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X-RAY FLUORESCENCE METHOD AND THERMAL ANALYSIS OF CONCRETE PREPARED BASED ON A SHARE OF FLY ASH AND VARIOUS CHEMICAL ADMIXTURES

The utilization of fly ash in concrete as partial cement replacement has many benefits. It leads to increase of a binder´s amount and improves workability (pumpability, keepability and others) of fresh concrete, as fly ash behaves as a solid fluidifier. Application of fly ash in combination with a fluidifier is very effective, because it improves the workability of fresh concrete significantly. Regarding characteristics of lower class fresh concrete the main benefit of fly ash utilization with fluidifier is complement of fine binder, especially particles up to 0,25mm. At the same time, fly ash hinders segregation and flowing of very soft and liquid fresh concrete (cone consolidation 100 mm and more) contributes to the higher structure homogeneity and higher quality of concrete construction surfaces. The phases of hydrate created in pozzolanic reaction cause higher strength of fly ash mixtures, structure concretion, and finer porosity.

However, results of our research of mechanical properties of fly ash – concrete composites by various chemical (plasticizers and aeration) additives showed deviations in the resulting strengths. The aim of this paper is monitoring of these deviations by the X-ray fluorescence method and thermal analysis and their subsequent evaluation.

Key words: X-ray fluorescence method, fly ash, concrete, chemical admixture.

Використання золи в бетоні для часткової заміни цементу має багато переваг. Це призводить до збільшення кількості в’яжучого і покращує оброблюваність свіжого бетону, тому що зола поводиться як твердий розріджувач. Застосування золи в поєднанні з розріджувачами є дуже ефективним способом, оскільки вона значно покращує оброблюваність свіжого бетону. Що стосується характеристик нижчого класу свіжого бетону, основна перевага використання золи з розріджувачми є доповненням в’яжучого, особливо часток розміром до 0,25 мм. У той же час зола перешкоджає сегрегації м'якого та рідкого свіжого бетону, та сприяє більш високій однорідності структури і кращій якості бетонних поверхонь. Пуццоланова реакція викликає підвищену міцність сумішей з золою, структуру і пористость.

Тим не менш, результати наших досліджень механічних властивостей золи – бетонних композиційних матеріалів з різними хімічними домішками показали відхилення в міцності. Метою даної роботи є моніторинг цих відхилень за допомогою рентгенівського флуоресцентного методу і термічного аналізу та їх подальша оцінка.

Ключові слова: рентгенівський флуоресцентний метод, зола, бетон, хімічні домішки.

Introduction

The large volumetric in-waste or by-product materials from industry are going to landfills and have been increasing with time. Recycling and reusing of construction waste is a viable option in construction waste management. Rawshan et al. investigated the effect of prefabrications in building systems in reducing waste [1]. They showed that large amount of material wastage can be reduced by the adoption of prefabrication and revealed that the rates of reused and recycled waste materials are relatively higher in projects that adopt prefabrication. Kumaran et al. investigated the feasibility of using waste tires (chips and fibers) in concrete to improve its strength [2]. They outline the use of rubberized concrete in structural and non-structural members and show how it is suitable for the concrete and its uses. Sustainable materials are one of the strategies to be considered by the construction industry to help circumvent waste problem. A couple of ways to achieve the goal of reducing volumetric in-waste is to introduce Recycled concrete from the largest sources of Fly Ash (FA) from burning coal into the production of concrete [3].

Fly ash is an industrial waste and a material of puzzolanic characteristic occurring due to burning the pulverized coal in the thermal power plants. In the construction sector, the fly ash is used in the production of cement as an additive-material, in production of concrete instead of some of the cement or instead of some of the fine aggregate, as a base and sub-base material in highway construction, as a filling material in dams, in retaining walls, and for production of light construction materials [4]. The fly ash, similar to other pozzolans, affects the technical properties of the concretes and mortars by its pozzolanic characteristics and filler effect. It is known that the filler effect of the fly ash is more effective than the pozzolanic characteristics when affecting the properties of concrete [5, 6]. The fly ashes have pozzolanic activity because they contain surplus amount of silica, alumina and iron oxide; they have a structure with very fine particles and amorphous. Materials with silica and alumina in the fly ashes structure make additional calcium silicate hydrate (C-S-H) by reacting with calcium hydroxide occurring as a consequence of hydration of the cement. The resultant C-S-H gels cause increase in strength of the concrete.

Furthermore, the fact that fly ash contains very fine particle increases compactness in the concretes or mortar and causes filling of the spaces. Using the fly ash in the concrete generally increases the workability of the fresh concrete, decreases the bleeding, decreases the hydration temperature, decreases the permeability of the hardened concrete, increases resistance of the concrete to the chemical effects, and decreases the costs (ACI Committee 1987) [7, 8]. Although more than 52 million tons of wastes (there 66.4% of fly ash) are generated from coal burning power stations in a year in Europe, the use of fly ash in concrete is still limited, because of difficulty in quality control of fly ash concrete.

In this paper, the study of fly ash concrete and its mechanical properties is presented. Results shown the slight deviations probably caused by various admixtures in concrete. Dependence on the composition of the admixtures has been tested by the analytical methods (X-ray fluorescence method; Thermal analysis) and results are presented later in the article.

Material and Methods

To study the possibility of fly ash utilization in concrete (max. 15% cement replacement) was chosen Slovak fly ash. In accordance to the proposed prescription, the C30/37 grade concrete was prepared with 0 – 15% fly ash replacement of special kind of Portland cement CEM I 42.5 N. Water cementations material ratio was 0.36 and natural gravel aggregate from stone – pit Soporna and Hanisberk in specific ratio of the fine to coarse aggregate 40 (0/4): 10 (4/8): 50 (8/16, 16/32) was used in the mixture [9]. Specifications of tested chemical (plasticizers and aeration) additives are the following:

Admixture 1: Plasticizer 1 is superplasticizer based on polycarboxylates modified especially for the production of road concrete. It is presented by a minimal decrease of the consistency of the concrete in the summer. Aeration admixture 1 based on synthetic surfactants, which must be used wherever concrete comes into contact with weathering, respectively aggressive chemical. Substantially it contributes to the increased resistance of concrete to frost and de-icing substances.

Admixture 2: Plasticizer 2 is a plasticizer based on sodium salt of naphthalene sulphate formaldehyde condensate. It has a strong plasticizing effect and significantly improves the consistency of fresh concrete. Aeration admixture 2 is an aeration additive that allows air dispersion of large quantities of stable and separated microscopic bubbles in fresh concrete. It can be used for long-term construction suffer adverse climatic conditions. Increases frost resistance, durability and resistance to road salt (cement-concrete roads, construction of bridges, concrete structures, water works, concrete for roads).

Admixture 3: Plasticizer 3 is high-performance special superplasticizer and concrete-plasticizer for ready-mix concrete and the prefab industry. Increase of the early and final strengths beacuse of the possible reduction of the w/c-value. Aeration admixture 3 is a synthetic aeration ingredient that entrains very finely distributed air micro-pores (< 0.3 mm) into the concrete. Typical areas of application are the construction of concrete road surface, bridge curbs, parking lots or runways or concretes with a high resistance against frost and de-icing salts.

X-ray fluorescence method

XRF was used for the chemical compositions investigation of concrete samples and admixtures. The samples of concrete were pulverised by using planetary ball mill SFM (MTI corp., USA) and prepared as tablets of diameter 32 mm by mixing of 5 g of concrete powder and 1 g of dilution material and pressing at pressure of 0.1 MPa/m^2. The chemical composition was determined by using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite – HOPG target. The prepared samples were measured during 300 sec. at voltage 25 and 50 kV, at current 0.5 and 1.0 mA, respectively. The standardized cement method of fundamental parameters was used for the measurements. The admixtures were measured during 180 sec. the same way by using the method of fundamental parameters for liquid samples.

Thermal analysis

Thermogravimetry continuously measures the mass of a sample subjected to a steady increase of temperature in order to quantify reactions involving gaseous emissions. Thermogravimetric analysis (TG) is thus a convenient method to determine concrete carbonation, because it quantifies the calciumcarbonates and portlandite contents in a sample of mortar extracted from concrete ("concrete mortar") and reduced into powder [10, 11].

Determination of the thermal behavior of the concrete samples prepared with different chemical admixtures was studied. Thermal properties of prepared concrete composite were studied by using STA 449F3 (Netzsch, Germany) in the temperature range from 25 to 1000 °C with the heating rate of 10 K/min under nitrogen atmosphere using DSC/TG mode.

Results and Discussion

X-ray fluorescence method (XRF)

The results of first three experiments show significant differences in the measured values of the strength for concrete composites with the same portion of fly ash. The differences in strength values result from various admixture constitutions probably. The results of XRF chemical analysis of admixtures used in tested concrete samples are summarized in Table 1.

Obviously, the chemical composition of admixtures 1 and 3 was very similar. The concentrations of elements measured in admixture 2 were quite different. Silicon, phosphorous, manganese and iron contents were measured to be much higher in admixture 2. On the contrary, the calcium and sulphur concentrations reached lower values when comparing to the admixtures 1 and 3. The high sulphur content in admixtures 1 and 3 can influence the surface of particles negatively as well as hydration reactions. Along with the Si content seems to be crucial in terms of the strength parameters evaluation.

The measured compressive and flexural strength of tested sample are shown in Table 2 (the reference sample represents always the best results).

Considering the results of chemical composition of prepared composites, it can be stated that composites based on various admixtures were similar to the chemical composition of the assessed Portland cement [12]. Differences in composition depend on the structure of the composites as well as on the processes that take place in composite materials during hardening. Mixtures 1 – 3 are presented by the different value of CaO / SiO_2 ratio (0.50 – mixture 1; 0.43 – mixture 2; 0.6 – mixture 3). The lowest value of CaO / SiO_2 ratio corresponded with the highest value of compressive and flexural strength (Table 2 – admixture 2). As consequence, the strength differences by the thermal analysis were monitored [13].

Table I

XRF chemical analysis of tested admixtures

Chemical composition	Admixture 1 [mg/kg]	Admixture 2 [mg/kg]	Admixture 3 [mg/kg]
Mg	<101	2140	<101
Si	<8.3	113	<5.1
P	<3.0	473.4	<3.0
S	93 160	47 280	99 680
Cl	188.9	294.4	195
K	222	324.2	224
Ca	5 799	2 476	5 130
Mn	<5.1	184.1	39.7
Fe	30.4	129.3	57.4
Co	15.5	8.1	14.7

Table 2

Results of mechanical properties of composites based on various admixtures

Strength [MPa]/ Mixtures based on various admixtures	Sample 1 (admixture 1)	Sample 2 (admixture 2)	Sample 3 (admixture 3)
Compressive strength – reference sample	19.3	28.2	19.9
Compressive strength – sample with 15% wt. FA	13.0	23.0	15.7
Flexural strength – reference sample	7.2	8.0	7.2
Flexural strength – sample with 15% wt. FA	5.8	7.4	4.5

Thermal analysis

The prepared concrete samples with 15 % of cement replacement by fly ash and concrete samples without fly ash replacement, respectively with various chemical admixtures were chosen for the thermal properties testing. As examples, the DSC/TG spectrum of concrete sample with 15 % of cement replacement by fly ash containing admixture 2 and 3 are illustrated in Figure 1.

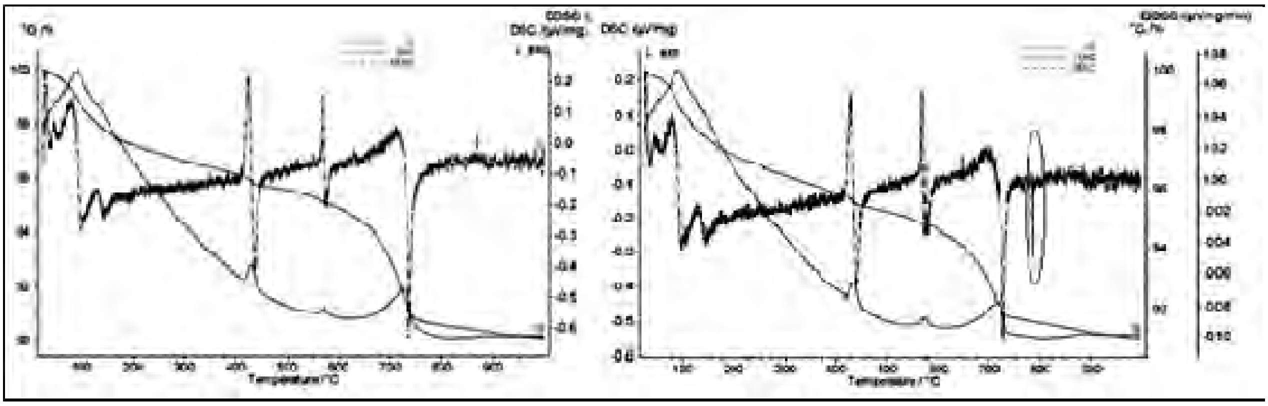

Fig. 1. DSC/TG spectrum of concrete sample with 15 % wt. of FA (admixtire 2 right; admixtire 3 left;)

The comparison DSC curves (endothermic processes courses) and TG curves (mass of losses) of the concrete samples 2, 3 (sample with admixture 1 is very similar to sample based on admixture 3) as well as the reference concrete are presented in Figure 2.

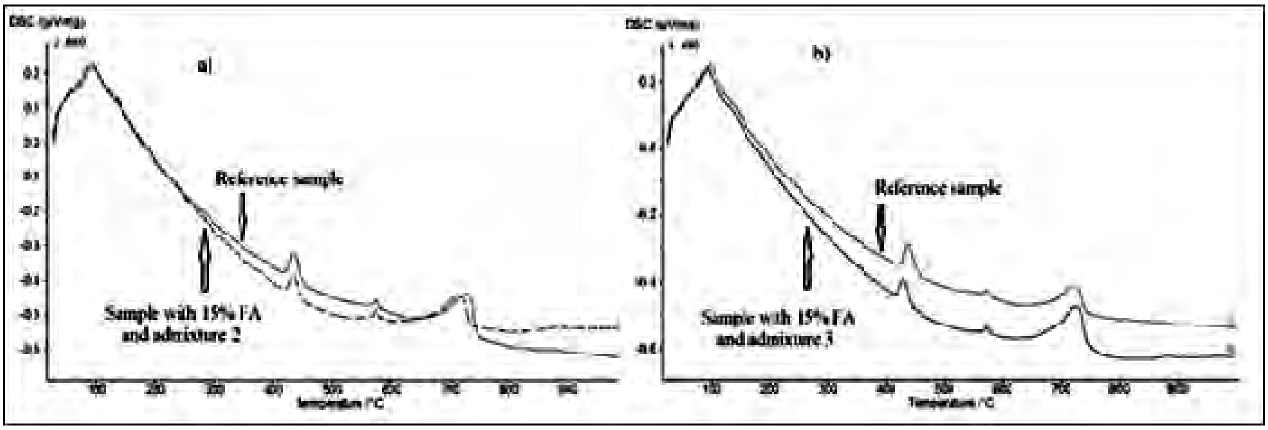

Fig. 2. Comparison of the DSC curves of the concrete samples with 15 % of cement replacement by fly ash to the reference samples without fly ash

Several endothermic processes in the range 25 to 1000°C were detected during heating of all measured concrete samples. The peaks and onset temperature values as well as the related mass changes for studied concrete composites with 15 % of cement replacement by fly ash are summarized in Table 3. Similar DSC curves with four principal peaks were observed for all studied concrete samples. The most significant shift in peak temperature towards to the higher temperature by 6°C was detected in process 4 in case of sample with admixture 2 (Figure 2b) for reference sample. The other related peak temperatures for all processes and each measured sample were very close to each other [13].

No significant differences in peak temperatures were detected for the investigated samples evaluating the endothermic processes (Table 3). The TG measurements expressed in mass of lost gases for tested powdered samples show to be similar; the higher percentage difference was detected only in case of sample with admixture 3 at process 4. Residual mass after the heating process ranged in close interval from 90.1 to 92.02 %. Admixtures are likely not to be the factor of importance in terms of thermal behavior of concrete composites.

Table 3I

Characterization of the thermal processes of studied concrete samples

		Sample 1 (admixture 1)	Sample 2 (admixture 2)	Sample 3 (admixture 3)
Process 1	Peak [°C] Onset [°C] Mass loss [%]	87.6 71.9 1.32	90.6 75.6 1.87	91.4 70.8 1.87
Process 2	Peak [°C] Onset [°C] Mass loss [%]	431.2 419.0 0.33	432.8 420.9 0.47	430.0 418.3 0.42
Process 3	Peak [°C] Onset [°C] Mass loss [%]	573.0 568.7 0.44	573.0 568.7 0.4	572.8 569.3 0.29
Process 4	Peak [°C] Onset [°C] Mass loss [%]	720.8 683.4 2.67	715.4 680.0 2.4	728.0 690.0 3.62
	Residual mass [%]	92.02	90.98	90.1

When comparing the TG curves of the samples with and without fly ash addition, the results are very similar for all studied samples. The total mass losses after heating process were measured 9.35, 9.88 and 9.73 % for reference samples with admixture 1, 2 and 3, respectively; 7.98, 9.02 and 9.9 % for fly ash samples with admixture 1, 2 and 3, respectively. In summary, the mass loses of reference samples were measured to be higher (except for sample with admixture 3).

Courses of TG curves (Figure 3, left) are consistent with the curves (Figure 3, right) published in work [14]. TG method supplement by chemical analysis, its comparison to gamma-ray absorption method and using FT IR spectroscopy as well as X-ray diffraction analysis was applied to identify of dehydration and decarbonation processes occuring during thermal behaviour study of an ordinary Portland cement paste, and three concrete mixes, containing siliceous or calcareous aggregates. A is seen from Figure 3, the mass of a carbonated concrete powder sample containing siliceous aggregates subjected to a steady increase of temperature in order to quantify reactions during its thermal decomposition. Each phase is characterized by its own temperature range of decomposition and by a specific mass loss. In the first stage of the thermal processes (Figure 3, left), the release of physical bounded water from concrete sample occurs at low temperatures (up to 100°C).

In the temperature range of ≈430-570°C (process 2), the dehydration of the residual portlandite ($Ca(OH)_2$) occurs.

Decomposition of the calcium carbonates measured between 570°C and 730°C (process 3) results mainly from the dissociation of the poorly crystallized and thermally unstable forms of $CaCO_3$ such as vaterite and aragonite resulting from carbonation of calcium silicate hydrates (C-S-H phase) which dissociate between 500 and 700 °C according to literature sources [15].

The more stable calcite ensuing from portlandite carbonation decomposes between 730 and 1000°C (process 4). The obtained decomposition temperatures of carbonated products are a little shifted in comparison to the literature data [14], where calcite formed from portlandite by carbonation reaction dissociates between roughly 760 and 950°C (or 650-950°C). It is difficult to determine a precise temperature range of decarbonation processes because they depend on the kinetics of the carbonation process of hydrated products (portlandite and C-S-H) [16].

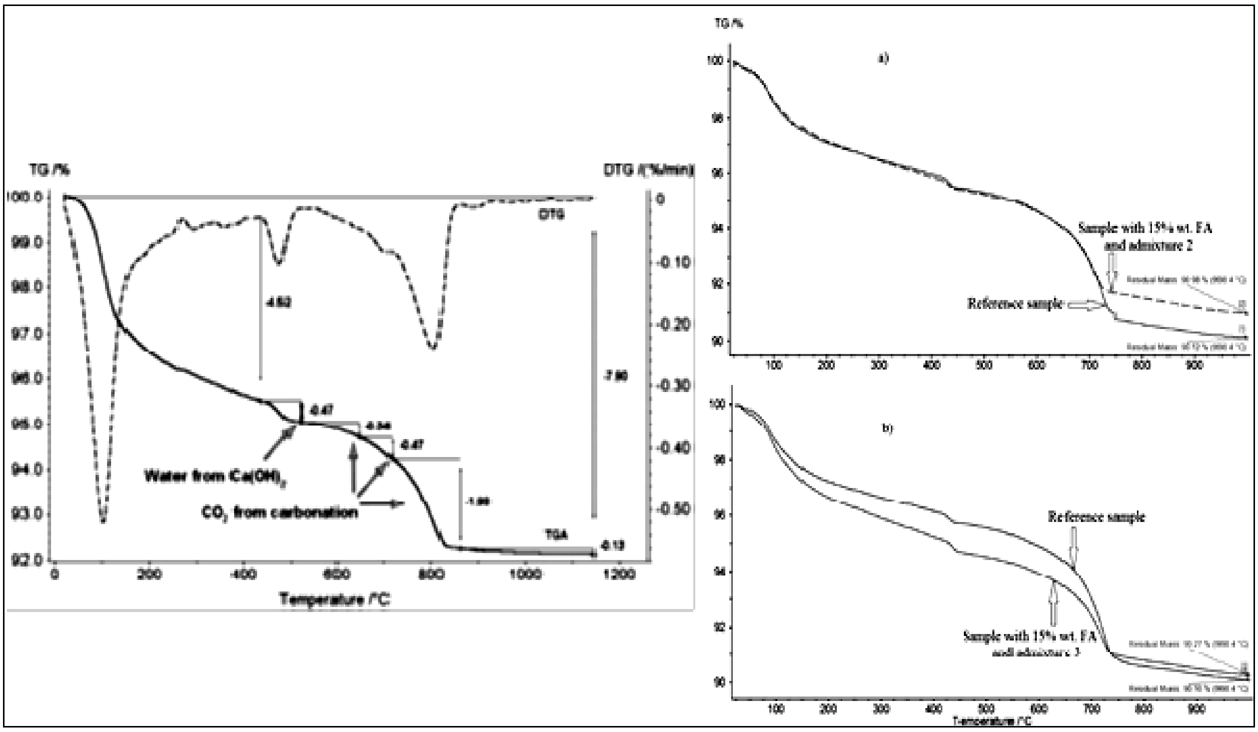

Fig. 3. Dissociation of a carbonated sample of crushed concrete mortar during a TGA test: concrete containing siliceous aggregates (right, source: Villain et al., 2007), Comparison of the TG curves of the concrete samples with 15 % of cement replacement by fly ash to the reference samples without fly ash (left)

Conclusion

Based on these results, especially from XRF results, it is clear that in addition to the requirements on the quality of fly ash concrete is also necessary to focus on the chemical composition of the admixtures. Based on our research we found that order to achieve the required mechanical properties of fly ash concrete needs follow the CaO/SiO_2 ratio in admixtures, because of the value of CaO/SiO_2 ratio closely related to the compressive and flexural strength of concrete. It indicates that the lowest value of CaO/SiO_2

ratio corresponded with the highest value of compressive and flexural strength like it is presented in the paper.

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