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Environmental Assessment of Fly Ash Concrete

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Costs and environmental impacts are currently the critical parameters of construction works. One way to fulfill these criteria is the use of alternative materials. In the Slovak Republic, it is primarily the waste from the power industry, which landfilling fees are still high as well as increasing negative impact on the environment. Fly ash (FA) is defined as a fine grained residue of coal combustion in thermal production stations of electrical energy, which particles are smaller and almost totally spherical in shape, allowing them to fill voids, flow easily, and blend freely in concrete mixtures. Fly ash, a by - product of the coal-burning power industry, is a rich cementitious industrial waste which has the great potential to substitute Portland cement, a major producer of CO_2. Research in Slovakia showed that despite the strict criteria and the requirements of technical standards (maximum use of Slovak FA of 5 %; the currently worldwide information say about high volume concrete with 60-80 % of FA cement replacement), the Slovak brown coal fly ash due to its characteristics can be used in the building industry as a replacement for cement component in concrete with minimum of 15 % FA. Based on the calculations, the substitute by fly ash represents for the construction companies of the area of High Engineering, savings tens of thousands of euros/km of roads. It is true; however, only meeting the specific standard criteria i.e. mechanical (strength characteristics), chemical (frost and chemical resistance) and economic indicators are not sufficient for the concluding statement of FA utilization. In terms of comprehensive assessment, it is necessary to draw attention to the analysis of its life cycle. The study of main environmental parameters, but also of the FA-concrete durability is the aim of this paper. Obtained results again confirm that in terms of hazardous elements content and of calculated environmental profiles (environmental impact), the fly ash is a suitable cement replacement in concrete.

1. Introductions

The current level of carbon dioxide (CO_2) in the atmosphere is approaching 380 ppm. Without drastic market, technological, and social changes CO_2 concentrations are projected to increase to over 800 ppm by the end of the century. Approximately 5 % of global carbon emissions originate from the manufacturing of cement (Ondova and Stevulova, 2012). The calcinations process (driving off CO_2 from $CaCO_3$ to form CaO) accounts for roughly half of the CO_2 emitted, while the remaining carbon results from energy usage during the production process (Huntzinger and Eatmon, 2009; Worrell et al., 2001). According to the International Energy Agency's (IEA) Greenhouse Gas R&D Program cement production generates an average world carbon emission of 0.81 kg CO_2 per kg cement produced. Approximately 1 ton of concrete is produced for every human being in the world each year on average (Lippiatt and Ahmad, 2004).
Fly ash, a by-product of the coal-burning power industry, is a rich cementitious industrial waste which has the great potential to substitute Portland cement, a major producer of CO_2 (Pattanaik and Sabat, 2010). It is a pozzolan, which 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 (Helmuth, 1987). However, this reaction is slower than the hydration of clinker minerals. The products of pozzolanic reaction seal up the pore structure of the cement stone gradually and ensure the high strength of concrete, its water resistance and resistance to aggressive

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elements compared to straight Portland Cement concrete mixtures. At the same time fly ash application leads to the reduction of cement consumption and heat hydration (by reduction of cement dose).
Environmental concerns have increased awareness of different means of preventing pollution and protecting the environment and have caused some to change behaviour accordingly. One tool that is being used more frequently as a result of this environmental concern is life cycle assessment (LCA). For globally significant products such as cement, environmental life cycle assessment is a valuable tool for improving our understanding of the environmental hazards posed by a product's life stages (Weiland and Muench, 2010). In addition it allows cement producers to optimize the manufacturing process by reducing adverse environmental impacts. Life cycle assessment is method of evaluation used to assess the environmental impacts of technologies from ''cradle to grave'' and may be performed on both products and processes. This method belongs to a group of analytical instruments for environmental management that evaluate potential environmental impacts independent from the place of manufacture or product use (Kridlova and Vilcekova, 2012; Estokova and Porhincak, 2012).

2. Materials and Methods

Backgrounds of information for this article are our research results presented in work (Ondova et al., 2012a). Research of utilization of fly ash (FA) as a partial cement replacement in concrete was oriented on preparing of 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 coal combustion process was tested. The fresh concrete mixture was tested before forms filling (slump test, air-volume, density and temperature). After 28 days (time is required of Slovak Technical standards) of hardening, the composites were tested for the required properties resulting from the special purpose of concrete (compressive and flexural strength, de-icing salts and frost resistance). The measurement results met all the requirements of Technical Standards (Table 1, 2). Positive conclusions were evaluated also the results of economic field (Ondova et al., 2011).

Table 1: Results of fresh concrete tests

Parameter	Unit	Required value	5 wt. % of FA	10 wt. % of FA	15 wt. % of FA
Consistency	[mm]	S1 (10-40 mm)	30	40	40
Air content	[%]	4.8	6.0	6.4	6.5
Temperature	[°C]	$+5 \leq T \leq +30$	22.5	19.5	19.5

Table 2: Results of concrete composites tests

Parameter	Unit	Time of testing	Required value	5 wt. % of FA	10 wt. % of FA	15 wt. % of FA
Flexural strength	[MPa]	28	4.5	6.6	6.4	6.0
Compressive strength	[MPa]	28	32	44.2	42.4	40.2
De-icing salts resistance - Scaling	[g/m^2]	1	max. 300	90.7	209.1	257.0
Frost resistance - Flexural strength	[MPa]	2	-	6.5	6.2	5.8
		1	-	5.9	5.6	5.1
Frost resistance - index	[%]	-	min 0.85	0.91	0.90	0.88
Frost resistance - Compressive strength	[MPa]	2	-	45.3	42.7	38.2
		1	-	50.6	50.6	42.7

2.1 Environmental assessment

As part of the environmental assessment of harmful elements in human health, the environmental assessment of fly ash as well as CEM 42.5N (content of hazardous elements: Cr^{VI} and ^{40}K, ^{226}Ra, ^{232}Th) were determined. The principle of the determination is given below:

Hexavalent water-soluble chromium

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 content of soluble hexavalent chromium was determined in fly ash leachates, according to STN EN 196-10 (STN EN, 2007). The same amount of fly ash and of re-destilled water (Rodem 6) with conductivity of 5.72 µS/cm and pH of 6.81 was mixed during 15 min at laboratory temperature. The prepared fly ash paste was separated by vacuum filtration through the glass filter with porosity 4 (Morton). The obtained filtrate was adjusted to final volume of 250 mL and the concentration of soluble hexavalent chromium was measured in fly ash leachates by the DR 2800 spectrophotometer (Hach Lange, Germany) at 540 nm (Palascakova et al., 2011).

Radioactivity

Human exposure to ionizing radiation is one of the scientific subjects that attract public attention, since radiation of natural origin is responsible for most of the total radiation exposure of the human population (UNSCEAR, 2000). Measurement of radioactivity was carried out using a detection system EMS-1A SH (Empos) with a multichannel analyzer MC4K with optimized resolutions of 818 V, 4,096 channel and with 0.9 cm of lead shielding and internal lining of 2 mm tinned copper. The emphasis was on the determination of specific activity concentration of ^{226}Ra, ^{232}Th and ^{40}K. The radioactivity of ^{40}K was measured directly through its gamma ray energy peak at 1,460.8 keV, while activities of ^{226}Ra and ^{232}Th were calculated based on the mean value of their respective decay products. Activity of ^{226}Ra was measured using the 351.9 keV gamma rays from ^{214}Pb and the activity of ^{232}Th was measured using the 238.6 keV gamma rays of ^{212}Pb. To assess whether the safety requirements for building materials are being fulfilled, a gamma index proposed by the European Commission (1999) was used. It is defined by Eq(1):

$$I\gamma = \frac{ARa}{300} + \frac{ATh}{200} + \frac{AK}{3000} \tag{1}$$

where ARa, ATh and AK are the specific activities of isotopes ^{226}Ra, ^{232}Th and ^{40}K in the building material.

The limit values depend on the dose criteria, the way and amount of the material and the manner in which it was used. For material used in bulk amounts (concrete) Iγ ≤ 1 as well as superficial and other materials with restricted use (tiles, boards, etc.) Iγ ≤ 6 corresponds to an absorbed gamma dose rate of 1 mSv y-1. Thus the material with Iγ > 6 should be avoided to use as building material, since these values correspond to the dose rates higher than 1 mSv y-1, which is higher than recommended values.

2.2 Life cycle assessment

Life Cycle Assessment (LCA) is a tool that can be used to identify ways to decrease the environmental impact of a product or process and to inform decision makers of the consequences of changes to the product or process. LCA encompasses all aspects of a process or product from “cradle to grave”, including material extraction, transport, production, maintenance, and removal or recycling (Weiland and Muench, 2010). The issue of life cycle assessment of materials is difficult process. Only some indicators (GWP - Global Warming Potential, PEI - Primary energy intensity, AP - Acidification Potential) and one phase of our overall evaluation (Table 3) has been selected for the publication.

GWP - The most common substances contributing to global warming are also defined using the term Global Warming Potential. This parameter is expressed in relation to carbon dioxide (CO2) emissions. GWP defines the contribution of a given substance to global warming in comparison to the contribution of an equal amount of CO2.

PEI - The energy consumed from “cradle to gate” of a product or service is called primary energy content. It is derived accounting for both renewable and non-renewable sources of energy. Oil, natural gas, coal and uranium are defined as non-renewable resources, whereas renewable resources are wood, hydroelectric power, solar and wind energy. The primary, non-renewable energy content - PEI ne - is calculated by adding the gross calorific value of all the non-renewable resources used in the process. Similarly the primary, renewable energy content - PEI e - sums all renewable energy sources used (Estokova et al., 2011).

AP - Acidification occurs primarily through the reaction of nitrous oxides (NOx) and sulphur dioxide with other components in the air such as hydroxyl (radical). The Acidification Potential is a measure of the tendency of a component to become acidified (Sjunnesson, 2005).

In this paper the LCA are very general and approximate, the boundaries were established only in the interval "cradle to gate". The application phase of concrete road cover with and without share of fly ash (15 % wt.) as cement replacement was assessed and compared. Functional unit 1m2 was determined. The calculations of the environmental profiles used input data from the catalogue of an international database of building materials Ecoinvent (Czech database ENVIMAT). Values of chosen indicators were calculated on 1m2 of road.

Table 3: Proposed field of life cycle assessment of fly ash in concrete

LCA phase	Assessed section	Assessed parameters
1. Extraction	Production cost	Manufacturing costs
		Raw materials cost
		Costs to fly ash certification
		Costs of properties modification
	Hazardous elements	Radioactivity: ^{226}Ra, ^{232}Th, ^{40}K
		Hexavalent water-soluble chromium
	Environmental impact	GWP, AP, PEI, POCP, ODP, EP
2. Concrete production	Hazardous elements	Radioactivity: ^{226}Ra, ^{232}Th, ^{40}K
		Hexavalent water-soluble chromium
	Environmental impact	GWP, AP, PEI, POCP, ODP, EP
	Transport and storage	Transport costs
		Optimal distance
		Special container for fly ash
	Hazardous elements	Radioactivity: ^{226}Ra, ^{232}Th, ^{40}K
		Hexavalent water-soluble chromium
3. Disposal / recycling	Concrete recovery	Concrete recovery costs
	Concrete disposal	Concrete disposal costs
		Fly ash disposal costs
	Environmental impact of concrete disposal	GWP, AP, PEI, POCP, ODP, EP

3. Results and Discussion

3.1 Environmental assessment

Results of hazardous elements content is summarized in Table 4. Determination of hexavalent water-soluble chromium as well as of radioactivity (226Ra, 228Th, 40K) of cement CEM I 42.5 N and fly ash meet all the world criteria. For the comparison, the gamma index of concrete composites without (reference sample) and with a 15 %wt. fly ash as substitution of cement were measured. Table 4 presents the additional stabilization formed during the hardening of concrete composites. Gamma index decreased to the value 0.146 (fly ash sample) and 0.140 (reference sample). Based on these results of the environmental assessment is the fly ash suitable for its use as cement substitute in concrete.

Table 4: Summary of toxicity tests

Tested hazardous elements	Unit	Fly ash	CEM I 42.5N	Reference sample	Fly ash sample
Cr^{VI}	mg/kg Cr^{6+}	0.01	2.46	-	-
Radioactivity: ^{226}Ra	[Bq/kg]	39.259	13.081	8.609	6.463
^{232}Th	[Bq/kg]	10.144	19.839	22.258	24.925
^{40}K	[Bq/kg]	698.167	169.232	397.18	199.41
Gamma index I_γ	-	0.411	0.198	0.140	0.146

Hexavalent water-soluble chromium

The total content of Cr^{VI} was measured. The value of CEM I 42.5 N is 2.46 mg/kg and 0.01 mg/kg of fly ash. Taking into account the maximum value for packed cements 2.0 mg per kg of cement (2.0 ppm = 0.0002%) stated by Slovak legislative (Notice no. 275/2004 Collection of Laws), CEM I samples had higher content of chromium (VI). That means this cement is not too dangerous for human health, but it may be distributed only in the fully automated operation without cement contact with the skin of workers. On the other side the fly ash is used without a greater threat to human health.

Radioactivity

The activity concentration index should be used as a screening tool for identifying materials which might be of concern. It is known that the material with Iγ>6 should be avoided to use as building material because it doesn´t meet specified requirements. The results of measured gamma index of CEM I 42.5 N (0.198) and fly ash (0.411) presented in Table 4 showed that both of tested materials have value of Iγ less than 1 and are suitable for use in building construction.

3.2 Life cycle assessment

The results of calculated environmental profile of two different concrete roads are showed in Tables 5, 6. The calculated profile of fly ash concrete road showed a reduction of emissions PEI, GWP as well as AP. Emission reduction per m^2 was: PEI 35.1 MJ/m^2 (2.7 %), GWP 6.54 $kg.CO_2.eq/m^2$ (2.6 %), AP 0.011 $kg.SO_2.eq/m^2$ (2.8 %). In considering the conditions used in the economic assessment (the real construction of Tunnel with length: 698m and width 9m) the result of calculation of real savings will be following: PEI 217663.36 MJ/m^2, GWP 41103.04 $kg.CO_2.eq/m^2$, AP 70.52 $kg.SO_2.eq/m^2$. Currently, in Slovak road construction "Boom", as well as in terms of the impact on the environment, these calculated values are not insignificant. They showed also, that the fly ash as cement replacement in road concrete markedly reduces the negative impact on our environment in evaluated multiple spheres.

Table 5: LCA in "application phase" of concrete roads without fly ash

CR without FA	Density	Thickness	Mass	PEI	GWP	AP
Layer	kg/m^3	mm	kg/m^2	MJ/m^2	kg CO_2eq/m^2	kg SO_2eq/m^2
2nd layer concrete cover	2,445	170	415.7	262.34	48.90	0.08
1st layer concrete cover	2,445	80	195.6	123.45	23.01	0.04
Coated intermediate aggregate - gravel	1,650	50	82.5	5.65	0.23	0.001
Infiltration road spray	1,160	1	1.2	57.54	1.28	0.007
Cement stabilization	1,200	180	216.0	777.26	177.55	0.25
Aggregate 2nd layer - macadam	1,650	150	247.5	30.76	1.09	0.006
Aggregate 1st layer - macadam	1,650	120	198.0	24.61	0.87	0.005
Sum		751	1,356.41	1,281.61	252.94	0.39

Table 6: LCA in "application phase" of concrete roads with fly ash

CR with 15%wt. FA	Density	Thickness	Mass	PEI	GWP	AP
Layer	kg/m^3	mm	kg/m^2	MJ/m^2	kg CO_2eq/m^2	kg SO_2eq/m^2
2nd layer concrete cover	2,280	170	387.6	238.47	44.45	0.08
1st layer concrete cover	2,280	80	182.4	112.22	20.92	0.04
Coated intermediate aggregate - gravel	1,650	50	82.5	5.65	0.23	0.001
Infiltration road spray	1,160	1	1.2	57.54	1.28	0.007
Cement stabilization	1,200	180	216.0	777.26	177.55	0.25
Aggregate 2nd layer - macadam	1,650	150	247.5	30.76	1.09	0.006
Aggregate 1st layer - macadam	1,650	120	198.0	24.61	0.87	0.005
Sum		751	1315.16	1,246.51	246.39	0.379
Difference (reduction)			41.25	35.10	6.54	0.011

4. Conclusions

In the European Union (EU) of the EU 15 (15 countries) the production was about 52 Mt of coal combustions products in 2009 and in the larger EU of 27 member states the total production is estimated to be about 100 Mt. Within the EU, the utilization of fly ash in the construction industry is currently around 48 % and of bottom ash around 45 %, while the utilization for boiler slag is 100 %. In the majority of cases

coal combustions products are used as a replacement for naturally occurring resources and therefore offer environmental benefits by avoiding the need to quarry or mine these resources.
The Slovak brown fly ash produced heat and power plant is useful in road construction too. Thanks to fly ash properties as well as thanks to our obtained results is the fly ash suitable partial replacement (minimal 15 wt. %) for cement in concrete road cover in Slovakia. The results of our study confirm the Slovak fly ash as appropriate resource material. Mechanical characteristics of concrete composites with fly ash fulfil the Slovak and European Technical Standards. Pointed economical benefits present fly ash as gainful alternative for building industry. Values of hazardous substances in fly ash as well as results of environmental profiles show other advantages and potential of fly ash utilization in the field of construction industry as well as in the field of construction materials production.
Based on the results of the processing of comprehensive analysis according to our proposed method in the field of fly ash concrete assessment could be possible to reconsider and modify the strict criteria of Slovak Technical Standards related to Slovak Highway Engineering.

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