ZESZYTY NAUKOWE POLITECHNIKI RZESZOWSKIEJ Nr 283
Budownictwo i Inżynieria Środowiska z. 59 (1/12/I) 2012

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PHOSPHOROUS CONTENT EVALUATION IN CEMENTS IN SLOVAK REPUBLIC IN FRAME OF ECO-LABELLING PROCESS

Phosphorous enters the clinker minerals and negatively affects the phase composition clinker, and thus the quality of cement. In environmental point of view, phosphates coming into the water cause the eutrophication processes. The environmental criteria including phosphorous content for materials and products are stated assessment of type I which determines is the most used evaluation process in Slovak Republic. Cements are one of the building product groups for which the required criteria are stated and the national eco-label is possible to obtain. Cements supplied on the market must fulfil the basic requirements stated by technical norms and regulations in order to achieve certain properties in concrete and human safety. Cements environmental criteria within the certification process include requirements for limit value of phosphorous (less than 3% of P_2O_5). The content of phosphorous expressed as P_2O_5 was in all measured cement samples less than stated limit in eco-labelling process.

1. Introduction

Environmental assessment and labelling of products is a voluntary environmental management tool. The environmental assessment of products should be a factor of importance in term of protection of the environment and human safety and may be performed at different levels with varying degrees of precision, and with special attention directed to different environmental effects, depending on the particular purpose and scope of the study.

There are three types of environmental assessment of building materials used nowadays [1]:

- type I a voluntary, multiple-criteria based, third party program that awards a license that authorizes the use of environmental labels on

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products indicating overall environmental preferability of a product within a particular product category,
- type II informative environmental self-declaration claims,
- type III voluntary programs that provide quantified environmental data of a product, under pre-set categories of parameters set by a qualified third party and based on life cycle assessment, and verified by that or another qualified third party.

Environmental assessment of type I which determines the criteria for materials and products is the most used evaluation process in Slovak Republic [1]. The eco-labelling is realized in Slovakia within the National Program of Environmental Assessment and Eco-labelling, approved by government of Slovak Republic in 1996 and amended in 2004. The national eco-labelling program is based on the Regulation No 880/92/EEC on a Community eco-label award scheme and on the Regulation No 1980/2000 of the European parliament and of the council of 17 July 2000 on a revised Community eco-label award scheme. The methodology of environmental assessment and eco-labelling in Slovakia is stated by law No 217/2007 and No 469/2002 on environmental assessment and eco-labelling and Notice No 258/2003 [2, 3].

The Slovak national eco-label award scheme is designed to:
- promote products which have a reduced environmental impact compared with other products in the same product group,
- provide consumers with accurate and scientifically based information and guidance on products.

Product labelling (eco-labelling) is based on creating a competitive environment in the market between products with comparable characteristics. The process of the evaluation results in eco-labelling, which is performed by an independent third side. The criteria for each product group have been identified on the basis of comprehensive studies of the environmental aspects related to the entire life cycle of the product. The label may be awarded to products which contribute significantly to improvements in relation to key environmental aspects. Eco-label criteria must be established by product group and be based on the product's prospects of market penetration, the technical and economic feasibility of the necessary adaptations and on the potential for environmental improvement. Eco-label certifies that the product is up to specific requirements in terms of environmental protection compared to other products of the same product group. The eco-label certification does not mean that the product has no impact on the environment, but ensures that the product is manufactured friendly manner and affects the environment less than other comparable products on the market [4].

Environmental requirements for products in Slovakia are specified in Notice, which are issued by the Ministry of the Environment of Slovak republic. Today there are seven groups of the building product for which are issued the specific requirements.

Cements are one of the building product groups in Slovak republic for which the required criteria are stated and the national eco-label is possible to obtain [1]. Notice of special requirements for the obtaining of national eco-label Environmentally Friendly Product No 04/2009 for group of cement products [5] characterize the cements as a mineral binder in powder form, which set to become solid when, mixed with water in a hydrating process and is produced from raw materials – limestone and clay. In the Notice, there are stated basic and specific environmental requirements as well as the methods to demonstrate compliance with these requirements.

The basic requirements including the technical standards, universal legislation on the protection of human health, consumer protection, the placing of chemicals and chemical products on the market and on legislation regarding the protection and care of the environment related to the product, its production, use and disposal must be fulfilled for all cements in Slovak republic.

The specific environmental criteria for the cements stated in the Notice are above standard criteria in terms of environmental issues and these specific criteria include [5]:

- the energy consumption limitation for burning process: 3600 MJ/t sinter,
- the alternative of the fossil fuel in combustion process by wastes or alternative fuel is required to be at least of 30% while respecting the requirements for waste incineration in cement furnace,
- carbon monoxide CO emissions must not exceed the value of 2000 mg/m^3 by burning process,
- odors resulting from the use of wastes in production mustn´t burden the surrounding environment and population,
- the maximum value of ^{226}Ra mass activity mustn´t exceed the limit value of 100 Bq/kg and the maximum value of the equivalent activity a_{ekv} mustn´t exceed the limit value of 250 Bq/kg,
- the maximum allowable index of mass activity of natural radionuclides in building products I = 1, in accordance with special regulation,
- the content of phosphorous in cement expressed as phosphorous pentaoxide P_2O_5 must be less than 3%,
- the content of water soluble Cr^{VI} in the packed cements with accordance with STN EN 196-10 must be less than 1,8 mg Cr^{VI} to 1 kg of cement.

The content of chromium in cements produced in Slovak Republic was studied in our previous works [6, 7] and there was exceeded the required limit in case of at about 30% of measured cements. This paper presents the part of the results of the study focused on the phosphorous content in cements produced in Slovakia.

The high content of phosphorous causes the main problem in burning the organic waste rich in organic phosphorus in a cement kiln. These include bone, muscle and entrails of animals processed into meat and bone meal in the autoclave at a rendering plant. Meat and bone meal may be fed to cement kilns scattered in the stream of air or fuel and the particles in the furnace burns spontaneously and ash particles, formed by calcium phosphate, especially in the form of mineral hydroxyl apatite, then react with the clinker in the whole its content [8]. P_2O_5 enters the clinker minerals and negatively affects the phase composition clinker, and thus the quality of cement [9]. In practice, the cement burns so far only the amount of organic waste rich in phosphorus, so a negative effect on the properties of clinker occurred only to a limited extent. Oversized amount of phosphates and nitrogen compounds in water environment cause the rapid growth of plants, especially algae. Excessive growth of certain plants violates the natural biological balance in the water. This process is called eutrophication of water [10].

2. Materials and methods

The most often used types of cements of selected Slovak producers A, B and C was assessed in this study. The cements of type CEM I – Portland cements, CEM II – Portland composite cements, CEM III – Blastfurnace cements and MC – Cement mortar were used for the experiments. The more detailed characteristics of studied cement composition are in Tab. 1.

Table 1. The characteristics of assessed cement types [11]

	Sample	**Type of cement**	**Composition**
Producer **A**	**1**	CEM I 42.5 N	Portland cement – contains only clinker and no other single constituents
	2	CEM II/A-LL 42.5 R	Portland limestone cement contains from 6 to 20% of limestone
	3	CEM II/B-M 32.5 R	Portland composite cement contains slag and limestone
	4	CEM III/A 32.5 N	Blastfurnace cement contains from 36 to 65% of slag
Producer **B**	**5**	CEM I 42.5 N	Portland cement – contains only clinker and no other single constituents
	6	CEM II/B-M 32.5 R	Portland composite cement contains slag and limestone
	7	MC 12.5	Universal cement binder to produce mortars and plasters
Producer **C**	**8**	CEM I 42.5 N	Portland cement – contains only clinker and no other single constituents
	9	CEM II /B-S 42.5 N	Portland composite cement contains slag, fly ash and limestone
	10	CEM III /A 32.5 N	Blastfurnace cement contains from 36 to 65% of slag

Other than for CEM I, the following codes are necessary in order to interpret the cement types: the suffix A means a low level of addition of the mineral addition and the suffix B means a high level of mineral addition. For CEM III blastfurnace cements, suffixes A and B indicate increasing proportions of slag. For the CEM II cement type, codes for the second main constituent (for example: blastfurnace slag, silica fume, pozzolana, fly ash) are specified as follows: L or LL – limestone (LL means high-purity limestone), S – blastfurnace slag, M – two or more of the constituents. The standard strength classes of studied cements based on the minimum 28-day mortar were 32,5 and 42,5 MPa. Additionally, early strength development was indicated by a suffix N (Normal early strength) and R (High early strength) [11].

The cement samples were prepared as pressed pellets with diameter of 32 mm by mixing of 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 10 tons. The chemical composition of cements were then determined by X-ray fluorescence spectrometry using SPECTRO iQ II (Ametek, Germany) with silicon drift detector SDD 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 samples were measured during 300 s at voltage 25 kV and 50 kV respectively and at current of 1,0 mA and 0,5 mA under helium atmosphere by using standardized method of fundamental parameters for cement pellets.

The selected cement samples were tested for phosphorous releasing into the water environment in accordance with STN EN 196-10 Methods of cement testing (Appendix C) [12]. Cement sample was prepared by mixing the same mass of cement and ultra-pure water (Rowapur 8) with conductivity of 5,72 μS/cm and pH of 6,81 during 15 minutes at laboratory temperature. The prepared cement 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 content of the phosphorous in cement leachates was measured by spectrofotometry by using Colorimeter DR/890 (Hach Lange, Germany).

3. Results and discussion

The chemical composition of studied Slovak producer’s cement samples measured by XRF spectroscopy is in Tab. 2 and it is similarly to the chemical composition of the ordinary Portland cements. The measured phosphorous pentaoxide average concentrations are summarized in Tab. 3.

The phosphorous pentaoxide content vary from 0,04% mass to 0,64% mass. The highest concentration of phosphorous pentoxide was measured for the sample 2 of producer A (CEM II/A-LL 42.5 R – Portland limestone cement). The least content of phosphorous pentoxide was measured for the sample 7 of producer B (MC 12.5 – Universal cement binder to produce mortars and plasters).

Table 2. Chemical composition of the studied cement samples [% mass]

Oxides [% mass]	Producer A				Producer B			Producer C		
	1	2	3	4	5	6	7	8	9	10
MgO	1,60	2,04	2,19	4,89	2,10	2,30	1,96	3,82	5,62	6,13
Al_2O_3	4,19	4,68	4,51	5,50	4,31	4,99	2,09	4,29	5,46	5,39
SiO_2	18,59	19,07	19,17	26,72	19,84	17,19	9,20	19,31	26,03	28,60
SO_3	3,31	3,10	3,16	2,25	2,96	2,61	2,17	3,26	3,22	3,34
Cl	0,04	0,04	0,02	0,02	0,05	0,04	0,03	0,02	0,01	0,01
K_2O	1,16	1,08	1,01	0,82	0,59	0,43	0,20	0,53	0,54	0,51
CaO	55,62	57,57	52,76	49,15	62,05	55,07	56,82	56,62	52,85	48,04
TiO_2	0,21	0,22	0,21	0,25	0,26	0,47	0,14	0,21	0,30	0,23
MnO	0,03	0,04	0,07	0,24	0,17	0,11	0,04	0,38	0,45	0,43
Fe_2O_3	2,66	2,77	2,28	1,63	3,01	2,44	1,60	3,30	2,46	1,58

Table 3. P_2O_5 content in studied cement samples

Sample	Type of cement	P_2O_5 [% mass]
1	CEM I 42.5 N	0,58
2	CEM II/A-LL 42.5 R	0,64
3	CEM II/B-M 32.5 R	0,43
4	CEM III/A 32.5 N	0,37
5	CEM I 42.5 N	0,09
6	CEM II/B-M 32.5 R	0,08
7	MC 12.5	0,04
8	CEM I 42.5 N	0,09
9	CEM II /B-S 42.5 N	0,08
10	CEM III /A 32.5 N	0,05

When comparing to the specific requirements in the process of Slovak eco--labelling, where the maximum value of phosphorous content in cements is 3% mass of P_2O_5 [5], the measured values of phosphorous pentoxide content were several fold lower than eco-labelling limit for all measured samples. So these cements fulfill the eco-labelling requirements related to the concentration of phosphorous in cements.

The comparison of phosphorous pentaoxide content in cements samples of type CEM I produced by various producers is illustrated in Fig. 1, Fig. 2 illustrate the comparison of the P_2O_5 content in CEM II samples and Fig. 3 presents the P_2O_5 content in CEM III cements samples.

The highest values of phosphorous pentoxide content were measured in cements of producer A. Lower values of the content of phosphorous pentoxide were measured in cements from producers B and C. That means that the content of phosphorous pentoxide depends on producing of these cements and especially depends on burning of the organic waste rich in organic phosphorus in a cement kiln.

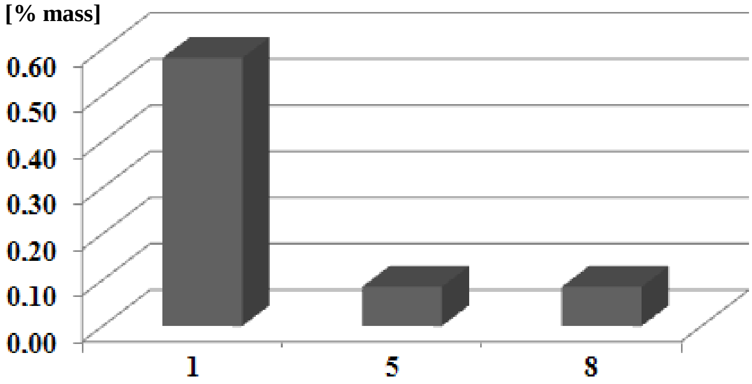

Fig. 1. Phosphorous content expressed as P_2O_5 in CEM I cements

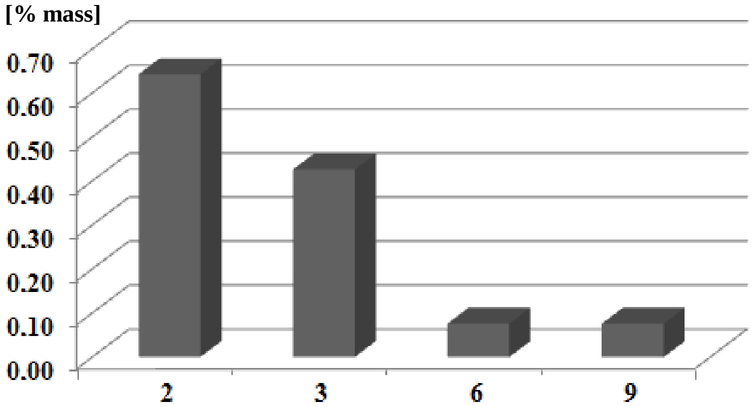

Fig. 2. Phosphorous content expressed as P_2O_5 in CEM II cements

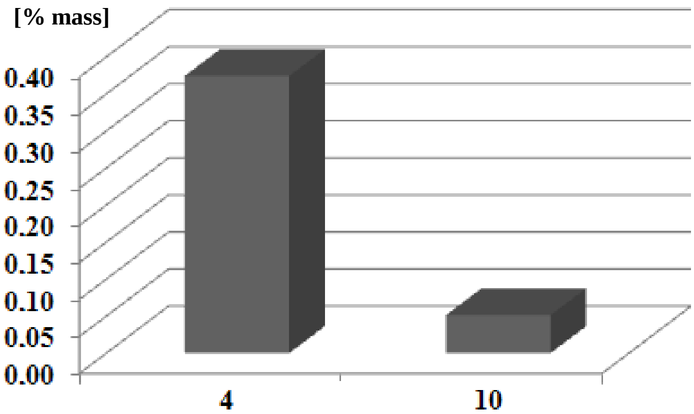

Fig. 3. Phosphorous content expressed as P_2O_5 in CEM III cements

The cements samples of Slovak producer C with low phosphorous content (samples 8, 9 and 10) were chosen for study of phosphorous leaching into the water environment. The measured concentrations of phosphorous expressed as P_2O_5 in water leachates range from 1,123 mg/l to 1,558 mg/l. The highest concentration of phosphorous was measured for the sample 9 (CEM II/B-S 42.5 N – Blastfurnace cement). The least content of phosphorous was measured for the sample 10 (CEM III/A 32.5 N – Blastfurnace cement). The comparison of phosphorous concentrations in water leachates are in Fig. 4.

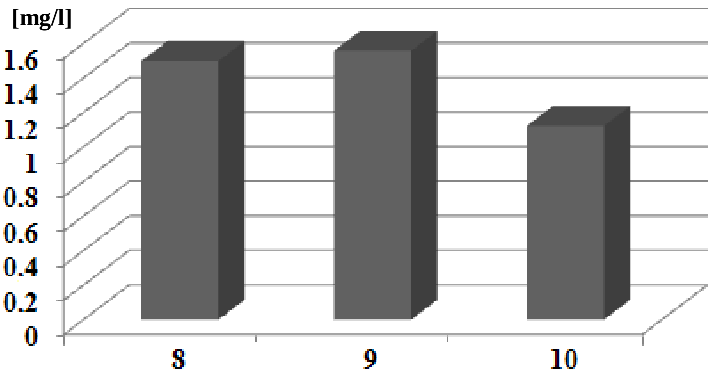

Fig. 4. Phosphorous (P2O5) concentrations in water leachates

Measured phosphorous concentrations in water leachates were counted over to the mass content related to the cement samples and compares to the initial mass content of phosphorous pentaoxide in cement samples. Comparison of phosphorous in cement pellets and water-soluble phosphorous in cement leachates is in Tab. 4.

Table 4. Phosphorous pentaoxide content in cement pellets and in cement leachates

P_2O_5 [mg/kg]	Sample		
	8	9	10
Pellets	852	763	513
Water leachate	14,98	15,58	11,23
Leaching rate [%]	1,75	2,04	2,19

The results of measurements of phosphorus content in water leachates showed that only a small part of phosphorous was extracted from the cement into the water environment. The leaching rate of phosphorous pentaoxide varies from 1,75% (sample 8) to 2,19% (sample 10). The comparison of leaching rate of phosphorous from cements for studied samples is illustrated in Fig. 5.

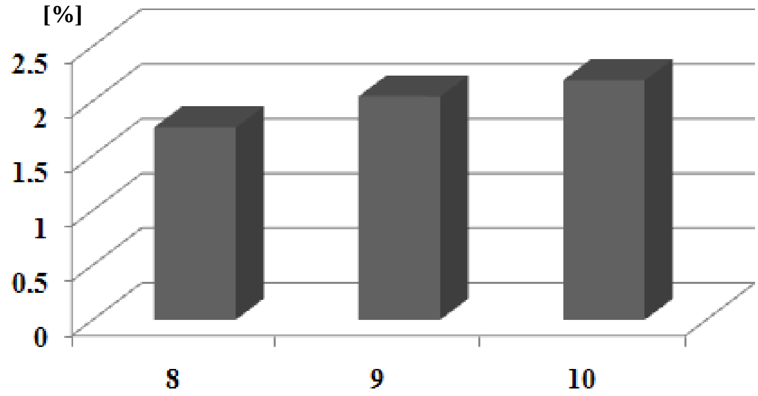

Fig. 5. Comparison of the leaching rate for the cement samples CEM I, CEM II and CEM III

The least leaching rate of phosphorous was measured for CEM I 42.5 N – Portland cement, the highest leaching rate was found out for the sample of CEM III/A 32.5 N – Blastfurnace cement. To make the relevant conclusion the more extended investigation is needed and is still in progress.

4. Conclusion

Summarizing the results of phosphorous concentration monitoring in selected types of cements, all of the assessed cements fulfill the eco-labelling requirements related to the phosphorous content. The content of phosphorous in cements does not seem to be a problem regarding to the process of eco-labelling in Slovakia, in contrast to the chromium (Cr^{VI}) for which the required concentration value is exceeded in 33% of studied samples [7].

The research has been carried out within the project NFP 26220120037 Centre of excellent integrated research of the progressive building structures, materials and technologies and supported from the European Union Structural funds and project No 2/0166/11 of the Science Grant Agency of Slovak Republic.

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