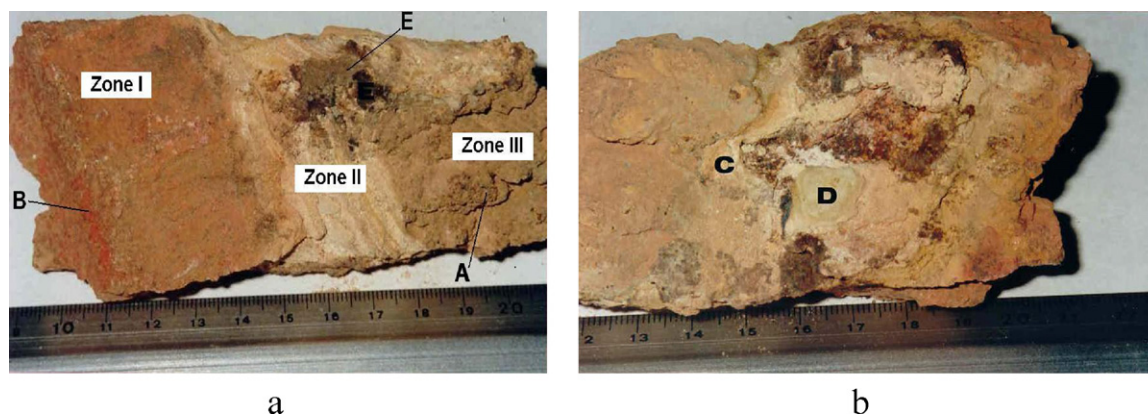


Fig. 1. Two sides of the same slagging deposit fragment from 25 m height of the burner.

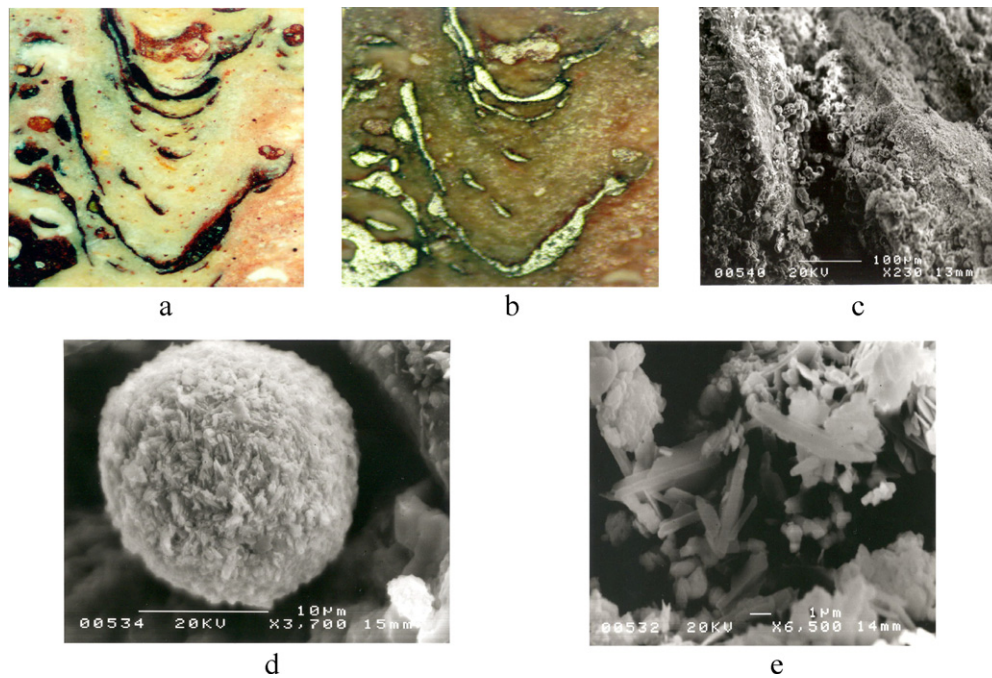


Fig. 2. Slag deposit from the burner (a, b) images in reflected light microscope, 25 \times , alternation of anhydrite (matrix) and hematite (dark in X Nicols and bright in //Nicols), (c) glass covered anhydrite- and hematite-rich zones (SEM), (d) spherical particles consisting mainly of Fe-rich particles $\leq 1 \mu\text{m}$ (SEM), (e) anhydrite crystals, covered with glass layers, rich in Fe_2O_3 and K_2O (SEM).

pared: a) initial samples representing the average composition of each deposit, and b) particular samples prepared from several distinct areas of the same deposit fragment. This was done in cases the deposit showed heterogeneous structure, including particular caverns or areas bigger than 1 mm or zones of variable aspect and cohesion (Fig. 1a–c). Additionally fly ash samples and lignite samples from representative lignite beams packages of the Kardias lignite mine and from the feedstock of the power plant were considered. In order to identify the minerals present in lignite, low-temperature-ashing [29] of the samples prior to mineralogical analysis was undertaken.

2.2.1. Deposits from the burner

The sample from the burner was a slag deposit fragment with a size of about 12 cm \times 6 cm \times 4 cm (Fig. 1). In this fragment distinct zones of varying structure were visible. At the one end of the fragment one zone was fine grained, very cohesive and red-dish brown coloured (Fig. 1a, zone I), while at the opposite end another zone (Fig. 1a, zone III) was greyish or blackish brown. (For interpretation of the references to colour in this text, the reader is referred to the web version of the article.) At the end part (zone III) a rather vitreous, botryoidal structure was seen. In a transition zone (Fig. 1a, zone II) between these two zones, caverns consisting of various areas differing in colour, structure or cohesion were visible (Fig. 1a, E and b, C, D). Seven specimens, each of them representative of the total fouling fragment and six specimens prepared from different zones or parts were analysed. The mineralogical composition of these specimens is shown in Table 2. From this table it is concluded that the major constituents of slag were a) Roentgen-amorphous, b) anhydrite (CaSO_4) and c) hematite (Fe_2O_3). All of them were present almost everywhere in various amounts. In all zones also Ca_2SiO_4 , anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), quartz, gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and diopside [$(\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6)$], were included in minor quantities. Furthermore brownmillerite [$\text{Ca}_2(\text{Al},\text{Fe})_2\text{O}_5$], mono-calcium-ferrite CaFe_2O_4 , and thenardite were only occasionally in traces present. The amorphous consisted mainly of glass,

having irregular forms, the form of sphaeroides or layers, or covering other particles of the fouling deposit. The phases in Table 2 except thenardite and mono-calcium-ferrite were also detected in fly ashes produced in the power plant. The red coloured zone of this fouling deposit (zone I, Fig. 1a) consisted mainly of amorphous, hematite and anhydrite, smaller quantities of plagioclase and very small quantities of quartz.

In the botryoidal formed zone (zone III, Fig. 2a) the main constituents were the amorphous and hematite, while Ca_2SiO_4 , gehlenite, brownmillerite, diopside, were included in minor quantities and only in traces anhydrite and seldom thenardite. In caverns of the transition zone (zone II, C–F, Fig. 1) Ca_2SiO_4 , gehlenite, diopside, brownmillerite or feldspare were the main constituents. The fouling fragment consisted mainly of fine coarse particles partially sintered or encapsulated in a glassy matrix. Anhydrite and hematite crystals were observed usually in a size of the order of μm or smaller, randomly distributed or in alternating wavy zones (Fig. 2a–c). Glass spherical formed accumulates (Fig. 2d) and some μm -long idiomorph anhydrite crystals (Fig. 2e) were sporadically observed.

Table 2
Mineralogical composition of the burner fouling deposit (25 m (B), Table 1).

	Total	Zone I, B	Zone II				Zone III, A
			C	D	E	F	
Anhydrite	27	22	57	10	5	22	tr.
Hematite	16	25	1	–	17	1	18
Anorthite	1	4	6	12	tr.	13	–
Diopside	6	4	19	1	5	15	3
Gehlenite	3	–	4	16	4	32	4
Brownmillerite	tr.	–	–	15	–	–	4
Ca_2SiO_4	2	1	–	30	5	–	6
Quartz	–	tr.	–	1	–	–	–
CaFe_2O_4	–	–	–	–	1	–	–
Thenardite	–	–	–	–	–	–	tr.
Amorphous	45	44	13	15	63	17	65

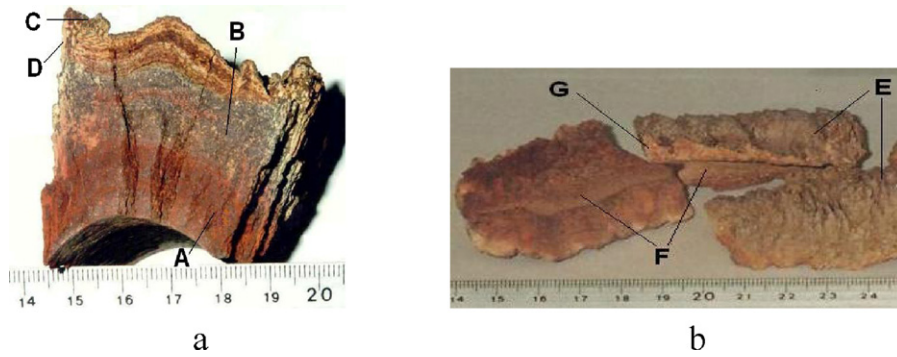


Fig. 3. Deposits from the superheater at heights of 42 m (a) and 46 m (b).

2.2.2. Deposits from superheater and reheater tubes

Samples taken from deposits on heat exchanger tubes at the height of 42 m (Fig. 3a), 46 m (Fig. 3b), 54 m of the boiler, from the superheater tubes (Fig. 5a), and 57 m from the reheater (Fig. 5b and c) were investigated. The deposits of the heights 42 m and 46 m were very cohesive. From each one of the samples taken from 42 m and 46 m height, which exhibited a non homogeneous composition 3–4 specimens from different areas of the sample were separated and additionally to the specimen of the total sample analysed (Table 3).

The major constituents of the total sample from 42 m and 46 m height of the boiler were amorphous, anhydrite, and hematite, while diopside and anorthite were minor constituents. Gehlenite, CaSi_2O_4 , brownmillerite, quartz or tridymite, were detected in small percentages or in traces in some parts of these deposit fragments. In both deposit fragments alternating layers of dark reddish brown, greyish yellow, ochre or brown colour were visible (Figs. 3a and 4a). (For interpretation of the references to colour in these texts, the reader is referred to the web version of the article.) The material of these layers mainly consisted of anhy-

Table 3

Mineralogical composition of deposits on tubes at 42 m and 46 m height.

	42 m				46 m				
	Total sample	Sample area			Total sample	Sample area			
		A	B	C	D		E	F	G
Anhydrite	28	30	16	9	26	39	29	35	56
Hematite	16	25	19	13	27	18	21	19	2
Anorthite	2	7	–	3	2	6	4	7	7
Diopside	4	3	6	9	8	6	9	2	13
Gehlenite	–	–	1	6	–	1	5	–	–
Brownmillerite	–	–	2	3	–	–	–	–	–
Ca_2SiO_4	–	–	–	6	–	–	–	–	–
Quartz	–	tr.	–	–	–	tr.	–	1	tr.
Tridymite	–	–	–	–	tr.	–	–	–	–
Amorphous	50	35	56	51	37	30	32	36	22

drite and hematite (Fig. 4b and c). Anhydrite crystals some times were a few μm long, while anhydrite as well as hematite usually formed sintered masses (Fig. 4b–d). Glass was detected almost everywhere either as cover of particles (Fig. 4d), or in spherical

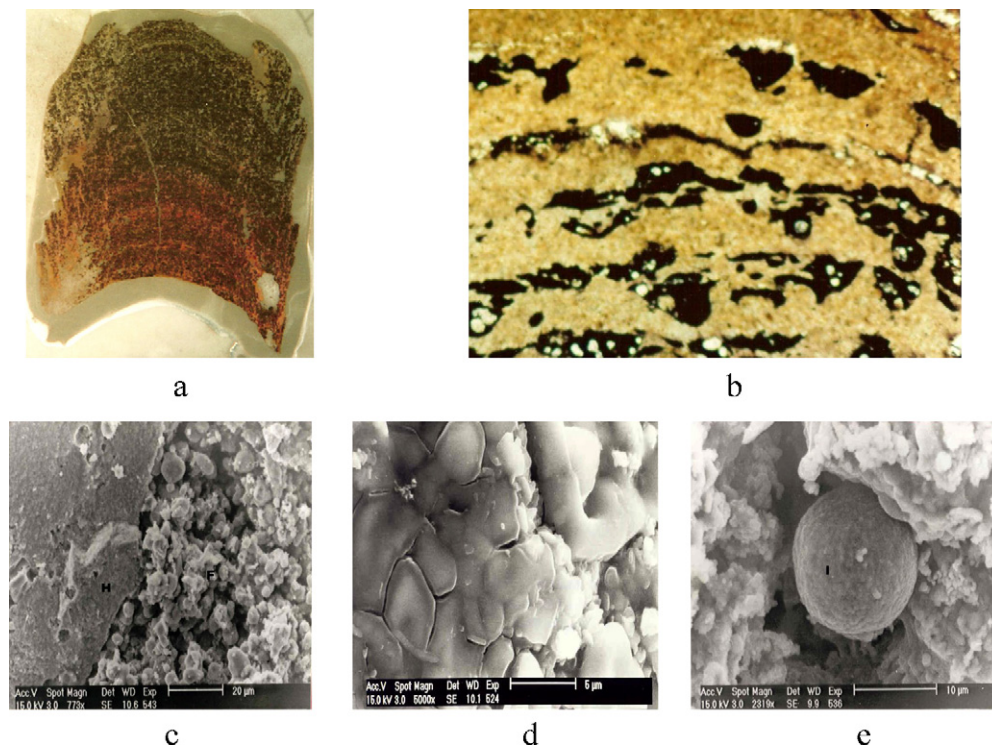


Fig. 4. Deposits from the boiler at 42 m height a) thin section about 4×5 cm, b) anhydrite (matrix) and hematite (dark areas), polarizing microscope, $25\times$, //Nicols, c) hematite (H)- and anhydrite-rich (F) areas (SEM), d) glass-covered particles (K- and Mg- and S-rich, SEM), e) spherical particles, rich in Si, Al, Ca, Fe and Mg (SEM).

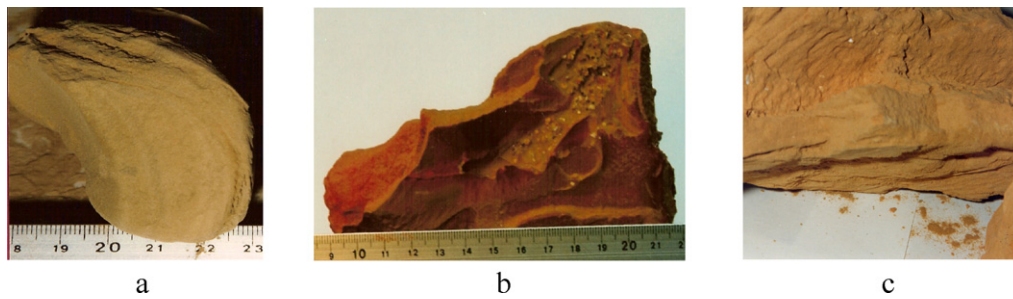


Fig. 5. Deposits from (a) 54 m and (b, c) 57 m height.



Fig. 6. Slag from the flue gas duct (a), and slag and fouling fragments from various boiler sections (b).

shape. Spherical particles were observed consisting of glass or glass matrix including fine particles, rich in Si, Al, Ca, Fe and Mg (Fig. 4e).

The investigated deposit fragments from 54 m (superheater) and 57 m (reheater) height of the boiler were 13–22 cm long, easy friable and mainly of a sandy structure (Fig. 5). Additionally to the total samples of three fragments (Fig. 5) a fourth specimen, taken from a cavern of the fragment at 57 m height, was investigated. The results of the mineralogical analysis of these deposits are shown in Table 4. All three deposits consisted mainly of anhydrite and amorphous, like the deposits of the lower boiler zones, but in contradiction to these, they included only traces of hematite. They also included lower percentages of anorthite, calcite, quartz, Ca_2SiO_4 , gehlenite, and traces of hematite. Additionally low amounts of brownmillerite (54 m sample), as well as enstatite (57 m sample, c), and traces of tridymite and cristobalite (57 m sample b) were detected.

2.2.3. Deposit fragments from various boiler parts

Fouling and slag fragments from a flue gas duct at a height of 32 m and from a heap of pieces selected from the boiler bottom under the ash hopper, where they had fallen from various boiler height levels (Fig. 6), were investigated.

As shown in Table 5, they had a diverse mineralogical composition. The major constituents in the slag from the flue gas duct were anorthite, amorphous, diopside, gehlenite, and pseudowollastonite, while the minor constituents were anhydrite, and mullite; Ca_2SiO_4 , quartz, hematite and thenardite were detected in traces. In all deposit fragments selected from the boiler bottom high percentages of amorphous phases were seen and in almost all of them high percentages of anhydrite were detected. Furthermore, in most fragments low amounts of diopside and anorthite, and in some of them quartz, mullite, gypsum, cristobalite, calcite, gehlenite and thenardite were present.

2.2.4. Fly ashes

The mineralogical composition of these ashes (Fig. 7) is shown in Table 6.

The major constituents of the ashes were Roentgen-amorphous. Lime, brownmillerite, gehlenite, feldspars and anhydrite were present in considerable amounts, while quartz, Ca_2SiO_4 , calcite, periclase, merwinite, muscovite/illite and hematite were present in lower amounts. The main part of the Roentgen-amorphous consisted of glass in shape of spheres or other particles of various shape, and glass-layer covered crystalline particles.

Table 4

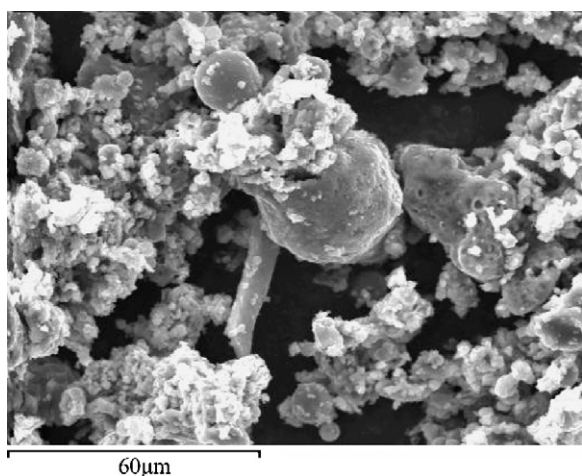
Mineralogical composition of deposits at (a) 54 m and (b, c) 57 m height.

Sample		A	He	Pl	Ge	C	Q	Cc	Cr	En	Tr	B	Am
a (Fig. 5a)	Total	39	tr.	7	4	2	3	6	–	–	–	5	34
b (Fig. 5b)	Total	43	tr.	10	4	6	3	5	tr.	–	tr.	–	29
	Cavern	21	1	11	–	–	14	12	–	–	2	–	39
c (Fig. 5c)	Total	45	1	2	3	2	3	4	tr.	5	–	2	33

A = anhydrite, He = hematite, Pl = plagioclase, Ge = gehlenite, C = Ca_2SiO_4 , Q = quartz, Cc = calcite, Cr = cristobalite, En = enstatite, Tr = tridymite, B = brownmillerite, Am = Roentgen-amorphous.

Table 5
Mineralogical composition of flue gas duct slag (F) and of diverse deposits fragments (1–9).

Sample	F	1	2	3	4	5	6	7	8	9
Anhydrite	2	57	55	17	1	25	39	42	29	28
Hematite	tr.	4	6	30	Sp.	23	1	1	5	27
Plagioklase	30	4	1	–	–	–	4	–	7	2
Diopside	17	4	7	6	–	6	5	–	14	12
Gehlenite	15	–	–	–	–	–	–	–	3	–
Brownmill	–	–	–	–	–	–	–	–	–	–
Quartz	tr.	–	–	–	6	–	2	–	1	–
Calcite	–	–	–	–	–	–	–	5	–	–
Mullite	2	–	–	–	29	–	–	–	–	–
Cristobalite	–	–	–	–	12	–	–	–	–	–
Gypsum	–	2	–	–	–	–	–	17	7	–
Pseudowollastonite	9	–	–	–	–	–	–	–	–	–
Thenardite	tr.	–	–	–	–	–	–	–	–	–
Ca ₂ SiO ₄	tr.	–	–	–	–	–	–	–	–	–
Amorphous	24	25	31	47	52	46	49	34	34	31

**Fig. 7.** Accumulation of fly ash particles (REM).**Table 6**
Mineralogical composition of fly ashes (average values of 5 week samples, standard deviation).

Lime	12.6 ± 2.1
Brownmillerite	9.3 ± 1.5
Gehlenite	7.9 ± 0.7
Feldspars	6.6 ± 1.2
Anhydrite	6.4 ± 0.6
Ca ₂ SiO ₄	3.2 ± 0.9
Quartz	3.9 ± 0.4
Calcite	2.7 ± 0.9
Periclase	2.1 ± 0.2
Merwinite	1.5 ± 0.5
Muscovite/illite	1.1 ± 0.1
Hematite	1.1 ± 0.3
Amorphous	41.9 ± 4.2

3. Discussion

The investigations of slag and fouling deposits from various boiler height levels have shown diverse cohesions, structures and compositions. The slag deposit of the lower boiler height levels (25 m, Fig. 1) was very cohesive, including caverns of very different composition. The major chemical constituents were Fe₂O₃, CaO and SO₃, while considerable contents of SiO₂ and Al₂O₃ were detected (Table 1). The major mineralogical phases were anhydrite, and hematite, since diopside, gehlenite, Ca₂SiO₄ and anorthite were found in lower quantities. The amorphous of the deposits consisted mainly of glass. The very cohesive deposits of the intermediate height levels (45 m, Fig. 1, and 46 m, Fig. 3), formed also alter-

nated zones consisting mainly of anhydrite and hematite and had a similar qualitative composition. Alternating zones of tube deposits, consisting mainly of anhydrite as adhesive mass between various iron rich phases, were already observed by Pollmann [4], while typical tube slags of a similar macroscopic view are described by Heap et al. [30], Benson et al. [14] and others. The particles were usually covered with a glass layer, which obviously held them cemented contributing thus to a high consistence of the slag deposits. On the contrary the deposits from the higher boiler levels (54 m and 57 m height, Fig. 5) contained higher percentages of anhydrite although their SO₃ content was quite similar, less amorphous, more plagioclase, quartz, and additionally calcite, and only a minor percentage (1%) or traces of hematite. The phase composition and the friable texture of these deposits is obviously due to the fact that the major part of their matter originated from non reacted and non essentially sintered minerals included in the lignite. Since the lignite of the Ptolemais Basin contains high percentages of calcite, gypsum, minerals of the kaolinite group, as well lower percentages of chlorites, muscovite/illite, and low percentages of pyrite (≤5%) [20,31], the formation of the deposits may be explained, as follows: the high anhydrite content in the deposits results from the reaction $\text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4$ as well as from gypsum dehydration. The calcium oxide for this chemical reaction results from the disintegration of calcite and from the organically bounded calcium. Hematite is obviously formed mainly from the oxidation of pyrite. SO₂ results from the oxidation of pyrite and the organic matter of the lignite. Anhydrite resulting from the dehydration of gypsum may cause the formation of eutectic mixtures with alkali sulfates. At least a part of the glass phase formed this way on fly ash particles, is seen in fragments from the combustion chamber and the lower levels of the boiler, where the temperature is high. This is based on the observation of the potassium- and sulfur-rich glass covered mineral grains or the grain conglomerates (Fig. 4d), as well as on the detection of thenardite traces in the slag deposit of the burner (Table 2). Since iron oxide formed by the oxidation of pyrite is a potential flux, lowering the viscosity of slag deposits significantly [14,19,32], and iron is found in spheroids (Fig. 4e), it is obvious that iron also contributed to the formation of glass particles. In parallel to this, glass may have been formed from muscovite/illite [33] and chlorites [34], as well as a result of the fluxing action of pure minerals contained in a given particle. The formation of glass, besides sintering, contributes to the formation of the cohesive deposits in the combustion chamber and in boiler zones at middle heights. In the opposite, in the highest boiler zones (deposits at 54 m and 57 m heights) where lower temperatures predominate, CaSO₄ does not contribute to glass formation, so that friable deposits were created from anhydrite, glass and other particles, transported from the flow gas from lower boiler zones. The comparison of the mineralogical

composition of the deposits with the mineralogical composition of the ashes (Table 6) and of the lignite burned in the power plant [20,31], lead to the conclusion that in the ashes two kinds of solid phases are present: a) phases which were present in the lignite and were not destroyed during burning in the boiler; these are quartz, anorthite, muscovite/illite, and b) phases resulted mainly by decomposition or reaction of mineral phases, and in a lesser degree by reaction of liberated organically bound matter; these phases are the amorphous (glass, derivatives of kaolin minerals, and char), lime (decomposition of calcite, dolomite, aragonite, and from organically bound calcium), anhydrite (reaction of CaO with SO₃, as well as dehydration of gypsum), gehlenite (reaction of lime with Al-silicates), and Ca₂SiO₄. Hematite, brownmillerite, and the rarely detected minerals mullite, cristobalite, wollastonite and thenardite must be also formed in the boiler, because they were not detected in the lignite [20,31].

4. Conclusions

The deposits investigated varied in their structure and cohesion. Most of them had complex qualitative phase composition, often varying in different areas of one deposit fragment. They included almost always amorphous, anhydrite and hematite, while in a number of deposits gehlenite, brownmillerite, anorthite, diopside, quartz, Ca₂SiO₄, as well other calcium silicates and other crystalline phases were detected in low amounts or in traces. Most of the deposits can be distinguished in two main types according to their mineralogical composition, which depends on the height level of the boiler unit they were formed: a) the deposit fragments of the burner, and the lower and middle zone of the boiler and b) the deposits of the highest zone of the boiler. The slag fragments of the burner and the lower and the middle zone of the boiler as well, were very cohesive, while their major constituents were the amorphous, anhydrite and hematite, which were usually covered with glass layers and often formed alternated zones. The fragments of the highest zone were relatively friable and consisted mainly of amorphous and anhydrite. Only a minor weight percentage of each deposit consisted of non reacted minerals, since the major part of the mass consisted of phases formed by the combustion of the lignite. The formation of glass was mainly due to iron oxide resulted from the oxidation of pyrite, and sheet silicates, whereas for the formation of most of the crystalline phases the contribution of CaO, originating to a large extent from the disintegration of calcite contained in the lignitic fuel, was the decisive factor.

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