TRANSFORMATIONS IN OIL SHALE ASH AT WET DEPOSITION

R. KUUSIK[*1] [(1)], A. PAAT[*2] [(2)]
H. VESKIMÄE [(1)], M. UIBU [(1)]

[(1)] Tallinn Technical University
Institute of Chemical Engineering
5 Ehitajate St., Tallinn 19086, Estonia

[(2)] Tallinn Technical University
Centre for Materials Research
5 Ehitajate St., Tallinn 19086, Estonia

Estonian oil shale ash contains chemically active compounds which would undergo different spontaneous transformations in the atmosphere of air. For explaining these processes the system ash–water–air was studied storing moistured samples of ash in laboratory in open-air as well as hermetic conditions. The samples of dry ash formed at pulverized combustion of oil shale at the Baltic Power Plant, and samples obtained from ash storing plateau from different depth of different boreholes were under investigation. The mineral composition of both initial and stored samples was determined by XRD. The content of CaO_{free} and CO_2 in the samples was determined by chemical analysis. The CO_2-binding degree and the slaking rate of samples were calculated.

At open-air storing ash samples contact with H_2O and CO_2. Substantial changes, especially upon lime, take place during the initial period of storing. The content of $Ca(OH)_2$ increases rapidly and thereafter, approximately during the following four weeks, it carbonates completely forming calcite. Numerous other compounds of complicated composition form as well. At hermetical storing of samples, due to the absence of CO_2 in the gaseous phase, the changes in the mineral composition of ash are much less intensive. $Ca(OH)_2$ formed at hydration of dry ashes preserves throughout the all period of sample storing. Storing conditions as well as the properties of initial samples have a great influence upon the processes taking place at storing of ashes. The results obtained could be used to explain and control the processes taking place at storing of ashes under atmospheric (wet) conditions.

[*1] Corresponding author: e-mail *rkuusik@edu.ttu.ee*
[*2] E-mail *apaat@edu.ttu.ee*

Introduction

Huge amounts of ash (42–48% of oil shale mass burnt) form during decomposition of Estonian oil shale. During the 1980s 10-11 million tons of oil shale ash were formed annually in four oil-shale-fired power plants (Estonian, Baltic, Kohtla-Järve and Ahtme). At the beginning of the 1990s the amount of oil shale burnt and therefore the amount of ash formed decreased, and now it is on the annual level of 5-6 million tons [1, 2]. A part of the oil shale ash is used in the industry of construction materials, in agriculture and road building [3]. However, most of the ash formed in power plants is transported to the nearby ash fields.

As oil shale ash is characterized by a complicated mineral composition and the presence of chemically active compounds [3], some spontaneous chemical reactions can take place in certain conditions, and the composition of ash changes in time. It is important to establish these changes in order to use ash industrially and, particularly, to decrease the environmental concerns – CO_2 and SO_2 emissions and strongly alkaline ash fields – related to oil shale combustion in Estonia. Solid wastes formed at oil-shale-fired power plants have a considerably high reactivity towards SO_2, and therefore they could be applied as potential sorbents for further desulfurization of flue gases [4–6]. The CO_2 binding in the carbonation process at ash deposits and in water suspensions of ash formed during hydrotransportation and deposition in ash fields has been shown earlier [7–9].

Various authors have studied the composition of oil shale and its ash using different analysis methods: chemical, thermal and technical, spectrum and neutron-activation analysis, petrography and X-ray diffractometry (XRD) [3]. However, only XRD allows a direct spectrum-based determination of the mineral composition of the investigated materials. Unfortunately, XRD has been very rarely used to determine the mineral composition of ash [10–12]. The first systematic use of XRD to analyze oil shale ash is presented in paper [13]. An attempt was made to determine the mineral composition of the ash and follow its changes along the nodes of the whole ash-handling system.

Mainly the developers of new construction materials have studied the changes taking place in ash, because they were interested in the cement minerals formed during ash processing [14–19]. The main subject of research was the mixture of ash and water, to which other substances used in production of construction materials were added. Usually these materials were heated or processed in autoclave. At first, the development of new formations was studied mainly by thermographic, in some cases also by petrographic methods. XRD has been seldom used for determining the composition of oil shale ash, but quite widely for studying new formations formed in it: at first, only as an assistant method [17, 18], but since the 1970s very often as a main one [20], taking into use new X-ray apparatus, so-called difractometers. The results of using XRD in solving these problems (e.g. the

behavior of ettringite [21] and anhydrite [22] during processing in autoclave are presented in a collection of papers [23].

The use of XRD is best discussed and presented in Dilaktorski's thorough review on the composition of ash and reactions taking place in it, and in the studies of the school of Kikas.

As the conditions in nature and in our imitative experiments differ from those used in the previously described studies, it is expected that the processes taking place in ash in nature could significantly differ from these taking place in construction materials. This is also confirmed by the few XRD studies related to binding of carbon dioxide by ash in carbonization process [7] and keeping ash in moist environment [13]. Taking into account huge ash fields of Narva power plants and the hazardous effect of ash deposition on the environment [24], it is important to understand the processes taking place in ash at storage. The aim of this study was to investigate hydration and carbonation of oil shale ash, especially the reactions occurring at the beginning of ash–water–air interaction by chemical and XRD methods.

Materials and Experimental Methods

The ash used was a mixture of Estonian Power Plant (PP) ashes of the mass ratio of furnace ash : superheater ash : cyclone ash : electrostatic precipitator ash 15 : 15 : 60 : 10. The content of CaO_{free} and CO_2 in the mixed ash (on dry basis) was 19.40 and 1.21%, respectively. The dry ash was hydrated with an amount of water exceeding the stoichiometric ratio ten times considering the content of CaO_{free} in the ash (10 g ash and 6 g water).

The samples of hydrated ash were set:
1) on the sample-holder in open air in laboratory conditions, mixing and moistening them once a day to preserve the initial mole ratio of CaO_{free} and water;
2) 2) in a hermetic bag without air access. The room temperature was 18–20 ºC. For analyses the samples were taken after 2, 4, 6, 24, 48 and 72 hours, and after 1, 2, 4, 6, 8 and 12 weeks of exposition. For both series the content of moisture, CaO_{free} and CO_2 were determined and X-ray analyses were made.

CO_2-binding degree (BD_{CO_2}) was calculated by the change in CO_2 content of the sample:

$$BD_{CO_2} = CO_2/CO_{2max} \times 100 \ (\%)$$

where CO_2 is analytically determined CO_2 content of the sample in current time, %;

CO_{2max} is the maximum possible CO_2 content of the sample calculated on the basis of CaO_{free} in the initial sample, %:

$$CO_{2\,max} = \frac{CaO_{free} * M_{CO_2} / M_{CaO} + CO_2}{100 + CaO_{free} * M_{CO_2}/M_{CaO}} *100 \ (\%)$$

where CaO_{free} and CO_2 are the content, %, of CaO_{free} and CO_2 in the initial sample, respectively.

All values used are given on dry basis.

XRD data were collected on a *Bruker AXS* difractometer 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 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, 2Θ 11–69° or 15–65°, rotating object. The samples were prepared in a standard sample holder.

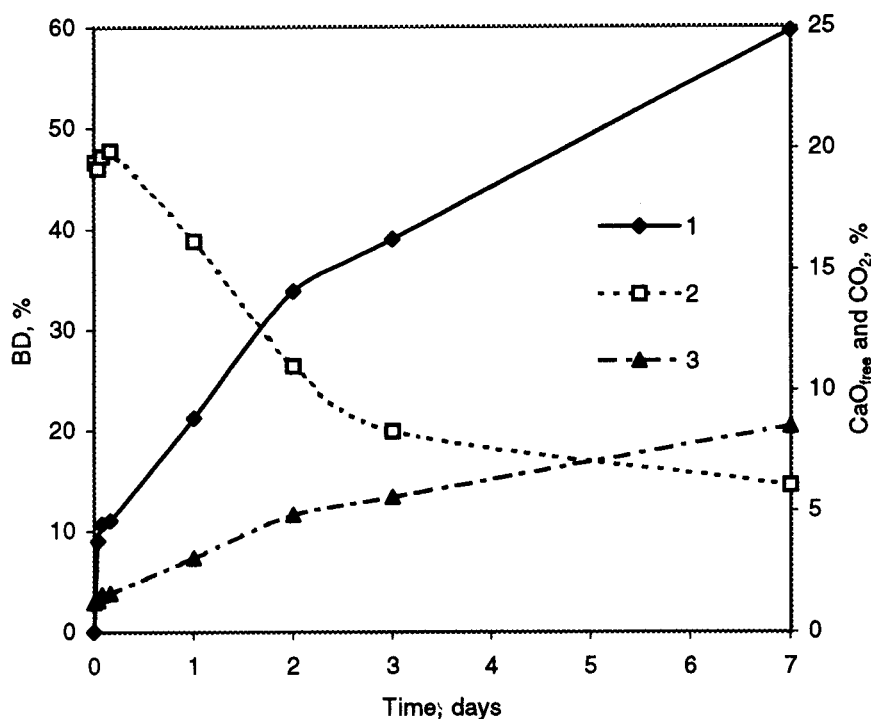## Results and Discussion

Fig. 1. Dependence of CO_2-binding degree BD (*1*), content of CaO_{free} (*2*) and CO_2 (*3*) of hydrated ash on the storing time in open-air conditions

Investigations with the previously hydrated ash indicated that in the open air the ash carbonated almost completely in the case of periodic moistening and mixing – in four weeks the content of CO_2 increased from 1.52 to 15.35%, or the BD_{CO_2} reached 96.5%. The rapid increase in BD_{CO_2} occurred in the first days – in three days the BD_{CO_2} reached 40% (Fig. 1).

The most intensive binding of CO_2 occurs during some hours of the contact with air. As expected, the carbonation process does not take place while storing the hydrated ash in hermetic conditions without air access (Fig. 2). In the following steps of the current study, the changes in the composition of samples were surveyed by XRD.
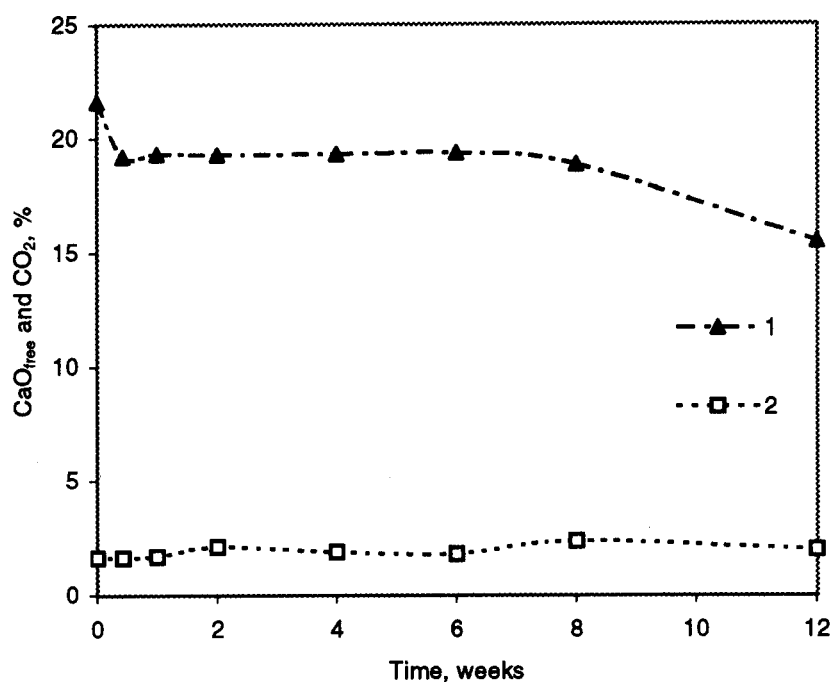

Fig. 2. Changes in the content of CaO_{free} (*1*) and CO_2 (*2*) of hydrated ash depending on the storing time in hermetic conditions

X-ray spectra of initial ash and some typical hydrated ash samples are shown in Fig. 3, where the changes in composition of ash during hydration are easy to follow. The content of a chemical compound in the sample was estimated by the intensity of the strongest line of its X-ray spectrum [13].
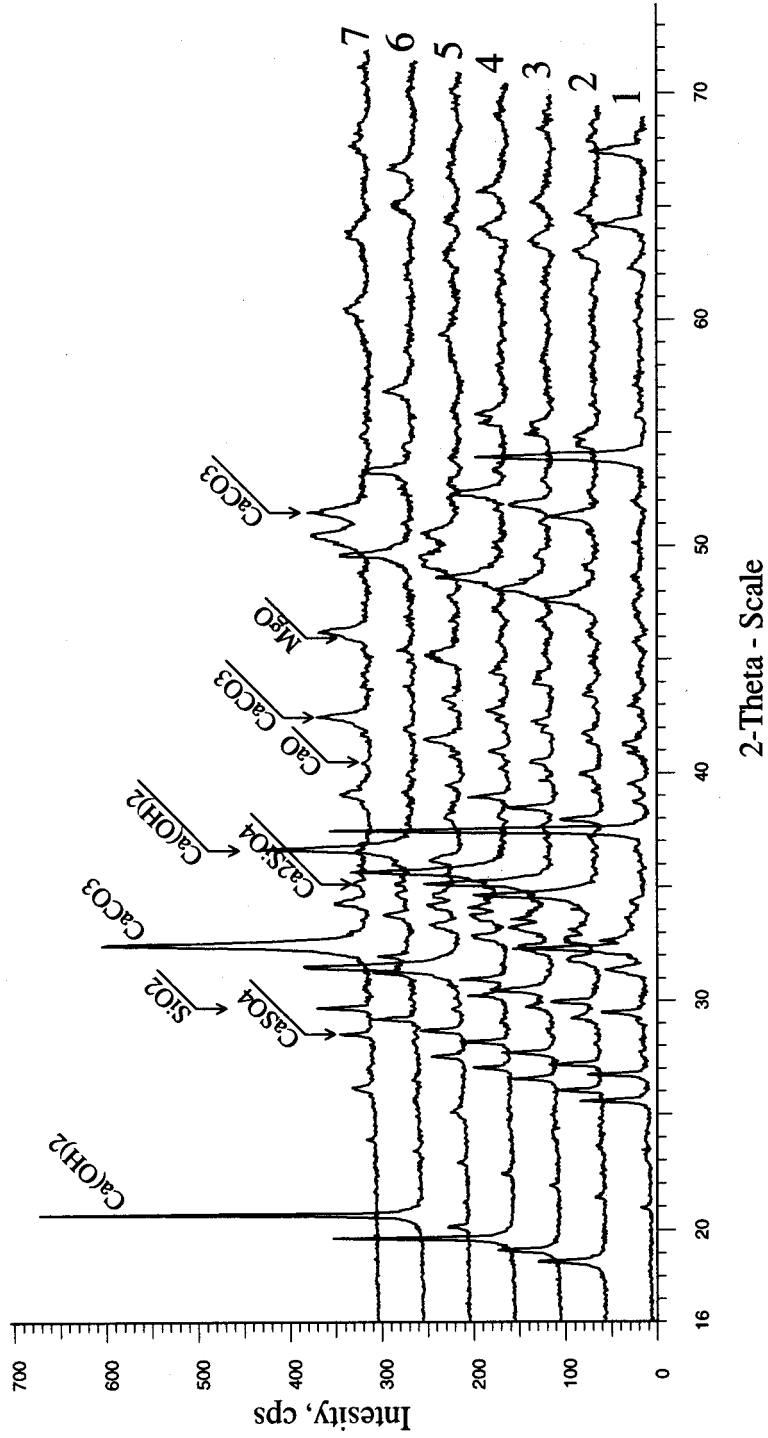
Fig. 3. X-ray spectra of initial ash and some hydrated ash samples: *1* – initial ash; *2* – open-air hydration during 6 hours; *3* – hermetic hydration during 3 days; *4* – open-air hydration during 3 days; *5* – open-air hydration during 14 days; *6* – hermetic hydration during 84 days; *7* – open-air hydration during 84 days

The Composition of Initial Ash

Initial ash contains quantitatively fixable amounts of lime CaO, quartz SiO_2, anhydrite $CaSO_4$, calcite $CaCO_3$, larnite Ca_2SiO_4 (dicalcium silicate $2CaO \cdot SiO_2$) and periclase MgO.

Gypsum $CaSO_4 \cdot 2H_2O$, dolomite $CaMg(CO_3)_2$, bassanite $CaSO_4 \cdot 1/2H_2O$, magnesite $MgCO_3$; as for calcium silicates tricalcium silicate $3CaO \cdot SiO_2/Ca_3SiO_5$ and monocalcium silicate $CaO \cdot SiO_2/CaSiO_3$ (wollastonite); dicalcium ferrite $2CaO \cdot Fe_2O_3/Ca_2Fe_2O_5$ (srebrodolskite); as for calcium aluminates monocalcium aluminate $CaO \cdot Al_2O_3/CaAl_2O_4$ and tricalcium aluminate $3CaO \cdot Al_2O_3/Ca_3Al_2O_6$ are also present in minor amounts.

It is highly probable that ash contains also oldhamite CaS, hematite Fe_2O_3, magnetite Fe_3O_4, potassum calcium sulfate $K_2Ca_2(SO_4)_3$, marcasite FeS_2, rutile TiO_2, zircon $ZrSiO_4$ and portlandite $Ca(OH)_2$. Troilite FeS, brookite TiO_2, siderite $FeCO_3$, iron sulfate $Fe_2(SO_4)_3$, aluminium oxide Al_2O_3 and many magnesium compounds – clinoenstatite $MgSiO_3$, bredigite $Ca_{14}Mg_2(SiO_4)_8$, merwinite $Ca_3Mg(SiO_4)_2$, huntite $Mg_3Ca(CO_3)_4$, calcite magnesian $(Ca,Mg)CO_3$, sodium calcium magnesium silicate $Na_2Ca_4Mg_2Si_4O_{15}$ are probably also present.

The list above is shorter than that presented in the paper [13]. It can be explained by the following factors:

- Longer step and shorter time of gathering the impulses were used in X-ray measurements.
- In [13] the ash samples taken from every step of the ash separation system were analyzed separately. As the composition of ash in different units differs significantly, some compounds can be found only in a certain type of ash.
- The ash was heated twice during the experiment (500 and 105 ºC).

In the study [13], in turn, no tricalcium silicate, aluminium oxide or the last-mentioned magnesium compounds were found.

Some more lines are found in X-ray spectra that could refer to new formations in ash. As these lines are more intense in the case of hydrated ash, their identification is discussed below.

Changes in Ash at Open-Air Hydration

As the changes in the content of lime CaO, quartz SiO_2, anhydrite $CaSO_4$, calcite $CaCO_3$, larnite Ca_2SiO_4 and portlandite $Ca(OH)_2$ in ash during 3–84 days of open-air hydration (Fig. 4) confirmed the conclusions made already on the basis of chemical analysis that the main processes in hydrated ash occur quickly (in less than three days), the next series of experiments were conducted under short-term open-air hydration (2–48 h) conditions (Fig. 5).
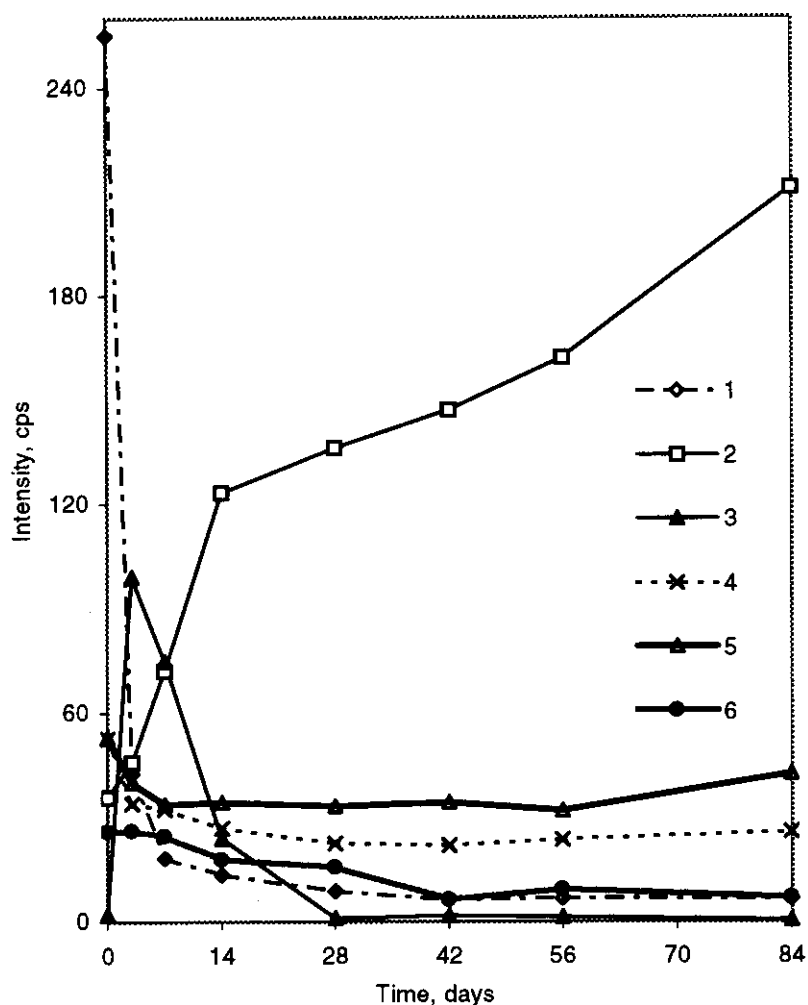
Fig. 4. Changes in the content of the main components during 3-84 days of open-air hydration: *1* – CaO; *2* – $CaCO_3$; *3* – $Ca(OH)_2$; *4* – $CaSO_4$; *5* – SiO_2; *6* – Ca_2SiO_4

In addition to the compounds found in initial ash, a lot of new formations form during hydration. These are, in general, complex compounds containing several elements present in ash. Most of them are hydrates/hydroxides. Calcium silicate hydroxide hydrate $Ca_{4.5}Si_6O_{15}(OH)_3 \cdot 2H_2O$ represents the silicates. Calcium aluminium oxide carbonate hydrate $Ca_6Al_2O_6(CO_3)_3 \cdot 32H_2O/3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 32H_2O$, calcium aluminium oxide sulfate $Ca_4Al_6O_{12}(SO_4)/3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ are probably also present. Calcium aluminium iron oxide hydroxide $Ca_{12}Al_{13.8}Fe_{0.14}O_{32}(OH)_2/11CaO \cdot 6.9Al_2O_3 \cdot 0.07Fe_2O_3 \cdot Ca(OH)_2$, brownmillerite $Ca_2(Al,Fe)_2O_5$ and calcium aluminium iron oxide $CaAl_8Fe_4O_{19}/CaO \cdot 4Al_2O_3 \cdot 2Fe_2O_3$ are probable Ca, Fe and Al compounds. Also aluminium hydroxide $Al(OH)_3$ as nordstrandite or vesuvianite ferrian

$Ca_{19}(Al,Mg,Fe)_{11}(Si,Al)_{18}O_{69}(OH)_2$ are found. The lines of ettringite, proposed by the researchers of ash-containing construction materials as a new formation, are too weak for reliable identification, although it probably exists in some samples.
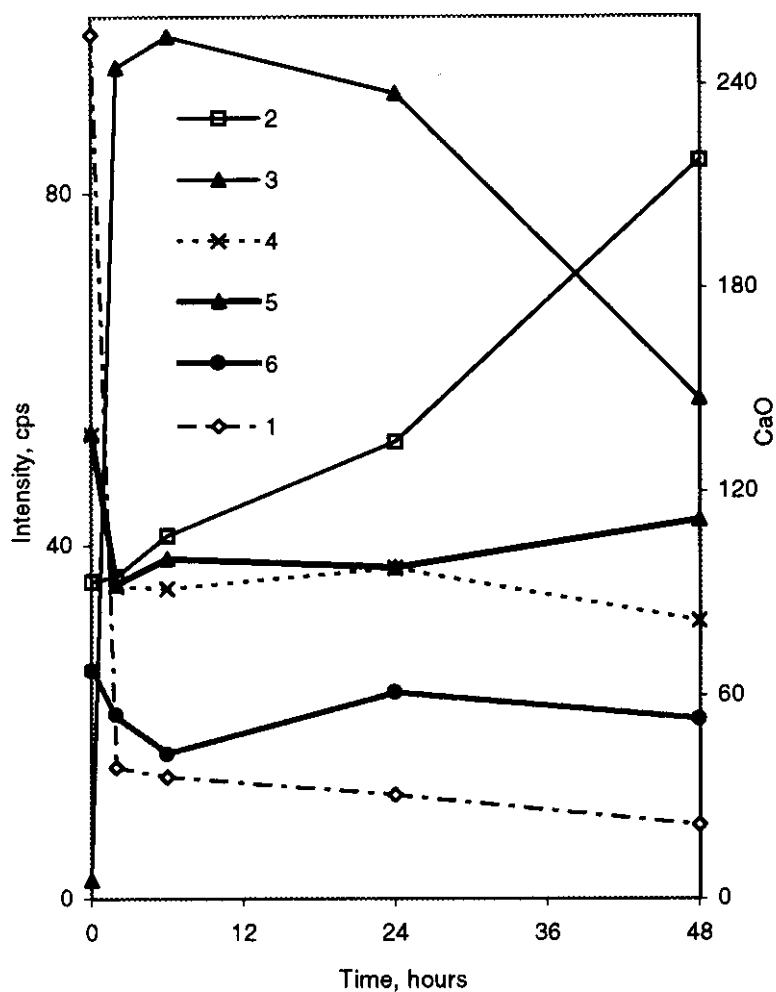

Fig. 5. Changes in the content of the main components during 2-48 hours of open-air hydration: *1* – $CaCO_3$; *2* – $Ca(OH)_2$; *3* – $CaSO_4$; *4* – SiO_2; *5* – Ca_2SiO_4; *6* – CaO

The changes occurring during ash hydration can be followed in Figs 4 and 5. During the first hours, the speed of the main processes is high, and especially rapid slaking of lime occurs. The same, rather surprising conclusion was drawn from determination of the slaking rate of ash by the method used to determine that of lime. As for ash, the maximum increase in temperature was achieved at approximately the same time as in the case of pure lime. The result is in accordance with the research [16], where the formation of hexagonal sheets of calcium hydroxide around the particles of

free lime was observed to take place in the samples containing a lot of water (1 : 10) in a few minutes. It is noticeable that a certain part of calcium oxide persists even during long-term hydration.

The amount of calcium hydroxide, the reaction product of calcium oxide and water, increases rapidly, and binding of CO_2 from air with formation of calcite occurs simultaneously. In four weeks all the $Ca(OH)_2$ has reacted, and rapid increase in the amount of calcite ceases. The further increase in calcite content can be explained by the reaction between calcium silicates and carbon dioxide from air. It is shown in Fig. 4 that the amount of larnite decreases during long-term hydration, but that of quartz increases. It can be thermodynamically explained by the following reactions, where the equilibrium is shifted towards the formation of $CaCO_3$ and SiO_2 at temperatures below 250 ºC:

$$Ca_2SiO_4 + 2CO_2 \rightarrow 2CaCO_3 + SiO_2$$

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$
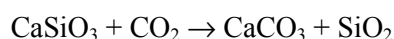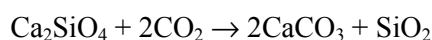
The concentration of quartz, larnite and anhydrite at the beginning of hydration decreases, that refers to the formation of the above-mentioned new formations like silicates, calcium and aluminium carbonates, sulfates and ferrites. On the contrary to the spread opinion that anhydrite binds water in moist conditions forming gypsum, the tendency towards the decrease in gypsum content was followed in the present study.

The changes in periclase MgO content were minor. This is in accordance with the statement that MgO preserves in free form [15]. However, some decrease in the amount of MgO can be detected during long-term hydration, because a part of periclase can combine with quartz forming clinoestatite and/or bredigite. No increase in the amount of dolomite was detected. The hydrosilicates present in construction materials were not found in the studied samples, probably because they are gel-like and give no strong spectrum lines.

Changes in Ash During Hermetic Hydration

Changes concerning the main compounds are presented in Fig. 6. It is evident that the processes in hermetic conditions differ greatly from those in open-air conditions, because no water was added later on and CO_2 from air was absent. The amount of water added initially is sufficient for the formation of calcium hydroxide, but the process occurs somewhat slower. The amount of calcium hydroxide reaches the maximum during approximately one week and does not change henceforth. Therefore, no more calcite can form. On the contrary, its content rather decreases, which could be explained by the increase in its mass due to the formation of hydroxide.

The decrease in the content of quartz and larnite is smaller than in the case of open-air hydration, whereat additional quartz does not form during

long-term hydration. Anhydrite disappears during three weeks. Possible that new formations forming at the expense of quartz, larnite, anhydrite, part of lime and aluminium- and ferrum-containing compounds cause the decrease in CaO_{free} content not involved in CO_2 binding (see Fig. 2). The content of these compounds is generally lower in the case of hermetic hydration as compared to open-air hydration and therefore their identification is more difficult. In difference, it can be noted that aluminum hydroxide occurs as gibbsite and vesuvianite ferrian is replaced by vesuvianite $Ca_{19}Al_{11}Mg_2Si_{18}O_{69}(OH)_9$.
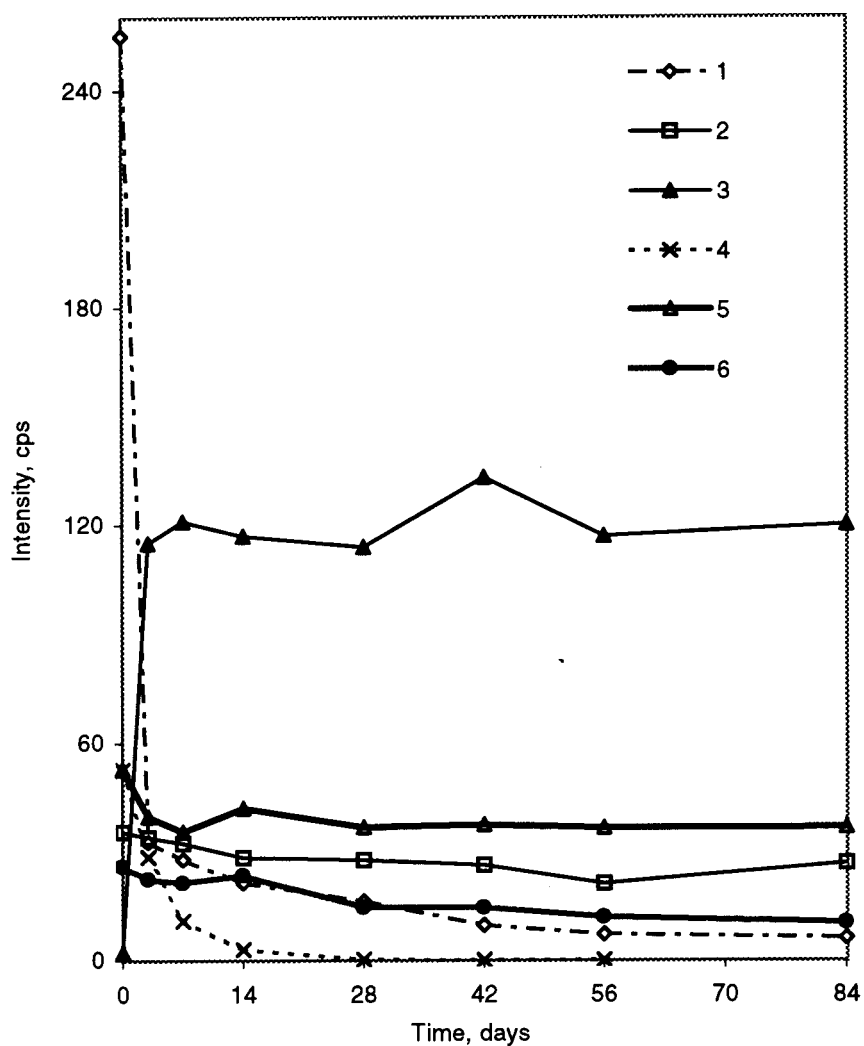
Fig. 6. Changes in the content of the main components during hermetic hydration: *1* – CaO; *2* – $CaCO_3$; *3* – $Ca(OH)_2$; *4* – $CaSO_4$; *5* – SiO_2; *6* – Ca_2SiO_4

In some samples aluminium hydroxide (gibbsite) was added to the initial ash. After long-term hermetic hydration calcium aluminium oxide carbonate hydrate $Ca_4Al_2O_6CO_3 \cdot 11H_2O/3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, calcium aluminium oxide carbonate hydroxide hydrate $Ca_4Al_2O_6(CO_3)_{0.5}(OH) \cdot 11.5H_2O/3CaO \cdot Al_2O_3 \cdot 0.5CaCO_3 \cdot 11.5H_2O$ and monticellite $CaMgSiO_4$ were found in the samples.

Comparison of Changes in Ash in Different Experiments

The experiments confirmed the fact that chemically active substances cause several changes in ash. These changes depend strongly on the process conditions and previous deposition of ash. Significant changes occur even during preservation of ash in ordinary laboratory conditions. Starting, for example, from the transformation of free lime (calcium oxide) to portlandite (calcium hydroxide) because of the impact of water vapor present in air. The transformation of portlandite to calcite because of the air CO_2 and more difficult processes involving the new formations will follow. Without taking into account the preserving conditions of ash, comparison of the results of different experiments is very difficult. The difference between the results of XRD analyses in the studies [12] and [13] can be explained by the disparity of the preserving conditions. In [12] the ash was kept years in ordinary laboratory conditions, but the ash used in [13] was preserved for a shorter period in desiccator on silica gel.

Ash could be preserved without changes in its mineral composition only in H_2O- and CO_2-free environment. The experiment [13] showed a few percent decrease in free lime content during 21-month preservation in desiccator on silica gel. Significant changes involving the decrease in free lime content by almost ten times, the increase in portlandite and calcite content (the latter by two times) took place in the case of 4.7-month preservation in desiccator at 85% moisture content. The poor increase in calcite content as compared to the present study can be explained by the limited access of CO_2.

Several processes like the almost full transformation of free lime into portlandite, the decrease in the content of quartz, the full disappearance of anhydrite and the formation of some new formations took place in the case of one-time addition of water and following hermetic preservation, but the normal course of these processes was hindered because of the absence of carbon dioxide. In [16] the disappearance of portlandite was observed petrografically during long-term preservation under hermetic condition and explained by the incidental access of CO_2 in the experiment.

Various reactions occur during open-air preservation with periodical addition of water to keep the moisture content at the same level. Some of them occur rapidly and can be closely followed by XRD analysis, because the changes in the content are remarkable (6-7 "main compounds"). The changes in the content of other compounds are small, and can often be followed only during long-term experiments (new formations, minor compounds).

The rates of hydration and carbonation depend besides the experimental conditions even in greater extent on the properties of ash. It was well demonstrated by additional open-air storage experiments with a fresh ash (collected in 2002) from Estonian PP (for the above-mentioned series the ash collected in 1998 was used). The samples were taken after 1, 2, 4, 24, 48, 72 an 168 h, additional moistening was carried out more often and the samples were dried at 105 ºC with duration less than in the case of previous series. Basically, the changes were similar to those shown in Figs 4 and 5, but there are some differences as well. The changes taking place during first hours were similarly rapid, but further changes were not as rapid as described above. The reaction of free lime occurred slower and, therefore, the following processes were inhibited as well. The new samples had somewhat lower content of free lime and higher content of glaze phase, their slaking took more time and also the rise of temperature was lower (2-3 and 5-6 ºC, respectively). Therefore, the results of XRD measurements and conclusions drawn from the other measurements coincide well and, besides, the use of XRD gives a more detailed information about the mineralization processes.

It is difficult to compare the results given in this paper with the data presented earlier by construction material researchers because they studied the mixture of ash enriched with different components and heated or autoclaved. The amount of ettringites formed in the samples of the present study was so small that their reliable identification was impossible. The fast reaction of free lime not detected in the case of construction materials was also dissimilar.

Cement minerals determined by previous researchers cannot be found in modern databases of chemical compounds, e.g. in the Powder Diffraction Database (PDF-2) of the International Center of Diffraction data (ICDD) used in the present study. The composition of complex compounds presented in several papers and given in databases differs in the number of molecules, especially, in that of crystallization water.

For example, the formula used for ettringites in almost every paper is $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O/3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$, but PDF gives $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O/3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

Some practical conclusions about the processes taking place during ash wet deposition can be drawn from these results. Although the contact between ash and water is good and the hydration of CaO occurs fast during hydrotransportation, the reaction is still not complete and ends only after long-term deposition in ash fields. The process occurs even slower in the case of solid pulp (the technology of Hungarian EGI) deposition, which caused the deformation and rise of a pilot field in Baltic PP giving no monolithic and even ash-rock that was expected [24]. As the carbonation of ash during deposition is only partial, because of its short contact with air (quickly arriving new amounts cover the hydrated ash), the ash deposited is chemically highly active due to the content of portlandite (Fig. 7).
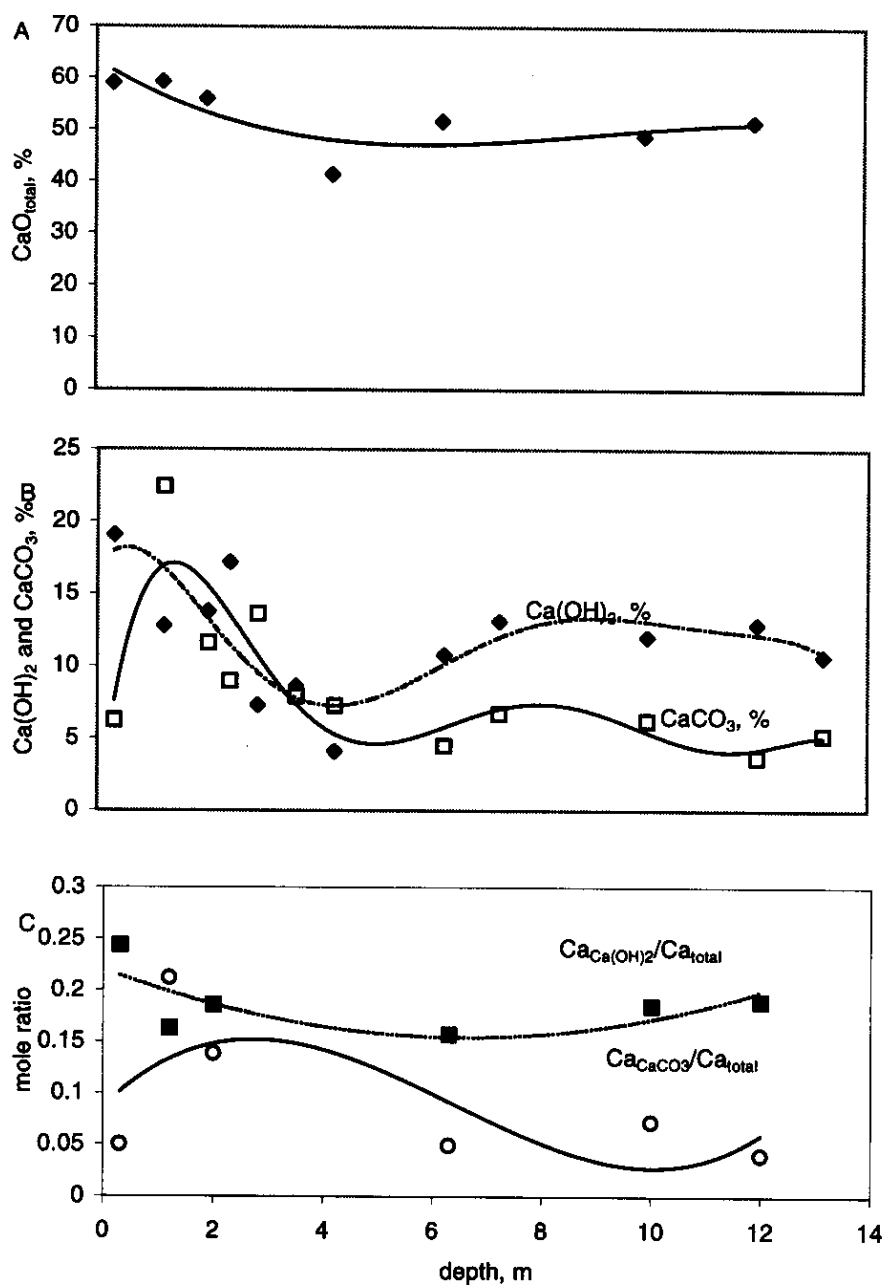
Fig. 7. Content and mole ratios of different Ca compounds *vs.* sampling depth (ashfield 2, Baltic PP, borehole No. 3, 25.10.2001): *a* – CaO_{total} content, *b* – $Ca(OH)_2$ and $CaCO_3$ content, *c* – mole ratios of Ca-compounds

Changes in the content of calcium compounds (Fig. 7*a*) as well as in multicomponent compounds stabilize in the depth of several meters (Fig. 7*b,c*). Several new compounds form in the covering layer in interactions

with Ca(OH)$_2$, however, portlandite remains mainly in its free form, making the whole mass alkaline and being the source of formation of highly alkaline wastewater. This can be avoided using deeper carbonation of ash, which could be accomplished only by using additional technological methods.

Conclusions

1. XRD method can be recommended as a good tool for description of rapid transformations occurring during the starting period of hydration and carbonation process of the oil shale ash. The adequate quantitative picture can be achieved in combination with chemical analysis methods.
2. The dynamics of the content of main wet ash components (lime, portlandite, calcite, quartz, anhydrite, larnite) during hydration and carbonation processes in open-air and hermetic conditions has been elucidated. The important role of process conditions as well as of initial ash properties has been pointed out.
3. The results of the present investigation can be used for explanation of the transformations taking place in the mineral part of ash during wet deposition as well as for their possible guidance and control.

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