

# Durability of concretes prepared with crystalline admixtures

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**Abstract.** The objective of this work was to study the influence of crystalline admixtures on the durability of concrete. Four concrete mixtures – two reference concretes and two alternative mixtures-were produced during the first phase of the research. Influence of curing on the activation of the crystals was investigated on concrete slab specimens. The properties measured were the compressive strength and different durability indicators. The results revealed that crystalline admixtures enhanced the strength and the durability of the alternative mixtures.

## 1 INTRODUCTION

Concrete is the most commonly used construction material worldwide and the material with the second greatest consumption globally, just after water. One can say that it is concrete that has been used for the major infrastructures built during the last century all over the world and therefore is the material strongly connected with the development of our society and the improvement of our way of living. However concrete structures do not last forever; deleterious substances penetrate from the surrounding environment into concrete and react with its components resulting in its deterioration and/or corrosion of the embedded steel. In almost all cases, the reactants responsible for concrete deterioration penetrate into the concrete matrix with water. Since durability of concrete is of major concern, both for financial as well as for sustainability issues, reducing or even better minimizing the penetration of water should be of major priority. Water can enter concrete through the network of pores and capillaries that forms during cement hydration, or through cracks and other voids in the concrete. Therefore, almost all concrete structures require protection from water.

It is well known that a carefully designed concrete mixture which is properly produced and executed (transferred on site, cast, vibrated and cured) using a low w/cm ratio will result in a final product with low permeability and enhanced durability. However, no concrete is absolutely waterproof [2]. Concrete is a porous material and water can penetrate into its mass through pores and microcracks (formed initially or during the service life of the structure) due to capillary absorption, or due to hydrostatic pressure. Capillary absorption is the movement of water through the small pores in concrete in the absence of an externally applied hydraulic pressure. This is the result of surface tension between the water and the pore walls [3]. Permeability of concrete is the movement of water due to a pressure gradient, such as water in contact with a concrete structure installed underground [3]. A well-known and

widely accepted method for reducing the permeability of concrete mixtures and therefore increase their durability is the addition of supplementary cementing materials (SCMs) into concrete mixtures [4,5]. As stated in ACI212.3R-16, a class of materials referred to as permeability-reducing admixtures (PRAs) have been developed to improve concrete durability through controlling water and moisture movement [6] as well as by reducing chloride ion ingress [7-8] and permeability [4]. According to ACI212.3R-16 [3], admixtures intended to reduce water ingress split into two subcategories: PRAs for concrete exposed to nonhydrostatic conditions (PRAN) and PRAs for concrete exposed to hydrostatic conditions (PRAH) [3].

## 2 EXPERIMENTAL PROGRAM

The research was divided into two phases. During the first phase of this research, four concrete mixtures were produced [7] - two conventional and two alternatives with added crystalline admixtures. The concrete mixtures were of C25/30 and C30/37 strength class, according to EN206-1. CEM I 42.5R and CEM II 32.5 (B-M) N cements were used to produce the mixtures. Aggregates were of limestone origin with a maximum grain diameter of 31.5 mm. Appropriate doses of retarder and polycarboxylate superplasticizer were used to achieve the desired workability and setting time.

The mixing ratio as well as the properties of the fresh concrete mixtures are shown in Table 2. The C30/37 PRAH mixture was produced with CEM II 32.5N cement instead of CEMI 42.5R in order to reduce the production cost of the alternative mixture.

Cubic specimens of 150X150X150mm and cylindrical specimens of 100x200mm were prepared. All samples were maintained in a curing chamber (T = 20°C, RH> 98%) until the test age. Cylindrical specimens with dimensions of 60X100mm were also used for measuring the carbonation depth.

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The 150mm cubes were used to measure the compressive strength at the ages of 2 and 28 days as well as to determine the water absorption. Resistance to chloride penetration of concrete was measured in cylindrical specimens with a diameter of 100mm and a height of 50mm cut off from the 100x200mm specimens. These specimens were maintained as above until the age of 28 days. The chloride diffusion coefficient  $D_{nssm}$  was then evaluated according to the procedure described in NT Building 492.

**Table 1.** Mixing ratio of concrete mixtures.

kg/m <sup>3</sup>	C 25/30	C 25/30-PRAH	C 30/37	C 30/37-PRAH
CEM I 42,5R	0	0	330	0
CEM II/(B-M) 32.5N	400	320	0	350
Sand	1042	1105	1133	1133
Gravel	180	190	195	195
Coarse	575	610	625	625
Water	200	160	165	160
superplasticizer	1.40	1.12	1.16	1.16
retarder	5.60	4.80	5	3.5
PRAH	--	2.56	--	2.8
W/C	0.50	0.50	0.50	0.46
S0 (cm)	25	23	24	21
S30 (cm)	20	22	22	19

Carbonation resistance was measured in cylindrical specimens 60x100mm. These specimens were maintained in the above-mentioned wet chamber for 3 days and then remained in a laboratory environment until the age of 28 days. After this age they were inserted into the accelerated carbonation chamber (RH = 55-60%, T = 20°C, CO<sub>2</sub> = 1%) where they remained for 60 days.

During the second phase of this research we wanted to examine the effect of curing on activating the crystals. For this reason we produced five concrete slabs (5.0X5.0X0.15m) (Figure 1). The reference concrete used was a C20/25 strength class concrete according to EN206-1. CEM II 32.5 (B-M) N cement was used. Aggregates were of limestone origin with a maximum grain diameter of 31.5 mm. This concrete was used for casting of two slabs. The remaining three slabs were cast using the same concrete with the addition of crystalline admixtures (P-c20/25) at a percentage of 0.8% per weight of cement. The mix design characteristics of both concretes are presented in Table 2.



**Fig. 1.** Concrete slab specimens produced

**Table 2.** Mixing ratio of C20/25 concrete mixtures.

kg/m <sup>3</sup>	Reference-R-C 20/25	PRAH C20/25 P-C 20/25
CEM II/(B-M) 32.5N	280	280
Sand	1150	1150
Gravel	180	180
Coarse	655	655
Water	180	180
superplasticizer	1.10	1.10
retarder	0.56	0.56
PRAH	--	2.24
W/C	0.64	0.64
S0 (cm)	19	19
S30 (cm)	15	16

Cubic specimens of 150X150X150mm were prepared and used for measuring the compressive strength at different ages. All samples were maintained in a curing chamber (T = 20°C, RH > 98%) until the test age.

After casting, the concrete slabs were cured using different curing scenarios. Slabs 1 and 2- cast with reference concrete- were cured under wet burlap for one and seven days respectively. Slab 3- cast with the concrete containing crystalline admixtures- was cured under wet burlap for seven days. Slabs 4 and 5 were cured using a water jet machine (Figure 2). In this case a water jet was applied four seven and fourteen days respectively. The water jet was applied three times per day, 10 minutes every time.



**Fig. 2.** Curing PRAH containing concrete slabs with water under pressure.

At the age of 28 days, core specimens were taken from all slab specimens. The core dimensions were 100X100mm and 60X100 mm and were used for measuring the durability indicators of the elements.

### 3 EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1 Compressive strength.

The compressive strength was measured for all concrete mixtures at the ages of 2 and 28 days. These values are shown in Table 3.

**Table 3.** Compressive strength of concrete mixtures (MPa)

(MPa)		C25/30	C25/30-PRAH	C30/37	C30/37-PRAH	REF-C20/25	C20/25-PRAH
2 days	$f_{c2}$	26.9	21.2	31.4	31.6	20.5	20.8
	$S_{dev}$	0.35	0.49	0.1	0.28	0.42	0.58
28 days	$f_{c28}$	39.3	41.1	54.2	64.0	32.8	34.6
	$S_{dev}$	0.3	0.1	0.7	0.5	0.51	0.28

The values of the above table show the positive effect of crystalline admixture on the compressive strength of the mixtures. Both C30/37 mixtures showed the same compressive strength at the age of 2 days. However, the mixture prepared with addition of crystalline admixtures exhibited an increased strength of 9.8 MPa (18.15%) relative to the reference mixture at the age of 28 days.

In the case of C25/30 mixtures, the 2-day strength of the alternative concrete is reduced by 5.65 MPa (21.04% reduction) relative to the reference mixture, due to the 20% reduced cement content in this mixture. However, the gradual growth of the crystals resulted in an increase in the later strength of the alternative mixture, which at 28 days was measured at 41.10 MPa, i.e. 1.8 MPa higher than the reference mixture (4.6 percent increase). In the case of C/20/25 concretes, both the 2 and 28 days compressive strengths were increased.

#### 3.2 Water absorption

The water absorption of the concrete mixtures was estimated according to EN 13057 on 150mm cube specimens. The specimens remained in the laboratory curing chamber until the age of 28 days. Then they were dried at 65 °C until their weight was stabilized. The specimens were then properly prepared (wrapped around the insulating tape to ensure absorption only from the bottom of the specimen) and after weighing they were placed in basins of clean water in such a way that the water covered 3-5 mm of height of the specimen.

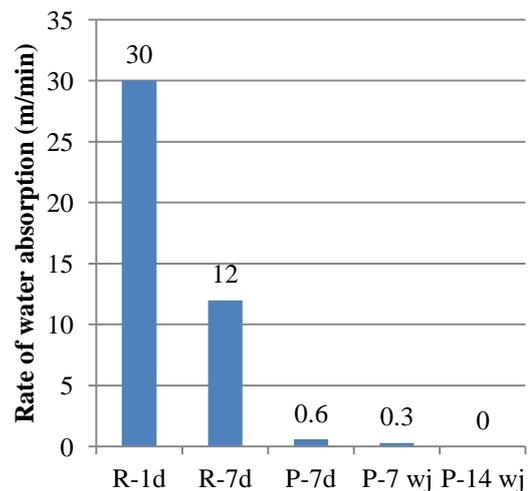
Measurements of weight change of the specimens were performed at 10 minutes, 30 minutes, 60 minutes, 90 minutes, 120 minutes, 180 minutes, 240 minutes, 480 minutes and 24 hours. These weights were divided by the exposed surface of the specimen into the water to calculate the water absorbance in  $gr/m^2$ .

**Table 4.** Water absorption of concrete mixtures

kg/(m <sup>2</sup> .h <sub>0,5</sub> )	C25/30	C25/30-PRAH	C30/37	C30/37-PRAH
$S_{coefficient}$	1.21	0.76	1.09	0.81

The rate of water absorption was measured on slab specimens using the Karsten method also described by EN1323. This method estimates the surface water absorption under atmospheric pressure. Plastic tubes were moulded on the surface of the slabs and filled with water

The rate of water absorption is presented for all slab specimens in Fig. 3.



**Fig. 3.** Water absorption of concrete slabs cured with different curing scenarios.

It is well known that extension of the wet curing period facilitates the hydration of cement and therefore the more proper closure of porosity. Thus the extension of wet curing decreased the rate of water absorption of R-7d concrete slab by 60%. In the case of concrete slabs produced with crystalline admixture concrete, water absorption against atmospheric pressure was almost completely diminished.

### 3.2 Chloride penetration coefficient

The Dnssm (non-steady-state migration) chloride diffusion coefficient values were measured according to NT Building 492 Standard [8] and are presented for all mixtures of the first phase in Table 5.

**Table 5.** Dnssm chloride penetration coefficient ( $\times 10^{-12} \text{m}^2/\text{s}$ ) of concrete mixtures.

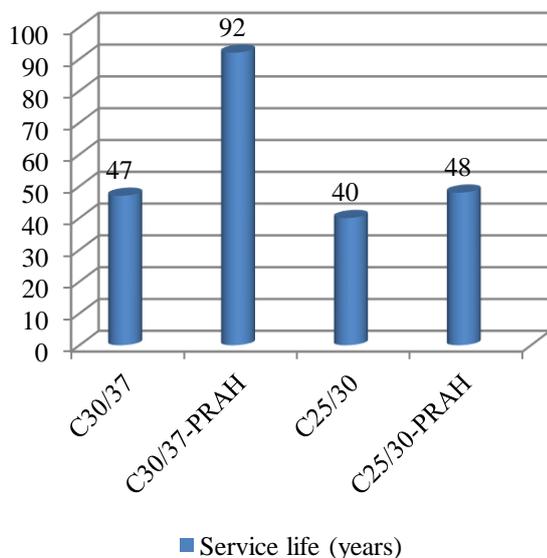
$\times 10^{-12} \text{m}^2/\text{s}$	C25/30	C25/30-PRAH	C30/37	C30/37-PRAH
Dnssm	15.27	12.54	11.6	8.61

The Dnssm chloride diffusion coefficient values were measured according to NT Building 492 on standard diameter concrete cores taken from the slab specimens and are presented for these mixtures in Table 6.

**Table 6.** Dnssm chloride penetration coefficient ( $\times 10^{-12} \text{m}^2/\text{s}$ ) of concrete slabs cured with different curing scenarios.

$\times 10^{-12} \text{m}^2/\text{s}$	R-1d	R-7d	P-7d	P-7dwj	P-14dwj
Dnssm	34.30	22.51	17.73	10.38	8.98

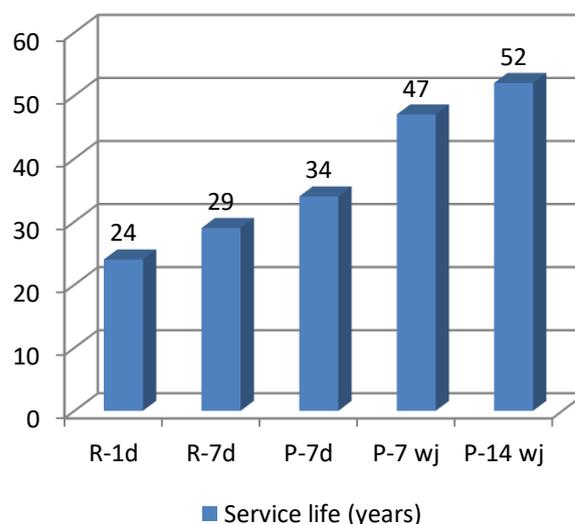
The above coefficients were used to calculate the lifetime of reinforced concrete constructions cast with these mixtures. For this purpose the Life 365 program was used. The following assumptions were made: Exposure class XS1, time for the propagation of corrosion 10 years, 50 mm reinforcement cover. The total service life time is shown in the following diagram.



**Fig. 4.** Service life of concrete mixtures.

The figure above shows the particularly positive effect of the crystalline admixtures on the service life of the concrete. The C30/37-PRAH mixture develops twice the lifetime of penetration of chlorides compared to the reference C30/37, while the C25/30-PRAH mixture has an increased lifetime of 20% over the reference C25/30.

Crystal activation in both cases led to a drastic reduction in porosity, thus preventing penetration of chlorides into the mixtures.



**Fig. 5.** Service life of concrete slabs cured with different curing scenarios.

The figure above shows the positive effect of the combination of using crystalline admixtures and extending the curing period on the service life of the concrete elements. Wet burlap curing increased the service life of the slab produced with crystalline admixture (P-7d) by 15% due to partial activation of the crystals. Since crystalline admixtures are hydrophilic at the beginning of their action, more water is needed for their activation. This additional water was provided by water jet. As indicated above, this method resulted in the formation of greater amounts of crystals that filled the pores and positively affected the resistance of concrete mixtures against ingress of chlorides. Thus the service life of P-7d wj and P-14d wj slabs was increased by 69% and 116% as compared with the reference slab (R-1d). What is more impressive is that even this poor concrete with the high w/c ratio fulfilled the requirements of Eurocodes for a design service life of 50 years when crystalline admixtures were added in the mixture and the concrete elements were properly cured.

### 3.3 Carbonation depth

The carbonation depth was measured according to the procedure described in EN 14630 Standard [9]. The specimens remained for 60 days in the Accelerating Carbonation Chamber. The carbonation depth of all mixtures of the first phase is shown in Table 7.

**Table 7.** Carbonation depth of concrete mixtures.

	C25/30	C25/30-PRAH	C30/37	C30/37-PRAH
Carbonation depth (mm)	8,7	9,1	2,9	4,5

The carbonation depth of the concrete slabs was evaluated on 60X100 mm core specimens drilled from the slabs at the age of 28 days. After this age, core specimens were inserted in the accelerated carbonation chamber and remained there for 60 days. The carbonation depth, measured according to the EN 14630 Standard, is shown in Table 8.

**Table 8.** Carbonation depth of concrete slabs cured with different curing scenarios.

	R-1d	R-7d	P-7d	P-7d wj	P-14d wj
Carbonation depth (mm)	19,8	18,8	16,5	14,2	12,5

Based on the values of Table 8, it appears that the carbonation depth of the prepared mixtures is affected by the addition of the crystalline admixtures in a different way. In particular, the C25/30-PRAH mixture exhibits a slightly increased 5% carbonation depth relative to the reference mixture while the C30/37-PRAH mixture exhibits a carbonation depth increased by 55% relative to the C30/37 reference mixture. This may be due to the non-activation of the crystals; the specimens remained in a wet curing chamber for only three days, unlike the specimens used in the previous tests and which were maintained in the laboratory's wet curing chamber for 28 days. In addition, it should be noticed that the alternative C25/30-PRAH mixture was prepared with a 20% lower cement, while the C30/37-PRAH alternative was prepared using CEM II (B-M) 32.5N cement more prone to carbonation due to its high pozzolan content.

The significance of curing slabs containing crystalline admixture with water under pressure for extended curing periods is clearly demonstrated in Table 7. Slabs produced with PRAH concrete (P-7d) showed a 5.3% lower carbonation depth as compared with slabs produced with the reference concrete (R-7d). In the case of PRAH concrete slabs cured under water pressure, the carbonation depth was decreased by 21.3% (P-7dwj) and 31.91% (P-a4dwj) respectively.

Long-term outdoor exposure experiments are underway in the Building Materials Laboratory in Xanthi in order to calculate the carbonation coefficient  $k$  and to assess more accurately the service life against carbonation of reinforced concrete structures exposed to environmental class XC4.

## 4 Conclusions

The crystalline PRAH additives used in the present study appear to be an effective way of sealing the porosity of the concrete prepared therewith. The presence of moisture is a catalytic factor for the activation of crystals which thus clog the pores of the cement and prevent the penetration of harmful fluids and gases. The alternative mixtures with crystalline PRAH additives that have been tested in the present study showed increased compressive strength, lower water absorption coefficient, and significantly lower permeability to chlorides than reference mixtures, thus enhancing the

lifetime against seawater originated chlorides of reinforced concrete structures. These mixtures also exhibited a higher carbonation depth, due to the use of a different dosage and type of cement as well as to the low water curing period, which did not help to activate the crystals.

It was also found that curing concrete specimens with water under pressure is essential for the formation of crystals and the increase of durability of concrete elements.

Crystal admixtures and chemical additives used in the above experiments were provided by Penetron Hellas SA and NORDIA SA. Their support to the research work of the Building Materials Laboratory is greatly acknowledged.

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