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The effect of wash cleaning and demagnetization process on the fly ash physico-chemical properties

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Summary

Problems related in this study concern the possibility of improving the physico-chemical properties of fly ash used as a base granular material in moulding mixtures. The investigations were carried out mainly to evaluate the process of the fly ash modification performed in order to stabilize its mineralogical and chemical composition. Changes in chemical composition, specific surface and helium density of fly ash after the process of its wash cleaning and demagnetization were examined. The analysis of the data has proved that the process of wash cleaning considerably reduces the content of sodium and potassium. Calcium and magnesium are washed out, too. The wash cleaning process of fly ash reduces also its true density. This fact can be due to the washing out of illite as well as some fractions of haematite (the grains weakly bonded to the glassy phase). The process of demagnetization allows removing about 25.7% of the magnetic phase calculated in terms of Fe_2O_3. The process of demagnetization is accompanied by a decrease in the content of aluminium, sodium, potassium and calcium, and a reduction in the size of the specific surface by over one half. The possible processes of transformation have also been discussed.

Key words: Fly ash, Wash clean, Demagnetization, Specific surface, Moulding sands

1. Introductiom

In traditional approach, moulding mixtures are based on sands of different mineralogical compositions, which determine their physical and chemical properties. The base materials used most frequently are silica sands of an acid reaction. In some specific cases, depending mostly on the type of the metal alloy cast, it is necessary to use sands of basic reaction (e.g. magnesite, chromite-magnesite) or sands of neutral reaction (e.g. sillimanite, mullite, corundum, olivine, zircon) [1]. The resources of natural raw materials are shrinking, while human interference in the natural environment is more and more drastic. The use of properly processed valuable waste as a base material for moulding mixtures can protect the natural resources, bring considerable savings in mining of the mineral raw materials and let the surrounding landscape preserve its genuine form and beauty. One of such waste materials is the fly ash of hard coal or brown coal. Given its physical and chemical properties, it is a full-value raw material used so far mainly by the industry of building materials and building constructions. The studies done recently [2,3] have indicated that it can be an alternative solution to the moulding sands used so far, acting as a substitute not only more friendly to the environment but also more profitable. An important factor deciding about the potential use of fly ash as a base granular material of moulding mixtures is the stability of its chemical and mineralogical composition and of the resulting physico-chemical properties. To know the effect of the fly ash modification, carried out in order to reduce the undesirable - in terms of the fly ash application as a base granular material of moulding mixtures - components, the processes of wash cleaning and magnetic separation were conducted.

2. Wash cleaning and demagnetization of fly ash

Tests were carried out on fly ash produced during combustion of hard coal (Figs.1-2) of the chemical composition given in Table 1. The sample of fly ash was washed clean in distilled, demineralized water, by stirring it intensely at a temperature of 20^0C. The duration of one stirring cycle was 10 was measured by means of an immersion pH-meter, model IP67. The changes in the values of pH are plotted in Figures 3 and 4.

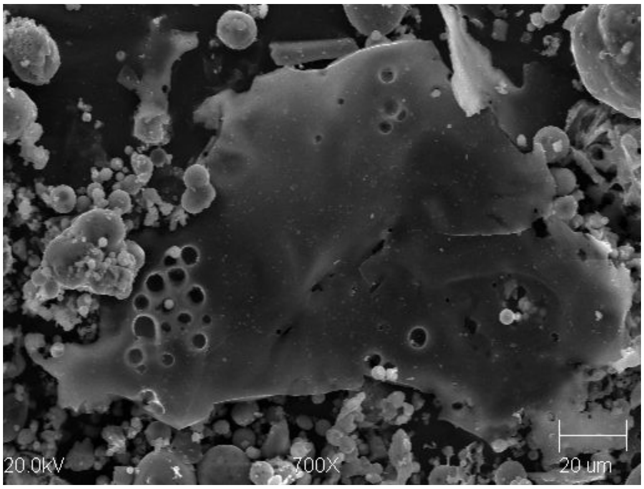

Fig. 1. Scanning photo of the fly ash grain (magnification 700x)

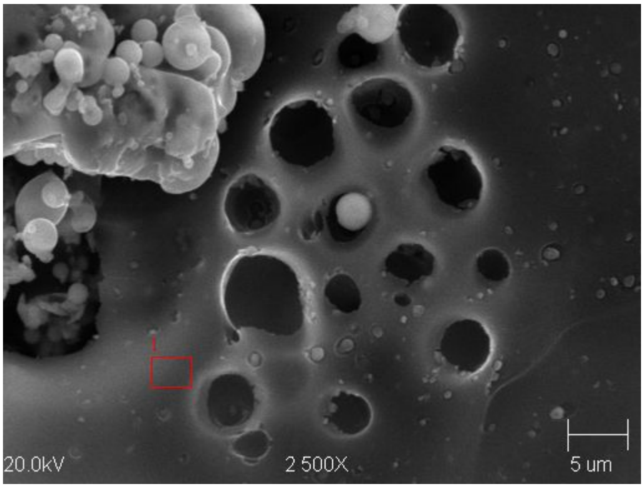

Fig. 2. Scanning photo of the fly ash grain (magnification 2500x)

Table 1.
Chemical composition of the investigated fly ash

SiO_2	81.66	ZnO	0.0103
Al_2O_3	6.690	CrO_3	0.0115
Fe_2O_3	4.374	CdO	3.214E-05
CaO	4.293	PbO	0.0081
MgO	1.577	As_2O_5	0.0010
Na_2O	0.2110	P_2O_5	0.2552
K_2O	0.4015	SO_3	0.2790

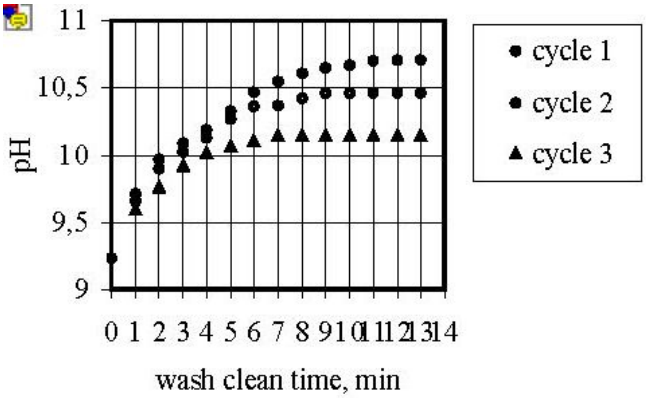

Fig.. 3. Changes of the water pH value during the first three cycles of wash cleaning of the fly-ash

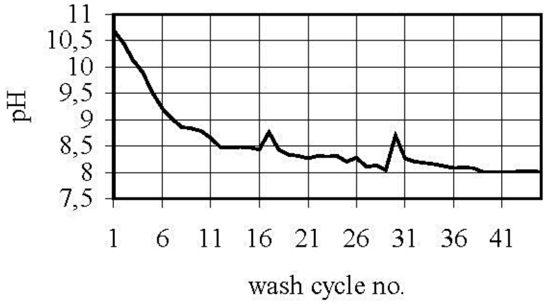

Fig. 4. Changes of the water pH value after 45 cycles of wash cleaning of the fly ash

To remove the magnetic phase from the fly ash, permanent magnets of barium ferrite were used. The chemical composition of the fly ash after the process of wash cleaning and demagnetization is given in Table 2. The phase constitution of the examined fly ash and of its derivatives was determined by X-ray technique on a PHILIPS APD X-Pert PW3020 X-ray diffractometer with CuKα radiation monochromatized by reflexive graphite monochromator. The following drawings (Figs.5 - 7) show the X-ray diffraction patterns of fly ash.

The investigations carried out examined the effect that the applied processes are expected to have on changes in the value of helium density and specific surface. Table 3 gives the values of helium density d_{He} determined on an AccuPyc 1330V.01 apparatus made by Micrometrics and the values of the specific surface, S_{BET}, determined from low-temperature isotherms of nitrogen adsorption plotted at a temperature of 77.3K using an ASAP 2010 V4.00 G apparatus made by Micrometrics and nitrogen as adsorbate within the range of its relative pressures, p/po, equal to 0,6 – 0,20. The measurement of the specific surface was done twice, and for discussion mean values obtained from these measurements were adopted.

Table 2.
Chemical composition of the fly ash after wash cleaning and demagnetization

Element	Fly ash after wash cleaning, %	Fly ash after demagnetization, %
SiO_2	78.5	79.2
Al_2O_3	5.862	6.764
Fe_2O_3	5.354	3.247
CaO	3.707	3.625
MgO	1.408	1.309
Na_2O	0.1678	0.2055
K_2O	0.2833	0.3724
ZnO	0.0311	0.0104
CrO_3	0.0099	0.0111
CdO	1.8E-05	1.54E-05
PbO	0.0008	0.00149
As_2O_5	<0.0010	<0.0010
P_2O_5	0.2297	0.2646
SO_3	0.2207	0.2265

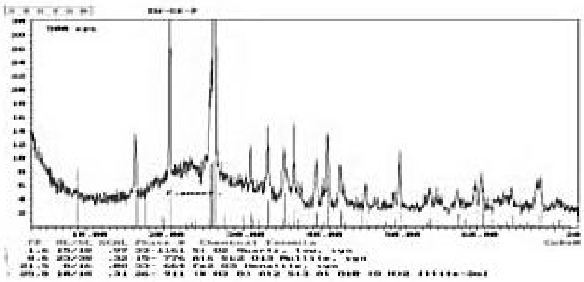

Fig. 5. X-ray picture of the investigated fly ash

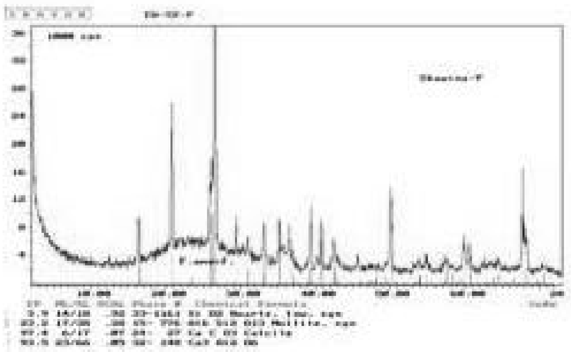

Fig. 6. X-ray picture of the fly ash after wash cleaning

Table 3.
The values of the helium density d_{He} and specific surface S_{BET} of the investigated fly ash

Fly ash	d_{He} [m^3/g]	S_{BET-I} [m^2/g]	S_{BET-II} [m^2/g]	$S_{BET-AV.}$ [m^2/g]
before processing	3.0275	4.759	3.396	4.077
after wash cleaning	2.2527	2.130	2.396	2.263
after demagnetization	2.2438	2.964	3.260	3.112

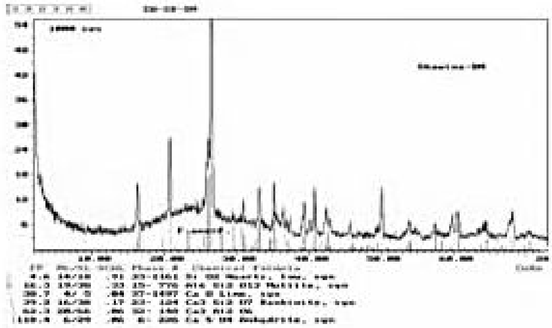

Fig. 7. X-ray picture of the fly ash after demagnetization

3. Conclusions from the investigations

3.1. The effect of wash cleaning process

The analysis of the data indicates that this process has caused a significant decrease in the content of sodium and potassium (by 20.4% and 29.4%, respectively). Calcium and magnesium were also washed out (the content of these elements decreased by 13.6% and 10.7%, respectively). It can be supposed that they are washed out mainly from the glassy phase. The content of sulphur and phosphorus in the examined fly ash was at a level of 0,2552 and 0,2790 %, respectively, and as such it was too low to make calcium assume the form of a low-soluble anhydride and/or calcium carbonate or phosphate. This is also confirmed by a very low kinetics of the pH value drop.

The data in Table 2 also indicate the decreasing content of aluminium and silicon, which confirms the hypothesis of a low dissolution rate of the glaze and/or illite. The content of iron increases (iron is as a rule present in fly ash in the glaze, and partly as hematite or magnetite). Zinc content raises, too. The decreasing content of Cr, Pb and Cd is caused by changes in the solubility of these ions due to the changed pH of the solution. In their case, the drop in pH value increases the washing out power.

The obtained results confirm the output of the examinations of phase constitution. The examined phase may be present in fly ash but in an amount either undetectable and/or in the form not sufficiently well crystallised. As observed in Figures 5 and 6, the phase constitution of the base fly ash consists, besides an amorphous phase, mainly of quartz and mullite (recrystallised glaze), which form the basic components, and of hematite and the derivatives of illite and aluminosilicate.

After wash cleaning, the disappearance of magnetite and illite is accompanied by the appearance of $CaCO_3$. This possibly indicates the presence in the base fly ash of free calcium (CaO), either not crystallised well enough, or in amounts too small to be detected in the examined sample. Its presence may contribute to the drop of pH value. The lack of hematite in the phase constitution of the sample after wash cleaning accompanied by a simultaneous increase of the iron content may be due only to the heterogeneity of the examined materials. The process of wash cleaning of the base fly ash results in decrease of the true density of the examined material. This fact can be attributed to washing out of illite and partly also of hematite (the grains whose bonds with the glassy phase are too weak). This process also makes the specific surface decrease in size by over one half (Table 3 : S_{BET-I}). The process of the fly ash wash cleaning is usually accompanied by an increase of the surface. The growth of CaO crystals may reduce the value of the specific surface. If during wash cleaning, illite is washed out, too, this can be responsible for a drop in the value of this parameter since materials in this group are characterised by a large specific surface.

3.2. The effect of demagnetization process

The process of demagnetization enabled removing about 25.7% of iron calculated in terms of Fe_2O_3.(Table 2) Its removal was accompanied by a decrease in the content of aluminium, sodium, potassium and calcium, thus indicating that iron was present in the glaze and as such became separated. In the phase constitution (Fig.7) after the removal of magnetic phase, like in the case of sample washed clean, no presence of hematite has been identified. On the other hand, weak reflexes from CaO and $CaSO_4$ (anhydride) have appeared. The process of demagnetization is accompanied by further decrease of the true density as well as a drop in the value of the specific surface, though it is smaller than in the case of the process of wash cleaning of the base fly ash.

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