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CONCRETE DETERIORATION DUE TO AGGRESSIVE ENVIRONMENT AND CYCLIC LOADING – THEORETICAL STUDY

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Abstract: *With the usage of modern cementitious materials, structural elements are designed more slender. For structures subjected to cyclic loadings this means higher stress ranges and thus higher probability of fatigue failure. Structures of transport infrastructure which are mainly exposed to cyclic loading are often located in places of aggressive environment. The paper presents a theoretical study, part of a long-term experimental research focused on the effect of coupled deterioration by aggressive environment and cyclic loading on the concrete specimens. The evaluation of the deteriorative effect of aggressive environment is based on kinetics of chemical reaction between concrete and aggressive solution of hydrochloric acid.*

Keywords: Concrete, Deterioration, Aggressive environment, Cyclic loading.

1. Introduction

Fatigue can be defined as a process of permanent progressive changes in the structure of material subjected to cyclic loading. The influence of fatigue on changes in material structure has been studied by many authors as has been described in Foglar & Göringer (2013). The influence of cyclic loading on the deflections of concrete samples was developed by Holmen (1979) and further extended by Foglar (2010).

The influence of aggressive environment can be divided into two types of deterioration mechanism, mechanical – agents contained in aggressive environment crystallize in the pores of the material and cause pore pressures and consequently lead to the formation and propagation of cracks in the material matrix, chemical – the material is exposed e.g. to acid solution which reacts with concrete components and successively weakens composition of the binder. The phenomenon of chemical deterioration has been extensively investigated with regard to the effect of acid rain on concrete structures, the summary can be found in Göringer & Foglar (2014).

Both areas of material damage (fatigue caused by cyclic loading, deterioration due to the aggressive environment) are widely explored. However, the interaction of these two adverse effects has not yet been properly quantified.

For evaluation of the interaction of the mentioned phenomena, a long-term experimental program was proposed.

2. Methodology

2.1. Aggressive environment and its definition.

The set of European standards, namely EN 206-1, defines the exposure classes of aggressive environment. The most severe class XA3 is defined as environment with value of pH equals to 4.0 which corresponds to concentration of H^+ ions, which cause the acidity of solution, $c_{H+} = 10^{-4}$ mol/dm^3.

In the developed (and below described) experimental program, an aggressive environment consisting of hydrochloric acid (*HCl*) solution of pH 2.0 is considered to speed up the deterioration process.

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2.2. Chemical deterioration of concrete

The rate of chemical deterioration of concrete is primarily affected by the concentration of H^+ ions. As a main deteriorative reaction which weakens the composition of binder, the neutralization defined in (1) can be assumed. The dissolution of ferrite or aluminate hydrates occurs at lower values of pH and in a lesser extent than the dissolution of calcium hydroxide ($Ca(OH)_2$). This assumption was proposed and verified by Pavlík (1994). This assumption will be used in the research.

$$2HCl + Ca\left(OH\right)_2 \Rightarrow CaCl_2 + 2H_2O \tag{1}$$

With the depletion of calcium hydroxide from the concrete surface layers, it can be assumed that the rate of deterioration of the concrete ceases to be primarily dependent on the solution pH and that it will switch to the diffusion phenomenon that is mainly influenced by the concrete permeability.

2.3. Formulation of the problem to be solved

Let it be assumed that the major effect on the strength of the concrete can be attributed to the content of calcium hydroxide (CaO) in the cement, which during the hydration process changes to hydration products. When using the known concrete mix design, it is possible to determine the initial concentration of Ca^{2+} ions and thus determine the maximum capacity for neutralization from the amount of cement and its content of $Ca(OH)_2$.

To determine the kinetics of reaction it is appropriate to use the rate equation, which in the case of neutralization according to (1) has the following form:

$$-\frac{dc_{Ca}}{dt} = k_{Ca} c_H^{\alpha} c_{Ca}^{\beta} \tag{2}$$

where c_{Ca}, c_H = Ca^{2+}, H^+ ions concentration, t = time, k_{Ca} = rate constant, α, β = reaction order.

In the case, that the proposed mechanism is correct and corresponds to the experimental data set, it is possible to use the relation established in (2) for further calculations e.g. loss of calcium ions. The rate constant k_{Ca} have to be determined experimentally using additive properties, for example the change of pH over time, or with use of chemical analysis methods as flame atomic absorption spectroscopy (AAS).

Returned to the assumption that the total amount of CaO in the mixture affects the compressive strength of the concrete, it is possible to develop the relationship between the time loss of Ca^{2+} ions from the material matrix caused by the aggressive environment and decrease of the compressive strength. The result of the chemical deterioration process is from this viewpoint primarily the reduction of compressive strength as outlined below.

For the description of fatigue deterioration the compressive strength is used in all previously mentioned approaches for modeling fatigue damage. Prerequisite for coupled deterioration due to aggressive environment and fatigue caused by cyclic loading is to combine reduction of compressive strength of both damage components. The principle of interaction of both types of damage can be seen in Fig. 1.

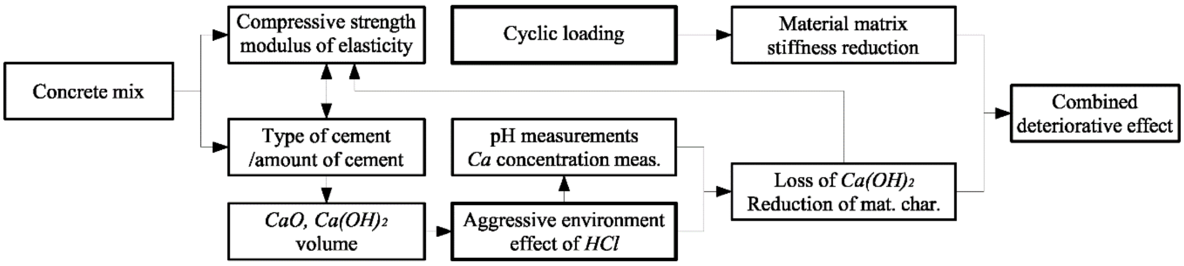

Fig. 1: Principle of interaction of damage components due to fatigue and material deterioration.

2.4. Diffusion and corroded layer

Due to the nature of concrete as a material, the basic problem for evaluation of specimen deterioration degree is diffusion of aggressive agents through material matrix.

Pavlík (1994) states that the transport of H^+ ions may be considered as steady-state diffusion due to slow increase of the corroded layer thickness. Two boundary conditions are proposed – on the surface of the concrete specimen the concentration of H^+ ions is equal to concentration of aggressive solution; in contact of the corroded and uncorroded layer the concentration pH value is due to neutralization around 7 ($c_{H+} = 10^{-7}$ mol/dm^3). The gradient dc_{H+}/dx is nearly constant. The pH distribution through the corroded layer according to mentioned assumptions can be seen in Fig. 2.

From the viewpoint of the conventional diffusion it is possible to describe the transport process of H^+ ions with the Fick's second law of diffusion (3). Mathematical solution considering constant diffusion coefficient, boundary and initial conditions is stated respectively in (3).

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \Rightarrow \qquad c(x,t) = c_0\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{3}$$

where c = is concentration, D = diffusion coefficient, x = location from surface, c_0 = solution concentration, erf = Gauss error function.

The time and location dependent pH distribution according to (3) and the comparison of the pH distribution according to (3) and Pavlík (1994) for time t = 365 days and initial concentration $c_0 = 10^{-4}$ mol/dm^3 (pH = 4) can be seen in Fig. 2. This comparison shows disagreement in both mentioned approaches. The suitability of the applicable approaches will be tested in the experimental program.

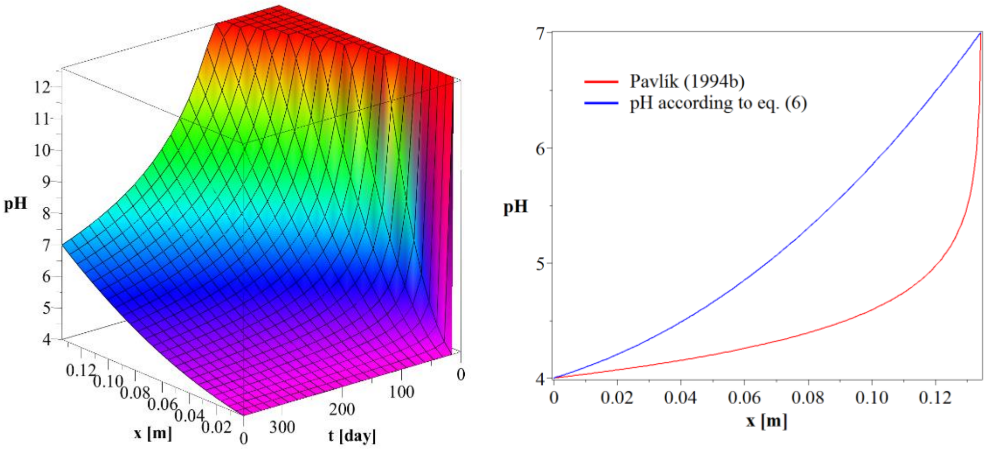

Fig. 2: In time pH distribution for (4) (left), comparison of (4) and approach in Pavlík (1994) (right).

If the pH distribution through the corroded layer according to Pavlík (1994) proves to be valid, there is a possible presumption that for the deterioration degree evaluation, the time variable surface exposed to aggressive environment can be used. At the basis of the kinetics of chemical reaction (1) (experimental data are required) the amount of dissolved Ca^{2+} ions can be determined. For known mix design, it is then possible to identify the possible thickness of the layer with almost none Ca^{2+} ions. This layer may be eliminated from further diffusion process.

Evaluation of the compressive strength. The compressive strength is the decisive characteristics both for its fatigue and deterioration performance. For the mix design of concrete the Féret equation (Féret, 1892) for compressive strength of concrete is commonly used (4).

$$f_{ck}(t) = k_f(t)\, f_{mc}\left[\frac{v_c}{v_c + v_w + v_a}\right]^2 \tag{4}$$

where f_{ck} = compressive strength of concrete (function of time) k_f = Féret coefficient (function of time), f_{mc} = resistance of cement in 28 days, v_c, v_w, v_a = cement, water and air volume in mix design.

With the mentioned assumption, that the compressive strength of concrete is dependent on total amount of CaO in concrete volume the value of v_c in (4) can be modified by amount of dissoluted Ca^{2+} from concrete matrix into the aggressive storage solution. With a constant pH of aggressive environment the solution of (2) substituted into (4) yields the function of compressive strength of concrete as a function of time and H^+ ions concentration, thus the value of pH of aggressive storage solution (5).

$$f_{ck} = k_f \, f_{mc} \left(\frac{X_{cem} V_c \exp\left(-k_{Ca} c_H t\right)}{V_c \left(X_{cem} \exp\left(-k_{Ca} c_H t\right) + X_w + X_a \right)} \right)^2 \tag{5}$$

where X_{cem}, X_w, X_a = volume fraction of cement, water, air in mix, V_c = volume of specimen.

The Féret coefficient k_f is evaluated from the tests of compressive strength of cube specimens. The rate constant k_{Ca} is evaluated from the analysis of periodic sampling of storage aggressive solution. As a comparative data, some cubes are stored separately in aggressive solutions of different pH. According to (1) and (2) the rate constants k_{Ca} is to be evaluated from the time development of the pH value.

3. Experimental Program

Several sets of concrete specimens (strength class C25/30-X0) were designed for the long-term experimental program. All sets are stored in dry or aggressive environment and consequently exposed to cyclic loading. To maintain the stable value of the pH = 2 during the storage of specimens in aggressive environment, the pH value was regularly measured. According to these measurements hydrochloric acid was added each time. Based on the pH measurements and the amount of added acid, the volumes of dissolved Ca^{2+} ions were calculated as well as determined using AAS. The comparison of calculated and measured volumes can be seen in Tab. 1. The values correspond with assumptions from section 2.2.

Tab. 1: The Calculated and analyzed volumes of Ca^{2+}, Al^{3+}, Fe^{3+} and Si^{4+} ions

Specimen no.	**Added *HCl***	**Calculated volume of Ca^{2+} ions**	**AAS volume of Ca^{2+} ions**	**AAS vol. of Al^{3+}, Fe^{3+}, Si^{4+} ions**
	[cm^3]	[g]	[g]	[-]
A1	1240	238.764	235.660	2.8 / 1.2 / 5.1
A2	1720	390.264	402.612	4.4 / 1.3 / 5.5
A3	1085	246.197	248.643	0.9 / 0.1 / 3.0

4. Conclusions

This paper described the theoretical study, part of a long-term experimental program focused on the interaction of deterioration caused by aggressive environment and cyclic loading. The paper presented the outline of a new approach to describe the coupled problem of both types of deterioration which will be based on an ongoing experimental program.

Acknowledgments

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