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Sustainable Usage of Slag in Concrete for Higher Resistance in Aggressive Environment - Mathematical Evaluation

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A number of important properties of the made mortar and concrete used with among others compressive strength, sulphate resistance, carbonation, corrosion resistance, and resistance to acid attack need to be studied. Slag is one of the promising sustainable solutions as it can improve a durability of concretes and is obtained as solid waste generated by industry. Concrete sets of specimens were prepared based on the Portland cement only and also with 65% wt. cement replacement by granulated blast-furnace slag. Chemical acid corrosion, simulated by H_2SO_4, was investigated in terms of basic concrete´s elements leachability (calcium and silicon). Sulphuric acid solutions were prepared in two concentrations (0.005 wt. % H_2SO_4 with pH 3 and 0.0005 wt. % H_2SO_4 with pH 4). Dissolved amounts of elements due to chemical corrosion attacks measured in the period of 3 months represented the deterioration parameters used for the mathematical evaluation regrading dependency of leaching the elements based on different concentration of acid solution or based on specimen composition. In spite of the same chemical composition of leachates, the leaching performance of concretes regarding silicon was fully independent when exposed to solution of sulphuric acid with pH of 3 and 4, respectively. The finding revealed the similar leaching trend and behaviour of dissolved calcium in the studied solutions of sulphuric acids for concrete sample with slag addition.

1. Introduction

External sulphate attack is the more common type and typically occurs where water containing dissolved sulphate penetrates the concrete. An assessment method for concrete sustainability is developed as a technique to ensure the manufacture of highly durable and sustainable concrete, while minimizing both the load on the ecological environment and manufacturing costs. Development of more sustainable cementitious systems in order to curb the negative environmental impacts and disintegration of concrete structures associated with ordinary Portland cement plays a key role in material engineering nowadays. Sulphate attack on concrete represents a chemical breakdown mechanism where sulphate ions attack components of the cement paste. The compounds responsible for sulphate attack on concrete are water-soluble sulphate-containing salts, such as sulphates of alkaline earth metals (calcium, magnesium) and alkali metals (sodium, potassium) that are capable of chemically reacting with components of concrete (The Constructor - Civil Engineering, 2015). Yu et al. (2016) studied the samples of ordinary Portland cement mortar fully immersed in sodium sulphate solutions of different concentrations (0%, 5% and 15%) for up to 270 days. Properties of the samples as compressive strength, static modulus of elasticity, stress-strain behaviour, hardened density, water permeability coefficient, and length changes were investigated. An increase in the concentration of the sodium sulphate solution was found to reduce the time needed to reach peak properties and to accelerate deterioration of the properties at the late stage (Yu et al., 2016). Brown (1981) compared the rates of sulphate attack of mortar specimens exposed under typical immersion and environmentally controlled conditions. It was observed that environmental control significantly increased the rate of sulphate attack as measured either by strength loss or linear expansion. The sulphate resistance of concrete was tested also by Loser and Leeman, 2016. They used drying-immersion cycles of varying duration in different sulphate solutions. The measured expansion in the different protocols

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showed a correlation to the sulphate profiles in the test specimens determined by EDX. The test of matrix of 20 concrete mixtures permitted to distinguish the effect of cement type, water to cement ratio and paste volume on expansion.
Structures in potentially aggressive environments must be designed to recognise the risk of sulphate attack, and specific precautions taken in the design process to manage that risk (Ash development association, 1995). Best practice to minimize the harmful impact on concretes is to use alumino-silicate by-products, such as silica fume, fly-ash and ground granulated blast-furnace slag, in combination with Portland cement to improve aspects of performance (Rodríguez-Camacho, 2002). Natural pozzolans and industrial by-products are generally available at substantially lower costs than Portland cement. Ground granulated blast-furnace slag is a by-product of the steel industry. Use of ground granulated blast-furnace slag as a cementitious material blended with Portland cement is based on its activation with alkalis (mainly $Ca(OH)_2$) released from hydration of the Portland cement (Bostanci et al., 2016). A number of research studies have shown that the addition of pozzolans and industrial by-products enhances the strength and durability of mortars exposed to sulphate attack. Ondrejka Harbuľáková et al. (2015) studied various cement composites (with and without fly ash cement replacement) exposed to two environments (distilled water and sulphuric acid) using statistical study of dependence concentration of the elements in leachate and pH of leachate. Binici et al. (2011), in their paper they studied the effect of using blast furnace slag, ground basaltic pumice and its combination as a fine aggregates on the durability of concrete pipes. Properties as ultimate load capacity, sulphate resistance, permeability, and weight changes were measured and evaluated. Various techniques including mercury intrusion porosimetry (Duan et al., 2013), microhardness testing or scanning electron microscopy are used to investigate and predict the concrete deterioration (Bazant and Steffens, 2000). Evolutionary polynomial regression (EPR) was used to predict degradation of concrete subject to sulphuric acid attack in paper by Alani and Faramarzi (2014). The results show that the EPR model can successfully predict mass loss of concrete specimens exposed to sulphuric acid. Other different methods of maintaining the reliability of critical infrastructure were presented in (Kong et al., 2002; Valis and Pietrucha-Urbanik, 2014; Pietrucha-Urbanik, 2014; Pietrucha-Urbanik 2015).
The objective of the paper is an application of statistical method for an evaluation of deterioration processes of slag-based concrete composites exposed to chemical sulphate attack. Leached-out amounts of calcium and silicon ions from the concrete specimens exposed to sulphuric acid of different concentrations were measured. Statistical investigation was focused on a relation between leached-out ions in dependence on the pH value of sulphuric acid and concrete’ s composition.

2. Material and Methods

2.1 Concrete samples

Concrete specimens used for the experiment were prepared as two sets of specimens: 1) concretes of mixture according to a standard recipe based only on Portland cement (marked as SR) and 2) concretes of a mixture where 65 wt. % of cement was replaced by granulated blast-furnace slag (marked as S65). Standardized concrete prisms with dimensions 100 x 100 x 400 mm were cured for 28 days in a water environment prior to leaching testing. Subsequently, the concrete prisms were cut into smaller prisms measuring 50 x 50 x 10 mm for deterioration testing. The test specimens were slightly brushed in order to remove polluting particles, and dried at 105 ºC to a constant weight. The composition of both concrete mixtures without and with cement replacement by slag is presented in detail in Table 1. The water-to-binder ratio of both mixtures was set to 0.47, the water absorbability of slag-based composites was of 3.3 %.

Table 1: The proportions of concrete mixture for 1 m^3 of fresh concrete

Components	SR mixture	S65 mixture
Cement (kg)	360	126
Slag (kg)	-	234
Water (L)	170	162
Aggregate - fr. 0/4 mm (kg)	825	825
Aggregate - fr. 4/8 mm (kg)	235	235
Aggregate - fr. 8/16 mm (kg)	740	740
Plasticizer (L)	3.1	-

2.2 Sulphate attack

For the purpose of accelerated testing of the sulphate attack, a solution of sulphuric acid of two different concentrations was used: the solution with a concentration of 0.005 wt. % H_2SO_4 (pH value 3) and the solution with a concentration of 0.0005 wt. % H_2SO_4 (pH value 4). Sulphuric acid with pH=3 is marked as MC (more concentrated solution) and sulphuric acid with pH=4 is marked as LC (less concentrated solution). The samples of concrete composites were placed into prepared solutions of sulphuric acid while the volume of liquids was strictly calculated based on the volume of the immersed sample. According to the standards dealing with corrosion of concretes, the ratio of volumes of liquid solutions (400 - 500 mL) to volumes of tested samples were set to 10:1. The experiments were conducted in glass containers closed with aluminum foils. Exposure of the tested concrete samples to liquid aggressive sulphate media proceeded over a period of 270 days under laboratory temperature of 23 °C. The concentrations of dissolved Ca^{2+} and Si^{4+} ions in leachates were measured periodically during whole experiment. The leached-out amounts of Ca and Si, converted to unit quantities per 1 g of concrete sample, represented deterioration parameters in mathematical evaluation of concrete´s deterioration.

2.3 Analytical method

The concentrations of Ca and Si in leachates were determined by X-ray fluorescence analysis (XRF) using SPECTRO iQ II equipment (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses. 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 concrete leachates.

2.4 Mathematical approach

A statistical 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. Correlation between sets of data is a measure of how well they are related. The most common measure of correlation in statistics is the Pearson Correlation R_{xy} as is shown in Eq(1) (Kreyszig, 2011). The full name is the Pearson Product Moment Correlation or PPMC. It shows the linear relationship between two sets of data.

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

Pearson's Correlation Coefficient is a linear correlation coefficient that returns a value of between -1 and +1. A -1 means there is a strong negative correlation and +1 means that there is a strong positive correlation. A 0 means that there is no correlation (this is also called zero order correlation). Than degree of the correlative closeness is defined as: 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

3.1 Deterioration parameters

Deterioration parameters - quantities of leached Si^{4+} and Ca^{2+} from reference samples (SR) and samples with 65% cement replacement by granulated blast-furnace slag (S65) during 270-day experiments corresponding to 1 g concrete specimen, due to chemical corrosion caused by more concentrated solution of sulphuric acid (MC) and by less concentrated solution of sulphuric acid (LC), are given in Table 2. Data presented in Table 2 were used as input data for correlation analysis of the trend of leaching basic elements from the both types of concrete specimens.

3.2 Correlation analysis

Based on measured concentrations, the correlation coefficient of the mutual relationship between the elements was established. Calculation was done for specimens prepared according to standard recipe (SR) and also for specimens with 65% cement preplacement by granulated blast-furnace slag. The leaching trends of calcium in

LC and MC and, analogically, of silicon in LC and MC were considered for both types of samples. The results are presented in Table 3.

Table 2: Quantities of leached-out Ca^{2+} and Si^{4+} corresponding to 1 g of concrete samples

		Ca mg/g		Si mg/g				Ca mg/g		Si mg/g	
solution	days	S65	SR	S65	SR	solution	days	S65	SR	S65	SR
MC	7	0.31	0.74	1.73	2.59	LC	7	0.30	0.40	2.07	2.28
	14	0.59	1.19	1.50	2.03		14	0.46	0.30	1.61	2.01
	21	0.71	1.77	1.40	2.21		21	0.48	1.23	1.63	2.17
	28	0.83	2.09	1.91	2.43		28	0.58	0.66	1.79	2.48
	35	0.94	2.05	1.56	2.39		35	0.65	0.99	1.79	2.94
	42	1.11	1.87	2.10	1.64		42	0.75	0.93	1.97	2.05
	49	1.33	1.94	1.84	1.59		49	0.80	0.94	1.82	1.53
	56	1.46	2.30	2.01	2.19		56	0.87	3.40	1.49	4.33
	63	1.82	2.40	2.61	2.24		63	0.92	1.45	1.25	2.28
	70	1.76	2.77	1.52	2.74		70	1.04	1.57	1.46	2.72
	77	1.97	3.39	1.92	4.59		77	1.11	1.58	1.42	3.93
	84	2.03	3.58	1.47	3.65		84	1.22	1.56	1.96	2.58
	91	2.11	4.28	1.26	4.18		91	0.88	1.57	1.08	2.99
	120	2.37	4.21	1.83	6.40		120	1.44	1.85	2.46	3.42
	150	2.26	3.81	1.63	7.12		150	1.56	1.82	2.45	3.70
	180	2.70	51.23	2.41	19.38		180	1.63	2.05	1.66	3.16
	270	2.65	27.12	1.07	10.95		270	1.76	1.13	0.89	2.63

Table 3: Correlation coefficients of Ca and Si leaching, respectively, in LC and MC

sample	ions	ions	R_{xy}
SR	Ca	LC/MC	0.22
	Si	LC/MC	0.30
S65	Ca	LC/MC	0.95
	Si	LC/MC	0.16

The very low correlation coefficients (R_{xy} = 0.16 and 0.30) calculated for silicon points to the fact that there is a big difference in Si leaching and consequential behaviour of silicon in the solutions studied. That was found for both concretes without and with slag addition. In spite of the same chemical composition of leachates, the leaching performance of concretes regarding silicon was fully independent when exposed to solution of sulphuric acid with pH of 3 and 4, respectively. This was quite surprising, because we assumed the similar leaching mechanisms of silicon in the acidic solutions, just more intensive in the more concentrated solution. The finding was observed also for calcium leaching from reference concrete sample (SR), as seen in Table 3, since the correlation coefficient reach a very low value equal 0.22. The different leaching performance of concretes depending on the composition of the concretes has been presented also in our study (Ondrejka Harbuľáková et al., 2014).

On the other hand, a very high correlation with the correlation coefficient $R_{xy} > 0.9$ was found for calcium leaching regarding concrete sample with slag addition (S65). The finding revealed the similar leaching trend and behaviour of dissolved calcium in the studied solutions of sulphuric acids.

The correlation coefficients were calculated also for relation between calcium and silicon for both liquid media and for both types of concrete specimens. The results are reported in Table 4.

Table 4: Correlation coefficients of Ca/Si leaching in LC and MC, respectively

acid	*ions*	samples	R_{xy}
LC	Ca/Si	SR	0.96
	Ca/Si	S65	0.04
MC	Ca/Si	SR	0.78
	Ca/Si	S65	-0.02

A high correlation with R_{xy} > 0.7 was calculated for the Ca/Si leaching from reference composites exposed to more concentrated solution of sulphuric acid with pH of 3 (Table 4). In case of the same concrete type (SR) exposed to less concentrated acidic solution this correlation is even stronger, having a high correlation coefficient R_{xy} > 0.9. This means that the more massive was leaching of silicon the more massive was leaching of calcium. The analogical relation was not found for specimen with slag addition, where the correlation was not confirmed. Concrete consisted of slag is then more sensitive to the concentration of aggressive media and need to be more studied in detail for its suitable usage in aggressive environment. As mentioned in (Estokova et al., 2016), slag-based concretes exposed to bacterial sulphate environment proved better performance compared to reference samples even when evaluating physico-mechanical parameters e.g. water absorbability.

4. Conclusion

The study investigated the resistance of concrete specimens prepared according to standard recipe and specimens where 65% of cement were replaced for ground granulated blast-furnace slag when considering the influence of sulphuric acid (of two pH values). Leaching of the elementary components of the cement matrix (Ca^{2+} and Si^{4+}) due to aggressive environments effect for 270 days under model laboratory conditions were measured and was established as a basic data for mathematical evaluation. Correlation coefficient was calculated for two tasks; (i) determination of dependency between leaching the same elements (Ca or Si respectively) considering the less or more concentrated acidic solution and (ii) determination of the dependency between Ca and Si ions leaching considering the same concentrated sulphuric acid for every calculation.
Based on the correlation analysis it can be concluded (i):

- The significant differences were found between Ca leaching trend from concrete with or without slag cement replacement.
- Similar Ca leaching rate considering the concentration of sulphuric acid was proved for slag-based concretes only.
- The hypothesis that the trend of Si leaching will be more intensive when exposed to more concentrated acid was not proven.

Regarding the dependency between Ca and Si leaching the findings revealed (ii):

- Ca/Si leaching trends of reference composites without any slag addition showed high (more concentrated acid solution) and very high correlation (less concentrated acid solution). This points to the similarity in leaching performance of calcium and silicon under acid solution attack regardless the concentration of acid.
- On the other hand, these correlations were not confirmed for the slag-based concretes. Specimens with partial replacement of cement by slag proved more sensitivity to the concentration of aggressive media.

More studies of the relation of elements each other as well as their influence on concrete matrix considering its usage in aggressive environment will be done in the future research. However, based on these experimental results, slag produced by industry worldwide may be one of the sustainable solution of using it in concrete structures with the aim to improve the properties ensuring the higher resistance of material to aggressive sulphate environment.

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References

Alani A. M., Faramarzi A., 2014, An evolutionary approach to modelling concrete degradation due to sulphuric acid attack, Applied Soft Computing, 24, 985–993.
Ash development association, Barry Butler W., 1995, Sulphate attack on concrete - What is and how to stop it, Fly ash technical notes, No. 2, Australia
Bažant Z. P., Steffens A., 2000, Mathematical model for kinetics of alkali–silica reaction in concrete, Cement and Concrete Research 30(3), 419-428.
Binici H., Durguan M.Y., Rizaoglu T., Kolucoak M., 2012, Investigation of durability properties of soncerete pipes incorporation blast furnance slag and ground basaltic pumice as fine aggregates, Scientia Iranica, Transactions A: Civil Engineering, 1(3), 366-372.

Bostanci S.C., Limbachiya M. and Kew H., 2016, Portland slag and composites cement concretes: engineering and durability properties, Journal of Cleaner Production, 112, 542-552.
Brown P.W., 1981, An evaluation of the sulfate resistance of cements in a controlled environment, Cement and Concrete Research, 11(5-6), 719-727.
Duan P., Shui Z., Chen W., Shen C., 2013, Enhancing microstructure and durability of concrete from ground granulated blast furnance slag and metakaolin as cement replacement materials, Journal of materials research and technology, 2(1), 52-59.
Estokova A., Smolakova M., Luptakova A., Strigac J., 2016, Analysis of water absorption capacity of cement composites made with waste material after the exposure in bacterial sulphate environment, SGEM 2016 Sofia : STEF92 Technology Ltd., 25-31.
Kong J. S., Ayman N., Ababneh D. M., Frangopol Y. X., 2002, Reliability analysis of chloride penetration in saturated concrete, Probabilistic Engineering Mechanics17(3), 305-315.
Kreyszig E., Eds., 2011, Advanced Engineering Mathematics, 10th edition, John Wiley and sons, United States of America
Loser R., Leemann A., 2016, An accelerated sulfate resistance test for concrete, Materials and Structures/Materiaux et Constructions, 49(8), 3445-3457.
Ondrejka Harbulakova V., Estokova A., Stevulova N., Luptakova A., 2014, Different aggressive media influence related to selected characteristics of concrete composites investigation, International Journal of Energy and Environmental Engineering, 5(2), p. 1-6.
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 Transaction, 43, 2221-2226, DOI: 10.3303/CET1543371
Pietrucha-Urbanik K., 2014, Assessment model application of water supply system management in crisis situations, Global NEST Journal 16(5), 893-900.
Pietrucha-Urbanik K., 2015, Failure Prediction in Water Supply System – Current Issues, Theory and Engineering of Complex Systems and Dependability, Advances in Intelligent Systems and Computing 365, 351-358.
Rodríguez-Camacho R.E., 2002, Importance of using the natural pozzolans on concrete durability, Cement and Concrete Research, 32, 1851-1858.
The Constructor- Civil Engineering Home, 2015, Sulphate attack on concrete - Process and control of sulphate attack <http://theconstructor.org/concrete/sulphate-attack-on-concrete-prevention/2162/> accessed 2.01.2016
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.
Yu X., Zhu Y., Liao Y., Chen D., 2016, Study of the evolution of properties of mortar under sulfate attack at different concentrations, Advances in Cement Research, 28(10), 617-629.
Winter, N., 2009, Understanding Cement, WHD Microanalysis Consultants Ltd, United Kingdom, 182.