An Overview on Effects of Water Repellent Concrete Protective Coatings in the Durability of Concrete Structures

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Abstract: The emergence of concrete structures is increasing day by day. Out of these, some of them under go faster deterioration based on the environment in which it is placed. So it is very important to protect and maintain the structures to make it durable throughout its service life. Durability is the ability of structures to resist the environmental attacks without deterioration. Lack of durability is the major concern faced by most of the structures. Durability is achieved by preventing the attack of environmental factors like weathering, freeze and thaw reaction etc. One of the methods to prevent these attacks is by the application of water repellent protective coatings on the surface of concrete, which gets exposed to environmental attacks. This paper is a review about the various studies on the effect of different types of concrete protective coatings on the durability of concrete.

Keywords: Concrete structures, Environmental attacks, Durability, Protective coatings, Mechanisms

1. Introduction

The present world in its hand carries a large number of different types of structures especially reinforced concrete structures. These may be of different size, shape and texture with one another. The major problem facing these structures is the lack of durability.

Durability is the property by which the concrete can withstand the external factors without deterioration for a long period of time. The external factors include environmental factors like weathering, chemical attacks, freeze- thaw process etc. If durability is not achieved, the wastage of money occurs.

Marine environment are the places mostly suffering the deterioration problem. Sea water containing salt contents comes in contact with the structures acts as an essential agent for causing deterioration. Water entering through pores of concrete structures acts as a transport medium in transferring the harmful chemical agents like chlorides, sulphates etc into the concrete. Thus the steel embedded inside is affected by the chemical agents and leads to deterioration. Also the carbonation process, alkali silica reaction etc imparts a part of damage into the concrete.

Research about these concrete were studies by many researchers and they found that there is no substitute for good concrete. The one of the suitable method to protect concrete is by the application of protective coating on the concrete.

Protective coatings are chemical substances used for protecting the concrete from external attacks and thereby improving durability of the concrete. There are many types of protective coatings available in the market. The main problem is some coatings may provide protection but may not be durable. So it requires a special knowledge for the selection of coatings for various applications. This paper is a review about various studies conducted by different researchers on the applications of various types of protective coatings on the durability of concrete. Figure 1 shows the various types of deterioration of concrete structures.



Figure 1: Deterioration of concrete structures (anticlockwise from top left) (Chemical reactions, Aggressive water attack, Freeze and thaw process and alkali silica attack)

2. Deterioration of Structures

Durability of a reinforced concrete structure depends on the environment in which it is exposed. Permeability is an important property in determining resistance of concrete to external factors. For high durability, concrete should have low permeability that is strongly linked to porosity of the concrete paste. The extent of the damage depends on concrete quality

The reduction in the useful service life of reinforced concrete structures is of major concern to the construction industry worldwide (Mohammed Ibrahim et al, 1999). Much

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of the deterioration of concrete can only occur in the presence of water, since aggressive agents penetrate concrete and react harmfully with the concrete only when dissolved in water. Water, the main cause of deterioration contains chemical agents especially chloride ions diffuse into the concrete and cause reinforcement corrosion, leading to its deterioration and eventually reducing the load-carrying capacity of a structure. As reinforcement corrosion is dependent on the availability of moisture and oxygen, any methodology to reduce their diffusion into the concrete mass will reduce its deterioration.

Marine environment is one of the places where the durability factor is a major concern for concrete structures. The corrosion induced by salinity of marine environment is considered as a great hazard to reinforced concrete. Though the chlorides contributed by the mix constituents can be controlled by strict adherence to improved construction practices, the ingress of chloride ions from the service environment can only be avoided by using good quality concrete and/or coating it with an impermeable membrane which prevents the entry of water into the concrete (Mehdi Khanzadeh Moradllo et al, 2012).

One of the methods is to apply surface treatment materials on the concrete. This method can also be used to repair corroding structures.

3. Modes of Failure of Structures

Transport phenomena through the pores of concrete may occur by the penetration and diffusion of substances such as chloride ions, carbon dioxide and sulfate. These structures, whether immersed in or suspended over the sea are subjected to high levels of chlorides which is the major element causing deterioration of concrete.

The failure of structures occurs due to wave action. Concrete exposed to seawater may deteriorate from the combined effects of chemical and physical processes. The major attacks occurring in the structures are described in the following sections.

A. Attack on Concrete

Water, containing many chemical agents, acts as the major cause of deterioration of concrete structures. Some of the types of deteriorations are sulphate attack, leaching of lime, cavitation, erosion and abrasion from waves, chloride attack, carbonation etc. The details are described below.

Sulphate attack

This is the more common type and typically occurs where water containing dissolved sulphate penetrates the concrete. A fairly well-defined reaction front can often be seen in polished sections; ahead of the front the concrete is normal, or near normal. Behind the reaction front, the composition and microstructure of the concrete will have changed. These changes may vary in type or severity but commonly include: extensive cracking, expansion, loss of bond between the cement paste and aggregate as shown in Figure 2. Sulphate reacts with free calcium hydroxide which is liberated during the hydration of the cement to form calcium sulfate (gypsum). Gypsum combines with hydrated calcium aluminates to form calcium sulphoaluminate. This results in an increase in volume, development of cracks and eventual spalling.



Figure 2: Spalling due to sulphate attack

Leaching of lime (calcium hydroxide)

Leaching of lime compounds can lead to the formation of calcium carbonate or calcium sulphate on the surface of the concrete; this is known as ,efflorescence". Two forms occur, namely lime bloom and lime weeping. Lime bloom appears as white patches or an over-all lightening of the surface of the concrete. This is a cosmetic problem. The aggregates will be visible without the cementitious matrix. Lime weeping is caused by water leaking through the concrete and dissolving calcium hydroxide from the matrix. On contact with the atmosphere the calcium hydroxide reacts with carbon dioxide to form calcium carbonate, which is precipitated on the surface when the water evaporates, generally at cracks or joints. Serious leakage of water through joints can lead to the formation of stalactites. Significant leakage may be symptomatic of a more severe problem and can lead to durability problems. Leaching is shown in Figure 3.



Figure 3: Leaching of concrete

Alkali-silica reaction

Some of the siliceous aggregates contain reactive silica, which on interaction with lime from cement hydration, form a solid non expansive alkali-silica complex which can imbibe considerable amounts of water and then expand, disrupting the concrete. Its symptoms are map or pattern cracking on concrete and concrete swelling. The alkali-silica attack on a concrete member is shown in Figure 4.

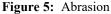


Figure 4: Alkali silica attack

Erosion and abrasion from waves

It is caused due to the action of debris rolling and grinding against a concrete surface in the stream environment as shown in Figure 5. The major symptoms are smoothening of surface, formation of localized depressions and the remaining of spherical and smooth debris in the structure. Due to continuous exposure, the cement film gets eroded in the initial step, and thereafter larger and larger aggregates are rubbed, knocked or washed out.





Chloride attack

Chlorides are introduced when the members come in contact with environment containing chlorides such as seawater. The penetration depends on amount of chloride coming into contact with concrete, permeability of concrete, amount of moisture present. Figure 6 represents the attack of chloride on concrete.



Figure 6: Corrosion of steel reinforcement due to chloride attack

Carbonation

Carbonation occurs in concrete because the calcium bearing phases present are attacked by carbon dioxide of the air and converted to calcium carbonate. Cement paste contains 25-50 wt% calcium hydroxide (Ca (OH) $_2$), which mean that the pH of the fresh cement paste is at least 12.5. The pH of a fully carbonated paste is about 7.

The concrete will carbonate if CO_2 from air or from water enters the concrete according to:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

When Ca (OH) $_2$ is removed from the paste hydrated CSH will liberate COO which will also carbonate. The rate of carbonation depends on porosity & moisture content of the concrete. Normal carbonation results in a decrease of the porosity making the carbonated paste stronger. Carbonation is therefore an advantage in non-reinforced concrete. However, it is a disadvantage in reinforced concrete, as pH of carbonated concrete drops to about 7; a value below the passivation threshold of steel.

B. Attack on steel

Chloride Induced Corrosion

Chloride ion, present in marine breeze and seawater is considered as the main external agent to damage reinforced concrete in marine environments. It affects the passivity of steel film and provokes the initiation of corrosion (M Sosa et al, 2011). For corrosion to be initiated, the passivity layer must be penetrated. Chloride ions activate the surface of the steel to form an anode, the passivates surface being the cathode. Chloride ions destroy the passive steel layer. Chlorides act as catalysts to corrosion when there is sufficient concentration at the rebar surface to erode the passive layer. These ions are not consumed in the process and allow the corrosion process to quickly proceed. Corrosion involving chloride attack is thus a continuous process because chloride ions are not consumed as explained by the chemical reactions represented below (M.H.F. Medeiros, 2009). → FeCl₃+ FeCl₂

Fe³⁺+ Fe²⁺+ 6Cl⁻ For hydrolysis:

FeCl₃+ FeCl₂ + H₂O → 6Cl⁻+Fe (OH)₂+Fe(OH)₃

After the second reaction, chloride ions remain free to react again. Consequently, the corrosion caused by chloride ions is one of the most dangerous and deleterious processes in reinforced concrete. One of the main mechanisms governing chloride ion penetration in a reinforced concrete structure is diffusion, which the transport stimulated by a difference in concentration of the species is considered.

However, there are other important mechanisms such as capillary suction and permeability that can act on the chloride ingression a reinforced concrete structure. Capillary absorption is an important mechanism related to the chloride ingress into concrete. Non-saturated concrete in contact with a salt solution will absorb this solution by capillary forces. The simultaneous action of diffusion and capillary suction thus causes a mixed transport mode, which is present in most exposure conditions to which reinforced concrete structures are subjected. The initial mechanism appears to be suction, especially when the surface is dry and salt water is rapidly absorbed by dry concrete. Next, the capillary movement of the salt water through the pores is followed by a more substantial diffusion. A possible means of extending the service life of reinforced concrete structures submitted to chloride ion attack is by surface protection of the concrete, which inhibits chloride penetration by diffusion and

absorption of contaminated water (M.H.F. Medeiros et al, 2009).

There are two consequences of the corrosion of steel. First, the products of corrosion occupy a volume of several times larger than the original steel so that their formation results in cracking, spalling or delamination of the concrete. Secondly it reduces the cross sectional area of the concrete there by reducing the load carrying capacity and collapse of the structure (Adam Neville, 1995).

4. Coatings for Concrete

In order to prevent concrete from deterioration due to chemical attack, it should be protected from water. One of the methods is to apply coatings on the surface of concrete which can prevent entry of water into concrete. Such coatings are called water repellent surface coatings. Many types of water repellent coatings, based on various chemicals/ polymers, are available for application on concrete. The coatings can be classified into two groups namely Barrier type and Non- Barrier type.

A. Barrier Type Coatings

These are coatings which act as a barrier against the movement of water, and water vapour in and out of the concrete. The different types of barrier coatings are:-

Epoxy Coatings

Epoxy coatings are generally packaged in two parts that are mixed prior to application. The two parts consists of 1) an epoxy resin which is cross linked with 2) a co- reactor or hardener. When properly catalyzed and applied, epoxies produce a hard, chemical and solvent resistant finish. They can typically be used on concrete to give resistance to water, alkali and acids. It is the specific selection and combination of the epoxy component and the hardener component that determines the final characteristics and suitability of the epoxy coating for a given environment.

Epoxy resins are sensitive to UV-light, a characteristic that reduces their performance outdoor. Despite their sensitivity to photo oxidation amine-cured epoxies are used extensively in exterior coatings. Epoxy resins absorb at about 300 nm resulting in chain scissoring, cross linking and eventual chalking. Pigments that absorb in the same UV region contribute to the degradation reaction.

Poly Urethane

They are commonly referred to as urethane, are thermosetting or thermoplastic and demonstrate moderate chemical resistance and good resistance to shrinkage and flexibility. They have many desirable properties including fast cure times, outstanding life expectancy, strong adhesion, high abrasion resistance and toughness, and good chemical resistance. They are typically the most resistant to water exposure, high humidity, temperature extremes, and fungus. The first essential component of the polyurethane polymer is the isocyanate. Isocyanates are toxic but they are treated with special formulating technology and make the use of polyurethane safe. Polyurethanes containing ester linkages may react with water leading to scission of the polymer chain and formation of a polymeric acid and a polymeric alcohol. The reaction is acid-catalyzed which means that since it produces an acid, it is autocatalytic and can produce runaway degradation. Since the reaction is reversible, re esterification of hydrolytically damaged ester-based polyurethanes is at least theoretically possible.

Acrylic Copolymer

They are binders comprised chiefly of esters of acrylic and methacrylic acid that are polymerized addition, polymerization, usually using a free radical mechanism. They are good weathering resistant and provide durability to concrete. It is due to their resistance to hydrolysis and their lack of absorption of UV light.

Coal tar epoxy

They have both properties of coal tar and epoxy. They have good adhesion to concrete and chemical resistance. They are applied by roller, conventional means or by airless pray. They are applied in two coats having total thickness of 15 to 20 microns.

B. Non-Barrier Coatings

These are coatings which allow the movement of water vapour in and out of the concrete which makes the concrete to be breathable one. The different types of non-barrier coatings are:-

Silicates

Silicates, which contain silicon, oxygen, and one or more metals, are primarily used for densification purposes in the concrete industry. Sodium, potassium, and lithium silicates are available and can be applied topically to hardened concrete. When applied to concrete, silicates diffuse into the concrete, react with hydroxyl ions present in the pore solution, and produce calcium-silicate-hydrate (C-S-H). C-S-H, which is also the primary product of Portland cement hydration, is a permanent cementitious product that provides both strength and durability to concrete. Formation of C-S-H in the pores of the treated concrete reduces the pore volume, or densities the concrete, and consequently reduces the permeability of the concrete within the treated depth, which can approach 25 mm (1 in.). While sodium and potassium can aggravate aggregate durability problems, such as alkalisilica reaction, lithium has been shown to mitigate this problem in concrete; therefore, applications of lithium silicate may have additional benefits beyond just reducing the permeability of the concrete.

Silanes

Silanes consist of a monomer silicon-centered molecule with four attached groups. Like silicates, silane can be applied topically to hardened concrete. When applied to concrete, silane forms a covalent bond with the concrete substrate and forms a polymer with adjacent silane molecules. Silane not only exhibits the deepest penetration of the silicon compounds, but it also provides excellent hydrophobicity while still allowing the treated concrete to remain breathable; the silane polymer structure inhibits the movement of liquid water but permits water vapour to move through the concrete matrix.

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Lithium Silicate and Silanes

Dual treatment systems involving the applications of silicates and silane together or in combination with other products can offer advantages, such as greater permanency and greater reductions in permeability, over the use of a single treatment. For example, although the actual scope of experimentation was not described, a silane base coat with an acrylic top coat was reported to be beneficial in one study, while the benefits of a lithium silicate base coat with a silane top coat were documented in another study. In both cases, applications of the sealers were expected to significantly reduce the occurrence of chloride-induced corrosion of reinforcing steel in the treated concrete structures, but data specifically evaluating the resistance to chloride ingress were not presented.

5. Merits and Demerits of Coatings

Among the above discussed coatings, the barrier coatings form a barrier film on the surface of concrete which prevents the entry of water into concrete and provides excellent hydrophobicity. The barrier coating also prevents the expulsion of water vapour from the concrete due to the changes in humidity in the atmosphere and thereby prevents the ability of concrete to breathe. But this creates a thin film of water vapour between the concrete surface and barrier coating, thereby affecting the bond between the coating and the concrete and eventually making the coating to fail in due course of time. On the other hand, non-barrier coatings such as silanes, silicates, do not form film on surface of concrete and allow breathing of concrete.

6. Protective Coatings

Coatings are used to improve the durability of the whole structure other than for cosmetic reasons. They are beneficial to seal the surface against the penetration of harmful species such as oxygen, carbon di-oxide, chloride ions, sulphate ions, and water entering into the concrete. At the same time, coatings should enable the concrete to breathe and allow water vapour to escape for preventing formation of blisters.

They should provide good bond, abrasion resistant, chemical resistant, UV resistant etc. Coatings may be classified based on the application to the structures in the dry environment and also to the structures existing in the wet environment especially marine environment. The availability of a wide range of coatings raises problems in their choice since they can provide different levels of protection while presenting different characteristics among similar generic chemical composition. This means that their "barrier" properties and their effect on concrete must be evaluated. In recent years, several test methods as well as some requirements have been issued as drafts standards for CEN (European Committee for Standardization) public enquiry. Those related with coatings for concrete protection are:

1) preen 1504-2, 2000 - Surface protection systems

2) ENV 1504-9, 1997 - General principles for the use of products and systems.

The aforementioned EN standards will help the selection of products to be used in new or repaired structures as long as

the intended use or main function required from the protection system is defined and the type of exposure is known. According to those standards, coatings can be used for protection and / or repair of concrete structures, making use of one or more of the following five basic principles which are based on the chemical or physical laws allowing the prevention or stabilisation of the chemical and physical deterioration processes in the concrete surface ingress protection, moisture control, physical resistance, resistance to chemicals, increasing resistivity (D. B. Mc Donald, 2011).

7. Application of Protective Coatings

The application of surface treatments on the concrete surface improves the life expectancy of the concrete. There are so many types of surface treatments available in the present time. Based on the cost and performance of surface treatments, they can be used in the concrete.

A. Selection of Protective Coating

When selecting methods to protect structures against the deterioration of concrete, factors such as performance, sustainability, initial and life cycle, cost, and availability should be evaluated (D. B. Mc Donald, 2011).

- *Performance* Concrete with an appropriate low watercement ratio is the most cost effective method for adding additional service life. However, poor mixture design and placement practices may result in less than expected performance (D. B. Mc Donald, 2011). The coatings selected should perform effectively in providing protection to the concrete structure.
- *Life Expectancy* The coatings should provide good life expectancy to the concrete. The more the life expectancy provided, more it will be preferred.
- *Sustainability* It should be economically and environmentally suitable. It should not cause any pollution or harm to the occupants.
- *Cost* The economy must be considered as a major factor, perhaps the single most important factor. At times, low-cost systems will prevail at the expense of more durable systems. The thicker the application better will be the protection.
- *Availability* The availability of coatings in a particular region enhances the use of a particular coating.

8. Mechanism of protective coatings

The use of superficial protection for concrete is a possible way of increasing the service life of reinforced concrete structures exposed to marine environments. This type of protection inhibits the penetration of aggressive agents by diffusion and capillary absorption.

The surface protection materials for concrete can be classified into three groups: Coatings (form continuous film on the concrete surface), Pore liners (make the concrete water-repellent), and pore blockers (react with some of the soluble concrete constituents and form insoluble products) (M. H. F. Medeiros et al, 2012).

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A. Coating and Sealers

The commonly used sealers are Epoxies Polyesters, Acrylics Polyurethanes, Vinyl's Butadiene, Polyethylene copolymers, Bitumen's etc. Figure 7 depicts a continuous film formed on application of a coating on concrete surface.

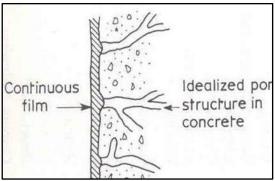


Figure 7: Coating and sealers

They form pinhole free film over concrete surface which acts as a barrier to the passage of water or diffusion of CO_2 . Some sealers penetrate in to the pores of concrete pores. Their dry film thickness ranges between 100-300 μ m (M. H. F. Medeiros et al, 2012).

Pore Liners

Hydrophobic materials: They line surface pores of the concrete and repel moisture. Silicone compounds: Silicone is dissolved in an organic solvent (5 % solids ethanol or white spirit) which on evaporation deposits water repellent silicone resin on the walls of the concrete pore structure.

Water repellent treatments: The materials based on the solutions of complex stearates (8% solids in white spirit) are also used. Their behaviour is similar to silicone compounds (M. H. F. Medeiros et al, 2012). Figure 8 shows the diagrammatic representation of pore liners.

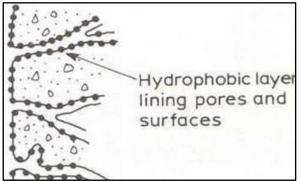


Figure 8: Pore liners

Pore Blockers

Pore blockers are family of products which penetrate to concrete and block pores. Some materials like liquid silicates and liquid silicofluorides react with $Ca(OH)_2$ to form Calcium Silicate Hydrate (CSH) gel products or insoluble calcium silicofluoride, respectively. Some special formulations of epoxies and acrylics also function in similar way. They are principally used as surface hardeners to prevent the dusting of concrete floors and to improve their abrasion resistance, besides as a part of the repair and protection systems for corrosion affected structures (M. H.

F. Medeiros et al, 2012). Figure 9 shows the diagrammatic representation of pore blockers.

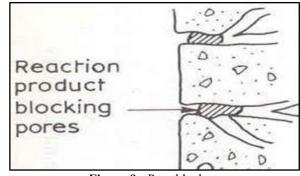


Figure 9: Pore blockers

Renderings

Rendering is a thick cementitious coating, generally applied by trowel or by spraying as in gunite process. Provides an additional barrier to the concrete cover against the ingress of aggressive agents may sometimes be enhanced by polymer compounds.

Water repellents or hydrophobic agents always result from silicon resins that are chemically bound to the concrete base. Currently, the most commonly used are silanes, siloxanes, oligomerics and a mixture of these two components (M. H. F. Medeiros et al, 2012). Figure 10 shows the diagrammatic representation of renderings

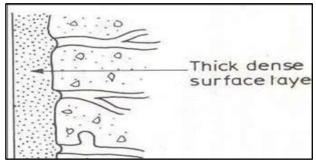


Figure 10: Renderings

9. Testing the efficiency of protective coatings

The efficiency of the protective coatings is often tested by carrying out certain performance tests on coated concrete specimen. The tests, as collected from literature, are as follows:

A. Capillary Water Absorption Test

This test is used to determine the capillary water absorption of concrete specimen whose surface is treated by different water repellent coatings. This test is conducted in accordance to standard DIN 52617/87. Cylindrical specimens of 200 mm in length and 100 mm diameter are used. The lateral side of the specimens is sealed with silicon up to 3 cm in height so that only one circular face of the specimen is exposed to water. The water level during the test is kept constant and 5 mm above the surface of the specimen in contact with water.

The weight of specimens is monitored in a period of time (0-16 days) throughout the contact with water. Before applying the protective products, the specimens are kept in an oven at 60° C until constant mass was obtained.

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Afterwards, they are kept in chamber $(23 \pm 2^{0}$ C and $50 \pm 4\%$ HR) to cool down before the application of the products. Then, the surface protection materials are applied on one of the circular surfaces of specimens. Seven days after the application of protection, the specimens are tested (M.H.F. Medeiros et al, 2009).

B. Pipette absorption test

The test helps to select an appropriate protective coating by determining water absorption capacity of the coated specimen with respect to time (M. H. F. Medeiros et al, 2012). Cylindrical specimens are mould (100 mm diameter and 200 mm length). 50-mm thick slices are cut from the base of the specimens. This test is carried out on the surface of the specimen's base. Figure 11 shows the slice and the surface tested. The test is only appropriate for horizontal surfaces.

The apparatus is fixed on the concrete surface using silicon as shown in Figure 12. The volume of water absorbed is measured as a function of time.

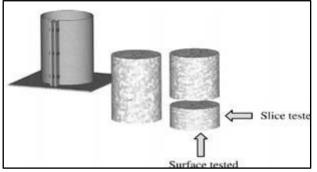


Figure 11: Specimen

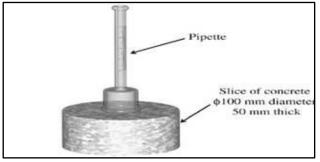


Figure 12: Pipette Apparatus

C. Rapid chloride penetration test

This test is conducted according to standard ASTM C1202/97.The test is used to determine the best protective coating among others based on the charge passing through the specimen. The specimen similar to the capillary water absorption test is taken. After the curing time, each cylindrical specimen (100 mm diameter and 200 mm length) is cut into two 50 mm-wide slices from the central nucleus of the original specimen.

After the drying procedure, the protection materials are applied on only one of the circular surfaces of the specimens. Afterwards, the specimens are vacuum-saturated for 24 h. This procedure consisted in conditioning specimens in a vacuum desiccators and applying a vacuum pressure of 1 mmHg for 3 h. Then, the desiccator is filled with deaerated water until all specimens are immersed, and the vacuum pressure is maintained for one additional hour. Afterwards, the vacuum pump is turned off, and the specimens are maintained immersed for 20 h.

Seven days after the application of the surface treatment, the50 mm-thick specimen is placed between two acrylic cells, each cell with 280 cm³ solution volume. One cell is filled with 0.3 NaOH aqueous solutions and the other with 3.0% NaCl aqueous solution. The cells are connected to a 60 V power source for6 h, in which the electrode immersed in NaOH aqueous solution is the anode and the electrode immersed in 3.0% NaCl aqueous solution is the cathode. The schematic presentation of the chloride migration test cell is illustrated in Figure 13. After 6 h under test, the total charge passed through the specimen (in coulombs) is obtained by integrating the current passed through the specimen during the test period (M. H. F. Medeiros et al, 2012).

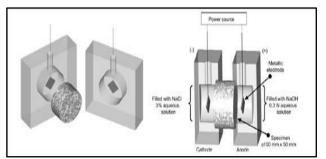


Figure 13: Rapid Chloride Penetration Test

10. Conclusions

Based on the studies conducted on the water repellent coatings, the following conclusions were obtained:

- 1) Surface treatments have the potential to improve the durability of concrete.
- 2) The tests depicted were useful for the evaluation of performance of protective coatings.
- The environmental attacks causing deterioration of concrete can be prevented by using the protective coatings
- 4) Selection of protective coatings depends on the economy, performance, availability, life expectancy etc.
- 5) The protective coatings enables the sustainability of concrete structures.

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