CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
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ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543371

Using a Statistical Method for the Concrete Deterioration Assessment in Sulphate Environment

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Corrosion is generally considered as a natural process of decay and progressive degradation of materials by the surrounding environment activity. This irreversible process however can be prevented by adequate measures.

This paper is focused on the investigation of the influence of aggressive sulphate environment on the concrete material (with and without coal fly ash replacement). Si, Ca, Al, Fe, Mn and Cu ions dissolved from the cement matrix into leachate during the various aggressive media exposition were measured in the experiment. At the beginning and at the end, the concentration of same ions has been measured in the liquid phase of each media in five 7-days cycles. Determination of concentration of selected ions considering mutual dependence on pH and its dependency on time (measured after each cycle) is presented in the paper. Correlation between the chemical elements and pH for calcium ions was measured and discussed. Significant correlation was found out in case of samples with no fly ash replacement related to the dependence Si-pH.

1. Introduction

ACI Committee Report 201 (2001) has classified chemical attacks into several types that include; acidic attack, alkali attack, carbonation, chloride attack, leaching and sulfate attack. It can be accepted as a general rule that acids are deleterious to concrete (Verma, A et al., 2013).

Concrete corrosion is mainly caused by salt water or acidic ground water, microbes in sewer pipes, sulphates, chlorides, nitrates, fluorides, sulphides, industrial waste like slag and corrosive gases.

Preventive measures include:

- Paint application such as varnish, oil or lacquer-based paint
- Surface treatment
- Appropriate choice of cement mix and chemicals during cement production
- Action to prevent attack of corrosive water or other liquids and gases

Biological sulphuric acid attack is a chronic problem in sewage pipes, leading to rapid deterioration of concrete. Because of the role of bacteria in the corrosion reaction, mechanical engineers have focused on the study of corrosion resistance of different concrete mixes in an effort to prevent this type of corrosion (web page corrosionpedia, 2014).

As a general simple description the physicochemical processes of corrosion of porous hydrated inorganic materials which are relatively heterogeneous and brittle consists of three steps. The first step is convective and diffusional transport of aggressive medium (gas or liquid) through interconnected pores to the corrosion front. In the second step the aggressive substance reacts with the material resulting in the formation of some soluble and/or insoluble products (Allahverdi, A. and Škvara, F., 2010). Diffusion processes are part of mathematics in the area of stochastic processes (Valis, D. and Pietrucha-Urbanik, K., 2014).

Please cite this article as: Ondrejka Harbulakova V., Purcz P., Estokova A., Luptakova A., Repka M., 2015, Using a statistical method for the concrete deterioration assessment in sulphate environment, Chemical Engineering Transactions, 43, 2221-2226 DOI: 10.3303/CET1543371

Constructing a suitable continuous stochastic process by generalizing Wiener's existence result for one-dimensional Brownian motion was published in Grow, D. and Sanyal, S., (2011).

In the paper by Lefebre, M. and Perotto, S. (2011) numerical methods were used to illustrate the analytical findings of assumed period between two repairs is the time. Also many studies have been conducted to evaluate the properties of concrete with supplementary cementitious materials mechanical (Arezoumandi, M. and Volz, J.S., 2013), chemical (Bhatty, J.I. and Taylor, P.C., 2006), and durable perspectives (Sumer, M., 2012). Fly ash and slag were found to be able to increase concrete's strength and sulphate resistance (Saraswathy, V. and Song, H.W. 2006). Osborne, G.J. (1999) presented guidance oriented on the design, specification, application and performance of concrete in practice where slag can also help to reduce costs and energy demands in the production of cement compared with normal Portland cement. The influence of using ground granulated blast furnace slag in reinforced concrete structures from the durability aspects such as chloride ingress and corrosion resistance, long term durability, microstructure and porosity of ground granulated blast furnace slag concrete has been reviewed and discussed in Song, H.W. and Saraswathya, V., (2006). Fly ash and slag can significantly reduce the sulphate deterioration by reducing the amount of free lime and reactive aluminates for sulphate reaction and reducing concrete permeability. In addition to improve concrete's sulphate resistance, fly ash was also found to mitigate alkali-silica reaction (ASR) in concrete (Thomas, M. et al., 2012), and decreases the shrinkage of cement paste (Li, Y., 2012). Nie, Q. et al. (2014) studied chemical, mechanical and durability properties of concrete made with local mineral admixtures. They proved that sulphate resistance could be effectively improved by adding local mineral admixtures or using sulphate resisting cement.

Recently there has been a growing trend towards the use of supplementary cementitious materials, whether natural, waste or by-products, in the production of concrete because of ecological, economical and diversified product quality reasons. Fly ash which is a by-product of combustion of pulverized coal in the thermal power plants, is used for these reasons. Fly ash is removed from the effluent gases of these power plants by electrostatic precipitators. Fly ash, along-with coal dust, is also collected from the furnaces of the thermal power plants. The intrusion of fly ash in concrete affects all aspects of concrete properties. Study of chemical corrosion of concrete with 10% of coal fly ash replacement was investigated in our previous paper (Eštoková, A. et al., 2013).

2. Material and Methods

Concrete composites with/without coal fly ash were studied in the laboratory corrosion experiments. Reference samples without coal fly ash and samples with 5% of cement replacement by coal fly ash having the same shape and size were investigated. Concrete cylinder samples of a 32 mm diameter and 15 mm height were formed as a drilled core from concrete cube (150x150x150 mm) using drilling mechanism STAM. The cylinder samples were rid of impurity. The characterization of concrete composites is in Table 1.

Table 1: Characterisation of concrete composites used for the experiment

Composites sign	Fly ash addition	Aggressive medium
0 DW	0%	distilled water (DW)
5 DW	5%	distilled water (DW)
0 AC	0%	sulphuric acid (H_2SO_4)
5 AC	5%	sulphuric acid (H_2SO_4)

Used coal fly ash with volumetric weight of 2381 kg/m^3 originates from black coal's burning process in Košice city heating plant (Novaky Power plant, ENO). The percentage of basic oxides and total amount of sulphur in coal fly ash used in cement composites was as follow: 37.5% SiO_2, 15.6% Al_2O_3, 7.67% Fe_2O_3, 1.3% TiO_2, 22.94% CaO, 2.77% MgO, 1.21% K_2O, 0.112% MnO, 0.63% Na_2O, 0.18% Pb_2O_3, and 2.76% S_{tot}. The concrete samples used for the experiments were prepared in accordance with Slovak standard STN EN 206-1 using cement CEM I 42.5 R.

Prepared concrete samples were treated by standard procedures, weighted and then immersed into two aggressive media representing two models of corrosion: distilled water DW (pH value of 6.25) simulating corrosion caused by leaching and 0.5% solution of H_2SO_4 (pH value of 0.99) simulating acid corrosion.

The volumes of liquids at the beginning of the experiment were 20 ml. Experiments runs in five consecutive cycles during (five 7-days cycles). Each of the cycle consists of following steps: seven day-exposition of sample to liquid media, removal the sample from the liquid, two-day drying of samples at room temperature and afterwards removing of precipitations by little brush, re-immersion of sample into the media and finally adjustment of pH back to the initial values. The values of leachate pH were measured by pH meter PHH – 3X Omega.

The chemical composition of liquid media before and after the leaching and corrosion simulation was investigated by X-ray fluorescence method (XRF) using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector. Concentration of basic chemical elements as calcium, silicon, iron, manganese and copper were evaluated. The relation between each concentration and pH increase of decrease were researched in each one of 7day cycle.

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.

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 [6]. 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, Y., 2003). Even when a data analysis draws its main conclusions using inferential statistics, descriptive statistics are generally also presented.

In statistics, the correlation ratio ($\mu_{x/y}$) is the most general measure of the closeness, which is possible to determine without regression analysis Eq(1).

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

The correlation ratio $\mu_{x/y}$ 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 ratio of the correlation are approximately equal (Closs, G., et al., 2003). Information about two dimensional statistical data set gives correlation coefficient R_{xy} as is shown in Eq(2).

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

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

3. Results and Discussion

The results of the leaching of studied parameters in distilled water and suphuric acid are given in Tables 2 and 3.

Table 2: Concentrations of studied elements dissolved in distilled water

Sample			**0 DW**						**5 DW**		
Parameter						**mg/L**					
Cycle	**0**	**1**	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Ca	55.6	52.1	134.0	104.5	262.1	197.5	45.2	197.8	88.5	256.9	90.6
Si	-	164.2	398.8	291.0	575.8	466.8	119.3	439.8	283.6	521.2	378.8
Al	79.4	41.0	166.4	124.3	241.6	368.6	28.5	169.2	107.9	216.1	166.1
Fe	-	-	4.3	-	7.5	7.3	-	5.5	-	4.8	4.9
Mn	36.6	31.1	29.1	30.0	32.1	39.0	47.2	25.4	21.8	25.9	29.6
Cu	9.9	13.8	16.0	-	-	-	14.3	13.3	-	-	9.5
pH	6.25	8.36	8.4	8.56	8.22	8.11	8.01	8.27	8.49	8.24	8.12

Table 3: Concentrations of studied elements dissolved in sulphuric acid

Sample	0 AC						5 AC				
Parameter	mg/l										
Cycle	0	1	2	3	4	5	1	2	3	4	5
Ca	49.3	710.7	935.4	863.1	1264	2501	8761	7323	6281	761	2501
Si	0	264.4	528	489.9	874.4	637.8	1946	2548	2601	1010	637.8
Al	298	295.2	462	406	544	198.1	753	794	864	693	198.1
Fe	-	394.4	420.6	450.4	500.6	121.2	320.4	375.8	469.2	393	121.2
Mn	29	49.7	44.1	38.4	47.2	39.6	24.2	26.6	24.8	36.4	39.6
Cu	14.7	2.9	14.3	-	-	11.1	-	10.1	16.4	15.4	11.1
pH	0.99	2.16	1.85	1.82	1.52	3.3	2.72	2.54	2.0	1.92	3.3

Figures 1 - 4 illustrate a dependency between concentrations of calcium ions in leachates of the concrete composites studied during the experiment and pH values.

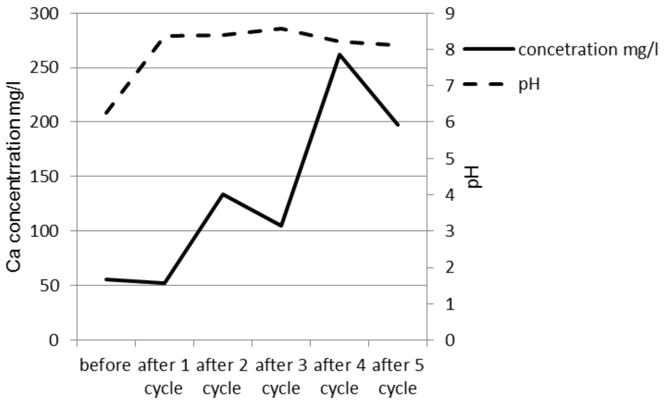

Figure 1: Dissolving trend of Ca from the 0 DW sample (0% coal fly ash) in distilled water and pH

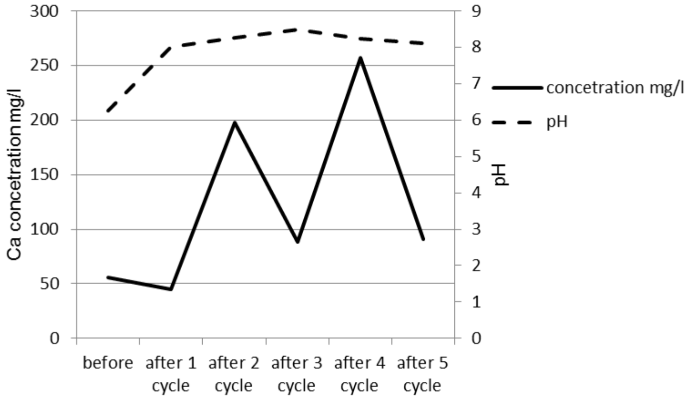

Figure 2: Dissolving trend of Ca from the 5 DW sample (5% coal fly ash) in distilled water and pH

As shown in graphs in Figures 2 – 4, no visible correlation between pH and leaching of the calcium ions was observed, except for the sample 5 AC. Thus the data presented in Tables 2 and 3 were used for the theoretical statistical investigation of degrees of the correlative closeness between each other. The correlation calculated between chemical elements and pH in each kind of liquid media and for case of each kind of concrete sample is shown in Table 5.

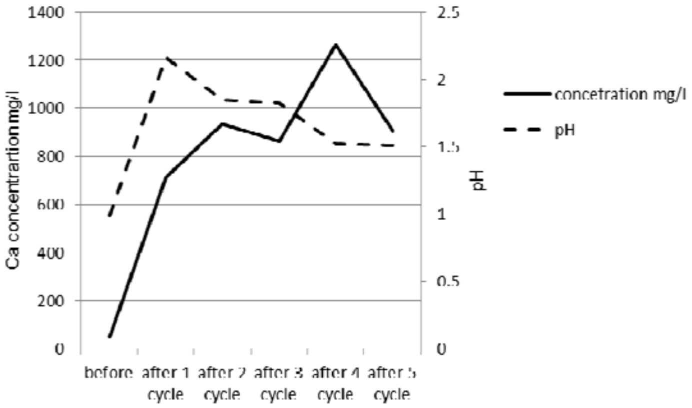

Figure 3: Dissolving trend of Ca from the 0 AC sample (0% coal fly ash) in sulphuric acid and pH

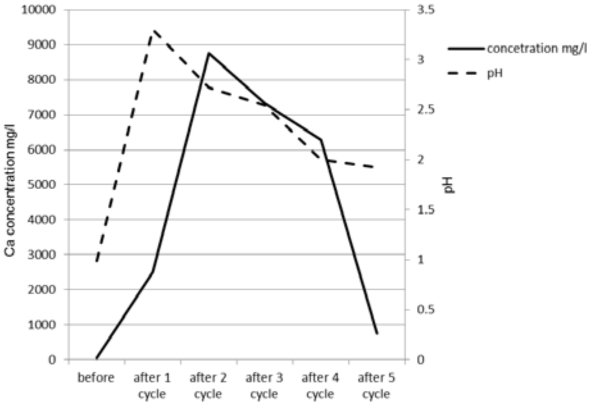

Figure 4: Dissolving trend of Ca from the 5 AC sample (5% coal fly ash) in sulphuric acid and pH

Correlation is high in case of relation between Si and pH in deionized water leachate of concrete sample with 5% of coal fly ash replacement (0.75) and Mn-pH in sulphuric acid of concrete sample without coal fly ash replacement (0.71). Significant correlation was in case of samples with no fly ash replacement relation Si-pH (0.65) as well as in cases of relation Fe-pH (0.67) but after sulphuric acid influence. Significant, but non-linear correlation is shown in case of samples 0 DW and 5 DW between relation Mn-pH (0.57 respectively 0.44).

Also total correlation between all values of selected chemical elements and pH were calculated. Despite the fact that not all values evince high of significant correlation the total one was high with value of correlation 0.96 for liquid medium – deionized water. Similar results were found out in case of sulphuric acid, where the total correlation was 0.96 which means significant closeness.

Table 5: Correlation coefficient of chemical element(s) and pH

correlation	0 DW	5 DW	0 AC	5 AC
Ca-pH	0.35	0.42	0.51	0.49
Si-pH	0.65	0.75	0.24	0.33
Al-pH	0.24	0.39	-0.02	-0.01
Fe-pH	0.28	0.42	0.67	0.21
Mn-pH	-0.57	-0.44	0.71	0.27
Cu-pH	-0.16	-0.29	-0.46	-0.53
TOTAL	0.96		0.76	

In deionized water there is little importance correlation between Al-pH, Fe-pH and Cu-pH in case of concrete samples with no fly ash replacement. Same little significant correlation was calculated for pairs exposed to sulphuric acid Si-pH (0 DW) and Fe-pH, Mn-pH (both 5 DW).

In sulphuric acid values of correlation between Al-pH for both concrete samples are fully independent on each other. In the other combinations medium dependency was proved.

4. Conclusion

The data obtained from the laboratory experiment of the leaching the elements from the various cement composites due to two environments were used for the statistical study of dependence or any statistical relationship between two sets of data: concentration of the elements in leachate and pH of leachate. Significant correlation was found out in case of samples with no fly ash replacement related to the dependence Si-pH.

Acknowledgements

This research has been carried out within the Grant No. 2/0166/11 of the Slovak Grant Agency for Science.

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