FINAL REPORT

Title: Testing Methods to Assess the Durability of Concrete Permeability Reducing Admixtures

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DISCLAIMER

SI (MODERN METRIC) CONVERSION FACTORS (FROM FHWA)

Symbol	When You Know	Multiply By	To Find	Symbol
Length				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
Area				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
mi^2	square miles	2.59	square kilometers	km^2
Volume				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: volumes greater than 1000 L shall be shown in m^3				
Mass				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
Temperature (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
Illumination				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
Force and Pressure or Stress				
lbf	pound-force	4.45	newtons	N
lbf/in^2	pound-force per square inch	6.89	kilopascals	kPa

TECHNICAL REPORT DOCUMENTATION

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16. Abstract

Hydrophobic pore blocking admixtures and crystalline admixtures are permeability-reducing admixtures (PRAs) marketed to reduce water ingress into and increase the service life of reinforced concrete. Because corrosion of steel reinforcement is the main cause of deterioration and repair expenses for reinforced concrete structures owned by the Florida Department of Transportation (FDOT), reducing the permeability and limiting cracking is important for concrete durability. The varied chemistry and mechanisms used by PRAs necessitate rigorous performance-based tests to determine their efficacy and potential benefits to FDOT. A literature review was performed to determine if there are existing test methods that can quantify the performance of chemical PRAs and what acceptance limits, if available, should be used to qualify PRAs for use in FDOT structures. It was found that among the hydrophobic pore blocking or crystalline admixtures examined, seven groupings of active ingredients and reaction types were identified. A review of penetrability tests used showed that nine different water absorption, six different water permeability, four different electrical tests, and three vapor/ gas permeability tests were used. PRA field studies examined did not systematically investigate the ability of these different tests to predict field performance of PRAs in the range of water-cementitious material ratios used by FDOT. Recommended acceptance criteria for PRAs with rapid laboratory penetrability and durability tests was not found in any of the literature examined. Recommendations for a future study to determine PRA test requirements and acceptance criteria are given.

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EXECUTIVE SUMMARY

Background

Permeability-reducing admixtures (PRAs) have begun to be marketed in Florida as products that can reduce water ingress into and increase the service life of reinforced concrete. Some are marketed to also help seal or autogenously heal fine cracks [1–6]. Because corrosion of steel reinforcement is the main cause of deterioration and repair expenses for concrete structures in Florida, reducing the permeability and limiting cracking is important for concrete durability. The American Concrete Institute (ACI) 212 Committee on Chemical Admixtures classifies PRAs based on mechanism: hydrophobic water repellents, polymer products, finely divided solids, hydrophobic pore blockers, and crystalline products [7]. The classification of finely divided solids includes many common supplementary cementitious materials such as silica fume, fly ash, and slag cement because they block pores through better particle packing; these mineral admixtures are routinely used to increase the service life of reinforced concrete structures in aggressive environments. PRAs classified in one of the other categories are chemical admixtures that in some cases are combined with cementitious materials. The use of chemical PRAs that reduce concrete permeability could extend the service life of concrete structures and provide an alternative to use of SCMs when there are shortages.

PRAs are categorized by performance into those that are effective when the concrete is exposed to water pressure gradients or hydrostatic conditions (PRAHs) and those that are nonhydrostatic (PRANs). This is more convenient for the end user because commercially available products often use multiple chemicals in one product that exploit multiple mechanisms. PRANs are considered to be dampproofing or efflorescence control admixtures intended for masonry blocks or pavers; their performance decreases substantially in the presence of even small pressure heads. PRAHs are designed to be used in concrete where water can pond, water-retaining structures, or below-ground structures. Florida Department of Transportation (FDOT) owns concrete structures that are exposed to ponded water, have below-ground substructures, or are exposed to seawater and could benefit from PRAs if they are proven effective.

The varied chemistry and mechanisms used by PRAs necessitate rigorous performance-based tests to determine their efficacy and potential benefits to FDOT. Traditionally, PRANs have been tested using water absorption tests because they cannot resist significant water pressure. PRAHs have historically been tested using water permeability tests by producers to demonstrate their benefits against penetrability [7]. These products are being marketed for use in new and hardened concrete to reduce permeability of uncracked concrete and heal fine cracks, which may require testing of cracked concrete to demonstrate efficacy. Many of these admixtures change the concrete pore solution composition and electrical conductivity, which makes it difficult to use current FDOT-required electrical tests to determine their durability. A thorough review of the state-of-the-art was performed to determine if there are existing test methods that can quantify the benefits of chemical PRAs.

Main Findings

The main findings from this study are summarized as follows:

- Test methods used for PRAs were categorized into penetrability, durability, mechanical, characterization, and supplementary techniques. Most studies that examined penetrability focused on using existing test methods to demonstrate PRAs performance against a reference concrete and did not discuss whether the test method used had been validated for use with this material.

- Penetrability test methods used to measure the performance of PRAs in concrete included water absorption, water permeability, electrical methods, porosity, and vapor/gas permeability. Water absorption and water permeability were the most commonly used test methods for measuring PRA performance with 30 and 23 occurrences, respectively. The other penetrability test methods were less common, but for all test method categories, there was no consensus on the standard or technique used for measurement.
- Durability test methods used to measure the performance of PRAs included simulated and field exposure cases measuring chloride ingress, corrosion potential, freeze-thaw resistance, abrasion, acid resistance, and sulfate resistance. The most frequent of these was exposure to chloride solution. This durability testing however takes a long time to perform, making it difficult to implement in a FDOT qualification test.
- There was a lack of consistency in the experimental methods employed by the studies found in the literature; the dosage, water-cementitious ratio (w/cm), testing age, and mixture designs found had a large range of methods used. Additionally, there were not many studies that had field and lab data on the same materials to correlate lab and field performance and determine the validity of using the test method. Overall trends were observed, but no discussion in the literature was found about acceptance criteria for PRAs.

Conclusions

The conclusions from this study are summarized as follows:

- There is no consensus on which laboratory test methods should be used to evaluate the performance of PRAs.
- The laboratory test results showed conflicting performance of the crystalline and hydrophobic pore blocker admixtures. There was no consistency with the control mixture for comparison to determine performance, thus thresholds for acceptance could not be determined.
- Due to the limited overlap between laboratory and field testing, there was not an established relationship between lab results and field performance that could be used to relate performance in an accelerated lab test to structure service life. Because of simplifications and assumptions used in laboratory tests and the unique properties imparted to the concrete by PRAs, work to determine the ability of laboratory tests used in the literature to predict field performance is still needed.

Research Significance

The number of companies marketing chemical PRAs has grown considerably in the last decade, but there is no standardized testing regimen to qualify the products for use on FDOT projects. PRAs could provide an alternative method of protecting FDOT reinforced concrete structures from corrosion if they prove effective. If supplementary cementitious material shortages become more acute, PRAs could provide a solution to this issue.

Recommendations

Based upon the findings from this study, the following recommendations are suggested:

- Conduct an experimental project to measure the efficiency of PRAs for a range of concrete mixture designs and testing methods. Establish acceptance thresholds based on mechanism or intended function of admixture.

Benefits to the State

The literature review provides recommendations for test method development to measure the performance and establish acceptance criteria to allow the use of chemical PRAs for improving concrete durability. PRAs could provide an alternative method of protecting FDOT reinforced concrete structures from corrosion if they prove effective. If supplementary cementitious material shortages become more acute, PRAs could provide a solution to this issue and reduce repair costs for FDOT structures.

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1. INTRODUCTION

1.1. BACKGROUND

Permeability-reducing admixtures (PRAs) have begun to be marketed in Florida as products that can reduce water ingress into and increase the service life of reinforced concrete. Some are marketed to also help seal or autogenously heal fine cracks [1–6]. Because corrosion of steel reinforcement is the main cause of deterioration and repair expenses for reinforced concrete structures owned by the Florida Department of Transportation (FDOT), reducing the permeability and limiting cracking is important for concrete durability. The American Concrete Institute (ACI) 212 Committee on Chemical Admixtures classifies PRAs based on mechanism: hydrophobic water repellents, polymer products, finely divided solids, hydrophobic pore blockers, and crystalline products [7]. The classification of finely divided solids includes many common supplementary cementitious materials such as silica fume, fly ash, and slag cement because they block pores through better particle packing and pozzolanic reactions; these mineral admixtures are routinely used to increase the service life of reinforced concrete structures in aggressive environments. Polymer products such as latex or epoxy are sometimes used in repair applications. PRAs classified in one of the other categories are chemical admixtures that in some cases are combined with cementitious materials. The use of chemical PRAs that reduce concrete permeability could extend the service life of concrete structures.

PRAs are categorized by performance into those that are effective when the concrete is exposed to water pressure gradients or hydrostatic conditions (PRAHs) and those that are nonhydrostatic (PRANs). This is more convenient for the end user because often commercially available products use multiple chemicals in one product that exploit multiple mechanisms. The varied chemistry and mechanisms used by PRAs necessitate rigorous performance-based tests to determine their efficacy and potential benefits to FDOT. Traditionally, PRANs have been tested using water absorption tests because they cannot resist significant water pressure. PRAHs have historically been tested using water permeability tests by producers to demonstrate their benefits [7]. These products are being marketed for use in new and hardened concrete to reduce permeability of uncracked concrete and heal fine cracks, which may require testing of cracked concrete to demonstrate efficacy. Many of these admixtures change the concrete pore solution composition and electrical conductivity, which puts the use current FDOT-required electrical tests to determine their durability in question. A thorough review of the state-of-the-art was performed to determine if there are existing test methods that can quantify the benefits of chemical PRAs.

1.2. RESEARCH OBJECTIVES

The objectives of this project were to perform a thorough literature review to determine if there are existing test methods that can quantify the performance of chemical PRAs, and if so, what acceptance limits should be used. Candidate test methods were evaluated based on their ability to measure the performance of uncracked concrete, concrete with autogenously healed cracks, admixed materials, and surface-applied materials. Preference was given for test methods that can be performed in a short time period (~28 days), are low-cost, and quantify fundamental transport properties.

1.3. RESEARCH APPROACH

The research approach included a literature review (Chapter 2) of admixture marketing and technical data, patent applications, published journal and conference papers, and reports from other universities and departments of transportation (DOT). The PRAs were classified based on composition, function, and method of application. The test methods found in the literature were compiled to determine frequency of use and discuss performance of PRAs. The test results were used to evaluate the efficacy of the admixtures and determine if acceptance threshold criteria could be established.

Chapter 2 documents the mechanisms of permeability reduction and crack healing, test methods that have been used for PRAs, performance of PRAs based on the test methods, and recommendations for potential test method development. Chapter 3 presents the conclusions and recommendations.

2. LITERATURE REVIEW

2.1. BACKGROUND

Reinforced concrete structures are often exposed to harsh environments, yet the service life of these structures is expected to exceed 50 years or in some cases 100 years. As a result, establishing reliable methods to accurately measure durability, the ability of a structure to remain in service with minimal repair and maintenance for its design life, is essential for improving the design life of structures. Research has shown that the transport properties of concrete are good indicators of durability for problems commonly encountered in Florida [8–14]. Transport is defined as the movement of substances, fluids, or solutions, through concrete. Of particular importance is the movement of chloride ions through concrete to the reinforcing steel. Chloride ions cause corrosion of the reinforcing steel. The volume of the corrosion reaction products is greater than that of the reactants, which results in a net volume increase that causes cracking in the surrounding concrete [15,16]. Cracking produces easier pathways for the chloride ions to reach the reinforcing steel, thereby corroding more steel, and thus continuing the deleterious cycle. Steel corrosion, and subsequent formation of cracking in the concrete, results in reduced load capacity, serviceability, and aesthetics of the structure [8,10,16].

Concrete transport properties have traditionally been reduced through a reduction in the water-cementitious material ratio (w/cm) and/or use of supplementary cementitious materials (SCMs) [7,8,17]. A reduction in the w/cm reduces the amount of water-filled porosity in the concrete from the time of mixing on throughout the life of the concrete. SCMs reduce permeability through pore blocking and by reacting to create additional hydration products that reduce the volume and connectivity of the concrete pore system. FDOT has traditionally used fly ash, slag cement, and silica fume as SCMs to improve durability [18], with fly ash being the most used SCM. Fly ash shortages have been reported recently, making it difficult for some material suppliers to comply with FDOT concrete durability requirements. Additional materials and methods of making low-permeability concrete would give FDOT more options for preventing work stoppages because of material shortages.

2.2. PERMEABILITY-REDUCING ADMIXTURE CLASSIFICATION

A potential option for improving the concrete durability is the use of permeability-reducing admixtures (PRAs). While concrete must still be proportioned with low w/cm and cured properly to achieve good performance in extremely aggressive environments, PRAs can further improve the performance by limiting water penetrability. PRAs encompass a wide range of mineral and chemical admixtures, which vary in mechanism, performance, and acceptance by the concrete industry. ACI Committee 212 on Chemical Admixtures classifies PRAs into five main categories as shown in Figure 1: hydrophobic water repellents, polymer products, finely divided solids, hydrophobic pore blockers, and crystalline products. The miscellaneous category was added by the authors because of the development of new types of admixtures since the publication of the ACI 212 document. Hydrophobic water repellants and polymer products include surface applied liquid sealers and coatings such as boiled linseed oil, epoxies, synthetic resins, latex, and silicones; sealers and coatings in these categories have been studied for over 40 years [19–23]. These PRAs are generally solvent-based chemicals and require safety precautions during application [19]. FDOT has approved for use Class F fly ash, slag, silica fume, metakaolin, and ultra-fine fly ash in the finely divided solids category [18]. Hydrophobic pore blockers and crystalline products are chemical admixtures that are relatively new to the concrete industry in Florida and are the focus of this literature review (highlighted orange in Figure 1). PRAs are further subcategorized into dampproofing and waterproofing; however, because concrete is never completely waterproof, more appropriate subcategories are PRAs exposed to nonhydrostatic (PRAN) and hydrostatic (PRAH) conditions [7]. Hydrophobic pore blockers are typically considered PRANs for dampproofing and are not designed to withstand large hydrostatic pressures. Crystalline products are hydrophilic and absorb water to react with hydration products in the concrete to form crystalline deposits in the pores; these admixtures become integrated into the concrete matrix and are considered PRAHs [7,24].

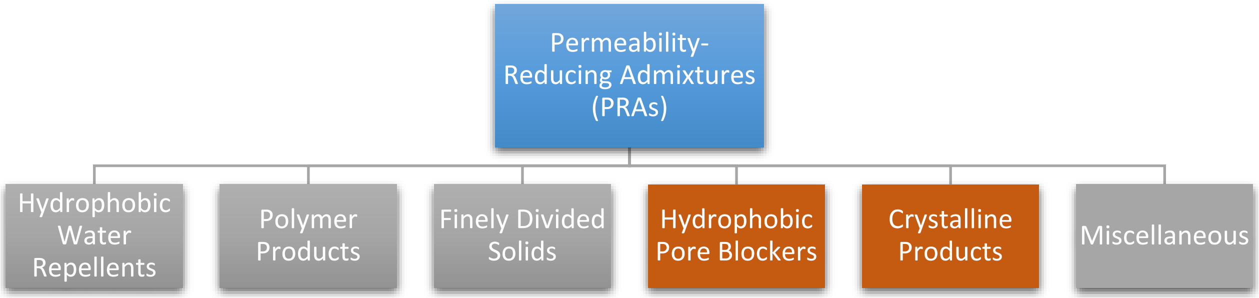

Figure 1. Classification of PRAs by ACI Committee 212 on Chemical Admixtures (Miscellaneous Added) [7]

Miscellaneous PRAs that do not fall into the ACI categories, but could be beneficial in reducing permeability include carbon nanotubes, precipitating bacteria, and microcapsules containing self-healing agents. Carbon nanotubes seem to be targeted more for improving mechanical strength and resistance to abrasive wear, but by filling the voids with flexible carbon nanotubes, the permeability and crack propagation is reduced [25]. Studies have shown that the water absorption, water permeability, and chloride ingress can be reduced with the addition of carbon nanotubes [26,27]. However, a concern with using carbon nanotubes is that the conductivity of the concrete is increased, thus increasing the corrosion potential in reinforced concrete structures [28]. While the porosity and permeability of concrete incorporating carbon nanotubes may be reduced and time to corrosion initiation increased, once chlorides reach the steel, corrosion will likely accelerate. Precipitating bacteria and microcapsules containing a variety of healing/sealing agents (bacteria, epoxy, etc.) are present in the literature as well as potential admixtures that can improve concrete permeability, crack healing, and thus overall durability [29–36].

2.2.1. Composition and Reaction

The hydrophobic pore blocker and crystalline admixtures being marketed in Florida consist of various chemicals, often in combination with portland cement and sand to improve dispersal. The active chemicals in these admixtures that reduce the permeability are proprietary and are listed as trade secrets or not included on the safety data sheets (SDS). In order to gain a better understanding of the mechanisms behind these admixtures, a literature review of PRA patents was performed to determine their general composition. The patent numbers, group of chemicals used, composition, and general reaction of the active ingredients is summarized in Table 1; portland cement, sand, and SCMs were excluded from the composition.

Table 1. Compositions and general reactions of PRAs by patent number

Patent No.	Year	Group	Composition		Reaction/Product
WO2003104159A, US5560773A, US5356716A, WO2002083808A, KR100975477B1 [37–41]	2002, 1995, 1992, 2002, 2008	Silicate and siliconate or silane mixture	- Alkali metal silicate (sodium, potassium, lithium) - Alkyl siliconate (sodium or potassium methyl) - Silane	- Tartaric acid - Surfactant - Emulsifier - Retarder	- Silicate reacts with CH to form additional C-S-H - Siliconate reacts with CO_2 to form silicone resin which reacts with CH to form siloxane resin along pore surfaces - Surfactant reduces surface tension to increase depth of penetration - Retarder slows reaction to increase penetration depth
ES2663840T3, JP2001294461A, JP2012006767A [42–44]	2002, 2000, 2010	Silicate and acid	- Alkali metal silicate - Polycarboxylic acid (tartaric, citric, oxalic) - Sodium carbonate	- Surfactant - Emulsifier - Retarder	- Silicate reacts and forms C-S-H - Acid enhances reaction of silicate and reacts with sodium carbonate to form crystals - Emulsifier opens pores for penetration
CN1122785A, CN101891432B, CN105645825A [45–47]	1995, 2010, 2015	Silicate, acid, and other additives	- Sodium silicate - Stearic acid - Polyvinyl acetate - Alum - Gypsum - Polycarboxylic acid	- Slaked lime - Copper sulfate - Expansive agent (calcium aluminate) - Surfactant	- Silicate and stearic acid generate insoluble crystalline product - Polyvinyl acetate has hydrophobic effect - Gypsum, aluminum salt increase density at top layer
KR100788021B1, JP2521274B2, KR101337376B1, CN1077700A [48–51]	2006, 1987, 2012, 1992	Silicate and expansive agent	- Sodium silicate - Sodium sulfate - Alumina (bauxite) - Magnesium oxide - Aluminum oxide	- Sulfur trioxide - Titanium oxide - Lime - Surfactant	- Sodium sulfate promotes filling in gel pores by enhancing permeability of silica - Bauxite reacts with CH to form C-A-S-H and is able to bind Cl & form Friedel's salt - Magnesium oxide reacts with CH to form insoluble crystals and expand
CN1228270C, CN110183139A [52,53]	2002, 2019	Silicate and fatty acid salt	- Silicate - Higher fatty acid metal salt (stearate, oleate) - Fatty acid alkali salt (sodium soap)	- Redispersible resin - Corrosion inhibitor, inorganic salt (calcium nitrite) - Antioxidant	- Fatty acid, stearate or oleate, bonds to CH to form higher fatty acid calcium which is water repellent - Sodium soap forms hydrophobic layer - Calcium nitrite (or sodium) corrosion inhibitor - Tannin as antioxidant, prevents carbonation, bonds to $CaCO_3$
US2508480 [54]	1947	Sulphate	- Sulfate (calcium and magnesium) - Sodium chloride - Ammonium alum	- Retarder	- Sulfates cause rapid hardening and expand in pores - Sodium chloride contributes to hardening, dissolves and seals pores - Ammonium alum dissolves from heat and fills pores
AT212766B [55]	1956	Carbonate and acid	- Sodium carbonate - Tartaric acid		- Tartaric acid reacts with sodium carbonate to produce sodium tartrate crystals

The compositions of admixtures found in patents marketed as hydrophobic or waterproofing varied greatly; however, overall trends were observed to sort the compositions into groups. The majority of groups had some type of alkali metal silicate with supporting ingredients, including siliconates, acids, expansive agents, and stearates. Surfactants, emulsifiers, and retarders were commonly used to enhance performance. Less frequently found groups included sulfates and carbonates as the main active ingredient.

The different reactions of hydrophobic pore blockers and crystalline product admixtures are due to the different compositions and functions. Hydrophobic pore blockers function as a combination of hydrophobic compounds that repel water and compounds that collect in the capillaries to form a physical plug. The benefit of these admixtures is that water is repelled, which minimizes the ingress of water and deleterious substances (e.g., chlorides). However, high hydrostatic pressure can overcome the effect of the hydrophobic pore blockers. Crystalline admixtures are hydrophilic and require water to react to form additional cement hydration products and/or pore-blocking precipitates. While crystalline admixtures can withstand hydrostatic pressure, some water ingress is needed for the admixtures to react and form the crystalline deposits.

Sodium silicate was the most common form of alkali metal silicates, but potassium and lithium silicates were also used. Lithium silicate was preferred for patent US 5560773A due to lower alkalinity and smaller size compared to sodium and potassium silicate, allowing it to penetrate deeper during topical application [38]. The silicates react with the calcium hydroxide in the concrete matrix to form additional calcium silicate hydrate (C-S-H) crystals as shown in Eq. 1. Thus, admixtures with silicates in the composition are typically classified as crystalline admixtures. The general process for crystalline admixtures where the composition is unknown (crystalline promoter) is given in Eq. 2; these admixtures react with calcium silicates or aluminates and water to form calcium silicate hydrate (C-S-H) or calcium-alumino-silicate hydrate (C-A-S-H) and pore-blocking precipitates [7,24,56]. The crystalline admixtures also react with the cement hydration product calcium hydroxide to form additional C-S-H [56].

$$\mathrm{Ca(OH)_2 + Silicate \rightarrow C\text{-}S\text{-}H} \qquad (1)$$

calcium hydroxide (lime) + silicate → calcium silicate hydrate

$$\mathrm{3CaO\text{-}SiO_2 + M_xR_x + H_2O \rightarrow Ca_xSi_xO_xR\text{-}(H_2O)_x + M_xCaR_x\text{-}(H_2O)_x} \qquad (2)$$

calcium silicate + crystalline promoter + water → modified calcium silicate hydrate + pore-blocking precipitate

Alkyl siliconates (sodium or potassium methyl) induce hydrophobicity and work in conjunction with the silicates to increase efficiency of both ingredients (WO 2002083808A) [37]. One patent was found that included 2%-8% silane along with 33%-43% silicate to improve the waterproofing performance [41]. The siliconates initially react with carbon dioxide to form silicone resin, which then reacts with calcium hydroxide in the concrete to form siloxane resin as given in Eq. 3. The siloxane resin lines the pores and induces hydrophobicity.

$$\mathrm{CO_2 + Siliconate \rightarrow Silicone\ Resin + Ca(OH)_2 \rightarrow Siloxane\ Resin} \qquad (3)$$

carbon dioxide + siliconate → silicone resin + calcium hydroxide (lime) → siloxane resin

Silicates with an acid and sodium carbonate are used together as PRAs. There are a few forms of polycarboxlic, tartaric, citric, and oxalic acid used, but tartaric acid was the most commonly found in patents for PRAs. Tartaric acid enhances the reaction of the silicates and reacts with sodium carbonate to form sodium tartrate crystals. These crystals fill the voids and reduce the porosity and permeability of the concrete. Sodium carbonate is used as an accelerator in concrete to decrease setting times, but can also reduce the overall strength; addition of tartaric acid balances the reaction to activate the beneficial effects of reduced permeability [37,55]. A few other patents listed other additives in addition to silicates and acids. Stearic acid reacts with the silicates to form insoluble crystalline products while polyvinyl acetate has a hydrophobic effect. Gypsum and alum is included to increase the density at the top layer for surface-applied admixtures. Slaked lime is an activator for the hydration reaction and helps create a denser pore structure for reducing permeability. Copper sulfate can be used as a dye to make sure the admixture is mixed or applied evenly. Calcium aluminate provides rapid hardening and good resistance to acid attack and abrasion [57]. Sodium sulfate promotes filling of gel pores with silicate particles by enhancing the permeability of silica and is used as an accelerator to harden and expand in pores [48,58]. One patent was found to include bauxite (KR 100788021B1), which reacts to form additional hydration products and binds chlorides to form Friedel's salts [48]. The various oxides including magnesium, aluminum, sulfur, and titanium are included as expansive agents that form crystals in the concrete [51,59,60].

A fatty acid metal (stearate or oleate) and alkali (sodium soap) salts are used to form water repellent layers in the pores [7,52,61,62]. These compositions classify as hydrophobic pore blockers. Redispersible resin was also found as a means to induce hydrophobicity. Calcium nitrite (or sodium) was found in one patent composition as an additional measure to prevent corrosion. A tannin agent was included to prevent carbonation. Some of the most frequently used hydrophobic materials are fatty acid salts; both metal and alkali salts of fatty acids were found in patent compositions. In the case of stearate-based admixtures, the stearate admixture reacts with calcium hydroxide in the concrete matrix to form an insoluble calcium stearate hydrophobic layer on the walls of the concrete pores according to Eq. 4 [7].

$$\mathrm{Ca(OH)_2 + RCOOH \rightarrow Ca^{+}COOR^{-} + H_2O} \tag{4}$$

calcium hydroxide (lime) + stearate admixture → insoluble calcium stearate + water

US 2508480 used calcium and magnesium sulfate to cause rapid hardening and expansion in the pores to reduce permeability [54]. Sodium chloride was used to also contribute to hardening and dissolves to fill the pores. Ammonium alum dissolves from the heat of hydration and fills small pores, further reducing the permeability.

Sodium carbonate and tartaric acid are used to produce sodium tartrate crystals as given in Eq. 5; this composition is for a simple crystalline product admixture. The sodium tartrate crystals are insoluble hygroscopic crystals that fill and block the pores, reducing porosity and permeability in the concrete [37,55].

$$\mathrm{2NaHCO_3 + C_4H_6O_6 \rightarrow Na_2C_4H_4O_6 + 2CO_2 + 2H_2O} \tag{5}$$

sodium carbonate + tartaric acid → sodium tartrate + carbon dioxide + water

Surfactants, emulsifiers, and retarders were included in many of the compositions of patents found for PRAs. Surfactants serve as a wetting agent to reduce the surface tension of the chemicals in the PRA and allow deeper penetration of the admixture into the pores; these chemicals are important for surface-applied PRAs, which must penetrate into the pore network of hardened concrete [37]. Surfactants include nonylphenol polyethylene glycol ether and isopropyl alcohol.

Emulsifiers are also important for surface-applied PRAs to increase penetration depth for better and longer-lasting performance; this component emulsifies dirt and impurities within the concrete pores to open the pores for better penetration of the admixture [37]. Emulsifiers include alkylbenzene sulfonic acid, sodium hydroxide, and sodium hypochlorite.

Retarders such as potassium bitartrate are included to control the reaction of the other components and prevent setting for topical applications before desired penetration depth is achieved [54]. For surface-applied PRAs, if the reaction occurs too quickly, then the admixture will not penetrate far and will be easily removed with abrasion and wear.

Another ingredient that was seen in PRA patent compositions was an antifoaming agent to reduce bubble formation and minimize air entrapment during application; isopropyl alcohol was found listed for this function. The full compositions with weighted percentages for two patents are given in Table 2 to provide an idea of the range of components and typical proportions.

Table 2. Examples of full PRA compositions from two patents with weighted percentages

WO 2003104159A [37]	US 5560773A [38]
Water – 65-82.5% Sodium silicate solution (40% solids) – 7.5-25% Potassium methyl siliconate (40% aqueous sol.) – 1.65-7.5% Tartaric acid – 0.75-3.5% Anhydrous sodium carbonate – 0.532-2.482% Isopropyl alcohol – 0.05-0.3% Nonylphenol polyethylene glycol ether – 0.005-0.075% Alkylbenzene sulfonic acid – 0.004-0.02% Sodium hypochlorite (12.5% aqueous sol.) – 0.003-0.025% Sodium hydroxide (50% aqueous sol.) – 0.002-0.025%	Water – 45-90% Alkali metal silicate – 10-50% Sodium methyl siliconate – 0.5-2% Surfactant mixture – 0.06-5% Potassium dichromate – 0.05-1.05%

2.2.2. Method of Application

Permeability-reducing admixtures have two means of application to concrete mixtures: surface-applied to set concrete and integrally-mixed into fresh concrete.

Surface-applied PRAs are applied to set concrete either by spraying or brushing an aqueous or slurry solution. For this method of application, the surface typically must be pretreated to achieve adequate penetration and reaction. Some PRAs require the surface to be dried for several days to a predetermined moisture content while others must remain saturated. The depth of penetration is critical as abrasion and wear will affect the performance. Surface-applied PRAs are only beneficial as long as there is a minimum penetration depth. Over time, wear of the surface will necessitate reapplication of the PRA. This incurs additional costs to maintain performance. Furthermore, the surface pretreatment and surface application may create safety concerns.

PRAs that are integrally-mixed into fresh concrete before placement have the benefit of dispersal throughout the concrete matrix. As a result, wear of the surface should not affect the performance of the PRAs within the concrete; however, significant wear may still require concrete repair. The cost is lower for integrally-mixed PRAs compared to surface-applied because there is not additional equipment, worker time, or surface treatment required. Manufacturer recommendations should be followed to determine the proper time to add the PRAs into the fresh concrete mixture to ensure suitable dispersion and placement. Although this method of application has many benefits, it can only be used for new structures or repair.

2.3. DESCRIPTION AND FREQUENCY OF TEST METHODS

Numerous test methods have been documented in the literature for evaluating the performance of PRAs with varying degrees of frequency and standardization. These methods include measuring penetrability or waterproofing capability, mechanical properties, durability performance for various exposure conditions, and material characteristics of reaction products formed. Due to the difference in function of crystalline and hydrophobic pore blocker admixtures as well as the method of application, there is no single test method applicable to all situations. Therefore, a standard testing regimen must be established that incorporates the functions and applications of these admixtures. The effect of PRAs on fresh concrete properties such as workability and setting time are also important but not well documented; PRAs that meet the requirements for hardened concrete properties should be investigated for their effect on fresh properties, especially for conditions like hot weather concreting frequently encountered in Florida.

Although the goal of permeability-reducing admixture use is to improve the watertightness and durability of concrete, there are many test methods that have been used to measure the properties of concrete incorporating PRAs. For each property, a range of standard and non-standard test methods have been previously used; standard acronyms for the test methods found are defined in Table 3. Test methods can be categorized into penetrability, durability, mechanical, characterization, and supplementary techniques as shown in Table 4.

Table 3. Definitions for standard test method acronyms with country of origin

Acronym	Definition	Country of origin
ASTM	American Society for Testing and Materials	International
AASHTO	American Association of State Highway Transportation Officials	United States
BS	British Standard	United Kingdom
EN	Europaischen Normen (European Standard)	European Union
UNE	Una Norma Española (Spanish Association for Standardization)	Spain
UNI	Ente Nazionale Italiano di Unificazione (Italian Organization for Standardization)	Italy
ABNT NBR	Associação Brasileira de Normas Técnicas Norma Brasileira Regulamentadora (Brazilian Association of Technical Standards)	Brazil
DIN	Deutsches Institut für Normung (German Institute for Standardization)	Germany
NCH	Instituto Nacional de Normalización (Chilean Standards)	Chile
CRD	Concepts and Requirements Division (Army Corps of Engineers)	United States
ACCI	Australia Centre of Construction and Innovation	Australia
NT Build	Nordtest Build	Nordic
ISO	International Organization for Standardization	International
CSN	Czech Standards Institute	Czech
AS	Australian Standard	Australia

Table 4. Frequency of test methods used for analysis of crystalline and hydrophobic pore blocker admixtures

Property	Standard/Description	Company	References	No.
Penetrability				
Water absorption	ASTM C1585, ABNT NBR 9778, BS 1881-208, BS 1881-122, ASTM C642, EN 1015-18, BS 1881-5, UNE 83982, UNI 10859	Vandex, Euclid, BASF, Xypex, Hycrete, Kryton	[23,36,61–82]	30
Water permeability	EN 12390-8, DIN 1048-5, CRD-C48-92, ABNT NBR 10787, ACCI water permeability, NCH 2262	Vandex, Hycrete, Xypex, Kryton, Penetron, BASF, Maxon	[69,73,75–78,81,83–91]	23
Electrical methods	ASTM C1202, AASHTO T 277, NT Build 492, AASHTO T 358	Vandex, Xypex, BASF, Kryton, Penetron	[35,64,71,78,82,90,92]	12
Porosity	ASTM C642, mercury intrusion porosimetry		[36,61,67,68,70,73,83,86,90,93]	10
Vapor / gas permeability	ISO 12572, ASTM E96, gas permeability		[71,85,94,95]	4
Durability				
Chloride penetration	AASHTO T 259, AASHTO T 260, ASTM C1556, EN 480-10, NT Build 443	Wicktek, Maxon, Foxfire, Penetron, Vandex, Xypex	[22,82,91–93,96–98]	14
Freeze-thaw and deicing chemical	ASTM C666, NYDOT Method 502-3P, ASTM C672, CSN 73 1326	Wicktek, Vandex, Xypex, Euclid, Maxon, Foxfire, Penetron	[63,64,72,93]	8
Corrosion, salt spray, abrasion	UNE-EN ISO 9227, EN 480-14, ASTM G109, ASTM C779	Maxon, Euclid, Penetron, Foxfire, Xypex, Vandex	[63,82,99]	8
Sulfate and acid resistance	ASTM C1012	Vandex, Penetron, Kryton, Xypex	[79,92]	5
Self-healing	Crack healing/width monitoring	Xypex, Penetron	[58,75,82,89,96,100]	6
Other exposure	Wet/dry cycles, air fan, carbonation, etc.		[22,72,76,80,81,92,93,96,101]	9
Mechanical				
Compression	ASTM C39, ASTM C873, ASTM C42, EN 12390-3	Vandex, Hycrete, Xypex, Euclid, BASF, Kryton, Foxfire, Penetron, Wicktek	[35,36,58,59,61,64,65,68,69,71,73,74,76,77,79–81,83–85,89,91,92,94,95,97,98,102]	37
Flexure/bending	ASTM C78, ASTM C293		[36,59,61,64,89,94,100,103]	8
Tension	ASTM C496		[58,104,105]	3
Characterization				
SEM/EDS and petrography	ASTM C856, scanning electron microscopy, energy dispersive spectroscopy	Penetron, Wicktek	[35,36,56,58,61,63,65,67,68,75,79,81,83,84,88,94,95,100,104,106–110]	26
XRD	X-ray diffraction		[35,56,58,61,65,67,68,70,75,79,83,88,94,95,105,109,110]	17
FTIR	Fourier-transform infrared spectroscopy		[56,61,70,73,94,109]	6
TGA	Thermogravimetric analysis		[61,70,94,95,102,109]	6
Supplementary				
Length change and drying shrinkage	ASTM C157, AS 1012.13	Vandex, Hycrete, Kryton, Penetron	[76,91,92,97,102]	9
Contact angle	Contact angle of water on specimen surface		[23,61,111–113]	5
Pulse velocity	ASTM C597	Hycrete	[59,105]	3

2.3.1. Penetrability

2.3.1.1. Water absorption

Water absorption is one of the easiest and most efficient means for assessing concrete penetrability [10,114], and as such was the most frequently used evaluation technique category found with 30 authors (including companies) choosing this test method. The general mechanism for water absorption test methods is unsaturated flow due to capillary forces. For some crystalline admixtures, water absorption may underestimate the permeability-reducing effect because these admixtures are hydrophilic and absorb water to react and swell to block pores [37,115,116]. Water absorption tests that measure the mass gain would see the water absorption by the admixture as water penetration, whereas it would actually be beneficial for some swelling admixtures in reducing further ingress, illustrating the difficulty in finding one sole test that can judge the performance of all admixtures. In contrast, hydrophobic pore blockers repel water, so water absorption tests may overestimate the effect of these admixtures. Despite the differences in absorption properties for these admixtures, water absorption was commonly used for both crystalline and hydrophobic pore blocker admixtures. There was no consensus on the standard test method used; nine standards with varying conditioning and measurement procedures were used in the literature examined to give an indication of the efficiency of PRAs. The following standardized methods were reported to be used on PRAs:

- ASTM C1585 – Standard test method for measurement of rate of absorption of water by hydraulic-cement concretes [117]
- BS 1881-208 – Recommendations for the determination of the initial surface absorption of concrete [118]
- BS 1881-122 – Method for determination of water absorption [119]
- BS 1881-5 – Methods of testing hardened concrete for other than strength [120]
- EN 1015-18 – Determination of water absorption coefficient due to capillary action of hardened mortar [121]
- UNE 83982 – Determination of the capillary suction in hardened concrete [122]
- UNI 10859 – Determination of water absorption by capillarity [123]
- ASTM C642 – Standard test method for density, absorption, and voids in hardened concrete [124]
- ABNT NBR 9778 – Determination of water absorption, voids index, and specific mass [125]

Specimens are typically conditioned according to a drying procedure, then placed in contact with water, and weighed at intervals to determine the mass increase due to absorption. While the measurement of mass change was similar for the majority of test methods, the specimen conditioning procedure varied greatly. ASTM C1585 has a mild specimen conditioning procedure of three days drying at 50 ± 2°C followed by 15 days at 23 ± 2°C in a sealed container before exposing to water [117]. BS 1881-208, BS 1881-122, and UNE 83982 use a more aggressive conditioning procedure of drying at 105 ± 5°C for a specified amount of time before returning to room temperature to test [118,119,122]. The other British Standard listed, BS 1881-

5, was superseded by BS 1881 Parts 122 and 208, but was found referenced by one of the companies. ASTM C642 has the harshest conditioning procedure, drying the specimens at 110 ± 5°C until constant mass before immersing in room temperature water (approximately 21°C) for 48 hours. ABNT NBR 9778 is similar to ASTM C642 in concept.

Differences in specimen conditioning can result in different absorption values. A study by Zhutovsky and Hooton investigated the importance of sample preparation in water absorption tests by comparing the effect of two drying procedures used in standard test methods [114]; it was concluded that drying at 60°C until constant mass was a more appropriate conditioning procedure and had better correlation with other transport properties [114]. Castro et al. also examined the specimen conditioning procedure used prior to water absorption testing and found that the conditioning procedure, specifically the relative humidity, can substantially influence the results [126]. Specimens with a lower relative humidity before the start of the test showed higher total absorption [126,127]. Another factor that can influence the results is the aggregate content; specimens with higher cement paste content will absorb more water [126].

Subsequent to the conditioning procedure, the specimen is exposed to water to measure the absorption. The overall testing procedure for the majority of water absorption methods examined is similar and involves measuring mass change due to partial or fully immersed water exposure; Figure 2 shows a typical setup for partial water exposure (one face) for water absorption. ASTM C1585, EN 1015-18, UNE 83982, and UNI 10859 use partial water immersion of one face (Figure 2) and measure mass at specified time intervals to determine absorption [117,121–123]. The measured absorption with time is then used to find the initial absorption rate and secondary absorption rate.

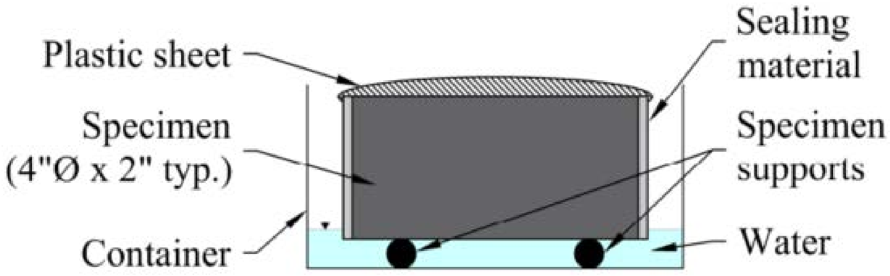

Figure 2. Diagram of partial water exposure for water absorption test ASTM C1585 [117]

BS 1881-208 is the only test method used with PRAs that does not use change in mass to determine water absorption; rather, a capillary tube and scale are attached to the water source to measure absorption rate as shown in Figure 3 [118]. For this method, a cap is clamped onto a smooth horizontal surface and a water reservoir is filled to apply a small constant head to the surface of the specimen. The rate of absorption is recorded as the scale divisions on the capillary tube at different time intervals; as the test proceeds, the moisture content of the specimen will increase at the exposed surface and the rate of surface absorption will decrease over time [118].

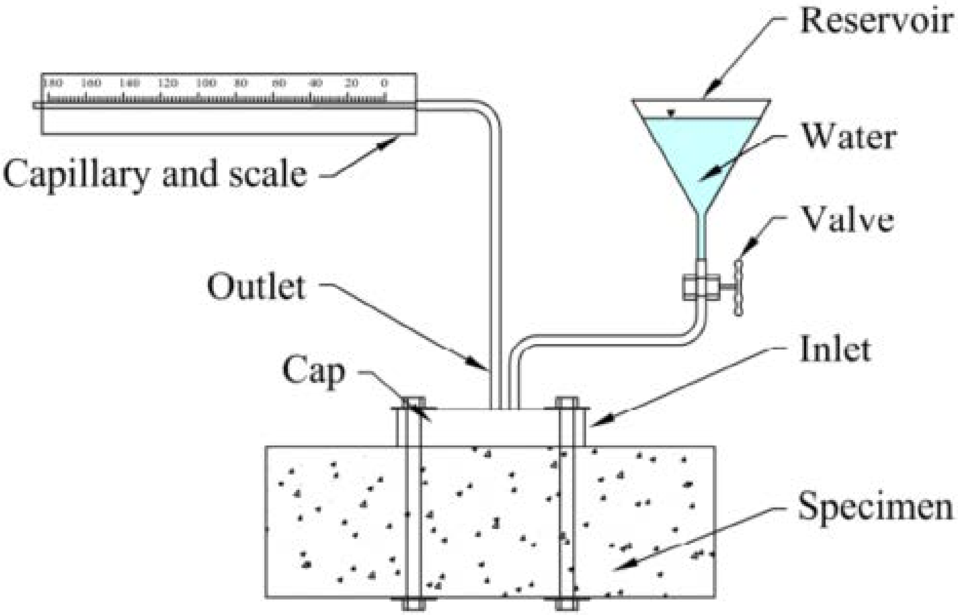

Figure 3. Diagram of BS 1881-208 initial water surface absorption test method [118]

ASTM C642 only attempts to measure the concrete absorption %, and not the rate of absorption like in the other water absorption tests described and is thought to be less predictive of concrete transport, especially at low permeabilities [124]. After drying, ASTM C642 continues to immerse the specimens for 24 hour intervals until constant mass is achieved; the specimens are then placed in boiling water for five hours and weighed before suspending the specimen in water to determine the apparent mass. The specimen masses from each step of ASTM C642 are used to calculate the absorption as well as the density and voids [124].

While water absorption tests are easy measurements of concrete penetrability, they might not be applicable for measuring the performance of both crystalline and hydrophobic pore blocker admixtures. Crystalline admixtures are hydrophilic and absorb water to react and form crystals to fill the pores, so water absorption may underestimate the permeability-reducing effect [37,115,116]. Hydrophobic pore blockers repel water and do not need moisture to react, so these admixtures would perform well in water absorption tests. Due to the difference in the admixture mechanisms, the performance for water absorption between the two admixtures would not be comparable.

2.3.1.2. Water permeability

The second most frequently used technique in the penetrability category was water permeability with 23 occurrences. There is no consensus on the standard or test method used to measure concrete water permeability, and specimen conditioning plays a large role in the resulting permeability measured. A total of six standardized test methods for water permeability were reported to be used on PRAs in the literature examined. Water permeability measurements of concrete can have high variability, consequently care should be taken with specimen conditioning and flow/penetration measurement to obtain accurate results [128–130]. Some tests are not able to measure water flow below a threshold water permeability. For these tests, specimens that show no water flow do not necessarily mean that the concrete is impervious, only that the test is not capable of measuring the flow. Caution is thus urged in interpreting water permeability results.

There are two principle categories of water permeability tests that have been used on PRAs. The first category is for methods that measure water penetration depth over a defined period of time. The second category is water flow-through tests that measure flow rate until steady-state is achieved. For both categories, a uniaxial, pressurized water gradient is applied to one surface of the specimen. While the hydrophobic pore blocker admixtures are typically considered non-hydrostatic and not effective under pressure head, water permeability was still reported being used for some materials in the literature; for these PRAs, the pressure head may need to be reduced for testing.

Penetration depth test methods are relatively short-term tests that apply water pressure to the specimens for 3-4 days before splitting the specimen and measuring the penetration depth. The applied pressure gradient for these methods ranges from 65 to 80 psi, but is typically reported as the average, 72.5 psi. Although not a direct measurement of water permeability, the penetration depth gives a good indication of the permeability of the specimen. The standardized test methods used in this category include:

- EN 12390-8 – Depth of penetration of water under pressure [131]
- DIN 1048-5 – Testing of hardened concrete [132]
- ABNT NBR 10787 – Determination of penetration of water under pressure [133]
- NCH 2262 – Determination of the impermeability to water – method of penetration of water under pressure [134]

Because water pressure is only applied for 3-4 days, the specimen sides do not need to be sealed. However, to ensure flow does not leak out of the sides, there are minimum specified dimensions. EN 12390-8 requires the surface of the specimen to be tested to have a minimum dimension of 150 mm (6 in.) and no other dimension less than 100 mm (4 in.) [131]. An example of an unsealed specimen set up for water penetration depth testing is shown in Figure 4. The water inlet is at the bottom and a watertight O-ring seals the test area to be approximately half the dimension of the surface of the specimen; the reduced test area helps prevent flow from occurring out of the specimen sides. However, specimens with high permeability may still have leakage out of the sides, in which case, this test method is not appropriate. After the specified period of 3-4 days, the specimens are split in half and the maximum depth of water penetration is measured. Because of specimen drying on the sides and pressurized water only applied to the center half of the sample, water penetration depth will not be uniform throughout the cross-section. The water penetration depth is measured to be the maximum depth penetrated.

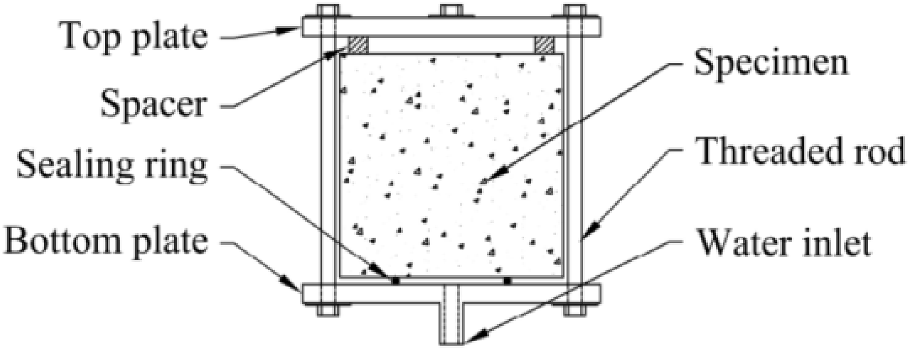

Figure 4. Diagram of unsealed specimen for water penetration depth test per EN 12390-8 [131]

Steady-state water permeability test methods use the flow rate during testing to calculate the permeability. Permeability is calculated using Darcy's law, which relates the flow to the hydraulic pressure gradient for steady-state, laminar flow through a saturated porous medium [8,9,135]. While this category of test methods directly measures the water permeability, there are drawbacks. The first is that the test takes a long time to conduct and depends on the quality of concrete tested; steady-state is typically achieved in 14-20 days, but high quality concrete, with low permeability, may take longer or exhibit no flow. Another factor to consider is that there is continued hydration during the testing period, consequently it is difficult to achieve steady-state flow, especially for early ages. Specimens can be vacuum saturated prior to testing to reduce the time to reach steady-state conditions. It may be difficult to saturate the concrete containing hydrophobic pore blockers. Due to the length of test and applied pressure, these test methods may not be appropriate for hydrophobic pore blockers. On the other hand, the length of these tests may be beneficial for measuring self-healing capabilities. The two water permeability flow-through test methods in this category with documented use with PRAs are listed below.

- CRD-C48-92 – Standard test method for water permeability of concrete [136]
- ACCI water permeability test [137]

The U.S. Army Corps of Engineering developed the first standardized water permeability test in the early 1970's as CRD-C48-73, which is now CRD-C48-92 [136,138]. According to CRD-C48-92, the sides of the specimens are first sealed with a paraffin-rosin mixture before securing the specimens in the testing chamber [136]. The specimens are secured using additional paraffin-rosin, plaster, and asphalt to ensure a good seal around the perimeter. A water pressure of 200 psi is then applied to the specimen via a water inlet and the resulting flow rate is measured until steady-state is achieved, typically 14-20 days [136]. A full schematic of the water permeability test assembly for CRD-C48-92 is shown in Figure 5.

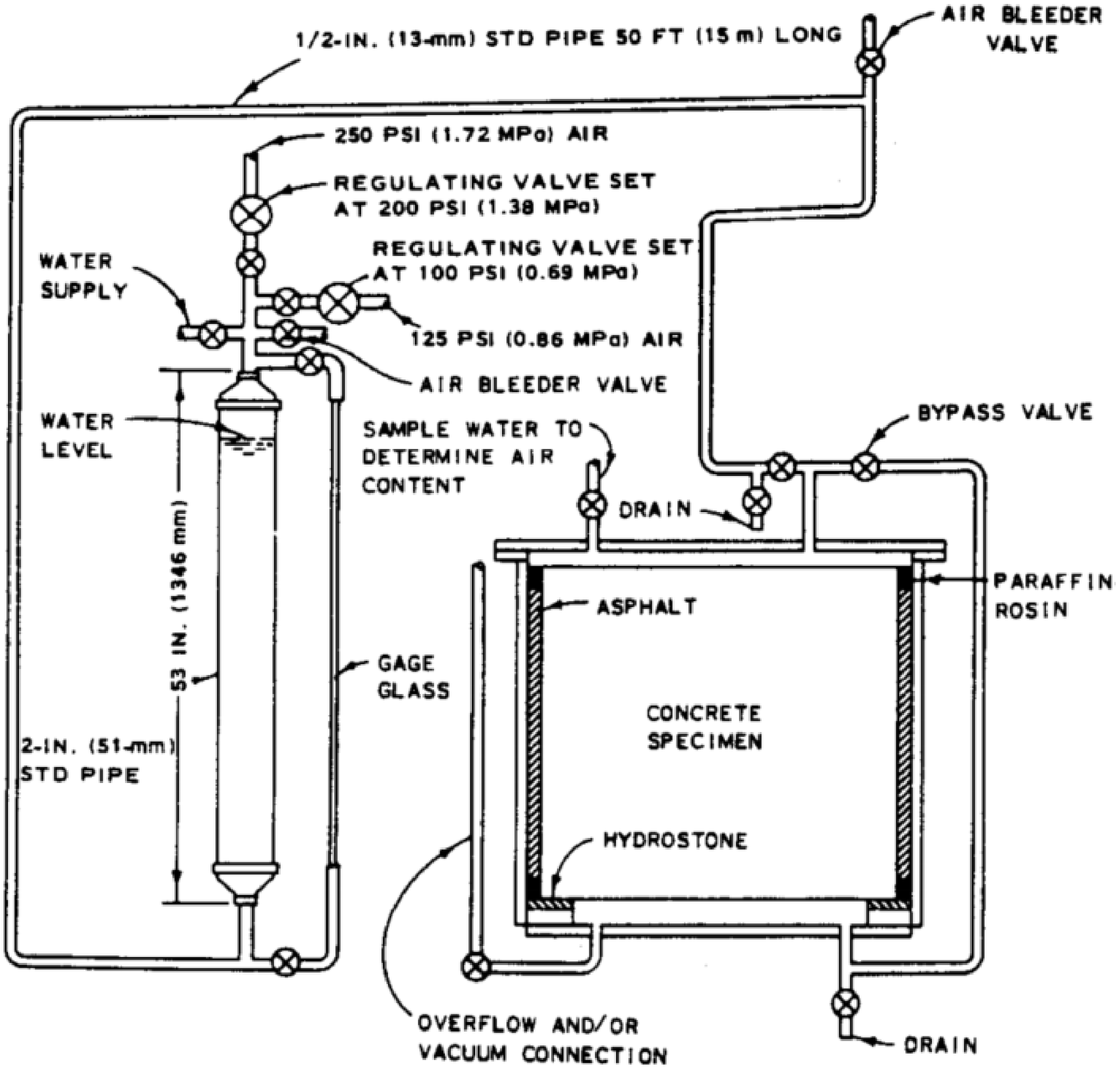

Figure 5. Diagram of water permeability test assembly for CRD-C48-92 [136]

The ACCI water permeability test was adapted from the Taywood test and also measures flow rate under constant pressure to calculate permeability directly [137,139]. This test appears to be similar in many ways to the method developed at the University of Florida (UF) [135,140]. For these methods, the specimen sides are sealed using an epoxy ring, which restricts flow through the specimen face and provides a bearing surface for sealing the specimens with an O-ring between two plates as shown in Figure 6. Subsequently, water pressure is applied and the flow rate is measured until steady-state is achieved; water pressure ranges from 85 to 145 psi.

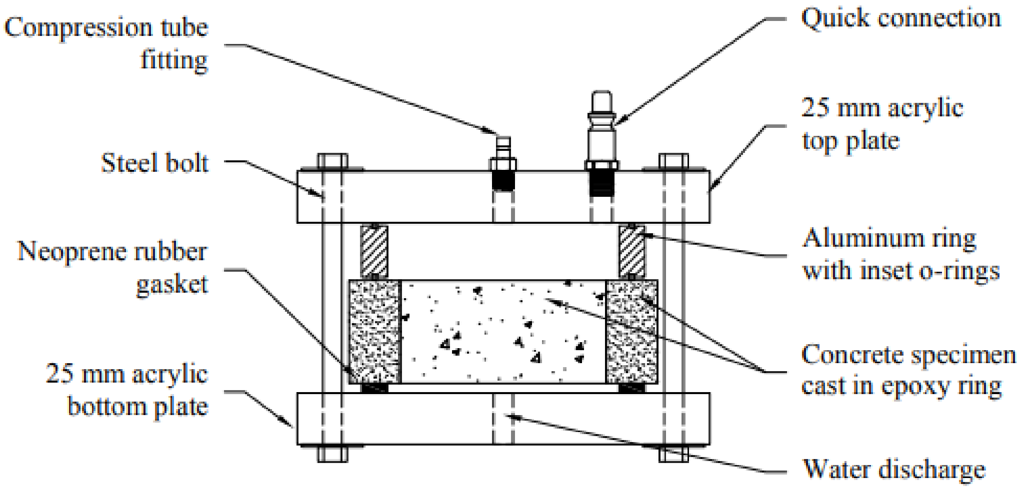

Figure 6. Diagram of UF water permeability cell with concrete specimen cast in epoxy ring (similar to the ACCI water permeability test)

2.3.1.3. Electrical methods

Electrically-based test methods were developed as an alternative to long-term exposure tests and have been used as index tests for concrete penetrability for many years. These test methods measure the electrical resistance of concrete. Since electricity is conducted by the pore solution, the electrical conductivity is proportional to the chloride diffusion. As such, the electrical resistance can be used as a qualitative indicator of the chloride ion penetrability [141,142]. However, electrical resistivity measurements are affected by the differences in chemistry due to cement source, inclusion of SCMs, and certain chemical admixtures [8,141,143]. Concrete that uses the chemical admixture calcium nitrite, a corrosion inhibitor, is known to produce misleading results in electrically-based test methods [141,142]. Since the composition of PRAs is not well documented and changes to the pore solution chemistry affect the conductivity, use of electrically-based methods for measuring penetrability of concrete with PRAs must be used with caution. There were 12 occurrences of electrical tests for penetrability being used on PRAs (made by five companies) listed in Table 4, with the following standardized test methods used:

- ASTM C1202 – Standard test method for electrical indication of concrete's ability to resist chloride ion penetration [141] or AASHTO T 277 – Standard method of test for electrical indication of concrete's ability to resist chloride ion penetration [144]
- NT Build 492 – Chloride migration coefficient from non-steady-state migration experiments [145]
- AASHTO T 358 – Standard method of test for surface resistivity indication of concrete's ability to resist chloride ion penetration [142]

ASTM C1202 (equivalent to AASHTO T 277) was the first electrical test method for estimating concrete penetrability to become widely adopted [141,144,146]; however, in addition to being influenced by the ionic solution of admixtures, can give misleading results for surface-treated specimens [141]. For these two methods, the specimen sides are first sealed with epoxy before the specimens are conditioned as per the vacuum water saturation procedure. After vacuum saturation, the specimens are assembled into cells that allow for a 3% sodium chloride solution on one face and 0.3 N sodium hydroxide solution on the other as shown in Figure 7. The specimen cell has lead wires that are attached to a power supply, which applies 60 V across the specimen for six hours. The current is recorded at intervals to calculate the total charge passed in coulombs for the test duration. A qualitative indication of the chloride ion penetrability is then based on the range of total charge passed, which was established from research done by Whiting [146].

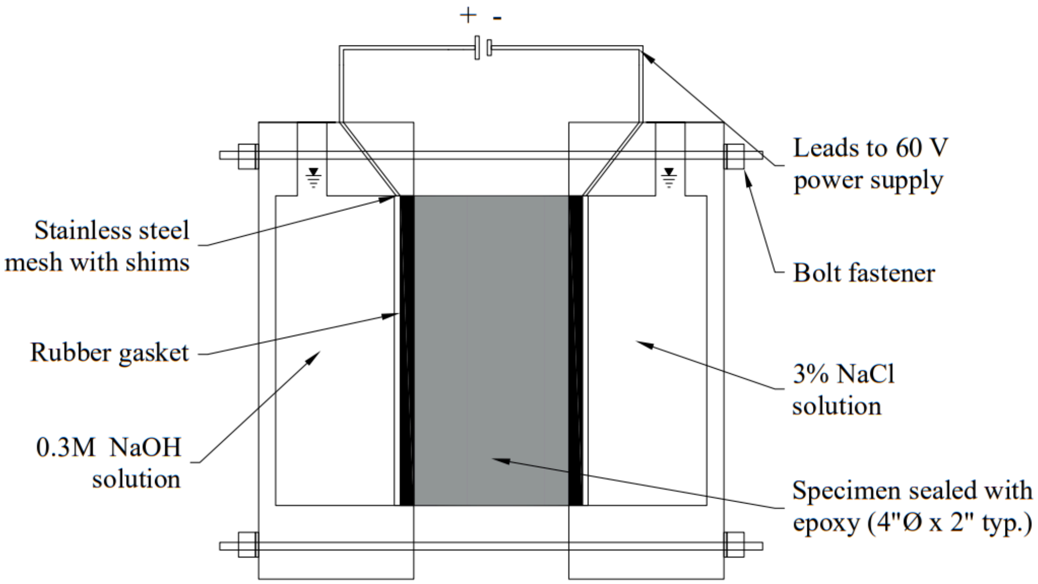

Figure 7. Diagram of ASTM C1202/ AASHTO T 277 specimen cell setup with rubber gaskets [141,144]

An alternative to ASTM C1202, the NT Build 492 method measures the chloride penetration depth instead of the total charge passed [145]. For this method, the specimen sides are not sealed with epoxy and saturated calcium hydroxide solution is used in the vacuum saturation conditioning procedure instead of water. Once conditioned, a sleeve is clamped around the specimen and the test is set up as shown in Figure 8. The catholyte is 10% sodium chloride solution and the anolyte is 0.3 N sodium hydroxide. The leads are connected to the power supply with 30 V, the current is recorded (and adjusted if necessary), and the test duration is chosen (typically 24 hours). After the test duration is complete, the specimen is removed from the sleeve and split in half axially. The exposed face is sprayed with a silver nitrate solution, which reacts with chloride ions to display the chloride penetration depth. NT Build 492 measurements are less affected by conductive ions in concrete than ASTM C1202 (AASHTO T 277), so the test method is applicable to a wider range of concrete mixtures [147]. As a result, the NT Build 492 test method may be more appropriate for testing the effect of PRAs, which could alter the pore solution conductivity.

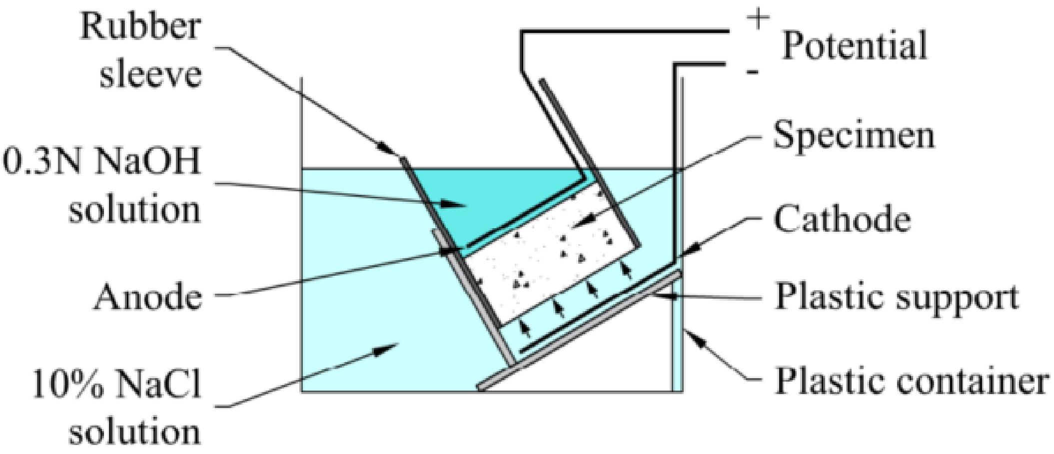

Figure 8. Diagram of NT Build 492 test setup [145]

AASHTO T 358, or surface resistivity, was also used as an electrical method to determine the effect of PRAs on penetrability [142]. This method applies a current to the surface of the specimen by means of a four-point Wenner probe as shown in Figure 9. The current is applied through the outer pins and the resulting potential is measured across the inner pins to determine the electrical resistance of the specimen. AASHTO T 358 is a quick, easy, non-destructive test that relates the resistivity to a qualitative rating of chloride ion penetrability. Since surface resistivity only provides a measure of electrical resistance, like ASTM C1202, it is also affected by source of cement, SCMs, chemical admixtures, and pore solution conductivity [8,142,143,148]. Additionally, specimen conditioning is very important for accurate measurement; temperature and degree of saturation fluctuations can significantly affect the results [15,149–152].

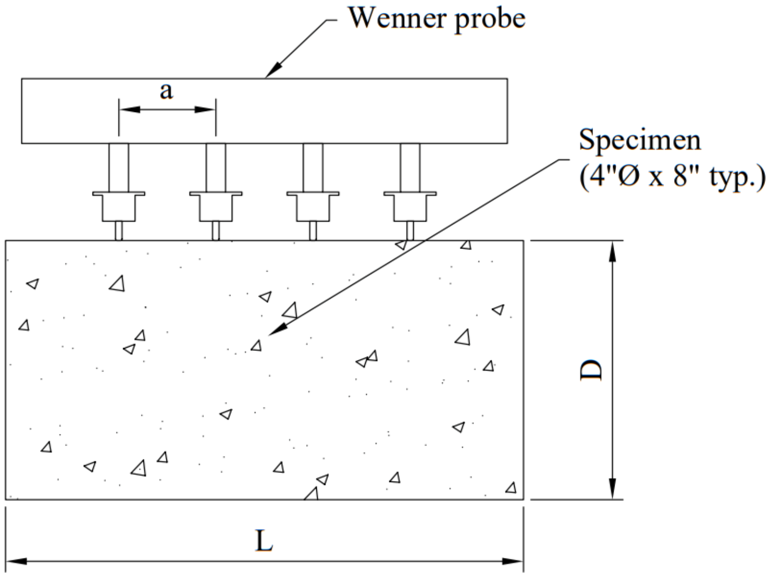

Figure 9. Diagram of four-point Wenner probe for AASHTO T 358 surface resistivity test [142]

2.3.1.4. Porosity

Porosity measurements were used to evaluate PRAs in 10 studies. Although there is not a direct relationship between the permeability and pore structure of concrete, the pore structure is one of the most important factors influencing the properties in terms of penetrability, strength, and durability [9,153,154]. Therefore, the effect of PRAs on concrete porosity can provide an indication of durability performance; however, the effect of the two classifications of PRAs would be expected to be different. Crystalline admixtures react with moisture and cement hydration products to form additional crystalline formations in the pores, thus reducing the porosity. Hydrophobic pore blockers line the pores to repel water, but do not necessarily alter the porosity. Another consideration is the specimen conditioning procedure; the drying method used is known to significantly affect the pore system [155–157]. Drying specimens with some types of PRAs could reverse the crystals formed by the crystalline admixtures, minimizing the effect seen on the porosity results.

The majority of research studies measured porosity using mercury intrusion porosimetry (MIP), but the percent voids was also calculated per ASTM C642 using the procedure described in Section 2.3.1.1 [124]. MIP uses a non-wetting liquid, mercury, to penetrate the open pores of the specimen under vacuum and measure the porosity characteristics. The benefit of using a non-wetting liquid, as opposed to water, is that mercury does not enter the pores by capillary action; instead, the mercury must be forced into the pores by applying external pressure. The mercury pressure is incrementally increased and the resulting intrusion into the pores is measured; the Washburn equation is used to relate the applied pressure to an equivalent cylindrical pore diameter given the surface tension and contact angle [158]. Another benefit of using mercury is that there is not continued hydration of the specimen during testing, which can occur for other methods, especially steady-state water permeability that can last for several weeks.

2.3.1.5. Vapor and gas permeability

Vapor transmission and gas permeability were not commonly used tests with PRAs, with only four studies reporting to have used the technique in the literature. The two standardized test methods reported, ISO 12572 and ASTM E96, are similar methods for determining the water vapor transmission of materials using the cup method [159,160]. For these methods, the test specimen is sealed to the side of a test cup containing either desiccant (dry method) or an aqueous saturated solution (wet method) as shown in Figure 10. The assembly of the specimen in the test cup is placed in an environmental chamber and the difference in vapor pressure between the chamber and inside of the cup results in vapor transmission through the specimen. The transmission is determined by measuring the change in mass of the specimen over time. Pressure-driven gas permeability is another measure of concrete penetrability; however the disadvantage of measuring gas permeability is that the results are highly dependent on the moisture condition of the specimens during testing [9,128]. Moisture remaining in the pores will act as a barrier, reducing the pore size and volume, thus reducing the gas permeability artificially.

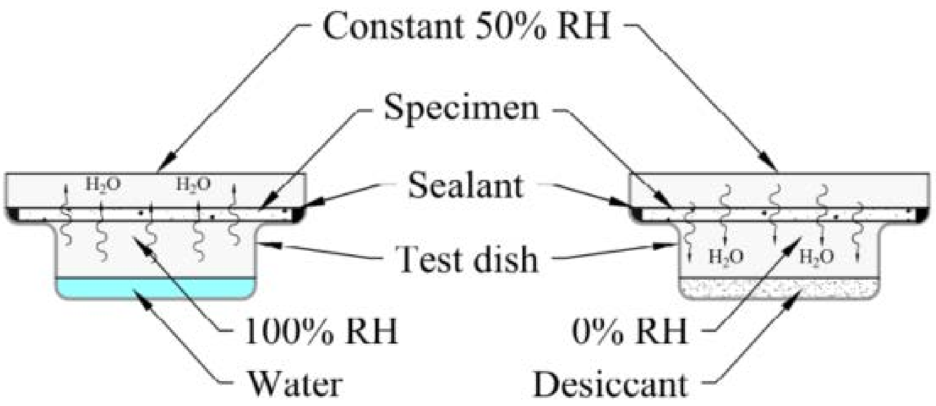

Figure 10. Diagram of cup method for vapor transmission using water (wet method) and desiccant (dry method)

2.3.2. Durability

2.3.2.1. Chloride exposure

Test methods included in the durability category include simulated and field exposure cases. The most common, with 14 occurrences in Table 4, was exposure to chloride solution. Resistance to chloride ingress is important for the durability of reinforced concrete structures because chlorides can cause corrosion of the steel reinforcement. Chloride induced corrosion is the leading cause of deterioration and repair costs for reinforced concrete, and the majority of Florida’s infrastructure is near a coastline, in an aggressive environment. Therefore, chloride exposure test methods are beneficial for measuring the penetrability for a more realistic case. The maximum depth of chloride penetration or the apparent diffusion coefficient can be calculated from the chloride profile after the exposure period. Both crystalline and hydrophobic pore blocker admixtures should decrease chloride ingress since their purpose is to reduce permeability. Chloride binding can be determined as well by measuring the water-soluble and total chloride contents. Since bound chlorides are not free to cause steel corrosion, the binding capacity of PRAs could be measured. The following standardized methods were reported:

- AASHTO T 259 – Standard method of test for resistance of concrete to chloride ion penetration [161]
- AASHTO T 260 – Standard method of test for sampling and testing for chloride ion in concrete and concrete raw materials [162]
- ASTM C1556 – Standard test method for determining the apparent chloride diffusion coefficient of cementitious mixtures by bulk diffusion [163]
- NT Build 443 – Accelerated chloride penetration [164]
- EN 480-10 – Determination of water-soluble chloride content [165]

AASHTO T 259 has conventionally been the most widely used method for chloride ion resistance in concrete and entails salt ponding slab specimens for a specified duration [161]. The specimens are moist cured for 14 days and then stored for 14 days in a drying room with 50% relative humidity. A dam is attached around the top perimeter of the slab (Figure 11) and then the slab is returned to the drying room for 14 more days. The 28 days of drying is intended to provide better definition of the chloride ingress. After the conditioning period, the specimens are exposed to continuous ponding with a 3% sodium chloride solution for 90 days [161]. Two samples are taken at progressive 0.5 in. depths and the chloride content is measured (via AASHTO T 260) [162]. Although the test provides a basic one-dimensional chloride ingress profile, two samples is not enough to provide an accurate chloride profile. Another drawback to AASHTO T 259 is that the conditioning procedure overemphasizes the importance of absorption, but the effect cannot be isolated as the test is a combination of diffusion, absorption, and wicking [10,147].

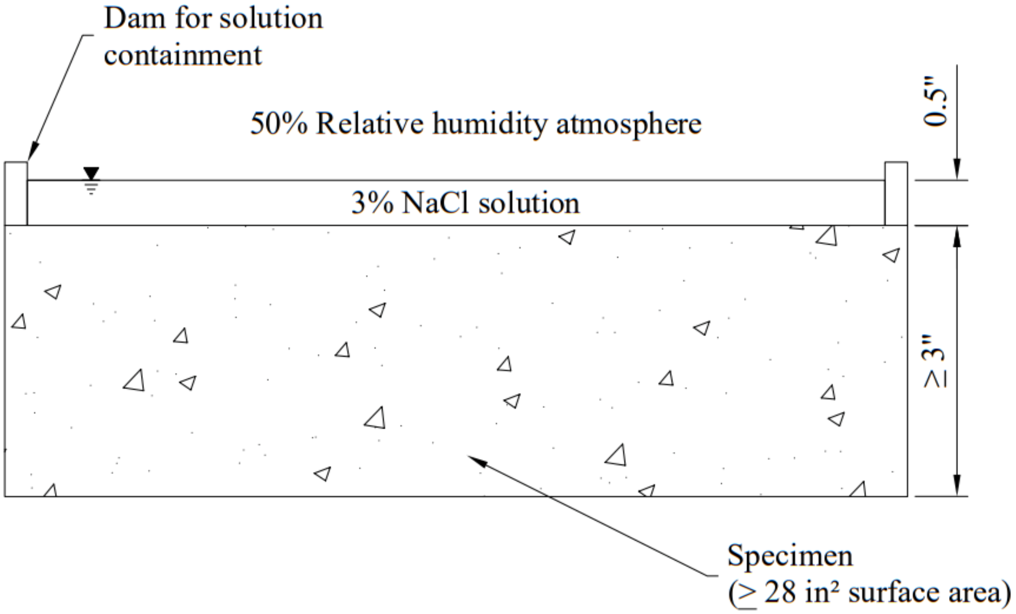

Figure 11. Diagram of AASHTO T 259 salt ponding test setup [161]

ASTM C1556 and NT Build 443 are chloride exposure test methods that use cylindrical specimens immersed in a 16.5% sodium chloride solution [163,164]. For these methods, cylindrical samples are moist cured for 28 days and then sealed with epoxy on all faces except one before exposing to 16.5% sodium chloride solution as shown in Figure 12. The specimens are exposed to the chloride solution for a minimum of 35 days; higher quality concrete should be exposed for at least 90 days to achieve sufficient chloride ingress [10,147]. After the exposure period, the chloride profile is determined by profile-grinding the specimen in layers parallel to the exposure surface so that there are at least six points between the surface and depth at which the chloride content is equivalent to the baseline. ASTM C1556 (NT Build 443) provides an actual profile of the chloride penetration, which is more accurate than the two layers obtained from AASHTO T 259. The surface concentration and apparent chloride diffusion coefficient can then be calculated from the chloride profile. AASHTO T 260 and EN 480-10 are standard methods for determining chloride content from powdered samples taken from exposed specimens [162,165]. AASHTO T 260 includes a procedure for measuring the acid-soluble (total) and water-soluble chloride contents [162]; the difference in these measurements give an indication of the chloride binding capacity of the system.

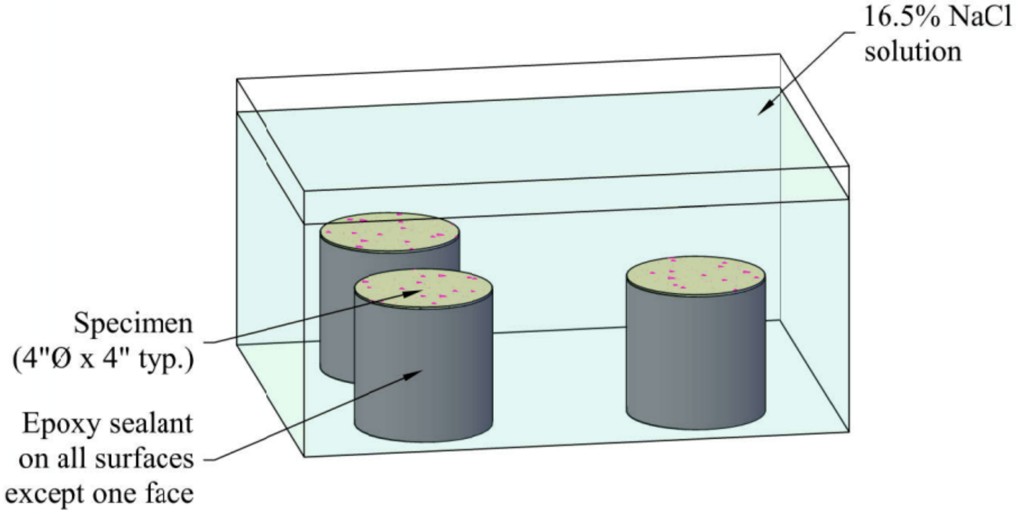

Figure 12. Diagram of ASTM C1556 (NT Build 443) bulk diffusion chloride exposure [163,164]

2.3.2.2. Other

Additional durability test methods used on PRAs and reported in the literature include: freeze-thaw, deicing chemicals, abrasion, corrosion, and sulfate exposure. These test methods are simulated field exposure methods to accelerate durability performance. Multiple standardized test methods were reported in literature (Table 4); however, many researchers have developed their own methods to create realistic exposure conditions such as wet/dry cycles. Measurement of the self-healing performance was also reported [75,89,94,95,100,106,166,167]; this was typically done by monitoring crack width over time with different exposure conditions or pre-cracking specimens and then measuring transport or strength properties. Since PRAs are relatively new to the market and have not established field performance, these harsh exposure conditions provide an accelerated measurement of durability. The chemical interactions and potential for leaching can be evaluated for the test methods using an exposure solution.

Although not applicable for Florida, freeze-thaw and deicing chemical exposure are important durability measures for locations that experience freezing temperatures and utilize deicers. ASTM C666 and NYDOT Method 502-3P are test methods for the resistance of concrete to rapid freezing and thawing cycles [168,169]. ASTM C666 cycles specimens between 40°F and 0°F, measuring the fundamental transverse frequency, length change, and mass every 36 cycles [168]. The test is continued for 300 cycles or until the relative dynamic modulus of elasticity reaches 60% of the initial modulus. The New York DOT Method 502-3P accelerates the damage by immersing the specimens in 10% sodium chloride solution and cycling between 70 ± 5°F and -10 ± 5°F [169]. The percent weight loss is measured and the test is continued for 25 cycles. ASTM C672 and CSN 73 1326 are test methods for determining the resistance of concrete surfaces exposed to deicing chemicals [170,171]. These methods expose the specimens to a deicing chemical solution and freeze-thaw cycles to evaluate the mass loss and/or visual deterioration.

UNE-EN ISO 9227, EN 480-14, and ASTM G109 are different corrosion test methods which could be used to determine the efficiency of PRAs at extending the time to corrosion initiation [172–174]. UNE-EN ISO 9227 is a salt spray test that subjects specimens to 5% sodium chloride solution at 23°C inside a climatic chamber for 82 days [173]. The chamber is filled with compressed air, and the specimens are periodically removed, weighed, and returned in a different position to homogenize the exposure. EN 480-14 determines the corrosion susceptibility of reinforcing steel by using a potentiostatic electrochemical test [175]; a steel bar is embedded in the test specimen and held at an increased potential in an electrochemical cell [174]. ASTM G109 attaches resistors to embedded steel in prism specimens that are ponded with 3% sodium chloride solution as shown in Figure 13 [172,176]. The voltage is measured across the resistor, and the current is calculated as a function of time until corrosion occurs.

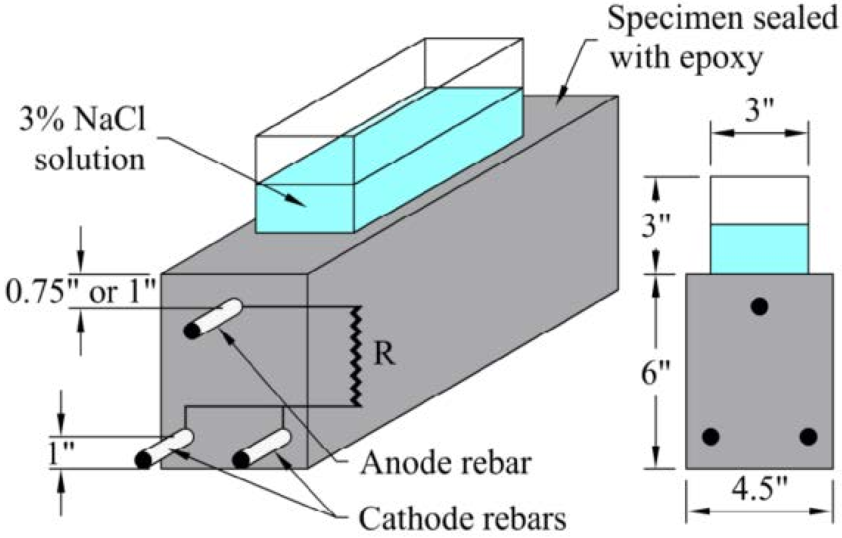

Figure 13. Diagram of test setup for ASTM G109 [172]

Abrasion resistance is measured according to the test procedure ASTM C779; three methods (revolving disk, dressing-wheel, and ball-bearing) provide simulated abrasion conditions [177]. This test method is particularly applicable for surface-applied treatments to ensure the penetration depth is adequate for exposure conditions and design life.

ASTM C1012 is the standard test method for length change of mortars exposed to a sulfate solution [178]. The expected environmental conditions for the structure should dictate the type of durability and exposure tests performed to give a reliable indication of performance in the field. Additionally, the self-healing capability can be measured by pre-cracking the specimen and measuring the crack width over time; however, this is not comparable to current FDOT requirements for aggressive environments.

2.3.3. Mechanical Properties

While it is not the objective of crystalline and hydrophobic pore blocker admixtures to significantly increase the mechanical properties of the concrete, it is important to ensure the strength characteristics are not compromised by their inclusion. The most frequently measured property is compressive strength with a total of 37 occurrences (nine companies) in Table 4. Compressive strength is the most frequently used quality control measure and can be used to compare performance of concrete mixtures with different types and dosages of admixtures. Although several test methods are listed for compressive strength (ASTM C39, ASTM C873, ASTM C42, and EN 12390-3), the testing procedure and loading rate follow or are similar to that of ASTM C39 [179–182]; ASTM C873 and C42 are for cylinders cast in place and drilled cores, respectively [180,181]. Flexural and tensile strength were measured to a lesser extent in eight and three studies, respectively. ASTM C78 and ASTM C293 are the standard test methods for measuring the flexural strength of concrete using a simple beam with third-point and center-point loading, respectively [183,184]. ASTM C496, the splitting tensile test, although an indirect measure of tensile strength, is more commonly performed and easier than the direct tension method [185,186].

2.3.4. Characterization

Various characterization techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) were used to describe the raw materials and reaction products formed when PRAs were used. SEM occasionally accompanied with EDS was a popular technique (26 cases) for imaging hydration products and monitoring self-healing of micro-cracks. Aside from measuring crack healing via SEM, these methods are for research to understand mechanisms of action of the admixtures and do not provide quantitative measures of performance for acceptance. The information from these test methods is beneficial for gaining insight into these new admixtures that do not document their composition or the reaction process. By expanding the knowledge base of crystalline and hydrophobic pore blockers, the long-term performance can be better predicted. XRD can measure the crystalline composition before and after hydration to determine admixture composition and reaction products, respectively. TGA peak analysis can be performed similar to XRD to identify the composition present and changes due to hydration. FTIR spectrum provides transmittance or absorbance over a range of wave numbers to investigate the chemical bonds and determine composition.

2.3.5. Supplementary

Supplementary techniques found in the literature included length change, drying shrinkage, contact angle, and pulse velocity. Nine authors (including four companies) measured either length change or drying shrinkage effects. ASTM C157 is the test method for measuring length change of mortar or concrete specimens in water or air storage over time [187]. The Australian standard AS 1012.13 provides a test method for determining the drying shrinkage of concrete specimens [188]. The effect of PRAs on length change and drying shrinkage is important to ensure there are not large volumetric changes that could cause cracking. Contact angle and pulse velocity were less frequently used with five and three occurrences, respectively. The contact angle of water can provide a measure of surface wettability; if the angle is greater than 90°, the liquid is non-wetting, indicating water repellency or hydrophobic behavior whereas an angle less than 90° indicates hydrophilic/wetting behavior as shown in Figure 14. However, measuring the contact angle is only applicable for hydrophobic pore blocker admixtures and would not be useful for comparing all PRAs. The pulse velocity is measured according to ASTM C597 and is used to determine the uniformity and presence of voids and cracks; this method was used to assess self-healing performance of cracks [189].

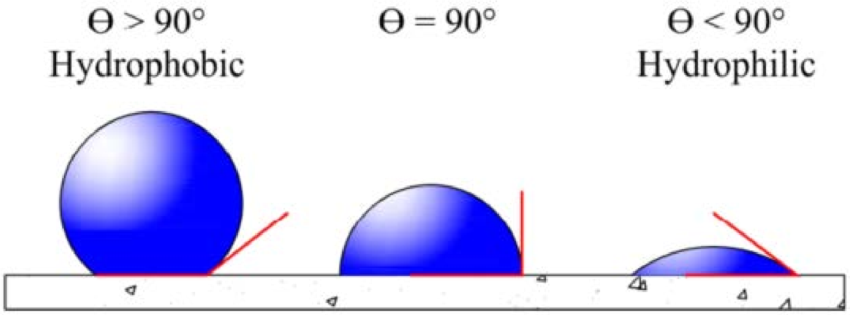

Figure 14. Diagram of contact angle for hydrophobic, borderline, and hydrophilic surfaces

2.4. PERFORMANCE OF ADMIXTURES

In an effort to assess the performance of the PRAs under investigation, crystalline and hydrophobic pore blockers, numerous test methods have been evaluated in the literature. However, for the various test method categories examined (i.e., water absorption, water permeability, chloride exposure, etc.), there was no consensus on the test method procedure to use. For water absorption alone, there were nine standardized test methods reported. In addition to the differences in specimen conditioning and procedures of the test methods, there was a lack of consistency in the experimental methods employed by the researchers found in the literature. There was a large range in dosage, water-cementitious ratio (w/cm), testing age, and mixture designs found. Therefore, the actual performances observed varied greatly and were specific to the individual research conditions. Overall trends were observed, but the performance of PRAs could not be quantified to establish acceptance criteria.

Two key factors were lacking to quantify performance of PRAs. The first was a scarcity of field studies and consequently scarcity of relationships between field and laboratory performance. As a result, there was not sufficient data in the literature examined to select appropriate, reliable lab tests for predicting PRA field performance. The second research gap identified was a shortage of experimental data that meets current FDOT concrete mixture requirements for aggressive environments (i.e., maximum w/cm and usage of SCMs). The objective of acceptance criteria would be for the PRAs to perform equal to or better than current FDOT concrete mixtures; therefore, performance of PRAs should be relative to concrete mixtures that meet the current standards. The FDOT Standard Specifications for Road and Bridge Construction specify cement type, pozzolans, and concrete class for each environmental classification: slightly, moderately, and extremely aggressive environments [18]. For moderately and extremely aggressive environments, the specifications require Concrete Class IV or higher, which use pozzolans and/or cement type to reduce permeability; approved pozzolans include Class F fly ash, slag, silica fume, metakaolin, and ultra-fine fly ash. Durability criteria requires concrete mixtures to meet or exceed an electrical resistivity of 29 kOhm-cm at 28 days as per AASHTO T 358 [18,142]. While purely electrical test methods may not be applicable to all PRAs, this threshold limit equates to low chloride ion penetrability according to the standard [142] and should be used when establishing performance criteria for concrete mixtures incorporating PRAs.

2.4.1. Laboratory Test Results

The results of the main laboratory test methods identified in the literature examined were compiled in Table 5 and Table 6. The test methods included: water absorption, water permeability, electrical resistance, porosity, compressive strength, flexural strength, and crack healing measurement. The results were divided by crystalline, dual, and hydrophobic pore blocker admixtures; Table 5 presents the results for crystalline and dual-acting admixtures while Table 6 presents the results for hydrophobic pore blockers. Dual-acting admixtures are those that were described as having crystalline and hydrophobic properties. The results were further divided by method of application (integrally-mixed or surface-applied), then by w/cm range. If given in the literature, the dosage percentage for integrally-mixed admixtures was listed along with the maximum age of testing. The supplier of the admixture was listed in the final column of the tables when specified.

For each test method, the performance of the PRAs in Tables 5 and 6 are indicated by arrows where an up arrow (↑) is an increase, down arrow (↓) is a decrease, and side arrow (↔) is no change in measurement compared to the respective control mixture; range of percent increase/decrease was listed beneath the arrows. Results within 10% of the control mixture were considered to have no change (↔) due to typical test method precision. For w/cm ranges that had multiple studies or conflicting results, multiple arrows are shown with dashed lines to separate results for the different performance measured. This shows the inconsistency in the PRA results that was found in the literature. The control mixture was typically 100% ordinary portland cement (OPC), but there were instances where the w/cm was not the same and SCMs were used for the control mixture.

Table 5. Laboratory test results for crystalline and dual admixtures

	w/cm	Dosage (% cm)	Age	Water absorption	Water permeability	Electrical resistance	Porosity	Compressive strength	Flexural strength	Self-healing	Ref.	Supplier
Crystalline	0.69-0.65	1, 1.5, 2%	118	↔				↔			[79]	2
	0.64-0.6	1.1%	28	↓ 13-22 ↔	↓ 25-75 ↔ ↑ 60		↔	↓ 24 ↔ ↑ 10-47	↑ 28-89	↑	[69,73,89]	1, 5
	0.59-0.55	0.8, 1.2%	28			↑ 10-16		↔ ↑ 10-15			[92]	2
	0.54-0.5	0.8, 1, 1.2%	28	↓ 10-24 ↑ 15	↓ 70 ↔	↑ 26-43	↔	↔ ↑ 10-47	↑ 10-41	↑	[69,89,92]	1, 2, 5
	0.49-0.45	0.8, 2, 3, 4, 5, 8%	28	↓ 20	↓ 33-83 ↔					↑	[75,190]	1
	0.44-0.4	0.8, 1, 1.2%	28, 91	↓ 11 ↔ ↑ 14	↓ 15-90 ↔ ↑ 11	↑ 26	↓ 10 ↔	↔ ↑ 10-30			[69,73,77, 91,97,191]	2, 5
	None	2%	28		↓			↔			[85]	1, 2
	0.74-0.7	Surface-applied	30		↓						[107]	1
	0.69-0.65	Surface-applied	28		↓ 21	↑ 19	↓ 20				[90]	
	0.54-0.5	Surface-applied			↓ 75			↑ 15	↑ 12-38	↑	[89]	1
	0.49-0.45	Surface-applied	28				↓ 20-40				[93]	
	0.44-0.4	Surface-applied	28	↓ 10	↔			↔			[77]	
	0.34-0.3	Surface-applied				↑ 81					[192]	2
	None	Surface-applied	210	↓ 20-50		↑ 42					[78]	2
Dual	0.49-0.45	1, 2, 8%	28	↓ 95				↓ 20-25			[65]	
	0.49-0.45	Surface-applied	28	↑ 200	↔ ↑			↓ 32 ↔			[80,81]	4

Supplier numerical identification: 1 = Penetron, 2 = Xypex, 3 = Krystalline Technology, 4 = International Chemcrete Corporation, 5 = Sika, 6 = Kryton, 7 = Hycrete

Table 6. Laboratory test results for hydrophobic pore blocker admixtures

	w/cm	Dosage (% cm)	Age	Water absorption		Water permeability		Electrical resistance			Porosity		Compressive strength			Flexural strength		Self-healing	Ref.	Supplier
Hydrophobic pore blocker	0.8	1%	28	↓ 71-93							↔	↑ 18	↓ 14-24	↔		↓ 11	↔		[61]	
	0.75	1%	28	↓ 65														↑	[82]	
	0.64-0.6	0.5, 1, 1.5, 2%	28	↓ 10-32		↓ 17-40	↔				↔		↔	↑ 10-26					[69,73,74]	5
	0.59-0.55	1 %	28	↓ 85															[72]	
	0.54-0.5	0.3%	90	↓ 10-15		↓ 50	↔				↔		↔	↑ 20					[69,83]	3, 5
	0.49-0.45	1, 2%, 0.25 g/L	28, 180, 365	↓ 10-50				↓ 20	↔	↑ 36			↓ 12-20	↔		↔		↑	[64,82,193]	7
	0.44-0.4	1%, 1 & 2 g/L	28, 90	↓ 10-84	↔	↓ 20-40	↔	↓			↔		↓ 10-28	↔	↑ 10				[69,72,73,97,194]	5, 7
	0.39-0.35	2, 4, 8, 12, 16%, 1 & 2 g/L	28, 90	↓ 45-90				↔	↑ 26-85				↓ 18-27	↔					[71,194]	7
	0.34-0.3	0.25, 1, 2 g/L	28, 90, 180	↓ 10				↔	↑ 10				↓ 15			↔			[64,194]	7
	0.75	Surface-applied	28	↓ 0-38														↑	[82]	
	0.49-0.45	Surface-applied	28	↓ 30-50														↔	[82]	
	0.39-0.35	Surface-applied	28	↓ 80-99															[71]	

Supplier numerical identification: 1 = Penetron, 2 = Xypex, 3 = Krystalline Technology, 4 = International Chemcrete Corporation, 5 = Sika, 6 = Kryton, 7 = Hycrete

A study by García Calvo et al. showed a 50% decrease in water permeability and 20% increase in compressive strength when using a crystalline PRA; however, the OPC control mixture had a w/cm of 0.55 and the test mixture with the PRA had a w/cm of 0.51 [83]. This makes it impossible to differentiate the performance due to the crystalline admixture from the effect of the lower w/cm. For the studies that used the same mixture proportions (w/cm) for the OPC control and test mixture incorporating PRAs, the performance (increase or decrease) could be directly attributed to the PRAs. However, while the comparison to an OPC control mixture alone may have showed the PRAs were beneficial to performance, they did not show if performance would be equal or better than current mixtures used by the FDOT that incorporate SCMs. Cappellesso et al. addressed this issue by comparing the performance of a mixture using a crystalline admixture to an OPC control and 10% silica fume mixture and found that while inclusion of the crystalline admixture did enhance performance overall compared to the control mixture, it did not perform as well as the 10% silica fume mixture [77]. For this study, water permeability, water absorption, porosity, and compressive strength were measured and silica fume was the solution for best performance [77]. Hassani et al. did an experimental investigation with two different w/cm, SCMs, and PRAs: concrete mixtures were made with w/cm of 0.4 and 0.6, 25% fly ash and 40% slag, and crystalline and hydrophobic pore blockers [73]. The study found that the efficiency of the PRAs was dependent on w/cm and type of SCM used for the mixture; the use of the crystalline admixture for the concrete mixtures with w/cm of 0.6 showed a 53% decrease, 59% increase, and 13% increase in maximum depth of water penetration when compared to respective control mixtures of OPC, 25% fly ash, and 40% slag. It was also found by factorial ANOVA that the w/cm and SCM type had a greater influence on the properties measured (water penetration, permeable voids, and compressive strength) than the inclusion of PRAs [73]. The interaction between PRAs and SCMs must be considered and evaluated to ensure there are not detrimental effects on the properties of the concrete. To meet current FDOT standards, maximum w/cm and use of SCMs is required, thus performance of PRAs should meet or exceed these standards.

Since it was the most commonly performed test method in the literature, water absorption was assessed first. The results showed a wide range of performance, but overall a decrease in absorption values. For crystalline admixtures, literature reported decreased, increased, and no change in water absorption values compared to controls. Most studies examined the performance of concrete made with a w/cm higher than what is currently allowed by FDOT specifications in extremely aggressive environments. This makes it difficult to extrapolate performance from the literature-reported values to FDOT structures. However, the majority of results exhibited a decrease in water absorption, ranging from approximately 10 to 25%. One study showed a reduction of up to 50% for a surface-applied crystalline admixture, but the w/cm was not given [78]. The dual admixture category had conflicting results; one study using an integrally-mixed admixture indicated a large decrease in absorption of 95% [65], while the other study using a surface-applied admixture showed an increase of 200% [81]. For the hydrophobic pore blockers, the results were overwhelmingly positive, showing reduction in water absorption ranging from approximately 10 to 100%. No trend was observed for performance based on the w/cm or method of application. Water absorption results were reported for every category of hydrophobic pore blockers, but only about half of the crystalline admixtures. The discrepancy in frequency and percent decrease in absorption, highlights the difference between the two admixture classifications. As stated in the description of the test methods, water absorption tests could have polarizing results that do not reflect the true field performance of these admixtures due to their differing mechanisms. Since crystalline admixtures need water to react and swell to block pores, it is understandable that the reduction in water absorption, if any, is less than that for the hydrophobic pore blockers. Likewise, the purpose of hydrophobic pore blockers is to repel water, so it was expected that these admixtures would perform well for this test method. However, the results for water absorption alone do not provide a complete picture of field performance in FDOT structures.

Water permeability results varied as well, indicating better, worse, and comparable water permeability with the inclusion of PRAs. The majority of literature showed a reduction in water permeability; however, many publications also showed no change for the same w/cm categories. For the literature reporting a decrease in water permeability, the percent ranged from approximately 15 to 90% for the crystalline admixtures and 20 to 50% for the hydrophobic pore blockers. The relatively worse performance of the hydrophobic pore blocker admixtures was expected as these admixtures are not typically designed for hydrostatic conditions. This suggests that hydrophobic admixtures could potentially be suitable for exposure conditions with minimal or occasional hydrostatic pressure without adversely affecting the performance. There was also less data in the literature on water permeability of concrete with hydrophobic pore blockers, which was the opposite of the water absorption data and likely due to the difference in mechanisms and expected performance. The inconsistency in results for water permeability is probably due in part to the large coefficient of variation typically seen in these test methods. It is difficult to obtain quantitative results for high quality, low w/cm concrete with permeability of 10^{-14} m/s or less [128,135]. Additionally, there was minimal data in the w/cm ranges (< 0.44) that would be of primary interest for concrete suitable for exposure to aggressive environments.

Another penetrability method investigated was electrical resistivity. Although there was less data reported in the literature, the majority of the results showed an increase in electrical resistivity with the use of PRAs. The increase in electrical resistance ranged from 10 to 85%; however, two of the largest increases of 80 and 85% were seen in mixtures using hydrophobic pore blockers with high dosages of 8 and 12%, respectively [71]. For the majority of results, the electrical resistance increased by approximately 10 to 40%. The one case of the surface-applied crystalline admixture with an increase in electrical resistance of approximately 80% was from a durability study in China [192]. Wu et al. measured the chloride penetration per NT Build 492 before and after the surface application of the PRA; however, the control mixtures had a w/cm of 0.32 and included slag and fly ash, but showed almost one inch of chloride penetration. The low w/cm with SCMs of the control mixtures would be expected to have lower penetrability, so the enhanced performance of the PRA seems high for this study [192]. Sharp and Ozyildirim investigated the performance of a hydrophobic pore blocker according to ASTM C1202 and found conflicting results between the mixtures with and without fly ash; the control mixture was 25% fly ash with w/cm of 0.45, and two dosages of the hydrophobic PRA with and without the 25% fly ash were compared [193]. For the two mixtures incorporating the PRA and fly ash, the measured total charge passed was comparable-to-slightly higher than the control mixture; however, when the fly ash was not included, the PRA mixtures had a total charge three to four times higher than the control mixture [193]. The results suggest the hydrophobic pore blocker is ionic and affects the electrical conductance [193,194]. Overall, both types of PRAs performed well in the electrical test methods, but the pore solution conductivity should be taken into consideration. Since electrically-based penetrability tests are influenced by the conductivity of the pore solution and there is considerable variability and uncertainty in the composition of the PRAs, the electrical resistivity results are inconclusive about performance without additional testing. Hydrophobic pore blockers may also reduce water ingress during saturation before testing, which would result in higher measured electrical resistivity due to a lower degree of saturation.

Porosity results were fairly consistent and predominantly comparable to the control mixtures. Decreases in total porosity were observed ranging from 10 to 40% in a few studies using crystalline admixtures [73,90,93]. As crystalline admixtures react with moisture and hydration products to form additional crystalline formations in the pores, the total porosity would be expected to decrease. The largest reduction in porosity for the crystalline admixtures was reported for the surface applied studies (20-40%), suggesting the concentration of the admixture may have been higher due to the localized application [90,93]. Since hydrophobic pore blockers line the pores to repel water, the porosity would not be expected to differ; the majority of literature reported comparable porosity for hydrophobic admixtures. One study measured an 18% increase in porosity using a hydrophobic pore blocker; however, the w/cm was 0.8, which is already high and the increase was attributed to an air entraining effect of the admixture [61]. Although the drying procedure for porosity measurements was not well documented in the literature examined, the specimen conditioning could alter the crystals formed by the crystalline admixtures and influence the results.

Concrete mechanical properties were assessed to ensure the strength characteristics were not negatively affected by the use of PRAs. Compressive strength was the most frequently used test to evaluate mechanical properties and was reported by most of the integrally-mixed categories. The majority of literature reported no change in compressive strength, and several researchers stated an increase ranging from 10 to 50%. There were also a few cases of decreased (approximately 10 to 30%) compressive strength. Only one study reported a decrease in compressive strength when using a crystalline admixture; Hassani et al. measured a 24% decrease in 28-day compressive strength for a w/cm of 0.6 concrete mixture containing 25% fly ash when compared to an identical mixture without the PRA [73]. This research study used the same crystalline admixture and dosage in another concrete mixture (w/cm 0.6) containing 40% slag and a 21% increase in 28-day compressive strength was measured (when compared to another 40% slag mixture) [73]. Since the FDOT specifies pozzolans for concrete exposed to moderate and extremely aggressive environments, it is critical to understand the interaction between PRAs and pozzolans using typical FDOT concrete mixtures.

The flexural strength was measured in several studies to assess PRA efficiency. Crystalline admixtures increased the flexural strength results for one study that investigated three mixture types. The hydrophobic admixtures had either comparable or slightly reduced (11%) flexural strength. A few studies used the flexure test loading method to crack, but not fail specimens and subsequently monitor self-healing performance. Mačanovskis et al. performed an initial and secondary (after additional curing) four-point bending test until crack formation to measure the flexural strength and crack healing; it was found that initially there were slight increases in flexural strength, but secondary loading produced substantial increases of approximately 40 to 90% higher than control [89]. The increase in flexural strength for the initial loading may have been due to inconsistencies in stopping the test when crack formation was observed; however, the secondary increases clearly demonstrate the benefit of self-healing capabilities.

All but one study showed a noticeable improvement in self-healing capability by using PRAs. Tittarelli and Moriconi investigated the effect of surface-applied and integral hydrophobic pore blockers for concrete mixtures with a w/cm of 0.45 and 0.75 and found that there was significant improvement for the w/cm 0.75 concrete, but the good quality (w/cm 0.45) concrete masked the beneficial effect of the hydrophobic surface treatment [82]. Jiang et al. measured the change in permeability over time for cracked specimens exposed to various curing conditions to determine the self-healing performance of crystalline PRAs [75]. The study found that cracked specimens exhibited better healing performance when exposed to alkaline and standing water conditions instead of acidic and flowing water. It also demonstrated that the healing performance was better for specimens cracked at an age of 7 days compared to 28 days, which was attributed to more unhydrated cementitious particles and void space present for crystal products to react and form in the early age specimens [75]. The self-healing capability of crystalline PRAs could be an added benefit that is not currently considered in the FDOT specifications for durability; however, the amount and density of the crystals will depend on the admixture dosage, remaining unhydrated admixture chemicals, and moisture conditions [24].

2.4.2. Field and Simulated Field Test Results

The results of the simulated field (exposure or weathering) lab tests and field performance identified in the literature examined are compiled in Table 7 and Table 8. The simulated field exposure tests are accelerated and used to provide a more realistic estimate of durability. The durability exposure tests included are chloride penetration, corrosion, freeze-thaw resistance, abrasion, acid resistance, sulfate length change, and other exposure (i.e., air fan, wet/dry cycles, and carbonation). A separate column was dedicated to actual field performance for studies that used a field durability site. The results were divided into categories in the same fashion as Table 5 and Table 6: crystalline, dual, and hydrophobic pore blocker admixtures were separated into method of application and w/cm range. Dosage and age were included, and the same reporting method was used for the arrows. Results within 10% of the control mixture were assumed no change (↔) due to typical test method precision. For w/cm ranges that had multiple studies or conflicting results, multiple arrows are shown with dashed lines to separate results for the different performance measured.

Table 7. Field and simulated field test results for crystalline and dual admixtures

	w/cm	Dosage (% cm)	Age	Chloride penetration / diffusion	Corrosion potential	Freeze-thaw and deicing chemical resist.	Abrasion / acid / sulfate resist.	Other exposure (air fan, wet/dry, carbonation)	Field perform. (outside)	Ref.	Supplier
Crystalline	0.69-0.65	1, 1.5, 2%	118				↑ 15-36			[79]	2
	0.59-0.55	0.8, 1.2%	28, 35, 140	↓ 10-77 ↔			↔ ↑ 35-58	↓ 10 ↔		[92]	2
	0.54-0.5	0.8, 1, 1.2%	28, 35, 140	↓ 18-50			↔ ↑ 27	↓ 18-22		[92]	2
	0.49-0.45	2, 4%	28				↑ 15-54	↑ 30-38		[75]	
	0.44-0.4	0.8, 1, 1.2, 2%	28, 35, 263, 1, 2, & 10 yr.	↓ 17-75 ↔ ↑ 20-25	↓ 23-48 ↑ 24				↔ ↑	[91,97,99,191,195]	2, 6
	0.39-0.35	None	2 & 4 yr.		↔				↔	[176]	2
	None	None	5 yr.						↔ ↑ 55	[196,197]	2
	0.49-0.45	Surface-applied	28, 1 yr.	↓ 25-70		↑ 10-100		↑ 15-45	↑ 30-60	[93]	
Dual	0.49-0.45	Surface-applied	28					↓ ↑		[80,81]	4

Supplier numerical identification: 1 = Penetron, 2 = Xypex, 3 = Krystalline Technology, 4 = International Chemcrete Corporation, 5 = Sika, 6 = Kryton, 7 = Hycrete

Table 8. Field and simulated field test results for hydrophobic pore blocker admixtures

	w/cm	Dosage (% cm)	Age	Chloride penetration / diffusion	Corrosion potential	Freeze-thaw and deicing chemical resist.	Abrasion / acid / sulfate resist.	Other exposure (air fan, wet/dry, carbonation)	Field perform. (outside)	Ref.	Supplier
Hydrophobic pore blocker	0.75	1%	28	↓ 85	↓ 200-400					[82]	
	0.59-0.55	1%	28			↓				[72]	
	0.49-0.45	1%, 0.25 g/L	28, 180	↓ 80	↓ 55-97	↔ ↑			↑ 40-44	[64,82,193,198]	7
	0.44-0.4	1%	28, 1 & 2 yr.	↓ 25-65 ↔ ↑ 55	↓ 177-4,300	↓ 77-250 ↔				[72,97,194]	7
	0.34-0.3	0.25 g/L	180			↓ 211 ↔				[64,194]	7
	None	2 & 3 g/L			↔ ↑					[194]	7
	0.75	Surface-applied	28	↓ 95	↔					[82]	
	0.49-0.45	Surface-applied	28	↓ 95	↔					[82]	

Supplier numerical identification: 1 = Penetron, 2 = Xypex, 3 = Krystalline Technology, 4 = International Chemcrete Corporation, 5 = Sika, 6 = Kryton, 7 = Hycrete

The most common exposure condition used on concrete containing PRAs in the literature was a chloride solution. Because corrosion is the leading cause of deterioration in reinforced concrete structures, chloride ingress is the primary concern. The maximum depth of chloride penetration as well as the apparent chloride diffusion coefficient were quantified in the literature examined. Although the majority of results showed a decrease in penetration depth or diffusion, there were a few instances of comparable or increased chloride ingress. Munn et al. tested the chloride penetration resistance of an integrally-mixed crystalline admixture in three concrete mixtures with two w/cm according to NT Build 443 and by using a cyclic wet/dry chloride exposure test [92]; the three concrete mixtures were OPC at 0.55 w/cm, 35% slag at 0.55 w/cm, and 20% fly ash at 0.5 w/cm. The slag and fly ash mixtures had much better chloride penetration resistance than the OPC mixture, though the fly ash mixture also had a lower w/cm. The inclusion of the crystalline admixture in each of these concrete mixtures resulted in further improvement to chloride resistance with maximum penetration depths decreasing between 10 to 38% across the mixtures for the cyclic and NT Build 443 tests. The calculated apparent chloride diffusion coefficients from the NT Build 443 test showed better performance for the PRA with reductions of 30%, 77%, and 50% for the OPC, slag, and fly ash mixtures, respectively. This indicates that while the maximum penetration depth might only be slightly improved, the slope of the chloride profile is much steeper and the chloride contents are reduced at each depth when using the PRA [92].

The corrosion tests on PRA-containing concrete in the literature also involved exposure to chloride solution; however, the specimens contained steel reinforcement and the focus of these studies was to measure corrosion due to chloride ingress. A study by Dao et al. compared the effect of a crystalline and hydrophobic pore blocker to an OPC control concrete mixture with a 0.44 w/cm with 25% fly ash by casting approximately 14 in. square by 30 in. tall reinforced columns exposed to a simulated coastal environment [97]. The simulated tidal action created a more realistic exposure of concrete in the field and samples were taken from three heights at ages 28 days, 1 year, and 2 years to represent the submerged, tidal, and high tide zones. Chloride profiles from the samples were used to calculate chloride diffusion coefficients, which were then input into a model to estimate the time to corrosion initiation. The results showed the hydrophobic pore blocker considerably improved the concrete durability with respect to chloride-induced corrosion, and corrosion potential was reduced by 177% and 4,300% for the high tide and tidal zones, respectively [97]. The hydrophobic pore blocker had exceptional performance in the submerged zone, giving slightly less than half the chloride concentration at 1.18-1.57 in. (30-40 mm) depth after 2 years of exposure, with a concentration of 0.09% chlorides by mass of cementitious material compared to 0.19% for the control [97].

While Florida does not experience many annual freeze-thaw cycles or use deicing chemicals, this exposure condition is an important durability measure and can indicate overall durability. One freeze-thaw study was performed for surface-applied crystalline admixtures and showed an increase in freeze-thaw resistance by 10 to 100% [93]. The results for the hydrophobic pore blockers were inconclusive with visual inspections showing relatively better, worse, or no change with respect to the control mixture. Sharp and Ozyildirim investigated the freeze-thaw resistance of a hydrophobic pore blocker admixture and found comparable results; the durability factor and surface rating for the PRA mixtures met the acceptance criteria and were similar to the control mixture [193]. Another study showed that the w/cm 0.40 mixtures performed well in the frost resistance test regardless of the hydrophobic PRA, but the w/cm 0.55 mixture with the PRA performed worse than the respective w/cm 0.55 control [72]. Civjan and Crellin measured the freeze-thaw performance for hydrophobic pore blockers and found that the mass loss percentage was much higher (77-250%) for the mixtures containing the PRA and to a lesser extent had a lower durability factor compared to the control mixtures [194].

Resistance to abrasion, acid exposure, and sulfate exposure showed either no change or moderate improvements to the performance for integrally-mixed crystalline admixtures. Results were not reported in this category for the hydrophobic pore blockers. Jiang et al. exposed cracked specimens to an acidic environment and found that the inclusion of crystalline PRAs had better self-healing performance and thus lower permeability than the control mixture [75]. The study also showed that when using PRAs, the measured permeability of pre-cracked specimens was lower when the specimens were conditioned in alkaline environments vs. acidic [75]. A study by García-Vera et al. exposed specimens to a 3% sulphuric acid solution and showed less mass loss and greater compressive strength for the mixtures containing crystalline PRAs compared to the control mixture [79]. Expansion due to sulfate exposure showed mixed results; one crystalline PRA had similar performance to the control mixture while the other had reduced expansion [92]. When the crystalline admixture was included with fly ash and slag, there were reductions in expansion; however, the fly ash and slag mixtures without the PRA already showed much lower expansion, approximately seven times lower, compared to the portland cement control [92].

Other exposure conditions in Table 7 included specimens subjected to air flow from a fan, wet/dry cycles, and carbonation chambers to measure PRA efficiency where an up-arrow indicates better performance and down-arrow is worse performance compared to a control. Data was only found for crystalline PRAs with conflicting results from the different studies. Munn et al. performed a wetting-and-drying cyclic chloride penetration test on 0.55 w/cm OPC, 0.55 w/cm 35% slag, and 0.5 w/cm 20% fly ash concrete specimens with two crystalline PRAs [92]. The first PRA in one of the 0.55 w/cm OPC and slag mixtures had approximately 10% lower chloride penetration depth after the cyclic testing compared to the respective controls; however, the other OPC mixtures containing PRAs had comparable performance to the OPC control. The 0.5 w/cm 20% fly ash mixtures containing PRAs showed approximately 20% better performance for both of the crystalline PRAs [92]. Another study investigated the effect of wetting-and-drying cycles with water on the self-healing performance of mixtures containing PRAs. Jiang et al. found that the mixtures with PRAs performed better than the control when exposed to wet-dry cycles; however, the self-healing performance of the PRA mixtures was much worse when exposed to wet-dry cycles vs. standing water [75]. There was a 75% increase in permeability when the PRA mixtures were subjected to the wet-dry cycles, indicating the crystal formation is affected by moisture cycles. The study also showed that the permeability decreased faster when the specimens were in standing water compared to flowing water, suggesting the water movement may be leaching the chemicals required for crystal formation [75].

Actual field performance (as opposed to simulated lab exposure) data was very limited for crystalline and hydrophobic pore blocker admixtures. Although the simulated field exposures provide more realistic conditions than typical lab tests, they were still performed in controlled lab conditions and did not take into consideration factors such as barnacle growth, temperature swings, etc. One long-term field exposure study was conducted by the Hawaii DOT to evaluate the durability of 25 reinforced concrete panels placed in the tidal zone of the Honolulu Harbor [195]. The panels were removed after 9-10 years and monitored for half-cell potential, chloride concentration, and visible inspection [99,195]. Nine types of concrete mixtures using two aggregate sources and two w/cm were made using eight types of admixtures; out of these mixtures, two crystalline PRAs were included. One PRA panel performed well, significantly better than the control, while the other PRA panel exhibited high half-cell readings, surface cracking, rust, and corrosion of reinforcing steel. The PRA that did not perform well in the field also had lab specimens made and tested according to ASTM G109; the lab specimens performed much better than the field panel and did not fail per ASTM G109 [99,172]. Unfortunately, the other PRA did not have lab specimens for comparison. These results show the importance of having lab and field specimens to judge the utility of a test method.

A study by the University of Wisconsin-Milwaukee examined the field performance of nine bridges, of which three integrally-mixed PRAs were used [196,197]. One bridge was divided into thirds, where one third used a crystalline admixture, one third used a hydrophobic admixture, and the last third was a control. For this bridge, the PRAs were not effective in reducing chloride ingress and showed comparable performance to the control portion of the bridge deck [197]. The second bridge to use integrally-mixed PRAs utilized a crystalline admixture in half of the bridge deck and the other half was a control mixture without PRAs; at a depth of 2 in. the average chloride content for the mixture using the PRA was approximately 55% lower than the control mixture [196,197]. It is important to note that for these bridge decks, the concrete did not contain fly ash or slag, which “does not reflect the current state of practice that the department [WisDOT] is currently employing” [197]. As a result, the one PRA that showed improved performance might not perform equal to or better than mixtures containing fly ash or slag.

The New Jersey DOT conducted a research study on the effectiveness of four commercially available corrosion reduction admixtures, where one was a crystalline PRA [176]. Five bridge decks were constructed, one for each admixture and one for a control, with a w/cm of 0.38. A corrosion rate meter, surface air flow permeability indicator, and electrical resistance test were performed to assess the corrosion potential for the admixtures in the field. However, the length of the study was only four years and was not sufficient to induce corrosion. Laboratory specimens were also made from the same mixtures and tested in an accelerated corrosion test according to ASTM G109 [172]; due to the low w/cm, only the control mixture with no admixtures was beginning to show signs of corrosion at the end of the study [176]. The differences observed among the concrete mixtures with the admixtures were not statistically significant, and therefore, the effectiveness of the admixtures at reducing corrosion could not be determined. The crystalline PRA used did create a denser concrete, thus the authors recommended the use of the PRA as long as no cracks are present [176].

The Maine DOT examined the field performance of an integrally-mixed crystalline admixture in a reinforced concrete bridge deck [191]. Due to the highly reactive aggregate used, the control mixture had a w/cm 0.40 with 50% slag replacement. The control and PRA-containing concrete mixtures were compared against a low permeability mixture with w/cm 0.40, 38% slag, and 4% silica fume. Field inspection showed signs of cracking after three years of service, but it was not attributed to the PRA. Test specimens were made from the same concrete batches and tested for chloride penetration resistance by performing salt ponding tests. The results showed that the use of the PRA had no detrimental effect and performed similarly to the control mixture. Lab specimens were also tested per AASHTO T 277; the PRA mixture had a 26% decrease in total charge passed compared to the control. However, the low permeability mixture incorporating slag and silica fume performed the best, showing a reduction in chloride penetration and 51% reduction in total charge passed [191].

Sharp and Ozyildirim at the Virginia DOT compared ASTM G109 lab and outdoor conditions and found performance of the hydrophobic pore blocker PRA was affected by the environmental conditions [193]. Outdoor exposure increased the current in the mixtures, although the higher dosage PRA mixture with fly ash performed the best in the lab and outdoors. In lab conditions, the mixtures including the hydrophobic pore blocker and fly ash had a 59% and 97% reduction in charge passed compared to the control fly ash mixture for the lower and higher PRA dosages, respectively. When the specimens were moved outside, the charge passed increased substantially for the PRA/fly ash mixtures; however, the average charge passed for these mixtures was still 40-44% lower than the control mixture. The authors concluded that the PRA restricted moisture intake while fly ash reduced the movement of moisture within the system; although the PRA showed some benefits, it was not recommended to be used as a replacement for fly ash [193].

A corrosion study for reinforced concrete structures by Civjan and Crellin evaluated the performance of a hydrophobic pore blocker PRA in several projects [194]. The half-cell potentials measured for one project showed higher corrosion for the mixtures incorporating the hydrophobic PRA; however, the exposure for the mixtures with the PRA was approximately one year longer than the control mixtures. Thus, the effect of the PRA on the corrosion potential of the concrete is difficult to assess. Another project site as part of the same study also had lower initial half-cell potential readings for the hydrophobic PRA mixtures, indicating higher corrosion potential, but the mixtures had higher electrical resistance [194]. These results are conflicting and additional measurements should be made after longer exposure to determine the actual field performance.

A study by O’Reilly et al. evaluated the corrosion rates of various corrosion inhibitors, one of which also functioned as a hydrophobic pore blocker, and found that the hydrophobic pore blocker admixture was the most effective of the admixtures at reducing corrosion rates [198]. The corrosion inhibitor admixtures were less effective in cracked concrete and when used in concrete mixtures with epoxy-coated reinforcement instead of conventional steel reinforcement. This was expected as hydrophobic pore blockers do not have self-healing capabilities, so once cracks form in the concrete, the effectiveness diminishes. The study found that although the corrosion inhibitors (including the hydrophobic pore blocker) increased the design life of the structure, the concrete with the admixtures did not outperform the design life of epoxy-coated reinforcement [198].

Moon et al. investigated the difference in carbonation depth for specimens subjected to an accelerated lab test and those placed outside for one year for surface-applied crystalline coatings; results showed decreased depth of carbonation for the coated specimens for both exposure conditions [93]. Improved performance due to the PRA was similar, decreasing carbonation depth by 15-45% and 30-60% for the accelerated lab test and outside exposure, respectively [93].

2.5. RECOMMENDED TESTING REGIMEN

The laboratory and simulated field test methods found in the literature were evaluated for the ability to measure the performance of uncracked and cracked concrete and determine the difference between integrally-mixed and surface-applied PRAs. Although the main function of permeability-reducing admixtures is to improve the watertightness and durability of concrete, there were many test methods used to measure the properties of concrete incorporating PRAs. There was a wide range of standardized and non-standardized test methods, ages, w/cm, control mixtures, and results found in the literature. There was also limited field performance data with corresponding lab results for the PRAs investigated. Consequently, no consensus was established for lab test methods to evaluate the performance of PRAs or to establish thresholds for acceptance criteria.

To determine the efficacy and potential benefits of PRAs to the FDOT, the penetrability of concrete mixtures incorporating PRAs must be measured and compared to concrete mixtures that meet the current FDOT requirements. Based on the mechanisms of the PRAs and test methods evaluated, the applicability of the various penetrability test methods for each PRA type was summarized and is presented in Table 9. The check marks indicate test method categories that are likely appropriate for the PRA category, the approximate symbols are for test methods with mixed results, and the X's are for test methods not appropriate for that PRA category. The cells are also highlighted for identification of test method categories that are good measurements of performance, potentially good, or not good with green, yellow, and red, respectively.

Table 9. Applicability of penetrability test method categories based on PRAs

Test methods	Crystalline		Hydrophobic pore blocker	
	Integrally-mixed	Surface-applied	Integrally-mixed	Surface-applied
Water absorption*	X	X	✓	~
Water permeability	✓	~	X	X
Electrical methods*	~	X	~	X
Porosity	X	X	X	X
Vapor and gas permeability	~	~	X	X
Chloride exposure*	✓	✓	✓	✓
Corrosion*	✓	✓	✓	✓

*Indicate recommended tests for experimental study

Due to the difference in function of crystalline and hydrophobic pore blocker admixtures as well as the method of application, it is difficult to select a lab test method applicable to all situations. For the crystalline admixtures, the water absorption test method is not the most appropriate because these admixtures are hydrophilic and absorb water to react and form crystals that in some cases may block pores, reducing transport. Surface-applied hydrophobic pore blockers may also have inconsistent results with water absorption testing depending on the depth of penetration of the admixture. Because hydrophobic pore blocker admixtures typically cannot withstand high hydrostatic pressures, water permeability does not give an indication of performance for these admixtures. Water permeability test methods are applicable for crystalline admixtures; however, water permeability results for surface applications will depend on which face is exposed to water pressure and how far the admixture penetrated into the concrete. Additionally, the water permeability of concrete mixtures of interest (low w/cm) might be too low to be able to easily distinguish the effects of PRAs. A water penetration-under-pressure test such as EN 12390-8 could serve as a rapid and simple-to-run test that indicates the concrete resistance to fluid transport; however, research is needed to determine how much variability is caused by the drying method, and the environment around the sample during water exposure.

Electrical test methods are influenced by the conductivity of the pore solution. Given that the composition of most PRAs is proprietary, the ability of pure electrical tests to gauge PRA performance is unknown without additional testing. NT Build 492 may hold more promise as a rapid measure of the concrete transport properties when PRAs are used because it measures the transport of chloride ions through the concrete, not just the concrete resistivity. Electrical test methods are not appropriate for surface-applied admixtures because the electrical current passes through the entire specimen giving an average sample resistivity, while a treated surface would have an outsized effect on the overall. Although porosity is an indirect measure of penetrability, it is not a good indication of PRA performance because the drying method used to prepare samples may affect the crystalline products and hydrophobic pore blockers typically have a minimal effect on porosity. Porosity measurements can be used as verification that the admixtures do not have negative effects on the concrete relative to a control mixture. Vapor and gas permeability were not commonly used tests for PRAs and would not be appropriate performance tests because the admixtures are designed to let the concrete breath. Crystalline admixtures will absorb moisture, affecting the vapor transmission, but once the reaction takes place and crystals form, the penetrability will decrease. Hydrophobic pore blockers have a minimal reduction of porosity, thus they would not decrease the vapor and gas permeability.

The most appropriate test method categories found in the literature for measuring PRA performance were simulated field tests that expose specimens to chloride solutions to measure chloride penetration or corrosion potential. The simulated field tests provide a more realistic measure of performance and are appropriate for the different PRA categories, but typically require longer testing times. The main concern for the FDOT is chloride ingress in reinforced concrete structures and the simulated field test methods can determine if there is a reduction in chloride ingress due to PRAs, whether integrally-mixed or surface-applied. For surface-applied admixtures, the surface can be abraded before measurement to ensure a minimum depth of penetration of the admixture for effectiveness over time.

While the simulated field test methods are appropriate for PRAs, the best indication of field performance of structures is the performance of specimens at a durability site or trial implementation project. Because there is limited field data, it is recommended to create enough specimens to be placed on a durability site to take cores periodically for testing to establish relationships between lab tests and field performance at multiple ages. A simulated chloride exposure test method such as NT Build 443 is recommended for assessing the benefit of the PRAs investigated in the research; however, this method is not rapid and would be difficult to implement into specifications.

The following test methods and exposure conditions are recommended for an experimental project to determine the most appropriate rapid performance test for PRAs and benchmark it against field performance to determine an acceptance criteria:

- Field exposure tests for benchmarking
    - Fabricate samples for exposure at a marine durability site and monitor for any surface wear, chloride profile, and corrosion of embedded reinforcement with time. Any laboratory test methods should be benchmarked against results from the field samples.
- Candidate rapid penetrability qualification tests
    - NT Build 443 to determine if there are additional mechanisms beyond simple diffusion that affect chloride transport in field samples.
    - Surface resistivity (AASHTO T 358) samples should be made because this test method is currently used for concrete mixtures. While it is not expected that this test would work for all PRAs, this should be shown through testing.
    - Rapid chloride migration test (NT Build 492) to determine the concrete non-steady state diffusion coefficient. NT Build 492 could provide a rapid indication of the penetrability of the concrete because measurement of chloride penetration depth makes its results less affected than AASHTO T 358 by conductive ions in concrete [147].
    - Water absorption (ASTM C1585) with different specimen conditioning procedures to account for the concrete initial state of saturation before drying.
    - Water penetration under pressure using a modified version of EN 12390-8 could provide a rapid measure of PRAH admixture efficacy. The test method should be modified to provide a repeatable degree of saturation before being exposed to water under pressure.
- Other fresh and hardened concrete tests to ensure concrete properties are not negatively affected
    - Air content (ASTM 231)
    - Slump (ASTM C143)
    - Setting time (ASTM C403)
    - Compressive strength (ASTM C39)
    - Drying shrinkage (ASTM C157)
    - Sulfate exposure (ASTM C1012)
    - Carbonation exposure

Self-healing capabilities can also be determined by pre-cracking specimens before measurement; specimens can be cracked, cured for a period, and then tested with the same methods to measure the penetrability and strength retention due to crack healing. Different curing conditions (e.g., flowing vs. standing water) and cracking cycles are recommended to provide a more realistic indication of healing capability and longevity.

3. CONCLUSIONS AND RECOMMENDATIONS

3.1. CONCLUSIONS

The objectives of this project were to perform a thorough literature review to determine if there are existing test methods that can quantify the performance of chemical PRAs, and if so, what acceptance limits should be used. This study examined test methods for and performance of PRAs when used integrally as an admixture or topical application.

The composition and reaction products of the crystalline and hydrophobic pore blockers were researched through PRA patents and journal articles. The majority of the PRA chemical composition groups had alkali metal silicates with supporting ingredients, including siliconates, acids, expansive agents, and stearates. Surfactants, emulsifiers, and retarders were commonly used to enhance performance and achieve better penetration for surface-applied admixtures. The literature documented numerous test methods for evaluating the performance of PRAs with varying degrees of frequency and standardization. Although the goal of permeability-reducing admixtures is to improve the watertightness and durability of concrete, there were many test methods used to measure the properties of concrete incorporating PRAs.

The test methods found to be used with PRAs were categorized into penetrability, durability, mechanical, characterization, and supplementary techniques. Most studies that examined penetrability focused on using existing test methods to demonstrate PRA performance against a reference concrete and did not discuss whether the test method used had been validated for use with this material. Penetrability test methods included water absorption, water permeability, electrical methods, porosity, and vapor/gas permeability. Water absorption and water permeability were the most commonly used test methods for measuring PRA performance with 30 and 23 occurrences, respectively. The other penetrability test methods were less common, but for all test method categories, there was no consensus on the standard or technique used for measurement. Test methods in the durability category included simulated and field exposure cases measuring chloride ingress, corrosion potential, freeze-thaw resistance, abrasion, acid resistance, and sulfate resistance. The most frequent of these was exposure to chloride solution. Chloride induced corrosion is the leading cost of repair for reinforced concrete, and the majority of Florida’s infrastructure is in an aggressive environment, thus resistance to chloride ingress is important for structural durability. Mechanical properties were measured and used to qualify the concrete; compressive, flexural, and tensile strength were reported for concrete containing PRAs. The most frequently measured mechanical property was compressive strength with a total of 37 occurrences. Various characterization techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) were used to describe the raw materials and reaction products formed when PRAs were used. SEM accompanied with EDS was a popular technique (26 cases) for imaging hydration products and monitoring self-healing of micro-cracks. Additional test methods for PRA performance included drying shrinkage, contact angle, and pulse velocity.

The results from the lab test methods and field exposure were summarized to gain an understanding of the performance of PRAs under different conditions. There was a lack of consistency in the experimental methods employed by the studies found in the literature; the dosage, water-cementitious ratio (w/cm), testing age, and mixture designs found had a large range of methods used. Therefore, the actual performances observed varied greatly and there were conflicting results. The field data was limited and there is still a need for verification of long-term performance. Additionally, there were not many studies that had field and lab data to establish relationships between lab results and field performance and determine the validity of using the test method to measure performance of PRAs. Overall trends were observed, but no discussion in the literature was found about acceptance criteria for PRAs.

From the literature examined, the following conclusions were drawn from this study:

- There is no consensus on which laboratory test methods should be used to evaluate the performance of PRAs.
- The laboratory test results showed conflicting performance of the crystalline and hydrophobic pore blocker admixtures. There was no consistency with the control mixture for comparison for determining performance, thus thresholds for performance could not be determined.
- Due to the limited overlap between laboratory and field testing, there was not an established relationship between lab results and field performance that could be used to relate performance in an accelerated lab test to structure service life.

3.2. RECOMMENDATIONS

Based upon the findings from this study, the following recommendations are made:

- Create lab and field specimens to establish a relationship between lab test results and actual field performance for concrete including PRAs. Place field specimens at a durability site to measure the difference in PRA performance in saturated, tidal, and splash zones.
- Measure the efficiency of PRAs for a range of concrete mixture designs and test methods.
- Establish PRA acceptance thresholds based on mechanism or intended function of admixture that gives comparable service life to that of a concrete mixture that meets current FDOT requirements for extremely aggressive environments, namely an electrical resistivity of 29 kOhm-cm at 28 days per AASHTO T 358.

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