Crystalline Water Resisting Admixture

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Study on effects of PRAHs on concrete durability by Ararat Company – Research and Development Department

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١. Concrete durability

Concrete durability is its resistance to deterioration due to external and internal factors. ACI states that “Durability of hydraulic-cement concrete is determined by its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration. Durable concrete will retain its original form, quality, and serviceability when exposed to its environment. Properly designed, proportioned, placed, finished, tested, inspected, and cured concrete is capable of providing decades of service with little or no maintenance”. (ACI Committee 201, 2008)

٢. Factors affecting concrete durability

Concrete performance and durability is greatly affected by its exposure conditions. “Certain conditions or environments exist that will lead to concrete deterioration. Attacking mechanisms can be chemical, physical, or mechanical in nature, and originate from external or internal sources”. (ACI Committee 201, 2008)

٢,١ Freezing and Thawing of concrete

Repeated freezing and thawing cycles cause cracks, spalling and further increase fluid ingress. “Deterioration of concrete exposed to freezing conditions can occur when there is sufficient internal moisture present that can freeze at the given exposure conditions. The source of moisture can be either internal (water already in the pores of concrete that is redistributed by thermodynamic conditions to provide a high enough degree of saturation at the point of freezing to cause damage) or external (water entering the concrete from an external source, such as rainfall).” (ACI Committee 201, 2008)

٢,٢ Chemical Attack

Chemical compounds or ions exist in soil, water and concrete surrounding environment which penetrate the concrete and are detrimental to concrete’s durability. “There are some chemical environments that will shorten the useful life of even the best concrete unless specific measures are taken. An understanding of these conditions permits measures to be taken to prevent deterioration or reduce the rate at which it takes place. Concrete is rarely, if ever, attacked by solid, dry chemicals. To produce a significant attack on concrete, aggressive chemicals should be in solution and above some minimum concentration.” (ACI Committee 201, 2008)
ACI sets the factors that accelerate or aggravate chemical attack in Table 6.2, and they are outlined as concrete’s high porosity in the form of high-water absorption,

permeability and voids, concrete cracks and spalling due to stress concentration and liquid penetration due to flowing liquid, ponding, and hydrostatic pressure. (ACI Committee 201, 2008).

Among one of the chemicals is water soluble Sulfate, if present at the surrounding of a concrete structure, it penetrates the structures through pores and capillaries and causes expansion and cracks in the concrete. "Naturally occurring sulfates of sodium, potassium, calcium, or magnesium, that can attack hardened concrete, are sometimes found in soil or dissolved in groundwater adjacent to concrete structures. Sulfate salts in solution enter the concrete and attack the cementing materials". (ACI Committee 201, 2008).

Another chemical is chlorine which can penetrate the concrete through capillary ingress and results in a decrease in the pH of the cement paste. The main effect of chloride attack is the corrosion of reinforcement in the concrete. (ACI Committee 201, 2008)

٢,٣ Steel Corrosion

Corrosion is initiated when the normal protective mechanism is eliminated, then it starts to grow and propagates through the steel which ultimately causes damage to the steel and additionally the rust could cause expansion that, in turn, may cause cracking and spalling of the concrete cover. ACI states that the primary causes of film breakdown (i.e., normal protective mechanism elimination) include: "• Chemical, physical, or mechanical degradation of the concrete cover."(ACI Committee 201, 2008)

ACI categorizes exposure conditions based on freeze and thaw exposure, sulfate and chloride presence, water, and humidity presence. They are all factors for durability of concrete, and ACI sets restrictions and parameters such as maximum water cement ratio, minimum compressive strength, etc. on the concrete exposed to each category to reduce permeability of concrete.

Table 19.3.1.1—Exposure categories and classes

Category	Class	Condition	
Freezing and thawing (F)	F0	Concrete not exposed to freezing-and-thawing cycles	
	F1	Concrete exposed to freezing-and-thawing cycles with limited exposure to water	
	F2	Concrete exposed to freezing-and-thawing cycles with frequent exposure to water	
	F3	Concrete exposed to freezing-and-thawing cycles with frequent exposure to water and exposure to deicing chemicals	
Sulfate (S)		Water-soluble sulfate (SO_4^{2-}) in soil, percent by mass[1]	Dissolved sulfate (SO_4^{2-}) in water, ppm[2]
	S0	$SO_4^{2-} < 0.10$	$SO_4^{2-} < 150$
	S1	$0.10 \le SO_4^{2-} < 0.20$	$150 \le SO_4^{2-} < 1500$ or seawater
	S2	$0.20 \le SO_4^{2-} \le 2.00$	$1500 \le SO_4^{2-} \le 10{,}000$
	S3	$SO_4^{2-} > 2.00$	$SO_4^{2-} > 10{,}000$
In contact with water (W)	W0	Concrete dry in service	
	W1	Concrete in contact with water where low permeability is not required	
	W2	Concrete in contact with water where low permeability is required	
Corrosion protection of reinforcement (C)	C0	Concrete dry or protected from moisture	
	C1	Concrete exposed to moisture but not to an external source of chlorides	
	C2	Concrete exposed to moisture and an external source of chlorides from deicing chemicals, salt, brackish water, seawater, or spray from these sources	

[1]Percent sulfate by mass in soil shall be determined by ASTM C1580.

[2]Concentration of dissolved sulfates in water, in ppm, shall be determined by ASTM D516 or ASTM D4130.

Table R19.3.1—Examples of structural members in Exposure Category F

Exposure class	Examples
F0	• Members in climates where freezing temperatures will not be encountered • Members that are inside structures and will not be exposed to freezing • Foundations not exposed to freezing • Members that are buried in soil below the frost line
F1	• Members that will not be subject to snow and ice accumulation, such as exterior walls, beams, girders, and slabs not in direct contact with soil • Foundation walls may be in this class depending upon their likelihood of being saturated
F2	• Members that will be subject to snow and ice accumulation, such as exterior elevated slabs • Foundation or basement walls extending above grade that have snow and ice buildup against them • Horizontal and vertical members in contact with soil
F3	• Members exposed to deicing chemicals, such as horizontal members in parking structures • Foundation or basement walls extending above grade that can experience accumulation of snow and ice with deicing chemicals

١. Concrete Permeability

The porosity nature of concrete enhances fluid ingress into the concrete through capillary absorption and diffusion under non hydrostatic pressure, penetration is further amplified under hydrostatic pressure. ACI concludes that fluid penetration into concrete has a significant effect on durability.

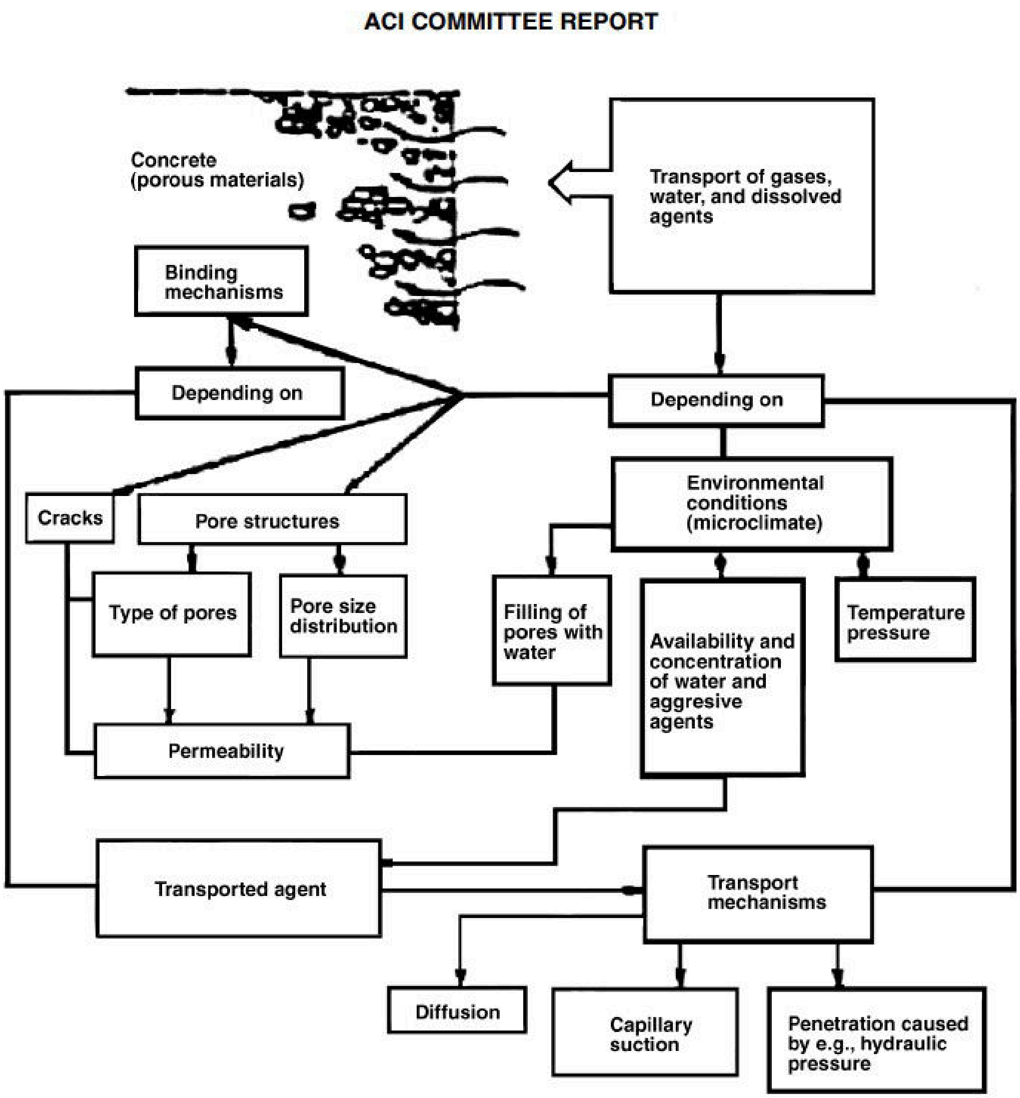

Fig. 3.1—Transport phenomena in concrete (Schiessl 1992).

According to ACI “no concrete structure is absolutely waterproof or “bottle tight” (Perkins 1986). Concrete is a porous material, and water can penetrate concrete through pores and micro cracks due to capillary absorption (often referred to as wicking) 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 head and is the result of surface interactions between the water and the pore wall. The permeability of concrete is the movement of water due to a pressure gradient, such as water in contact with a concrete structure installed underground. In some cases, porosity may be exacerbated by external factors such as incomplete consolidation and curing, which may ultimately lead to reduced durability”. (ACI Committee 212, 2010)
In another paragraph ACI states that “The transport of deleterious agents into and within hardened concrete has an important influence on the durability of concrete structures. The rate, extent, and effect of the transport are largely dependent on the pore structure of the concrete (amount, shape, size of pores, and pore-size distribution), the presence of cracks in the concrete.” (ACI Committee 201, 2008)
Moreover, in another section it attests that “Durability of concrete is impacted by the resistance of concrete to fluid penetration.” (ACI Committee 318, 2019)

٣. Permeability Reducing Admixture

Different post cast approaches have been developed to deal with permeability, but recent approaches focus on solving the issue by transforming the concrete chemical structure. “A class of materials referred to as permeability-reducing admixtures (PRAs) have been developed to improve concrete durability through controlling water and moisture movement (Roy and Northwood 1999) as well as by reducing chloride ion ingress (Munn et al. 2003) and permeability (Munn et al. 2005).” (ACI Committee 212, 2010)
Permeability reducing admixture consists of Portland cement, and various active chemicals, these chemicals react with the cement hydration by products, which results in a crystalline formation in the capillary tracts and pores of the concrete. Thus, the concrete becomes permanently sealed against the penetration of water or liquids from any direction and will eliminate the need to apply any waterproofing membrane after the concrete is cast. Moreover, the concrete is protected from deterioration due to harsh environmental conditions. ACI defines PRAHs (permeability reducing admixture under hydrostatic pressure) as “Crystalline materials [that] consist of proprietary active chemicals provided in a carrier of cement and sand. The hydrophilic nature of these materials causes them to increase the density of calcium silicate hydrate (CHS) and/or generate pore-blocking deposits that resist water penetration.” (ACI Committee 212, 2010)

PRAHs must conform to ASTM C494 and BS EN 934-2, These standards focus on the reliability of the admixtures used in concrete and sets limits on the admixture effects on initial and final setting time, compressive strength, drying shrinkage, capillary absorption and air content of the concrete etc. as well as chemical content of the admixture like alkali and chlorine etc. the standards for PRAHs are outlined in ASTM C494 table 1 under (TYPE S specific performance) and in BS EN 934-2 in Table 1 and Table 9.

TABLE 1 Physical Requirements$^{A, B}$

	Type A, Water-Reducing	Type B, Retarding	Type C, Accelerating	Type D, Water-Reducing and Retarding	Type E, Water-Reducing and Accelerating	Type F, Water-Reducing, High-Range	Type G, Water-Reducing, High-Range and Retarding	Type S Specific Performance
Water content, max, % of reference^{A}	95	...	...	95	95	88	88	...
Time of setting, allowable deviation from reference, h:min:								
Initial: at least	...	1:00 later	1:00 earlier	1:00 later	1:00 earlier	...	1:00 later	
not more than	1:00 earlier nor 1:30 later	3:30 later	3:30 earlier	3:30 later	3:30 earlier	1:00 earlier nor 1:30 later	3:30 later	1:00 earlier nor 1:30 later
Final: at least	...	...	1:00 earlier	...	1:00 earlier	...	...	
not more than	1:00 earlier nor 1:30 later	3:30 later	...	3:30 later	...	1:00 earlier nor 1:30 later	3:30 later	1:00 earlier nor 1:30 later
Compressive strength, min, % of reference:^{C}								
1 day	...	...	...	...	...	140	125	...
3 days	110	90	125	110	125	125	125	90
7 days	110	90	100	110	110	115	115	90
28 days	110 (120)^{D}	90	100	110 (120)^{D}	110	110 (120)^{C}	110 (120)^{D}	90
90 days	(117)^{D}	n/a	n/a	(117)^{D}	n/a	(117)^{C}	(117)^{D}	n/a
6 months	100 (113)^{D}	90	90	100 (113)^{D}	100	100 (113)^{C}	100 (113)^{D}	90
1 year	100	90	90	100	100	100	100	90
Flexural strength, min, % reference:^{C}								
3 days	100	90	110	100	110	110	110	90
7 days	100	90	100	100	100	100	100	90
28 days	100	90	90	100	100	100	100	90
Length change, max shrinkage (alternative requirements):^{E}								
Percent of reference	135	135	135	135	135	135	135	135
Increase over reference	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Relative durability factor, min % of reference^{F}	80	80	80	80	80	80	80	80

^{A} Requirements in this table apply to the averages of three or more test results for each category of concrete. Comparisons are not to be made between pairs of single test results of reference and test concretes. The indicated maximum water contents are not to be interpreted as requiring exactly that amount; they are maximum values and testing at lower water content is permitted. Further, there is no requirement that either test or reference concretes be prepared at the same water contents. Because requirements in this specification apply to the average test results for each category of concrete, adjustment of mixtures within the tolerances of this specification are permitted if necessary to make the averages fall within requirements.

^{B} The values in the table include allowance for normal variation in test results. The objective of the 90 % compressive strength requirement for a Type B and Type S admixture is to require a level of performance comparable to that of the reference concrete while allowing for variability in test results.

^{C} The compressive and flexural strength of the concrete containing the admixture under test at any test age shall be not less than 90 % of that attained at any previous test age. The objective of this limit is to require that the compressive or flexural strength of the concrete containing the admixture under test shall not decrease with age.

^{D} Alternative requirement. If the physical requirements are met and any of the measured relative strengths are greater than the requirement in parentheses, the admixture shall be considered provisionally to meet the requirements of this specification until the one-year strength test results are obtained.

^{E} Alternative requirements, see 17.1.4. The % of reference limit applies if length change of reference concrete is 0.030 % or greater; increase over reference limit applies if length change of reference concrete is less than 0.030 %.

^{F} This requirement is applicable only if the admixture is intended for use in air-entrained concrete that may be exposed to freezing and thawing while wet.

Table 1 – General Requirements

No	Property	Test method	Requirements
1	Homogeneity[a]	Visual	Homogeneous when used. Segregation shall not exceed the limit stated by the manufacturer
2	Colour[a]	Visual	Uniform and similar to the description provided by the manufacturer
3	Effective component[a]	EN 480-6[b]	IR spectra to show no significant change with respect to the effective component when compared to reference spectrum provided by the manufacturer
4	Relative density[a] (for liquids only)	A2 ISO 758[i] A2	$D \pm 0{,}03$ if $D > 1{,}10$ $D \pm 0{,}02$ if $D \leq 1{,}10$ where D is manufacturer's stated value
5	Conventional dry material content[a]	EN 480-8[c]	$0{,}95\ T \leq X < 1{,}05\ T$ for $T \geq 20\ \%$ $0{,}90\ T \leq X < 1{,}10\ T$ for $T < 20\ \%$ T is manufacturer's stated value % by mass; X is test result % by mass
6	pH value[a]	ISO 4316	Manufacturer's stated value ±1 or within manufacturer's stated range
A2 7	Total chlorine[a d]	ISO 1158[e]	Either ≤ 0,10 % by mass or not above the manufacturer's stated value
8	Water soluble chloride (Cl^-)[a]	EN 480-10	Either ≤ 0,10 % by mass[h] or not above the manufacturer's stated value
9	Alkali content (Na_2O equivalent)[a]	EN 480-12	Not above the manufacturer's stated maximum
10	Corrosion behaviour	[f g]	No corrosion promoting effects on steel embedded in concrete[g] A2

BS EN 934-2:2009+A1:2012
EN 934-2:2009+A1:2012 (E)

Table 9 — Specific requirements for water resisting admixtures
(at equal consistence or equal w/c ratio [a])

No	Property	Reference mortar/concrete	Test method	Requirements
1	Capillary absorption	EN 480-1 mortar	EN 480-5	Tested for 7 days after 7 days curing : test mix ≤ 50 % by mass of control mix Tested for 28 days after 90 days curing : test mix ≤ 60 % by mass of control mix
2	Compressive strength	EN 480-1 reference concrete I	EN 12390-3	At 28 days : test mix ≥ 85 % of control mix
3	Air content in fresh concrete	EN 480-1 reference concrete I	EN 12350-7	Test mix ≤ 2 % by volume above control mix unless otherwise stated by the manufacturer

[a] All tests shall be performed either at equal consistence or equal w/c ratio.

١. Effect of Permeability Reducing admixture on Concrete

ACI demonstrates the effects of PRAHs, and states that “PRAHs can result in a significant reduction in water penetration under pressure compared to a reference concrete. Reductions in the depth of water penetration of 50 to 90% have been reported using penetration methods such as BS EN 12390-8 or DIN 1048-5 (Morelly 2003). (ACI Committee 212, 2010)

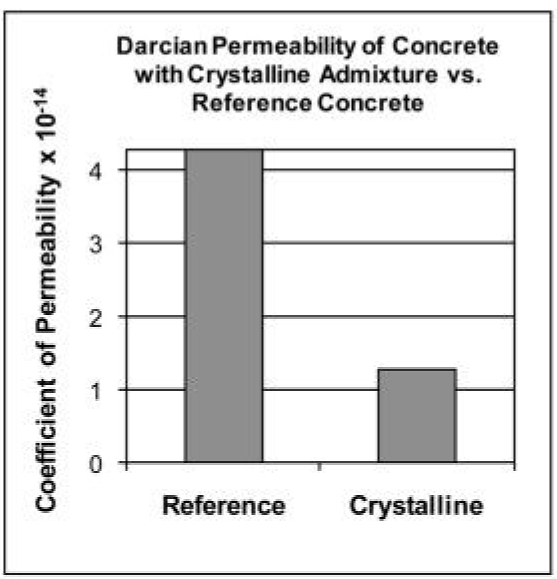

Table 15.1—Reduction in permeability of concrete using PRAs

Admixture type	Coefficient of permeability of reference concrete	Coefficient of permeability of test concrete	Percent reduction in permeability
Crystalline	4.29×10^{-14}	1.28×10^{-14}	70

Therefore “PRAs can be incorporated into virtually any concrete mixture. Usage of these admixtures, however, is usually limited to structures that will be exposed to moisture, salt, salt water, wicking, or water under hydrostatic pressure. Prevention of water-related problems such as water migration, leaking, freezing-and-thawing damage, corrosion, carbonation, and efflorescence are reasons to choose a PRA. PRAHs are appropriate for water-containment structures, below-grade structures, tunnels and subways, bridges and dams, and recreational facilities such as aquatic centers.” (ACI Committee 212, 2010)

References

ACI Committee 201. (2008). Guide to Durable Concrete. *ACI* 201, 1--49.

ACI Committee 212. (2010). Report on Chemical Admixtures. *ACI* 212, 46-50.

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ASTM International. (2019). Standard Specification for Chemical Admixture for Concrete.

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