STUDIA UBB CHEMIA, LIX, 2, 2014 (p. 7-16)
(RECOMMENDED CITATION)

# ASPECTS OF IMPROVING CONCRETE DURABILITY

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**ABSTRACT.** Concrete, under certain conditions, may degrade due to corrosion processes. Corrosion protection can be achieved by providing a suitable concrete composition. In this paper the influence of supplements, added to concrete preparation, in the hydration-hydrolysis processes during their setting and hardening, is presented (the evolution of the mechanical strengths). The influence of supplements on the concrete stability in aggressive environments is also studied (two solutions of $(NH_4)_2SO_4$, with the following concentrations: $C_1$ = 8.25 g/L – corresponding to a high chemical aggressive environment – $XA_3$ [1], and $C_2$ = 24.75 g/L, corresponding to an aggressive chemical environment three times as high). Finally, it is noted which supplements can improve concrete durability for use, without serious consequences, in the proposed highly aggressive environments.

***Keywords:*** *supplements, concrete, durability, aggressive environments*

## INTRODUCTION

According to A.C.I. 201.2R-01 [2], concrete durability is defined as its property to resist climatic, chemical and abrasion actions, or any other deterioration processes. So, a durable concrete is a concrete that retains its initial shape, features and functionality in the environments for which it was designed. If we define concrete quality as its ability to meet the users' needs, durability is responsible for maintaining this quality in time.

An important aspect of the study is the fact that the durability of concrete buildings is not regarded as a problem only in the case of aggressive environments, but also in the case of current environments, in which the most buildings with worrying degradation phenomena were found [3].

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Concrete is designed to be durable under certain in environmental conditions, with the possibility of its use being inadequate under different conditions. For instance, a concrete designed to withstand in aggressive chemical environments will not be suitable for use in environments, characterized by repeated cycles of freeze-thaw and de-icing agents. For this reason it is necessary for the concrete to be designed also regarding composition, depending on the environmental conditions and use. Achieving the projected service time (making only current repairs) in the given environmental conditions and maintaining the original performances can be regarded as synonymous with assuring the required durability.

The modern concepts and the actual trends of durability design [4] can consider two basic strategies against concrete corrosion:

**A.** Avoiding the chemical reactions of the mineralogical constituents of the cement, with the aggressive external environment which lead to decreased durability.

This strategy can be applied considering the following aspects:

- Eliminating the contact between the concrete and the aggressive environment by applying coatings with protective films on the concrete elements;
- Selecting unreactive materials such as: stainless steel, coated reinforcement steel, unreactive aggregates and sulfate resistant cements;
- Air entrainment in the preparation of fresh concrete to achieve a high resistance to freeze-thaw, reaction inhibition by cathode protection, etc.

**B.** Selection of the materials, of the optimal composition and of the suitable operating conditions for the concrete to withstand the aggressive action of the environment.

Strategy B may cover a series of categories of intervention, for example: selecting a suitable concrete composition – this being found in main objective proposed by this work – and making an appropriate concrete coating over the reinforcement with its weight determined by environmental conditions. The standards and the European norms for concrete production are based on this strategy.

Thus, concerning the selection of a suitable concrete composition that can ensure its protection against corrosion in highly aggressive environment, this paper aims to study the influence of different additives on the quality of cement concrete, regarding its use in optimal conditions, in the analyzed aggressive environment.

## RESULTS AND DISCUSSION

After introducing of the hardened concrete, prepared with cement CEM I 42.5 and additives, in an ammonium sulfate aggressive environment, of different concentrations, the concrete's surface was studied from a visual point of view. It was found that the corroded surface layer, after 60 days but especially after 90 days, was bounded from the uncorroded layer by an quantitatively insignificant area given by the presence of compounds like ferric hydroxide, gypsum and ettringite, but also by compounds resulting from the chemical reactions between the aggressive environments and the substances added as additives in the concrete preparation [5, 6].

The main factors determining the corrosive attack on the concrete are: the chemical composition of the cements, the type of aggressive environment and its concentration, exposure time, but also the water/ cement ratio used. Therefore the analysis of the concrete's stability, in the mentioned corrosive environments, will be made by following these factors.

In table 1 the mass variations values (Δm) in time of the concrete exposed in the aggressive environments: ammonium sulfate $(NH_4)_2SO_4$ with concentration $C_1$ = 8.25 g/L (corresponding to a high chemical aggressive environment – $XA_3$ according to SR. EN. 206-1) and concentration $C_2$ = 24.75g/L (corresponding to an environment with a chemical aggressively three times as high) are presented.

**Table 1.** The variation in time of the concrete mass (Δm) subjected to $(NH_4)_2SO_4$ aggressive environment action with the following concentrations: $C_1$ = 8.25g/L and $C_2$ = 24.75g/L

| **CONCRETE** | **$\Delta m = m_{60 days\ agrs} - m_0$, g** | | **$\Delta m = m_{90 days\ agrs} - m_0$, g** | |
|---|---|---|---|---|
| | **$C_1$** | **$C_2$** | **$C_1$** | **$C_2$** |
| **I. Reference sample (no additives)** | -2.7 | 1.5 | 0.7 | 5.0 |
| **II. With sodium silicate additive** | -2.0 | 3.0 | 1.2 | 1.2 |
| **III. With sodium soap and $AlCl_3$ additives** | 0.0 | 3.0 | 4.5 | 7.6 |
| **IV. With sodium carbonate additive** | -0.7 | 1.7 | 1.4 | 4.2 |
| **V. With $FeSO_4$ additive** | -0.9 | 0.8 | 0.2 | 2.0 |

where:

$m_0$ - the mass of the concrete sample hardened in water for up to 28 days;

$m_{60days\ agrs}$ - the mass of the concrete sample hardened in water for up to 28 days and kept in the aggressive environment for up to 60 days;

$m_{90days\ agrs}$ - the mass of the concrete sample hardened in water for up to 28 days and kept in the aggressive environment for up to 90 days.

Table 1 shows an increase in mass of the samples kept in high concentrated aggressive environment, $C_2$. The explanation may be due to either the formation of new compounds which bind an additional amount of water on the surface of the samples (gypsum type compounds, $NH_4(OH)$ or ettringite, but also compounds resulting from the chemical reactions between the aggressive environment and the additives introduced in the concrete) or, most likely, to the superficial corrosion of the samples so that their porosity increases allowing water absorption in their structure.

The stability of the concrete in aggressive environments is also represented by variation in time of the mechanical strengths (Table 2).

**Table 2.** The variation in time of the mechanical strengths (compressive, $R_c$ and tensile, $R_{ti}$) of the concretes subjected to $(NH_4)_2SO_4$ aggressive environment action at different concentrations

| **CONCRETE** | **$(NH_4)_2SO_4$ aggressive environment (Conc. g/L)** | **Compressive strength, MPa** | | | **Tensile strength, MPa** | | |
|---|---|---|---|---|---|---|---|
| | | **$R_{c,}$ 28 days** | **$R_{c,}$ 60 days** | **$R_{c,}$ 90 days** | **$R_{ti,}$ 28 days** | **$R_{ti,}$ 60 days** | **$R_{ti,}$ 90 days** |
| **I. Reference sample (no additives)** | $C_0 = 0$ | 44.53 | 49.35 | 51.64 | 4.96 | 8.2 | 11.43 |
| | $C_1 = 8.25$ | | 47.89 | 44.14 | | 12.32 | 11.71 |
| | $C_2 = 24.75$ | | 41.79 | 41.80 | | 11.62 | 11.64 |
| **II. With sodium silicate additive** | $C_0 = 0$ | 24.53 | 35.71 | 37.42 | 3.89 | 6.31 | 9.23 |
| | $C_1 = 8.25$ | | 34.53 | 30.07 | | 11.27 | 10.07 |
| | $C_2 = 24.75$ | | 27.96 | 29.76 | | 14.47 | 10.82 |
| **III. With sodium soap and $AlCl_3$ additives** | $C_0 = 0$ | 43.75 | 44.23 | 44.84 | 4.45 | 8.23 | 9.60 |
| | $C_1 = 8.25$ | | 41.09 | 39.84 | | 9.98 | 8.71 |
| | $C_2 = 24.75$ | | 36.09 | 25.62 | | 9.09 | 7.21 |
| **IV. With sodium carbonate additive** | $C_0 = 0$ g/L | 21.09 | 23.45 | 27.89 | 3.32 | 6.84 | 7.78 |
| | $C_1 = 8.25$ | | 22.89 | 26.32 | | 8.39 | 7.73 |
| | $C_2 = 24.75$ | | 21.87 | 23.35 | | 8.95 | 7.54 |

| **CONCRETE** | **$(NH_4)_2SO_4$ aggressive environment (Conc. g/L)** | **Compressive strength, MPa** | | | **Tensile strength, MPa** | | |
|---|---|---|---|---|---|---|---|
| | | **$R_c$, 28 days** | **$R_c$, 60 days** | **$R_c$, 90 days** | **$R_{ti}$, 28 days** | **$R_{ti}$, 60 days** | **$R_{ti}$, 90 days** |
| **V. With $FeSO_4$ additive** | $C_0 = 0$ | 38.75 | 43.94 | 48.35 | 4.21 | 7.92 | 10.03 |
| | $C_1 = 8.25$ | | 42.81 | 43.79 | | 8.43 | 13.45 |
| | $C_2 = 24.75$ | | 41.79 | 46.79 | | 10.68 | 10.64 |

From the standpoint of the exposure time over a period up to 90 days in $XA_3$ aggressive environment, with concentrations $C_1$ and $C_2$ respectively, the values of the compressive strength fluctuate during the corrosion process, as depicted in table 3.

**Table 3.** The variation of the concretes compressive strength values ($\Delta R_c$) up to 60 days and up to 90 days respectively (in $XA_3$ aggressive environment with $C_1$ and $C_2$ concentrations)

| **CONCRETE** | **$\Delta R_c = R_{c\ 60days\ (c1,\ c2)} - R_{c\ 28days\ (water)}$, MPa** | | **$\Delta R_c = R_{c\ 90days\ (c1,\ c2)} - R_{c\ 28days\ (water)}$, MPa** | | **$\Delta R_c = R_{c\ 90days} - R_{c\ 60days}$, MPa** | |
|---|---|---|---|---|---|---|
| | **$C_1$** | **$C_2$** | **$C_1$** | **$C_2$** | **$C_1$** | **$C_2$** |
| **I. Reference sample (no additives)** | 3.36 | -2.74 | -0.39 | -2.73 | -3.75 | 0.01 |
| **II. With sodium silicate additive** | 10.00 | 3.43 | 5.54 | 5.24 | -4.45 | 1.80 |
| **III. With sodium soap and $AlCl_3$ additives** | -2.66 | -7.66 | -3.91 | -18.12 | -1.25 | -10.47 |
| **IV. With sodium carbonate additive** | 1.8 | 0.78 | 5.23 | 2.3 | 3.43 | 1.48 |
| **V. With $FeSO_4$ additive** | 4.06 | 3.04 | 5.04 | 8.05 | 0.98 | 5.00 |

According to tables 2 and 3, from point of view of the aggressive environment concentration, after 60 and 90 days respectively, the mechanical strengths, generally, decrease with the increase of the aggressive environment's concentration. Lower values of the compressive strengths variation ($\Delta R_c$) for the concretes subjected to the corrosion process in

$(NH_4)_2SO_4$ aggressive environment with $C_2$ concentration were found, as against to those subjected to the same environment but with concentration $C_1$. The same situation not happened with the concrete in whose composition the $FeSO_4$ was introduced. In this case, the strengths values were comparable to the ones of the concretes hardened in water, after 60 and 90 days and used as reference samples. Likewise, for the concrete with $FeSO_4$ additive, mass losses are insignificant (see table 1).

Compared with mechanical strengths (compressive and tensile) increase of the concretes kept in water, against mechanical strengths of the concretes in aggressive environment they vary according with data from table 4.

Loss in of the reference samples compressive strengths with sodium silicate, sodium soap and $AlCl_3$ additives can be observed and, minor variations of samples with sodium carbonate and $FeSO_4$ additives are obtained. There weren't any significant drops of the tensile strength values because the corrosion did not occur in the deepness of the concrete. However, there are increases of the tensile strength for samples with $FeSO_4$.

**Table 4.** The mechanical strengths variation (compressive and tensile) of the concretes kept in aggressive environments with $C_1$ and $C_2$ concentrations, for 90 days, compared with values of the mechanical strengths of the same concretes kept in water for 90 days

| **CONCRETE** | **$\Delta R_c = R_{c\ 90days\ (c1,\ c2)} - R_{c\ 90days\ (water)}$, MPa** | | **$\Delta R_{ti} = R_{ti\ 90days\ (c1,\ c2)} - R_{ti\ 90days\ (water)}$, MPa** | |
|---|---|---|---|---|
| | **$C_1$** | **$C_2$** | **$C_1$** | **$C_2$** |
| **I. Reference sample (no additives)** | -7.5 | -9.87 | 0.28 | 0.21 |
| **II. With sodium silicate additive** | -7.35 | -7.65 | 0.87 | 1.6 |
| **III. With sodium soap and $AlCl_3$ additives** | -5 | -19.2 | -0.89 | -2.38 |
| **IV. With sodium carbonate additive** | -1.57 | -4.54 | -0.05 | -0.23 |
| **V. With $FeSO_4$ additive** | -4.56 | -1.56 | 3.42 | 0.61 |

## CONCLUSIONS

The aim of this study was to investigate the behavior of concrete in a highly aggressive environment – $XA_3$ –according to SR EN 206-1. To create a corrosive environment, the ammonium sulfate solution with concentrations $C_1$ = 8.25 g/L (corresponding to a high chemical aggressive environment - $XA_3$) and $C_2$ = 24.75 g/L (three times $C_1$) were used. The concrete subjected to these aggressive environments, was prepared with CEM I 42.5 cement and following additives: sodium silicate (8%), sodium soap and $AlCl_3$ (2%), sodium carbonate (8%) and $FeSO_4$ (8%) respectively, mass percentage of cement.

The results led to the following observations, regarding to the stability of concrete in aggressive environments:

- Through increase the concentration of aggressive environment leads to a lower concrete stability, appreciated by reducing the mechanical strengths for the same exposure time;
- In terms of exposure time, after 60 and 90 days, the stability of the concrete, expressed as a variation of the mechanical strengths, shows no constancy in the evolution of the corrosion process, regardless of the acid concentration.

The presented data show a good behavior, in the ammonium sulfate aggressive environment with $C_1$ = 8.25 g/L and $C_2$ = 24.75 g/L concentrations, of the concrete in whose composition the $FeSO_4$ was introduced. In this case the obtained values of the mechanical strengths are similar to those of mechanical strengths of the concrete hardened in water and used as a reference sample; the mass losses are insignificant.

The reason underlying the protective effect of the iron compounds ($FeSO_4$) to the concrete in aggressive environments can be explained by the following chemical reaction:

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4$$

Thus, $Fe(OH)_2$ turns into a colloidal gelatinous precipitate, which has tendency to clog the pores of the concrete thus increasing its resistances to corrosion by elutriation [7, 8].

The $CaSO_4$ formation and any volume increases it may have created, as a result of the combination with tricalcium aluminate in the cement, occurred probably, during the cement binding.

The decreases of mechanical strength for the ***sodium silicate concretes*** are due by the slow curing of the sodium silicate in air. The hardening process of sodium silicate is due to the silicic acid forming, resulted from hydrolysis of the sodium silicate according to reaction:

$$Na_2O \cdot nSiO_2 + (2n+1)H_2O = 2Na^+ + 2HO^- + nSi(OH)_4$$

that provides strength of the structure (cementation), by the polycondensation processes with $SiO_2$ hydrate gel formation with binding properties. In time, the gel is crystallized in a form characterized by mechanical strengths and stability to acids. Through its combination with calcium compounds of the concrete, the gelatinous calcium silicates are obtained, are impermeable to water and by increasing the volume, occlude the concrete capillary pores contributing to increasing of its impermeability [7].

By introducing of $Na_2SiF_6$ compound, a good acceleration occurs at the silicate strengthening [9], involving the next reactions:

$$Na_2SiO_3 + 3H_2O = 2NaOH + Si(OH)_4$$
$$Na_2SiF_6 + 4H_2O = 2NaF + 4HF + Si(OH)_4$$
$$HF + NaOH = NaF + H_2O$$

***The soluble sodium soaps in combination with $AlCl_3$*** turns into insoluble aluminum soaps [7] with hydrophobic action that leads to an improvement in the surfaces resistance to aggressive actions. The $(NH_4)_2SO_4$ aggressive environment, used in this work, did not allow this improvement causing the sulphatic corrosion.

Based on all research, it is recommended that for the concrete exposed to highly corrosive environments, a correlation between the binder types and the aggressive environment characteristics, a key element for assuring the buildings durability.

## EXPERIMENTAL SECTION

### *Experimental conditions and procedures*

The researches in this field have suggested the important role of the additives to concrete behavior during the strengthening process and to their properties [7, 8, 10, 11, 12]. Therefore the investigations were performed on concrete containing the following categories of binder systems:

a) cement CEM I 42.5 (reference sample);
b) cement CEM I 42.5 with following additives: sodium silicate (8%), sodium soap and aluminum chloride (2%), sodium carbonate (8%) and $FeSO_4$ (8%), mass percentages in relation to the cement.

The chemical, physical and mechanical characteristics of CEM I 42.5 cement are presented in table 5:

**Table 5.** The characteristics of CEM I 42.5 cement (cement supplied by HOLCIM)

| Chemical Composition (%) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CaO | $SiO_2$ | $SO_3$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $Na_2O$ | $K_2O$ | $Na_2O$ eq | Free CaO | P.C. | Insoluble residue | $Cl^-$ |
| 62.79 | 20.57 | 2.80 | 4.45 | 6.11 | 1.91 | 0.18 | 1.10 | 0.90 | 0.61 | 0.46 | 0.22 | 0.018 |

| Physical characteristics | | | |
|---|---|---|---|
| Specific surface (Blaine) ($cm^2/g$) | Stability (mm) | Vicat setting time (minutes) | |
| | | Initial | Final |
| 3022 | 1.0 | 190 | 235 |

| Compressive strength ($N/mm^2$) | | |
|---|---|---|
| 2 days | 7 days | 28 days |
| 24.8 | 35.6 | - |

On the binder systems listed above, experimental studies have been made regarding their availability to develop strengthened structures, assessed by strength measurements made on the concrete obtained with these binder systems. The water/cement ratio is constant and equal with 0.5, for all obtained concretes. Also the influence of some aggressive environments on the concrete's durability was studied.

The chemical aggressive environments were given by two ammonium sulfate solutions $(NH_4)_2SO_4$ with $C_1$ = 8.25 g/L (corresponding to a high chemical aggressive environment – $XA_3$ according to SR EN 206-1), and $C_2$ = 24.75 g/L (three times C1) concentrations.

In order to emphasize the durability of the obtained concrete with above mentioned binder systems, the influence of the environmental aggression was investigated through:

- The mechanical strengths (tensile and compressive) variations at 28, 60 and 90 days respectively;

- The mass variations of the concrete samples at 28, 60 and 90 days respectively.

The obtained results were compared with those of the similar measurements made on the concrete subjected to a normal environment exposure: water.

The tensile strengths have been carried out on prismatic samples (40x40x60 mm), and the compressive strengths have been carried out on the prism pieces. Were used three samples for each determination; their average was calculated and used for results comments.

## REFERENCES

[1] *** Standard SR EN 206-1, „Concrete Part 1: Specification, performance, production and conformity”, **2002.**

[2] *** Report of American Concrete Institute Committee ACI 201.2R-08, „Guide to Durable Concrete”, **2008.**

[3] D. Georgescu, „Guide to design the concrete durability in conformity with the National Annex application, EN 206-1. Durability classes” (In Roumanian), Ed. Everest, Bucureşti, **2001.**

[4] S. Rostam, “Service Life Design in Practice Today and Tomorrow” *International Conference: Concrete Across Borders*, Copenhaga, **1994.**

[5] I. Biczok, “Corrosion and concrete protection” (In Romanian), Editura Tehnică, Bucureşti, **1965.**

[6] T. Yamaguchi, K. Negishi, S. Hoshino, T. Tanaka, *Cement and Concrete Research*, **2009**, *39*, 1149.

[7] D. Georgescu, A. Apostu, *Romanian Journal of Materials,* **2009***, 39(2),* 119.

[8] I. Neamţu, N. Rujenescu, I. Lazău, D. Becherescu, **“**Using the thermoelectric power station ash in concrete roof tiles production” *The 8th International Conference of Constantin Brâncuşi University*, Târgu Jiu, May 24-26, **2002**.

[9] I. Robu, M. Popescu, “Materiaux de Construction 2 – Liants, mortieres et beton”, Editura Conspress, București, **2005.**

[10] M. Amăreanu, *Romanian Journal of Materials,* **2010**, *40(3)*, 203.

[11] I. Robu, G. Ilie, I. Pordea, *Romanian Journal of Materials,* **2011***, 41(23)*, 110.

[12] G. Guslicov, C. Ioniţă, D. Mârza, *Romanian Journal of Materials,* **2009***, 39(2), 98.*