UNIVERSITÀ POLITECNICA DELLE MARCHE

MASTER'S DEGREE COURSE IN ENVIRONMENTAL ENGINEERING

Corrosion behavior of steel and galvanized steel reinforcement in Calcium sulfoaluminate and Portland cement in comparison

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Summary

1.Chapter: SUSTAINABILITY IN BUILDING MATERIALS

1.1. Introduction

In the last decades, plethora of attention is being paid to the environmental impact of the construction sector as one of the most energy-intensive on the planet. This sector can even estimate the consumption of 40% of energy resources.

To achieve environmental sustainability, energy consumption must be reduced. Energy production requires the use of fossil fuels responsible for the emission of carbon dioxide (CO_2).

The continuous use of ordinary Portland cement (OPC) results in a high energy consumption and a large emission of $CO_{2,}$ and this leads to a huge concern in the field of construction.

The challenge was faced by cement companies in synergy with the scientific community and resulted in different types of approaches:

[1] increase in mixtures with a lower percentage of Portland binder.

[2] use of alternative energy sources and raw materials in the production of OPCs.

[3] development of alternative cements at low CO_2.

The continuous need to find technologies that are eco-sustainable has led to the development of materials that determine a lower environmental impact, among these we find calcium sulfoaluminate (CSA).

It is possible to use this material, managing to respect the environment while maintaining high performance with fast commissioning times and operating on both modern and historical structures, with the same performance effectiveness.

The objective of this report studies the development of alternative cements with low $CO_{2,}$ including calcium sulfoaluminate (CSA), allows environmental benefits and valuable technical properties.

This report directly describes the comparison between Portland cement (CEM) and calcium sulfoaluminate (CSA), showing the materials and production processes to which, they are attached.

2. Chapter: CEMENT MIXTURE

2.1. Introduction

Mortar is generally produced by mixing cementing or binding material (lime or cement) and fine aggregate (sand, sawdust, etc.) with water. Mortar is used to bind different building blocks like bricks, stones, etc. It can also add a decorative pattern in brick or stone masonry.

In the building environment, mortar together with concrete, are the most used materials; in fact, they also have an important Italian and international regulatory framework.

Properties of Good Mortar

- The main quality that mortar should possess is adhesion.
- Mortar should be water resistant.
- Deformability of mortar should be low.
- Mortar should be cheap.
- Mortar should be easily workable in the site condition.
- The mobility of mortar should be good.
- It should possess high durability.

Concrete differs from mortar in its composition, having within the Mix design a coarser aggregate (gravel, crushed stone) natural or artificial (granules between 5-30 mm)

According to the kind of binding material, mortars are classified into the following categories:

(i) Lime mortar
(ii) Cement mortar
(iii) Gypsum mortar.

(i) Lime Mortar:

In this type of mortar, the lime is used as binding material. The lime may be fat lime or hydraulic lime.

The fat lime shrinks to a great extent and hence it requires about 2 to 3 times its volume of sand. The lime should be slaked before use. This mortar is unsuitable for water-logged areas or in damp situations. This mortar should be consumed within one hour after mixing.

It possesses more strength and can be used in damp situations. The lime mortar has a high plasticity, and it can be placed easily. It possesses good cohesiveness with other surfaces and shrinks very little. It is sufficiently durable, but it hardens slowly. It is generally used for lightly loaded above-ground parts of buildings.

(ii) Cement Mortar:

In this type of mortar, the cement is used as binding material. Depending upon the strength required and importance of work, the proportion of cement to sand by volume varies from 1:2 to 1:6 or more.

The proportion of cement with respect to sand should be determined with due regard to the specified durability and working conditions. The cement mortar is used where a mortar of high strength and water-resisting properties is required such as underground constructions, water saturated soils, etc.

(iii) Gypsum Mortar:

These mortars are prepared from gypsum binding materials such as building gypsum and anhydrite binding materials.

2.2. Regulations

During the last twenty years the mortars have been the subject of many legislative investigations, a consequence of their massive use in construction.

The current standard UNI EN 1504:2006 defines the mechanical compression (Mechanical strength of mortar) of characterization of mortars through four resistance classes:

R_1 is 10MPa $\leq R_C$ <15MPa
R_2 is 15MPa $\leq R_C$ <25MPa
R_3 is 25MPa $\leq R_C$ <45MPa

2.3. Applications

Mortar is traditionally used for binding building blocks and for plastering the masonry surface, which is an intimate mixture of inert cementing material like mud, lime, cement or a combination of these and fine aggregates like sand and water.It is used to give a soft even bed between different layers of brick or stone masonry for equal distribution of pressure over the bed. It is used to fill up the spaces between bricks or stones for making walls tight. It is used in plastering works to hide the joints and to improve appearance.It is used for molding and ornamental purpose.

2.4. Mortars based on Portland cement

Mortars based on Portland cement have good mechanical performance, they are also very waterproof, for this reason they are widely used in the construction sector more than the others.

Mortar is characterized by two stages:

- The gripping phase is the phase in which the mortar passes from a plastic consistency to a rigid one that maintains the shape
- The hardening phase is in which the shape acquires progressively mechanical strength and therefore the ability to withstand stress.

2.5. Mortar based on sulfoaluminate cement

An alternative to Portland cement mortar is sulfoaluminate cement-based mortar, which we will study in detail later.

Calcium Sulfoaluminate cement (CSA) has been known as a low carbon and energy cementitious material as it can be produced at lower temperature, lower lime content, and improved grindability compared to ordinary Portland cement (OPC)

The cements that are used for these mortars contain calcium carbonate in different quantities. Thanks to Sulfoaluminate cement, they are able to reach high performance resistances after a short curing; in fact, the development of resistance is much faster than other types of concrete.

The advantage of use derives from possibility of replacing part of the cement with particular cementitious materials, deriving from waste from power plants or metal industries (ruffle ash, blast furnace slag or silica smoke) with two substantial benefits:

- Reduction of clinker that will limit the emission of carbon dioxide.
- Recycling of slag.

This can represent a valid alternative to normal mortars by paying attention to problems that affect human.

3.Chapter: TRADITIONAL CEMENTS

3.1.Introduction

Cement is one of the few materials that, in its history, has seen the relationship between man and nature emphasized. Nature, with its extraordinary raw materials and man, with his creativity and research skills.

Already the Egyptians and Romans were looking for a binder to strengthen their constructions and at that time they understood that the mixture of different materials could be the right key to get what they were looking for. The Romans first used mud-based mix and stone materials extracted from the volcanic rock of Pozzuoli, from which the name of pozzolana derived.

From those first experiments to be able to talk about real cement we have to wait until 1756 when the engineer John Smeaton, found a mix particularly resistant to water.

However, it will be expected in 1824 when an English bricklayer, Joseph Aspdin, came to perfect the mix until it reached that level of quality and resistance handed down to the present day. Aspdin's creativity is responsible for the discovery of Portland Cement.

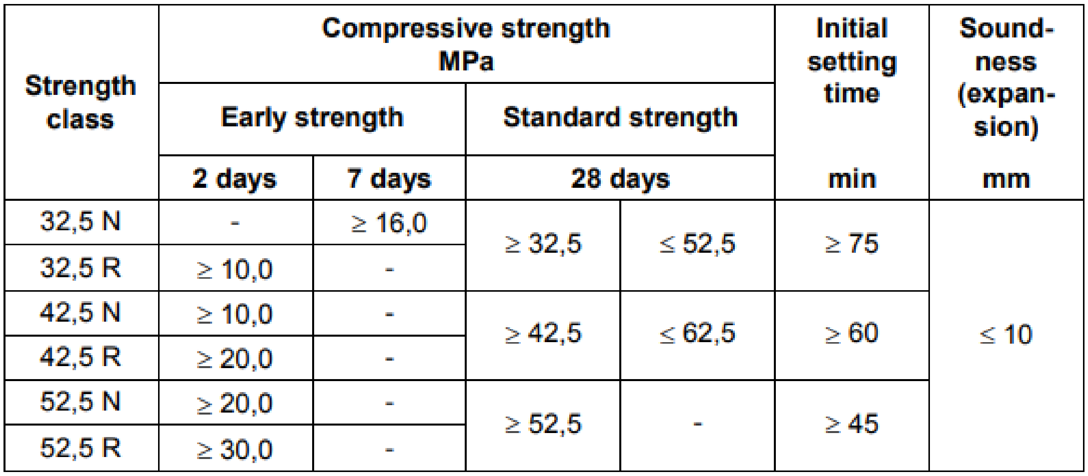
Aspdin mixed, carefully studying its proportions, limestone and clay which, cooked in an oven similar to that used for lime, provided a binder with superior characteristics to the others hitherto experienced.

3.2. Classification

It is recognized that different cements have different properties and performance. Those performance tests now available (i.e., setting time, strength, and soundness), have been included in EN 197-1. In addition, work is being carried out by CEN/TC 51 to identify any additional tests which are needed to specify further performance characteristics of cement. Until further performance tests are available it is necessary that the choice of cement, especially the type and/or strength class in relation to the requirements for durability depending on exposure class and type of construction in which it is incorporated, follows the appropriate standards and/or regulations for concrete or mortar valid in the place of use.

The standard strength of a cement is the compressive strength determined in accordance with EN 197-1 at 28 days and shall conform to the requirements in Table.1. Three classes of standard strength are included: class 32,5, class 42,5 and class 52,5 (see Table.1).

The early strength of a cement is the compressive strength determined in accordance with EN 197-1 at either 2 days or 7 days and shall conform to the requirements in Table.1. Two classes of early strength are included for each class of standard strength, a class with ordinary early strength, indicated by N, and a class with high early strength, indicated by R (see Table.1).



Strength class	Compressive strength MPa				Initial setting time	Sound-ness (expan-sion)
	Early strength		Standard strength			
	2 days	7 days	28 days		min	mm
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5	≥ 75	≤ 10
32,5 R	≥ 10,0	-				
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5	≥ 60	
42,5 R	≥ 20,0	-				
52,5 N	≥ 20,0	-	≥ 52,5	-	≥ 45	
52,5 R	≥ 30,0	-				

Table.1: Resistance(strength) classes according to EN

3.3. *Portland cement*

3.3.1 Introduction

On a global scale, it is one of the most commonly used products in the construction industry, with Italy ranking first among European cement producers and twelfth overall.

3.3.2. Hydration reaction for Aluminates and Silicates

The chemical composition of concrete is primarily defined by the presence of 80 percent silicates (C3S and C2S), whose hydration is important for the development of mechanical performance, and 20 percent aluminates in Portland clinker (C3A and C4AF).

A cement paste is made by mixing water and Portland cement, which undergoes hydration processes of the various elements included in the cement over time. The mix is initially plastic and manageable, but as it hydrates, the amount of free water decreases. The paste loses flexibility and becomes less and less workable as a result, until it freezes completely; this phase is known as the gripping phase and is characterized by the chemical formula below.

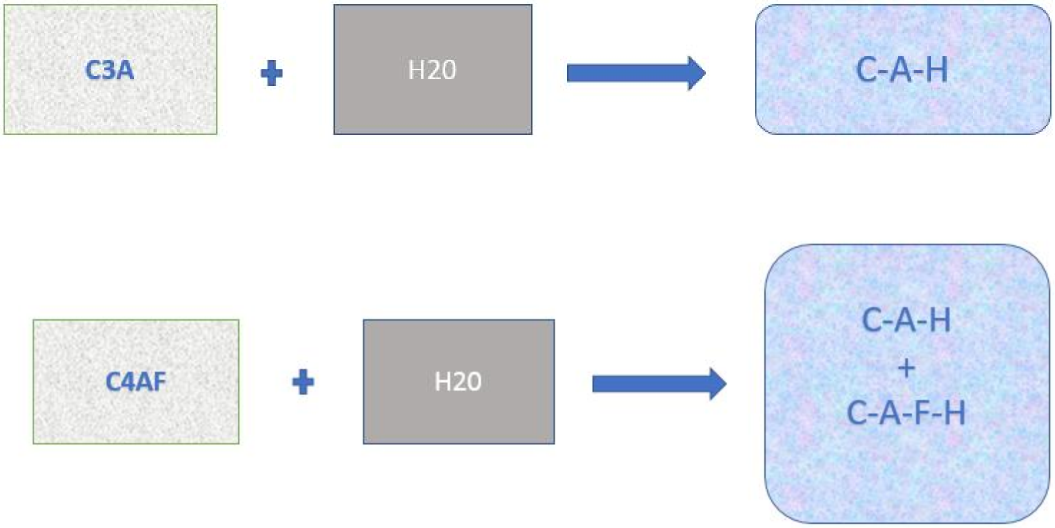


Figure.1: Hydration of aluminates responsible for setting.

The hydration process continues after the setting, although at a slower rate; this phase is known as the hardening phase, and it might extend for months or even years. There is seasoning and curing at this stage, during which the mechanical strength of the cement paste develops and consolidates, as described by the chemical formula:

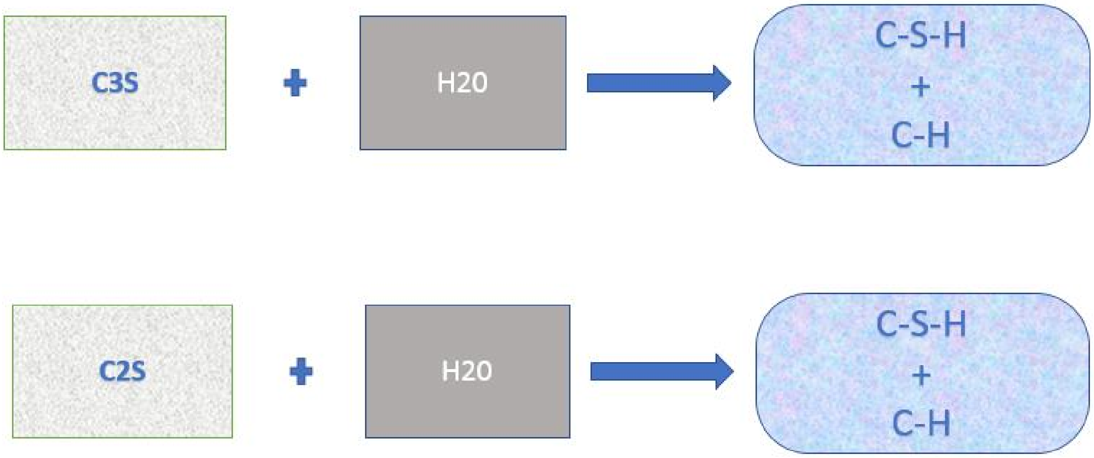


Figure.2: Hydration of silicates responsible for hardening

The setting phase of Portland cement is characterized by the hydration of aluminates, as seen above.

C3A and C4AF are the major components involved in hydration.

C3A generates crystalline hydrates and is very exothermic when it reacts with water. Even the hydration of calcium aluminoferrite C4AF yields crystalline hydrate analogues; in fact, the hydration products of the two ingredients are heavily intermingled.

Except for a rapid but minor increase during the initial hours, aluminate's mechanical strength does not contribute considerably to the development of the material's final mechanical strength. This is dependent on the morphology of the C-A-H crystals, which is primarily determined by the existence of hexagonal laminae or cubic crystals, making it less conducive to the development of mechanical resistance than C-S-H fibrous materials.

This hydration process is quite quick, and the mix loses its plasticity in a matter of minutes, leaving inadequate time to put it in position, generating a slew of issues on the job site. Gypsum (CaSO4) is added to the clinker as a gripping regulator to prevent this action and allow the cementitious material to be installed.

When gypsum comes into contact with water, it releases sulphate ions SO4 and calcium ions Ca2+, which combine with the aluminate ions present (AlO4)- to generate ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), which covers the responding cement grains and decreases their hydration rate.

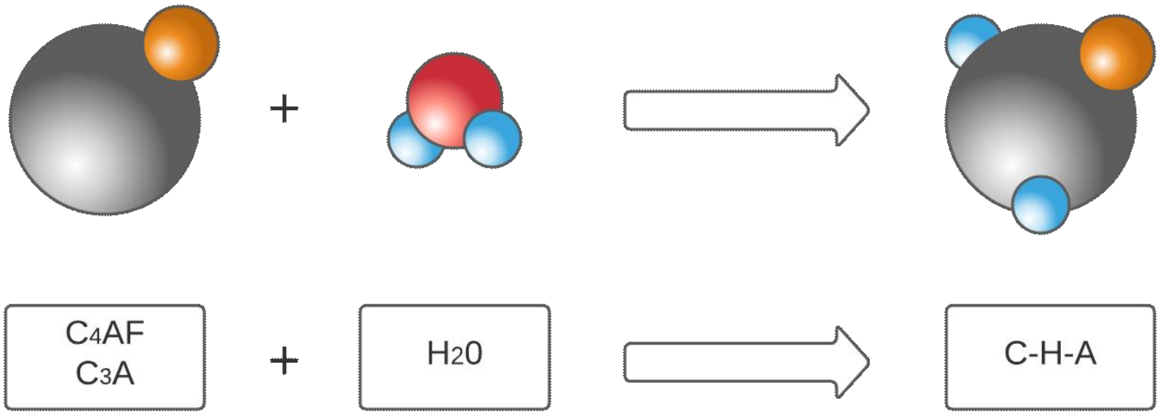


Figure.3: Formula of ettringite production

The "primary" ettringite that forms during the initial hours of aluminate hydration in cement is distinguished from the "secondary" ettringite that might occur later in adverse conditions.

The hardening phase of Portland cement is characterized by the hydration of silicates, as seen above.

C_3S and C_2S are the primary components involved in hydration.

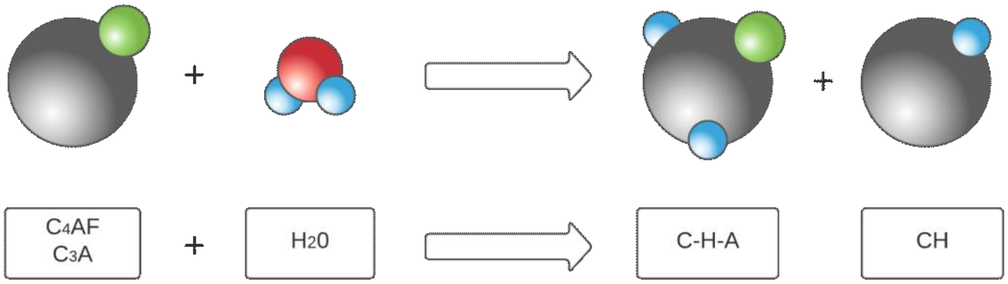


Figure.4: Formula of silicate production

The C-S-H or cement gel product of silicates is responsible for the mechanical strength of the cement paste; it is formed by fibrous products consisting of small solid particles in the form of extremely thin lamellae, with spaces of the same order of magnitude, known as gel pores, between the latter.

The fibers begin to come into contact once the mix is mixed and the gripping phase begins, and the system loses its initial suppleness; hardening begins when the fibers interweave and induce stiffness.

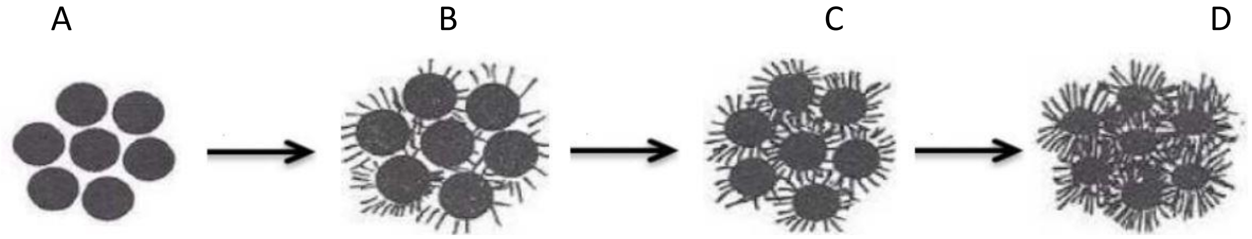


Figure.5: Schematic hydration of C3S or C2S: immediately after mixing with water (A), Start of taking (B), During hardening (C) and Hardening (D).

Advantages of Ordinary Portland Cement

1. It has great resistance to cracking and shrinkage but has less resistance to chemical attacks.
2. Initial setting time of OPC is faster than PPC (Portland pozzolana cement) so it is recommended in projects where props are to be removed early.
3. Curing period of OPC is less than PPC and curing cost reduces. Hence recommended were curing cost prohibitive.

Disadvantages of Ordinary Portland Cement

1. It cannot be used for mass concreting as it has high heat of hydration as compared to PPC.
2. The durability of concrete made using OPC is less than that of the concrete made using PPC.

3. It produces comparatively less cohesive concrete than PPC, hence concrete pumping becomes a little difficult.
4. OPC has lower fineness, hence has higher permeability and as a result it has lower durability.
5. OPC is costlier than PPC.

4. Chapter: SULFOALUMINATE CEMENTS

4.1. Introduction

Sulfoaluminate cement was invented in the 1930s, but it wasn't until the 1970s and 1980s that it became widely used. Unlike the most well-known Portland cements, the hydraulically active mineralogical phase is made up of manufactured calcium sulfoaluminate derived from raw materials like bauxite, limestone, and gypsum.

The production of CSA clinker takes place in rotary ovens at a temperature of 1300° C, with potential environmental benefits compared to the production of Portland clinker, due not only to a lower cooking temperature of the raw material (1300° C vs. 1500° C for Portland clinker), but also to lower CO2 production linked to the fact that the limestone content in the raw materials is significantly lower than that of Portland clinker.

4.2. Eco-sustainability

In the cement manufacturing process, considerations such as energy prices, pollution, and raw material use are critical.

The cement conglomerate is typically made up of 20% cement and 80% water and aggregates.

The extraction of raw materials for the production of clinker and aggregates has a direct influence on the environment, mostly in the landscape. In 2012, there were 5592 operational quarries in Italy, with sand and gravel extraction accounting for around 50 million cubic meters, or 62 percent of the materials mined on the national territory (AITEC 2016, AITEC 2017, Nanni et al. 2014).

The extraction of raw materials, packing the resulting conglomerate, and transporting it to the construction site all consume a modest amount of energy and produce a minor amount of carbon dioxide.

Cement manufacture accounts for the majority of emissions and consumption. The production cycle of this binder has an impact on the environment due to direct and indirect greenhouse gas emissions. In fact, the fire of limestone to produce calcium oxide (calcination) produces CO_2directly:

$CaCO_3 \rightarrow CaO + CO_2$

This reaction accounts for roughly half of all emissions from cement manufacturing and accounts for around 4% of global emissions; about 4 billion tons of cement are produced each year.

In addition, when fossil fuels such as coal, natural gas, or oil are used to heat the furnace, CO_2 is released indirectly. This contributes around 4% of world CO_2 emissions and accounts for about 40% of cement manufacturing cycle emissions. Finally, electricity needed to power machinery and energy used in the final conveyance of cement is another source of indirect emissions, accounting for around 5-10% of the sector's emissions.

It is estimated that 60 to 130 kilograms of fuel and about 110 kWh of electricity are used to create one ton of Portland cement, resulting in emissions of 900 to 1100 kg of CO_2 (about 220 – 240 kg per cubic meter of conglomerate produced).

Approximately 40% of the materials now in use are projected to be recycled.

The following pollutants can be released by building materials and products:

- Physical pollutants: degradation products.
- Organic pollutants: fungi, molds, and bacteria.
- Chemical Agents: volatile and semi-volatile organic molecules, in particular benzene, carbon monoxide, carbon dioxide, nitrogen dioxide, and various anhydrides.

- Natural and artificial minerals: asbestos, glass wool, stone wool.

Building materials can wreak havoc on houses in three ways:

- Direct waste of contaminating or hazardous materials (volatile organic compounds, radon, dust, and fiber).

- Absorption and subsequent release of compounds already in the air and those originating from other sources.
- Promote the accumulation of dirt and the growth of microorganisms.

Materials and products used in construction may emit:

- Highly toxic compounds (carcinogens or allergens).
- composts that can induce general symptoms.
- irritating compounds: compound that create poor air quality (unpleasant odors).
- compounds with unknown hazardous qualities may be released by materials and products used in building.

Hydraulic binders based on calcium Sulfoaluminate (CSA) are considered low-impact hydraulic binders that provide good mechanical performance.

A CSA clinker can save 68 percent on limestone and 40 percent on fuel consumption when compared to a Portland clinker.

Furthermore, due to the contained presence of calcium carbonate ($CaCO_3$) among the raw ingredients and the lower use of fossil fuel during the cooking phase, it provides for a large reduction in CO2 emissions into the atmosphere, of roughly 62 percent.

Furthermore, the temperature attained by the oven during the heating process for the synthesis of sulfoaluminate is around 1200 ° C, which is around 150 ° C to 200 ° C lower than the temperatures used in the manufacturing of standard Portland clinkers, allowing for a smaller energy effect.

This results in more friable clinkers that require less grinding energy, as well as the possibility of utilizing a variety of waste and industrial by-products that are difficult to dispose of throughout the production cycle.

Because of the lower energy requirements for the dissociation of limestone. CO2 emissions are reduced by roughly half, and the entire clinker grinding process saves a significant amount of electricity.

4.3. Composition of sulfoaluminate cements

Unlike regular cements, sulfoaluminate cement hardens quickly and has a high initial strength.

Ettringite ($C_6AS.3H_{32}$), which is produced by the hydration of C_4A_3S -, and calcium sulfates added to the clinker, are the main regulators of this behavior.

Sulfoaluminate clinker is composed of around 35% limestone, 30% natural gypsum, and 35% bauxite; alternatively, Portland clinker is composed of 80% limestone and 20% clay.

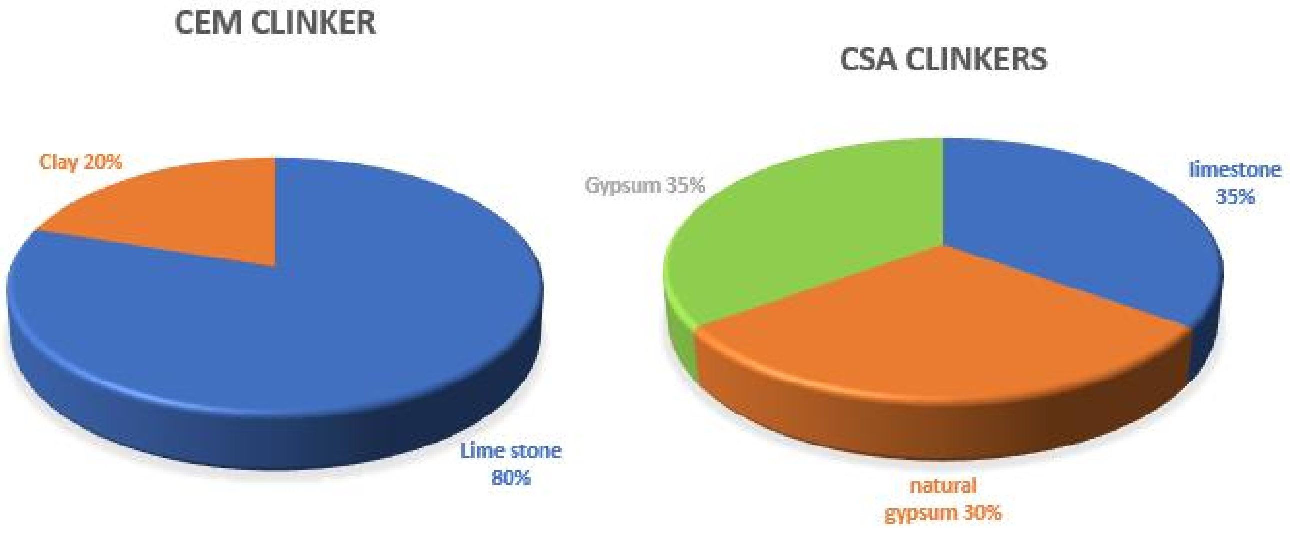


Figure.6: CSA and Portland clinker components

4.4. Applications

A defect of the CSA is the aluminum component present in bauxite. So, it's hidden in a hard-to-find rock, which could raise production costs, but it's a minor consideration compared to the many benefits:

- The cement matrices longevity.
- Good waterproofing.
- Great resistance to frost-thaw cycles.
- Excellent chemical resistance.
- Fast bond
- Rapid Strength Development
- Low shrinkage.
- Short curing phase
- Reduced CO2 emissions
- Cost

It is gaining traction in the building industry as a result of these properties. It's employed in high-performance self-leveling screeds, expanding binders, and fiberglass composites.

Advantages of CSA:

Rapid Strength Gain

The main benefit of CSA cements over Portland cement is that they can acquire compressive strengths of over 5000 psi in less than 24 hours; in fact, CSA cements can achieve 28-day strength in less than 24 hours. For some applications, this is the primary reason that CSAs are utilized instead of conventional Portland cement (OPC). In circumstances where an airport runway, a bridge repair, or a damaged freeway must be returned to operation in a short length of time, rapid strength gain is crucial.

Low Carbon Footprint:

Another big advantage of CSA cements is that they are substantially greener. Portland cement is burnt at roughly 1500°C (2700°F) in kilns, whereas CSA cements only need to be fired at around 1250°C (2250°F) in kilns. The CSA clinker that results is softer than OPC clinker, which requires less energy to grind.

Cement production accounts for a modest but considerable fraction of total global CO2 emissions. The natural synthesis of carbon dioxide is revealed by the chemical conversion of limestone to calcium oxide. Regardless of the technique employed or the fuel efficiency, the chemical reaction produces 579 kilograms of CO2 gas for every 1000 kg of calcium trisilicate (C3S) produced from limestone.

The chemical calcium trisilicate (C3S) is responsible for Portland cement's early strength growth. Calcium disilicate (C2S), the second component, forms more slowly and is responsible for longer-term strength. C3S makes up about 50-60% of Portland cement composition, whereas C2S makes up a lower portion of OPC, usually around 18-20%.

The chemical conversion of limestone to calcium oxide generates around 48 percent of the CO2 emissions created in the production of regular Portland cement, as seen in the breakdown of CO2 emission sources. An additional 42 percent is attributed to the use of fossil fuels to attain the high kiln temperatures. The chemical conversion of limestone into cement is directly responsible for 90 percent of CO2 emissions.

In comparison to OPC, generating 1000 kg of CSA produces just 216 kg of CO2, a reduction of around 62 percent. This reduction is significantly more than that achieved by employing industrial waste-derived pozzolans as OPC substitutes, such as fly ash and blast furnace slag, which are typically used to replace just 10% to 30% of the Portland cement. OPC that has had a large amount of cement replaced with pozzolans, including "green" pozzolans such fly ash and slag, is 2 to 6 times greener than concrete composed entirely of CSA. In fact, out of nine different cements tested, CSA cements had the lowest carbon emissions, including magnesia (Sorel cements), sodium metasilicate (water glass), and calcium aluminate cements.

Lower Alkalinity

Anhydrous calcium sulfoaluminate (4CaO3Al2O3CaSO4), dicalcium silicate (2CaOSiO2), and gypsum (CaSO42H2O) are the principal mineral components of CSA cement. Because the lime in CSA cement is bound rather than loose, the alkali content is lower. The pH of CSA cement is only 10.5-11; standard Portland cement (OPC) has a pH of roughly 13, which is 100 to 300 times alkaline than CSA cement. Alkali aggregate reaction is naturally minimized due to the low alkalinity. When glass is utilized in concrete and the concrete is exposed to moisture, this is critical.

CSA cements do not work in the same way as Portland cement does. They don't work with pozzolans because of the decreased alkalinity, therefore employing pozzolans like silica fume, metakaolin to raise strength or reduce cement content (and hence restore or even improve the strength relative to 100 percent OPC) won't work.

Lower Shrinkage

CSA cements hydrate stronger and faster than OPC cements, and they have very low shrinkage properties. This is due to a combination of factors. The first is that CSAs require around 50% more water for optimum hydration than Portland cement. The lowest recommended water-to-cement ratio (w/c) for OPC is 0.35, but the minimum recommended w/c for Portland cement is around 0.22-0.25. Because of the higher hydration requirements, most of the mix water is absorbed for hydration, leaving less extra water to produce shrinkage issues. The second reason is that the rapid strength gain can prevent shrinkage fractures because concrete strength increases faster than shrinkage strains in the concrete.

If the w/c ratio is less than 0.35, however, considerable shrinkage can occur. This can include curling as well as significant fissures and discoloration. There is a precise minimum water requirement for CSA cements that should not be overlooked.

Shorter Curing Time

Although CSA curing is crucial, wet curing times are generally assessed in hours rather than days or weeks. When the CSA concrete is maintained wet for at least 3 to 4 hours after casting, it achieves optimal hydration and slab stability. The concrete wants moisture during the first hydration phase, and the quick reaction generates a lot of heat. If not, enough moisture is delivered during the curing process, cracking and curling may occur. Long-term stability and strength are kept and ensured when moisture is delivered through ponding or recurrent wetting during the initial few critical hours.

Direct Portland Cement Replacement

CSA cements can and should be used as a direct, 100% Portland cement substitute.

Because CSAs do not react with pozzolans, they are not required for high strength and environmentally friendly concrete. Mix design is simplified, and inventory is reduced as a result. Simply eliminate the pozzolans by replacing 100 percent of the cementitious material in your present mix design. It's preferable not to use pozzolans with CSA cements because they can weaken the concrete.

Superplasticizers, particularly polycarboxylates, and viscosity modifiers act in CSAs in the same way they do in Portland cement. Other unusual admixtures, such as liquid silicates or accelerating agents, are unnecessary and incompatible with CSA cements. Cement retarders of the past are incompatible. Only citric acid-based retarding admixtures designed specifically for CSA cements will work.

Color Considerations

Only a light tan/buff hue of CSA cement is available. White is not an option. When switching to CSA cements, be sure to play around with your color formulae.

CSA cements can be colored, and acid stained like Portland cements and are compatible with concrete colors. Specialty embedment’s and exposed aggregate appearances are achievable since decorative aggregates, metal, and glass are all compatible.

Cost

While rapid strength gain, high "green" value, and low shrinkage are all desirable characteristics, such great performance comes at a cost. An 88-pound bag of white CSA can cost more than double the price of a 94-pound container of white Portland cement. Saving days spent waiting for the concrete to build strength may be important in the commercial world, especially if shorter turnaround times are required. Concrete that is poured today can be stripped and processed the next day, and in many cases, it can be poured and stripped on the same day. This boosts the production rate of your casting tables while reducing the number of tables required.

5. Chapter: STUDY OF MIXTURES

5.1. Objectives

The purpose of this thesis is to compare the physical, chemical, and mechanical properties of the CSA and CEM mixtures, while keeping in mind that the CSA mixture is more environmentally friendly.

Three distinct mortar resistance classes were used in the comparison:

R1 > 10 MPa,

R2 > 15 MPa,

R3 > 25 MPa.

5.2 Raw materials

For the production of mortars, it is necessary to mix proportionally different raw materials such as, inert water and binder. In order to improve its performance, there is the possibility of adding other components such as chemical additives and fibers.

Mix-design is literally the "project of the mixture"; more extensively is the "calculation of the composition of mortars starting from the required performance (workability, mechanical strength, durability, etc.) and the characteristics of the available raw materials (cement, aggregates, additives)"

5.2.1 Water

Water is a colorless and tasteless liquid made of two oxygen atoms bonded to one hydrogen atom, with the formula H2O. Due to its molecular structure, it comes in the form of a colorless and tasteless liquid under ordinary conditions.

Water influences the workability and mechanical resistance of mortars, making it an essential component of the improved Mix design.

The characterization of the workability in the fresh state is an indication of the moldability of the mixture, making it more plastic or less plastic.

The porosity of the mixture is indirectly proportional to its mechanical strength, with the latter being greatly impacted by the water-cement ratio.

The mixing water is required to maintain adequate cement hydration, to wet the aggregate in order to improve cement paste adhesion, and to bring the mix to the ideal consistency in order to assure its processing and subsequent installation. The water must be dosed properly in order to get the proper water/cement ratio, which determines the final strength of the cement conglomerate.

Furthermore, the mix water must be clear, free of salts, particularly sulphates and chlorides at hazardous concentrations, and meet the criteria of current standards. In particular, according to the UNI EN 1008:2003 standard, which specifies the requirements of slurry water for the production of mortars and concretes, drinking water is considered suitable for the production of cementitious composites, and does not need to be subjected to specific tests.

5.2.2. Inert

The inert, also known as aggregate, is a stone component that does not react with the other components and is mostly utilized as a passive component in the combination.

They are mineral substances that are either natural, manufactured, or recycled from demolition materials.

One of the most significant benefits is cost savings, since increased aggregate content allows you to lower the amount of binder, which is more expensive. Their utility is not limited to cost savings; rather, the function they play in dimensional stability by decreasing the effects of heat hydration or withdrawal during the first phase is critical.

The UNI EN 12620 standard governs the inert requirements for mix, which are divided into three categories:

- Coarse aggregate: d≥ 2 mm; D ≥4 mm;
- Fine aggregate (sand): d = 0; D ≤ 4 mm;
- Natural particle size 0/8: d = 0; D ≤ 8 mm;
- Mixed aggregate (all in): d = 0; D ≤ 63 mm;
- Filler: ≤ 0.063 mm through the section.

5.2.3. Sand

For the preparation of the mortars studied we used calcareous sand, with a diameter of less than 8 mm. Having been taken directly from the bag, it was not completely dry.

With this procedure you will have a dose of water more than the weight of the saturated sand on a dry surface, which in proceeding with the mixture must be taken into account.

Generally, the absorbed by sand to reach the saturated dry surface condition In fact, the term sand indicates the dry inert (dried in the oven) with about 2% of its water mass.

5.2.4. Filler

Calcium carbonate was employed as a filler.

Carbonic acid's calcium salt is calcium carbonate. It's a white solid at room temperature that's not very soluble in water and has a somewhat basic reaction with it: a suspension of 100 grams in a liter of water at 20°C has a pH of roughly 10. In reality, the production of OH ions by the carbonate ion (CO_3^{2-}) generated by the dissociation of salt in water makes the aquatic environment basic.

Because it is free of dangerous chemical agents, it has no health hazards, and it is suited for use in natural-source environmental protection applications; as a result, it has become a material with steadily increasing consumption over time.

We may find it in nature in the forms of calcite and aragonite (minerals) as well as limestone and marble (rocks).

Calcium carbonate is an ionic compound generated by the $Ca^{2+ \text{ cation}}$ and the polyatomic anion CO_3^{2-}. when analyzed chemically.

As a result, it dissociates in aqueous solution as follows:

$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$

$CaCO_3$ is also easily destroyed in the presence of acids. Carbonic acid H_2CO_3 is formed as a result of the reaction, which decomposes into calcium oxide and carbon dioxide almost quickly.

5.2.5. Binder

The binder is a finely crushed inorganic ingredient that, when mixed with water, forms a paste that sticks to the surface and hardens over time due to reactions and hydration processes.

5.2.6. Portland Cement

Portland cement is the most common type of cement in general use around the world as a basic ingredient of concrete, mortar, stucco, and non-specialty grout. It was developed for other types of hydraulic lime in England in the early 19th century by Joseph Aspdin, and usually originates from limestone. It is a fine powder, produced by heating limestone and clay minerals in a kiln to form clinker, grinding the clinker, and adding 2-3% percent of gypsum. Several types of Portland cement are available. The most common, called ordinary Portland cement (OPC), is grey, but white Portland cement is also available.

The inventor of Modern Portland Cement:

Portland cement was developed from natural cements made in Britain beginning in the middle of the 18th century. Its name derives from its similarity to Portland stone, a type of building stone quarried on the Isle of Portland in Dorset, England.

The production cycle of Portland cement:

The most common way to manufacture Portland cement is through a dry method. The first step is to quarry the principal raw materials, mainly limestone, clay, and other materials. After quarrying the rock is crushed. This involves several stages. The first crushing reduces the rock to a maximum size of about 6 inches. The rock then goes to secondary crushers or hammer mills for reduction to about 3 inches or smaller.

The crushed rock is combined with other ingredients such as iron ore or fly ash and ground, mixed, and fed to a cement kiln.

The cement kiln heats all the ingredients to about 2,700 degrees Fahrenheit in huge cylindrical steel rotary kilns lined with special firebrick. Kilns are frequently as much as 12 feet in diameter—large enough to accommodate an automobile and longer in many instances than the height of a 40-story building. The larger kilns are mounted with the axis inclined slightly from the horizontal.

The finely ground raw material or the slurry is fed into the higher end. At the lower end is a roaring blast of flame, produced by precisely controlled burning of powdered coal, oil, alternative fuels, or gas under forced draft.

As the material moves through the kiln, certain elements are driven off in the form of gases. The remaining elements unite to form a new substance called clinker. Clinker comes out of the kiln as grey balls, about the size of marbles.

Clinker is discharged red-hot from the lower end of the kiln and generally is brought down to handling temperature in various types of coolers. The heated air from the coolers is returned to the kilns, a process that saves fuel and increases burning efficiency.

After the clinker is cooled, cement plants grind it and mix it with small amounts of gypsum and limestone. Cement is so fine that 1 pound of cement contains 150 billion grains. The cement is now ready for transport to ready-mix concrete companies to be used in a variety of construction projects.

Although the dry process is the most modern and popular way to manufacture cement, some kilns in the United States use a wet process. The two processes are essentially alike except in the wet process, the raw materials are ground with water before being fed into the kiln.

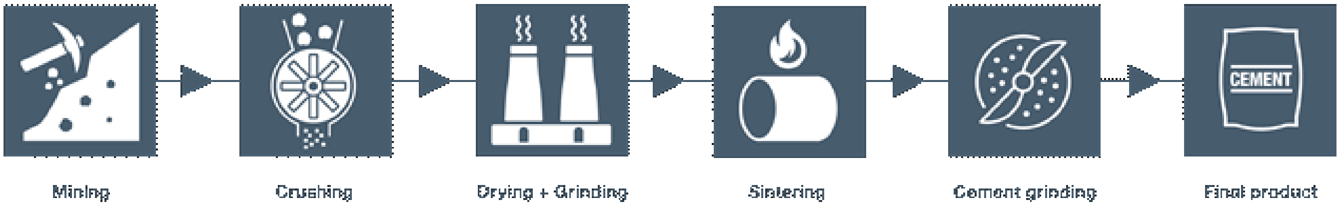


Figure.7: Portland cement production cycle

As previously stated, the theoretical energy required to form clinker is around 1700 Joules per gram, however the actual amount is substantially higher due to dispersions. This necessitates a high energy demand for cement manufacturing, as well as a significant release of carbon dioxide into the atmosphere, a chemical that causes the greenhouse effect.

5.2.7.Hydraulic Lime

Natural hydraulic lime is the name of the alternative to cement. Both are made with cooking stones, but the materials and techniques are significantly different.

The hydraulic limes are obtained from marly limestones or calcareous marls (natural mixtures of limestone and clays) subjected to burning process at temperatures generally between 1100 and 1250° C. In such conditions calcium oxide is formed, which subsequently combines in part with the silica and the alumina of the clay, forming hydraulic silicates and calcium aluminates, that is compounds which, reacting chemically with water, form stable and insoluble hydrates. That allow the material to harden and remain stable even under water (hydraulic behavior).

On leaving the kiln, the hydraulic lime is subjected to extinction, such as aerial lime, but, given the presence of hydraulic compounds, the extinguishing water is only the stoichiometrically necessary to transform the calcium oxide, left as quicklime, in calcium hydroxide. If, in fact, even the silicates and the aluminates are hydrated, they would not be able to provide hydraulic characteristics during use.

According to the EN 459-1:2010 standard, natural hydraulic lime is available in three different types: NHL 2, NHL 3.5 and NHL 5. The acronym NHL is, in fact, synonymous with Natural Hydraulic Lime. The numbers 2, 3.5 and 5 represent the compressive strength expressed in N/mm2 and are associated with the traditional terms of ‘weakly hydraulic lime’, ‘moderately hydraulic lime’ and ’eminently hydraulic lime’.

The merit of the NHL is that each grade is suitable for different types of use and boundary conditions. This means that it is possible to obtain different mortars, adapting them to the type of use, the required performances and the expected durability.

6. Chapter: CORROSION BEHAVIOUR OF REINFORCED CONGLOMERATES

6.1. Introduction

Initially the corrosion tests were conducted in a non-aggressive environment during the curing period, which was defined as the first 28 days in which the specimens were kept in the curing chamber at a constant temperature and humidity, then defined for 12 weeks for the comparison.

Following that, measurements were made using dry-wet cycles in a solution imitating sea water (containing 3.5 percent NaCl) to assess the status of corrosion of the reinforcements caused by chlorides. Measurements were taken both with dry specimens and with specimens immersed in the solution.

The corrosion tests were carried out on six mortar specimens in the experiment:

- R1 CEM;
- R2 CEM;
- R3 CEM;
- R1 CSA;
- R2 CSA;
- R3 CSA.

6.2 Final mix

6.2.1. Mix-design of mortars

As previously stated, after performing some tests to achieve the needed resistances, a Mix-design was chosen that met all of the criteria.
The compositions of mortars for corrosion testing are listed in the table below.

Table.2: Table of Mix Designs(g/L), where the tests were carried out once the appropriate Mix design was found.

Materials	Cement OPC (g)	NHL 5 (g)	CSA Cement (g)	Limestone filler (g)	Water (g)	Sand Wet (g)	w/c	w/l*	Slump (mm)
R1 CEM	223	231	-	-	299	1833	1,70	0,84	150
R2 CEM	304	162	-	-	299	1833	1,25	0,82	135
R3 CEM	493	-	-	-	299	1833	0,77	0,77	130
R1 CSA	-	-	218	273	277	1833	1,64	0,73	180
R2 CSA	-	-	363	121	283	1833	1,00	0,75	160
R3 CSA	-	-	478	-	287	1833	0,77	0,77	145

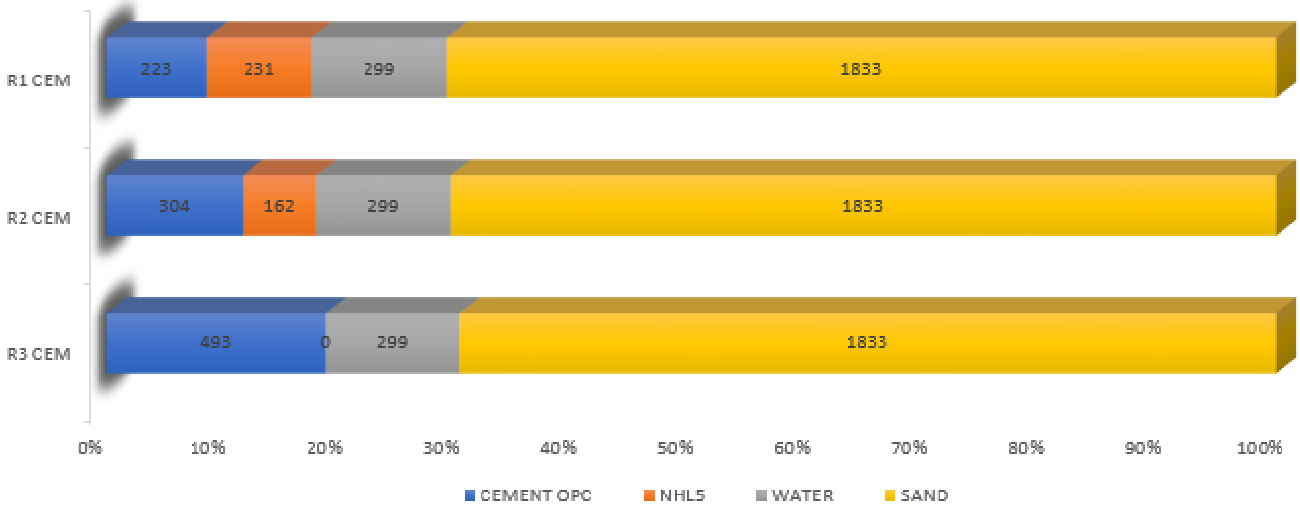


Figure.8: Mix Design of CEM Mortars

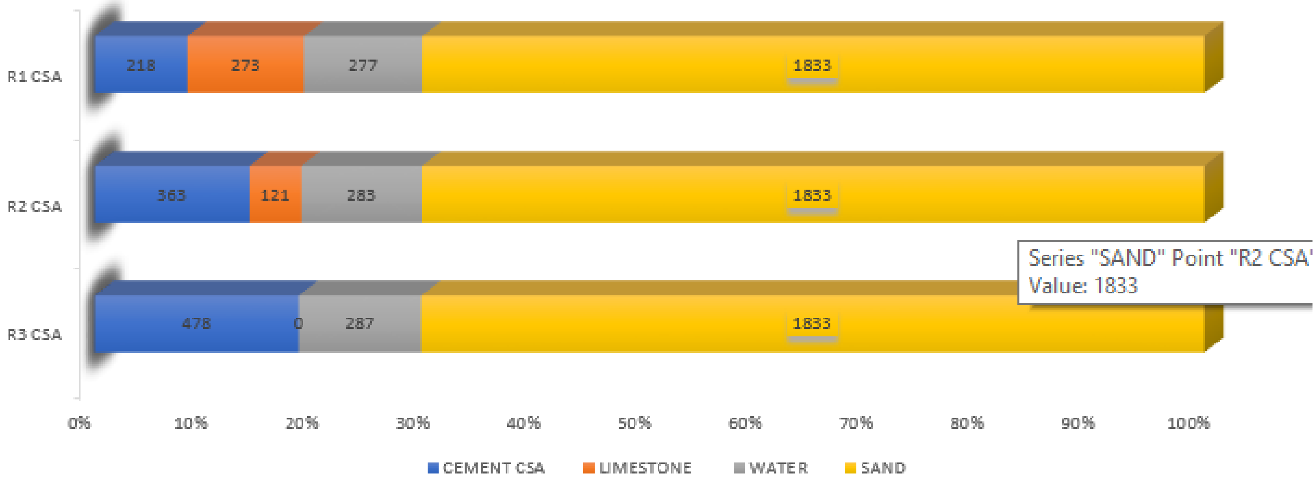


Figure.9: Mix Design of CSA Mortars

6.2.2. Preparation of formwork

A reinforced cylindrical specimen with a diameter of 11.5 cm and a height of 12.5 cm was created for each mortar mix.

The measurements of the formwork have been evaluated in order for us to have enough area to study our specimens more thoroughly.

The figure depicts the dimensions that have been adhered to.

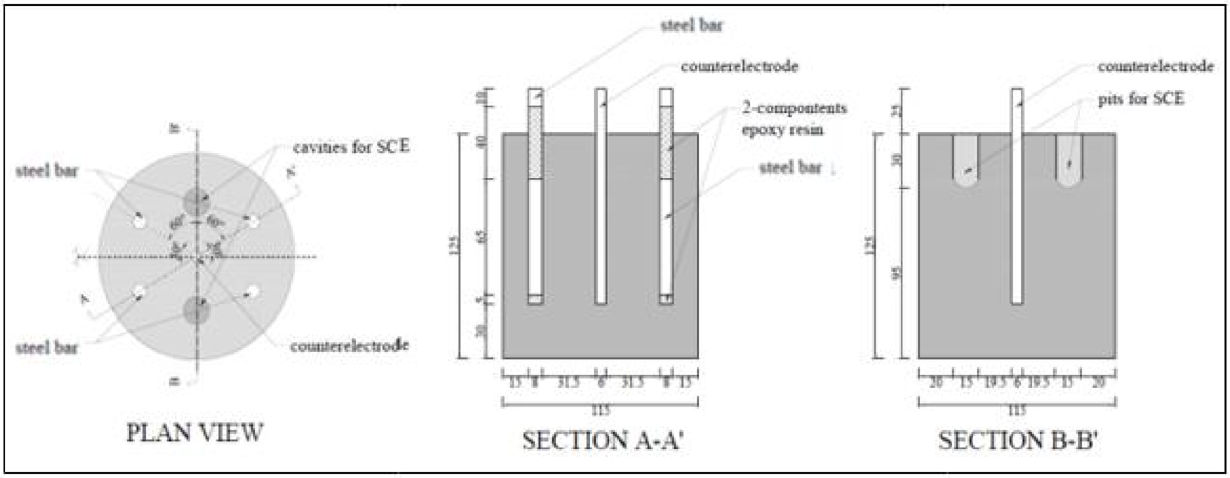


Figure.10: Size of the cylindrical specimens.

A pvc pipe and lids were used to create the formwork for the casting; to achieve a watertight formwork, the pipe and lid were bonded together with silicone to prevent the mortar from escaping after casting.

Figure.11: Cylindrical specimen formwork

Then holes were drilled in the top cover, which were used for the slot during the casting, and reinforcing bars were inserted, two corrugated iron reinforcements (Ø=8 mm), two corrugated galvanized reinforcements (Ø=8 mm), and one stainless steel AISI 316 counter-electrode (Ø=6 mm), which acts as a counter-electrode for measuring polarization resistance (Rp).

Two slots were made in addition to the bars, into which the titanium reference electrodes were afterwards installed.

Figure.12: Cover of cylindrical specimens

Two slots were created for the reference SCE electrode to be placed during corrosion tests. In total, nine holes were drilled, all the bars and reference electrodes were fixed to the top cover by means of elastomer rings, so as to prevent their movements.

Figure.13: Reference SCE electrode

Before being inserted into the slot holes, the reinforcing bars, to be insulated, were resigned, with a two-component epoxy resin, so as to delimit on them a measuring area of 16 cm^2.

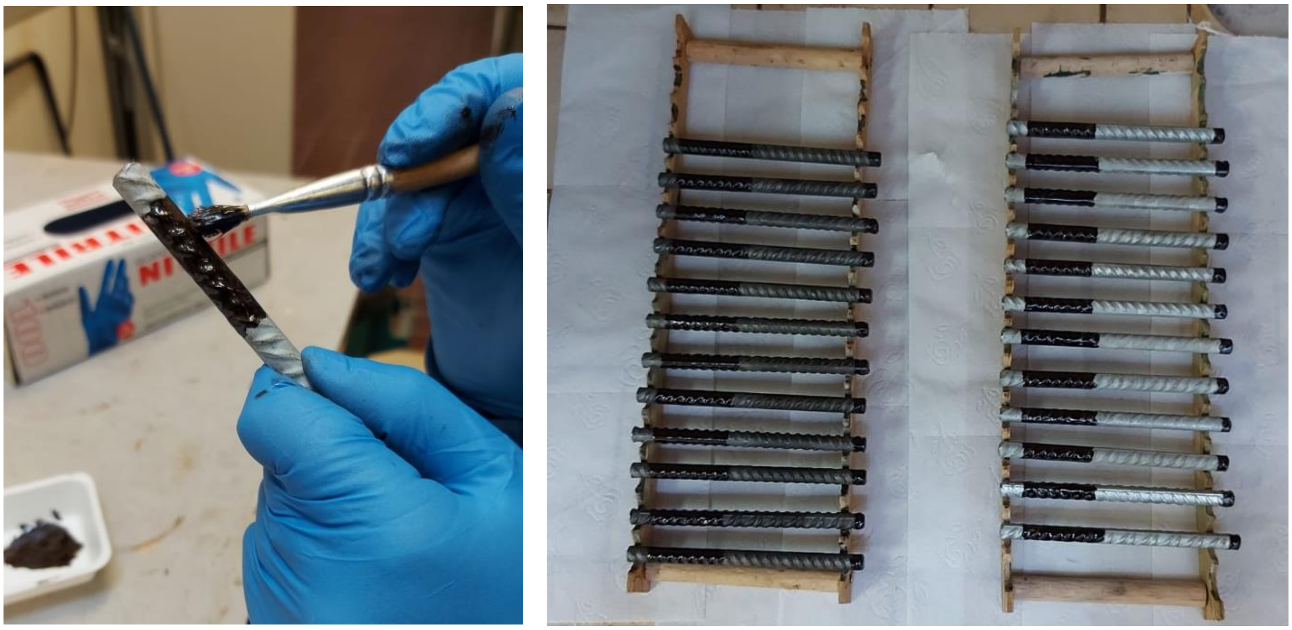


Figure.14: Resin reinforcing irons

7. Chapter: CORROSION OF METAL REINFORCEMENT

7.1. Introduction

The Inter-European Committee of Concrete and the International Federation of Prestress (FIP) define durability as the ability of a work to withstand aggressive agents of different nature while maintaining the mechanical and functional characteristics. In general, for reinforced concrete structures, durability is linked to the ability of concrete to protect metal reinforcement from corrosion processes caused by the attack of aggressive agents present in air, water and soil. Durability, therefore, is closely linked to the environmental exposure of the structure.

7.2. The classes of environmental exposure

To ensure the durability of concrete for a useful life of about 50 years for ordinary works and 100 years for sensitive works, the rules governing the design of reinforced concrete structures have identified for the three parameters Characteristic strength, W/C ratio and Cement content C, the constraints that must be respected to obtain a concrete that allows to create durable structures.

Durability in reinforced concrete is determined by the ability of the concrete to protect metal reinforcements from corrosion processes, which can be severe or mild depending on the climatic conditions at the building site. The UNI-EN 206 standard defines six environmental exposure classes (XO, XC, XD, XS, XF, and XA), each of which has its own set of criteria.

Concrete is characterized by the phenomenon of passivation, when conditions are created for which a passive ferric oxide film is created on the reinforcing irons which makes them impermeable to the passage of water and air.

The rate of corrosion is greatly reduced due to a layer of oxide or surface hydroxide that "deactivates" the metal.

This condition is created when the concrete is perfectly packaged, put in place and is located in an environment with a strong basicity, that is, with a pH greater than 13.

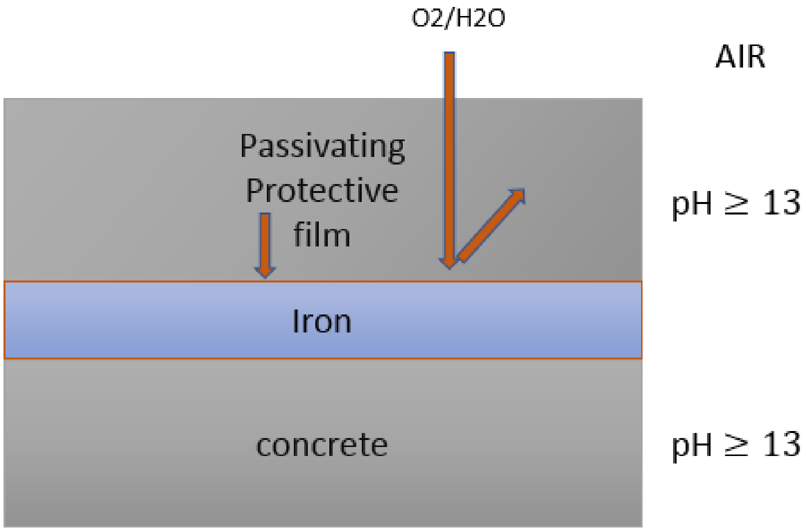
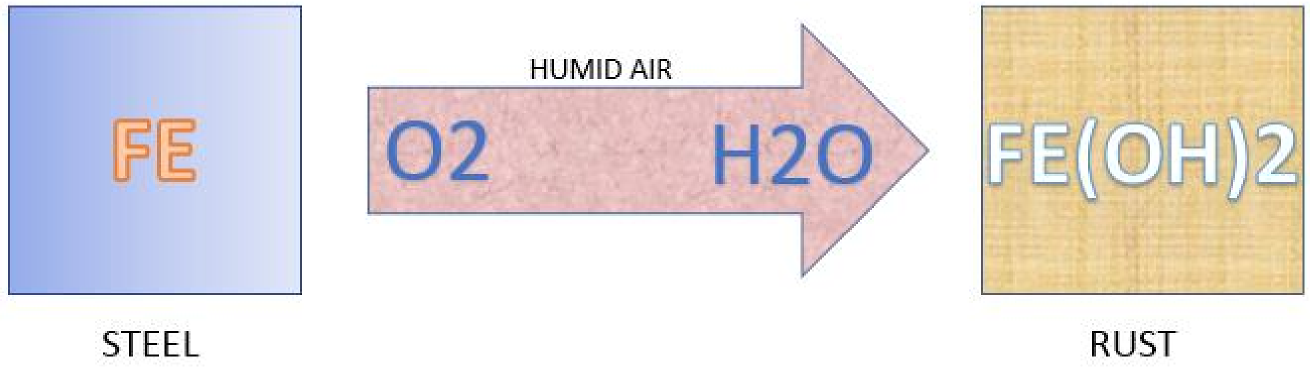


Figure.151: Passivating protective film formed under pH>13

When concrete loses its protective properties, metal reinforcement begins to corrode.

Corrosion of metal reinforcement occurs when porous, inconsistent, and voluminous ferric oxides turn steel (mostly comprised of metallic iron, Fe) into rust. The following report describes this transformation:



In order for this process to trigger, one of two mechanisms must be present:

- Carbonation of concrete;
- Penetration of chloride.

Carbonation of concrete means the formation of calcium carbonate in the mass of this material in the hardened state. As a result of carbonation, the pH of the concrete decreases and favorable conditions are established for the oxidation of the metal reinforcements present in the structures. In particular, the substances that provoke the phenomenon are carbon dioxide, oxygen and water, contained in the form of steam in the air. During the setting and hardening of concrete, cement components, such as compounds C2S and C3S, are affected by hydration reactions and form the C-H-S (Calcium-Silicate-Hydrated) family of compounds, and calcium hydroxide Ca (OH)2:

$$C_3S + H_2O = \text{C-H-S} + Ca(OH)_2$$

$$C_2S + H_2O = \text{C-H-S} + Ca(OH)_2$$

Calcium hydroxide lowers the acidity of concrete, up to pH values greater than 13, and the basicity of the compound favors the passivation of metal reinforcements, or the formation of an iron oxide film, F_2O_2, which comes to cover the metal rods. The film, waterproof and compact, isolates the mass of the reinforcement from contact with oxygen and water, preventing the formation of rust. However, the presence in the concrete mass of both calcium hydroxide resulting from the hydration of cement and carbon dioxide linked to air penetration causes the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3$$

which raises the acidity up to pH values of less than 11. The reduction of pH causes the change of the passive state of the iron, which was the protective film of the reinforcement, in a porous and inconsistent layer, allowing oxygen and water to attack the metal reinforcement. Water and oxygen cause the oxidation of iron according to the well-known reaction:

$2Fe$ (STEEL) + O_2 +$2H_2O$ =$2Fe\ (OH)_2$ (RUST)

Passive state of metal reinforcements can also occur as a result of the presence of Cl ions- on the surface of reinforcing irons after exposure to chlorides found in de-icing solutions used on floors or in marine waters during the winter. The corrosion process must be supplied by oxygen and water in this situation as well.

In this situation, the chlorides penetrate deeply and inflict significant damage.

In electrochemistry, the Pourbaix diagram (or potential/pH diagram or Eh/pH diagram) is used to predict the corrosion behavior of a metallic material, which is a representation of the possible stable conditions (at equilibrium) of an electrochemical system in aqueous solution, at constant temperature and pressure (usually at T = 25 °C and P = 1 atm).

The primary redox reactions that might occur in an electrochemical system are represented by "equilibrium curves," which can be straight lines or have more complex geometries, when the Pourbaix diagram is taken into account.

As a result, the electrical potentials associated with the reduction and oxidation semi-reactions that can occur in an electrochemical system are represented by the equilibrium curves.

Continuing to read the picture, we can observe that it is separated into zones delimited by metal equilibrium curves, which indicate the electrochemical system's circumstances, which can be:

- Corrosion: the metal material is attackable by corrosion;
- Immunity: the metal material is not attackable by corrosion;
- Passivation: the process of coating a metal surface with a layer of oxides or hydroxides.

Through material research, it was feasible to create a diagram for each type of metal that precludes its behavior, allowing for the remediation of any potential repercussions.

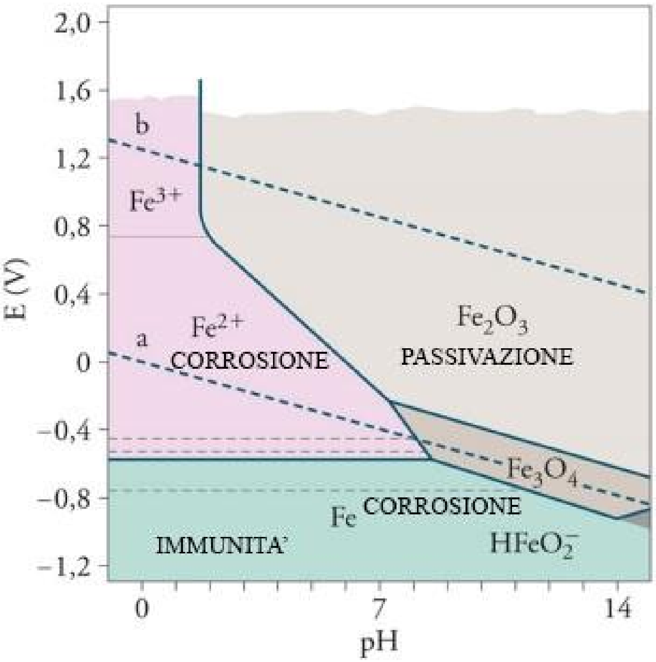


Figure.16: Pourboix diagram for iron

From the diagram it is visible how corrosion is possible in two zones respectively:

- At low pH values, through the formation of Fe^{2+} with low potential or Fe^{3+} with higher potentials.
- At high pH values, with origin of $HFeO_2^-$.

Iron is stable at low potentials (immunity zone) and can be protected in passivation zones where Fe_3O_4 and Fe_2O_3 oxides may form at low and high potentials respectively.

7.3. Electrochemical process

Corrosion is an electrochemical process that consists of two semi-reactions (anodic and cathodic), to which are added two charge transports: the transport of electrons in the metal and the transport of ions in the electrolyte in contact with it.

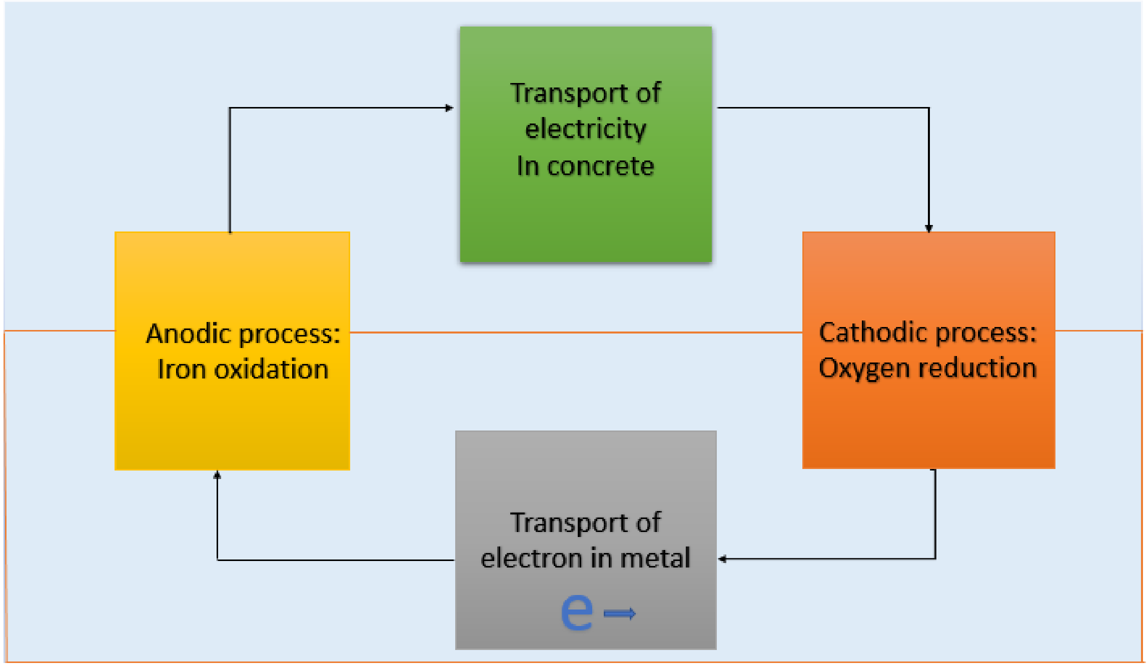


Figure.17: Processes in corrosion

Corrosion is caused by four processes that follow an electrochemical mechanism:

- An anodic metal oxidation reaction that produces metal ions and allows other reactions to take place:

  $Fe \rightarrow Fe^{+2} + 2e^{-}$

- A cathodic reaction of reduction of a chemical species (typically oxygen and hydrogen) that consumes the electrons made available by the anode process:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^{--}$
$2H^+ + 2e^- \rightarrow H_2$

- The conduction of electrons in the metal from the anode to the cathode:

- The current circulation in the electrolyte from the anodic zones to the cathodic zones.

The overall reaction of the corrosion process is as follows:

$Fe + O_2 + 2H_2O \rightarrow Fe^{2+} + 4OH^-$.

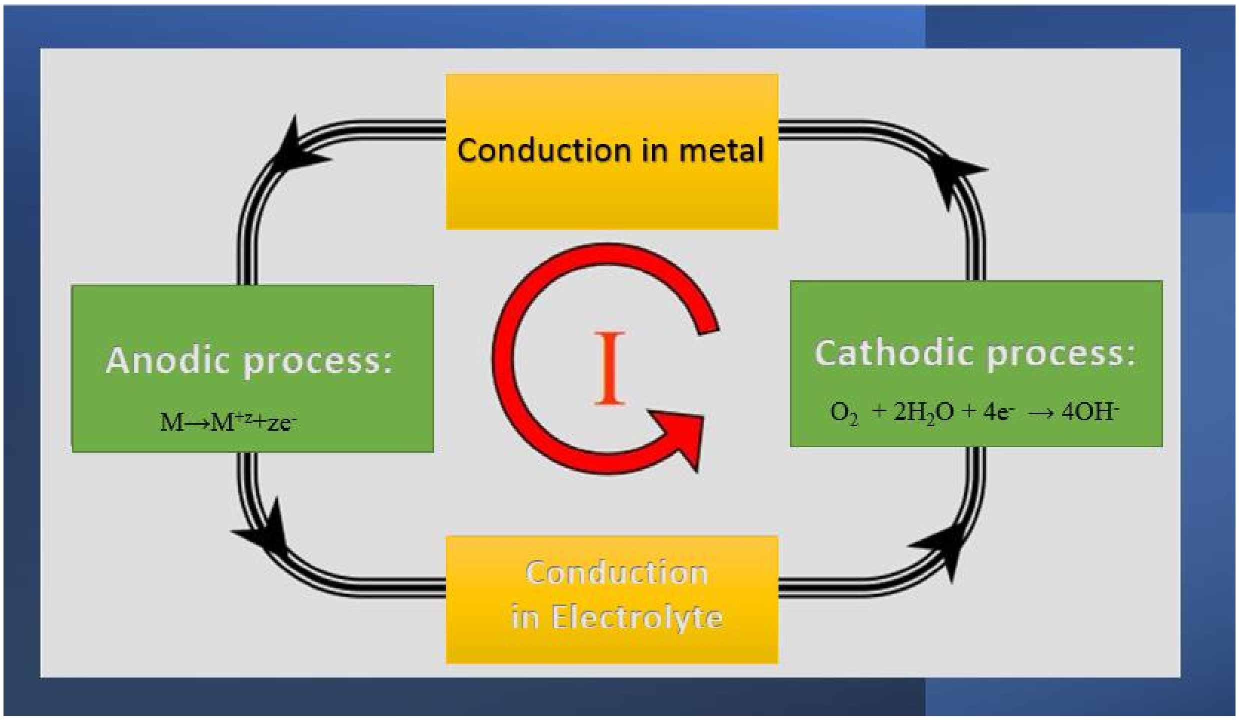


Figure.18: The four processes of the electrochemical mechanism

7.4. Corrosion analysis methods

Electrochemical evaluations are carried out using the following approaches to determine the corrosive process:

- measurement of corrosion potential.

- indirect electrochemical measurements.

7.4.1.Measurement of corrosion potential

The voltmeter is a device that allows you to monitor the potential of a metal that comes into contact with a solution. Through this electrochemical analysis, the potential difference at the two points of a circuit is measured.

To carry out the measurement, a reference electrode is used, put in contact with the concrete surface, which is immersed in a solution in which the compatible electrolyte is present.

The positive pole is connected to the metal whose potential you want to measure, while the reference electrode is connected to the negative pole.

The surrounding environment closes the circuit and allows the high-impedance voltmeter to measure the potential of the metal relative to the electrode.

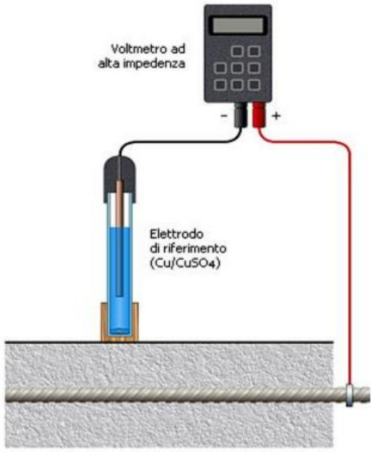


Figure.19: Instruments for measuring corrosion potential

The saturated calomel electrode (SCE), which has a potential of +241 mV when compared to the conventional hydrogen electrode, is a common universal reference electrode (Standard Hydrogen Electrode).

The measurement is defined as the free corrosion potential $E_{corr,}$ index of the probability of corrosion.

By detecting the potential value of the bars for their length and representing their values using color scales, it is possible to map the potential.

This makes it possible to identify the damage, before it spreads, causing major corrosion and degradation.

7.4.2. Indirect electrochemical measurements

- **Linear polarization measurements**

The diagram's validity is limited to reactions involving pure metals, pure water, and species that can result from these interactions; impurities and alloying elements in the metal, as well as compounds dissolved in water, can have a substantial impact on the diagram. Furthermore, they are solely based on thermodynamic data and do not include information on reactions: the considerations are limited to equilibrium conditions in specific environments, and variables such as temperature and flow rate, which are not taken into account, can have a significant impact on the rate of corrosion.

The electrochemical method of measuring linear polarization allows the corrosion rate to be determined.

It entails providing an external current to the metal, which affects its corrosion condition somewhat while leaving its potential unchanged, allowing the corrosion rate to be determined.

Electrochemical methods (such as linear polarization measurement) can be used to measure the corrosion rate, which allows tracing the corrosion rate of the reinforcement without changing its potential by slightly altering the corrosion conditions of the metal through the application of an external current.

This test requires a potentiostat, which is made up of three electrodes:

1. Electrode W = working electrode, i.e., the element being evaluated.

2. Electrode R = reference electrode
3. Electrode C = counter electrode, which has the task of delivering the current during the evaluation of the test, alternating cathodic (positive) and anodic (negative) polarization to the metal.

This approach requires the use of three electrodes: in addition to the metal to be evaluated (working electrode, W = working) and the reference electrode (R), a counter electrode (C) is employed to polarize the metal cathodically or anodically during the test.

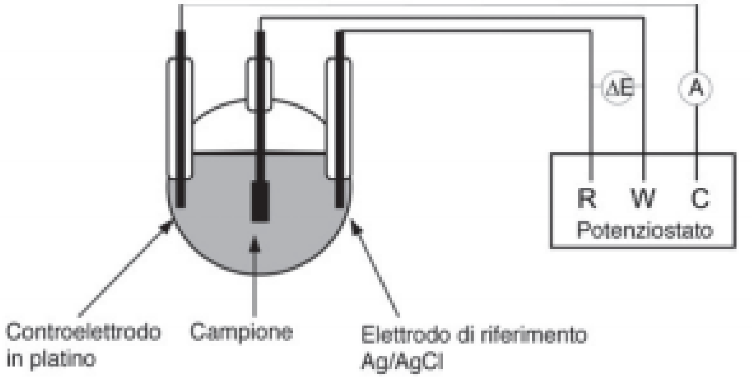


Figure.20: Scheme of potentiostat and a chemical cell

By passing current through the potentiostat, the metal is polarized in a very tiny range at a fixed value (10mV).

The current is supplied by a potentiostat, which can impose a certain potential on the metal while circulating the current required to polarize it at that value.

The relationship between potential (E) and external current (i_{corr}) is almost linear in this very small interval, and the theory developed by Stearn and Geary states that the slope of the line that connects the potential E and the current I around Ecorr (called polarization resistance Rp measured in $\Omega \cdot m^2$) is inversely proportional to the corrosion rate (i_{corr}) through the expression:

$$\boxed{i_{corr} \quad \frac{B}{R_p}}$$

Where,

i_{corr} is the external current supplied (mA/m^2),

B is a characteristic constant of every environment-metal (mV).

This method, known as the polarization resistance method, is the most extensively used among electrochemical analysis techniques.

The polarization resistance method, invented by Stern and Geary, is an electrochemical method for evaluating corrosion rate.

The potential/current polarization curves of a metal can be obtained using this technique, from which the polarization resistance and corrosion rate can be calculated.

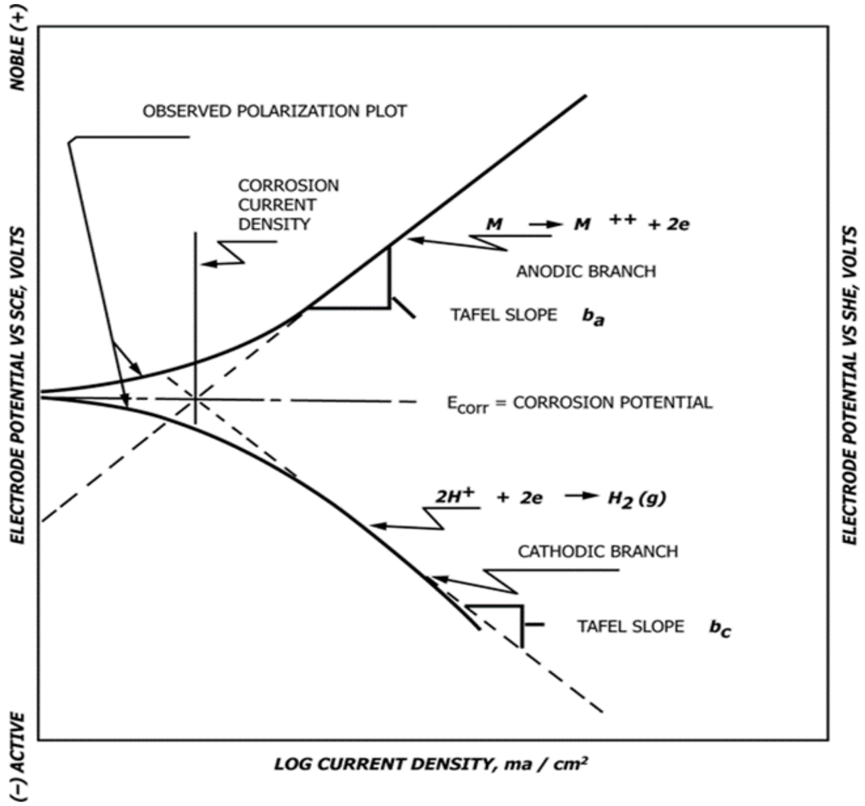


Figure.21: Polarization curves in logarithmic scale

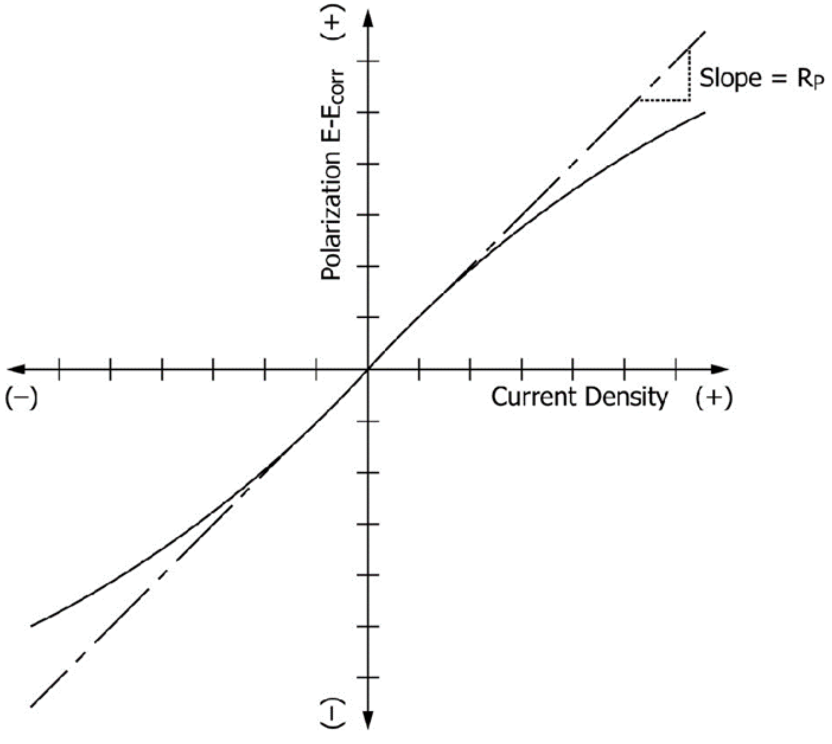


Figure.22: Linear polarization curve

As shown in the figure, the test involves polarizing the metal in a limited range (10 mV) around its free corrosion potential, where the relationship between the potential (E) and the external current (i external) is practically linear.

The slope of the line connecting E and I around Ecorr (called polarization resistance, Rp, measured in m2) is inversely proportional to the corrosion rate [mA/m2], according to the following formula discovered by Stern and Geary:

$$\boxed{i_{corr} \quad \frac{B}{R_p}}$$

where the constant B [mV] is characteristic of any material-environment coupling.

7.5. Corrosion tests on mortars

The corrosion experiments on mortars, as well as the results obtained in a previous paper, are presented in the following paragraphs for completeness. These tests were conducted in a variety of environments, including those where corrosion is aided by the presence of chlorides.

7.5.1Method of measuring corrosion under environmental conditions

The Autolab PGSTAT 204 potentiostat/galvanostat was used for the analysis.

Through the three terminals, the equipment described in the preceding paragraph was connected to the specimen being measured.

1. A working electrode (W) is linked to the analysis bar object.

2. Calomel reference electrode (R) with saturated calomel (SCE, +0.241 mV versus SHE).

3. counter-electrode (C)

The Autolab PGSTAT 204 potentiostat/galvanostat was used to do corrosion testing. Three terminals connected to the specimen:

Figure.23: Instrumentation used for corrosion testing and connections with the specimen to be tested.

- One connected to the reference electrode.
- One connected to the counter electrode.
- The remaining connected to the steel bar under analysis.

The polarization resistance (Rp) measurements are used to calculate the corrosion resistance of the bars.

The reference electrode is placed into holes in the specimen that have been filled with a saturated Ca(OH)2 solution, allowing for proper electrolyte contact between SCE and the cement matrix.

This enables the free corrosion potential to be determined, which in turn defines the corrosion trend.

Measurements of polarization resistance were used to test the corrosion resistance of the reinforcing bars (Rp). Measurements of the free corrosion potential (Ecorr) in steel rods were used to assess the corrosion trend, with a saturated calomel electrode (SCE, +0.241 mV versus SHE) serving as a reference. The pores in the specimen for inserting the reference electrode were filled with a saturated solution of sodium chloride to ensure electrolyte contact between the SCE and the cement matrix.

Figure.24: SCE electrode

The linear polarization method was used to measure Rp, and the potential was changed from -10 mV to +10 mV with respect to Ecorr.

Corrosion tests were conducted on each sample in each of the four reinforcing bars.

For two months, measurements were taken at regular intervals, then again during the maturation period (28 days after casting) and the following month.

The samples were matured in the formwork and cell for the first 7 days before being evaluated under environmental conditions for the remainder of the evaluation.

7.5.2 Results of corrosion tests under environmental conditions

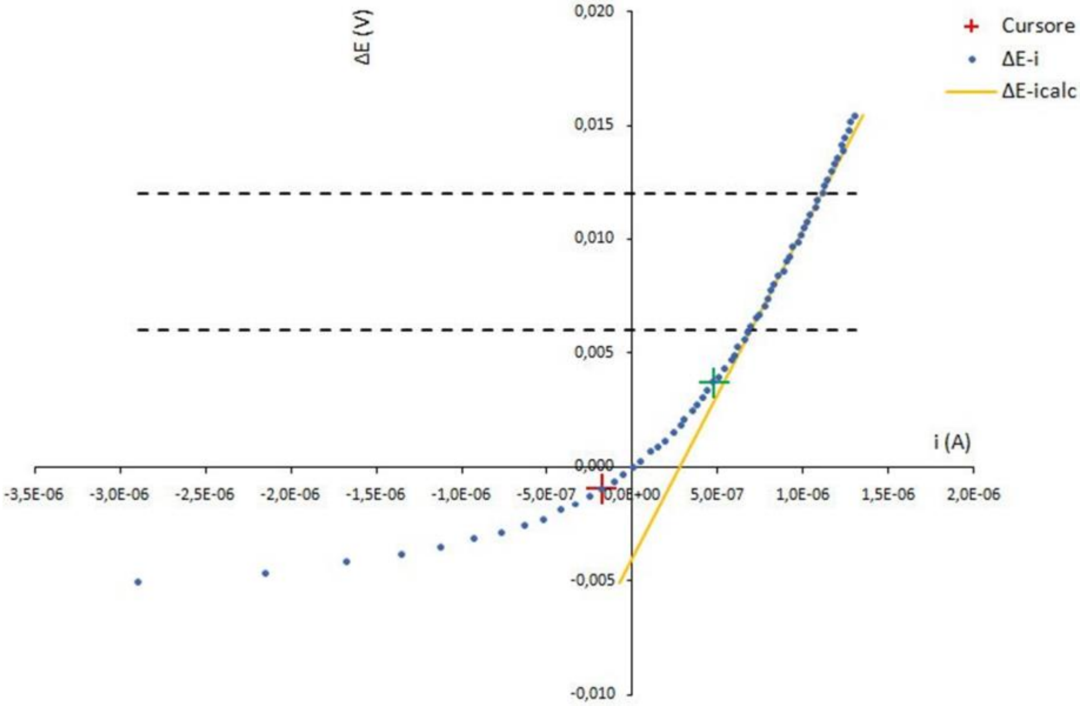


Figure.25: Polarization Curve Obtained from Excel Spreadsheet

It should be noted that the ASTM G3-14 standard describes the determination of resistance using the linear polarization curve, which is done by evaluating both the anode and cathode branches.

For the determination of the polarization resistance in the reinforcing bars immersed in a cement matrix, only to the anode branch has been considered.

As a result, the resistance (R) was computed using the value of the slope in a linear segment of the curve far from the zero circle in the anode branch:

$$R[\Omega] = \frac{\Delta \mathrm{E}}{\Delta I}$$

The polarization resistance was calculated by multiplying R by the surface area of the corrosion-prone bar (16 cm2):

$$R_p[\Omega \cdot cm^2] = R \cdot A_b$$

Furthermore, the medium's electrical resistance is defined as a material's ability to resist the passage of electric charges and is measured in ohms (Ω).

Electrical impedance tests using the Autolab instrument were used to determine the resistance of the medium to current passage in this experiment. The electrical impedance (Z) was measured over a frequency range of 10 to 100000 Hz.

The average values of Z in the range where the phase is approximately 0° were used to determine the value of Z, which takes into consideration the influence of the ohmic fall (values circled in Figure). The resistive behavior of the investigated sample is shown by these Z values.

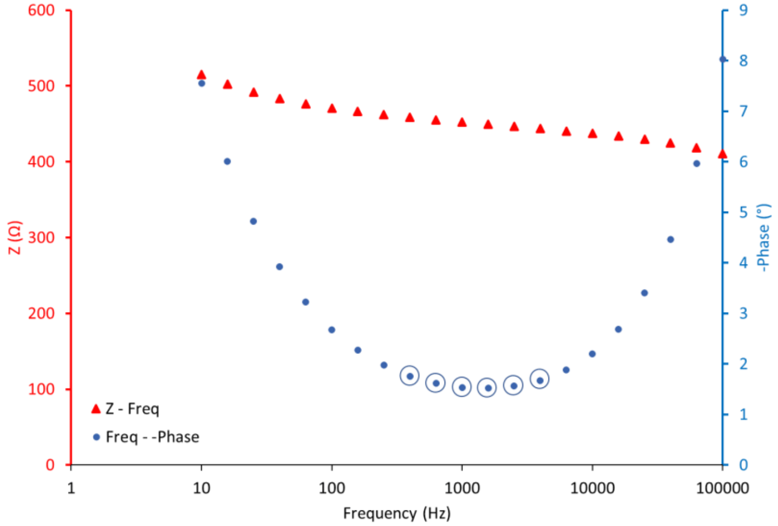


Figure.26: Example graph of Z impedance and phase as frequency changes. The values circled in the phase curve are those at which the average value of the resistance of the medium has been calculated

The average value of Z was multiplied by the area of the reinforcing bar exposed to corrosion (equal to 16 cm^2), the value thus obtained was then subtracted from the polarization resistance (R_p) to consider the ohmic fall.

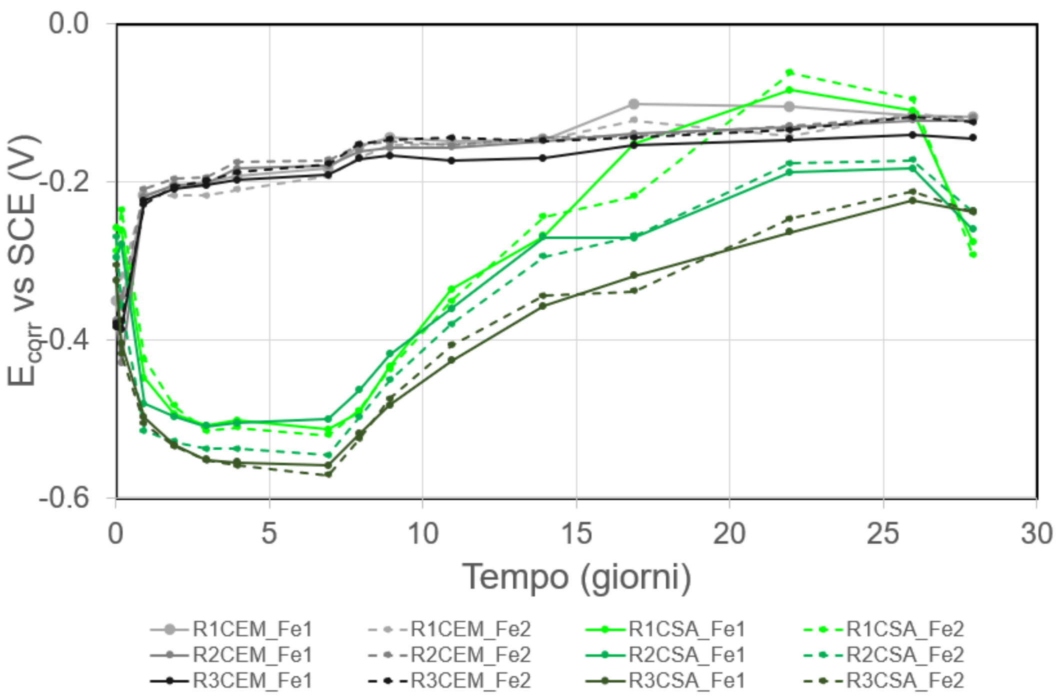


Figure.27: Graphs of the Ecorr trend, in the first 28 days of curing, for Fe reinforcement.

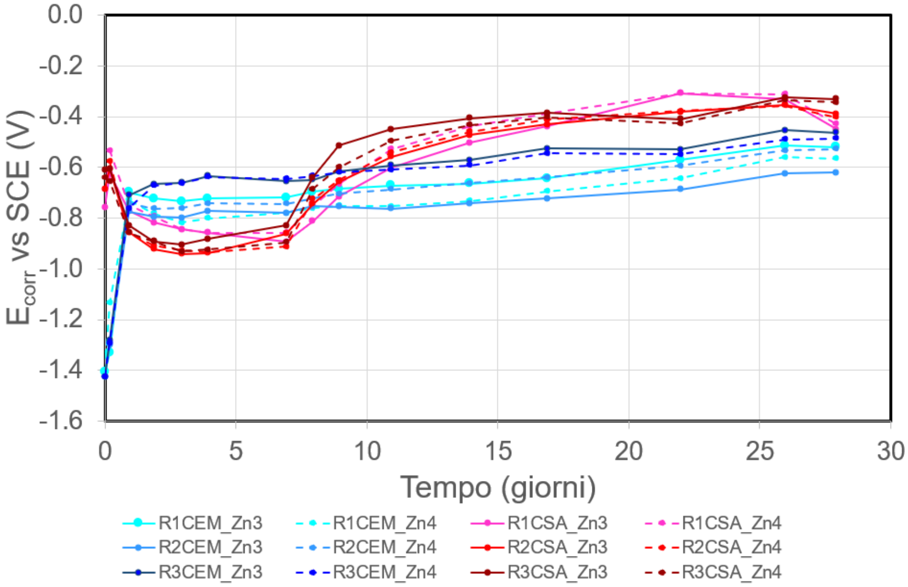


Figure.28: Graphs of the Ecorr trend, in the first 28 days of curing, for Zn reinforcements.

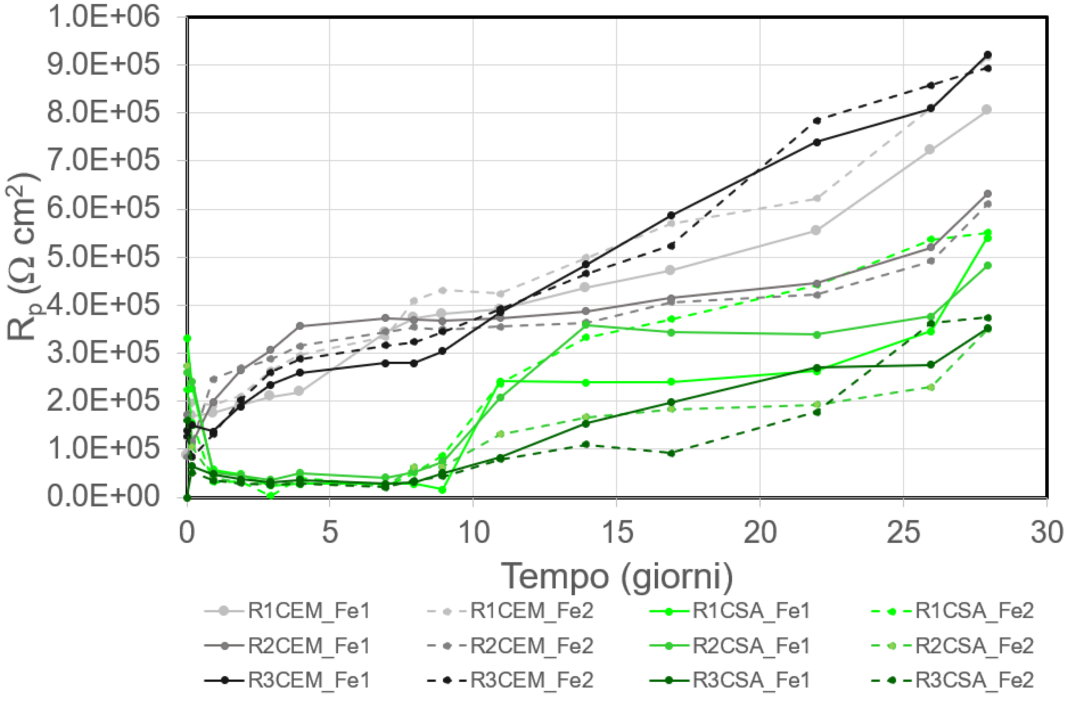


Figure.29: Graphs of the Rp trend, in the first 28 days of curing, for Fe reinforcement.

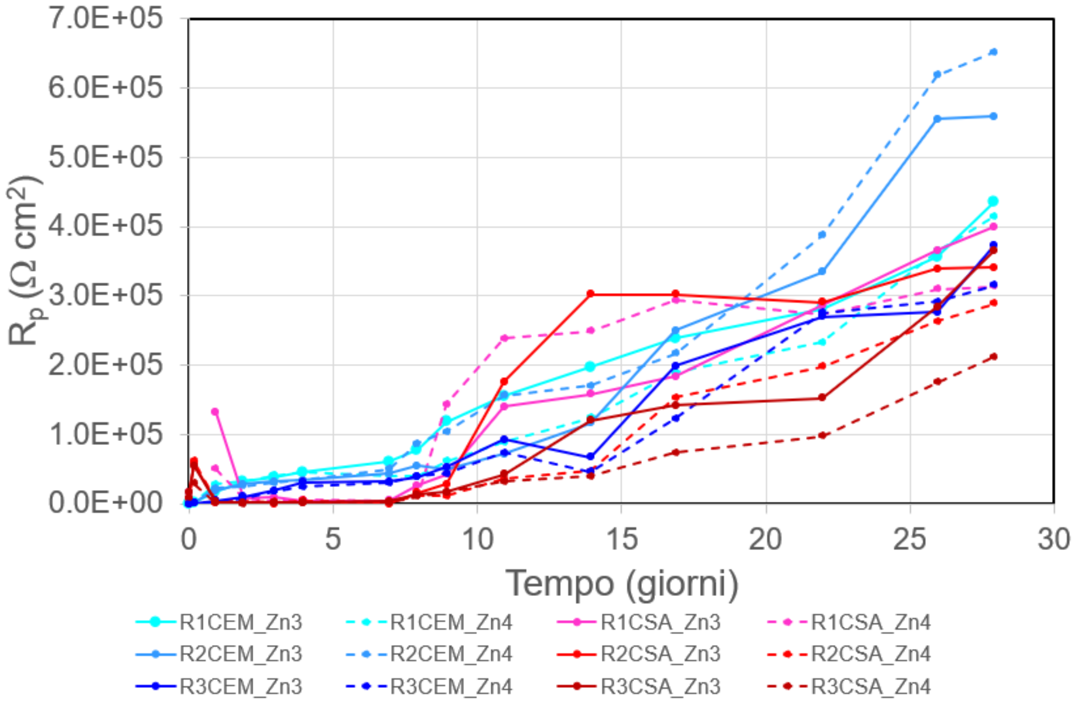


Figure.30: Graphs of the Rp trend, in the first 28 days of curing, for Zn reinforcements.

7.5.3 Discussion of results

The tables show the results of electrochemical tests performed on carbon steel and galvanized steel bar and reinforcement during the first month of maturity.

The reinforcing bars behave differently in the CEM and CSA matrices. Because the corrosion potential Ecorr -0.350 V/SCE is high for carbon steel bars immersed in concrete mortars immediately after casting, independent of the strength class, these reinforcements are active. After one day of curing, the corrosion potential rises to roughly -0.210 V/SCE, indicating that the reinforcements have become passivated. This is caused by the extreme alkalinity of the Portland cement matrix, which reaches a pH of greater than 13 after only one day of casting. Ecorr then increases during the course of the 28-day curing period, suggesting that the reinforcing irons are still passive.

The polarization resistance of the carbon steel reinforcements follows the Ecorr pattern; in fact, the values of Rp increase over time, reaching values of roughly $9 \cdot 10^5$ $\Omega \cdot cm^2$ for R3 CEM bars, $6 \cdot 10^5$ $\Omega \cdot cm^2$ for R2 CEM bars, and $8 \cdot 10^5$ $\Omega \cdot cm^2$ for R1 CEM bars. During the first 7 days of curing, the carbon steel bars immersed in the CSA matrices record very negative Ecorr values, ranging from -0.500 to -0.570 V / SCE, indicating an active state of the reinforcements. Ecorr begins to rise after this interval and reaches values around -0.260 V/SCE during the course of the curing. This is owing to the fact that the pH of CSA mortars is lower than that of cement during the first week, but as the curing progresses, it rises to around 12.5. In addition, the mortars were demoulded 7 days after casting, allowing air to progressively infiltrate the matrix and passivate the reinforcement. Because R1 CSA matrices are the most porous, this mechanism is more prominent. The polarization resistance of the bars submerged in the CSA matrices follows the Ecorr trend, with very low values during the first 7 days and steadily increasing values until the end of the 28-day curing period.

The risk of corrosion of galvanized steel bars immersed in CEM matrices is high immediately after casting, with Ecorr -0.950 V/SCE, indicating that Fe is active because the matrix pH is extremely alkaline. The irons show increasing values of Ecorr after a day of curing because zinc hydroxide (Zn (OH)2) or calcium hydroxyzincated (CAHZn) forms, causing the galvanized steel reinforcements to passivate. The trend of Ecorr is mirrored by the movement of Rp, which increase for the past 28 days.

The reinforcing bars appear to be passive immediately after the cast, but due to the limited availability of Ca and OH after a day of curing, they become active, and Ecorr drops to around -0,900 V / SCE up to 7 days after the cast. The entrance of oxygen into the matrix after 7 days, because the specimens have been dismoulded, allows the passivation of the galvanized bars; in fact, as you can see from the graph, Ecorr grows progressively until the end of the curing. Although the polarization resistance of galvanized steel bars immersed in CSA mirrors the trend of Rp, it does not reflect the trend of Ecorr.

When the Rp values of carbon steel and galvanized steel reinforcements are compared, it is clear that with the same type of matrix in both CEM and CSA mortars, the polarization resistance of carbon steel bars is always higher than that of galvanized steel bars.

7.6 Corrosion tests in the presence of chlorides

7.6.1.Resin coating of specimens

A two-component epoxy glue was applied to the bases of the cylindrical specimens to prepare them for corrosion tests, limiting the entry of the chloride-containing solution to only the lateral surface of the samples.

The four steel bars were put into the specimens to ensure a 1.5 cm iron coating.

Figure.31: Specimens after resin coating

7.6.2.Corrosion tests

Corrosion experiments were performed on six cylindrical specimens with steel reinforcement bars inside.

Several cycles were carried out on the specimens in the following manner to better examine the corrosion due to the presence of chlorides:

- Initially, dry measurements were taken.
- then, the specimens were immersed in a 3.5% NaCl aqueous solution.
- the second measurement was taken two days following the immersion.
- and finally, the samples were removed from the solution and permitted to dry for five days.

In order to ensure an adequate stable concentration over time, we tried not to vary the level of the solution inside the containers, adding adequate amounts of solution

The corrosion behavior of both bare and galvanized steel reinforcements embedded in geopolymer and ordinary Portland cement-based mortars with three different strength classes (R1≥10 MPa, R2≥15 MPa and R3≥25 MPa) was investigated and compared both in the first month of curing and during 12 weekly wet-dry cycles in a 3.5% NaCl solution.

Figure.32: Specimens in 3.5% NaCl aqueous solution.

Twice during each cycle, measurements of corrosion potential (Ecorr)and polarization resistance (R p) were performed.

Figure.33: wet and dry potential measurements

7.6.3.Final Results of corrosion tests in the presence of chlorides

Here showing some of the values i.e, RP and Ecorr got from the total 15 wet/dry cycles of **Fe** reinforcements from AUTOLAB:

Data e ora getto:	7/27/2021 9:30	R1CEM_Fe1					R1CEM_Fe2				
Data e Ora	**Tempo (giorni)**	**Ecorr (V)**	**Ecorr_m (V)**	**|Z| LF (ohm cmq)**	**Rp_NC (ohm cmq)**	**Rp (ohm cmq)**	**Ecorr (V)**	**Ecorr_m (V)**	**|Z| LF (ohm cmq)**	**Rp_NC (ohm cmq)**	**Rp (ohm cmq)**
7/29/2021 9:00	2.000000	-0.540	-0.542	467	55796	55329	-0.521	-0.524	427.5590043	57198.62367	56771.06467
8/3/2021 9:00	6.979167	-0.430	-0.433	2878	55279	52401	-0.402	-0.404	2479.346763	69676.88872	67197.54196
8/5/2021 9:00	8.000000	-0.583	-0.586	400	48481	48081	-0.578	-0.581	433.2665023	45313.09877	44879.83227
8/24/2021 9:00	27.979167	-0.448	-0.448	7355	55055	47700	-0.415	-0.415	6478.771942	74445.22474	67966.45279
8/26/2021 9:00	29.979167	-0.636	-0.639	414	13804	13390	-0.596	-0.599	429.4183349	21036.36261	20606.94428
8/31/2021 7:00	34.895833	-0.516	-0.518	2026	23695	21669	-0.5	-0.502	1960.370454	31412.46337	29452.09292
9/2/2021 7:00	36.895833	-0.628	-0.631	403	12483	12080	-0.605	-0.608	450.0650015	16639.06644	16189.00144

Graphs:

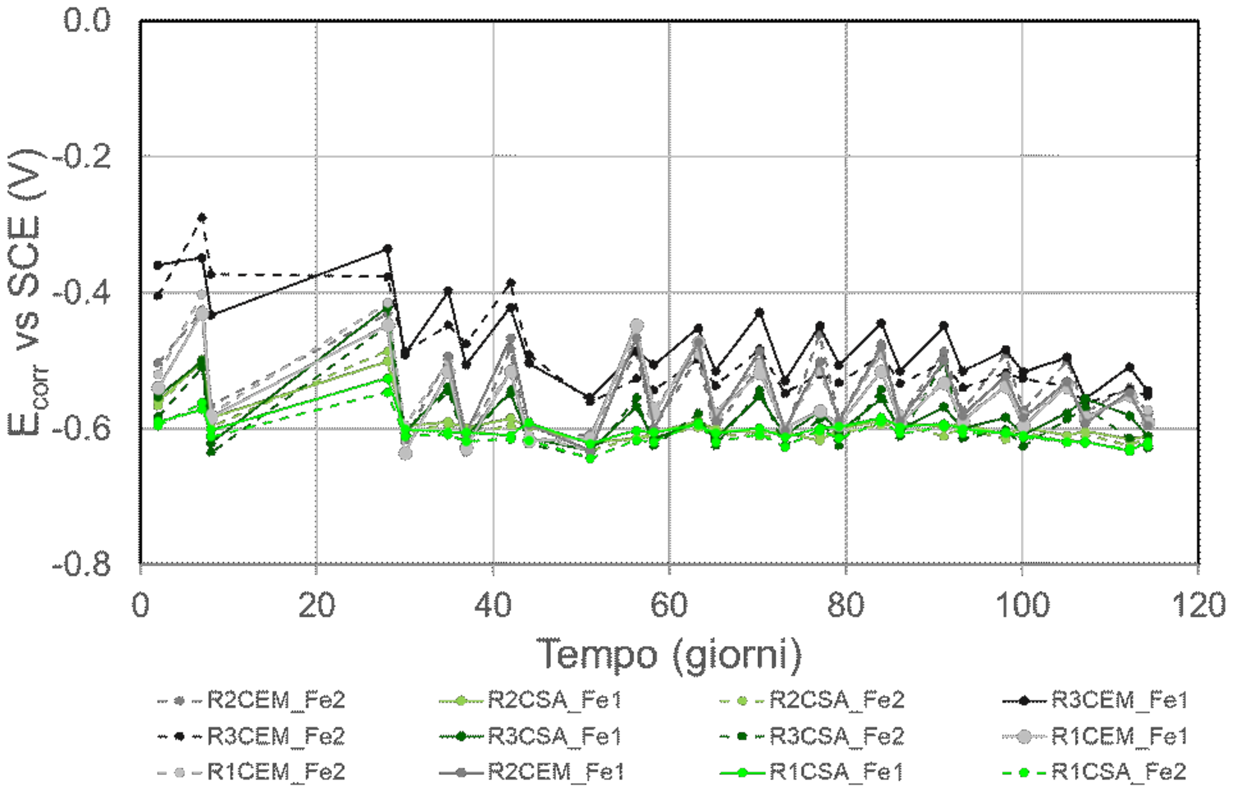


Figure.34: Graphs of the Ecorr trend, for Fe reinforcement.

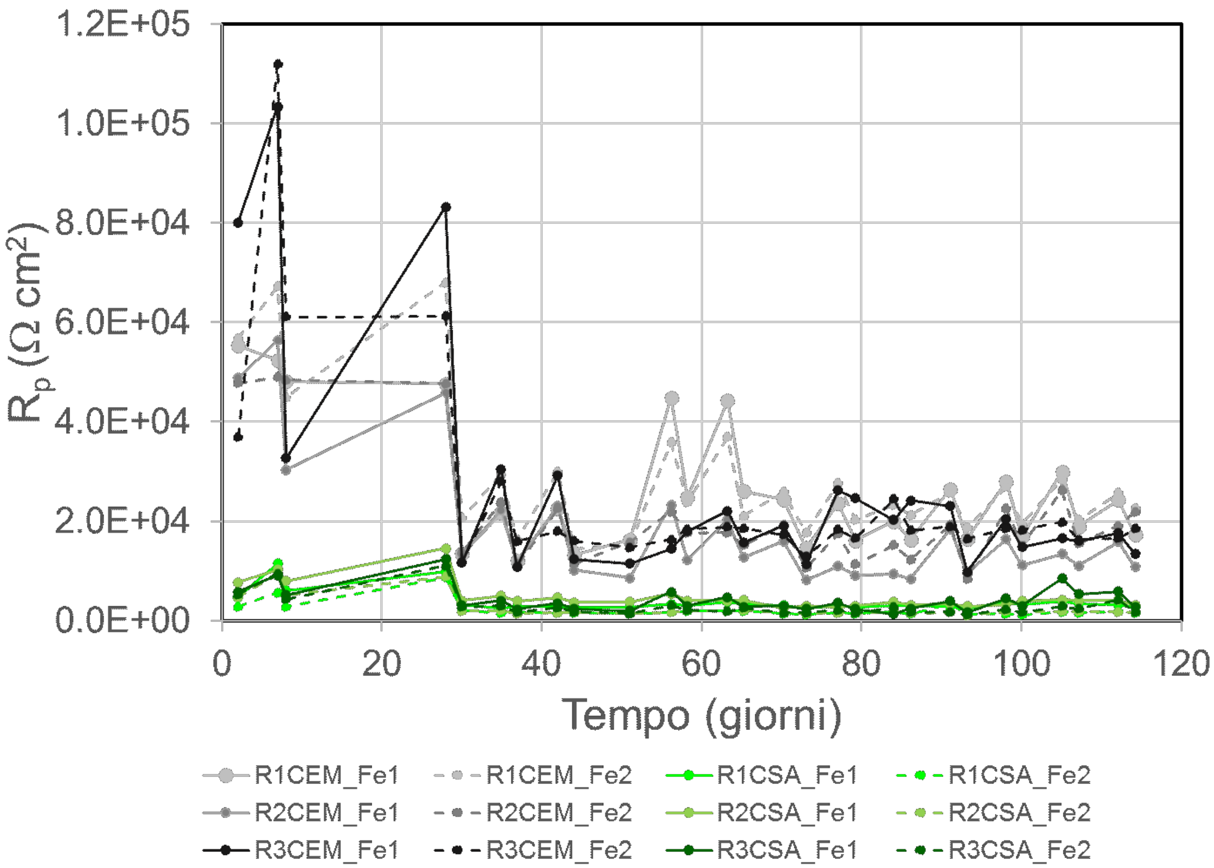
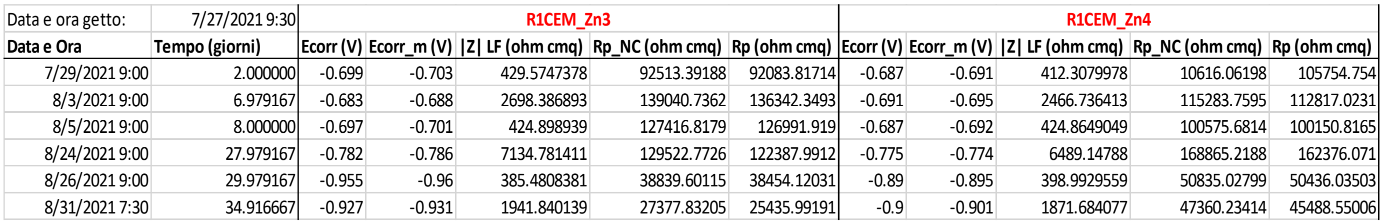


Figure.35: Graphs of the Rp trend, for Fe reinforcement

Then, showing some of the values i.e, Rp and Ecorr got from the total 15 wet/dry cycles of **Zn** reinforcements from AUTOLAB :



Data e ora getto:	7/27/2021 9:30	R1CEM_Zn3					R1CEM_Zn4				
Data e Ora	**Tempo (giorni)**	**Ecorr (V)**	**Ecorr_m (V)**	**|Z| LF (ohm cmq)**	**Rp_NC (ohm cmq)**	**Rp (ohm cmq)**	**Ecorr (V)**	**Ecorr_m (V)**	**|Z| LF (ohm cmq)**	**Rp_NC (ohm cmq)**	**Rp (ohm cmq)**
7/29/2021 9:00	2.000000	-0.699	-0.703	429.5747378	92513.39188	92083.81714	-0.687	-0.691	412.3079978	10616.06198	105754.754
8/3/2021 9:00	6.979167	-0.683	-0.688	2698.386893	139040.7362	136342.3493	-0.691	-0.695	2466.736413	115283.7595	112817.0231
8/5/2021 9:00	8.000000	-0.697	-0.701	424.898939	127416.8179	126991.919	-0.687	-0.692	424.8649049	100575.6814	100150.8165
8/24/2021 9:00	27.979167	-0.782	-0.786	7134.781411	129522.7726	122387.9912	-0.775	-0.774	6489.14788	168865.2188	162376.071
8/26/2021 9:00	29.979167	-0.955	-0.96	385.4808381	38839.60115	38454.12031	-0.89	-0.895	398.9929559	50835.02799	50436.03503
8/31/2021 7:30	34.916667	-0.927	-0.931	1941.840139	27377.83205	25435.99191	-0.9	-0.901	1871.684077	47360.23414	45488.55006

Graphs:

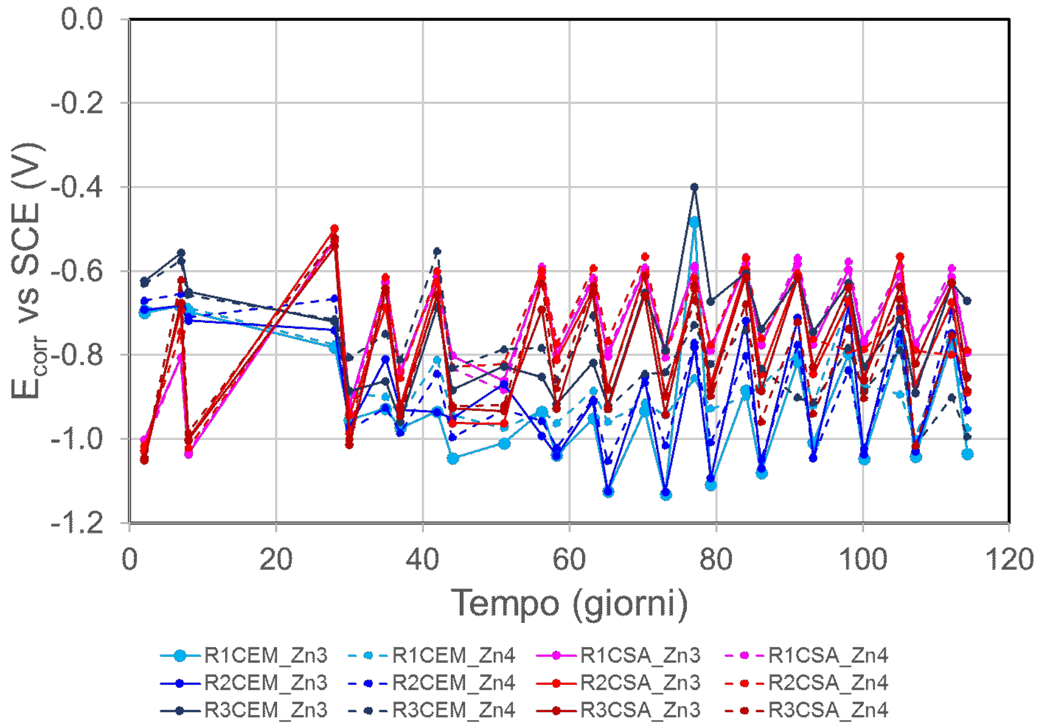


Figure.36: Graphs of the Ecorr trend, for Zn reinforcements;

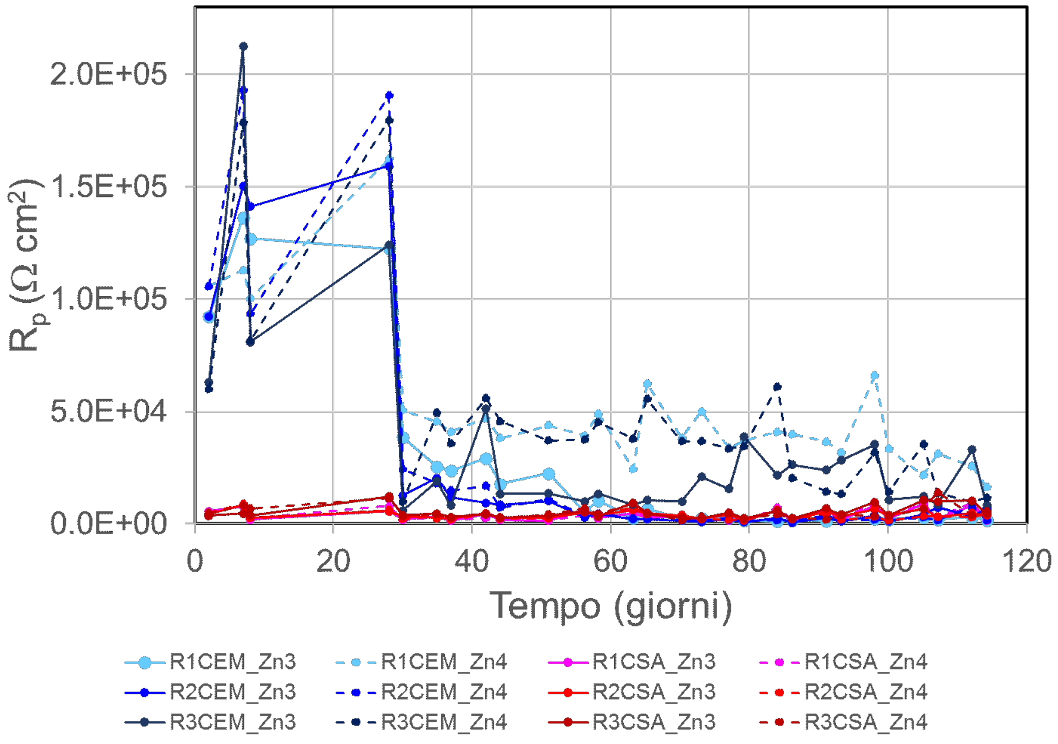


Figure.37: Graphs of the Rp trend, for Zn reinforcements.

7.6.4. Discussion of results

The graphs from Figure.34 to Figure.37 show the electrochemical behavior of the reinforcement bars during the wet/dry cycles i.e,15 cycles.

The graphs show the trend change in the measurements from day 8 to day 28, since they fell during the summer period when the University was closed, and between days 44 and 51, since the specimens remained immersed in the solution for a whole week.

In both types of matrices, the black steel reinforcement bars are immediately active as the Ecorr values are lower than -0.350 V / SCE and are all the more negative the lower the resistance class of the matrices in which they are immersed (Figure 34). This effect is probably due to the porosity of the mortars which is greater the lower the resistance class is, i.e., it increases from R3 to R1. Furthermore, for the bars immersed in the CSA matrices the Ecorr values are always lower than those of the bars immersed in the CEM matrices. The trend of the Ecorr values shows a decrease after two exposure cycles. By the end of the wet-dry cycles the values of steels in R3CEM is around -0.550 V/SCE, in R2CEM is around -0.580 V/SCE, in R1CEM is around -0.580 V/SCE, in R3CSA is around -0.620 V/SCE, in R2CSA is around -0.610 V/SCE and R1CSA is around -0.620 V/SCE.

As for the resistance to polarization Rp, the bars immersed in the CSA matrices show much lower values than the bars immersed in the CEM (Figure 35). Initial values in wet state for steels in CEM mortars are around 60000 $\Omega\cdot cm^2$ and in dry state the values are around 70000 $\Omega\cdot cm^2$ and the values for steels ins CSA mortars in wet state are around 5000 $\Omega\cdot cm^2$ and in dry state the value are around 10000 $\Omega\cdot cm^2$. in general, the differences in values between dry and wet measurements are much less noticeable for rebars immersed in CSA than in CEMs, probably because the CSA matrix is more compact than the CEM matrix. With the same type of matrix, black steel reinforcements immersed in Portland cement mortars are less affected by cycles if immersed in class R3 than in classes R2 and R1, since also in this case the matrix is more compact. On the contrary, in CSA mortars the trend is the opposite. At the end of the exposure the values of rebars embedded in CEM mortars are around 18000 Ω· cm^2 and for those embedded in CSA mortars are around 1700 Ω· cm^2, which is approximately one order of difference.

As regards the galvanized steel reinforcements (Figure 36), the results show that those immersed in the CSA matrices are active immediately during the first wet measurement, while those in the CEM matrices are activated after 3 exposure cycles. At the beginning, the values of galvanized steels are -0.690 V/SCE, and -0.670 V/SCE and -0.630 V/SCE in wet condition for those embedded in R1CEM, R2CEM and R3CEM, respectively. Conversely, the values are around -1.000 V/SCE for those embedded in CSA matrices. During the exposure it is noted that the bars immersed in the CSA mortars tend to passivate as the dry-wet cycles progress, while those immersed in the CEM show gradually decreasing Ecorr values. And at the end of the exposure the values in wet condition are -1000 V/SCE, -900 V/SCE and -800 V/SCE for rebars embedded in R1CEM, R2CEM and R3 CEM, respectively, whereas -900 V/SCE for those embedded in CSA mortars.

The Rp values of the CSA galvanized reinforcements are much lower than the CEM, and this difference is maintained throughout the exposure (Figure 37). At the beginning the values in wet are around 60000 Ω· cm^2 for those in R3CEM and

90000 Ω· cm^2 for those in R2CEM and R1CEM, whereas for rebars in CSA mortars values are around 5000 Ω· cm^2. The galvanized bars immersed in the CEM show a considerable lowering of the Rp values after 3 exposure cycles. This effect could be due to the aggressive action of the chlorides that have reached the reinforcement bars. The values at the end of the 15 wet/dry cycles are around 11000 Ω· cm^2 for rebars in R3CEM and 6000 Ω· cm^2 for rebars in R1CEM and R2CEM, whereas they remain around 5000 Ω· cm^2 for those embedded in CSA mortars.

By comparing the Rp values of the black steel (Figure 35) and galvanized steel (Figure 37) bars, it can be seen that for the same type of matrix in the CEM mortars during the first 3 cycles the galvanized reinforcements show Rp greater than those in steel black, this trend is reversed for subsequent cycles. On the contrary, in CSA mortars during the first 3 cycles the black steel bars show higher values than the galvanized steel bars, while later these trends are reversed.

Conclusion

During the period, comparing the carbon steel reinforcing bars immersed in the CEM and CSA matrices, it is clear that, regardless of the strength classes, the concrete matrices allow a greater passivation of the reinforcing irons, because they are more alkaline.

During dry-wet cycles, despite the fact that the bars lead to active values in both matrices, the greatest protection from chloride attack is given by CEM matrices.

As with carbon steel bars, galvanized steel bars are also more protected from corrosion when immersed in the cement matrix, regardless of the classes of mechanical strength.

In the curing period, the carbon steel bars show R_p always greater than the galvanized bars, with the same types of matrices.

At the end of the exposure of the cycles, the black steel bars show R_p greater than the galvanized ones when immersed in the CEM matrices.

This result is reversed for reinforcement bar immersed in CSA mortars.

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