Proceedings of the 14th International Conference on Environmental Science and Technology
Rhodes, Greece, 3-5 September 2015

CEST 2015

STATISTICAL DEPENDENCE INVESTIGATION OF DELETERIOUS PROCESS ON CONCRETE SAMPLES EXPOSED TO DIFFERENT MEDIA

ONDREJKA HARBULAKOVA V.[1], ESTOKOVA A.[1], PURCZ P.[2] and LUPTAKOVA A.[3]

[1]Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4, 042 00 Kosice, Slovakia, [2]Technical University of Kosice, Faculty of Civil Engineering, Department of Applied Mathematics, e-mail: pavol.purcz@tuke.sk [3]Slovak Academy of Science, Institute of Geotechnics, Watsonova 45, 043 53 Kosice, Slovakia, E-mail: vlasta.harbulakova@tuke.sk

ABSTRACT

Corrosion of concrete comprises a number of complex processes leading to reduction of engineering properties such as strength, elastic modulus and durability. It may happen due to a number of various physical, chemical, and physic-chemical factors and their interactions reflecting peculiarities of both material aspects and external factors.

The paper is focused on the investigation of the influence of different media (distilled water, sulphuric acid, aluminium sulphate) on the concrete samples deterioration. Si, Ca, Al, Fe, Mn and Cu ions dissolved from the cement matrix into leachate during the various media exposition were measured in five cycles. Determination of the XRF concentration of selected ions considering mutual dependence on pH is presented in the paper. Correlation between the dissolved ion concentrations and pH values was found out. Very high correlation was observed in case of Ca-pH dependency for samples exposed to aluminium sulphate while a high correlation for Si-pH in distilled water.

Significant correlation dependence was found out also studying dependence of Ca-Si (for distilled water and sulphuric acid). The study reveals that the leaching of the elements during sulphate based deterioration processes is mutually related.

Keywords: aluminium sulphate, correlation analysis, leachate, sulphuric acid

1. Introduction

Existing evidence (Zivica *et al.*, 2000; Collepardi, 2002; Beddoe *et al.*, 2005) has shown that in many concrete structures exposed to aggressive aqueous environments corrosion problems are present. The main categories of deleterious processes in concrete, by which the concrete deteriorates as the result of chemical attack, are cracking and shrinkage due to corrosion of steel reinforcement, alkali-silica reaction, carbonation, leaching and sulphate attack (Winter, 2009). Of course, concrete can also suffer from physical damage, for example through impact, abrasion or frost action.

Sulphuric acid is one of the significant corrosion media to concrete. Due to its complex corrosion law and multiple influencing parameters (Robin *et al.*, 2005; Hewayde *et al.*, 2003), there is no effective prediction method right now. A leaching process starts when water dissolves compounds in pore walls inside the concrete. A dissolution can be looked upon as a diffusion process where, (a) water molecules diffuses to the reaction place in the pore walls, (b) water molecules dissolve solid compounds, (c) the dissolved compounds are transported away from the reaction place to the pore solution (Ekström, 2001). Diffusion processes are part of mathematics in the area of stochastic processes (Valis *et al.*, 2014). Experimental results in paper by Kan C. (Kan *et al.*, 2013) showed that the addition of aluminium sulphate shorten the setting time of cement, increase the drying shrinkage and improve the early strength however it reduce the fluidity.

The paper is focused on the statistical investigation of different media´ influence on the concrete samples deterioration. Si and Ca ions, representing basic components of the concrete, leached

out from the cement matrix due to sulphate media exposition were measured in the experiment. The correlation between the chemical elements concentrations in leachates and leachates´ pH as well as between the concentrations of silicon and calcium each other was calculated.

2. Material and methods

Concrete cylinder samples of a 32 mm diameter and 15 mm height were formed as a drilled core from concrete cubes (150x150x150 mm), prepared according to a classic recipe, using drilling mechanism STAM. The cylinder specimens were rid of impurity, weighted to a constant weight and then immersed into three aggressive media representing three models of corrosion: distilled water simulating a corrosion caused by leaching (pH value 6.25), 0.5% solution of H_2SO_4 (a pH value of 0.99) simulating an acid corrosion and 0.5% solution of $Al_2(SO_4)_3$ (a pH value of 3.22) simulating a sulphate corrosion. The solution of 0.5% H_2SO_4 was prepared by dissolving of 98% H_2SO_4 of analytical grade in distilled water. The solution of 0.5 % $Al_2(SO_4)_3$ was prepared by dissolving 171.1g of $Al_2(SO_4)_3$ in distilled water and filled up to volume of 1000 mL.

Experiments proceeded in five consecutive cycles. Each of the cycle consists of the following steps: 7-day exposition of sample to the liquid medium, removal the sample from the liquid, 2-day drying of samples at room temperature and afterwards removing of precipitations by little brush, and re-immersion of samples into the media and adjusting the pH to the initial values. The values of pH in leachates were measured after every 7-day exposition using a pH meter PHH – 3X Omega. After each 7-day exposition, the dissolved concentrations of selected elements in leachates were measured using X-ray fluorescence analysis (XRF). The XRF measured concentrations used for the statistical analysis are presented in Table 1.

Table 1: Concentrations c(X) of studied elements in leachates

Cycle	c(Ca)	c(Si)	c(Al)	c(Fe)	c(Mn)	c(Cu)	Medium
			mg/L				
0	55.6	0.0	79.4	0	36.6	9.9	H_2O
1	52.1	164.2	41.0	0	31.1	13.8	
2	134.0	398.8	166.4	4.3	29.1	16.0	
3	104.5	291.0	124.3	0	30.0	0	
4	262.1	575.8	241.6	7.5	32.1	0	
5	198.0	467.0	368.6	7.3	39.0	0	
0	49.3	0	298.0	0.1	29.0	14.7	H_2SO_4
1	710.7	264.4	295.2	394.4	49.7	2.9	
2	935.4	528.0	462.0	420.6	44.1	14.3	
3	863.1	489.9	406.0	450.4	38.4	0	
4	1,264	874.4	544.0	500.6	47.2	0	
5	904.7	620.5	492.0	473.4	47.5	8.6	
0	57.5	0	608.0	0	28.1	0.1	$Al_2(SO_4)_3$
1	964.3	129.6	135.0	0	38.7	8.4	
2	633.2	733.6	4,027	7.5	28.6	0	
3	382.1	419.9	2,500	5.2	17.7	13.2	
4	464.8	602.6	952.0	7.7	23.5	13.7	
5	237.7	861.0	525.5	9.3	31.2	13.9	

In statistics, dependence refers to any statistical relationship between two random variables or two sets of data. Correlation refers to any of a broad class of statistical relationships involving dependence. Descriptive statistics is the discipline of quantitatively describing the main features of a collection of data (Kreyszig, 2011). Descriptive statistics are distinguished from inferential statistics (or inductive statistics), in that descriptive statistics aim to summarize a data set, rather than use the data to learn about the population that the data are thought to represent. This generally means that descriptive statistics, unlike inferential statistics, are not developed on the basis of probability theory (Dodge, 2003). Even when a data analysis draws its main conclusions using inferential statistics, descriptive statistics are generally also presented.

In statistics, the correlation index ($\eta_{x/y}$) is the most general measure of the closeness, which is possible to determine without regression analysis Equal 1. The correlation index $\eta_{x/y}$ takes values between 0 and 1. Increasing of the absolute value of the R_{xy} is proportional to linear correlation. In case of the linear correlation, both the correlation coefficient and the index of the correlation are approximately equal (Closs *et al.*, 2003). Information about two dimensional statistical data set gives correlation coefficient R_{xy} as is shown in Equal 2.

$$\eta_{x/y} = \sqrt{\frac{\sum_{i=1}^{m} \overline{y}_i n_i - n\overline{y}^2}{\sum_{i=1}^{m}\sum_{j=1}^{n_i} y_{ij}^2 - n\overline{y}^2}} \tag{1}$$

$$R_{xy} = \frac{n\sum_{i=1}^{n} x_i y_i - \left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_i\right)}{\sqrt{\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right]\left[n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2\right]}} \tag{2}$$

R_{xy} values are from the interval <-1,1>. If $R_{xy} = 1$, the correlation is full linear, if $R_{xy} = -1$, then the correlation is inversely linear and if $R_{xy} = 0$, the pairs of values are fully independent. Than degree of the correlative closeness is: medium, if $0.3 \leq |R_{xy}| < 0.5$; significant, if $0.5 \leq |R_{xy}| < 0.7$; high, if $0.7 \leq |R_{xy}| < 0.9$; and very high, if $0.9 \leq |R_{xy}|$.

A statistic method was used for evaluation of deleterious process and to determine the trend of chemical elements leaching as well for description of a relation among the selected parameters.

3. Results and discussion

The concentrations of silicon and calcium dissolved in distilled water, sulphuric acid and sulphate aluminium sulphate solution, given in Table 1, were used for the statistical analysis. With the aim of pursued and determining whether there is any correlation between the dissolved Si and Ca ions from the concrete matrix and increase/decrease in pH values the correlation coefficients for all three selected media were calculated. Found correlation coefficients (R_{xy}) for silicon ions and pH values relationship in studied media are presented in Table 2.

Table 2: Correlation coefficient R_{xy} of Si ions and pH dependence

medium	parameter	initial	after cycle 1	after cycle 2	after cycle 3	after cycle 4	after cycle 5	R_{xy}
H_2O	c(Si)	0	164.2	398.8	291.0	575.8	466.8	0.65
	pH	6.25	8.36	8.4	8.56	8.22	8.11	
H_2SO_4	c(Si)	0	234.4	528.0	489.9	874.4	620.5	0.21
	pH	0.99	2.16	1.85	1.82	1.52	1.51	
$Al_2(SO_4)_3$	c(Si)	0	129.6	733.6	419.9	602.6	861.0	0.24
	pH	3.22	4.5	4.21	4.16	3.89	3.87	

As seen in Table 2, the increasing growth in pH values was detected until cycle 3 for distilled water and cycle 2 for sulphuric acid and aluminium sulphate. After the cycles 3 and 2, respectively where the maximum pH increments have been measured, grow in the pH values decreased. It is known that the leaching rates are highly dependent on time. With time advancing, less and less alkali compounds were leached out. The concentrations of OH^- ions in distilled water ranged from 1.77×10^{-8} mol/L (pH of 6.25) at the beginning of the experiment to 363.1 mol/L in maximum measured after cycle 3 (pH of 8.56) and 128.8×10^{-8} mol/L measured after the experiment (pH of 8.11). OH^- concentrations observed in sulphuric acid ranged $9.7 \times 10^{-14} – 32.3 \times 10^{-14}$ mol/L (a pH range 0.99 – 1.51) with a maximum of 144×10^{-14} mol/L measured after the cycle 2 (pH of 2.16).

The pH course in aluminium sulphate solution corresponded to OH⁻ concentrations ranged $1.66 \times 10^{-11} – 31 \times 10^{-11}$ mol/L.

Despite of the similar trends in pH rise, different correlation were observed between dissolved ions and pH for the studied media. As concluded in Table 2, the degree of the correlative closeness (considering Si ions leaching and pH values) was calculated to be significant for distilled water ($0.5 \leq |R_{xy}| < 0.7$). However, no correlation between Si ions leaching and pH was detected for sulphuric acid or aluminium sulphate solution ($|R_{xy}| < 0.3$). This finding can be caused by building-in of the silicon ions into new sulphate precipitates formed on the surface of the cement composites samples in both sulphate environments. The correlation coefficients (R_{xy}) calculated for calcium ions dissolved and pH values are reported in Table 3.

Table 3: Correlation coefficient R_{xy} of Ca ions and pH dependence

medium	parameter	initial	after cycle 1	after cycle 2	after cycle 3	after cycle 4	after cycle 5	R_{xy}
H_2O	c(Ca)	55.6	52.1	134	104.5	262.1	197.5	0.35
	pH	6.25	8.36	8.4	8.56	8.22	8.11	
H_2SO_4	c(Ca)	49.3	710.7	935.4	863.1	1,264	904.7	0.51
	pH	0.99	2.16	1.85	1.82	1.52	1.51	
$Al_2(SO_4)_3$	c(Ca)	57.5	964.3	633.2	382.1	464.8	237.7	0.9
	pH	3.22	4.5	4.21	4.16	3.89	3.87	

As it shown in Table 3, the correlation closeness of Ca ions leaching in relation to pH values was calculated very high ($0.9 \leq |R_{xy}|$) in aluminium sulphate solution while significant ($0.5 \leq |R_{xy}| < 0.7$) in sulphate acid and only medium ($0.3 \leq |R_{xy}|$) in distilled water. Contrary to the Si ions, the increase in concentrations of the dissolved calcium ions was in strong correlation with the increase in pH of leachate in aluminium sulphate but only in weak correlation in distilled water. This fact points to totaly different behaviour of Si and Ca ions in aluminium sulphate solution. Based on these findings, correlation coefficients between Si and Ca ions leaching each other were determined and are presented in Table 4.

Table 4: Si - Ca correlation coefficients R_{xy}

medium	parameter	initial	after cycle 1	after cycle 2	after cycle 3	after cycle 4	after cycle 5	R_{xy}
H_2O	c(Ca)	55.6	52.1	134.0	104.5	262.1	197.5	0.93
	c(Si)	0	164.2	398.8	291.0	575.8	466.8	
H_2SO_4	c(Ca)	49.3	710.7	935.4	863.1	1,264	904.7	0.95
	c(Si)	0	234.4	528.0	489.9	874.4	620.5	
$Al_2(SO_4)_3$	c(Ca)	57.5	964.3	633.2	382.1	464.8	237.7	-0.04
	c(Si)	0	129.6	733.6	419.9	602.6	861.0	

As shown in Table 4, no correlation was found between dissolved Ca and Si ions in aluminium sulphate solution ($|R_{xy}| = 0.04$). Since mentioned above, in aluminium sulphate, the more calcium ions was dissolved the more OH⁻ ions was measured. This confirms the knowledge that $Ca(OH)_2$ is a main compound to be leached-out from the cement matrix not only in water but in aluminium sulphate solution as well. On the contrary, no relation was found between dissolved Si and OH⁻ concentrations (Table 2). Thus no correlation between Si-Ca was confirmed in aluminium sulphate. On the other hand, very high correlations ($|R_{xy}| = 0.93$ and 0.95, respectively) were found between dissolved Si-Ca concentrations in water and sulphuric acid (Table 4). This fact is likely linked to the similar behaviour of dissolved Si and Ca ions in water and sulphuric acid.

4. Conclusions
A strong correlation was calculated for dissolved Ca concentrations and pH but no correlation for dissolved Si concentrations and pH in aluminium sulphate solution. On the other hand, a very

high correlation was found for mutual Si-Ca concentrations in water and sulphuric acid. The results revealed that Si and Ca behaviour in aluminium sulphate is totally different while in water and sulphuric acid could be the leaching mechanism and consequently precipitation of the analysed ions similar.

Many problems related to the chemically influenced corrosion of concrete have not been solved until now, in spite considerable progresses in recognition of the corrosion kinetics and mechanisms. Thus, further research on corrosion processes and methods of protections against these processes are necessary.

ACKNOWLEDGEMENTS

REFERENCES

1. Beddoe R.E., Dorner H.W. (2005), Modelling acid attack on concrete: Part I. The essential mechanism, Cem. Concr. Res., **35**, 2333-39.
2. Collepardi M. (2002), Simplified modelling of calcium leaching of concrete in various environments, Materials and Structures/Materiaux et Constructions, **35**, 632-40.
3. Closs G., Downes B., Boulton A. (2003), Freshwater Ecology: A Scientific Introduction, Wiley.
4. Dodge Y. (2003), The Oxford Dictionary of Statistical Terms, OUP Oxford.
5. Ekström T. (2001), Leaching of concrete - Experiments and modeling, Report TVBM-3090, Lund University.
6. Hewayde E., Nehdi M., Allouche E.N. (2003), Experimental Investigations of the Effect of Selected Admixtures on the Resistance of Concrete to Sulfuric Acid Attack, Proceeding of International on Pipeline Engineering and Construction, Baltimore; ASCE, 2003:504-513.
7. Chang Yu Kan, Ch.T., Lan, M.Z., Kong, L.M., Yang, J.B. (2013), Effect of aluminiun sulfate on cement properties, Mater. Sci. Forum, **743-744**, 285-291.
8. Kreyszig E. (2011). Advanced Engineering Mathematics, John Wiley and sons, 10th edition.
9. Lee S.T., Moon H.Y., Swamy R.N, (2005), Sulfate attack and role of silica fume in resisting strength loss. Cem. Concr. Compos. **27**(1), 65–76.
10. Robin B.E., Horst W.D. (2005). Modelling Acid Attack on Concrete (Part I): The Essential Mechanisms, Cem. Concr. Res., **35**(12), 2333-2339.
11. Valis D., Pietrucha-Urbanik K. (2014), Utilization of diffusion processes and fuzzy logic for vulnerability assessment. Eksploatacja i Niezawodnosc – Maintenance and Reliability, **16**(1), 48–55.
12. Winter N. (2009), Understanding Cement. Suffolk: WHD Microanalysis Consultant Ltd, UK.
13. Zivica V., Bajza A. (2000), Acidic attack of cement based materials - a review. Part 1. Principle of acidic attack, Construction and Building Material, **15**, 331-40.