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Mineral and chemical composition of waste products formed by combustion of Maritsa East lignite coals in a low-oxygen environment at the TPP Maritsa East 2, Bulgaria

Минерален и химичен състав на отпадни продукти, формирани в нискокислородна обстановка при изгарянето на източномаришки лигнити в ТЕЦ „Марица-Изток 2“, България

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Introduction

This study presents data about waste products, formed in particular zones of the combustion chamber in the thermal power plant (TPP), where the combustion proceeds under oxygen deficient conditions due to limited air circulation and/or higher temperatures. As a result, these waste products have specific phase composition, characteristic for reduction processes.

Materials and methods

Two samples (P8/k1 and P8/k2), taken from the walls of the combustion chamber of boiler No. 8 (TPP Maritsa East 2) were studied (Fig. 1a, b). The samples have size as follows: P8/k1 20×8.5×2.5 cm and P8/k2 14×10×6 cm. They have dark gray-brown color, as P8/k1 is heavy, has fine grain massive texture, whereas P8/k2 is light, and has slaggy porous texture. The samples were studied using the following methods: 1) X-ray diffraction (XRD) (phase composition); 2) inductively coupled plasma mass spectrometry (ICP-MS) (major elements) and 3) laser ablation combined with ICP-MS (LA-ICP-MS) (trace elements).

Results and discussion

The phase composition of the studied samples (P8/k1 and P8/k2) is listed in Table 1 together with composition of coal for burning (P4F) and combustion wastes (fly and bottom ash) (P5FA and P7BA) also collected from TPP Maritsa East 2. Sample P8/k1 has high con-

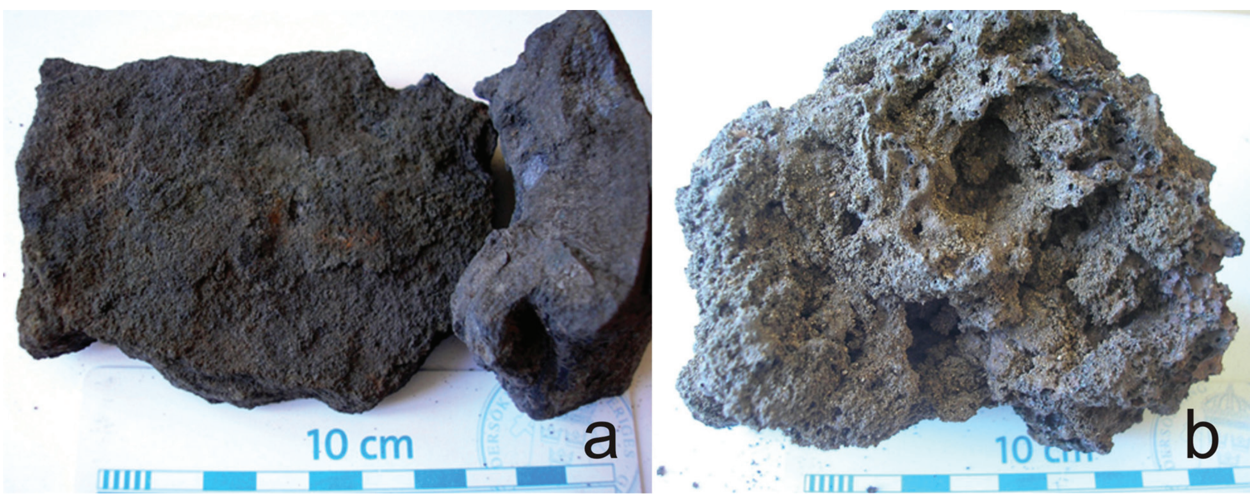

Fig. 1. Photographs of the studies samples: *a*, P8/k1 and *b*, P8/k2

Table 1. Phase composition of samples, vol.%

Sample No.	Phases (%)
P4F – fuel for TPP	illite (69.7), gypsum (15.9), quartz low (10.2), pyrite (2.2), jarosite (1.9)
P5FA – fly ash	quartz (46.2), enstatite (28.5), magnetite (7.9), anhydrite (7.6), gypsum (5.2), hematite (4.6)
P7BA – bottom ash	anorthite (19.9), muscovite (28.1), quartz low (22.4), gypsum (12.1), magnetite (10.7), anhydrite (7.0)
P8/k1	pyrrhotite (61.3), ferridiopside (35.2), quartz low (3.5), troilite 2H (<1.0), orthopyroxene (<1.0)
P8/k2	anorthite (79.3), hercynite (10.5), tridymite low (6.6), hematite (3.2), crystobalite low (<1.0)

tent of pyrrhotite and absence of magnetite and hematite, indicating formation in environment with limited air flow, where pyrite (from coal sample) have not be completely oxidized (Vassilev, Vassileva, 1996). The presence of troilite also denotes redox conditions. However, the airflow was sufficient to produce some Fe^{3+} that was incorporated at high temperature (>1000 °C) in the ferri-diopside (Huckenholtz et al., 1969).

Unlike P8/k1, sample P8/k2 contained a certain amount of hematite (3.2%), denoting that oxidation occurred, but was weaker than the conditions at which fly and bottom ash formed. In this case, bottom (P7BA) and fly (P5FA) ash contained hematite and/or magnetite 10.7 and 12.5%, respectively. A portion of Fe^{2+} was included in hercynite. The association anorthite-hercynite-tridymite-cristobalite suggests formation at temperature ~1400 °C. The formation of anorthite can be explained by the high contents of Ca and Mg in the Maritsa East coal ashes (Vassileva, 2002). Sample P8/k2 also contained glass as P5FA and P7BA.

The concentrations of 63 elements were determined and compared to average concentrations (clarkes) of elements in brown coal ashes (Ketris, Yudovich, 2009) to determine a coefficient of enrichment (CE). The concentrations of Fe, Si, S and Re were compared to clarkes for lignite coal ashes (Finkelman, 1994). The following elements have CE>1:

1) in P8/k1: $Re_{16.3} > Mo_{8.6} > Cu_{6.7} > Fe_{4.9} > Co_{3.3} > Mn_{3.1} > Se_{2.7} > (S, Au)_{2.3} > Pd_{1.7} > Ni_{1.5} > Ga_{1.2}$

2) in P8/k2: $(Mo, Cu)_{5.2} > Re_{3.8} > V_{2.7} > Rb_{2.4} > (Li, Cs)_{1.9} > Mg_{1.8} > (Cr, Mn)_{1.7} > Ga_{1.6} > (Ca, W)_{1.5} > Ti_{1.2} > (Al, Si)_{1.1}$.

The elements that have high CE in P8/k1 associate with Fe in pyrrhotite and probably originated from pyrite in coal and organic matter. Most of the elements with CE>1 in P8/k2 associate with the silicate/glass matter and came from mineral (silicate) and/or organic matter. The lithophile elements (Mo, Re, Rb, Li, Cs, Mg, Ca, W, Al, and Si) are dominant in P8/k2. The sum of REE+Y+Sc concentrations in the studied samples is lower than the clarkes. It is higher in P8/k1 (73.1 ppm) than P8/k2 (50.1 ppm). The REE are probably concentrated in ferri-diopside in P8/k1, as HREE are three times higher than P8/k2. On the other hand, REE in P8/k2 are preferentially included in glass and hercynite. Anorthite has the tendency to concentrate a certain portion of Eu (Linnen et al., 2014).

Conclusions

Combustion of coal was not completely even in the combustion chamber volume. There were zones where the airflow was reduced and phases typical for reduction processes were formed, such as pyrrhotite, troilite, hercynite. There were also zones, where the temperature of combustion was higher (1400 °C) than the usual temperature of formation of typical fly and bottom ash. Evidence for this fact is the association of anorthite, hercynite, tridymite and cristobalite. Trace elements characteristic for natural sulphides and silicates were also found in the same technogenically produced minerals.

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