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THE STUDY OF THE PROPERTIES OF FLY ASH BASED CONCRETE COMPOSITES WITH VARIOUS CHEMICAL ADMIXTURES

Madhan P, Aarthi R, Selvaram, P., Akila, V
Assistant Professor
Department of Civil Engineering
Nehru Institute of Technology
mckenziemyth.2292@gmail.com - Corresponding Author

Abstract

Technological developments in our society are still highly extensive nature and the forthcoming process of globalization affects the state of the environment significantly. Along with a slight increase in population, uncontrolled pumping of raw materials for production of materials and energy and urbanization of the environment, there is the increase of harmful emissions and waste generation. Mineral resources are limited considerably. The resources for feeding our growing population (the problem of drinking water and food) are limited as well as materials needed for construction of buildings, infrastructure development, and industry needed to ensure the people's welfare. This is also true for conventional raw materials for production of construction materials and fuel. One of the main challenges of the 21st century is oriented on the increasing effectiveness of the materials processing and significantly reduced energy usage. Because concrete is the most used building material in the world, the new approach consists in change in the design of concrete structures and in developing and implementing new concrete processing technologies based on cement reduction demand. Although new technologies are being developed to solve these problems, there is a viable solution for the present time utilization of alternative raw materials i.e. fly ash. The current annual worldwide production of by-products is estimated about 700 million tons of which 70 % is fly ash at least. Large quantities of fly ash are available at low costs around the world and the use of fly ash concrete seems to offer the best solution to reducing consumption of cement. The paper is aimed at the study of the mechanical properties (tensile flexural and compressive strengths) of hardened fly ash - concrete composites with various proportions of fly ash as well as the investigation of the chemical admixtures influence on the concrete properties.

Keywords: Fly ash; concrete; concrete strenght; X-ray fluorescence; thermal analysis

1. Introduction

Fly ash (FA) is a by-product of the combustion of pulverized coal in electric power generation plants [1]. When the pulverized coal is ignited in the combustion chamber, the carbon and volatile materials are burned off. However, some of the mineral impurities of clay, shale, feldspars, etc., are fused in suspension and carried out of the combustion chamber in the exhaust gases. As the exhaust gases cool, the fused materials solidify into spherical glassy particles called fly ash. Due to the fusion-in-suspension these fly ash particles are mostly minute solid spheres and hollow cenospheres with some particles even being plerospheres, which are spheres containing smaller spheres. The size of the fly ash particles varies but tends to be similar to slightly larger than type I Portland cement. The fly ash is collected from the exhaust gases by electrostatic precipitators or bag filters. Chemical make up of fly ash is primarily silicate glass containing silica, alumina, iron and calcium. Colour generally ranges from dark grey to yellowish tan for fly ash used for concrete. In addition it has a pozzolanic property [2]. A pozzolan is a siliceous or aluminosiliceous material that, in finely divided form and in the presence of moisture, chemically reacts with the calcium hydroxide released by the hydration of Portland cement to form additional calcium silicate hydrate and other cementitious compounds. The hydration reactions are similar to the reactions occurring during the hydration of Portland cement [3]. Thus, concrete containing fly ash pozzolan becomes denser, stronger and generally more durable long term when compared to straight Portland cement concrete mixtures. Fly ash has been used in many applications several years all over the world (ASCE, 1993; Linn and Symons, 1988), always aiming the most beneficial utilization and the protection of the environment (EC, 2000; European Committee for Standardization, 2000) [4]. Generally speaking, currently in the concrete industry, the percentage of fly ash as part of the total cementing materials in concrete normally ranges from 15 to 25%, although it can go up to 30-35% in some applications. The use of fly ash in concrete will improve some aspects of the performance of the concrete provided the concrete is properly designed. Therefore a common reason for using fly ash in concrete is to achieve the needed compressive strength at lower cement content. The well known information show that the replacement of Portland cement by fly ash on a one-for-one basis, either by volume or weight, results in lower compressive strengths at ages up to about 3 months, but greater strengths develop at 6 months and beyond [5- 9]. Some of the other fly ash concrete properties depend on the use of admixtures. Admixtures are ingredients other than water, aggregates, hydraulic cement, and fibres that are added to the concrete batch immediately before or during mixing. A proper use of admixtures offers certain beneficial effects to concrete, including improved quality, acceleration or retardation of setting time, enhanced frost and sulphate resistance, control of strength development, improved workability, and enhanced finish ability. Admixtures vary widely in chemical composition, and many perform more than one function. All admixtures to be used in concrete construction should meet specifications; tests should be made to evaluate how the admixture will affect the properties of the concrete to be made with the specified job materials, under the anticipated ambient conditions, and by the anticipated construction procedures. Two basic types of admixtures are available: chemical and mineral. The more important function have the chemical admixtures, which are added to concrete in very small amounts and could significantly affect the properties of concrete (mainly for the entrainment of the air, reduction of water or cement content, plasticization of fresh concrete mixtures, or control of setting time). The paper presents the overview of research results of properties of concrete based on fly ash with a share of different chemical admixtures with special regard to the assessment of dependence of mechanical concrete properties on the chemical composition of admixtures.

2. Material and Methods

Concrete samples preparation

Research of utilization of fly ash as a partial cement replacement in concrete was oriented on preparing of 3 experimental mixtures, in which the special kind of cement exploited for the Highway Engineering purposes (CEM 42,5 N) was used. The Slovak fly ash originated from the brown (Novaky) coal combustion process (chemical properties of fly ash are presented in Table 1) was tested. Specific ratio of the fine aggregate to stone 40: 10: 50 (40% fraction 0/4; 10% fraction 4/8; 20% fraction 8/16; 30% fraction 16/32) was used in mixture. In accordance to the proposed recipe the specified amount of cement (410 kg) was replaced by the 5–15% fly ash. Three different types of chemical admixtures from Slovak producers: experiment 1 (admixture 1), experiment 2 (admixture 2), experiment 3 (admixture 3) were used.

Table 1. Chemical compositions of fly ash

Component [wt. □]							
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
37.5	15.60	7.67	1.30	22.94	2.77	1.21	0.63
MnO	P_2O_5	SO_3 (S)	S_{total}	*LOD	*LOI	*C.Sub.	*ROC
0.11	0.18	7.29 (2.91)	2.91	0.16	2.59	2.14	0.28

*Loss of drying (LOD), Loss of ignition (LOI), Combustible substances: 830 □ C (C.Sub.), Residual organic carbon (ROC)

Methods for mechanical and chemical composites properties testing

In accordance to STN EN 12350 (parts 3 and 7) four base testing of consistence assessment (slump test), air-volume (compressive method), volume weight (relative compaction - STN EN 12350 - 6:2001) and temperature assessment (STN EN 206-1: 2002) of fresh concrete proceeded. After 28 days (d) of hardening (the Slovak technical standards requirement), the composites were tested on compressive strength (CS), tensile flexural strength (TFS) and on the frost resistance and determination of water activity and de-freezing substance resistance (STN 73 1326, STN 73 6123). For the comparative study, the reference composite (RC) of C 30/37 concrete class was prepared in accordance with requirements of Technical standards STN 73 6123 – Building of pavement (the required qualitative parameters of proposed class of concrete according to STN 73 1326 shows the Table 2).

Table 2. Specification of required parameters of concrete C 30/37

Parameters	Group of pavement				
	L	I	II	III	IV
Characterized combined stress strength f_{cf} [N/mm^2]	4.5	4.5	4.5	4.0	3.5
The least amount of period of water activity and de-freezing substance	100 / 75			75 / 50	75 / 50
Prism compressive strength f_{cc} [N/mm^2]	32			28	25
The biggest coefficient of spatial arrangement of air voids [mm]	0.25				
The least coefficient of frost resistance after 300 circles [%]	85			–	–
Cylindrical compressive strength [N/mm^2]	24			21	19

Analytical methods

X-ray fluorescence method (XRF) was used for the chemical compositions investigation of both concrete samples and admixtures used. The samples of concrete were pulverised by using planetary ball miller 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 (M-HWC) 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 s at voltage 25 and 50 kV, at current of 0.5 and 1.0 mA, respectively. The standardised cement method of fundamental parameters was used for the measurements. The admixtures were measured during 180 s the same way by using the method of fundamental parameters for liquid samples. 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.

3. Results and Discussion

Fresh concrete tests

The resulting measured values of fresh concrete mixture properties (consistence, air content, concrete temperature in comparison with the specific requirements of Technical Standard (TS) as well as the volume weight compared with reference composite (RC)) are presented in Table 3. The results of tests proved that prepared fresh mixture of concrete of strength class C 30/37 met the requirements of Slovak technical standards.

Table 3. Requirements according to Slovak TS and results of fresh mixture (C 30/37) tests

Type of test Requirements according to Slovak standard	Measured value (exp. 1)				Measured value (exp. 2)				Measured value (exp. 3)			
	0%	5%	10%	15%	0%	5%	10%	15%	0%	5%	10%	15%
Consistence [mm] / S1 (10 – 40 mm)	20	40	30	30	30	30	40	40	30	30	40	30
Air content [%] / maximal 7 – 8 %	7.9	5.6	4.7	6.5	6	6	6.4	6.5	6.4	6.2	6.2	6.5
Temperature [°C] / +5 °C to +25 °C	20.0	21.1	19.2	19.7	23.5	22.5	19.5	19.5	22.5	19.4	19.7	19.5
Volume weight [kg. m^{-3}] / RC	2340	2287	2287	2222	2330	2330	2310	2280	2380	2330	2280	2270

Water activity, chemical resistance of concrete surface and freezing and thawing

The results of water activity – with respect to all replacement (5 – 15% FA) and de-freezing substance resistance of concrete surface based on certificate interpretation of the test performance showed that the composites of 3 experiments met the requirements of Technical standard with results: slightly disturbed. The results of freezing and thawing tests showed that the requirements of Slovak Technical standard after 300 circles were fulfilled and in term of testing results of prepared composites on the base of 15% CEM 42.5 N replacement by FA are suitable (frost resistance coefficient of 0.85) for the using in the area of Highway engineering.

Mechanical properties

Overall developing of the compressive strength (CS) and tensile flexural strength (FS) of composites based on various coal fly ash portions after 28 days (average values of strength [N.mm^{-2}]) is shown in Table 4. Both strength characteristics of experimental composites are compared with values of reference composites (RC) and Technical standard requirements (CS – 37.0 MPa / 28 days; FS – 4.5 MPa / 28 days). Based on these results it can be stated that the utilization of FA with 5 wt. % as well as 15 wt. % of cement replacement is possible for using of cement-concrete, class C 30/37. Based on comparison of the current requirements of Slovak technical standard for TS (4.5 MPa / 28 days) valid for concrete road covers and the results of the experiment 2 and 3 it is clear that the prepared samples did not meet the required flexural strength parameters. Since the mixture were prepared on the same principle just the basis of various chemical additives, the results showed significant differences in the measured values of the strength for concrete composites with the same portion of fly ash with various chemical admixtures. The differences in strength values probably consisted in admixture constitution.

Table 4. Compressive and tensile flexural strengths results of 28 days hardened composites

Hardening time [d] 28 d	Mixture											
	Experiment 1				Experiment 2				Experiment 3			
	RC	5% FA	10% FA	FA	15% % RC	5 FA	10 % FA	FA	15% % RC	5 FA	10 % FA	15% FA
CS [MPa]	42.5	34.5	35.5	31.0	48.4	44.2	42.4	37.2	52.0	46.0	42.04	41.9
FS [MPa]	4.3	4.4	4.0	4.0	6.9	6.6	6.2	5.6	4.7	4.4	4.2	4.2

Chemical composition of admixtures and concrete composites

The results of first three experiments showed significant differences in the measured values of the strength for concrete composites with the same portion of fly ash. The differences in strength values probably resulting from various admixture constitutions. The results of XRF chemical analysis of admixtures used in tested concrete samples are summarised in Table 5.

Table 5. Comparison of the chemical analysis of admixtures

Chemical composition	Admixture 1	Admixture 2	Admixture 3
	[mg/kg]	[mg/kg]	[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

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 detected can negative influence the surface of particles as well as hydration reactions. Along with the Si content seems to be crucial in terms of the strength parameters evaluation.

Based on obtained outputs, the study of potential chemical admixtures influence on concrete properties has been started. The experiments were repeated and new composites were prepared with identical recipe, same value of FA replacement and with a variation of chemical admixture to confirm our previous results [10, 11]. The measured compressive and flexural strength of new tests is shown in Table 6 (the reference composites represent always the best results). The results of the chemical composition analysis by XRF are summarised in Table 7.

Table 6. Results of mechanical properties tests of concrete composites

	Compressive strength RC [MPa]	Compressive strength 15% FA [MPa]	Flexural strength RC [MPa]	Flexural strength 15 % FA [MPa]
Admixture 1	19.3	13.012	7.189	5.786
Admixture 2	28.176	23.005	8.028	7.444
Admixture 3	19.928	15.66	7.234	4.527

Table 7. Overall oxide concentrations of tested composites

Symbol	Element	Admixture 1 [concentration %]	Admixture 2 [concentration %]	Admixture 3 [concentration %]

		*0% FA	15 % FA	*0% FA	15 % FA	*0% FA	15 % FA
Na_2O	Sodium	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
MgO	Magnesium	1.880	2.084	2.051	2.101	1.731	1.762
Al_2O_3	Aluminum	5.180	5.995	5.696	6.591	4.378	5.442
SiO_2	Silicon	32.08	34.49	40.11	40.40	25.99	32.67
P_2O_5	Phosphorus	0.0835	0.0899	0.0869	0.0984	0.0795	0.0782
SO_3	Sulfur	2.865	2.853	2.782	2.792	2.952	2.897
Cl	Chlorine	0.00526	0.00477	0.00462	0.00471	0.00470	0.00424
K_2O	Potassium	0.7603	0.8642	0.7949	0.9262	0.6426	0.8624
CaO	Calcium	20.46	19.07	19.86	17.49	20.70	15.20
TiO_2	Titanium	0.3109	0.3276	0.3050	0.3446	0.3050	0.3333
MnO	Manganese	0.3630	0.3640	0.3643	0.3618	0.3679	0.3613
Fe_2O_3	Iron	3.501	3.997	3.444	4.068	3.230	4.083

Considering the importance of calcium and silicon in the concrete composite in terms of its strength parameters, the concentrations of calcium and silicon oxides are discussed. As it is seen from Table 7, the fly ash mixtures represented the lower content of calcium oxide comparing to the reference sample without fly ash. This likely result in the decrease of the strength characteristics for ash samples (Table 6). On the contrary, the silicon concentrations seem to be similar for the tested composites.

Thermal properties of concrete composites

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 an example, the DSC/TG spectrum of concrete sample with 15 % of cement replacement by fly ash containing admixture 2 is illustrated in Figure 1.

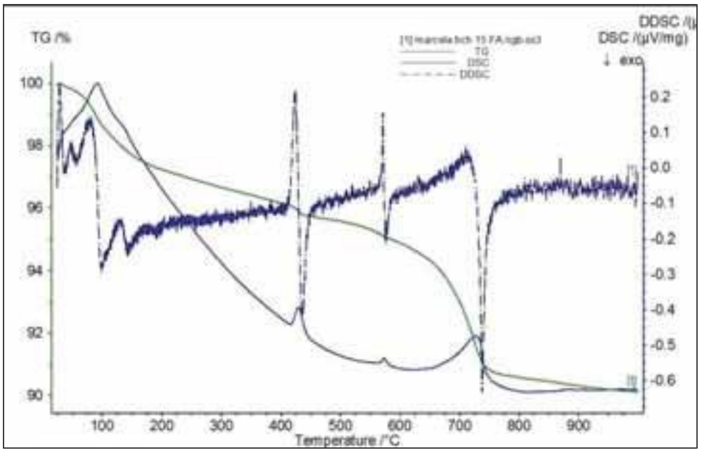


Fig. 1. DSC/TG spectrum of concrete sample with 15 % of cement replacement by fly ash

Several endothermic processes in the range 25 to 800°C were detected during heating of concrete samples with admixtures for all measured samples. The peaks and onset values measured as well as the related mass changes for studied concrete composites with 15 % of cement replacement by fly ash are summarised in Table 8.

Table 8. Characterisation of the thermal processes of studied concrete samples

	Admixture 1 (15% FA)	Admixture 2 (15% FA)	Admixture 3(15% FA)
Process 1			
Peak [°C]	87.6	90.6	91.4
Onset [°C]	71.9	75.6	70.8
Mass change [%]	1.32	1.87	1.87
Process 2			
Peak [°C]	431.2	432.8	430.0
Onset [°C]	419.0	420.9	418.3
Mass change [%]	0.33	0.47	0.42
Process 3			
Peak [°C]	573.0	573.0	572.8
Onset [°C]	568.7	568.7	569.3
Mass change [%]	0.44	0.4	0.29
Process 4			
Peak [°C]	720.8	715.4	728.0
Onset [°C]	683.4	680.0	690.0
Mass change [%]	2.67	2.4	3.62
Residual mass [%]	92.02	90.98	90.1

No significant differences in peak temperatures were detected for the investigated samples evaluating the endothermic processes (Table 8). The mass changes related to the peaks were measured to be similar; the higher percentage gap 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 behaviour of concrete composites. The comparison of the mass changes (TG curves) and endothermic processes (DSC curves) of concrete samples and relevant reference samples is illustrated in Figure 2 and 3.

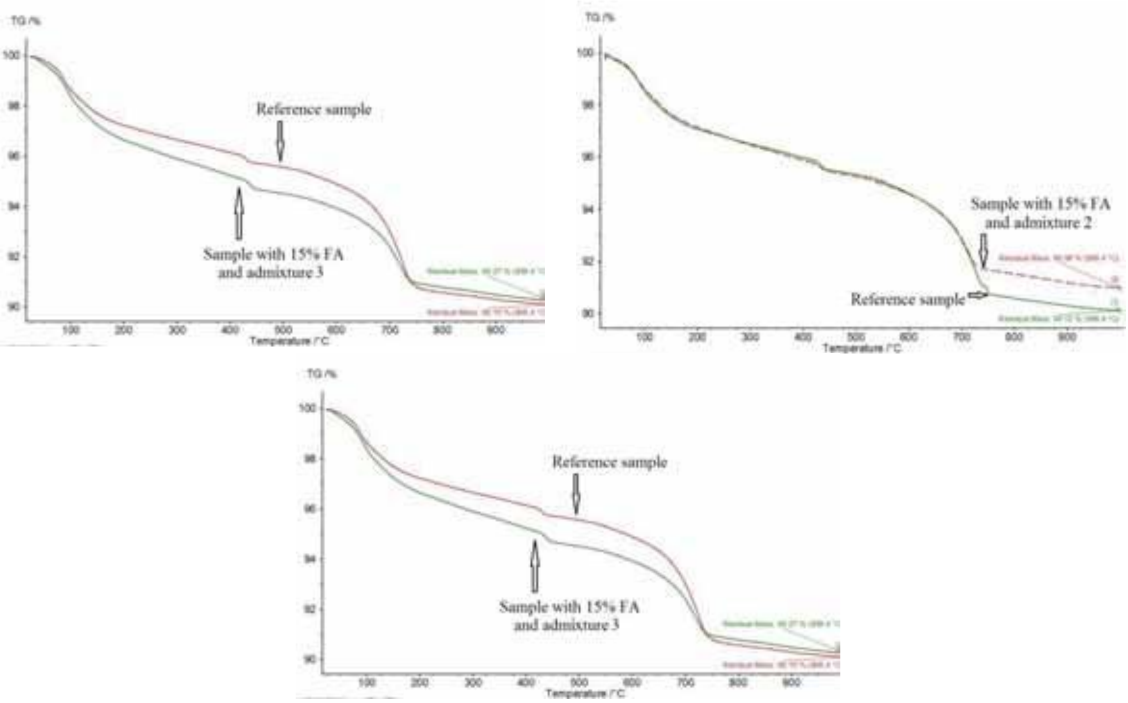


Fig. 2. Comparison of the TG curves of the concrete samples with 15 % of cement replacement by fly ash to the reference samples without fly ash

When comparing the TG curves of the samples with and without fly ash addition, the results differ for all studied samples. Almost identical curve course was detected in case of the sample with admixture 2 (25- 740 °C) with residual mass gap of 0.86 % (Figure 2b). The slightly shifted curves were observed for both the sample with admixture 1 and 3 (Figure 2a, 2c). The residual mass gap of samples with and without fly ash addition with admixture 1 was measured much higher (1.37 %) than in case of sample with admixture 3 (0.17 %). The total mass changes 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).

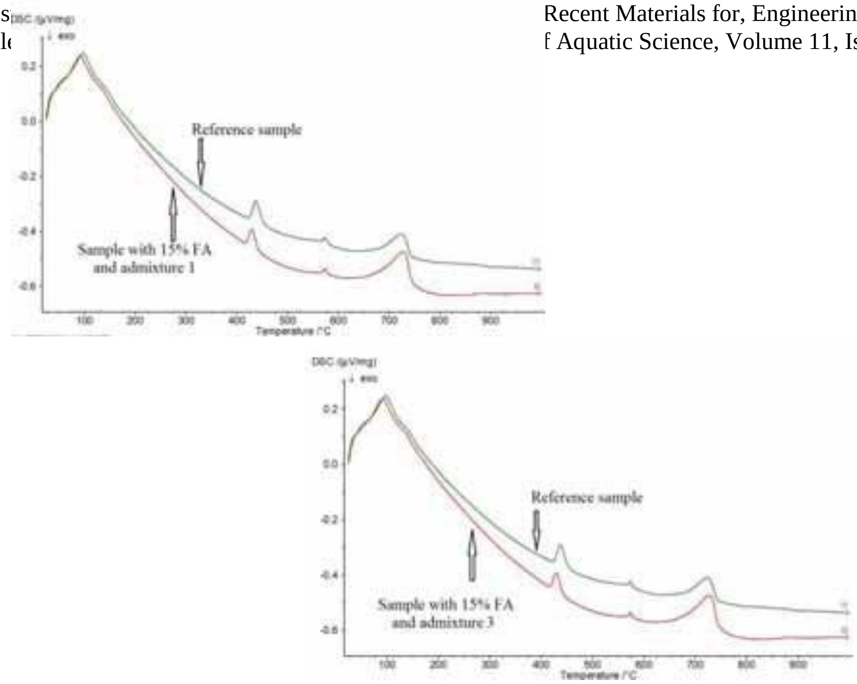


Fig. 3. Comparison of the DSC curves of the concrete samples with 15 % of cement replacement by fly ash to the reference samples without fly ash

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 3b) for reference sample. The other related peak temperatures for all processes and each measured sample were very close each to other.

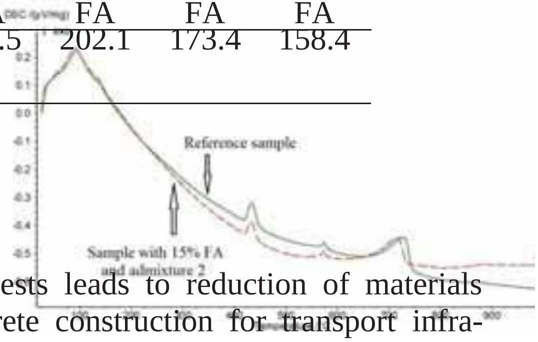
Environmental parameters of concrete composites

The chromium content in the concrete samples was chosen for the environmental assessment of the health safety. Chromium is an indelible non-volatile trace element of raw materials (clay, limestone and iron additives in particular) used in cement clinker production in the form of chromium (III). Naturally occurring chromium (III) is not initially harmful, since it is chemically stable. Only at high temperatures found in cement rotary kilns, inert trivalent chromium oxidizes to form reactive hexavalent chromium. The measured concentration is suggested to be the hexavalent water-soluble chromium which is harmful and allergenic. The total chromium concentrations in tested samples were measured in the range 158.4 to
232.6 ppm (Table 9).

Table 9. Environmental assessment FA-concrete composites based on chromium

Symbol Element	Admixture 1 [concentration mg/kg]	Admixture 2 [concentration mg/kg]	Admixture 3 [concentration mg/kg]

	*0% FA	15 % FA	*0% FA	15 % FA	*0% FA	15 % FA
$Cr2O3$ chromium	232.6	187.9	225.5	202.1	173.4	158.4



4. Conclusion

The development of new specifications and tests leads to reduction of materials related problems when fly ash is used in concrete construction for transport infrastructure. Additionally the rational tests based on documented research prove that the increase of the fly ash utilization provides a net of environmental benefits. Partial cement replacement with supplementary cementing materials reduces greenhouse gas emission proportionately and results in a more "green" concrete, through reduced energy consumption (energy required to produce cement) and prevents the depletion of natural resources. Testing of the interesting environmental parameter such as the hexavalent water-soluble chromium and its impact to health will be next aim of our study. The other - cost reducing of the road building is more important economic benefit [12].

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