The influence of the usage of secondary fuels for Portland clinker production on the emission value of heavy metals from cement and concrete

D Kalarus¹, A Tkocz¹, B Duszak¹ and M Najduchowska¹

¹Sieć Badawcza Łukaszewicz Instytut Ceramiki i Materiałów Budowlanych w Warszawie, Oddział Szkła i Materiałów Budowlanych w Krakowie, Poland
E-mail:d.kalarus@icimb.pl

Abstract. The influence of secondary fuels components used for Portland clinker production on emission value of heavy metals is presented in this paper. Analyses and studies of hazardous substances emission (heavy metals) from cements and concretes were conducted according to standards developed by Technical Committee CEN TC 351. The contents of following heavy metals were analyzed: Cr, Zn, Pb, Co, Ni, Cu, Sr, Ba and P in secondary fuels used by cement industry in Poland for Portland clinker production. Total heavy metal contents in cements and their leaching from cements CEM I were studied. Leaching of heavy metals from CEM I-based concretes to environment was also determined. Obtained tests results allow to conclude that changes in technology of cement clinker production leading to the usage of waste materials and secondary fuels does not cause an increase in heavy metals emission in level, which requires qualifying cement as material, which has to be regularly controlled for harmfulness on man and natural environment.

1. Introduction

Cretaceous, Jurassic and Triassic limestone rocks, marl, clay, as well as materials replaced “low” raw materials, which are industrial waste are used for Portland clinker production in Poland. Cement industry replaces conventional fuels, principally coal, by secondary fuels, mainly to reduce costs of clinker production, waste utilization and because of the need to reduction of CO₂ emission. According to the data of Polish Cement Association, in 2015, about 57.5% of thermal energy needed to burn clinker in rotary kilns came from combustion of secondary fuels [1]. Heat from secondary fuels in some cement plants in 2019 was even 85%, and principally old car tires, crushed and impregnated municipal waste, used oils, rubber powder, coal shale, sawdust and biomass were used [2]. Heavy metal contents in secondary fuels used for Portland clinker production in Poland after 2002 are given in Table 1. The data presented in Table 1 concerns minimum and maximum heavy metal contents for individual group of secondary fuels. Studies of heavy metal contents in secondary fuels use for Portland clinker production show large differences in the concentration of certain elements, especially: zinc, lead, manganese, cadmium, nickel and copper. Studies results also shown large differences in heavy metals concentration in individual samples of a given type of secondary fuel.

The usage of secondary fuels and post industrial recycled materials for clinker production raises concerns around increasing content of these ingredients in cement and their increasing emission from cement-based materials [4-7]. Presented issue suggests that studies on the effects of cement and
cement-based materials on man and natural environment are very important. Numerous research [5-7] and collected documentation [8, 9] confirm great immobilization of heavy metals in cement matrix and very high level of their retention for most elements, thus ecologically safe impact of cement-based products on the environment.

Table 1. Heavy metal contents in secondary fuels [3]

| Component | Type of secondary fuel | Municipal waste | Impregnated waste | Tires | Sawdust |
|-----------|------------------------|-----------------|-------------------|-------|---------|
| Cr        |                        | 70-2745         | 840-8200          | 130-640 | 130-200 |
| Zn        |                        | 245-9000        | 700-5300          | 1300-3500 | 1450-2200 |
| Cd        |                        | 8-60            | 4-20              | 1-20 | 9-15 |
| Pb        |                        | 10-240          | 270-2200          | 3-760 | 14-45 |
| Co        |                        | 30-100          | 14-25             | 5-207 | 15-38 |
| Ni        |                        | 7-790           | 17-1450           | 17-380 | 28-75 |
| Mn        |                        | 70-1660         | 91-1670           | 6-890 | 918-2460 |
| V         |                        | 10-120          | 170-390           | 1-60 | 14-19 |
| Cu        |                        | 30-12800        | 165-1780          | 10-300 | 54-78 |
| Sr        |                        | 120-420         | 175-400           | 240-310 | 550-700 |
| Ba        |                        | 100-990         | 245-1450          | 270-1480 | 2170-3690 |

Development of test methods concerning the release of dangerous substances (heavy metals) from cement-based materials have been performed from 2005 and coordinated by European Technical Committee CEN/TC 351 „Assessment of release of dangerous substances”. Technical Committee presented three test methods of the emission of dangerous substances from monolithic cementitious materials on natural environment [10]. This issue is continued for building materials and construction products by the same Technical Committee CEN TC 351: "Dangerous substances in construction" in Working Group WG 1 "Construction products - Assessment of release of dangerous substances". The aim of this work was determination of the effect of cement and cement-based materials (concrete) on man and natural environment and their influence on drinking water quality.

2. Experimental part

Raw materials and secondary fuels used for Portland clinker production were tested. Immobilization degree of heavy metals in cement and effects of heavy metals emission from cement produced with very high participation of secondary fuels were analyzed. Assessment of release of dangerous substances from concrete was conducted according to standards developed by Technical Committee CEN TC 351.

3. Scope of the study

Studies on raw materials for Portland clinker production and cements included:

- determination of total heavy metal contents in raw mix, conventional fuel, secondary fuels,
- determination of total heavy metal contents in cement,
- determination of leaching of heavy metals from cement (concentration of compounds soluble in water)
- determination of heavy metals emission from concrete.

3.1. Materials

Raw materials, conventional fuel, secondary fuels and Portland clinker were analytical samples, prepared and delivered by cement plant. Leaching tests of heavy metals released from cement were conducted for material produced by grinding in a laboratory mill. It was Portland clinker (95% by mass) with natural gypsum (5% by mass). Obtained cement sample had fineness below 90 µm and
specific surface area of 3450 cm$^2$/g. Concrete, which was studied for environmental impact, was prepared in laboratory from aforementioned cement.

3.2. Methods
Following tests methods were used:

- Digestion of samples according to PN-EN 13657 [11],
- Total heavy metal contents in solution were conducted according to PN-EN 11885 [12],
- Leaching of heavy metals from cement was determined in the eluate from cement with water in a proportion of 1:10 according to PN-EN 12457-2 [13],
- Releasing of heavy metals from concrete is determined in the eluate obtained by leaching of concrete cube size 10x10x10 cm with water, with proportion of water content to concrete cube surface of 80 dm$^3$/m$^2$. Leaching of heavy metals from concrete cubes was determined after storage in water for 1, 2, 7, 16, 32 and 64 days, according to Dutch standard NEN 7375 "Leaching characteristics - determination of the leaching of inorganic components from moulded or monolithic materials with a diffusion test - solid earthy and stony materials". Concretes were prepared and seasoning according to CEN/TR 15678 "Concrete. Release of regulated dangerous substances into soil, groundwater and surface water. Test method for new or unapproved constituents of concrete and for production concretes",
- Concentration of elements in solutions and eluates were performed by the ICP-OES method,
- All results of heavy metal contents in analyzed materials refer to analytical samples ground below 90 µm and dried at temperature of 105°C.

4. Results
Conducted tests of total heavy metal contents in raw materials, fuels and cement concluded following elements: Cr, Zn, Cd, Pb, Co, Ni, Mn, Cu, Sr, Ba and P. Assessment of the effect of cement and concrete on natural environment was analyzed for the same sequence of metals.

4.1. Heavy metal contents in studied materials
Heavy metal contents in raw mix, conventional fuel, secondary fuels used for Portland clinker production in cement plant are given in Table 2.

| Element | Raw mix | Calcareous fly ash | Secondary fuel | Coal dust |
|---------|---------|--------------------|----------------|----------|
| Cr      | 20      | 101                | 186            | 92       |
| Zn      | 476     | 136                | 782            | 176      |
| Pb      | 61      | 41                 | 145            | 10       |
| Cd      | 1.6     | 4                  | 5              | 1        |
| Co      | 2.8     | 23                 | 11             | 11       |
| Ni      | 11      | 57                 | 31             | 29       |
| Mn      | 254     | 201                | 145            | 48       |
| V       | 21      | 158                | 15             | 47       |
| Cu      | 12      | 33                 | 975            | 47       |
| Sr      | 760     | 592                | 73             | 143      |
| Ba      | 46      | 165                | 550            | 141      |
| P       | 289     | 600                | 1665           | 2804     |

Heavy metal contents in raw mix for Portland clinker production result from accumulation of heavy metals in natural raw materials and corrective materials. Increased contents of zinc, lead and
manganese in raw mix are caused by iron–bearing component which was steelmaking dust containing large content of these metals. Calcareous fly ash is enriched in heavy metals. Increased contents in this material concerns manganese, chromium, copper, lead, nickel, vanadium and zinc. Tests results concerning heavy metal contents in secondary fuels shown that these materials have very different contents of some metals, principally: zinc, lead, cadmium, manganese, copper and phosphorus.

4.2. Total heavy metal contents and their leaching from cement

Total heavy metal contents and their leaching from Portland cement CEM I are presented in Table 3. Calculated values of heavy metals retention in cement matrix are also given in Table 3.

| Element | Total content mg/kg | Leaching % | Element retention a % |
|---------|---------------------|------------|-----------------------|
| Cr      | 67                  | 11.06      | 83.49                 |
| Zn      | 824                 | 0.12       | 99.99                 |
| Pb      | 68                  | 0.32       | 99.53                 |
| Cd      | 2.0                 | <0.02      | -                     |
| Co      | 7                   | <0.1       | -                     |
| Ni      | 21                  | 0.12       | 99.43                 |
| Mn      | 407                 | <0.01      | -                     |
| V       | 39                  | 0.14       | 99.64                 |
| Cu      | 138                 | 0.12       | 99.91                 |
| Sr      | 1189                | 182.6      | 84.64                 |
| Ba      | 154                 | 13.4       | 91.30                 |
| P       | 675                 | 0.72       | 99.89                 |

a as % of element content remaining in cement after leaching.

Results presented in Table 3 confirm inconsiderable degree of the leaching of most heavy metals from cement. Leaching of elements from cement, measured for eluate of 1:10 is lower than concentrations required for ground water and sewage waste [14]. Immobilization of heavy metals exceeds 99% for most of them except Sr and Ba. Leaching of chromium from cement without application of chromium reductor, ranges from 15% to 25% of total chromium content [8, 15], while immobilization of zinc, cadmium and lead compounds is practically 100% [8, 9]. High alkalinity of solution causes high increase in solubility of Cr(OH)₃, thus the equilibrium change of reaction towards the chromates formation [14, 15].

4.3. Leaching of heavy metals from concrete

Assessment of the effect of concrete structures on natural environment, thus releasing of dangerous substances (heavy metals) from concrete to soil and ground water was studied according to requirements specified in Construction Products Regulation (CPR) from 2011. According to this Regulation, studies of the releasing of dangerous substances into ground water, marine waters, surface waters or soil should be performed with standards developed by Technical Committee CEN/TC351 WG1. In this paper, leaching measurements of heavy metals from concrete were conducted according to requirements of Technical Specifications developed by aforementioned Committee CEN. Portland cement CEM I, which concentration and leaching characteristics are discussed in p. 4.2, was used. Concrete mix composition and compressive strength are given in Table 4. Average concentrations of heavy metals in eluates and their comparison to requirements for drinking water with category A1, are presented in Table 5.
Table 4. Composition of concrete mix

| Concrete Component contents, [kg/m$^3$] | Compressive strength after 28 days [MPa] |
|----------------------------------------|----------------------------------------|
| Cement                                | 300                                    |
| Standardized sand                     | 609                                    |
| Aggregate 2/8                         | 522                                    |
| Aggregate 8/16                        | 609                                    |
| W/C                                   | 0.6                                    |
|                                        | 42.5                                   |

Table 5. Average concentrations of heavy metals in eluates from concrete stored in water

| Element | Component concentrations after storage in water [days] | Requirements for drinking water [mg/dm$^3$] |
|---------|--------------------------------------------------------|--------------------------------------------|
|         | 1           | 2           | 7           | 16          | 32          | 64          | mg/dm$^3$ | mg/dm$^3$ |
| Cr      | 0.021       | 0.024       | 0.023       | 0.026       | 0.022       | 0.025       | 0.05      |            |
| Zn      | 0.006       | 0.006       | 0.005       | 0.007       | 0.007       | 0.009       | 3         |            |
| Cd      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | 0.005     |            |
| Pb      | 0.025       | 0.028       | 0.031       | 0.026       | 0.024       | 0.023       | 0.05      |            |
| Co      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | -         |            |
| Ni      | 0.016       | 0.023       | 0.016       | 0.017       | 0.018       | 0.019       | 0.05      |            |
| Mn      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | <0.001      | 0.05      |            |
| V       | 0.039       | 0.033       | 0.054       | 0.064       | 0.062       | 0.065       | 1         |            |
| Cu      | 0.003       | 0.003       | 0.003       | 0.002       | 0.002       | 0.001       | 0.05      |            |
| Sr      | 0.085       | 0.173       | 0.386       | 0.467       | 0.663       | 0.728       | -         |            |
| Ba      | 0.024       | 0.026       | 0.046       | 0.042       | 0.057       | 0.064       | 0.1       | -          |
| P       | 0.049       | 0.064       | 0.084       | 0.077       | 0.074       | 0.072       | -         |            |

Data in Table 5 confirms that

- Heavy metal concentrations leached from hardened concrete are extremely low and they are better than requirements for drinking water [16]. Thus it shows that cement is ecologically safe for natural environment.
- Emission factors of metals from concrete (leaching of metals from unit of area), calculated and presented in table, are comparable or lower than values obtained by Verein Deutscher Zementwerke (VDZ) and concerning the assessment of emission of harmful components from concrete [17].

5. Conclusions

The following conclusions can be drawn from obtained results:

- The main source of heavy metals in clinker above geochemical level of raw materials and conventional fuels (coal dust) are some waste raw materials and secondary fuels.
- Secondary fuels have large influence on the increase in heavy metal concentrations in Portland clinker. Ash from secondary fuel introduces significant amounts of chromium, zinc, lead, manganese, copper, barium and phosphorus into the installation.
- Leaching measurements confirmed very high degree of immobilization of heavy metals in cement. Heavy metal retention in cement exceeds 99.5% except strontium and barium. Leaching of chromium from cement without the usage of chromium reductor, ranges from 15% to 25% of total chromium content in cement.
• Heavy metal emission from hardened concrete into water is extremely low. Concentration of analyzed heavy metals in eluates after storage of concrete in water is lower than permissible concentrations in surface waters used to supply people with drinking water.

• Results presented in this paper and extensive documentation collected in Institute of Ceramics and Building Materials [8, 9] shown that changes in technology of cement clinker production leading to the usage of waste raw materials and secondary fuels does not cause an increase in heavy metals emission from concrete.

Acknowledgements
Publication was supported financially under Contract No. 944/P-DUN/2019 from funds of MNiSW intended for dissemination of science (DUN).

References
[1] Informator SPC 2018 Wydawnictwo Stowarzyszenia Produkcentów Cementu, Kraków,
[2] Czajka K, Mokrzycki E, Uliasz-Bocheńczyk A 1999 Paliwa wtórne jako niekonwencjonalne źródła energii. Materiały XIII Konferencji, Sympozjum i Konferencje Nr 39, Wydawnictwo IGSMiE PAN, Zakopane, 17–20 października, str. 233-240, (in polish)
[3] Kalarus D 2010 Źródło metali ciężkich w klinkerze portlandzkim, Energia i środowisko w technologii materiałów budowlanych, ceramicznych, szklarskich i ogniotrwałych, Warszawa–Opole, str. 320, (in polish)
[4] Kanare H M, Howard M, and West P B 1993 “Leachability of Selected Chemical Elements from Concrete”, Proceedings of the Emerging Technologies Symposium on Cement and Concrete in the Global Environment, March 10 and 11, 1993, O'Hare Marriott, Chicago, Illinois, U.S.A., Portland Cement Association, pp. 198-214,
[5] Nocuń-Wczelik W 1997 Immobilizacja metali ciężkich przez fazę C-S-H, CWB, Nr 5, str. 188-191,
[6] Kopia B, Małołępszy J 1994 Metody badań immobilizacji metali ciężkich w materiałach budowlanych, CWG, Nr 5, str. 150-153, (in polish)
[7] Szczerba J, Kalarus D 2001 Obieg metali ciężkich przy utylizacji odpadów pogalwanicznych w piecu obrotowym do produkcji klinkieru portlandzkiego metodą mokrą, Ekologiczno-energetyczne kierunki rozwoju przemysłu materiałów budowlanych, Materiały Międzynarodowej Konferencji Naukowej, Lądek Zdrój–Opole, (in polish)
[8] Kalarus D 2001 Analiza zawartości metali ciężkich w cementach krajowych”, Raport z Programu badawczego – IMMB-SPCiW, Kraków, listopad, 2001, (in polish)
[9] Kalarus D 2015 Oznaczenie zawartości i wymywalności metali ciężkich w cementach krajowych”, Raport końcowy, ICIoMB, OSiMB – SPC, Kraków, grudzień, (in polish)
[10] DAFStb Guideline 2005 Assessment of the effect of construction product on soil and groundwater, Part II: Concrete and Concrete’s Constituent, Deutsches Institut fur Bautechnik – DIBt Berlin, December,
[11] PN-EN 13657 2006 „Charakteryzowanie odpadów. Roztwarzanie dalszego oznaczenia części pierwiastków rozpuszczalnych w wodzie królewskiej”
[12] PN-EN 11885, 2009 „Jakość wody. Oznaczanie 33 pierwiastków metodą atomowej spektrometrii emisyjnej z plazmą wzbudzoną indukcyjnie”
[13] PN-EN 12457-2 2006 „Charakteryzowanie odpadów. Wymywanie. Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów. Część 2: Jednostopniowe badanie porcji przy stosunku cieczy do fazy stałej 10 l/kg w przypadku cząstek materiałów o wielkości cząstek poniżej 4 mm (bez redukcji lub z redukcją wielkości)”
[14] Kalarus D, Nocuń-Wczelik W 2004 Problem redukcji chromu {Cr(VI)} w cementach w świetle Dyrektywy Europejskiej”, Energia i środowisko w technologii materiałów budowlanych, Materiały III Międzynarodowej Konferencji Naukowej, Szczyczyk-Opole, [27–29 września],
[15] Baetzner S, 2002 Ways of analyzing iron(II) sulphate hydrate in respect of its chromate-reducing action in cement, ZKG, Vol. 55, No 7, str. 80-88
[16] Dziennik Ustaw z 2002 nr 204 poz. 1728, in polish
[17] Activity Report 2005, VDZ.