

INVESTIGATION OF MINERAL COMPOSITION OF OIL SHALE ASH STORED IN ASH FIELDS OF THE BALTI POWER PLANT

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Mineral composition of oil shale ash stored in the ash fields of the Balti Power Plant was determined by X-ray diffractometry. Changes in the content of the main compounds and new compounds formed during the storage of ashes under natural conditions were investigated. The composition of the ash collected from the ash fields was substantially different from the composition of the ash discharged from power plants. Different compounds were detected in the various boreholes as well as at different levels of the same borehole. The results obtained could be used to explain and control the processes taking place in ash fields.

Introduction

Ash fields of Estonian oil shale-fired power plants induce a certain danger to the environment of the North-East Estonia. Narva power plants – the Balti Power Plant and the Eesti Power Plant produce about 4.5 million tonnes oil shale ash per annum. The total area of the ash field of Narva PP is more than 20 km². Environmental impact of ash fields is caused by highly alkaline ash-transporting water (pH 12–13). This water may reach the Narva River, soak into soil and groundwater.

The situation is particularly bad in the Balti PP (Fig. 1) where the total area of ash fields and setting ponds is larger (10.65 km²) [1]. The 2nd ash field of the Balti PP has not been in use for storing ash for a long time. This field consists of twelve ponds for evaporation the excess water from ash fields. Ash dams separate the ponds from each other. The 2nd ash field would be recultivated in the nearest future.

To reduce the amount of excess water the so-called technology of dense slurry was proposed by Hungarian EGI. Theoretically, all water must be bound into ash resulting in the formation of a layer of “ash stone”. A small

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test ash field and test cartridge was set up. However, the expectations were not realized, and the Balti PP decided to give up the idea of using this technology.

Oil shale ash is characterized by a complicated mineral composition and content of chemically active compounds. With time and in certain conditions some spontaneous chemical reactions can take place, which change the composition of ash. In paper [2] the system ash-water-air was studied by storing moistured samples of ash in laboratory both in the open air and closed hermetically. These investigations indicated that the processes in the ash strongly depended on the process conditions, and a number of new formations were formed.

The aim of this study was to investigate the changes in oil shale ash of the Balti Power Plant by X-ray diffractometry (XRD), paying special attention on the new formations. Borehole samples from the 2nd and test ash fields were studied. Mineral composition of these samples was determined to explain the processes taking place at deposition of oil shale ash.

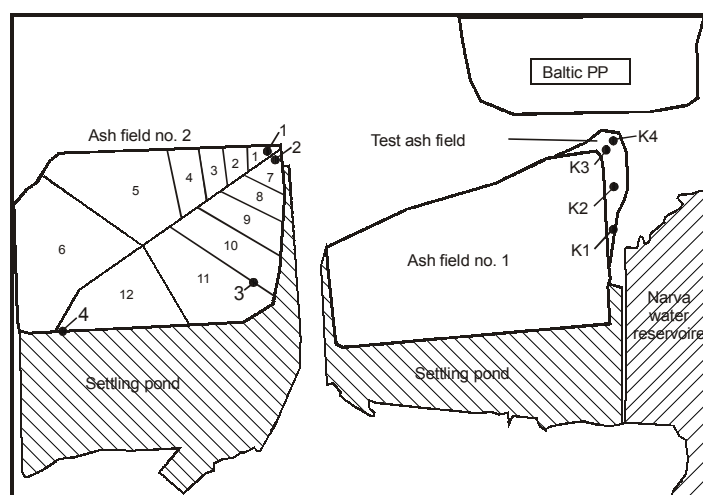


Fig. 1. Plan of the Balti PP ash fields. Numbers 1–12 indicate evaporation ponds, • – boreholes 1–4 and K1–K4

Experimental

Ash field samples provided by Thermal Engineering Department of Tallinn University of Technology were investigated. Core samples were taken from the boreholes No. 3 and No. 4 of the 2nd ash field of the Balti PP, and from the boreholes Nos K1, K2, K3 and K4 of the test ash field (see Fig. 1).

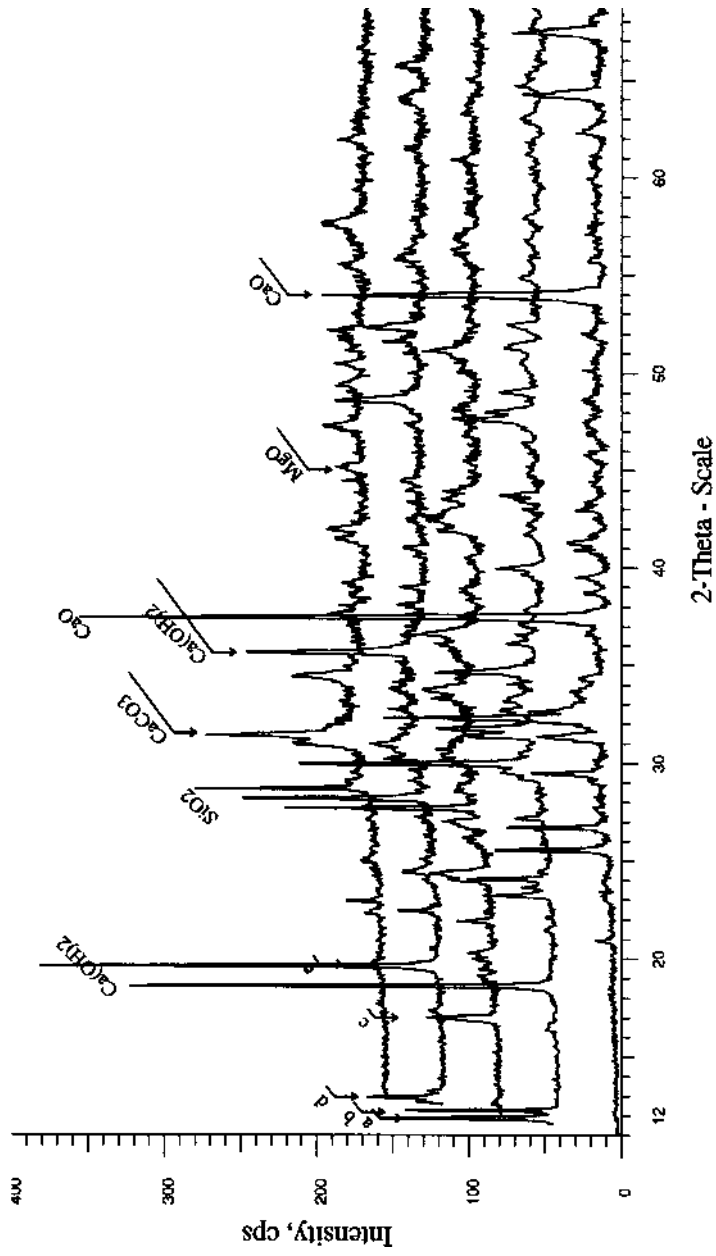


Fig. 2. X-ray spectra of some samples of oil shale ash: 1 – initial ash; mixture of ashes used in [2], 2 – ash from borehole No. 3 at depth 7 m, 3 – No. 4, 9 m, 4 – No. K3, 1 m, 5 – No. K4, 2.8 m. a – PDF pattern no. 41-0476, b – 41-0219, c – 41-0217, d – 31-0245, e – 38-0368

On the test cartridge only fine ash from the electrostatic precipitators was deposited (borehole No. K4). As the core samples were not taken all over the ash field, the results give only a general estimate of the mineral composition of the ash field.

Ash samples were studied by X-ray diffractometry as described in [3]. XRD data were collected on a Bruker AXS diffractometer D5005 with scintillation detector. Theta-Theta geometry, Cu tube, variable divergence and antiscattering slits and diffracted beam graphite monochromator were used. Data acquisition and data evaluation was achieved with a software package DIFFRAC^{plus}. For the identification of crystalline phases the Powder Diffraction Database (PDF-2) of the International Center for Diffraction Data (ICDD) was used. For measuring X-ray diffractograms the following parameters were used: tube current 40 mA, tube voltage 40 kV, step size 0.04°, time per step 4.0 s, 2 Θ (11–69)°, rotating object. The samples were prepared in a standard sample holder. To identify minor compounds special parameters 0.02°, 10.0 s, (9–70)° were used.

Results and Discussion

X-ray spectra of the initial ash and some ash samples from boreholes are shown in Fig. 2. As the initial ash a mixture of ashes was used in the study [2]. The content of chemical compounds in the sample was estimated by the intensity of the strongest line in the corresponding set of lines assigned to a certain compound [3].

The content of six main components: lime CaO, anhydrite CaSO₄, quartz SiO₂, calcite CaCO₃, periclase MgO and larnite Ca₂SiO₄ was determined. During the storage of ash in wet conditions portlandite Ca(OH)₂ as an important compound was formed [2]. X-ray diffractograms of the samples of the ash field reveal that the lines characteristic to lime, anhydrite and larnite disappear or become very weak.

According to the literature [2], a rapid reaction of lime with water and portlandite takes place. However, a very little amount of lime was present, especially in the upper layers. Anhydrite was missing, or only traces were recorded. It is stated in [4] that anhydrite participates in the formation of ettringite, alkali sulphates and calcium sulphoaluminates. The intensity of the lines of larnite decreased a few times. Probably larnite reacted with CO₂ from the air and calcite was formed. The changes in the content of the rest four compounds along the depth of deposited ash can be followed in Fig. 3a and 3b for boreholes No. 3 and No. 4, respectively. The changes in the content of portlandite and calcite in the boreholes of the test ash field are shown in Fig. 4.

The figures show that the changes in the content of the compounds along the depth are not smooth. The content of some compounds in the adjacent layers differ, and the ash field material has a stratified structure. The content

of periclase MgO varied very little. However, in boreholes No. 3, K2 and K4 the content of periclase had the tendency to decrease, i.e. a part of Mg ought to form other compounds.

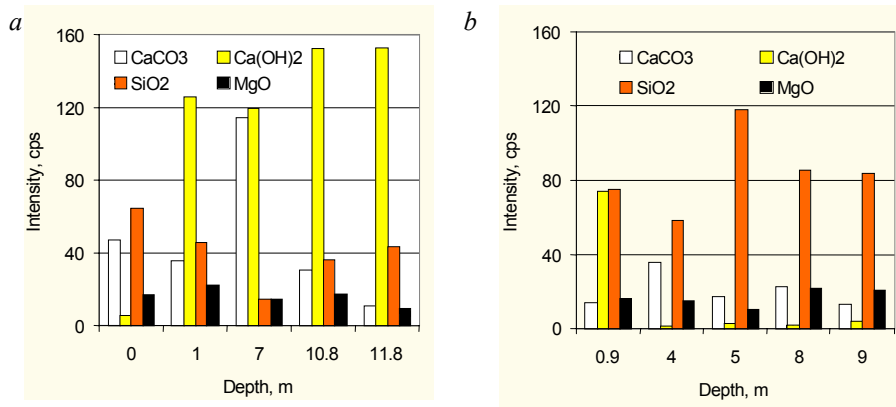


Fig. 3. Changes in the content of some compounds along the depth of deposited ash, boreholes No. 3 (a) and No. 4 (b)

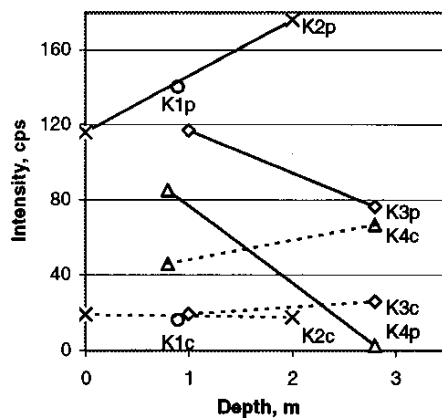


Fig. 4. Changes in the content of portlandite and calcite in the boreholes of the test ash field: p – portlandite, c – calcite

An essential finding was the formation of portlandite from lime and its further reaction with carbon hydroxide to form calcite. The ash field material contains portlandite in all layers. In contact with water it changes the aqueous solution highly alkaline. In most of the samples the content of portlandite was high and varied slightly with the depth. There is an analogy with laboratory experiments in hermetic conditions, as calcium hydroxide present in ash and stored in the ash pond is not able to react with carbon hydroxide from the surrounding air.

At the same time some exceptions exist. In the samples from borehole No. 4 of the 2nd ash field and from borehole K4 of the test ash field, high content of portlandite in upper layers was very small in the depth of 3–4 m. There is a partial analogy with laboratory experiments in open-air conditions. Consequently, in these places the access of carbon hydroxide is

possible. Occurrence of calcite in every sample leads to the conclusion that a part of portlandite is transformed everywhere. There is a possibility that another formation also may react [2].

From minerals occurring in the ash samples taken from the ash fields of power plants the following compounds are present in minor amounts: gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, magnesite MgCO_3 , dolomite $\text{CaMg}(\text{CO}_3)_2$, rutile TiO_2 , monocalcium silicate $\text{CaSiO}_3/\text{CaO} \cdot \text{SiO}_2$ (wollastonite), dicalcium ferrite $\text{Ca}_2\text{Fe}_2\text{O}_5/2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (srebrodolskite), monocalcium aluminate $\text{CaAl}_2\text{O}_4/\text{CaO} \cdot \text{Al}_2\text{O}_3$, tricalcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6/3\text{CaO} \cdot \text{Al}_2\text{O}_3$, clinoenstatite MgSiO_3 , and bredigite $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$.

Some of these minerals are not present in any sample. The samples from boreholes No. 4 and K4 are particularly interesting, as a lot of the initial compounds are still present, for example arcanite K_2SO_4 , marcasite FeS_2 , and potassium calcium sulphate $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$.

Many compounds that have been detected in the power plant ash were missing after ash has been stored on ash fields, for example, such compounds as feldspars, melilites, micas and many other freely soluble and leaching out compounds.

In addition to the compounds found in initial ash, a large number of new formations has been detected. Thereby in the various boreholes different compounds were formed. Even more, the samples from one borehole can contain different new formations. These are, in ground, complex compounds containing several elements present in ash. Most of these represent hydrate/hydroxides. New formations contain the groups of CO_3 , SO_3 , SO_4 , SiO_4 and some others.

Calcium aluminium oxide carbonate hydrate occurs in borehole No. 3 as $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}/3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ (PDF pattern no. 41-0219), but as $\text{Ca}_6\text{Al}_2\text{O}_6(\text{CO}_3)_3 \cdot 32\text{H}_2\text{O}/3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCO}_3 \cdot 32\text{H}_2\text{O}$ (PDF pattern no. 41-0215) in borehole No. 4. Calcium aluminium oxide sulphite hydrate $\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_3)_3 \cdot 32\text{H}_2\text{O}/3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_3 \cdot 32\text{H}_2\text{O}$ (PDF pattern no. 41-0217) occurs in borehole No. 4 as well as in others in larger quantities. Groups CO_3 and SO_3 both occur in the sample No. 268 from borehole No. 3 in the compound calcium aluminium oxide carbonate sulphide hydrate $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)_{0.67}(\text{SO}_3)_{0.33} \cdot 11\text{H}_2\text{O}/3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.33\text{CaSO}_3 \cdot 0.67\text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ (PDF pattern no. 41-0476). Calcium aluminium silicates are represented by silication katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (PDF pattern no. 38-0368), calcium aluminium silicate hydroxide $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (PDF pattern no. 32-0151), and clinozoisite $\text{Ca}_2\text{Al}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ (PDF pattern no. 44-1400). Calcium silicate hydroxide hydrate $\text{Ca}_{4.5}\text{Si}_6\text{O}_{15}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ (PDF pattern no. 43-1488) represents silicates. Chelyabinskite $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{OH})_6 \cdot 9\text{H}_2\text{O}$ (PDF pattern no. 44-1423), thaumasite $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$ (PDF pattern no. 46-1360), calcium aluminium oxide hydrate $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 19\text{H}_2\text{O}$ (PDF pattern no. 14-0631), hydrocalumite $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ (PDF pattern

no. 42-0558), magnesium aluminium hydroxide hydrate $\text{Mg}_4\text{Al}_2(\text{OH})_{14}\cdot 3\text{H}_2\text{O}$ (PDF pattern no. 35-0964), and hanksite $\text{KNa}_2(\text{CO}_3)_2(\text{SO}_4)_9\text{Cl}$ (PDF pattern no. 25-1348) were probably also present.

Only few compounds detected in ash fields coincided with the compounds detected in laboratory experiments. Only calcium silicate hydroxide hydrate (PDF pattern no. 43-1488), calcium aluminium oxides carbonate hydrate as (PDF pattern no. 41-0215) and (PDF pattern no. 41-0219) were present in both cases.

Conclusions

- The composition of the ash collected from ash fields was substantially different from the composition of ash discharged from power plants.
- A number of new formations were discovered. In different boreholes as well as at the different levels of the same borehole different compounds were detected.
- Laboratory experiments made it possible to observe the behaviour of the main compounds. The reactions taking place in ash fields and new formations could be observed analysing the samples taken from the ash fields.
- The results of the present investigation can be used for the explanation of the processes occurring in ash fields.

Acknowledgements

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REFERENCES

1. Arro, H., Prikk, A., Pihu, T. Reducing the environmental impact of Baltic Power Plant ash fields // *Oil Shale* 2003. Vol. 20, No. 3S. P. 375–382.
2. Kuusik, R., Paat, A., Uibo, M., Veskimäe, H. Transformations in oil shale ash at wet deposition // *Oil Shale* 2004. Vol. 21, No. 1. P. 27–42.
3. Paat, A., Traksmäa, R. Investigation of the mineral composition of Estonian oil shale ash using X-ray diffractometry // *Oil Shale* 2002. Vol. 19, No. 4. P. 373–386.
4. McCarthy, G., Solem, J. K. X-ray diffraction analysis of fly ash. 2. Results // *Adv. X-Ray Anal.* 1991. Vol. 34. P. 387–394.

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