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The influence of the chloride content in cement CEM III on the chemical resistance of concrete under conditions simulating the effect of acid rain and wastewater

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Abstract

Chlorides content in cement is related to the production process – the sources of chlorides are mainly fuels, especially alternative fuels. Some chlorides are drawn off with by-pass powder, which is a by-product not easy for utilization. To reduce the production of environmentally noxious waste, cement producers attempt to increase the chloride content in ground granulated blast furnace slag cement (CEM III) above the value of 0.10% by weight. In European standard (EN 197-1) the limit value of chloride content in cement is generally 0.10% by mass, however, for CEM III there is a note in this standard which permits higher content of chlorides in this type of cement. The accelerated tests on the effect of the chloride content in CEM III, in the range of 0.1 – 0.5%, on the chemical resistance of concrete in solutions simulating acid rain and wastewater were performed. The solution of nitric acid and sulfuric acid was used as a solution simulating the acid rain. Solution simulating the wastewater contained ammonium sulfate, magnesium sulfate and sulfuric acid. After five weeks of exposure of concrete to corrosive solutions, weight change and the strength of the concrete samples were determined. No significant effect of the chloride content in cement over a range of tested values on the chemical resistance of concrete in environment simulating acid rain and wastewater was found.

Keywords: Granulated blast furnace slag cement; chloride ions; chemical resistance; acid rain; wastewater

1. Introduction – research significance

Acid rains are one of significant reasons of chemical corrosion of concrete, including acidic and sulfuric mechanisms of corrosion. Acid rain contains usually following acids: nitric, sulfuric and carbonic. Their pH value range is 3-5 (Xie et al. 2004). Acid corrosion of concrete is observed during exposure in such a solution. The products of corrosion are easily soluble salts (which contains such ions as: Ca^{2+} , HCO_3^- , SO_4^{2-}), which are then leached from concrete. The rate of corrosion caused by acid rain depends on rain composition and its pH value. In laboratory tests intensified conditions are used for acceleration of corrosion processes (Xie et al. 2004; Fan et al. 2010) – namely some tests are conducted in the solutions with pH value as low as 1 (Xie et al. 2004). The solutions of nitric and sulfuric acids are usually used as simulation of acid rains (Xie et al. 2004; Fan et al. 2010).

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Concrete elements which do not have surface protection are usually exposed to acid rains influence, in particular it concerns concrete sewage systems elements. Typical environment of exploitation of such elements in civic conditions is related to the ground waters and to the mix of rain water and municipal wastewater. So, taking into consideration limit characteristics of waste water in domestic sewage, sewage concrete elements are exposed to contact with solutions having low pH value and containing SO_4^{2-} , Mg^{2+} , NH_4^+ ions (Woyciechowski et al. 2016). In such conditions there is a high risk of corrosion. Mechanism as well as an effect of sulfate attack depend on concomitant cation, SO_4^{2-} ions concentration and pH value (Santhanam et al. 2001).

Surface softening and expansion are observed as the effects of such a type of corrosion. In accelerated laboratory tests solutions with higher concentration and lower pH value are used as factors which intensifies corrosion (Santhanam et al. 2001; Xie et al. 2004; Fan et al. 2010; Woyciechowski et al. 2016).

Cement composition strongly influences the rate of concrete corrosion. In this paper the authors focused on the effect of chloride content in concrete on its corrosion. Chloride content in concrete and its constituents is limited due to the risk of reinforcement and concrete corrosion. The limit values are given in standards (Woyciechowski et al. 2012). In European standard (EN 197-1) the limit value of chloride content in cement is generally 0.10% by mass. However, for GGBS cement (ground granulated blast furnace slag cement - CEM III) there is a note in this standard which permits higher content of chlorides in this type of cement. Acceptance of higher chloride content in GGBS cement could be reasonable due to the fact that concrete with CEM III has higher resistivity against chemical corrosion (Gruener 1983), including chloride corrosion of concrete, as well as a consequence of slower penetration of chlorides through the concrete with CEM III as against to concrete with CEM I (Kurdowski 2014).

Chlorides content in cement is related to the production process – the sources of chlorides are mainly fuels, especially alternative fuels, which contain small particles of plastics and textiles (common name – “passers”). Some chlorides are drawn off with by-pass powder, which is a by-product not easy for utilization. To reduce the production of environmentally noxious waste, cement producers attempt to increase the chloride content in CEM III above the value of 0.10% by weight.

In the previous article (Kuziak et al. 2016) the authors have shown the results of investigation of chloride content influence (range of 0.1-0.5%) on concrete cover protective properties. The lack of influence of chloride content in cement in the tested range on reinforcement corrosion was found as an effect of the research program. Non-carbonated concrete with cement CEM III provides the protection of reinforcement against corrosion, even if chloride content in cement is as high as 0.5% of cement mass.

The aim of research program presented in this paper was to investigate the influence of chloride content in GGBS cement (CEM III) on chemical resistance of concrete in the environments which simulate acid rains and municipal wastes.

2. Materials and methods

Concrete samples were made with blast furnace slag cement (CEM III A 42,5), because this type of cement is recommended for concrete building elements exposed for acid aggression (Xie et al. 2004) and is considered to be more resistant to sulfuric corrosion than OPC (Gruener 1983; Xie et al. 2004). Test concrete samples with dimensions of 25 x 60 x 120 mm, made of cement with chloride content of 0.1, 0.2 and 0.5% by weight, were used. Water-cement ratio w/c was 0.4. Sand 0/2 mm and granite aggregate 2/8 mm were used. Samples were cured for one year in a climate chamber (temperature = $20 \pm 2^\circ\text{C}$, humidity > 95%). Water absorption of samples was determined before testing of the chemical resistance. Then three series of samples saturated with water were immersed in:

- 1) solution simulating acid rain – acid solution containing nitric acid and sulfuric acid in a molar ratio of 9:1 (concentration of nitric acid = $0,027 \text{ mol/dm}^3$, concentration of sulfuric acid = $0,003 \text{ mol/dm}^3$), with the pH of the solution of 1.5;
- 2) solution simulating municipal wastewater – salts solution containing the magnesium sulfate (concentration of 0.07 mol/dm^3), ammonium sulfate (concentration of 0.07 mol/dm^3) and sulfuric acid (concentration of 0.03 mol/dm^3) (Woyciechowski et al. 2016) to adjust the value of pH = 1.5;
- 3) distilled water.

In 1 dm^3 of each solutions 2 or 3 samples were immersed. Time of exposure was five weeks. During first four weeks of investigation all the solutions were replaced by fresh solution portion in 2-3 days intervals, due to the changes of solutions compositions. In the last (fifth) week of the investigation – the solutions were not

replaced, because the changes of solution pH were not very significant during this period. Samples were slightly dried with paper tissue and then they were weighted before each solution replacement and at the end of investigation.

After five weeks one of the samples was dried to constant weight to measure water absorption. Other samples were cut on to halves (25 x 28 x 120 mm) for flexural strength tests. The maximum size of aggregate (8 mm) was 3 times lower than the least dimension of specimen (25 mm). Samples dimensions were not standard. In the literature there are examples of use of different specimens size – for example: concrete cubes with dimensions 100 x 100 x 100 mm, concrete specimens with dimensions of 25 x 25 x 100 mm (Xie et al. 2004), 12.7 mm cement paste cubes (Monteiro et al. 2000). The size of specimens was not critical, as the aim of the research was the comparative study on influence of chloride content in cement on concrete properties. Dimensions ratio of specimens did not deviate strongly from the ratio of typical standard specimens. After that the test of depth of carbonation was performed on the surface of fraction using phenolphthalein and thymolphthalein indicator.

3. Results and discussion

3.1. Mass changes

The weight of saturated samples, which were immersed in distilled water was growing in time (Fig. 1). It could be related with progress of cement hydration (new hydrates growing). But after drying samples at 105°C, the loss of weight (in the range of 1.5-1.7%), as well as water absorption increase of two percentage points (Table 1) were observed. It is probably the effect of leaching of soluble compounds of concrete matrix by distilled water. It can be concluded that the increase in weight of the saturated samples is related to the increasing porosity and water absorption of the samples.

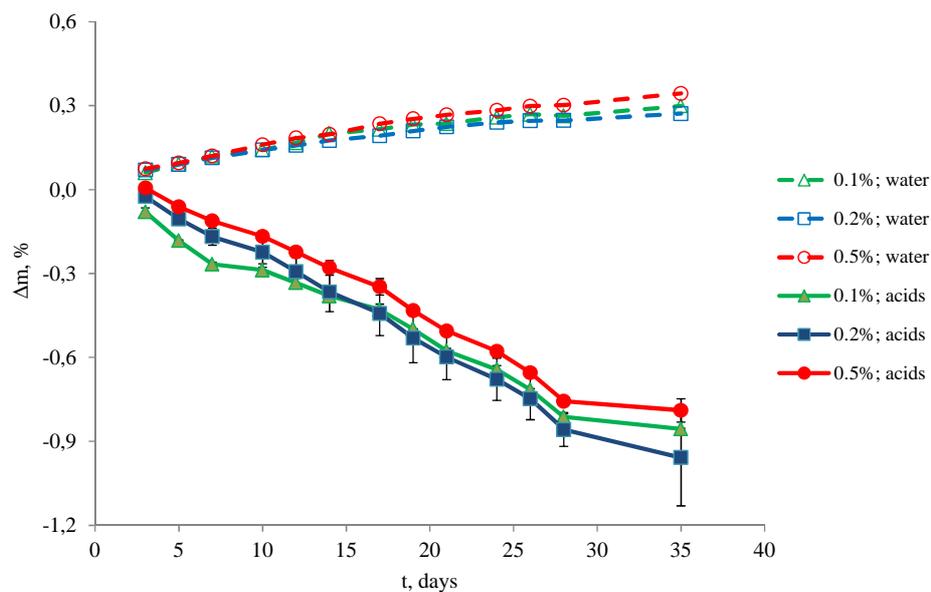


Fig. 1. Change of weight for concrete samples with cement CEM III with chloride content 0.1, 0.2 and 0.5%, immersed in distilled water and in acids solutions.

Weight of the samples immersed in a solution of acids decreased during the test (Fig. 1). For the first two weeks of testing the higher increase of weight loss was observed the lower the content of chloride in cement was. In later tests, there was no relationship between the weight loss and the chloride content in cement. Only in the case of acid solution weight loss was observed for both states of samples: the state of saturation with corrosive solution and dried state. The percentage loss determined after drying the samples was approx. three times greater than that determined in saturated state, and it was slightly decreasing with increase of chloride content in cement. The percentage loss of mass (after drying) of the samples exposed to the acid solution was approx. two-fold higher than for the reference sample immersed in distilled water. The weight loss is mainly caused by the reactions of nitric acid with the products of cement hydration and the creation of easy soluble nitrates. During the corrosion process increasing of porosity (measured as increasing of water absorption) was observed. It causes the lower observed weight loss in the saturated state then in dried state. Water absorption of samples made of cement

with chloride content of 0.1% and 0.2 %, immersed in a solution of acid, was higher than absorption of samples immersed in distilled water. However, in the case of samples of cement with chloride content 0.5% water absorption after the test was higher than before but at the same level as in the case of this series of samples immersed in distilled water (Table 1).

Table 1. Change of weight and absorption for concrete samples with cement CEM III with chloride content 0.1, 0.2 and 0.5%, after five weeks of exposure in distilled water and solutions of acids and salts.

Solution	Content of Cl ⁻ in CEM III [mass %]	Results before testing	Results after testing			
		water absorption [%]	water absorption [%]	Δm_{wet} [%]	Δm_{dry} [%]	Δ water absorption [%]
Distilled water	0.1	5.2	7.4	0.299	-1.7	2.2
	0.2	5.4	7.4	0.272	-1.6	2.0
	0.5	5.7	7.8	0.344	-1.5	2.1
Acids (HNO ₃ + H ₂ SO ₄ in a molar ratio of 9:1; pH = 1.5)	0.1	5.2	8.2	-0.856	-3.5	3.0
	0.2	5.4	8.2	-0.958	-3.3	2.8
	0.5	5.7	7.7	-0.789	-2.7	2.0
Salts (0.07 M MgSO ₄ + 0.07 M (NH ₄) ₂ SO ₄ + H ₂ SO ₄ ; pH = 1.5)	0.1	5.2	8.6	0.036	-3.3	3.4
	0.2	5.4	8.6	0.365	-2.5	3.2
	0.5	5.7	8.8	0.283	-2.7	3.1

Changes in the mass of samples in a state of saturation during exposure to salts solution for the first two weeks are similar to those immersed in distilled water (Fig. 2). In the next two weeks it was observed slightly higher weight increase than in the case of the reference samples. Crystals of salts were seen on the surface of concrete samples and gradually the grains of sand were bared and then trickled – in result the weight of the samples decreased. In Fig. 2 two values, for each series, of Δm after 35 days of exposure are drawn. Last Δm is the value of loss of mass after slight drying and removing of the loose material from surface of the sample. Earlier values of Δm were based on measurements of mass of dried samples without removing the loose material, in order to minimize the interference with the process of concrete corrosion (do not accelerate the process). Nevertheless, after the test at saturation state, the weight of the samples was slightly higher than before the test. After drying, the samples showed a weight loss and increased water absorption. The chloride content in the cement did not affect the water absorption after the test. The loss in weight of the sample (dry state) made of cement with chloride content 0.1% was higher than the mass loss of samples made of cement with higher chloride content. During corrosion in a saline solution weight changes were influenced by the following processes:

- crystallization of salts on the sample surface including the formation of compounds with lower weight because of the replacement of calcium ions (molecular weight of Ca²⁺ = 40 g/mol) by magnesium (molecular weight of Mg²⁺ = 24 g/mol) and ammonium (NH₄⁺ molar mass = 18 g/mol; one mole of Ca²⁺ is replaced by 2 moles of NH₄⁺) ions and the emergence of compounds with higher molecular weight (reaction of sulfate ions with the components of the hardened cement paste);
- ammonia gas evolution from the corrosion products;
- loosening of material from the surface of the sample (products formed during the magnesium and ammonium corrosion do not have binding properties).

Furthermore, due to the increasing of porosity, water absorption was increased (Table 1), resulting in an increase of weight of the saturated sample. Taking into account these processes influence on the weight change, it is better to specify the impact of concrete exposure to the solutions containing magnesium salts and ammonium salts, on the basis of other parameters than change of concrete weight. For example suitable parameter is the change of absorption or mechanical strength.

3.2. Change of porosity

On the basis of water absorption it is possible to conclude indirectly about concrete porosity. After exposure absorption of all samples was higher than before. The lowest increase was observed in case of samples immersed

in distilled water and the highest one – in case of samples immersed in slats solution. In all cases (in water and in both corrosive environments) the lower change of absorption was measured for concrete with higher chloride content (Table 1). The influence of chloride content on absorption is not very significant and its verification is necessary for larger number of samples.

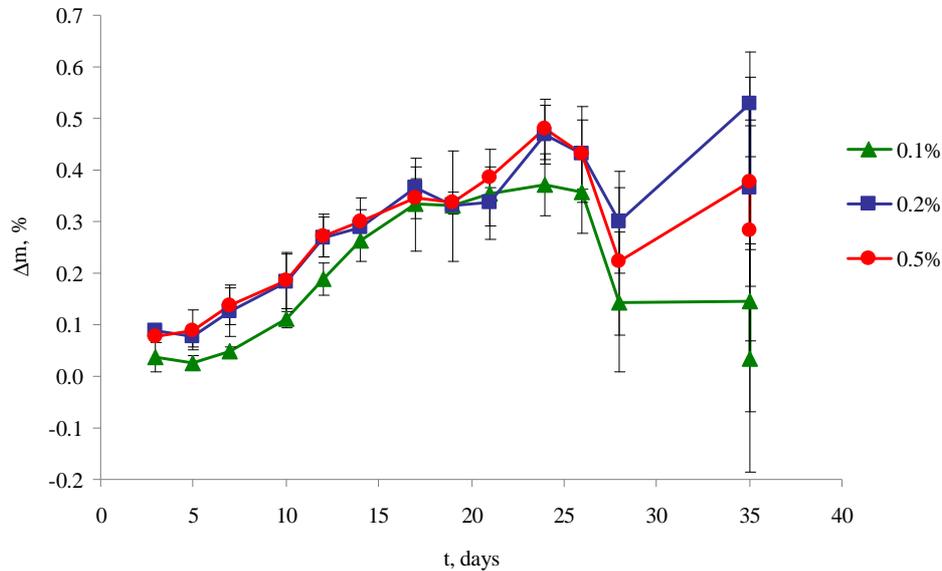


Fig. 2. Change of weight for concrete samples with cement CEM III with chloride content 0.1, 0.2 and 0.5%, during the exposure on the solutions of ammonium and magnesium sulfate and sulfuric acid with pH = 1.5.

3.3. Change of flexural strength

After five weeks of immersion of samples in acid and salt solution, the bending strength of concrete decreased by approx. 25% (exception: samples containing 0.2% of Cl⁻ in cement immersed in acids – in this case, the strength decreased by only approx. 6%) comparing to the reference sample i.e. samples immersed in distilled water (Fig. 3). A flexural strength of specimens containing 0.2% and 0.5% of Cl⁻ exposed in the saline solution were slightly lower than for the samples exposed in the solution of acids. There was no effect of chloride ion content in the considered range of values on flexural strength after exposure to corrosive solutions.

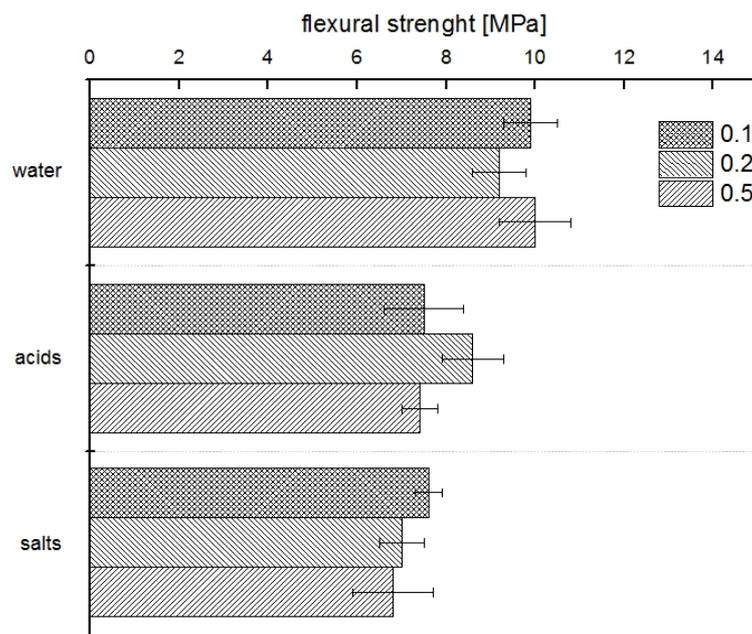


Fig. 3. Flexural strength of concrete with cement CEM III with different chloride ions content (0.1, 0.2 and 0.5%) after five weeks of immersion in distilled water, solutions of acids and salts.

3.4. Neutralization of concrete and visual inspection of concrete surface

Based on tests with both phenolphthalein and thymolphthalein indicators it was found that there is no effect of chloride content in cement on concrete neutralization for the samples immersed in water.

All the samples exposed to the acid solution were neutralized by the surface reaction of calcium hydroxide present in the concrete with acid. The depth of neutralization of these samples determined using the test of thymol- and phenolphthalein was approx. 0.5-1.0 mm and did not depend on the chloride content in cement. The maximum depth of neutralization was observed for samples immersed in acidic saline solution. The thickness of the neutralized layer measured by thymol- and phenolphthalein indicator (after removing "loose material" from the surface of the sample) was approx. 1-1.5 mm. Larger depth of neutralization for samples placed in a saline solution as compared to samples placed in a solution of acids with the same pH value was the result of different texture of concrete surface. For samples treated with an acidic salt solution more porous surface layer was observed. This is probably due to the interaction of cations present in the solution (Mg^{2+} , and NH_4^+).

Surface of samples immersed in water did not change noticeably during the study (Fig. 4). For samples immersed in acid solutions there were partly exposed aggregate grains and samples stained yellow-brown color. The largest surface changes for the samples immersed in saline solution were observed – surface of the samples became porous, crystallized salts were visible, surface material was easily crumbled (Fig. 5). After removal of "loose material" exposed aggregate grains became visible (Fig. 4).

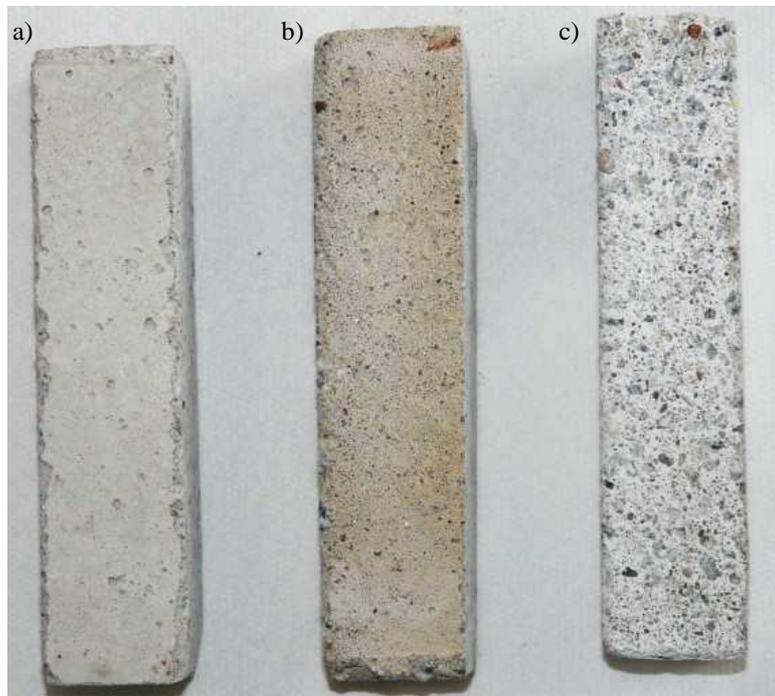


Fig. 4. Samples for bending tests after five weeks of exposure in a) distilled water, b) acids solution, c) salts solution – sample after removing "loose material" form the surface.



Fig. 5. Sample after five weeks of exposure in salts solution and after drying.

4. Conclusions

Based on the five-week exposure of concrete samples in salts and acids solutions with pH 1.5, to simulate the impact of acid rain and sewage, no significant impact of chloride content in cement CEM III (in range of 0.1 up to 0.5% by weight) on the chemical resistance of concrete was found. After testing in both solutions a reduction of flexural strength of the concrete as well as reduction of the weight of the sample in dry conditions, an increase in absorption and neutralization of the concrete surface were observed. The effects of the solution which simulates waste water (saline solution: ammonium sulfate (0.07 mol/dm^3), magnesium sulfate (0.07 mol/dm^3), sulfuric acid (0.03 mol/dm^3) were more significant comparing to the effects of a solution which simulates acid rain (a solution containing nitric acid (0.027 mol/dm^3) and sulfuric acid (0.003 mol/dm^3) in a molar ratio of 9:1). Loss of weight of concrete samples is accompanied by increased porosity of the concrete, and thus increased water absorption. Therefore, measurement of the mass in saturation state after exposure in corrosive solutions may not correlate with the change in weight of samples in the dry state. Changes in the weight of concrete samples after exposure to aggressive solutions have to be determined by measuring the weight of the dried samples. It was also observed a loss in weight and an increase in absorption in the case of the reference samples placed in distilled water, due to the leaching of components of the hardened cement paste by distilled water (soft water). These changes were smaller than in solutions of acids and salts.

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