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Deterioration of high-performance concrete subjected to attack by the combination of ammonium nitrate solution and flexure stress

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Abstract

The behavior of ordinary concrete and high strength concrete under a combinative effect of stress and chemical corrosion was studied in the present work. The concrete specimens were immersed in a variety of chemical solutions including 10%, 5%, 1% and 0.1% ammonium nitrate and simultaneously subjected to different flexural loads with load levels of 30%, 40% and 50% of their initial flexure strengths. The influences of the concentration of solutions, quality class of the concretes and load level of applied flexural stress on the strength of concretes were investigated. The relationships between life-time of the concrete and concentration of the solution, relative strength of the concrete and penetration depth of the ammonium nitrate solutions were determined. The mechanisms of stress corrosion of concrete exposed to ammonium nitrate solution and superimposed to a flexural stress was also discussed.

Keywords: High-performance concrete; Corrosion; Nitrate; Long-term performance; Durability

1. Introduction

It is known that materials, such as metals, ceramics, glass and polymers, are significantly affected by stress corrosion effect which generally takes place when the materials are exposed to a corrosive conditions with the addition of an external stress [1–3].

In practice concrete constructions are subjected to attack by the combination of chemical corrosion and mechanical stress. The study of simultaneous effects of chemical attacks and mechanical stresses was initiated and reported by Schneider and co-workers in 1984. It was reported [4–8] that several media, such as ammonium and sodium sulfate, sodium nitrate, magnesium sulfate and sodium chloride tended to cause stress corrosion.

As is well known [9–15,20–22], ammonium nitrate solutions are very corrosive to cementitious materials, which leads to dissolution of cement-based materials according to the following reaction:

$$2NH_4NO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O \quad (1)$$

The reaction products are calcium nitrate and ammonia, both of which are easily dissolved in water. Furthermore, the dissolution of calcium hydroxide in the ammonium nitrate solution is higher than that in pure water. It is clear from the above-mentioned chemical reaction that the ammonium nitrate decalcifies the hardened cement paste due to removal of calcium hydroxide (Eq. (1)). This results in decalcification and dissolution of other products of the hardened cement paste and leads to a reduction of the pH-value. Consequently, steel reinforcement corrosion may occur at an accelerated rate. The deterioration and damage of the cement-based material must be intensified and accelerated, when the material suffers under a corrosive attack superimposed with a mechanical load.

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2. Materials and mixture proportions

2.1. Portland cement

Two types of portland cements, ÖNORM B3310 type PZ375 and PZ475 (ASTM Type I), were used. The chemical analyses of both the PZ475 and PZ375 are given in Table 1.

2.2. Aggregates

The aggregates were from natural gravel 4/8 and natural sand 0/4. The grading of the aggregates is given in Table 2.

2.3. Superplasticizer (SP)

A superplasticizer based on melamine sulphonate was used for the high strength concretes.

2.4. Retarder (R)

A retarder based on lignosulfonate was used for the high strength concrete C95.

2.5. Silica fume (MS)

The physical properties of the silica fume slurry are shown in Table 3.

2.6. Mixture proportions

Refer to [16–18] about the mixtures of high strength concrete the tested concretes were designed as ordinary concrete C40 and high strength concretes C80 and C95. The proportions of the concrete mixtures are summarized in Table 4.

The water (W)-to-binder (B) ratios (W/B) is calculated as follows:

$$W/B = \frac{W + 0.5MS + SP + R}{C + 0.5MS}. \tag{2}$$

3. Test method

In the present work, ammonium nitrate was selected as aggressive medium. To test the effect of a number of parameters on stress corrosion, the research program was designed with varying the type of cement-based materials (mortar, ordinary concrete and high strength concrete), concentration of solutions and load levels.

Concrete prisms, 40×40×160 mm, were used as test specimens in this study. The concrete mixtures were designed to have compressive strengths of 40 MPa (ordinary concrete) and 80 MPa (HPC without silica fume), 95 MPa (HPC with silica fume). After 24 h of concrete placement, the models were stripped. The specimens were cured in water for the next 27 days.

At the age of 28 days, the flexural and compressive strengths were determined with three prisms of a series of the specimens and used as initial strength of the concrete. Thereafter, the test specimens were immersed into the aggressive solutions and simultaneously subjected to different flexural loads. The ammonium nitrate solutions were with various concentrations of 10% ($[NH_4^+]$=22,500 mg/l, $[NO_3]$=77,500 mg/l), 5% ($[NH_4^+]$=11,250 mg/l, $[NO_3^-]$=38,750 mg/l), 1% ($[NH_4^+]$=2250 mg/l, $[NO_3^-]$=7750 mg/l) and 0.1% ($[NH_4^+]$=1125 mg/l, $[NO_3^-]$=3875 mg/l), respectively. The load levels were 30%, 40% and 50% of their initial flexural strengths. The solutions were replaced as needed to maintain submersion of the samples, ensuring that the solution concentration was maintained. A series of specimens were immersed in water saturated by calcium hydroxide as reference. The flexural strength and compressive strength of the specimens were determined after immersion at regular intervals. The depths of penetration of the aggressive ions into the concretes were measured by

Table 1
Chemical analysis of the cement PZ 375(H)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	GV	C_3S	C_2S
PZ475	19.9	4.9	2.3	63.7	1.7	3.6	0.4	0.8	2.0	61.4	10.8
PZ375	21.7	5.7	2.1	59.8	2.5	3.4	0.5	0.9	3.4	27.6	41.5

Table 2
Grading of the aggregates

Sieve size (mm)	Cumulative percentage passage	
	Gravel 4/8	Sand 0/4
0.063	0.1	1.07
0.125	0.2	3.60
0.25	0.2	11.43
0.50	0.2	25.74
1	0.3	38.65
2	0.6	62.72
4	5.5	95.99
8	90.3	

Table 3
Typical physical properties of silica fume (slurry)

Property	Dimension	Liquid
Density of the slurry	kg/dm^3	1.41±0.02
Proportion of silica solids	%	50
In the slurry		
Specific surface	BET (m^2/g)	18–20
Dry substance	%	min. 99
Fineness		
<0.001 mm	%	60±15
<0.04 mm	%	min. 85

Table 4
Proportions of concrete mixtures

	Cement (kg/m^3)	Water (kg/m^3)	W/B	Sand (0/4) (kg/m^3)	Gravel (4/8) (kg/m^3)	Silica Slurry (kg/m^3)	VZ_4 (kg/m^3)	FM_{62} (kg/m^3)
C40	450(PZ375)	180	0.40	893	893	–	–	4.50
C80	450(PZ475)	150	0.37	893	893	–	–	14.80
C95	550(PZ475)	108	0.30	893	893	77	2.2	29.08

means of phenolphthalein [19]. The reported test data at each time are based on the average of 2 to 4 specimens.

4. Results and discussion

4.1. Effects of an external stress on concrete suffered from a chemical corrosion

The stress corrosion is a simultaneous effect by a combination of corrosive environment and mechanical stress. Without a chemical attack, the deterioration of concrete construction loaded in the elasticity could not exist in a certain time of loading. The strength of HPC Concrete C80 immersed in the water solution saturated by calcium hydroxide under flexural load with load level of 30% initial strength for 6 months was observed the same as that without load, either flexural strength or compressive strength (Fig. 1).

Ammonium nitrate solution is very corrosive to cementitious materials. Strength of the specimens of HPC C80 stored in water increased continually for 2 years, and however, the strength of the HPC C80 immersed in the 10%NH_4NO_3 solution decreased clearly. After 28 days of immersion, the strength of the HPC C80 was reduced by about 25% (Fig. 2). After 3-month immersion, the strengths were only the half of its initial strength.

An external load, applied to the specimens suffered from the chemical corrosion by the 10%NH_4NO_3 solution, accelerated significantly the rate of deterioration. The HPC C80 in the 10%NH_4NO_3 solution under a load with a load level of 30% of its initial strength lost 80% strength in 112 days, whereas 365 days required for the unloaded one (Fig. 2). It is seen that stress corrosion is much more detrimental than the chemical corrosion to the cement-based materials.

4.2. Influence of load level

The processes of stress corrosion of the cement-based materials immersed in ammonium nitrate solution can be described as those in Fig. 3. The high load levels accelerate stress corrosion and lead to intensive opening, propagation and growth of cracks in materials.

Fig. 4 shows the test results of concrete C40 in the 5%NH_4NO_3 solution under loads with different load levels. It can be concluded that the higher the load level, the greater is the reduction of strength, the earlier the failure. The flexural strength of concrete C40 immersed in the 5%NH_4NO_3 solution under a load with 30% of the initial strength reduced by 40% in 85 days, whereas under a load level of 40% in 60 days and under 50% in 32 days.

It was notable that the test samples subjected to stress corrosion broke down after certain period of immersion. The time to break depends on the concrete type, concentration of aggressive media and the load level. A high load level leads to a quick break of the specimens. With a load level of 30% of the initial strength, the specimens of concrete C40 immersed into the 5%NH_4NO_3 solution began to break at the 104th day of the immersion. With a load level of 40%, the breaking started at the 77th day, and with load level of 50% only at 21st day (Fig. 5). In the same solution, the first break of specimens of concrete C80 with a load level of

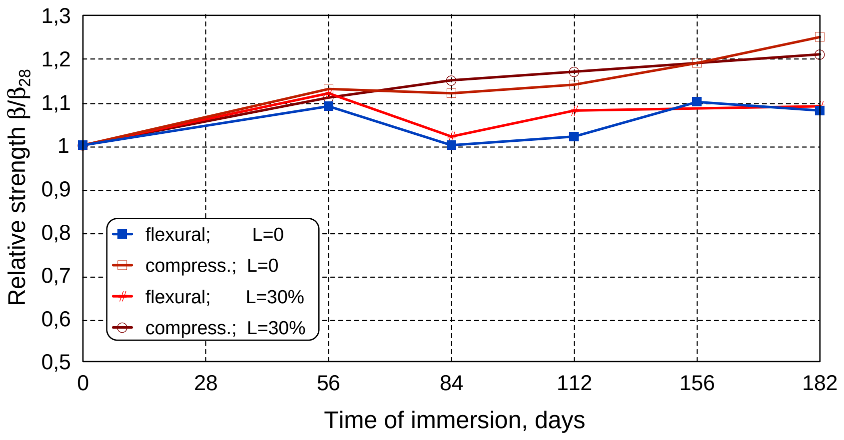

Fig. 1. Relative strength of HPC C80 immersed in the water saturated by $Ca(OH)_2$ with/without loading.

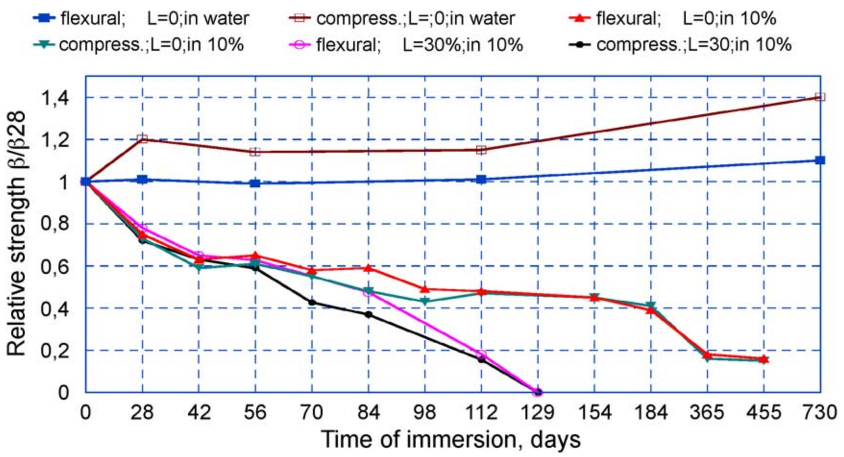

Fig. 2. Relative strength of the HPC C80 in water and in the $10\%NH_4NO_3$ solution with/without loading.

30% of the reference strength appeared at the 147th day of the immersion and with a load level of 40% at the 88th day of the immersion (Fig. 6).

The time to break of the specimens decreases with increasing in the load level. In the $10\%NH_4NO_3$ solution, the first breaking of the sample of the HPC C95 with a load level of 30% of its initial strength occurred at 105th day of immersion, and with a load level of 40% it appeared at 60th day, 45 days shorter. With a load level of 50%, the time to break was only at 16th day (Fig. 7).

4.3. Influence of initial strength of materials

High strength of concretes results generally from high compactness. A dense concrete has a low permeability and a high resistance to penetration of aggressive ions. The test results indicated that a high strength concrete has a high resistance to stress corrosion as well. Under loading with a load level of 30% of the reference strength, the service life of concrete C80 in the $5\%NH_4NO_3$ solution was 2 months more than that of the concrete C40. For C95, it was 3 months more than that for C80 (Fig. 8). In the $10\%NH_4NO_3$ solution, the life-time of the concrete C95 was 2 months more than that of the C80 (Fig. 9).

4.4. Influence of concentration of ammonium nitrate solution

The test results indicated that the concentration of aggressive media affect the stress corrosion of concrete more significantly than the pure chemical corrosion. Under a load of 30% of the initial strength, the highly concentrated ammonium nitrate solutions led to a very rapid reduction of the strength. This holds likewise for the ordinary concrete and high strength concrete (Figs. 10–12).

4.5. Life-time of concrete under stress corrosion

The life-time of concrete subjected to corrosion or stress corrosion is defined as the time interval, until which its initial strength is reduced by 50%. According to this definition, the life-times of HPC C80 and C95 subjected

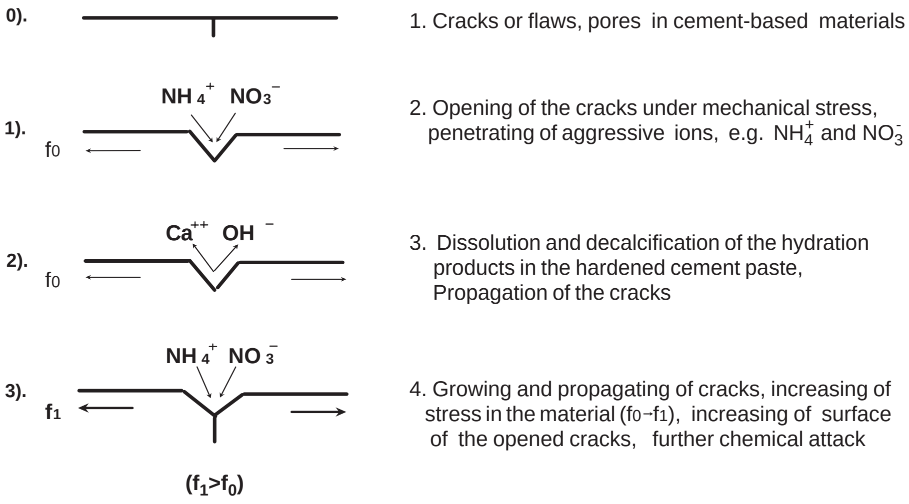

Fig. 3. Processes of stress corrosion of cement-based materials suffered from combination of ammonium nitrate solution and external stress.

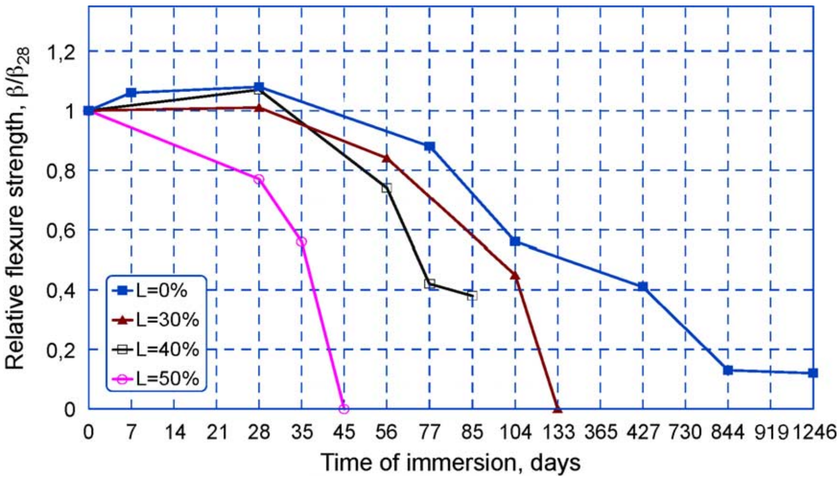

Fig. 4. The time to break of the ordinary concrete specimens C40 in the 5%NH_4NO_3 solution under loading with different load levels.

to attacks of ammonium nitrate solutions with different concentrations with/without loading are shown in Figs. 13 and 14, respectively. The results reveal the following:

- A higher concentration of the solution leads to a shorter life-time of specimens with loading or without loading.
- The external load accelerates the damage of the concrete due to chemical attacks. With a load of 30% of its initial strength in the 5%NH_4NO_3 solution, the life-time for HPC C80 was 91 days shorter than that without loading, and the life-time of HPC C95 was 87 days shorter under load compared to a zero load level.

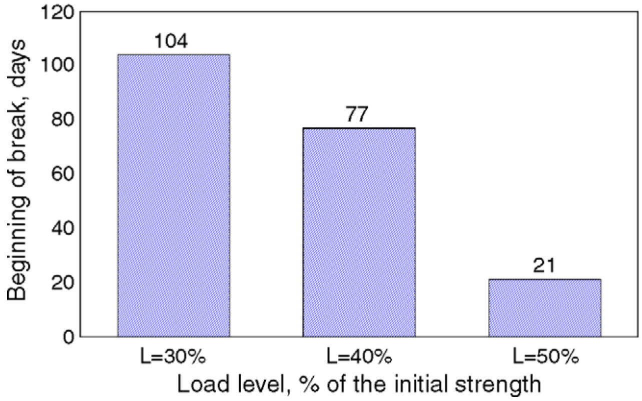

Fig. 5. The time to break of the specimens of the ordinary concrete specimens C40 in the 5%NH_4NO_3 solution under loading with different load levels.

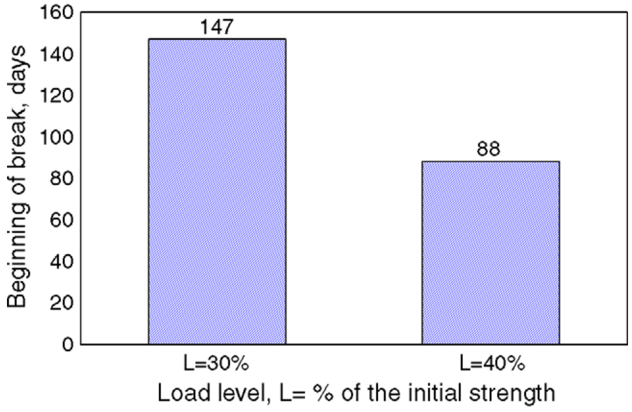

Fig. 6. The time to break of the specimens of the HPC specimens C80 in the 5%NH_4NO_3 solution under loading with different load levels.

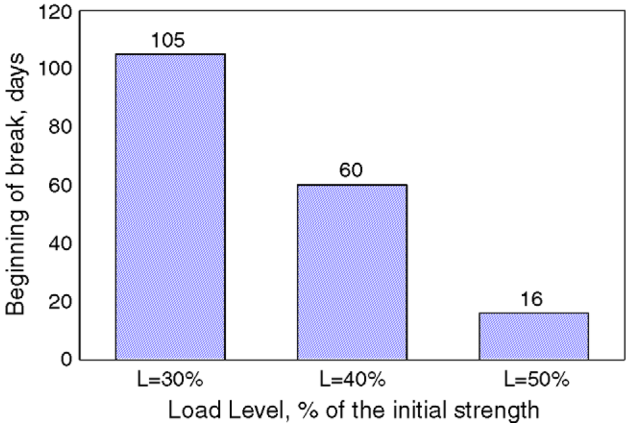

Fig. 7. The time to break of the specimens of the HPC specimens C95 in the 10%NH_4NO_3 solution under loading with different load levels.

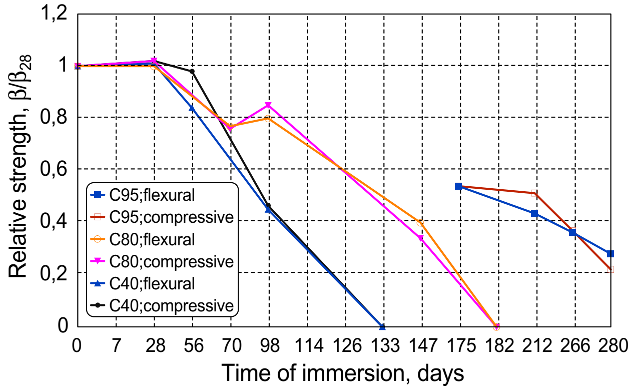

Fig. 8. Relative strength of the specimens of HPC C95, C80 and ordinary concrete C40 in the 5%NH_4NO_3 solution under loading with load level of 30% of its initial strength.

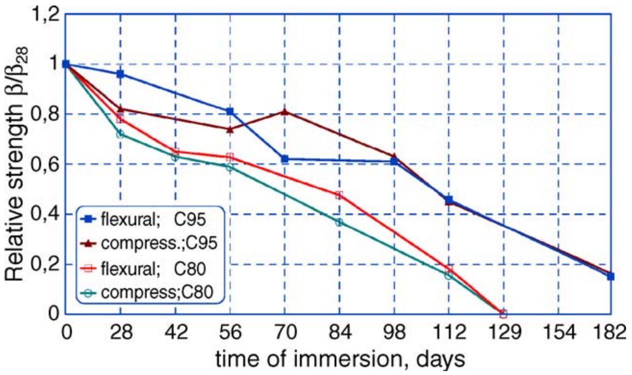

Fig. 9. Relative strength of the specimens of HPC C95 and C80 in the 10%NH_4NO_3 solution under loading with load level of 30% of its initial strength.

The results also indicate that the life-time of the concrete can be determined by exponential functions. In the present work, the life-times of the concretes, which were cured in water for 28 days in advance, immersed into the ammonium nitrate solutions with/without loading as a function of the concentration of the solutions can be described as follows:

HPC C80 in NH_4NO_3 solutions without loading (Fig. 13):

$$\tau = 360.496e^{-0.115L_c} = 360.496\exp(-0.115L_c) \quad (3)$$

HPC C80 in NH_4NO_3 solutions with loading of 30% of the initial strength (Fig. 13):

$$\tau = 306.141e^{-0.150L_c} = 306.141\exp(-0.150L_c) \quad (4)$$

HPC C95 in NH_4NO_3 solutions without loading (Fig. 14):

$$\tau = 461.300e^{-0.092L_c} = 461.300\exp(-0.092L_c) \quad (5)$$

HPC C95 in NH_4NO_3 solutions with loading of 30% of the initial strength (Fig. 14):

$$\tau = 430.787e^{-0.145L_c} = 430.787\exp(-0.145L_c) \quad (6)$$

with τ=life-time in days, L_c=concentration of solution in % ($0.01 \le L_c \le 10$).

The calculated values from the formulae are shown in Figs. 13 and 14 in comparison with the test values. In all cases, the standard deviations are less than 10 days.

4.6. The depth of penetration of the ammonium nitrate solution

The ammonium nitrate solution causes a pure dissolving corrosion by a neutralization reaction. This implies that the pH-value in the attacked part of the specimens is reduced by the neutralization reaction. In our work the penetration depths of the fractured sections were measured by means of a phenolphthalein solution after the mechanical tests.

The results show that a higher concentration of the solutions led to a deeper penetration of the aggressive ions after a certain period of immersion. The increase of concentration of the ammonium nitrate solution from 1% to 10% led to penetration depths from 2 to 8 mm until 252 days (Fig. 15). The penetration depths depend on the initial strengths of the specimens. Fig. 15 shows that the relation between penetration depth $D(t)$ in mm and immersion time t in days can be described by a simple root law:

$$D(t) = \alpha\sqrt{t} \quad (7)$$

with: $D(t)$—depth of penetration of the ammonium nitrate solutions in mm; t—time of immersion in days ($28 \le t \le 365$); α—experimental coefficient.

According to the experimental results α=0.58 and 0.50 for concrete C80 and C95 immersed in 10%NH_4NO_3 solution, α=0.19 for C80 and C95 immersed in 1%NH_4NO_3 solution, respectively (Fig. 15).

It was noted that the relative flexural strength β/β_{28} was nearly proportional to the penetration depth $D(t)$ in mm as shown in the following equation. The relation is independent of the initial strength of the concrete and the concentration of the aggressive solutions (Fig. 16).

$$\beta/\beta_{28} = -0.097D(t) + 1.102 (28 \le t \le 365). \quad (8)$$

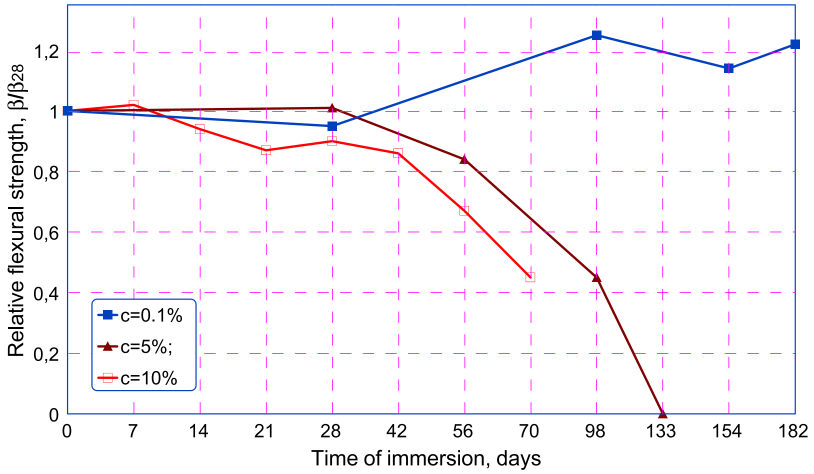

Fig. 10. Relative flexural strength of the specimens of the C40 in the NH_4NO_3 solutions with different concentrations under loading with a load level of 30% of the initial strength.

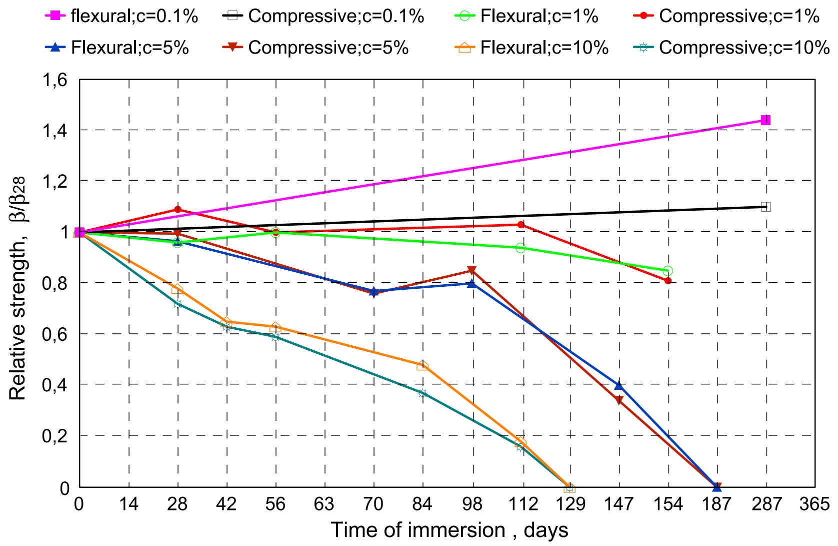

Fig. 11. Relative flexural strength of the specimens of the HPC C80 in the NH_4NO_3 solutions with different concentrations under loading with a load level of 30% of the initial strength.

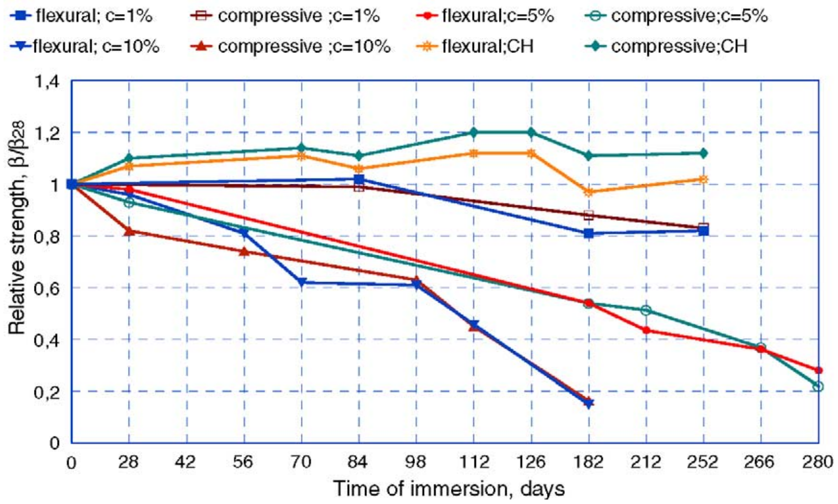

Fig. 12. Relative flexural strength of the specimens of the HPC C95 in the NH_4NO_3 solutions with different concentrations under loading with a load level of 30% of the initial strength.

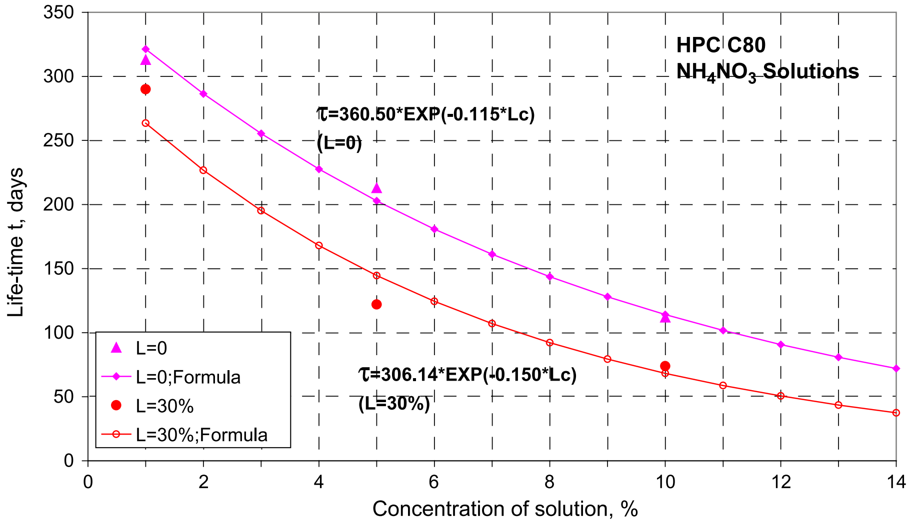

Fig. 13. Life-time of HPC C80 immersed into ammonium nitrate solutions with different concentrations, with/without load.

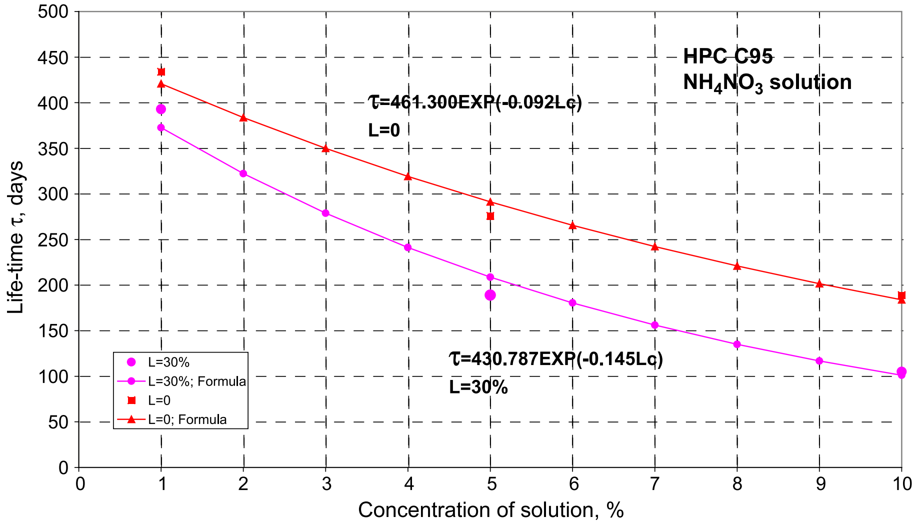

Fig. 14. Life-time of HPC C95 immersed into ammonium nitrate solutions with different concentrations, with/without load.

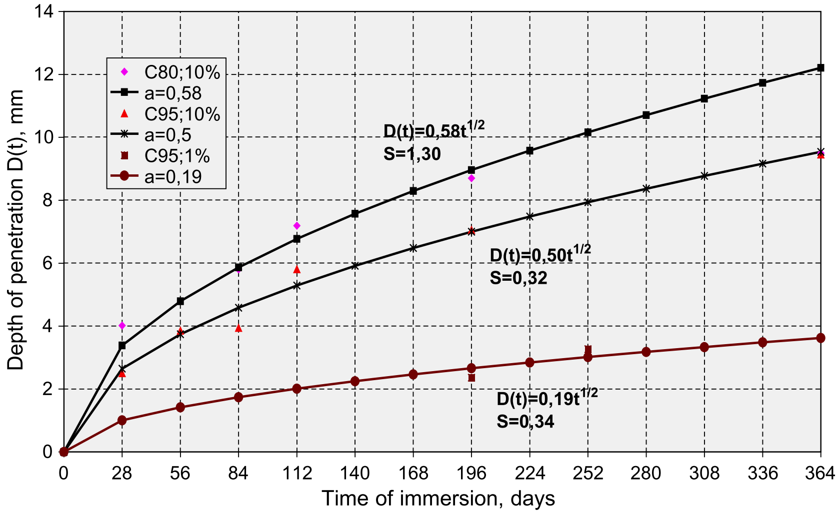

Fig. 15. Depth of penetration and time of immersion for concretes immersed into the $10\%NH_4NO_3$ solution.

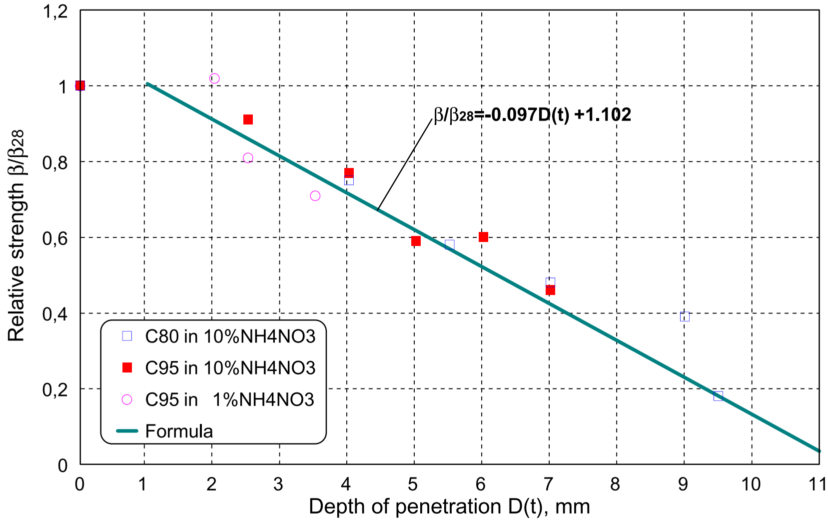

Fig. 16. Relationship between the relative strength and the depth of penetration for concretes immersed into the $10\%NH_4NO_3$ solution.

5. Concluding remarks

- The synergetic effects of an external stress during exposure in the aggressive medium increase and accelerate the deterioration and the failure of the concrete.
- The effects of stress corrosion on the concretes immersed into ammonium nitrate solution depend on the concentration of the solutions, quality class of the concretes and the load levels of the applied external stress, i.e. a high strength of concrete, a lower load level and concentration of the aggressive solution lead to a higher resistance against stress corrosion attacks and prolong the service life of the concretes.
- The life-time of the concretes decreases significantly with an increase in concentration of the ammonium nitrate solution, no matter whether with load or without load. The relations between the life-time and concentration of the solutions can be described by exponential functions.
- A higher concentration of the solutions led to a deeper penetration of the aggressive ions after a certain period of immersion. The penetration depths depend on the initial strengths of the specimens as well. The relation between penetration depth and the immersion time can be described by a simple root law.
- The relative flexural strength β/β_0 was nearly proportional to the penetration depth $C(t)$ in mm as shown in the following equation. The relation is independent of the initial strength of the concrete and the concentration of the aggressive solutions.

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