

Some Aspects of Study the Leaching and Acid Corrosion of Concrete

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Abstract—Although properly made concrete is inherently a durable material, there are many physical and chemical forces in the environment which can contribute to its deterioration. This paper deals with two aspects of concrete durability in chemical aggressive environment: degradation effect of particular aggressive exposure and role of particular mineral additives. Results of the study of leaching and acid corrosion processes in samples prepared with specific dosage of microsilica and zeolite are given in the paper.

Corrosion progress after 60-day exposition is manifested by increasing rate of both Ca and Si release, what is identified by XRF method. Kind and dosage of additions used in experiment was found to be helpful for stabilization of concrete microstructure. The lowest concentration of mean elements in leachates was observed for mixture V1 (microsilica only) unlike the V2 (microsilica + zeolite). It is surprising in the terms of recommendations of zeolite application for acid exposure. Using microsilica only seems to be more effective.

Keywords—Sustainability, durability, concrete, acid corrosion, leaching.

I. INTRODUCTION

THERE are three components of sustainability: environment, economy, and society. To meet its goal, sustainable development must provide that these three components remain healthy and balanced [1]. According to the concept of sustainable development, the environmental load of a building must be evaluated throughout its life cycle, i.e. from design to construction, maintenance or repair, demolition and rubble disposal. Therefore, sustainable construction means designing structures with appropriate durability during a specified service life [2].

Durability of concrete is defined as the ability of concrete to withstand damaging effects of environment without deterioration for a certain period of time. So, durability of concrete should be considered in two aspects. The first aspect is damaging factors; the second is the resistibility to damaging effects. The durability of concrete is determined by the confrontation between these two aspects [3], [4]. External damaging factors are generally considered as mechanical, physical or chemical. Resistibility is solved mainly by proper composition of concrete mix, as well as proper technique on working site.

Codes and specifications followed in different countries play an important role in ensuring the durability of concrete structures. The definitions of exposure conditions and then exposure classes in most of the international standards have

been expanded and are aligned with the anticipated severity of exposure during the service life of structures. The vast majority of international codes on structural concrete are basically “prescriptive” in nature, in that they specify the limiting values of the following four parameters for code-defined exposure conditions [5]:

- Minimum cement content
- Maximum free water-binder ratio
- Minimum grade of concrete
- Cover to reinforcement.

Other recommendations for concrete composition are usually given as well, e.g. for concretes to be exposed to chemical attack, mineral additives are recommended.

A lot of mineral additives come as wastes/secondary raw materials and they play a significant role in production of sustainable concrete by three main ways:

- They can save energy consumption and CO₂ production by substitution of cement
- They can help the concrete durability due to better quality (strength, impermeability, resistance to various impacts ...), and
- They can help to reduce the environmental burden by their incorporation in concrete.

Demonstration of concrete durability in specific environment then acts only through the demonstration of standard parameters, given by national standards. These are represented by limiting values of following: compressive strength class, frost and freeze-thaw resistance with NaCl solution, depth of penetration of water under pressure and so on. On the basis of own practical experiences, those parameters are not of informative value for users/contractors in praxis; they cause an uncertainty as regards a chemical resistance of concrete, moreover when the standard does not give dosage of additives for specific exposure classes.

Therefore this paper deals with two aspects of concrete durability in chemical aggressive environment: degradation effect of particular aggressive exposure and role of particular mineral additives. Results of the study of leaching and acid corrosion processes in samples prepared with specific dosage of two kinds of additives are given in the paper. The recipes of mixtures were verified in advance in terms of the meeting the standard criteria for defined exposure class.

Deterioration of concrete structures exposed to an aggressive solution is often characterized by the leaching of calcium and silicon compounds from cement matrix. Leaching as a diffusion-reaction phenomenon, which takes place when concrete is exposed to poorly mineralized or acid water, is one of the most significant parameters which affect the durability

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of cement pastes. Therefore it is suitable parameter for the study of corrosion processes under those conditions [6].

II. MATERIALS AND METHODS

Testing of resistance to chemical aggressive environments in standard laboratory praxis usually goes using small samples (40x40x40 mm or even smaller). This is because of space and capacity reasons, difficult curing of big samples in standard conditions, great demands on materials (samples and testing solution) and so on. However, using of so big samples as possible is recommended for finding more exact results. This is instructive considering approximation of results to real conditions in construction. Therefore using of 150x150x150 mm samples was verified and results given here are unique in this sense.

TABLE I
LIMITING VALUES FOR EXPOSURE CLASSES FOR CHEMICAL ATTACK FROM NATURAL SOIL AND GROUND WATER – ACID EXPOSURE [7]

Chemical characteristic	XA 1 (slightly aggressive)	XA 2 (moderately aggressive)	XA 3 (highly aggressive)
pH	5.5- 6.5	4.5 - 5.5	4.0- 4.5

Recipes for testing were designed following requirements of EN 206-1 [7] for XA2 exposure class. XA2 is moderately aggressive chemical environment intended for concrete to be used for treatment plants, slurry containers or in soil corrosive to concrete, etc. Limiting values are given in Table I.

Materials and composition of tested concretes are given in Table II. Both a microsilica and zeolite were used for improvement of acid resistance of concrete. Amounts of additives represent 5.5% or 11% of cement content respectively.

TABLE II
MATERIALS AND COMPOSITION OF TESTED CONCRETES

Materials	Samples		
	V0	V1	V2
CEM I42.5 N (kg.m ⁻³)	360	360	360
Water (L)	170	197	205
Zeolite (kg.m ⁻³)	-	-	20
Microsilica (kg.m ⁻³)	-	20	20
Aggregates D _{max} 16 (kg.m ⁻³)	1 800	1 775	1 725
Superplasticizer (%)	0.8	0.8	0.8

Required standard parameters for of XA2 class (min C 30/37, max depth of penetration = 50 mm and max. water absorption = 4%) were tested after 28 days of standard curing of samples and all recipes were found to comply them. These results were published previously in [8]. Meeting these criteria, tested concretes should ensure a sufficient durability in real structure under acid exposure.

For study of tested concretes in acid environment, samples (150x150x150mm cubes) after standard 28 days curing in water were immersed into the HCl solution of pH=5.5 within 60 days. In order to evaluate the influence of acid environment on tested concretes, one set of samples was cured for 60 days in water only, taking it as reference environment.

Although amount of acid solution corresponded with principles of testing the corrosion resistance of concretes (volume of the solution to volume of the samples should be 10:1), a pH of the solution was very quickly turning to alkaline due to large size of the samples. Therefore value of pH was being adjusted to the constant one during the whole testing process very precisely.

Samples after 28 days of standard curing (reference samples), as well as after extra 60 days of acid/water exposure was tested by X-ray fluorescence analysis (XRF). Samples for analysis were prepared by milling the concretes after particular exposures, then both the pellets and leachates were prepared from powdered material.

SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses was used here. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The pellets were prepared as pressed tablets of diameter 32 mm by mixing 5g of cement and 1g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m². The samples were measured during 300s 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.

III. RESULTS AND DISCUSSION

The results of XRF analysis regarding the composition of analysed concrete samples in terms of its main elements (calcium, silicon, aluminium, iron, and magnesium) for reference samples (after standard 28-day curing) are given in Table III and for samples after 60-day extra exposures in Tables IV and V.

TABLE III
CONCENTRATION MAIN ELEMENTS IN OXIDES FORM IN REFERENCE SAMPLES (%)

	Samples (%)		
	V0	V1	V2
CaO	31.27	26.17	25.12
SiO ₂	30.16	45.63	39.82
Al ₂ O ₃	5.21	5.39	5.25
Fe ₂ O ₃	4.04	3.75	4.63
MgO	3.04	2.73	2.38
Ca/Si	1.586	0.877	0.965

TABLE IV
CONCENTRATION MAIN ELEMENTS IN OXIDES FORM IN SAMPLES EXPOSED TO WATER (%)

	Samples (%)		
	V0	V1	V2
CaO	29.55	28.94	26.61
SiO ₂	31.33	36.38	39.65
Al ₂ O ₃	4.92	5.22	5.51
Fe ₂ O ₃	4.49	4.57	3.94
MgO	2.85	2.95	2.49
Ca/Si	1.443	1.217	1.023

TABLE V
CONCENTRATION MAIN ELEMENTS IN OXIDES FORM IN SAMPLES
EXPOSED TO HYDROCHLORIC ACID (%)

	V0	V1	V2
CaO	28.35	26.56	26.75
SiO ₂	34.92	37.84	40.38
Al ₂ O ₃	5.26	5.47	5.45
Fe ₂ O ₃	4.58	4.32	3.92
MgO	3.41	3.00	2.70
Ca/Si	1.241	1.074	1.013

The results of silicon, calcium, aluminium and iron ions concentrations leached from the concrete samples after the 60-day exposition to water and hydrochloric acid are presented in Figs. 1 and 2.

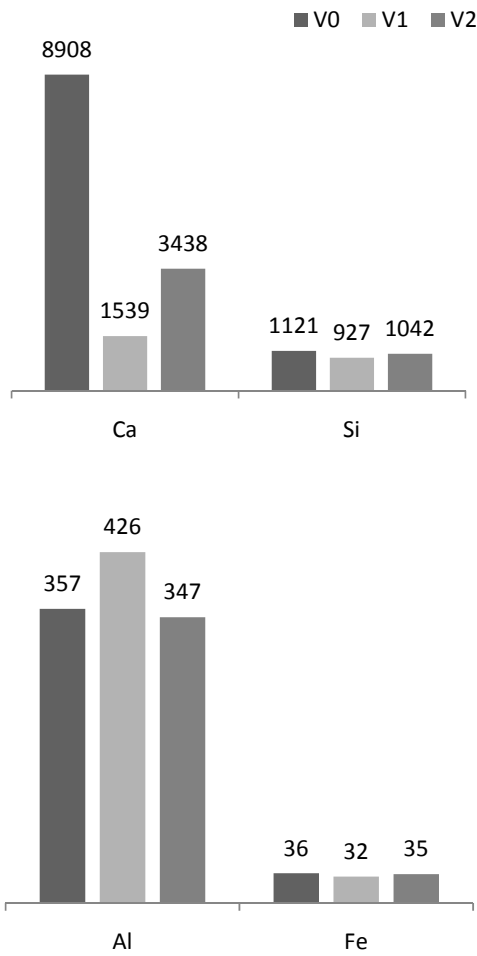


Fig. 1 Concentration of released ions (mg/L) from concrete composites after 60-day exposition to water

The highest concentrations of all analysed ions in leachates from the concrete samples after the 60-day exposition to water environment have been measured for V0 – reference mixture without any additions. Mixture V1 with microsilica addition was found to have the lowest concentrations in leachates for all analysed ions except for aluminium (Fig. 1).

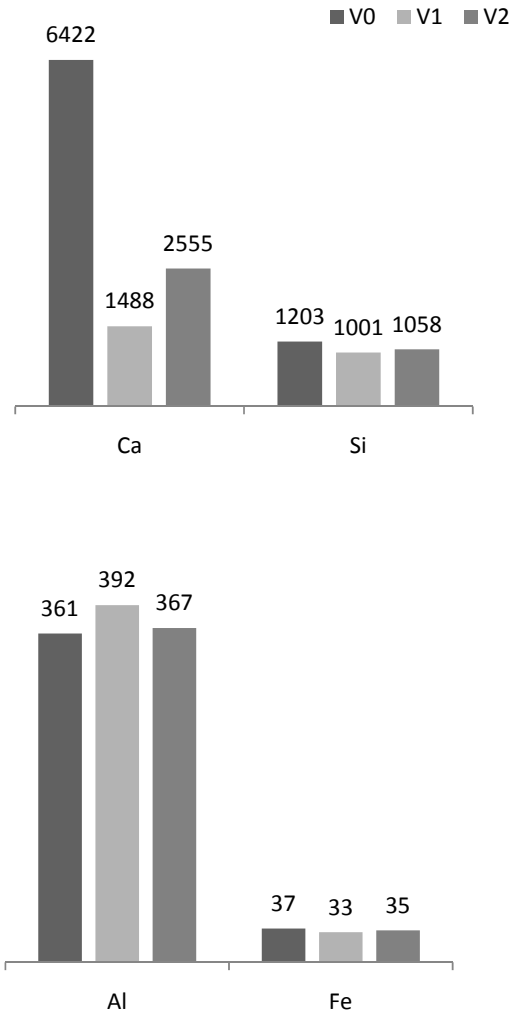


Fig. 2 Concentration of released ions (mg/L) from concrete composites after 60-day exposition to hydrochloric acid

Similarly to the water environment, V0 reference mixture after 60-day exposition to hydrochloric acid was confirmed to have the highest concentrations of analysed ions in leachates except for aluminium whereas for V1 mixture with microsilica the lowest concentrations of calcium, silicon and iron ions have been measured in leachates (Fig. 2).

Surprisingly, more significant leaching of calcium ions was observed in case of samples exposed to water environment compared to samples exposed to hydrochloric acid (8908 versus 6422 mg/L; 1539 versus 1488 mg/L and 3438 versus 2555 mg/L for V0, V1 and V2 samples, respectively). On the contrary, the highest concentrations of silicon ions released were found in case of samples exposed to HCl, as expected.

Percentage of calcium and silicon ions released to the total content of ions in concrete samples is presented in Table VI.

TABLE VI
PERCENTAGE OF ANALYSED IONS RELEASED

Sample	Exposition medium	Compress. strength (MPa)	Ca released (%)	Si released (%)
V0	Reference sample	41.2	1.02	0.67
	Water	47.3	4.22	0.77
	Hydrochloric acid	41.6	3.17	0.74
V1	Reference sample	46.9	1.47	0.38
	Water	49.6	0.74	0.55
	Hydrochloric acid	47.5	0.78	0.57
V2	Reference sample	49.9	1.21	0.54
	Water	46.2	1.81	0.56
	Hydrochloric acid	45.7	1.34	0.56

Percentage of calcium ions released ranged from 1.02 to 4.22, 0.74 to 1.47 and 1.21 to 1.81% for V0, V1 and V2 mixtures, respectively. Comparing the durability of concrete samples of various compositions after 60-day exposition to both environments (H₂O, HCl) in terms of released calcium ions percentage, it can be concluded that water exposition caused more intensive leaching of calcium than hydrochloric acid, excepting V1. However, this finding does not correspond to the compressive strength parameter values because of the fact, that higher compressive strength has been measured for samples immersed for 60 days in water than in HCl, as assumed. Water curing supporting the additional hydration processes in concrete samples likely still prevails over the calcium leaching.

Leaching of silicon ions was manifested by very close percentage intervals of 0.67 – 0.77, 0.38 – 0.57 and 0.54 – 0.56 % for V0, V1 and V2 mixtures, respectively. Significantly more intensive leaching of silicon ions was not confirmed after the exposition to hydrochloric acid compared to water.

According to Table VI, no correlation between the released amount of analysed ions and sample compressive strength was found except for the mixture V1. As it is seen in Fig. 3, the compressive strength of mixture V1 decreased with the increasing of calcium ions released percentage.

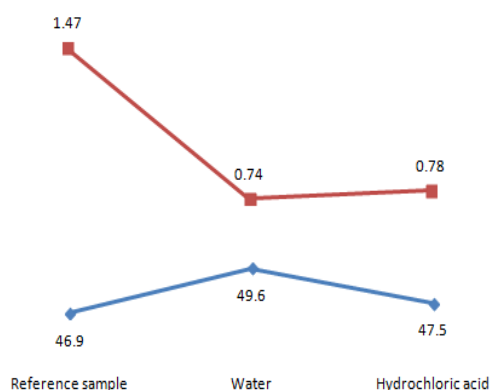


Fig. 3 Correlation between percentage of calcium ions released and decreasing of the compressive strength of mixture V1

Leaching of both silicon and calcium ions has been observed to be more intensive after the exposition of samples

to water and hydrochloric acid environments comparing to reference samples (Table VI), excepting calcium leaching from mixture V1.

IV. CONCLUSION

The observations mentioned above allow the following conclusions:

- Mixture V0 with no any addition shows in principle the highest release of main elements in both exposures, suggesting that kind and dosage of **additions used in experiment are helpful** for stabilization of concrete microstructure.
- The lowest concentration of main elements in leachates was observed for V1 (microsilica only), unlike the V2 (microsilica + zeolite). It is surprising in the terms of recommendations of zeolite application for acid exposure. **Using microsilica only seems to be more effective.**
- Concrete samples exposition to water environment resulted in more intensive leaching of calcium than to hydrochloric acid.
- Corrosion progress after 60- day exposition is manifested by increased leaching of both silicon and calcium ions when comparing to reference samples, what is relatively easy identifiable by XRF method.

ACKNOWLEDGMENT

This research has been carried out within the Grants No. 1/0767/13 and No. 1/0481/13 of the Slovak Grant Agency for Science.

REFERENCES

- [1] L. Struble and J. Godfrey, "How sustainable is concrete?" in *Proc. International Workshop on Sustainable Development and Concrete Technology*, Beijing, 2004, pp. 201-211.
- [2] V. Corinaldesi and G. Moriconi, "Influence of mineral additions on the performance of 100% recycled aggregate concrete," *Construction and Building Materials*, vol. 23, 2009, pp. 2869–2876.
- [3] X. Zhao, J. Wei and Liu Z., "Durability of Concrete under Multi-damage Action," *Journal of Wuhan University of Technology*, vol. 19/2, 2004, pp. 73-75.
- [4] K. Obla, C. Lobo and L. Lemay, "Specifying Concrete for Durability", *Concrete in Focus*, 2006, pp. 42-50.
- [5] V. R. Kulkarni, "Exposure classes for designing durable concrete," *The Indian Concrete Journal*, March 2009, pp. 23-43.
- [6] H. Yang, L. Jiang, Y. Zhang and Q. Pu, "Flexural Strength of Cement Paste Beam under Chemical Degradation: Experiments and Simplified Modeling", *J. Mater. Civ. Eng.*, 25(5), 2013, pp. 555-562. Technical Papers.
- [7] EN 206-1: Concrete. Part 1: Specification, performance, production and conformity, 2002.
- [8] A. Sicakova, E. Terpakova and J. Junak, "Verification of proposed concrete alternatives for XA2 specification - acid exposure," in *Proc. 13th International Multidisciplinary Scientific Geoconference: Ecology, Economics, Education and Legislation*, Albena, vol. 1P, 2013, pp. 1155-1160.