CHEMICAL ENGINEERING TRANSACTIONS
VOL. 26, 2012
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Guest Editors: Valerio Cozzani, Eddy De Rademaeker

ISBN 978-88-95608-17-4; **ISSN** 1974-9791
DOI: 10.3303/CET1226013

Content of Chromium and Phosphorus in Cements in Relation to the Slovak Cement Eco-Labelling

Adriana Eštoková*[a], Lenka Palaščáková[a]

[a]Technical University of Košice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovakia
adriana.estokova@tuke.sk

Cement meaningly affects the environment not only during its production, but also in the process of its consumption causing a negative impact on both the environment and human health.
The paper aims to present the results of assessment of the content of water soluble hexavalent chromium and phosphorous in cements commonly used in the Slovak Republic. Cement samples of various types (CEM I - CEM V) of the significant Slovak producers were taken into the evaluation.
The leaching of chromium was investigated in water environment by using the standard testing methods including the chromium concentrations determination by spectrometry. The content of phosphorous in cements was determined by X-ray fluorescence analysis.
The content of hexavalent chromium in observed samples ranged from 0.46 to 6.38 mg/kg of cement. The measured concentrations were compared to the eco-labelling limit in Slovakia and in 53 % of samples the concentration of hexavalent chromium was higher than the limit value. The content of phosphorous expressed as P_2O_5 varied from 0.04 to 0.64 % (mass) which was less than stated limit in the eco-labelling process.

1. Introduction

Environmental assessment and products labelling are one of environmental management tools. Environmental labels and declarations provide information about a product or service in terms of its overall environmental character, a specific environmental aspect, or any number of aspects. There are several types of environmental assessment of building materials used nowadays. The most comprehensive approach is based on the LCA analysis (De Benedetto and Klemes, 2008).
The environmental labelling program is a voluntary, multiple-criteria-based third party programme that awards a licence which authorizes the use of environmental labels and products indicating overall environmental benefits of a product within a particular product category based on the life cycle considerations. The objective of environmental labelling programmes is to contribute to a reduction in the environmental impacts associated with products; through the identification of products that meet specific eco-labelling programme criteria for overall environmental suitability (STN EN ISO, 1999).
The Slovak eco-labelling programme is under guarantee of Ministry of the Environment of the Slovak Republic. There are six groups of building products for which the specific environmental criteria are issued. The Slovak national eco-label “Environmentally Friendly Product” may be obtained if the product meets the specific environmental criteria stated (Palaščáková et al., 2011).
Cements are one of the building product groups for which the required criteria are stated in the Slovak Republic. The basic requirements for cements in the Slovak eco-labelling process include the technical standards and legislation related to the protection of human health compliance.

Please cite this article as: Estokova A. and Palascakova L., 2012, Content of chromium and phosphorus in cements in relation to the slovak cement eco-labelling, Chemical Engineering Transactions, 26, 75-80 DOI: 10.3303/CET1226013

Environmental criteria for cements include the energy consumption limitation for burning process (3600 MJ/t sinter), at which the alternative fuels portion is required to be at least of 30 %. Carbon monoxide CO emissions must not exceed the value of 2000 mg/m^3 by burning process. Both the mass radium ^{226}Ra activity value of 100 Bq/kg and equivalent radium activity value of 250 Bq/kg are stated as a maximum limit. The other requirements are concerned to phosphorous (less than 3 % of P_2O_5) and chromium contents (1.8 mg $Cr^{(VI)}$ to 1 kg of cement) (Palaščáková et al., 2011).
Chromium is present in raw materials used for the production of cement, especially in iron agents and clay, but also in limestone and various fuels. Naturally occurring chromium (III) is not initially harmful, since it is chemically stable. Only at high temperatures occurring in cement rotary kilns, inert trivalent chromium oxidizes to form reactive hexavalent chromium (Roskovic et al., 2011). This form of chromium in cement is harmful and having a very high water solubility can easily come into contact with the skin of masons. Hexavalent chromium is both carcinogenic and allergic, and it has also been found to promote the development of lung cancer (Wang et al., 2011). As reported (Frias and Sánchez de Rojas, 2002), the concentrations of hexavalent chromium in cements varied in a wide range from 0.9 to 24 ppm and were depending on several factors (Bentaieb et al., 2011) .
The high content of phosphorous causes the main problem in burning the organic waste rich in organic phosphorus in a cement kiln. This includes bones, muscles 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 burn spontaneously in the furnace and ash particles, formed by calcium phosphate, especially in the form of mineral hydroxyl apatite, then react with the clinker in its whole content (Staněk and Sulovský, 2009). P_2O_5 enters the clinker minerals and negatively affects the phase composition clinker, and thus the quality of cement (Lin et al., 2009). In practice, the cement burns only the amount of organic waste rich in phosphorus, so a negative effect on the properties of clinker occurred only to a limited extent (Winter, 2009). From an environmental point of view, phosphates coming into the water cause eutrophication process.
This paper is aimed at the evaluation of the content of water soluble hexavalent chromium and phosphorus in various types of Slovak cements in relation to the Slovak eco-labelling process.

2. Materials and methods

The content of phosphorous and soluble hexavalent chromium was assessed in the most frequently used types of cements of selected Slovak producers (*Table 1*). More than three samples of each type of cement were tested and the average values of phosphorous and hexavalent chromium were used for the evaluation.

Table 1: The characteristics of assessed cement types (STN EN, 2002)

Type of cements	Characteristic
CEM I	Portland cement - contains mainly clinker and no other single constituents
CEM II/A-S	Portland-slag cement: Portland cement with up to 20 % of blastfurnace slag
CEM II/B-S	Portland-slag cement: Portland cement with up to 35 % of blastfurnace slag
CEM II/A-LL	Portland-limestone cement: Portland cement with up to 20 % of limestone
CEM II/B-M	Portland composite cement: Portland cement with up to 35 % of other single constituents (blastfurnace slag, silica fume, puzzolana, fly ash, limestone, burnt shale)
CEM III	Blastfurnace cements: Portland cement with more than 35 % of blastfurnace slag
CEM V	Composite cements: Portland cement with more than 35 % of blastfurnace slag and pozzolana or fly ash

The basic chemical composition of tested cements as well as the phosphorous content was investigated by X-ray fluorescence analysis 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 of 25 kV and 50 kV respectively, at current of 0.5 and 1.0 mA under helium atmosphere by using the standardised method of fundamental parameters for cement pellets. Cement samples were prepared as pressed tablets of diameter 32 mm by mixing 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m^2.

The content of soluble hexavalent chromium was determined in cement leachates. Cement leachates were prepared in accordance to STN EN 196-10 (STN EN, 2007). The same amount of cement and of ultra-pure 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 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 concentration of soluble hexavalent chromium was measured in cements leachates by the DR 2800 spectrophotometer (Hach Lange, Germany) at 540 nm.

The prepared tablets were studied by X-ray fluorescence spectrometry. The content of phosphorous in cements was determined by using SPECTRO iQ II (Ametek, Germany).

3. Results

The percentage of basic components of tested cement samples measured by XRF spectroscopy is shown in *Table 2*.

Table 2: The basic chemical composition of studied cements

Oxides (%)	CEM I	CEM II/A-S	CEM II/B-S	CEM II/A-LL	CEM II/B-M	CEM III	CEM V
MgO	1.54–3.82	4.23–4.72	5.62–5.83	2.04–2.05	2.19–2.35	4.88–8.45	3.75–4.94
Al_2O_3	3.87–4.39	4.31–4.80	5.46–5.57	4.68–4.68	4.51–5.08	5.13–7.20	7.18–9.57
SiO_2	17.8–19.8	20.9–22.2	26.0–26.4	19.0–19.2	17.1–19.1	26.7–36.7	37.9–39.1
SO3	2.83–3.31	3.04–3.08	2.85–3.22	3.09–3.17	2.61–3.23	1.75–3.34	2.34–2.58
K_2O	0.45–1.16	0.53–0.55	0.54–0.56	1.08–1.09	0.43–1.01	0.51–0.82	0.92–1.01
CaO	54.2–63.6	55.8–56.4	52.8–53.1	57.5–58.2	52.7–57.7	46.1–52.4	40.0–42.6
TiO_2	0.21–0.26	0.21–0.22	0.26–0.30	0.21–0.22	0.21–0.47	0.23–0.37	0.24–0.32
MnO	0.03–0.38	0.35–0.36	0.38–0.45	0.04–0.33	0.07–0.33	0.24–0.49	0.35–0.38
Fe_2O_3	2.63–3.29	2.64–2.70	2.46–2.50	2.77–2.70	2.28–2.50	1.13–2.08	2.06–5.21

The chemical composition of investigated cement samples correlate to the standard chemical composition of particular cement types (Lam et al., 2010). The percentage of the oxides depends on both raw materials and constituents.

The results of the content of soluble hexavalent chromium in tested cements measured by spectrometry are shown in *Table 3*.

Table 3: The content of $Cr^{(VI)}$ (mg/kg) in cements

Type of cements	Minimum value	Maximum value	Mean
CEM I	0.23	3.22	2.15
CEM II/A-S	0.82	1.55	1.17
CEM II/B-S	0.26	2.31	1.01
CEM II/A-LL	0.73	1.28	1.01
CEM II/B-M	0.68	1.81	1.08
CEM III	0.38	1.45	0.79
CEM V	0.50	0.52	0.51

The chromium (VI) mean concentrations vary from 0.51 mg/kg of cement to 2.15 mg/kg. The highest concentration of chromium (VI) was measured for the samples CEM I - Portland cement. The least content of chromium (VI) was measured for the samples of CEM V - Composite cement.

The measured values correlate with those of foreign authors' works, where, for example hexavalent chromium concentrations in cements measured in Japan (Yamaguchi et al., 2006) and Australia (Tandon and Aarts, 1993) were determined in the range 0.2 to 20 mg/kg. Similarly, the concentrations of hexavalent chromium in cements in Spain ranged from 0.9 to 24 mg/kg of cement (Frias and Sánchez de Rojas, 2002). The results of authors (Potgieter et al., 2003) showed that the Cr (VI) form represents 30 % – 80 % of the total chromium content in cement clinker.
The average values of soluble chromium (VI) for each type of cements were compared to the requirement in the Slovak eco-labelling process – 1.8 mg chromium (VI) per 1 kg of cement (1.8 ppm) – see *Figure 1*.

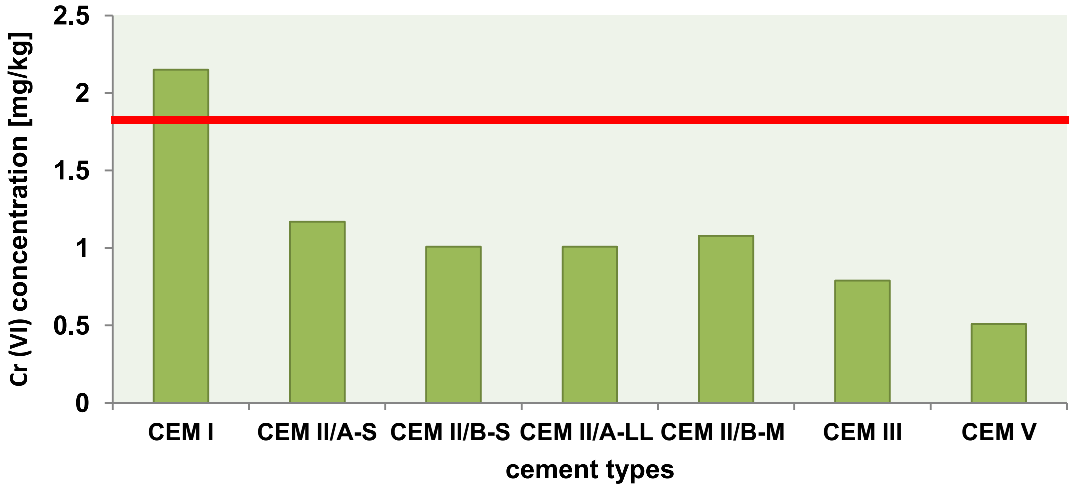

Figure 1: Comparison of the measured water-soluble content of chromium (VI) in cement types to the Slovak eco-labelling limit

The measured values of chromium (VI) content in commonly used cement types were higher than the eco-labelling limit only in CEM I cement type and therefore these cements couldn't obtain the Slovak national eco-label.
The concentration of soluble chromium (VI) in cement depends on the clinker content in cement. The sample of CEM I - Portland cement, which has the highest content of chromium (VI), contains only clinker as an important natural source of chromium. CEM III and CEM V cement types contain the least content of clinker but they contain high amount of slag and therefore the concentration of soluble chromium (VI) is lower in these samples.
The measured diphosphorous pentoxide mean concentrations are summarized in *Table 4*.

Table 4: The content of P_2O_5 (%) in cements

Type of cements	Minimum value	Maximum value	Mean
CEM I	0.0756	0.5812	0.2193
CEM II/A-S	0.0806	0.0865	0.0836
CEM II/B-S	0.0763	0.0805	0.0784
CEM II/A-LL	0.5907	0.6426	0.6167
CEM II/B-M	0.0761	0.4263	0.1963
CEM III	0.0513	0.3742	0.1810
CEM V	0.0628	0.1412	0.1020

The mean values of diphosphorous pentoxide were detected in the range 0.0784 % (mass) to 0.6167 % (mass). The highest concentration of diphosphorous pentoxide was measured for the samples CEM II/A-LL – Portland limestone cement. The least content of diphosphorous pentoxide was measured for the samples CEM II/B-S – Portland-slag cement.

When comparing to the specific requirements in the Slovak eco-labelling process (max 3 % (mass) of P_2O_5), the measured percentage of diphosphorous pentoxide content was several fold lower than the eco-labelling limit for all measured samples. Thus these cements meet the eco-labelling requirements related to the concentration of phosphorous in cements.

Three types of cements (CEM I, CEM II and CEM III) were chosen to study phosphorous leaching into water environment. The measurement results of phosphorus content in water leachates showed that only approximately 2 % of phosphorous was extracted from the cement into water environment. The least leaching rate of phosphorous was measured for CEM I – Portland cement, the highest leaching rate was found out for the sample of CEM III – Blastfurnace cement.

4. Conclusion

The measured concentration of water-soluble chromium (VI) in selected types of cements didn't excess the limit value (except CEM I cements) required in the Slovak eco-labelling process. Although the technical standard for the measurements in eco-labelling is stated, many authors refer that this detected concentration of hexavalent chromium represents only a small part of the real content of hexavalent chromium in cement and cement materials.

The evaluated concentrations of phosphorous in tested types of cements reached lower values than 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.

Acknowledgements

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.

References

Bentaieb N., Lachemet A., Zirour R., Belaadi S., Frances C., 2011, Thermal analysis of composite cements, Chemical Engineering Transactions, 24, 685-690, DOI: 10.3303/CET1124115.

De Benedetto L., Klemes J., 2008, LCA as environmental assessment tool in waste to energy and contribution to occupational health and safety, Chemical Engineering Transactions, 13, 343-350.

Frias M., Sánchez de Rojas M. I., 2002, Total and soluble chromium, nickel and cobalt content in the main materials used in the manufacturing of Spain commercial cements, Cement and Concrete Research, 32, 435– 440.

Lam H. K., Barford J. P., McKay G., 2010, Utilization of incineration waste ash residues as Portland cement clinker, Chemical Engineering Transactions, 21, 757-762 DOI: 10.3303/CET1021127.

Lin K. L., Lin D. F., Luo H. L., 2009, Influence of phosphate of the waste sludge on the hydration characteristics of eco-cement, Journal of Hazardous Materials, 168, 1105-1110.

Palaščáková L., Eštoková A., Bálintová M., Petriláková A., 2011, Assessment of the content of chromium (VI) in selected types of cement as a part of cement eco-labelling, Pollack Periodica, 6, 123-129 DOI: 10.1556/Pollack.6.2011.3.12.

Potgieter S. S., Panichev N., Potgieter J. H., Panicheva S., 2003, Determination of hexavalent chromium in South African cements and cement-related materials with electro thermal atomic absorption spectrometry, Cement and Concrete Research, 33, 1589-1593.

Roskovic R., Oslakovic I.S., Radic J., Serdar M., 2011, Effects of chromium (VI) reducing agents in cement on corrosion of reinforcing steel, Cement and Concrete Composites, 33, 1020-1025.

Staněk T., Sulovský P., 2009, The influence of phosphorous pentoxide on the phase composition and formation of Portland clinker, Article Materials Characterization, 60, 749-755.

STN EN ISO, 1999, STN EN ISO 14024: Environmental labels and declarations, Type I environmental labelling, Principles and procedures, Slovak Standard Institute, Bratislava, Slovak Republic (in Slovak).
STN EN, 2002, STN EN 197-1: Cement Part 1: Composition, specifications and conformity criteria for common cements, Slovak Standard Institute, Bratislava, Slovak Republic (in Slovak).
STN EN, 2007, STN EN 196-10: Methods of testing cement. Part 10: Determination of the water soluble chromium (VI) content of cement, Slovak Standard Institute, Bratislava, Slovak Republic (in Slovak).
Tandon R. and Aarts B., 1993, Chromium, nickel and cobalt contents of some Australian cements, Contact Dermatitis, 28, 201– 205.
Wang B. J., Wu J. D., Sheu S. C., Shih T. S., Chang H. Y., Guo Y. L., Wang Y. J. and Chou T. C., 2011, Occupational hand dermatitis among cement workers in Taiwan, Journal of the Formosan Medical Association, 110, 775-779.
Winter N., 2009, Understanding Cement: Introduction to cement production, hydration and deleterious processes in concrete. WHD Microanalysis Consultants Ltd, United Kingdom.
Yamaguchi O., Ida M., Uchiyama Y., Hanehara S., 2006, A method for the determination of total Cr(VI) in cement, Journal of the European Ceramic Society, 26, 785 – 790.