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PROCESSES OF COAL FLY ASH WEATHERING
IN WASTE DEPOSITS

In natural environment, where a long-term interaction of potentially toxic elements with surface water or groundwater systems may be of concern, ash can also be affected by weathering and certain secondary minerals can be formed.

In weathering processes, the structure of fly-ash changes considerably which determines their physical and chemical properties. Simulating the weathering by the freeze–thaw test allows the changes occurring in ash particles structure to be produced. The experiment presented shows that ash solubility during a long period of time provides evidence that in the ash–water system, a variety of precipitation processes dominate the solubility of solid mass. The simulation of field conditions in laboratory research explains the behaviour of fly ash on deposits. It has been confirmed that weathering is the reason for a specific grain destruction. As a consequence, the grains are more reactive and more reaction products encircle the individual/single grain.

The freeze–thaw test can be used as a helpful tool for predicting the behaviour of combustion by-product deposited on landfill, or temporal deposits and those subjected to weathering under natural conditions.

The changes in ash particles observed on SEM images after 5 to 10 freeze–thaw cycles were comparable to those typical of ashes exposed to weathering during field test for a period not shorter than 12 months. The practical conclusion is that disposed fly ashes, taken from landfill site or store place for further application, are characterized by another peculiarity and therefore cannot uncritically be used for a partial replacement of cement in concrete or for other applications.

1. INTRODUCTION

Recently, a growing interest in the utilization of fly ashes has been observed. Not only are used ashes collected directly under electrostatic precipitators, but those deposited in open locations for temporary storage as well. The dwell time of ashes in locations is from a few weeks to several months (3 years at maximum).

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Weathering processes may be significantly influenced by frost which when combined with high humidity affects the structure of ashes.

The purpose of the research was to estimate changes in the stored fly ashes and their effect on the environment and also such changes occurring in the very structure of ashes that considerably influence their physical and chemical properties in further applications.

Combustion by-products contain mobile compounds that may give rise to a significant pollution when disposed into environment. Chemical composition of fly ash obtained from energetic plants is presented in the table. It is known that a variety of toxic elements can leach out and contaminate soils as well as surface water and groundwater resources. But the amount of polluted materials depends on the time of contact of the waste material with water. Thus terrestrial disposal of the fly ash has been regarded as a potential source of contamination (PRAHARAJ et al. [25], QUEROL et al. [26] and [27]).

Table

Chemical composition and chosen physical features of fly ash taken from power plant
according to ŁĄCZNY [18]

Parameter	Fly ashes (%)		
	Siliceous	Aluminate	Limeness
SiO_2	40–58	45–50	35–50
Al_2O_3	15–25	30–35	5–10
Fe_2O_3	5–15	5–12	4–7
CaO	2–10	2–4	10–30
MgO	1–5	1–3	2–4
Na_2O	0.5–1.5	0.5–1.5	0.5–0.7
K_2O	1.5–3.0	1.5–3.0	1.5–3.0
SO_3	0.5–4	0.5–1	5–10
As	0.001	0.001	0.001
Cr	0.01–0.08	0.01–0.05	0.01–0.15
Be	0.001–0.003	0.001–0.020	0.001
Zn	0.01–0.09	0.01–0.02	0.002–13
Pb	0.04–0.03	0.007–0.02	0.0005–0.008
Ni	0.005–0.030	0.005–0.025	0.005–0.04
V	0.01–0.06	0.007–0.03	0.003–0.02
Cu	0.003–0.04	0.002–0.007	0.003–0.015
Loss on ignition	2–10	0.5–2	0.5–2
Density (kg/m^3)	2500–4500	2000–4000	2000–4000
Surface area (cm^2/g)	2250–2450	2250–2450	2250–2450

The disposal of fly ash causes significant economic and environmental problems and much attention has been paid to the leaching behaviour and the possible contami-

nation, especially in the aquatic environment, when ash is in contact with water (CHOI et al. [2]).

The distribution of minerals within the coal is not uniform and also varies from coal to coal. The different modes of the occurrence of a given element in different coals modify their behaviour during combustion. Fly-ash particles are inhomogeneous, highly diverse, dispersed in a broad range of size and have different morphologies (MIRAVET et al.[20], VASSILIEV et al. [36]). The properties of the fly ash depend on the physical and chemical properties of the coal source, the coal-particle size, the burning process, and the type of ash collector. General transformation of mineral matter in coal during combustion is presented in figure 1 (KUTCHKO and KIM [16]).
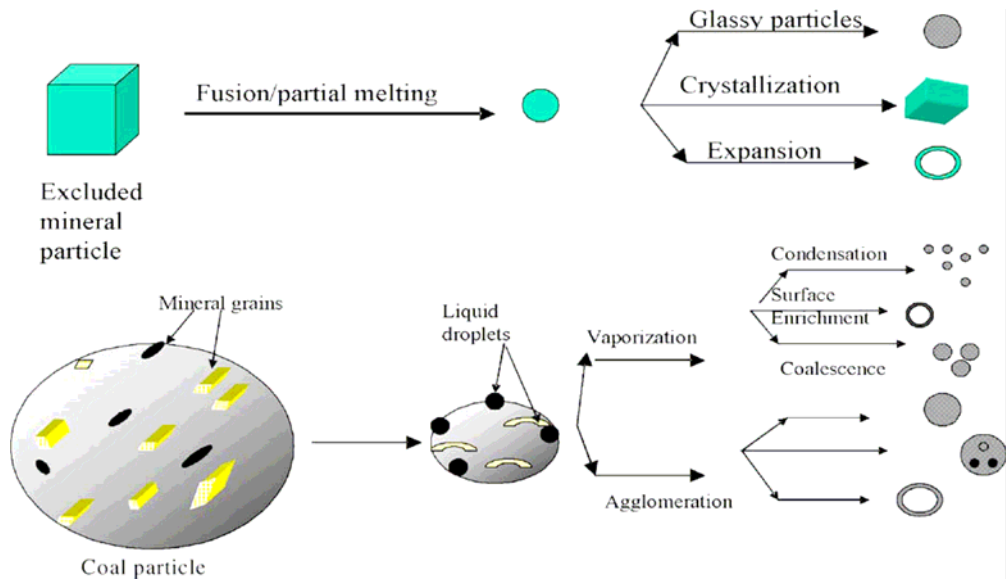

Fig. 1. Transformation of mineral matter in coal during combustion processes (KUTCHKO and KIM [16])

Fly ashes are complex inorganic-organic mixtures of polycomponent, heterogeneous and variable composition, containing closely associated and finely dispersed solid, liquid and gaseous components. According to VASILIEV and VASSILEVA [38] the phase and mineral composition of fly ashes can be described as follows:

• inorganic constituent comprises non-crystalline (amorphous) matter, namely different glassy particles and crystalline (mineral) matter such as crystals, grains, and aggregates of various minerals,

• organic constituent is composed of char materials (slightly changed, semi-coked and coked particles) and organic materials,

• fluid constituent comprises liquid (mixture), gas and gas-liquid inclusions associated with both inorganic and organic matter.

An empirical formula for fly ash based on the dominance of certain key elements has been proposed by IYER and SCOTT [12]:

$$Si_{1.0} \, Al_{0.45} \, Ca_{0.51} \, Na_{0.047} \, Fe_{0.039} \, Mg_{0.020} \, K_{0.013} \, Ti_{0.011}.$$

Two types of fly ash are identified: type F and type C. Type F is produced when anthracite, bituminous or sub-bituminous, low in lime (<7%), coal is burned. It contains more silica, alumina and iron oxide. Type C is a by-product of lignite coal burning and contains more lime (15–30%) (IYER and SCOTT [12]).

Trace elements are present in either organic or inorganic association. This association can change in different coals; moreover, in coal a trace element can occur in more than one form. Trace elements chemically bonded to organic matter may be present in association with organic groups or as complexes and chelates (XU et al. [42]). In mineral matter, trace elements can be found as discrete minerals, as replacement ions in other minerals or adsorbed on clay particles (OTER-REY et al. [22]).

The path of trace elements during coal combustion is of a serious concern for environmental protection.

Fly ashes as by-product of combustion include mainly glass, quartz, char, mullit, plagioclase, calcite and portlandite, and to a lesser extent illit + muscovite, melilite, hematite, anhydrite, lime, cristobalite, kaolinite and magnetite. Minor amounts of K-feldspar, dolomite, ankerite, Fe-spinel, gypsum, and Ca-K-Na phase also occur (VASSILIEV et al. [37]).

In fly-ash particles, fine-grained particles are known to have higher trace element concentration. According to SPEARS [31] in glass, V, Cr, Cu and Zn are found. Chromium and vanadium are thought to be concentrated in magnetite, although their major source in the ash is the glass. As, U, Pb, Tl, Mo, Se and probably, to a lesser extent, Ge and Ga are associated with the surface of the ash particles.

The mineral and glass phases that constitute fly-ash material are formed in a wide range of temperatures in a furnace environment. All these phases are unstable (IYER [11]). They dissolve and then precipitate as stable and less soluble secondary phases. The primary phases even though highly soluble in water dissolve very slowly as they are trapped in the glass and crystalline aluminosilicates. Secondary hydrous aluminosilicate products are shown to be only slightly soluble (HANSEN et al. [8]) and are formed on shells on the surfaces of primary phases. The dissolution of primary phases slows down as the mass transport of ions between water and solid phases becomes diffusion-controlled.

In the model, according to IYER [11], (figure 2), the leached ions traverse two spherical shells surrounding the particle, e.g. a double diffusion layer and bulk convective layer. It has been experimentally shown by exchange of ions that the ions, namely Ca^{2+} in the form of $Ca(OH)_2$, are retained in a double diffusion layer. The retention of ions coupled with the resistance of a double diffusion layer explains the delay in the achievement of steady state.
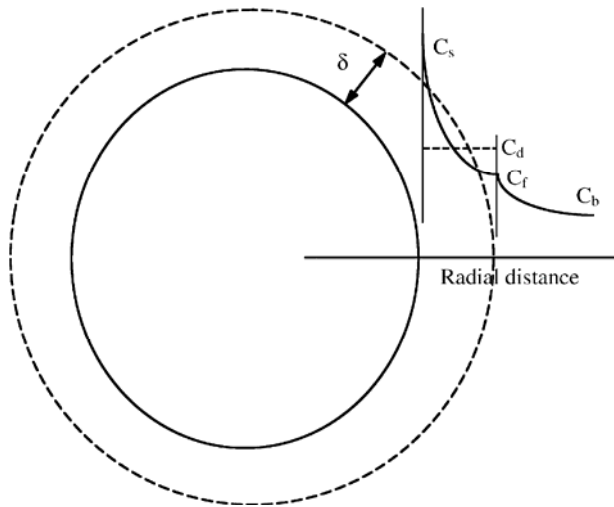
Fig. 2. Mass transfer across the surface of fly-ash particle (according to IYER [11]):
δ, double diffusion layer on the surface of fly-ash particle (nm); C_s, concentration of calcium hydroxide
(mg/dm^3) at particle surface; C_d, concentration of calcium hydroxide (mg/dm^3) in a double layer;
C_f, concentration of calcium hydroxide (mg/dm^3) at the double layer–boundary layer interface;
C_b, concentration of calcium hydroxide (mg/dm^3) in the bulk

Fly ash has a hydrophilic surface and highly developed surface area which are important physical parameters determining its reactivity (FERNANDEZ-JIMENEZ and PALOMO [6]). Particles of smaller diameters tend to be more reactive as they are more available for hydroxides. Another reason is that smaller particles cool faster upon exiting the combustor, which results in their more disordered and, therefore, reactive structure (IYER and SCOTT [12]).

2. MATERIALS AND METHODS

The fly ash was sampled from heat power plant in Kielce. The ashes taken from the hoppers of electrostatic precipitators were cured and underwent different expositions. Two kinds of ash samples were investigated: aged during 12 months and no aged.

External factors may be poorly reflected in leaching test when the combustion by-products are deposited on landfill. Freeze/thaw cycles were considered a tool allowing us to evaluate the impact of weathering on a total surface area and chemical activity of the ash investigated. During the test the solid/liquid ratio was kept on the same level of 1:2. Freezing and thawing cycles were repeated 20 times. One twenty-four hour cycle included:

- 14 hours of freezing at –15 °C,
- 8 hours of thawing at room temperature (20 ± 2 °C).

The structure of ash due to chemical activity can change with time. Thus, it was necessary to use a reference sample. The reference samples differed from other ones in one thing, namely in lack of exposition to freeze/thaw tests. The reference sample was cured under laboratory conditions at room temperature, but it was also exposed to CO_2 activity and air humidity.

Other ash sample was used as reference sample for ashes that underwent aging process named "aged" ashes and another one for "no aged" ashes. The reference samples had to be of the same age as the samples exposed to weathering. The reference sample was selected from a larger sample taken to examine the effect of exposition upon weathering agents.

One part of ash underwent long-term treatment under conditions simulating the deposition on landfill site in natural environment, including: contact with water, impact of CO_2 from the air, alternating temperature, freezing and thawing cycles.

The reference wet sample was cured under laboratory room conditions for the time as long as that of freeze/thaw exposition. Both samples were examined for leaching ability in order to estimate the influence of frost and thawing cycles.

The behaviours of the samples cured under different conditions were compared by chemical analyses of leachates, morphology, and structure.
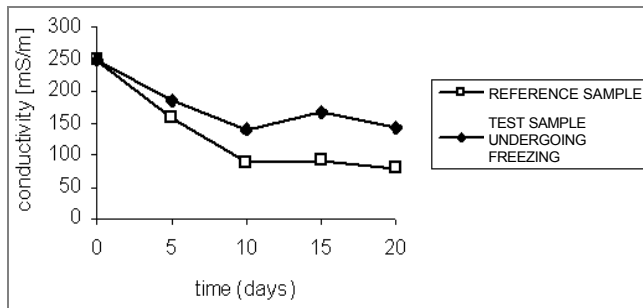

a)
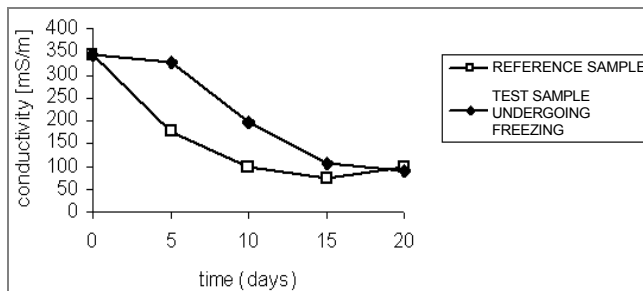
b)

Fig. 3. Influence of time on conductivity in effluent:
a) the samples aged 12 months, b) the samples not aged

Chemical analyses of leachates were conducted after 5, 10, 15 and 20 freeze/thaw cycles (figures 3 and 4). The leaching procedure used in this study was based on the works by ŁĄCZNY [17] and STEFANOWICZ et al. [33]. The leaching tests in our research involved extraction procedure with distilled water as a leaching medium. Dry ash was mixed with distilled water (solid:liquid = 1:100, by dry weight). In order to obtain the extract, a certain amount of fly ash was agitated in glass jars, each containing 100 cm^3 of distilled water, and the content of jars was shaken for 8 hours in a laboratory shaker. The temperature was controlled (20 ± 1 °C) during all extraction procedures.
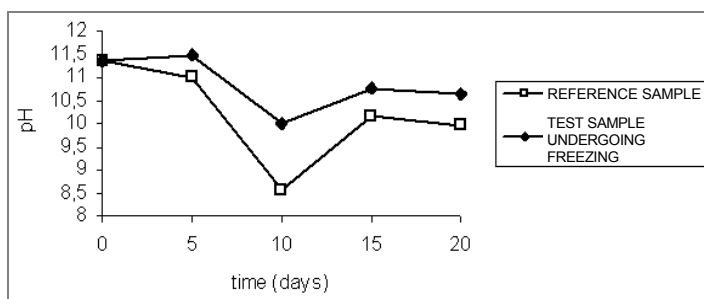
a)
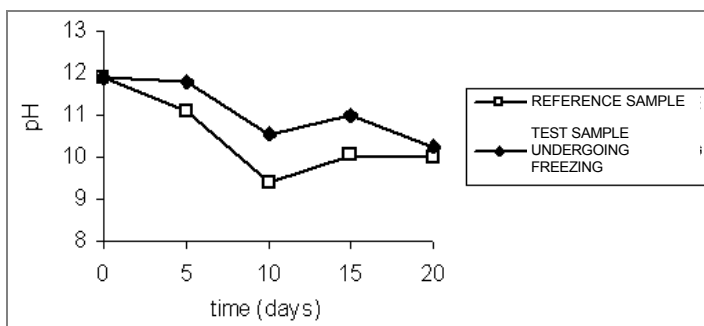
b)

Fig. 4. pH versus time in leachates from ash:
a) the samples aged 12 months, b) the samples not aged

After a fixed period of agitation had elapsed, the extracts were filtered through a filter paper. All extractions were carried out in triplicates. The volume of effluent was measured and a sample taken aside for further investigations.

In the resulting eluates, pH and conductivity were analysed. Conductivity was measured by means of conductometer according to Polish Standard PN-77/C-04542 with controller, type HJ 8819 N (HANNA instruments). pH was measured according

to Polish standard PN-91/C-04540/01 by potentiometer method using pH controller
(type OP-208/1).

3. RESULTS

Figures 3 and 4 illustrate the effect of time and weathering agents upon chemical
characteristics of ashes. Each point on the curve is the average of five determinations.
Figure 3a) and b) shows that the solubility of ash measured by conductivity test versus
time decreases for both reference and frozen samples, but the curve slope in the case
of ash undergoing freeze/thaw tests is distinct. This means that freeze/thaw test de-
creases the solubility of ash grains.

The analysis of pH changes shows that in the samples aged and not aged (figure
4a) and b)) alkalinity decreases, reaching its minimum after 10 cycles. It can also be
observed that in a frozen ash sample, pH decrease is smaller than in a comparable
reference sample.

It was confirmed that freeze/thaw tests accelerate the processes normally taking
place in ash–water system during weathering in landfill site. The most marked changes
in the parameters under examinations were observed after 10 cycles. A decrease in the
solubility of ashes and pH during the period of investigation supports the arguments
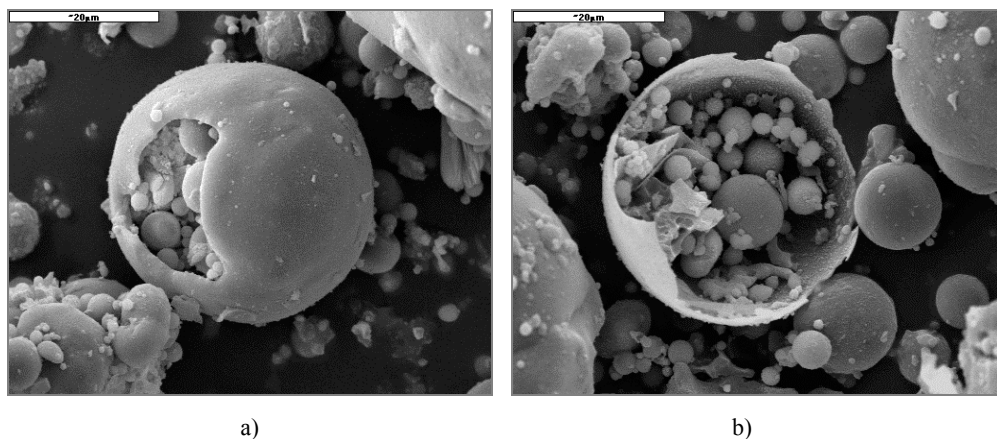that the cementitious processes occur, but they are enhanced by former grain destruc-
tion.

a)   b)

Fig. 5. SEM images of reference ash sample (a),
ash sample undergoing 20 cycles of freeze/thaw test (b). Magnification of ×2000

The results of SEM examination are illustrated in figures 5 and 6. They confirm
the impact of long-time test and freeze/thaw test on the condition of particles in ash,
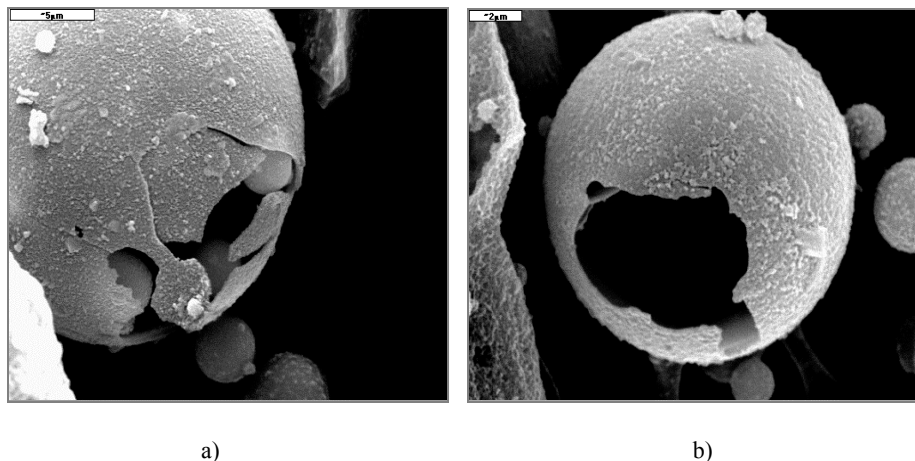which can be mirrored by the morphology of particles.

a)   b)

Fig. 6. SEM images of particular grain in ash sample after 20 cycles of freeze/thaw test.
Magnification of ×5000 (a) and ×7500 (b)

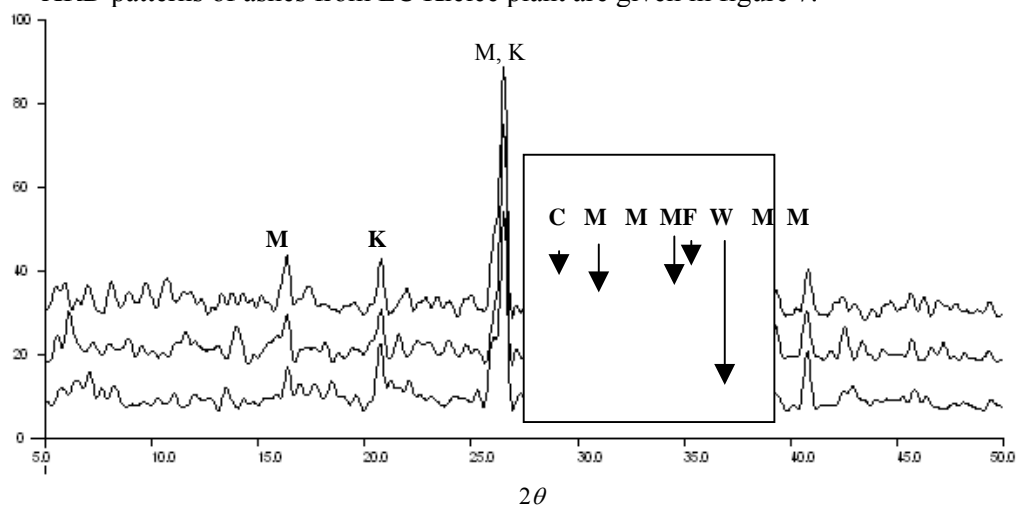XRD patterns of ashes from EC Kielce plant are given in figure 7.

2θ

Fig. 7. XRD patterns of ashes from Kielce plant:
a) sample taken from electrostatic hoper, b) reference sample (wet), c) sample that underwent
freeze/thaw cycles (wet). M – mullit, K – quartz, C – calcite, W – lime, MF – hematite

4. DISCUSSION

In the present experiment, the dynamics of ash solubility during a long period of time
provides evidence that in the ash–water system, a variety of precipitation processes

dominate the solubility of solid mass. Simulating the weathering by the freeze/thaw test allows the changes occurring in ash particles structure to be produced.

The leaching of particular ash components depends on reactions in the ash–water systems. Material solidification by compaction is often favoured because of the cementation properties of ashes being in contact with water and decreasing the initial conductivities and those observed during the time (figure 3). Calcium–silicate hydrates, aluminate hydrates and gypsum can occur as secondary minerals (STEENARRI et al. [32]). The solubility of such new phases and solidification process determine the leaching of the ash mass.

Secondary hydrated minerals such as ettringite, portlandite and calcite are formed during a contact with water. Ettringite is composed of calcium and aluminum sulphate ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). The presence of ettringite is due to the dissolution of Ca- and Al-containing minerals and a subsequent reaction that runs according to the following equation:

$$6Ca^{+2} + 2Al^{+3} + 3SO_4^{2-} + 38H_2O \leftrightarrow 12H^+ + Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O. \quad (1)$$

For ettringite formation an excess water is necessary. Chemical equilibrium calculations have shown that ettringite is not stable at pH below 10.5.

The portlandite $Ca(OH)_2$ formed by hydration of CaO subsequently reacts with CO_2 in air penetrating the wetted ash mass according to the reaction:

$$Ca(OH)_{2(cr)} \rightarrow Ca(OH)_{2(aq)} + CO_2 \rightarrow CaCO_{3(cr)} + H_2O. \quad (2)$$
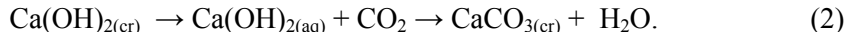
Both compounds, the portlandite and the carbon dioxide, are dissolved in the pore fluid of the wetted ash and the calcium carbonate crystallizes from the solution. The transformation of portlandite into calcite reduces high pH which can be observed in figure 4.

The attempts have been made to carry out the transformation by X-ray radiography but the changes observed were rather subtle (figure 7).

In order to establish pH of the leachate, two opposing processes have been proposed (IYER [11]):

• The dissolution and hydrolysis of oxide components such as CaO and MgO contribute to an increase in solution pH:

$$CaO + H_2O \Leftrightarrow Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-. \quad (3)$$
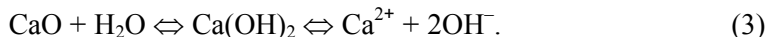
In contrast with pH increase caused by basic components, there occurs the dissolution of soluble acids components such as B_2O_3 and salts containing hydrolysable constituents such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$.

• There is a slow dissolution and outwashing of silica from fly-ash particles. This reaction occurs at both high and low pH, resulting in the formation of silicic acid:

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4. \quad (4)$$

The above reaction of silica with water is possible only in sinters like glass matter included in ash structure.

A change of grain morphology (figures 5 and 6) observed in the present experiment is conformable to that obtained during a field experiment (CHEERAROT and JATURAPITAKKUL [1]). The authors concluded that fly ashes disposed for 6–24 months have both different particle sizes and chemical composition. It was observed that some particles of disposed fly ashes were irregular and porous due to weathering. Fly ashes deposited over 6 or 24 months should not be used as a pozzolanic material since it results in low compressive strength of mortar. Thus the ashes taken from landfills differ in features from those taken immediately from precipitators.

5. CONCLUSIONS

Based on the results obtained, some differences between the fly ash taken immediately from precipitator and the fly ash undergoing weathering in deposits can be noticed.

It was observed that spherical particles of disposed fly ashes due to freeze/thaw stress became irregular and porous. Thus, it can be concluded that during this test fly-ash particles behave like disposed, weathered fly ashes and possess different features as the weathering changes their surface area in such a way that sorption and further reactions differ from the previous ones. Frost destruction of fly-ash particles results in their behaviour in they come into contact with water. Probably a "newly opened" structure possesses more active centres with higher ability to react with water and new water–ash reaction products can be formed. It has been confirmed that weathering in deposit site is the reason for individual grain destruction. As a consequence, the grains are more reactive and more products encircle an individual grain.

Freeze/thaw test can be used as a helpful tool for predicting the behaviour of combustion by-product deposited on landfill and subjected to weathering under natural conditions. The changes of ash particles observed on SEM images after 5–10 freeze/thaw cycles were comparable to those observed for ashes affected by weathering during field test for the period not shorter than 12 months.

The results of our experiment based on freeze/thaw tests seem to reflect a real behaviour in the field more adequately than a leaching test alone. The practical conclusion is that disposed fly ashes possess another peculiarity and cannot uncritically be used for a partial replacement of cement in concrete or for other application.

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