CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
Copyright © 2013, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-23-5; **ISSN** 1974-9791

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

DOI: 10.3303/CET1332267

Analysis of the Selected Characteristics Changes of Cement Composites Exposed to the Sulphate Environment

Adriana Estokova*,[a], Vlasta Ondrejka Harbulakova[a], Alena Luptakova[b], Nadezda Stevulova[a], Lenka Palaščáková[a], Marek Repka[a]

[a]Technical Univesity of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4, 042 00 Kosice, Slovakia
[b]Slovak Acadamy of Science, Institute of Geotechnology, Watsonova 45, 043 53 Kosice, Slovakia
adriana.estokova@tuke.sk

Many chemicals associated with manure are identified as having a detrimental effect on concrete. The major problem, however, is the effect of hydrogen sulphide and its derivatives, which leads to sulphuric acid corrosion. Sulphuric acid corrosion can be caused due to attack of aggressive media naturally existing in environment. Another possibility of corrosion formation is biogenic acid effect through the agency of microorganisms. The corrosion resistance of concrete depends on the type and chemical composition of the cement as well as the pH of the attacking acid.

The paper is focused on the study of chemical corrosion of concrete samples resulting in increased leaching due to sulphate environment. Sulphate aggressive environment was represented by 0.5 % solution of H_2SO_4 (pH value of 0.99) and 0.5 % $Al_2(SO_4)_3$ solution (sulphate concentration of 3,000 mg/L). Distilled water used as reference medium as proper leaching simulation environment. Concrete composites with/without coal fly ash cement replacement were used for the experiments. The laboratory experiments proceeded during the 60 days.

No significant differences in chemical composition of concrete samples before and after the experiment were observed except for the iron, aluminum and silicon concentrations. Summarizing the results of chemical composition of the liquid media before and after the experiments, the initial concentrations of Ca in leachates have been increased 2.0 to 3.5, 16.4 to 18.3 and 4.1 to 5.1 times for distilled water, sulphuric acid and aluminum sulphate, respectively. In point of view of calcium leaching, the concrete sample with fly ash was confirmed to be more resistant to sulphuric acid in comparison to the sample without fly ash. The initial concentrations of Si have been increased 1.9 to 1.91, 3.2 to 3.3 and 1.89 to 1.92 times for distilled water, sulphuric acid and aluminum sulphate, respectively. In case of all liquid media the increasing character of pH values have been noticed. The most visible increase of pH value to the alkali region was observed in case of distilled water (more than 1.8 times for both types of composites).

1. Introduction

Concrete as one of the basic construction materials is usually thought for decades and that is why strong resistance to even aggressive environment is expected. Despite these facts concrete does corrode mainly by exterior conditions influence. The leaching of calcium can be a matter of concern for the durability of concrete structures (Gérard et al., 2002). It increases the porosity of the surface layers, and detrimentally affects the resistance of the material to mechanical loads (Le Bellego, 2001).

The concrete degradation is common for structures located in aggressive environment and subject to, for instance, sulphate attack, chloride penetration or leaching. According to international standards the aggressive attack is mainly classified as: acidic attack; alkali attack; carbonation; chloride attack; leaching; sulphate attack (Zivica and Bajza, 2001). Acidic attack leads to spread damages of concrete structures all over the world. Due to interaction between certain aggregates (containing amorphous silica or strained quartz) and the highly alkaline solution of the pore aqueous phase, concrete can deteriorate and this reaction is known as "alkali-silica reaction" (*ASR*). The alkali content of the pore aqueous phase depends

Please cite this article as: Estokova A., Ondrejka Harbulakova V., Luptakova A., Stevulova N., Palascakova L., Repka M., 2013, Analysis of the selected characteristics changes of cement composites exposed to the sulphate environment, Chemical Engineering Transactions, 32, 1597-1602 DOI: 10.3303/CET1332267

primarily on the alkali content of the clinker phase and even on the exposure to environmental sodium salts (sea water and de-icing agents) (Collepardi, 2005). Carbonation occurs when carbon dioxide dissolves in the pore fluid of the concrete to produce carbon ions. These react with calcium to produce calcium carbonate, usually in the form of calcite, although aragonite can form in hot conditions (Winter, 2009). The penetration of chlorides into the concrete occurs by various transport mechanisms depending on the exposure conditions. There are significant amounts of chlorides in seawater but chlorides are more limited in groundwater and soil (Cement Concrete & Aggregates Australia, 2009). Leaching in concrete is the process by which soluble material is extracted from the concrete by flowing water. The water may flow over the concrete surface, or percolate through cracks. The major of instances of sulphate attack have two main effects on the cement paste:

- Sulphate reacts with hydrated aluminate phases, particularly monosulphate phase, and any unreacted aluminate (C_3A), to produce ettringite. Ettringite formation within the paste exerts and expansive force, causing cracking
- Calcium hydroxide (CH) in the paste supplies calcium to produce ettringite. When CH becomes scarce, the required calcium for continued ettringite formation is supplied by the C-S-H, which becomes partly decalcified (Winter, 2009).

In the contrast to inorganic aggressive components, the information about the deterioration caused by organic media is very limited and rare (Zivica, 2006). The analysis of the resistance of the cement composites with coal fly ash replacement against biological attack was also investigated in our previous works. In Estokova et al (2012) study of the concrete deterioration caused by biogenic sulphate attack were done, investigation of sulphur oxidizing bacteria as the causative factor of concrete biocorrosion were described in Estokova et al. (2011), and study of concrete samples changes after influence of wastewater in real conditions were published in Ondrejka Harbulakova et al. (2012). Other studies of these samples were aimed at economic calculation of the financial benefits of partial fly ash utilization in concrete road with orientation to building companies (Zelenakova and Ondova, 2010).

The paper is focused on the comparison of the concrete composites deterioration influenced by different aggressive media stands for two selected types of chemical corrosion – sulphate corrosion and proper leaching.

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 10 % 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.

Used coal fly ash with volumetric weight of 2,381 kg/m^3 originates from black coal's burning process in Košice city heating plant (Tepláreň Košice a.s. TEKO). The percentage of basic oxides and total amount of sulphur in coal fly ash used in cement composites was as follow: 36.6 % SiO_2, 16.06 % Al_2O_3, 10.82 % Fe_2O_3, 0.65 % TiO_2, 3.3 % CaO, 1.22 % MgO, 1.41 % K_2O, 0.27 % MnO, 0.56 % Pb_2O_3, 0.09 % 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 three aggressive media representing three models of corrosion: distilled water DW (pH value of 6.25) simulating corrosion caused by leaching, 0.5 % solution of H_2SO_4 (pH value of 0.99) simulating acid corrosion and 0.5 % $Al_2(SO_4)_3$ solution (sulphate concentration of 3,000 mg/L) stands for sulphate corrosion.

Table 1: Characterisation of concrete composites used for the experiment

Composites sign	Fly ash addition	Aggressive medium
DW-0	no	distilled water (DW)
DW-10	yes	distilled water (DW)
AC-0	no	sulphuric acid (H_2SO_4)
AC-10	yes	sulphuric acid (H_2SO_4)
SC-0	no	aluminum sulphate $Al_2(SO_4)_3$
SC-10	yes	aluminum sulphate $Al_2(SO_4)_3$

The volumes of liquids at the beginning of the experiment were 20 mL. Experiments runs in several consecutive cycles during 60 days. 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 both composites and liquid media before and after the corrosion simulation was investigated by X-ray fluorescence method (XRF) using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector. The concrete samples were pulverized by using planetary ball miller SFM (MTI corp., USA and 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 samples and liquids were measured during 300 s 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 cement pellets and liquids.

3. Results

Percentage of basic elements of concrete samples measured by XRF analysis before and after the experiment is presented in Table 2. The initial chemical composition of concrete samples with and without coal fly ash was quite similar except for silicon and iron concentrations. The samples with fly ash addition were expected to be more resistant to the aggressive environment in comparison to the samples without the coal fly ash. Comparing the results, no significant differences in chemical composition of concrete samples was observed except for the iron, aluminum and silicon concentrations. The decrease of iron concentration after the experiment was found out in case of concrete samples without fly ash for all three environments by 41.7 to 48.9 % in correlation to results presented by (Balintova et al., 2012). The decrease in silicon concentrations was observed for both samples (with and without fly ash) after the exposition to distilled water and sulphuric acid. The similar trend of concentration decrease was noticed in case of aluminium after the exposition to distilled water and sulphuric acid but only for the samples without fly ash addition. In case of sulphur, the increase of percentage in concrete samples was noticed after the exposition to sulphuric acid. This fact could be the result of the formation of sulphate compounds e.g. ettringite on the surface of samples or inside the concrete volume.

The more marked evidence of basic elements leaching from the cement matrix was observed when analysing the results of chemical composition of the liquid media before and after the experiments (Table 3 and Table 4). The initial concentrations of Ca have been increased 2.0 to 3.5, 16.4 to 18.3 and 4.1 to 5.1 times for distilled water, sulphuric acid and aluminum sulphate, respectively. In point of view of calcium leaching, the concrete sample with fly ash was confirmed to be more resistant to sulphuric acid in comparison to the sample without fly ash.

Table 2: The percentage of basic elements of composites before and after the experiment

	Composite	Mg	Al	Si	S	Ca	Mn	Fe
					%			
before	without fly ash	2.19	6.74	19.97	0.15	13.23	0.14	6.69
	with fly ash	2.16	6.65	21.42	0.31	13.76	0.12	3.97
after	DW-0	2.05	5.80	18.50	0.25	15.50	0.12	3.60
	DW-10	2.03	6.61	20.63	0.22	14.07	0.15	4.03
	AC-0	1.76	5.31	17.97	0.98	13.68	0.10	3.42
	AC-10	1.97	6.45	20.70	0.61	12.16	0.13	4.04
	SC-0	2.10	6.90	21.54	0.29	13.14	0.12	3.90
	SC-10	1.98	6.83	21.28	0.25	12.60	0.15	4.21

Table 3: Chemical composition of aggressive media before the experiment

Liquid	pH	Mg	Al	Si	S	Ca	Mn	Fe
				ppm				
DW	6.25	-	79.4	243.4	-	55.6	36.8	-
H_2SO_4	0.99	-	298	195.3	3683	49.3	29.1	-
$Al_2(SO_4)_3$	3.21	-	608	273.1	991.5	57.5	28.1	-

Table 4: Chemical composition of leachates after the experiment

composite	Mg	Al	Si	S	Ca	Mn	Fe
				ppm			
DW-0	-	205.4	460.8	48.0	111.4	25.8	6.5
DW-10	1468	368.6	466.8	205.1	197.5	39.0	7.3
AC-0	-	492	620.5	3270	904.7	47.5	473.4
AC-10	-	539	644.4	2522	807.4	48,9	481.3
SC-0	-	861	525.5	1027	237.7	31.2	9.3
SC-10	-	727	516.4	906.5	293.1	28.0	7.1

The initial concentrations of Si have been increased 1.9 to 1.91, 3.2 to 3.3 and 1.89 to 1.92 times for distilled water, sulphuric acid and aluminum sulphate, respectively. The very similar trend in increasing of final concentrations when comparing to the initial ones was observed for most of the studied elements except for sulphur. That is in correlation with the probable formation of sulphate compounds e.g. ettringite on the surface of samples or inside the concrete volume as mentioned above.

The course of pH values changes of leachates before and after the experiments is presented in Figure 1. pH values were measured after every week-cycle. In case of all liquid media the increasing character of pH values have been noticed. The most visible increase of pH value to the alkali region was observed in case of distilled water (more than 1.8 times for both types of composites). pH value increase for both samples with and without fly ash was comparable in case of distilled water and aluminum sulphate as medium. On the contrary, the more significant increase of pH was found out after the experiment for composite with coal fly ash (more than 1.3) in sulphuric acid when comparing to the composite without fly ash.

The results of the weight changes measurements after 60 day-experiment are presented in Figure 2. Both the decrease and slightly increase of concrete samples weight were observed after the corrosion experiment. The decreases of weight ranging from 0.25 to 0.33 g (1.06 to 2.88 %) were determined in both concrete composites immersed into the 0.5 % solution of H_2SO_4. The most visible decrease of 0.33 g was observed for the composite without coal fly ash immersed to the 0.5 % solution of H_2SO_4. In case of the composites exposed to distilled water and aluminum sulphate measured weight changes were not significant (+/- 0.02 g).

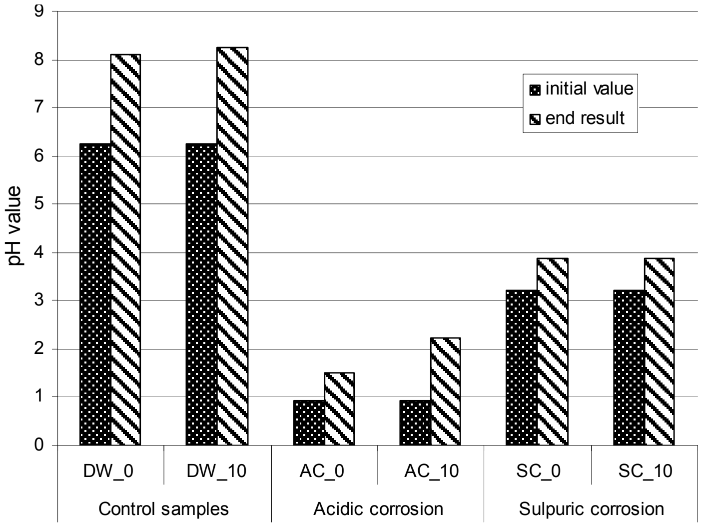

Figure 1: pH values changes of leachates

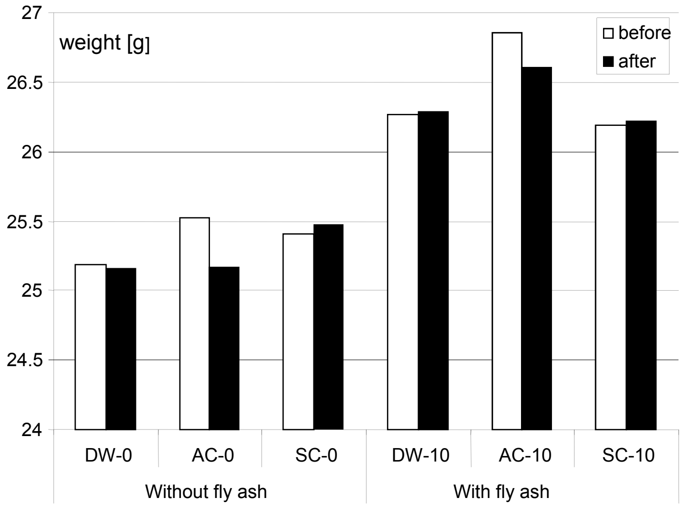

Figure 2: Weight changes of concrete composites without/with coal fly ash replacement

4. Conclusion

The chemical corrosion of concrete composites based on the three corrosive attacks was studied in this work: acidic attack representing by sulphuric acid, sulphate acid representing by aluminum sulphate solution and proper leaching representing by distilled water. Summarizing the results of the chemical composition of concrete composites and liquids before and after the corrosion, measured pH values and weight changes of concrete samples it is concluded:

- No significant differences in chemical composition of concrete samples were observed except for the iron, aluminum and silicon concentrations. The major decrease of iron concentration after the experiment was found out in case of concrete samples without fly ash for all three environments by 41.7 to 48.9 %;
- More marked evidence of basic elements leaching from the cement matrix was observed when analyzing the results of chemical composition of the liquid media. The initial concentrations of Ca have been increased 2.0 to 3.5, 16.4 to 18.3 and 4.1 to 5.1 times for distilled water, sulphuric acid and aluminum sulphate, respectively;
- The increasing character of pH values of all liquid media has been noticed, the most visible shift to the alkali region was observed in case of distilled water;
- Both decrease and slightly increase of concrete samples weight were observed after the corrosion experiment. The highest decrease was observed for samples exposed to sulphuric acid.

Acknowledgement

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

References

Balintova M., Holub M., Singovszka E., 2012, Study of iron, copper and zinc removal from acidic solutions by sorption, Chemical Engineering Transactions 28, 175-180. DOI:10.3303/CET1228030

CCAA Cement Concrete & Aggregates Australia, Report: Chloride Resistance of Concrete, June 2009, 37 pages, http://www.concrete.net.au/publications/pdf/ChlorideResistance.pdf, accessed 06.02.2013.

Collepardi M., 2005, Sulphate attack and alkali - silica expansion, Proceedings of Second International Symposium on Concrete Technology for Sustainable February - Development with Emphasis on Infrastructure, Hyderabad, India, 27 February - 3 March, 55 - 67.

Estokova A.,Ondrejka Harbulakova V., Luptakova A.,Prascakova M., Stevulova N. 2011, Sulphur oxidizing bacteria as the causative factor of biocorrosion of concrete, In: Chemical Engineering Transactions 24, 1147-1152. .DOI: 10.3303/CET1124192

Estokova A., Ondrejka Harbulakova V., Luptakova A., Stevulova N., 2012, Study of the deterioration of concrete influenced by biogenic sulphate attack, Proceedia Engineering 42, 1901-1908.

Gerard B., Le Bellego C., Bernard O., 2002, Simplified modeling of calcium leaching of concrete in various environments, Materials and Structures/Materiaux et Constructions 35, 632-640.

Le Bellego C., 2001, Chemomechanics of leached concrete structures, structural analysis and size effects. Ph.D. Thesis, ENS Cachan, France (in French)

Ondrejka Harbulakova V., Estokova, A., Stevulova, N., Foraiova., K. 2012, Study of concrete changes characteristics after biocorrosion processes affected by wastewater, Folia Scientiarium Universitatis Technicae Resoviensis 59 (2), 13-22.

Winter N., 2009, Understanding cement, e-book. Suffolk: WHD Microanalysis Consultant Ltd, UK.

Zelenakova E., Ondova M., 2010, The economic balance of the financial costs of concrete road construction with a part of fly ash in the cement component, Innovative approaches to modeling of intelligent structural elements in construction area 2010, Kosice: VUSI, 202-211.

Zivica V., 2006, Deterioration of cement-based materials due to the action of organic compounds, Construction and Building Materials 20, 634–641.

Zivica V., Bajza A.,2001, Acidic attack of cement based materials - a review. Part 1. Construction and Building Materials 15 Elsevier, Principle of acidic attack, 331- 340.