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VARIABILITY QUALITATIVE PHASE COMPOSITION OF THE DIFFERENT GRAIN CLASSES OF THE CALCAREOUS FLY ASHES

ZMIENNOŚĆ JAKOŚCIOWEGO SKŁADU FAZOWEGO POPIOŁÓW LOTNYCH WAPIENNYCH W ZALEŻNOŚCI OD WIELKOŚCI ICH UZIARNIENIA

The results of studies of the phases composition of the different grain classes of calcareous fly ash were presented in this article. It was necessary to use three analytical methods: thermal, X-ray and microscopic to identify properly additional mineral phases in different grain classes of fly ash. These mineral phases were not determined during analysis of the sample which was not devided into grain classes. The minerals: quartz, anhydrite, calcite, bassanite, hannebahite hematite, magnetite, gehlenite, anorthite and CaO were identified. The thickest grain class of the tested ash characterized by a higher content of unburned fragments of coal. The presence of coal grains has negative influence at any further applications of the ash.

Keywords: calcareous fly ash, phase composition, grain composition, unburned coal, thermal analysis

Powstawanie popiołów lotnych jest nieuniknioną konsekwencją produkcji energii elektrycznej. W przeszłości jedyną formą ich utylizacji było deponowanie na składowiskach. Od szeregu lat podejmuje się próby wielokierunkowego zagospodarowania tych ubocznych produktów spalania węgla, dostosowanego do ich właściwości. Na szczególną uwagę zasługują popioły lotne wapienne powstałe w wyniku spalania węgla brunatnego. Pomimo niepodważalnych zalet tego surowca, a także bogatej literatury poświęconej jego właściwościom fizykochemicznym, problem wykorzystania tych popiołów wciąż zostaje otwarty. Przydatność popiołów lotnych wapiennych do celów utylizacyjnych zależy m.in. od ich składu fazowego.

W ramach pracy przedstawiono rezultaty badań jakościowego składu fazowego różnych klas ziarnowych popiołu wapiennego. Jednoczesne wykorzystanie badań termicznych, rentgenograficznych i mikroskopowych do identyfikacji różnych klas ziarnowych popiołu pozwoliło na ujawnienie dodatkowych minerałów obecnych w próbce, nie ujawnionych podczas analizy próbki surowej. Przeprowadzone badania wykazały, że każda z metod rozpatrywana osobno daje pewien obraz jakościowego składu fazowego badanej próbki popiołu, jednak nie daje jego pełnej charakterystyki. Analiza otrzymanych wyników badań pozwoliła na stwierdzenie obecności w popiele następujących minerałów: kwarcu SiO_2, anhydrytu $CaSO_4$, kalcytu $CaCO_3$, bassanitu $CaSO_4 \cdot \frac{1}{2} H_2O$, hannebahitu $CaSO_3 \cdot \frac{1}{2} H_2O$, hematytu $\alpha\text{-}Fe_2O_3$, magnetytu Fe_3O_4, gehlenitu $Ca_2Al\,[(Si, Al)_2O_7]$, anortytu $Ca\,[Al_2\,Si_2O_8]$ i tlenku wapnia CaO.

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Umożliwiło to pełniejszą charakterystykę jakościowego składu fazowego badanego popiołu, a tym samym pozwoli na znalezienie bardziej ekonomicznego sposobu jego utylizacji. Klasa najgrubsza badanego popiołu charakteryzowała się podwyższoną zawartością okruchów niespalonego węgla. Ich udział jest niekorzystny przy jakichkolwiek dalszych zastosowaniach tego popiołu.

Słowa kluczowe: popiół lotny wapienny, skład fazowy, skład granulometryczny, niespalony węgiel, badania termiczne

1. Introduction

For many years a diverse range of utilisation applications of fly ash – defined in the literature as coal combustion residues remaining in suspension in furnace gases – have been exploited in Poland and beyond. Fly ash has been used to a large extent in mining technology (Chudek et al., 2001; Klimas, 2013; Mazurkiewicz, 2007), in order to, inter alia, fill caving goafs, liquidate and fill unnecessary narrow workings or as a self-hardening backfill material. One of the applications of fly ash includes the construction materials sector, where fly ash is utilized in the production of Portland cement, cellular concrete, construction ceramics or as a component in cementitious grouts used in drilling (Stryczek et al., 2009). Increasingly, research has focused on refinement of ash that is difficult to reuse by means of, for example, grinding, separating or mixing with other ashes, which results in obtaining a high-value product (Garbacik et al., 2011; Rajczyk et al., 2011). The problem of fly ash utilization is still open, despite undeniable benefits of this material as well as abundant literature on its physical and chemical characteristics. This is particularly true of calcareous fly ash produced during combustion of brown coal. Despite having both pozzolanic and hydraulic properties, this type of fly ash has been utilized only to a small extent. The majority of calcareous fly ash, i.e. about 4 million tonnes per year, is still stored in dumps, which can be explained by variations in the quality of this raw material associated with a variable chemical, phase and grain composition, as well as little experience in its disposal. However, based on the findings of the calcareous fly ash properties monitoring, which was conducted for the past several years in Belchatow power plant, the variability in the chemical composition of fly ash was found to be gradually decreasing (Giergiczny & Garbacik, 2012). Results of the research allow to anticipate the benefits of calcareous fly ash as an additive to cement. In order to use fly ash effectively, a detailed investigation of its properties is required, including, inter alia, its phase composition, which is an important criterion used to decide on the possible applications of this waste product. This article attempts to trace the variations of the qualitative phase composition of calcareous fly ash in relation to the particle size distribution using several research methods.

2. Results

2.1. Granulometric composition

The study was conducted on calcareous fly ash produced from combustion of brown coal. The granulometric study shows that a significant fraction (43.12%) of grains was smaller than 0.045 mm, but also a numerous fraction (23.91%) of coarse grains was larger than 0.125 mm (Table 1). Such fly ash does not conform to the Polish standard PN EN 14227–4 for calcareous fly ash, because only 66% of particles passes through the 90 μm sieve.

The granulometric composition of the fly ash sample with weight loss at 1000°C

Symbol of the sample	Grain class [mm]	Yield [%]	Total yield [%]	Weight loss [%]
1	>0.315	2.77	2.77	41.7
2	0.315-0.25	2.56	5.34	8
3	0.25-0.125	18.57	23.91	4.5
4	0.125-0.09	10.67	34.58	3.3
5	0.09-0.071	6.83	41.41	2.6
6	0.071-0.063	5.44	46.85	2.6
7	0.063-0.045	10.03	56.88	2.5
8	>0.045	43.12	100	2
W	Feed	—	—	3.7

2.2. Chemical composition

In conformity to BN–79/6722–09 standard, the content of basic components confirmed the lime character of ash ($SiO_2 > 30\%$, $Al_2O_3 < 30\%$, $CaO > 10\%$). According to the American ASTM C 618 Standard Specification, this is Class F fly ash, as the content of $SiO_2 + Al_2O_3 + Fe_2O_3$ exceeds 70% (Table 2). The most substantial components of fly ash include SiO_2 and Al_2O_3, which occur mainly in the glass phase. These components cause high reactivity of fly ash in the alkaline environment; hence, the higher the content, the better the pozzolanic properties of the waste. A high 18% content of CaO indicates that fly ash already has binding properties, because calcium oxide that is present in fly ash can react with silica and aluminium oxide (Roszczynialski et al., 2002). The tested fly ash sample contains a relatively low, about 2%, iron content, which would be beneficial in further applications of this fly ash in the cement industry. As to other components, their content rarely exceeds 1%. The quality of residues to be re-used is determined by low alkali content. In fly ash applications with a reactive aggregate, the content of Na_2O is a particularly important variable. Loss on ignition measured for the fly ash sample accounted for about 4%. Most standards pertaining to fly ash aiming at reducing the unburned coal residues in

The chemical composition of the calcareous fly ash sample

Chemical element	Calcareous fly ash W [%]
SiO_2	52.53
Al_2O_3	18.18
Fe_2O_3	3.40
CaO	18.07
MgO	1.43
SO_3	1.93
Na_2O	0.11
K_2O	0.08
Moisture	0.26
Loss on ignition	3.81
Total	99.80

fly ash, define requirements as regards loss on ignition. Note, however, that the change of weight is not only related to the unburned carbon content in the sample, but may also be associated with, for example, loss of moisture, dehydration of $Ca(OH)_2$, or decomposition of carbonates.

2.3. Phase composition

2.3.1. Phase studies using a derivatograph

The phase composition of fly ash is a function of the mineral composition of coal from which it was produced. The differences result mainly from thermal changes occurring during combustion, such as dehydroxylation of clay minerals, decarbonatization of carbonates, dissolution of iron sulphides. The emergence of new phases is dependent on the temperature and time of combustion as well as the atmosphere in the boiler. The phase composition of fly ash produced from brown coal is related to the chemical composition and deviates significantly from the phase composition of silica ash produced from hard (bituminous) coal (Galos, 2009; Strzałkowska, 2011).

The qualitative phase composition of each fraction of fly ash particles was determined using the MOM Budapest derivatograph and a PW-1050 Philips diffractometer with a copper lamp. A thermal analysis was carried out in corundum crucibles by means of heating the sample at the rate of 10°C/min, at temperatures ranging from 20 to 1000ºC in the atmosphere. The derivato-grams obtained for fly ash and its particular grain classes are shown in Figures 1-3, whereas the selected diffraction patterns are given in Figures 4-8. In addition to the X-ray diffraction and derivatography, microscopic analyses were performed using a ZEISS polarizing microscope for transmitted and reflected light microscopy (Figures 9-14). Thermal analyses of the output sample W and grain classes below 0.315 mm were carried out in identical technical conditions (sensitivity of galvanometers TG – 100 mg, DTG – 1/5 mg, DTA – 1/10 mg, test portion of 600
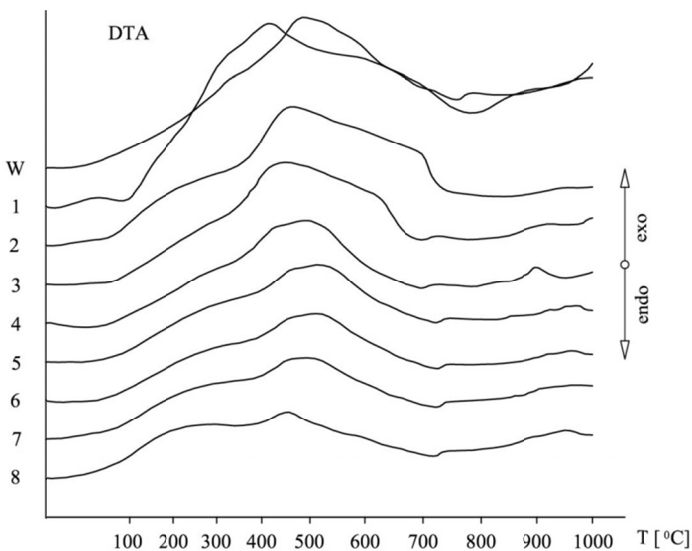

Fig. 1. DTA curves for the tested fly ash grain classes

mg, except for sample 2 which represented the grain class of 0.315-0.25 mm, and the test portion equalled 500 mg). Curves for the class > 0.315 mm (sample 1) were obtained at a smaller test portion 300 mg and with lower sensitivity of galvanometers TG 200 mg, DTG – 1/10 mg, DTA – 1/10 mg.

The general shape of the differential thermal curves for fly ash samples and particular grain classes of this ash is similar, and demonstrates both exothermic and endothermic reactions.

The analysis of the curves allows concluding that loss of moisture expressed by the endothermic effect on the DTA curve at about 100°C was explicitly noticeable only for the coarsest grain class >0.315 mm (Curve 1, Fig. 1). The deviation is negligible on other curves, which indicates that the samples had low moisture content. All DTA curves show an exothermic displacement between 180 and 500°C, which should be associated with organic matter combustion and oxidation of iron (II) content of the sample (Fig. 1). The aforementioned processes run relatively slow in a wide range of temperatures. With a higher percentage of the organic matter content, the aforementioned exothermic effect can significantly obscure other thermal effects or move endothermic reactions towards higher temperatures.

As expected, the larger the particle diameter, the larger the displacement, while the TG curves show sample weight loss, which indicates combustion of organic matter.
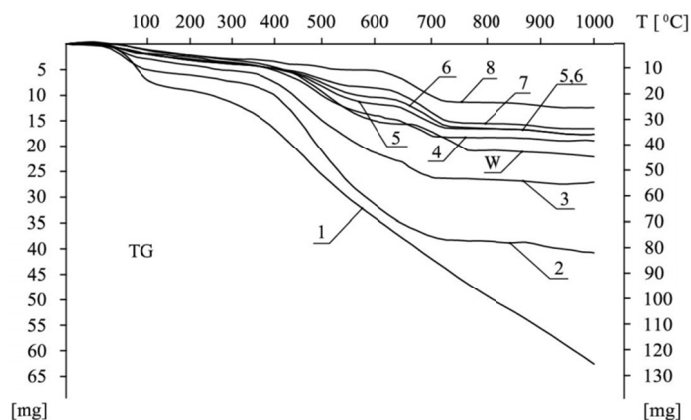

Fig. 2. Thermogravimetric (TG) curves of the tested fly ash grain classes
(on the right side – the scale for curve 1; on the left side – the scale for curves 2-8, W)

For the class >0.315 mm (Curve 1) the loss at temperatures ranging from 200 to 620°C accounted for up to 17% (Fig. 2). This indicates that unburned coal in the tested ash samples concentrated mainly in the coarsest grain classes. The carbon content is the main factor determining the usefulness of fly ash, especially in construction applications. The carbon content in fly ash is not desirable; firstly, because it indicates a lack of suitable optimization of the coal combustion process, and, secondly, it has negative effects on the quality of construction materials produced from such fly ash. A slight endothermic bend at about 350-370°C (Fig. 1) can be noted against the background of the exothermic effect caused by the combustion of organic substances. This can be associated with dehydration of hannebachite. This phase could not been clearly identified due to the negligible content of this phase and the masking exothermic effect. In addition, a small

endothermic displacement at 760°C combined with weight loss suggest that the sample contains little calcium carbonate content undergoing thermal decomposition. This effect is marked on the curve representing the output sample W and on all the curves representing the classes below 0.25 mm. This indicates that the calcium carbonate (calcite) content in fly ash is characterized by a fine particle size distribution. The calcite content is also characteristic of this mineral asymmetric effect at approx. 700°C on the DTG curve, Figure 3 (W, 3-8 curves). Calcite content may suggest that some part of the material did not pass through the kernel of the combustion chamber because of some turmoil in the boiler, and thus failed to reach the temperature required for its decomposition.
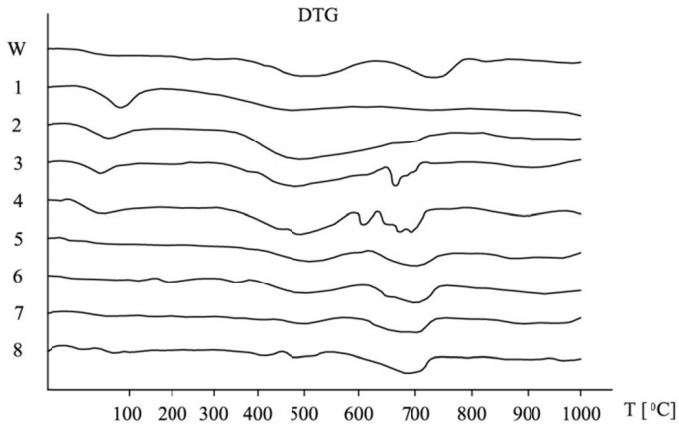

Fig. 3. Differential thermogravimetric (DTG) curves of the tested fly ash grain classes

For DTA curve 4 (Fig. 1), which represents thermal changes of fly ash fractions of 0.125-0.09 mm particle size distribution, at the temperature of 910°C, a sharp exothermic peak was marked very clearly, which can be attributed to a crystalline change of one of the components of fly ash. The TG curve (Fig. 2) can be divided into three stages of weight loss varying in size and intensity. The DTG curves (Fig. 3) show three minima indicating the temperatures at which the thermal decomposition rate was at the maximum. The first minimum observed at around 100°C is associated with evaporation of moisture, the largest second one, observed at about 500°C, was generated in combustion of organic matter, and the third minimum, observed at about 700°C, is associated with decarbonatization of carbonates. DTA curve 4, representing the grain class of 0.125-0.09 mm (Fig. 3) may indicate the simultaneous dehydration occurring in the sample in small amounts of silicate phases. The TG curves obtained for all the samples show that thermal decomposition of fly ash was completed at 700-720°C. Above this range of temperatures, no further decomposition of the tested samples, expressed as weight loss, was observed. An exception to this rule constitutes sample 1, which represents the grain class >0.315 mm (Fig. 2); here, even at 1000°C the mass of the sample could not be determined, which might have been caused by a continuous gas evolution from the sample. Based on the TG curve, the total loss of mass ranged from 41.7% for the coarsest grain class >0.315 mm, up to 2% for the finest grain class <0.045 mm (Fig. 2).

2.3.2. Phase studies using X-ray diffraction

Despite the similarity of diffraction patterns, XRD analysis showed some differences in the phase composition of each grain class in terms of quantity and quality. The test results indicate that the tested fly ash comprised both a crystalline phase and a small amount of the glassy phase. A glassy state is a state in which a substance has no long-range order. Such a chaotic domain orientation results in a slightly raised background of angles $2Q = 15\text{-}35°$ on the diffraction pattern. All diffraction patterns have reflections that are clearly indicative of the quartz content (Figs 4-8).

The quartz content has also been confirmed by microscopic examination. Quartz occurred most often as inclusions in cryptocrystalline aggregates or created dagger-like forms. In the coarsest grain class >0.315 mm, quartz occurred along with bassanite (Fig. 5). The presence of diffraction lines $d = 5.97$ Å; 3.003 Å; 2.80 Å; 3.47 Å (Fig. 5) is characteristic of this phase. A very clearly raised background on the diffraction angle in the range of $Q2 = 20\text{-}30°$ in the sample confirms the presence of a significant amount of amorphous carbon (Fig. 5). The most diversified in terms of the mineral content is the calcareous fly ash fraction <0.045 mm. Quartz occurs along with anhydrite and hematite, as well as compounds resulting from the reaction between the reactive oxides: gehlenite or anorthite. A small fraction of the latter is the reason that in most cases the corresponding reflections are barely visible, and thus difficult to interpret (Fig. 8). The fraction of anhydrite is, nonetheless, greater than it is in other grain classes, which is evidenced by significantly stronger reflections on diffraction patterns. The calcium oxide CaO content in fly ash, which is associated with this phase, may also occur in the glassy phase or in a free form.
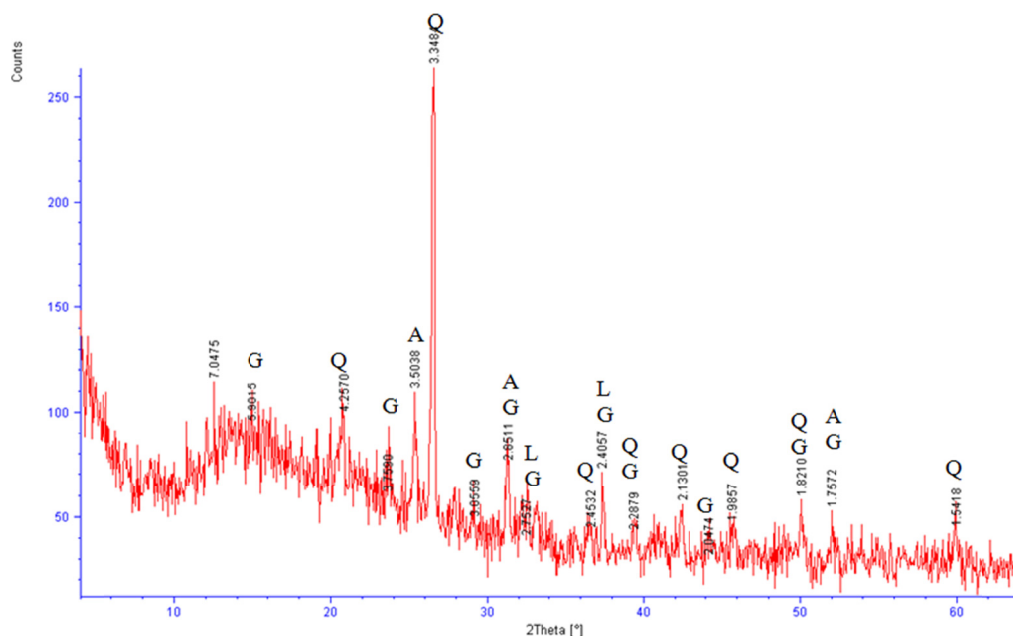

Fig. 4. The diffraction pattern of the calcareous fly ash sample W
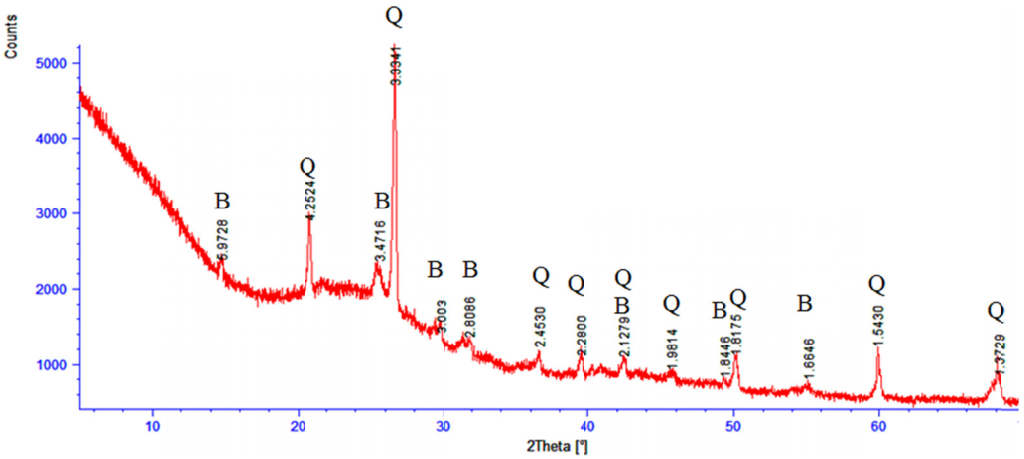(G – gehlenite, Q – quartz, A – anhydrite, L – CaO)

Fig. 5. The diffraction pattern of the grain class > 0.315 mm (B – bassanite, Q – quartz)
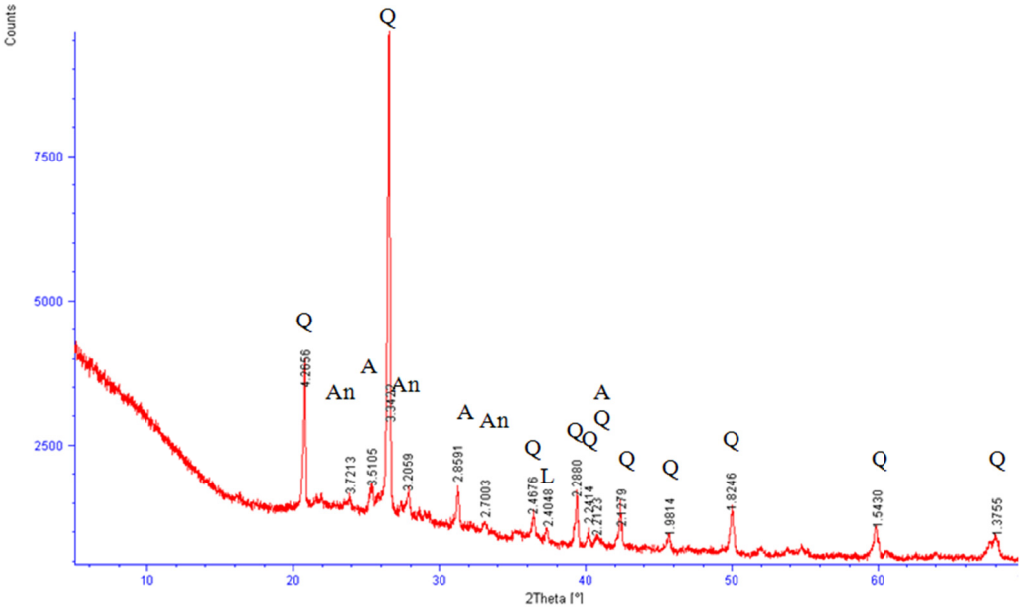

Fig. 6. The diffraction pattern of the grain class 0.125 – 0.09 mm
(Q – quartz, An – anorthite, A – anhydrite, L – CaO)

Due to the high fraction of calcium compounds, the finest grain class should therefore have the best hydraulic properties. The X-ray diffraction method is not able to clearly identify the calcite content, despite the fact that calcite was found in the course of thermal examinations. This indicates a low degree of crystallization, as well as a low content of this mineral in the sample. Despite the fact that magnetite was found during microscopic analyses, no peaks characteristic of this
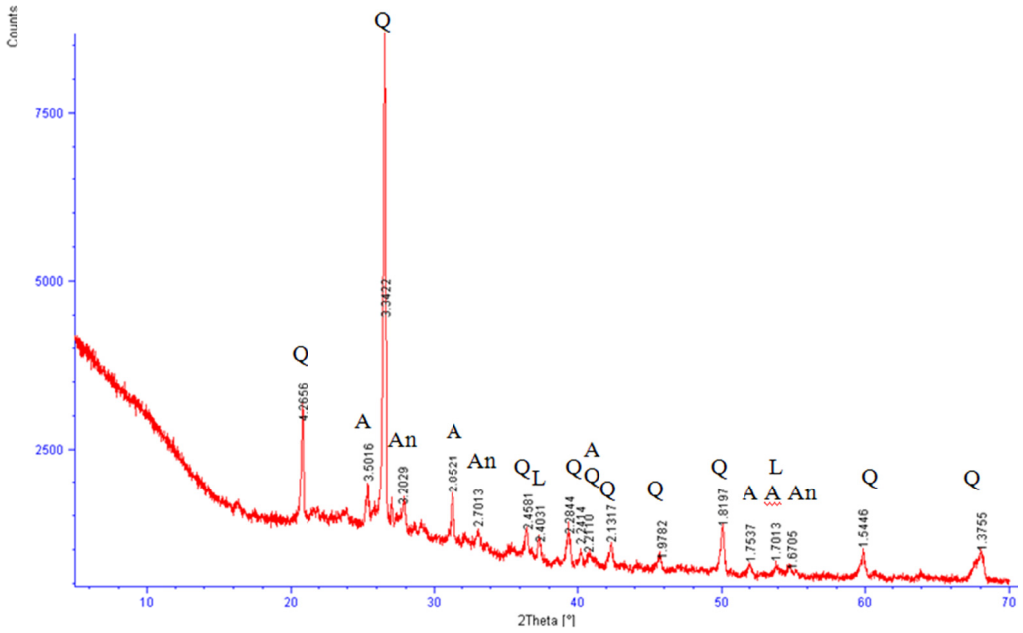
Fig. 7. The diffraction pattern of the grain class 0.09 – 0,071 mm
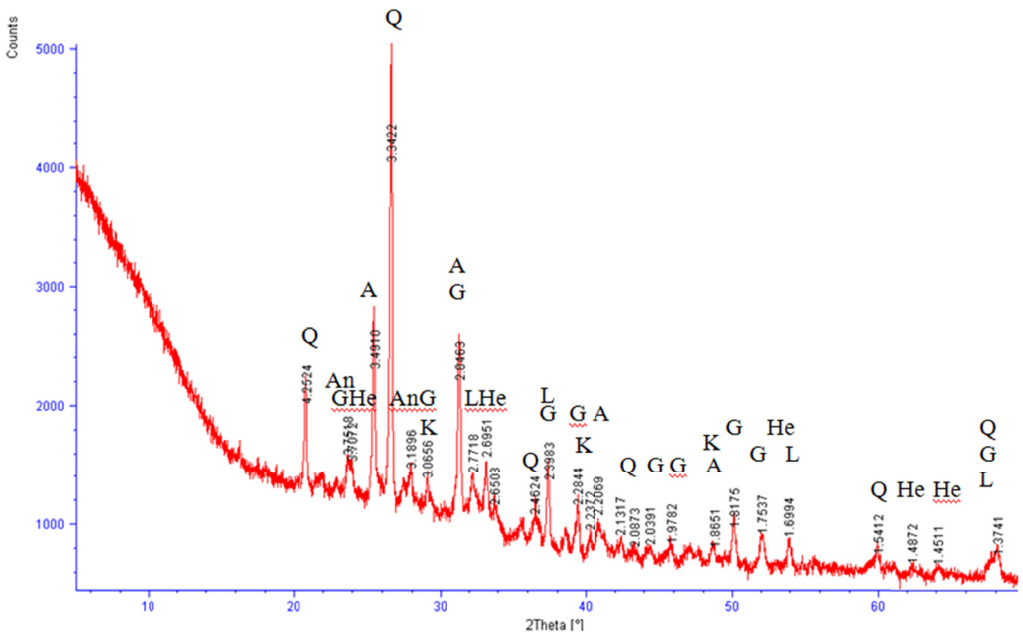(Q – quartz, An – anorthite, A – anhydrite, L – CaO)

Fig. 8. The diffraction pattern of the grain class < 0.045 mm
(Q – quartz, An – anorthite, A – anhydrite, L – lime, G – gehlenite, He – hematite, K – calcite)

mineral were observed. Microscopic observations, however, show that magnetite rarely occurs alone. More frequently, it creates interlayers with an aluminosilicate phase, which may be the reason for the lack of reflections that would correspond to this phase on the diffraction patterns.

2.3.3. Microscopic observations

Fly ash grains are highly diversified morphologically. The tested fly ash consists of both spherical and irregular particles. Spherical forms account for mainly the finest fly ash grain class (<0.045 mm) and comprise primarily enamel grains (Fig. 9). Its yellowish colour is caused by Fe^{3+} ions that are present in enamel, while the colourless spherical grains may have a chemical composition similar to gehlenite, as observed by the Russian authors cited in this work (Pachowski, 1976). Because of enamel isotropic properties, microscopic analysis of enamel gave limited results. If used, the spherical shape of grains would greatly improve workability of a concrete mix based on such fly ash. Pozzolanic properties of fly ash are associated with the enamel content and improve with the increase of its content (Tkaczewska & Małolepszy, 2009). In addition, most of magnetite grains create globular forms (Fig. 10), rather than dendritic ones with a diameter of up to several tens of μm, which is characteristic of the particles produced by rapid cooling of an alloy. Magnetite does not occur independently; as a rule, interlayers of this mineral were observed with silicate or aluminosilicate mass (Fig. 11). Irregular, porous and often jagged particles accumulate mainly in the coarser grain class and are represented primarily by fragments of unburned carbon (Fig. 12). Their content may have an adverse effect on any further applications of fly ash.
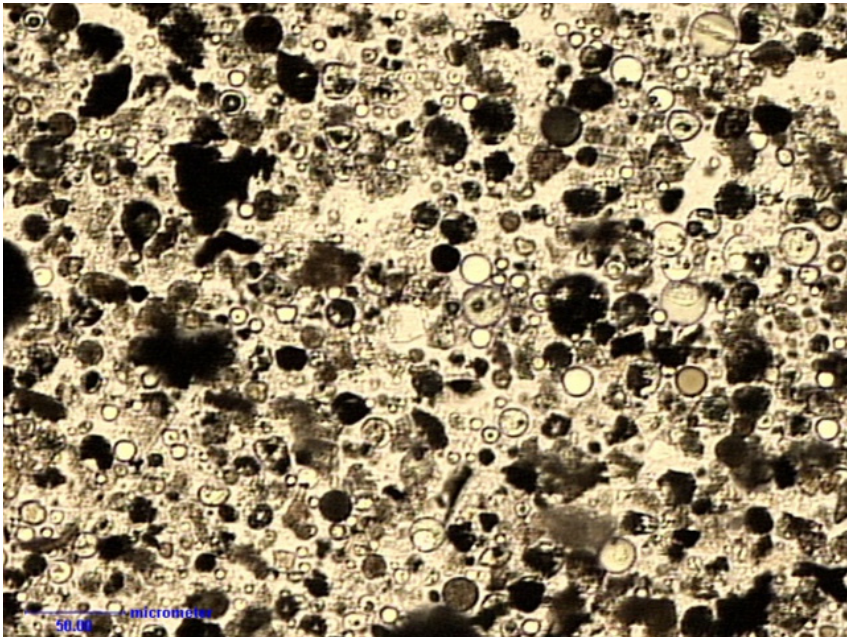

Fig. 9. Glaze of different colours. Black fields – unburned organic matter and opaque minerals. Grain class <0.045 mm. Microscopic analysis in transmitted light, magnification 400×, 1N
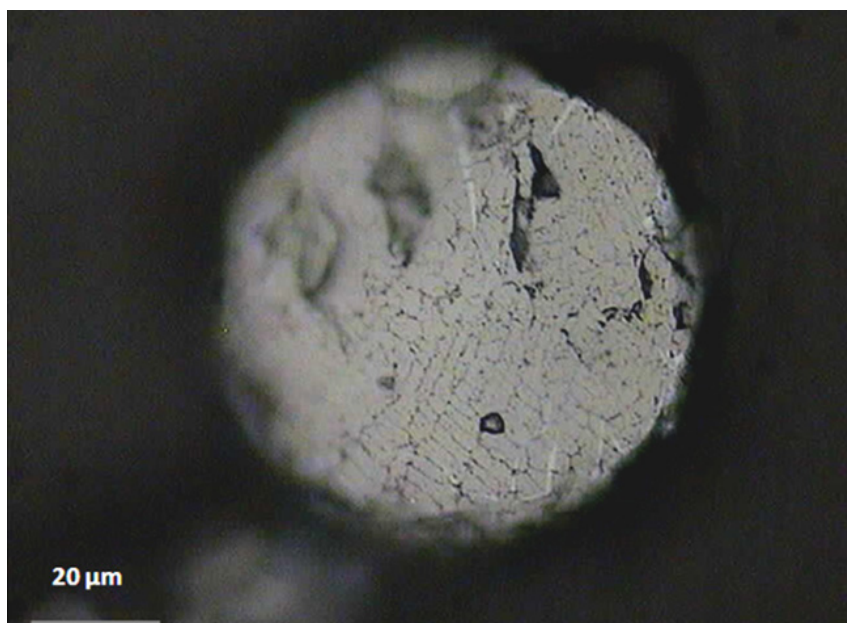
Fig. 10. White lamels of hematite in magnetite. Grain class 0.09-0.071 mm.
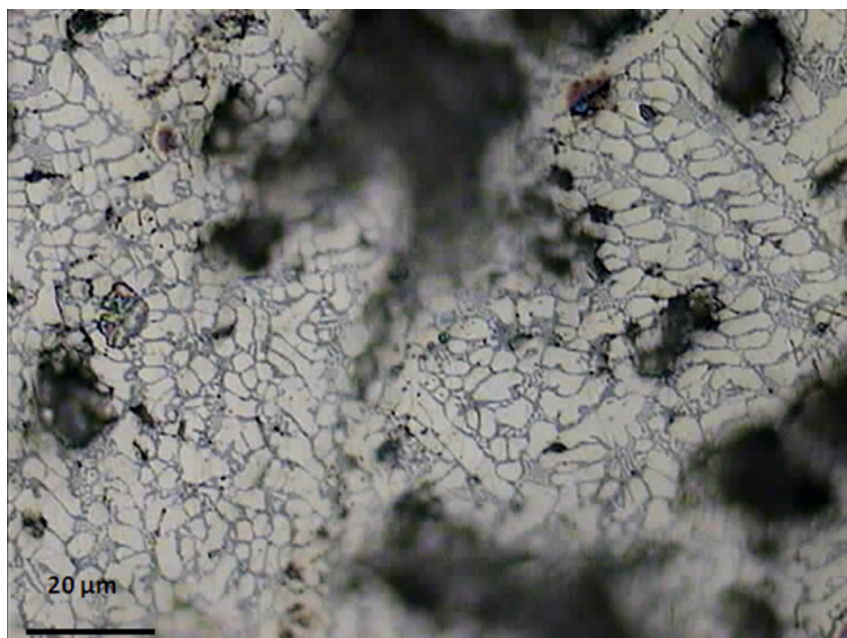Microscopic analysis in reflected light, dry lens, magnification 500×, 1N

Fig. 11. Magnetite (white fields) with an aluminosilicate phase (grey fields). Grain class >0.315 mm.
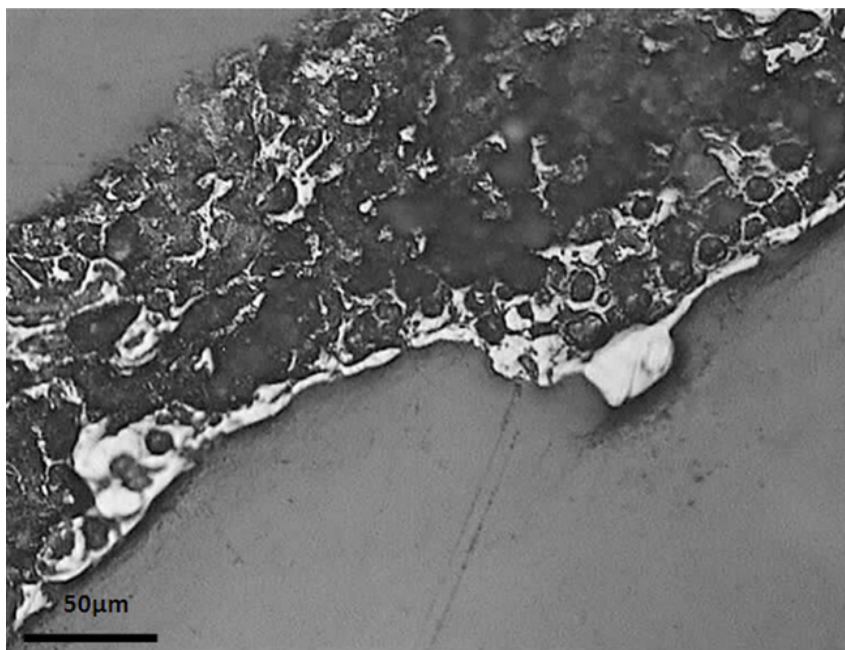Microscopic analysis in reflected light, dry lens, magnification 500×, 1N

Fig. 12. Unburned organic matter in the form of inertinite. Grain class >0.315 mm.
Microscopic analysis in reflected light, dry lens, magnification 200×, 1N

3. Conclusion

The tests conducted on fly ash samples revealed that prior fractionation of the tested material and the use of several research methods are necessary for gaining detailed knowledge of the composition of the phase. On the DTA curve of the multi-component material (i.e. the tested fly ash) in its natural state, only components occurring in large quantities can be identified or the ones that undergo very specific thermal changes. Endothermic effects of one mineral and exothermic effects of another mineral occurring at the same range of temperatures led to, in most cases, a distortion of the curves and inability to indisputably determine the existence of some minerals. For instance, thermograms did not show a small endotherm, which is characteristic of quartz at 575°C, as it was overshadowed by a large exothermic effect resulting from combustion of organic matter in the sample. The quartz content was confirmed only through X-ray and microscopic examinations. In addition, the use of X-ray diffractometry to identify the minerals in the mixture can be effective only for crystalline phases occurring in amounts greater than 5%, and for the phases for which at least some lines do not overlap with reflections of others. This was the case of the calcite content, which could not be unequivocally defined in the tested material solely based on X-ray, because the reflections corresponding to calcite overlapped in most cases with reflections of gehlenite or anhydrite. This problem can only be resolved by a thermal analysis. The study showed that each of the methods considered separately gives a qualitative picture of the phase composition of the sample, but does not give a complete characteristic.

Therefore, it seems advisable to use the method adopted in this article. Simultaneous use of thermal, X-ray and optical examinations to identify different fly ash grain classes allowed to identify additional minerals in the sample, which had not been revealed during the analysis of a raw sample, as was the case of bassanite, hematite, anorthite, gehlenite or calcite. This allowed a more complete characterization of the qualitative phase composition of the tested fly ash, and thus will enable to find a more economical method of its utilization. When seeking opportunities of fly ash applications, it is advisable to separate fractions >0.315 mm. This will significantly reduce the unburned carbon content in a sample, and thus reduce water demand and increase the freeze-thaw resistance of mortar and concrete containing fly ash. The smallest grain class of the tested fly ash < 0.045 mm, which has the largest yield, can be used in those applications where the anhydrite content (e.g. as a time regulator for setting of cement) and strong fragmentation of the sample are advisable.

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