



The 9th International Conference “ENVIRONMENTAL ENGINEERING”

22–23 May 2014, Vilnius, Lithuania

SELECTED PAPERS

eISSN 2029-7092 / eISBN 978-609-457-640-9

Available online at <http://enviro.vgtu.lt>

Section: Environmental protection

Monitoring of heavy metal concentrations in concrete leachates

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Abstract

The papers presents the results of monitoring of various heavy metals leaching from concrete samples based on ordinary CEM I Portland cement without any additives and with silica fume exposed to the sulphate environments. The leaching experiments of compact cement composites proceeded during 180-day period in various aggressive and reference media (H₂SO₄, MgSO₄, fresh water). The concentrations of manganese (Mn), iron (Fe), copper (Cu) and cobalt (Co) ions in liquid media were measured. Only a small part of total metal content was extracted from concrete samples into the liquid media (up to 17% for manganese and 0.3% for iron). Concrete samples with microsilica were found to have better performance in terms of leaching of Mn, Fe, Co and Cu ions than samples without microsilica. The most significant effect of sulphuric acid as aggressive environment causing analyzed metals releasing was confirmed.

Keywords: Cement; concrete; leaching; heavy metals.

Nomenclature

XRF	X-ray fluorescence analysis
Mn	Manganese
Fe	Iron
Cu	Copper
Co	Cobalt

1. Introduction

It is recognized that the cements commonly used in the building industry, especially the blended cements manufactured with mineral additions such as slags or coal fly ashes, are often characterized by a significant presence of heavy metals of particular environmental concern [1]. However, the use of mineral additions in blended cement formulations is an effective way of reducing the Portland cement clinker consumption and then reducing the related CO₂ emission [2].

Heavy metals are leached into water in contact with concrete surfaces by direct dissolution of surface phases and/or diffusion through the pore solution to the concrete surface. The solubility of heavy metals depends on their bonding in the hydration products as well as their ability to form aqueous complexes and precipitate solubility-controlling phases. Consequently, the evaluation of environmental risks cannot be based on the total amounts of trace metals contained in concrete alone, but requires better understanding of the mechanisms involved in leaching. In addition to this, leaching is affected by the actual environmental conditions at the surface of concrete structural components [3]. These include exposure to CO₂ or various aggressive environments.

Exposure of concrete structural components to external sulphates leads to deterioration owing to the formation of the expansive phases, ettringite and gypsum, whereas portlandite, AFm phases and C–S–H tend to dissolve [4, 5].

It is likely that external sulphates affect the solubility of trace metals and thus their leaching behaviour [3].

Cobalt is present in trace amounts in the human diet, primarily in vegetables and fish, and in drinking water. Cobalt is acutely toxic in larger doses, and cumulative, long-term exposure even at a low level, e.g. occupational exposure, can give rise to adverse health effects related to various organs and tissues. Manganese is an abundant element in the environment

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<http://dx.doi.org/10.3846/enviro.2014.033>

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and widely used throughout industry. Although manganese has relatively low toxicity, in chronic overdose or prolonged occupational exposure, it can cause severe disruption to the central nervous system [6]. Copper is an essential element for all known living organisms including humans and other animals at low levels of intake. However, exposure to higher doses can be harmful. Long-term exposure to copper dust can irritate nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhea [7]. Iron is the most abundant trace mineral in the body and is an essential element in most biological systems. Acute iron poisoning is common and potentially lethal in dogs, cats, and many other animals. Iron is also a leading cause of unintentional poisoning deaths in children less than 6 years old [6, 9].

This paper focuses on the leaching behaviour of Mn, Fe, Co, Cu from concretes made of ordinary CEM I Portland cement without any additives as well with silica fume addition due to concrete exposition to the sulphate environments.

2. Material and methods

2.1. Cement composites preparations

Two types of concrete mixtures (I and II) were used for the preparation of concrete samples for the experiment, using cement CEM I 42.5 N. The mixture I represented commonly used composition of concrete without special additives (except for plasticizer) containing 360 kg of CEM I 42.5N, 170 L of water, 825 kg of 0/4 mm aggregate, 235 kg of 4/8 mm aggregate, 740 kg of 8/16 aggregate and 3.1 L of plasticizer. Mixture II represented the concrete being considered more resistant in aggressive environment by addition of silica fume. Mixture II consisted of 360 kg of CEM I 42.5N, 200 L of water, 800 kg of 0/4 mm aggregate, 235 kg of 4/8 mm aggregate, 740 kg of 8/16 aggregate, 3.1 L of plasticizer and 20 kg of microsilica. The recipes of prepared cement composites were presented for 1 m³ of concrete. Concrete prisms of size 100x100x400 mm were prepared by using standardized procedure for concrete preparation. Prepared concrete samples have been cured for 28 days in water environment and afterwards cut into small prisms with dimensions of 50x50x10 mm. The test specimens were slightly brushed in order to remove polluting particles, cleaned, dried and weighted.

The cement composites were investigated in terms of the chemical composition and selected metals releasing.

2.2. Laboratory experiment

The leaching of cement composites was studied in compact composite form by immersion of concrete samples into the various liquid media: fresh water, sulphuric acid and magnesium sulphate solution. The characteristics of used liquid media and concrete samples are summarized in Table 1. The volume of liquid medium to concrete sample was set to 10:1. pH value of sulphuric acid solutions was kept on constant level of 4.2. The leaching experiments of compact cement composites proceeded during 180-day period.

Table 1: Characterization of samples

Sample	Mixture	Liquid medium	Characteristics of medium
S1	I	H ₂ SO ₄	pH 4.2
S2	II	H ₂ SO ₄	pH 4.2
S3	I	MgSO ₄	10 g/L of SO ₄ ²⁻
S4	II	MgSO ₄	10 g/L of SO ₄ ²⁻
S5	I	fresh water	pH 7.2
S6	II	fresh water	pH 7.2

The exposition of concrete samples proceeded at laboratory temperature of 23 °C. After each 7-day immersion period, the change in pH as well as the concentration of released metals were measured in leachates.

2.3. Analytical methods

X-ray fluorescence analysis (XRF) was used for the measuring of chemical composition of powdered concrete samples before and after the experiments and for trace concentrations of Co, Cu, Fe, Mn monitoring in liquid leachates. SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses was used for the analysis. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 and 180 s at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA, respectively under helium atmosphere by using the standardized method of fundamental parameters for pellets and concrete leachates. pH changes were measured by pH meter FG2- FiveGo (Mettler-Toledo, Switzerland).

3. Results

The chemical composition of concrete samples measured by XRF is in Table 2.

Table 2: Basic components of the studied materials (% mass)

Oxides (% mass)	Mixture	
	I	II
MgO	3.040	2.727
Al ₂ O ₃	5.209	5.385
SiO ₂	30.16	45.63
P ₂ O ₅	0.096	0.0941
SO ₃	2.889	2.718
Cl	0.016	0.0187
K ₂ O	0.766	0.794
CaO	31.27	26.17
TiO ₂	0.269	0.2583
MnO	0.375	0.364
Fe ₂ O ₃	4.037	3.748

The concentrations of selected metals released into the water and acid environment from the cement composites are summarized in Tables 3–6.

Table 3: Measured concentrations of Mn ions in liquid leachings during 180-day experiments

Exposition time [days]	Mn ions [mg/L]					
	Sample					
	S1	S2	S3	S4	S5	S6
30	34.4	48.4	32.8	37.3	40.6	34.8
60	32.5	39.5	34.6	33	42.9	48.7
90	45.4	43	25.2	25	37.4	42.8
120	44.7	47	29.6	15.4	36.5	32.4
150	34.1	32.9	20.1	36.4	45.6	41.6
180	40.2	29.2	31.7	25.3	23.5	28.3

The manganese ions concentrations in leachates ranged from 15.4 mg/L (leachate of sample S4 after 120 days of exposition) to 48.7 mg/L (leachate of sample S6 in fresh water environment after 60 days of exposition) as it is seen in Table 3.

The concentrations of manganese in sulphuric acid have been measured to be higher than in magnesium sulphate solutions for both studied concrete sample types, respectively. On the contrary, manganese concentrations in magnesium sulphate solutions have been measured to be lower than in water leachates for all type II concrete samples (S6 versus S4). Similarly, water environment seems to be more significant for manganese leaching when comparing to magnesium sulphate solution for type I concrete samples as well (S3 versus S5).

Table 4: Measured concentrations of Fe ions in liquid leachings during 180-day experiments

Exposition time [days]	Fe ions [mg/L]					
	Sample					
	S1	S2	S3	S4	S5	S6
30	8.2	6.4	7.8	7.7	8.4	8.4
60	4.9	5.8	6.7	5.5	6.3	4.9
90	8.5	UDL	4.8	4.8	6.6	8.8
120	9.1	5.8	8.9	5.1	6.6	10.2
150	7.3	7	9.1	4.7	9.1	7.7
180	5.9	7.1	8	6.9	8.7	9.4

Comparing the total content of manganese in concrete samples and released amount of manganese after 180-day exposition it can be concluded that percentage of manganese released from the concrete samples were 16.9, 10.6, 12.7, 9.1, 8.3 and 8.8 % for S1, S2, S3, S4, S5 and S6 samples, respectively.

The iron ions concentrations in leachates ranged from 4.7 mg/L to 10.2 mg/L. The highest concentration of Fe ions (10.2 mg/L) was measured in sample S6 after 120 days of exposition in water environment as it can be seen in Table 4, the lowest one in sample S4 after 150 days of exposition to magnesium sulphate solution. Iron concentrations in magnesium sulphate solutions have been measured to be lower than in water leachates for almost all type II concrete samples (S6 versus S4).

Percentage of iron released from the concrete samples were in very close interval 0.3, 0.32, 0.39, 0.31, 0.37 and 0.37% of total iron content for S1, S2, S3, S4, S5 and S6 samples, respectively.

Table 5: Measured concentrations of Co ions in liquid leachings during 180-day experiments

Exposition time [days]	Co ions [mg/L]					
	Sample					
	S1	S2	S3	S4	S5	S6
30	5.9	5	5.6	10.3	6.2	9.3
60	7.9	5.2	6.5	8.5	5.9	6.5
90	6.2	13.3	7.7	7.3	5.8	6.5
120	5	4.2	6.5	6.9	9.3	5.3
150	9.6	8	6.5	9.1	6.1	6.1
180	4.9	6.1	6.9	7.4	7.5	5.4

The concentrations of Co ions in liquid leachates reached the values from 4.2 mg/L (in leachate of sample S2 after 120 days of exposition) to 13.3 mg/L (in sample S2 leachate after 90 days of exposition). In contrast to manganese, the concentrations of cobalt in sulphuric acid have not been measured to be higher than in magnesium sulphate solutions for all concrete samples of type I or type II. Percentage of released cobalt was not calculated due to absence of total content data of cobalt in concrete samples.

Table 6: Measured concentrations of Cu ions in liquid leachings during 180-day experiments

Exposition time [days]	Cu ions [mg/L]					
	Sample					
	S1	S2	S3	S4	S5	S6
30	11.9	6.4	13.3	UDL	6.0	UDL
60	5.0	12.2	14.6	UDL	13.1	14.8
90	10.5	9.9	11.2	8.8	12.6	12.3
120	11	11	12.4	7.4	10	11.8
150	UDL	9.9	15.3	12.7	14.1	14
180	11.8	11.2	12.4	8.7	11.4	10.1

The copper ions in leachates ranged from 5.0 mg/L (in leachate of sample S1 after 60 days of exposition to H₂SO₄) to 15.3 mg/L (in leachate of sample S3 after 150 days of exposition to MgSO₄ solution) as it can be seen in Table 6. Percentage of released copper was not calculated due to absence of total content data of copper in concrete samples.

Summarizing the results, the concentrations of analyzed ions measured at the end of the experiment (after 180 days) were not higher for all samples than after 30 days of the experiment, that could point to the forming new compounds by precipitation in leachate or on the sample surface as referred by [8].

Calculated concentrations of studied metals released from samples S1 and S2 in sulphuric acid corresponding to 1 g of concrete sample are illustrated in Figure 1.

As assumed more significant releasing of studied ions (Mn and Cu) was noticed from sample S1. Released amount of manganese in acidic environment from sample without microsilica (S1) was 1.6 times higher than from sample with microsilica (S2). Thus sample with addition of microsilica was confirmed to be more resistant in sulphuric acid environment compared to sample without microsilica.

Figure 2 illustrates the leaching trend of Mn, Fe, Co and Cu ions in MgSO₄ solution.

In MgSO₄ solution, concentrations of all analyzed metals from concrete sample without microsilica (S3) have been measured to be higher comparing to concrete sample with microsilica (S4). Masses of released manganese and iron from sample S3 were 1.5 and 1.3 higher than from sample S4.

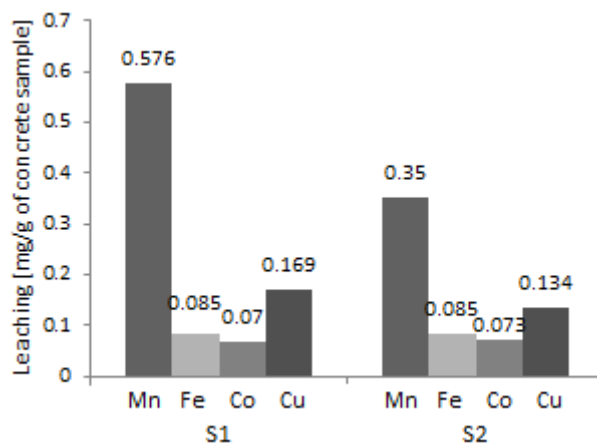


Figure 1 Comparison of studied metals leaching in solution of H₂SO₄ after 180 days-exposition

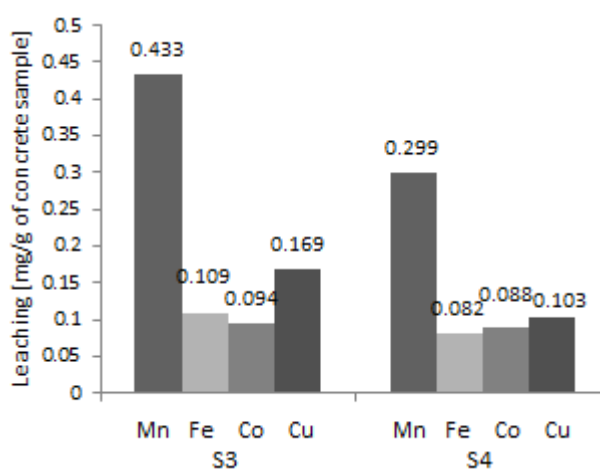


Figure 2 Comparison of studied metals leaching in solution of MgSO₄ after 180 days-exposition

Analogically as for sulphuric acid, concrete sample with microsilica was found to have better performance in leaching of Mn, Fe, Co and Cu ions than sample without microsilica.

The leaching of selected metal ions into water environment is presented in Figure 3.

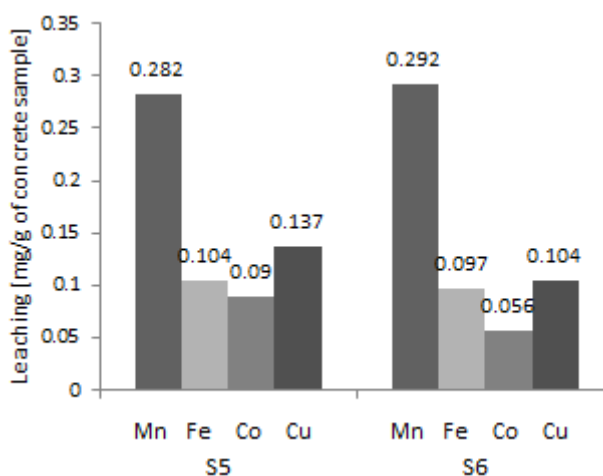


Figure 3 Comparison of studied metals leaching in fresh water after 180 days-exposition

The concrete sample with microsilica (S6) was found to have better performance of Fe, Co and Cu ions leaching. The concentrations of Mn ions was measured to be quite similar for both concrete samples.

4. Conclusion

Heavy metal contamination has become an environmental problem today in both developing and developed countries throughout the world. They are of considerable environmental concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviors. The paper aimed to present the results of the study of selected metals releasing from the cements composites into the water and acid environments. The results of measurements of selected metals concentrations in leachates showed that only a small part of their content was extracted from concrete samples into the liquid media (up to 17 % for manganese and 0.3% for iron). Samples with microsilica were found to have better performance in leaching of analyzed ions.

Acknowledgements

This research has been carried out within the Grant No. 1/0481/13 and No. 1/0882/11 of the Slovak Grant Agency for Science.

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