



ΕΘΝΙΚΟ ΜΕΤΣΟΒΙΟ ΠΟΛΥΤΕΧΝΕΙΟ

ΔΙΑΤΜΗΜΑΤΙΚΟ ΠΡΟΓΡΑΜΜΑ  
ΜΕΤΑΠΤΥΧΙΑΚΩΝ ΣΠΟΥΔΩΝ (Δ.Π.Μ.Σ.)

*"ΕΠΙΣΤΗΜΗ ΚΑΙ ΤΕΧΝΟΛΟΓΙΑ ΥΛΙΚΩΝ"*

# ΒΕΛΤΙΩΣΗ ΑΝΘΕΚΤΙΚΟΤΗΤΑΣ ΑΣΒΕΣΤΟΛΙΘΙΚΩΝ ΤΣΙΜΕΝΤΩΝ

ΜΕΤΑΠΤΥΧΙΑΚΗ ΕΡΓΑΣΙΑ  
**ΑΤΤΕΥΕΗOSSADAT SEYEDALHOSSEINI NATANZI**  
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**ΑΘΗΝΑ, Ιούλιος 2013**



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**NATIONAL TECHNICAL UNIVERSITY OF ATHENS**  
**SCHOOL OF CHEMICAL ENGINEERING**  
**M.Sc. IN MATERIALS SCIENCE AND TECHNOLOGY**

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**Improving Durability of Different Limestone Cement and  
Effects of it on Reinforcement**

**M.Sc. Thesis**  
**Atteyhossadat Seyedalhosseini Natanzi**

**Supervisor:**  
**Prof. George Batis**

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## ΠΕΡΙΛΗΨΗ

Το οπλισμένο σκυρόδεμα είναι παγκοσμίως το περισσότερο χρησιμοποιούμενο υλικό στις κατασκευές. Το Σκυρόδεμα αρχικά παρέχει ένα προστατευτικό αλκαλικό περιβάλλον γύρω από τον οπλισμό. Η διάβρωση του χάλυβα όμως, ως θερμοδυναμικά αυθόρμητο φαινόμενο, συμβαίνει είτε οφειλόμενη στην ενανθράκωση του σκυροδέματος που τελικά μειώνει το αλκαλικότητα, είτε στην διείσδυση των χλωριόντων που καταστρέφουν το προστατευτικό στρώμα οξειδίων του οπλισμού.

Η διάβρωση του οπλισμένου σκυροδέματος είναι ένα σημαντικό πρόβλημα σε όλο τον κόσμο, απαιτώντας σημαντικά οικονομικά ποσά επισκευής και αποκατάστασης. Η διάβρωση του οπλισμού μπορεί να αντιμετωπιστεί με μεθόδους όπως η χρήση επιφανειακών επικαλύψεων ή χρήση ανοξειδώτου χάλυβα, είτε με την χρήση αναστολέα διάβρωσης.

Ο κύριος σκοπός της παρούσας εργασίας είναι η σύγκριση των ασβεστολιθικών τσιμέντων με CEM II που εκτίθενται σε διαβρωτικό περιβάλλον.

Τα δοκίμια φτιάχτηκαν από CEMII και ασβεστολιθικά τσιμέντα. Τα ασβεστολιθικά δοκίμια παρήχθησαν με τη χρήση δύο ειδών τσιμέντου, του LC1 και LC 2. Σε μερικά δείγματα προστέθηκε αναστολέας διάβρωσης, προκειμένου να μειώσει τον ρυθμό διάβρωσης του οπλισμού στο διαβρωτικό περιβάλλον. Τα δοκίμια βυθίστηκαν σε διάλυμα 3.5% NaCl.

Η διαβρωτική συμπεριφορά των δοκιμίων ελέγχεται με την παρακολούθηση των δυναμικών διάβρωσης και της απώλειας μάζας. Η ανθεκτικότητα των δοκιμίων εκτιμήθηκε με ηλεκτροχημικές μεθόδους, όπως η μέτρηση δυναμικού διάβρωσης και γραμμική πόλωση.

Τα αποτελέσματα και οι μετρήσεις κατέδειξαν ότι : Οι οπλισμοί των δοκιμίων με τσιμέντο CEM II είχαν μικρότερη διάβρωση από ότι οι οπλισμοί των ασβεστολιθικών τσιμέντων. Η προσθήκη αναστολέα διάβρωσης σε τσιμέντα τύπου CEM II και LC 2 μείωσε την απώλεια μάζας των οπλισμών. Η προσθήκη αναστολέα διάβρωσης σε τσιμέντο τύπου LC 1 δεν είχε καμία επίδραση στην διάβρωση των οπλισμών.

## **Abstract**

Reinforced concrete is worldwide the most widely used constructional material. Concrete initially provides a protective alkaline environment around the reinforcements. The steel bars corrosion however, as thermodynamic spontaneous phenomenon, happens either due to the carbonation of concrete that finally decreases the alkalinity or due to the chloride migration through the concrete cover which destroys the protective layer of oxides of the steel bars. The corrosion of reinforced concrete structures is a major problem throughout the world, demanding significant amounts of repair and rehabilitation. Corrosion protection is commonly performed by coating the concrete, stainless steels or by using corrosion inhibitors.

The main purpose of the present thesis is to compare the corrosion resistance of limestone cement concrete to cement concrete type CEM II exposed to corrosion environments.

Specimens made from CEMII and limestone cement. Limestone specimens were produced using two type of cement LC 1 and LC 2. Corrosion inhibitor was added in some specimens in order to reduce the corrosion rate of steel reinforcement in chloride environment. Specimens were partially immersed in 3.5% NaCl solution.

The corrosion behaviour of specimens is investigated by monitoring corrosion potentials and mass loss. The durability of specimens was evaluated by electrochemical method such as potential measurement and measuring polarization resistance ( $R_p$ ) and corrosion current with linear polarization technique.

The result revealed that in CEM II and LC 2 cases the use of corrosion inhibitor reduced significantly corrosion of rebars. In the case of cement LC 1, adding corrosion inhibitor had not any beneficial effects on corrosion of steel bars.

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## **THEORETICAL PART**

## **Chapter 1**

# **CONCRETE**

Concrete is a composite material made with aggregate, cement, and water. The compressive strength of set concrete is dependent mainly on the type of the cement in the mortar, the type of aggregate, the cement/ aggregate band, the water/ cement ratio used in the concrete mix and the degree of compaction of the wet concrete.

As well as the factor which affects the compressive strength of the set concrete, it is also necessary to investigate the factors that affect the ease of pouring of the concrete, i.e. the workability of the concrete. (Gani, 1997)

Concrete making has undergone considerable change during the last forty years or so. There have been great improvements in the design, testing, placing and curing methods. Use of computer in concrete- making has already been adopted. Recently, considerable improvement in the understanding of the affect of selection and the testing of concrete-making materials, the effect of the water-cement ratio and the optimum placing and curing of concrete have led to the development of high strength concrete. Concrete is composed of three basic components: cement, aggregate and water.

## **1.1 CEMENT**

### **1.1.1 Portland cement**

A real advance was made when, in the early nineteenth century, it was discovered that if a mixture of clay and chalk was heated, a hydraulic cement was obtained which would develop excellent strength and durability in a reasonably short time without any atmospheric action being necessary. Such cements would set as well under water as they do in the air. (Taylor, 2002)

Portland cements are so named because concretes made from them have a colour similar to that of Portland stone. They remain by far the most important cements in current use.

The production of Portland cement involves the burning of calcareous material (normally limestone, sea shell etc.) with an argillaceous material (clay, an aluminosilicate). The solid raw materials are crushed and mixed in ball mills, and then heated in a kiln to about 1500°C. The firing result in the formation of a clinker which consists of a number of compounds which set or harden when the clinker is ground to a fine powder (cement) and then mixed with water.(Gani, 1997)

Portland cement concrete is composed of three basic components: Portland cement, aggregates, and water. In addition, there are a host of other materials, called additives, that may be added to obtain special properties. These include air entraining agents, accelerators, decelerators, carbon black, fly ash, pozzolans, silica fume, water-reducing agents, superplasticizers, among others.

### **CEMENTING MATERIALS**

Any material which can be made plastic and which gradually hardens to form an artificial stone-like material is referred to as a cementitious material. Hydraulic cements, namely Portland and natural, along with limes are the principal cementing material used in structures. They become plastic by the addition of water and then the mix hardens. The

other principal type of cementing agents are asphalt which are made plastic either by heating, emulsifying, or by the addition of a cutback agent Their hardening process is totally different from that of a hydraulic substance which requires a hydration mechanism to harden. This book is only concerned with one type of hydraulic cement, Portland, although natural cements will be mentioned briefly because of their historical significance.

The earliest cement known was pozzolans cement which was first used by the Romans more than 2000 years ago. It was produced by mixing lime with a volcanic ash called pozzolana which is found near the town of Pozzuoli, Italy. Natural cement in more recent times was produced by burning at limestone high in clay and magnesia to drive off the carbonic acid and then grinding the clinker to a fine powder. In comparison to Portland cement, natural cement possesses lower tensile strength, gains strength more slowly, and is less uniform.

Portland cement was first made in Portland, England from which it derived its name by Joseph Aspdin in 1824. It can be produced by either a wet or a dry process. In the wet method the raw materials are blended and ground in a slurry condition. In the dry process operations are carried out with the materials in a dry state. Adjustments to the constituents are made by the addition of clay or stone of known characteristics. Portland cement is obtained from finely pulverizing clinker produced by calcining to incipient fusion properly proportioned argillaceous and calcareous materials. The final constituents and properties of Portland cement are very carefully controlled during the manufacture.

Portland cement comes in five basic types and a number of specially varieties to fulfil different physical and chemical requirements. The most frequently used cements are:

Type I- Normal or general purpose

Type II- Moderate sulphate resistant

Type III- High early strength

Type IV- Low heat of hydration

Type V- Sulfate resistant

Type I, II, and III with an A after the number signifies that the cement contains an air-entraining agent. There also is a white Portland cement for special purposes in Type I and III. This does not exhaust the list of hydraulic cements that are available but it will suffice for the purpose here. ( Kett, 2000)

## **MANUFACTURING PROCESS**

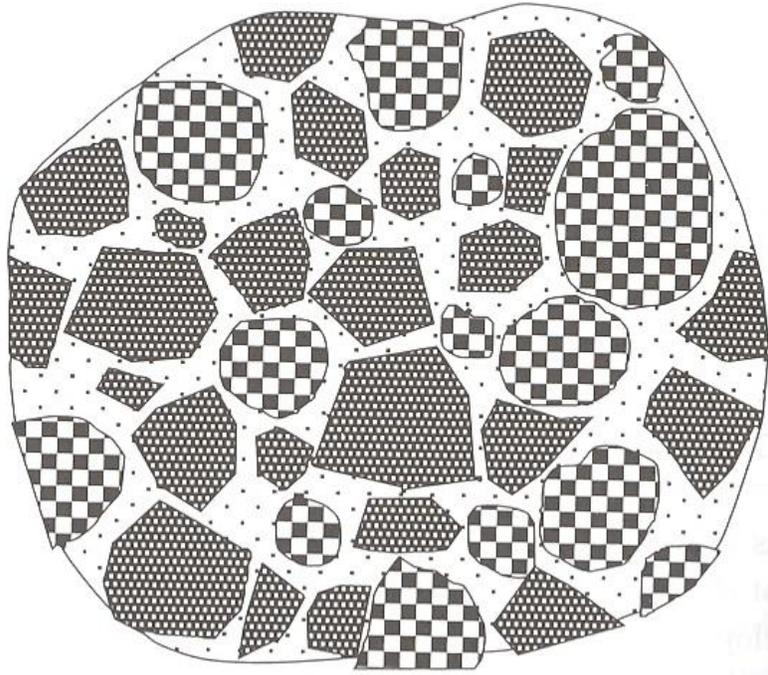
The manufacturing process is the same as that originally conceived, although by careful control cements of consistently high quality can now be achieved and various forms are obtainable according to application.

Cement chemists use specific chemical shorthand to describe the compounds in cement. The chief component of chalk or limestone is calcium carbonate,  $\text{CaCO}_3$ , which on heating yields calcium oxide  $\text{CaO}$ . This is referred to as C.

The chief ingredients in clay are, in order of decreasing amount: silica  $\text{SiO}_2$  abbreviated S, alumina  $\text{Al}_2\text{O}_3$  abbreviated A and ferrite  $\text{Fe}_2\text{O}_3$  abbreviated F.

These compounds, C, S, A and F, have little chemical interest in each other at normal temperatures but by heating to bright yellow heat (about  $1500^\circ\text{C}$ ) slow chemical combination occurs. All forms of chemical reaction take place much more readily when one of the constituents is liquid and in the case of cement manufacture the reaction begins when the metallic oxides, chiefly iron, fuse (melt). These materials are said to act as fluxes in the process. They combine with the calcium oxide to form liquid products and in this environment further reaction takes place with the silica. The latter slowly combines with calcium oxide to form two crystalline products based upon calcium silicate. The quantities of the raw materials are carefully chosen so that almost all the calcium oxide (derived from the chalk or limestone) is consumed chemically by the other ingredients. On cooling the liquid turns into a largely amorphous solid which encloses the crystalline calcium silicate forming a clinker. The crystalline materials formed at the high

temperature are: dicalcium silicate  $C_2S$  and tricalcium silicate  $C_3S$ . While the surrounding matrix contains: tricalcium aluminate  $C_3A$  and tetracalcium aluminoferrite  $C_4AF$ .



**Figure 1.1:** schematic representation of section through a grain of Portland cement

Figure 1.1 shows a schematic section of a grain of cement formed by crushing the clinker. The grain comprises angular crystals of  $C_3S$  together with more rounded crystals of  $C_2S$  in a non-crystalline background of  $C_3A$  and  $C_4AF$ . All four compounds are hydraulic though their behaviour is very different as summarised in Table 1.1.

Name	Abbreviation	Approximate percentage in OPC	Properties	Heat of hydration J/g
Dicalcium silicate	C <sub>2</sub> S	19	Slow strength gain responsible for long term strength	260
Tricalcium silicate	C <sub>3</sub> S	52	Rapid strength gain responsible for early strength (e.g. 7 days)	500
Tricalcium aluminate	C <sub>3</sub> A	10	Quick setting (controlled by gypsum) susceptible to sulphate attack	865
Tetracalcium alumino ferrite	C <sub>4</sub> AF	8	Little contribution to setting or strength responsible for grey colour of OPC	420

**Table 1.1: Properties and typical proportions of compounds in ordinary Portland cement in current use**

It is important in the production of cement to control the relative quantities of each compound produced. Some aspects of the ratios can be controlled fairly easily, for example, the ratio of C<sub>3</sub>S to C<sub>2</sub>S which will affect the rate of hardening and heat output, can be regulated by adjusting the chalk/ limestone: clay ratio. More of the former will tend to produce more C<sub>3</sub>S which contains more calcium oxide.

If iron oxide F is added specially as a separate ingredient, more C4AF and therefore less C3A will be produced, though manufacturers would prefer, if possible, to avoid the extra cost of additional ingredient to modify properties. It will be apparent that both the composition will affect the final product. In addition, the raw materials must be very finely ground in order to permit complete chemical reaction in the kiln the core of larger particles would be unable to react with surrounding materials. The temperature of the kiln must also be carefully regulated.

There are two chief aspects of the manufacturing process: the first is to produce a finely divided mixture of the raw materials-chalk/limestone and clay/ shale. The second is to heat this mixture to produce chemical combination. Two main processes may be used- the wet and the dry process- and the one chosen will be dependent on locally available materials and conditions. However, since the water used in the wet process must all be evaporated, there is now an increasing trend towards using the dry process where possible, in order to save fuel costs in production.

### **1.1.2 Hydration of Portland cement**

Hydration is the process of chemical combination between the cement and water. It result first in setting (the cement becomes solid) and then hardening (increase of strength and stiffness). The processes are gradual and require the continuous presence of water. The reaction rate is in fact so slow that unground cement clinker can be stored outside for some days, or under cover for longer periods, only a very thin surface film becoming hydrated. The hydration rate depends on the surface area of clinker exposed, hence the fineness of grinding has a very significant effect, especially on the rate of hardening.

It must be emphasised that the atmosphere plays no part in hydration and the quite common belief that strengthening is associated with drying out is erroneous, for drying out of concrete will bring the hydration process and therefore strength development to an end .

It will be recalled that there are four chief compounds in Portland cement and that these react quite differently with water.

Immediately after adding water, the pH value of the mixture rises and laboratory tests show that the temperature of the mixture also rises rapidly. These effects are caused by reaction between the  $C_3A$  and water which is initially quite rapid since it takes some minutes for the gypsum to dissolve sufficiently to control the reaction of the  $C_3A$ . Thereafter, setting and gradual hardening take place by reaction of the  $C_3S$  and  $C_2S$  with water. In the early stages the  $C_3S$  is chiefly responsible for hydration. There is still some uncertainty as to the precise nature of the reaction between these compounds and water. They dissolve slowly and react chemically with the water to form a hydrate as follows:



and



The hydration products shown here are the same in each case, though in practice a range of similar products may be obtained depending on the constituents, the presence of any impurities in them and the prevailing conditions. Evidence suggests that there may also be a bond between hydrated and unhydrated material indicative of some additional surface reaction of the cement with water rather than simple dissolution.

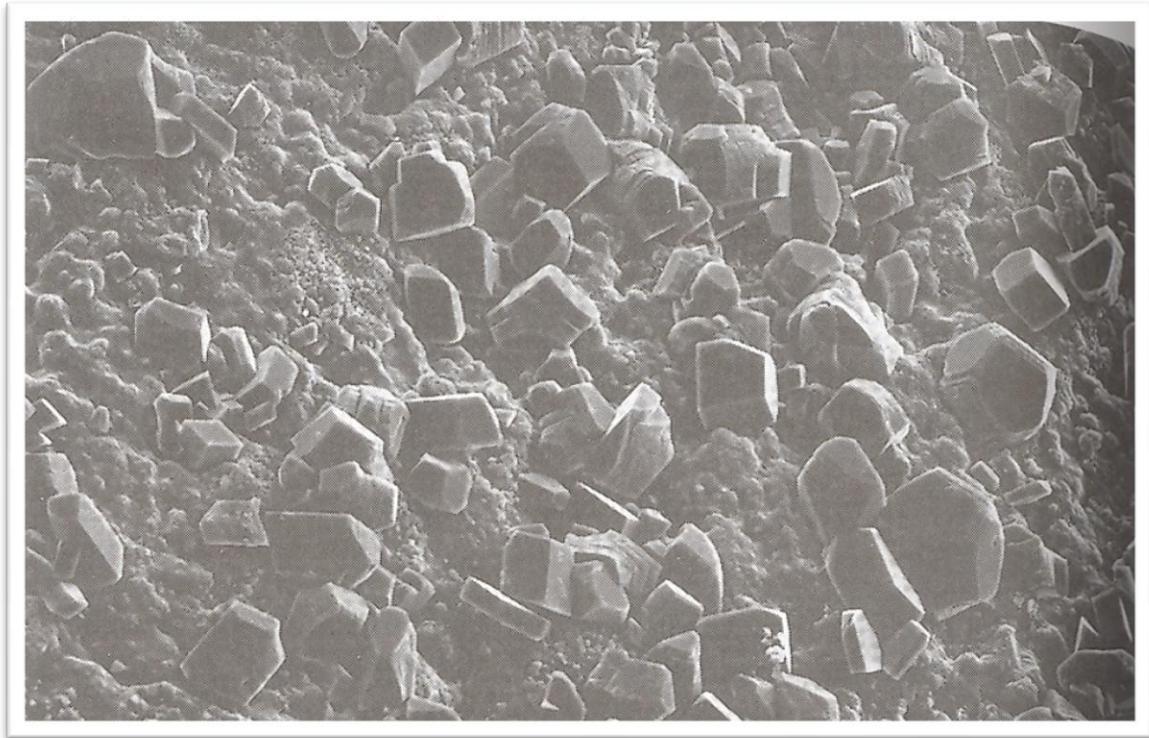
Both the chemical and physical nature of these materials have a decisive effect on the behaviour of the cement product.

The calcium silicate hydrate takes the form of extremely small interlocking crystals which grow out slowly from the cement grains to occupy previously water-filled spaces. An indication of fineness is obtained when their specific surface (about 200000  $m^2/kg$ ) is compared with that of unhydrated cement, about 300  $m^2/kg$ . This microcrystalline material is responsible for strength in the hardened concrete and also for its susceptibility to moisture, for it absorbs water very strongly. The term adsorption is used. It is described as a gel, the nearest natural equivalent being tobermorite gel.

Equally important is the other hydration product, calcium hydroxide, which forms much larger crystals. These acts as fillers in the hardened cement but do not interlock and therefore do not contribute directly to strength. However if moisture is present in the concrete, the crystals partly dissolve to form an alkaline solution which is protective to any steel present so preventing corrosion of the metal.

The pH value of saturated calcium hydroxide is approximately 12.5 though the pH of concrete pore water may be raised further to 13 or 14 by small quantities of sodium or potassium hydroxides which are present, especially in high alkali cements. Reinforced concrete depends on this alkalinity for its durability and it is unfortunate that calcium hydroxide at the surface of concrete is converted to calcium carbonate by atmospheric action, thereby becoming neutralised and ceasing to be protective to steel. To be durable the steel must be placed beneath this surface layer.

The contrasting physical forms of cement gel and calcium hydroxide crystals can be seen in Figure 1.2 which is scanning electron microscope photograph of the surface of hydrated cement.



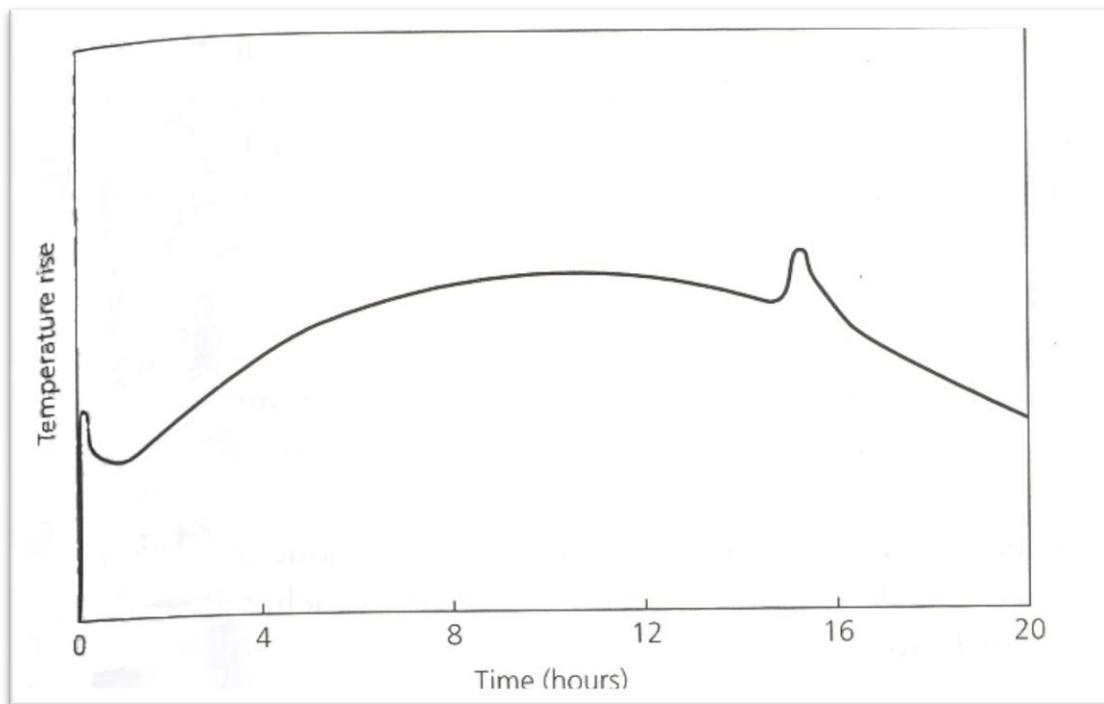
**Figure 1.2: Scanning electron microscope photograph of hydrated cement paste. Crystals of calcium hydroxide are surrounded by matrix of cement gel**

The reaction of  $C_3A$  was mentioned earlier in that it tends to produce a flash set. Although vigorous, the reaction produces little strength. The gypsum, added to prevent a flash set from occurring, forms an intermediate compound, calcium sulphoaluminate. Once the gypsum has been consumed, calcium aluminate monosulphate hydrate is formed. There should be sufficient gypsum for this reaction to occur fully- if gypsum becomes exhausted, the remaining  $C_3A$  may react quickly producing a sudden heat emission some hours after mixing. The monosulphate will revert to ettringite if the concentration of sulphates in solution rises as in sulphate attack. This will cause expansion and disruption of the hardened cement. It will be appreciated that the presence of  $C_3A$ , with its rapid setting, high heat emission and sulphate susceptibility, is undesirable in concrete. Alumina, the ingredient responsible, is found in most clays. It would be extremely difficult to remove it but the amount of  $C_3A$  in the cement can be reduced by addition of iron oxide as a raw material which combines with alumina in the

kiln to form  $C_4AF$  instead. Some  $C_3A$  is hopeful in manufacturing terms since it exists in the kiln as a liquid, facilitating silicate formation.

$C_4AF$  makes little contribution to setting or strength but acts as a flux in the kiln and is responsible for the grey colour of cement; hence higher  $C_4AF$  cements will be darker.

The sequential stages in the early hydration of Portland cements are illustrated by a heat output curve for cement paste. Three distinct sections may be visible (Figure 1.3). The initial peak is due to uncontrolled  $C_3A$  hydration, followed by a much more gradual output as the  $C_3S$  and  $C_2S$  hydrate. A final short peak may occur if the mixture becomes short of gypsum, resulting in a sudden reaction of the remaining  $C_3A$ .



**Figure 1.3: temperature rise in early stage of hydration of Portland cements. Three distinct are apparent.**

It should be added in conclusion to this section on the hydration of Portland cements, that the rate of hydration decrease continuously with age as the resistance to water penetration

of unhydrated cement grains progressively rises. It is unlikely that hydration penetrates to a depth of greater than 4  $\mu\text{m}$  even over long periods of time so grain of cement of size 10  $\mu\text{m}$  or larger will always contain an unhydrated kernel. ( Taylor, 2002)

## 1.2 AGGREGATES

Aggregate are the inert particles that are bound together by the cementing agent to form a mortar or a concrete. Mortar is a mixture of fine aggregate, a cementing material, and water. A mixture of only cement and water is referred to as “neat cement”. Concrete is composed of the ingredients of mortar plus coarse aggregates. The boundary size definition of fine aggregates is one that passes a 5 mm sieve. Coarse aggregate particle sizes are those that are retained on a 5 mm sieve opening. There is not real maximum size aggregate, but in most concretes for pavements and structures the upper limit is usually 5 cm, but may be larger.

Coarse aggregates are obtained from gravel or crushed stone, blast furnace slag, or recycled concrete. Trap rocks, granite, limestones, and sandstones are satisfactory for crushed stone. Fine aggregates are derived from the same sources except but in the place of gravel, naturally occurring sand is used. All aggregates should be composed of hard particles and free of injurious amounts of clay, loam, and vegetable matter. The principal characteristics of aggregates that affect the strength, durability, and workability of a concrete are cleanness, grading, hardness, and shape. Usually the aggregates are stronger than the concrete from which they are made. A coating of dirt or dust on the aggregate will reduce the strength of concrete because it prevents the particles from properly bonding to the mortar. A well-graded aggregate mix is essential to obtaining an economical concrete of good quality. If poorly graded, even clean, sound aggregates will require excessive water for workability, resulting in lower strength, or the mix will require an excessive amount of cement to develop a given strength. (Kett, 2000)

The aggregate component of a concrete mix occupies 60 to 80 percent of the volume of concrete, and its characteristics influence the properties of the concrete. The selection of

aggregates will determine the mix design proportion and the economy of the resulting concrete. It is therefore necessary to understand the importance of aggregate selection, testing, and handling.

Aggregates selected for use should be clean, hard, strong, and durable particles, free of chemicals, coatings of clay, or other materials that will affect the bond of the cement paste. Aggregates containing shale or other soft and porous organic particles should be avoided because they have poor resistance to weathering. Coarse aggregates can usually be inspected visually for weakness. Any aggregates that do not have adequate service records should be tested for compliance with requirements. Most concrete aggregate sources are periodically checked to ensure that the aggregates being produced meet the concrete specifications.

The commonly used aggregates such as sand, gravel, and crush stone produce normal-weight concrete. Various expanded shales and clays produce structural lightweight concrete. Much lighter concrete, using vermiculite, pumice, and perlite as aggregates, are called insulating concretes. The use of materials such as barites, limonite, magnetic iron, and iron particles produces heavyweight concretes.

Aggregate must possess certain characteristics to produce a workable, strong, durable, and economical concrete.

The most common test used to measure abrasion resistance of an aggregate is the Los Angeles rattler. A quantity of aggregate is placed in a steel drum with steel balls, the drum is rotated for a preset number of revolutions, and the percentage of material worn away is determined. Though the test is a general index of aggregate quality, there is generally no direct correlation with concrete abrasion using the same aggregate. If wear resistance is critical, it is more accurate to run abrasion tests on the concrete itself.

Porosity, absorption, and pore structure determine the freeze-thaw resistance of an aggregate. If an aggregate particle absorbs too much water, when it is exposed to freezing there will be little room for water expansion. At any freezing rate there may be a critical particle size above which the particle will fail if completely saturated.

There are two ways to determine the resistance to freezing-thawing of an aggregate: past performance records, if available, and the freeze-thaw test on concrete specimens containing the aggregates. Specimens are cast and cyclically exposed to freezing and thawing temperatures, with the deterioration measured by the reduction in the dynamic modulus of elasticity of the specimens.

Although aggregates are generally considered to be the “inert” component of a concrete mix, alkali-aggregate reactions do occur. Past performance records are usually adequate, but if no records are available or if a new aggregate source is being used, laboratory tests should be performed to determine the aggregate’s alkali reactivity.

Fresh concrete is affected by particle texture and shape more than hardened concrete. Rough- textured or flat aggregates require more water to produce a workable concrete than rounded or cubical, well- shaped aggregates. The National Ready Mix Concrete Association, based upon the use of well-shaped cubical aggregate as the standard, suggests that flat, elongated, or sharply angular aggregates will require more water, thus requiring more cement to maintain the same water- cement ratio. The use of rounded gravel aggregates will usually allow reduction in mixing water, with the resulting in cement, thus producing a savings to the concrete producer. It is recommended that long, flat particles not exceed 15 percent by weight of the total aggregate. This requirement is important when using manufactured sand because it contains more flat, elongated particles than natural sand.

The method of determining aggregate gradation and maximum aggregate size is by sieve analysis. The grading and maximum size of aggregates affect relative aggregate proportion as well as cement and water requirements, workability, economy, porosity and shrinkage of concrete. Variations in grading may seriously affect the uniformity of concrete from one batch to another. Harsh sands often produce unworkable mixes and very fine sands often produce uneconomical concrete. Generally, aggregates that have smooth grading curves, that is, no excesses or deficiencies, produce the most satisfactory results. For workability in leaner mixes, a grading that approaches the maximum recommended percentage passing through each sieve is desirable. Coarse grading is

required for economy in richer mixes. Generally, if the water-cement ratio is held constant and if the proper ratio of coarse to fine aggregate is chosen, a wide range in grading may be used with no effect on strength.

Usually more water is required for smaller aggregates than for larger maximum sizes. Conversely, the larger sizes require less water, and therefore less cement, to maintain a constant ratio with its economy. The higher cost of obtaining or handling aggregates usually offsets the saving in cement.

Generally, in higher-strength ranges, smaller aggregates will produce higher strengths than larger aggregates.

In certain cases, aggregates that have been gap graded may be used to produce higher strengths in stiff concrete mixes. Close control of gap-graded mixes is required because the variations may produce segregation. ( Marotta, 2005)

Aggregate may be described as clean, hard, inert material incorporated in concrete mixes. They usually serve the following main functions:

- They reduce the cost of concrete. Most aggregates are natural materials which require only extraction, washing and grading prior to transport to site.
- Well graded aggregates produce workable, yet cohesive, concrete.
- They reduce the heat of hydration of concrete since they are normally chemically inert and act as a heat sink for hydrating cement.
- They reduce the shrinkage of concrete since most aggregates are not affected by water and they restrain shrinkage of concrete since most aggregates are not affected by water and they restrain shrinkage of the hydrating cement. Additionally, aggregates may serve the following purposes for specific applications.
- Control of surface hardness. Most aggregates have better abrasion resistance than hydrated cement. Where heavy abrasion is anticipated, hard, high strength aggregates such as granite or corborundum can be incorporated.
- Colour or light reflecting properties. Aggregates can be exposed to utilise their visual properties.
- Control of density.
- Control of fire.

## 1.2.1 Types of aggregate

### NATURAL AGGREGATES

The great majority of aggregates used for concrete are obtained from natural sources, either in the form of rock which is crushed to obtain the desired maximum size or gravel which is processed by crushing or screening oversized material. In any particular area, there is only likely to be one type of aggregate which is readily available and, due to high costs of transportation of aggregate, normal concrete will be made with this type.

Natural aggregates are now briefly classified petrologically, since there are some important properties which are specific to the various groups. The simplest means of classification is according to the mode of formation of the rocks concerned.

Rocks which were at one time molten are described as igneous. Examples are granite and basalt, and the flint group of aggregates is igneous in origin, the rock being broken up into gravel and often worn smooth by glacial action. When fine particles become cemented together over a period of time, the resultant rock is described as sedimentary, limestone and sandstone being of this type. Limestone has several important characteristic properties: it results in a concrete with a relatively low coefficient of thermal expansion and also excellent fire resistance. Abrasion resistance, conversely, is not generally as good as that of other aggregate types. Sandstones vary greatly according to source, some sandstones being of high strength but others being less strong and exhibiting significant moisture movement which is not found in aggregates generally. Where stones have been formed or modified by heat and pressure, a metamorphic rock is produced. The most important of these is marble, which is formed from limestone and used widely for its decorative effect, for example, in terrazzo flooring.

Artificial aggregates may be manufactured from natural or materials and their use, mainly in the form of lightweight aggregates, is rapidly increasing. They are described under the heading of lightweight concrete.

## **RECYCLED AGGREGATES**

Quite large quantities of crushed material with the potential for use as concreting aggregates are now available. The chief sources are: demolition waste, crushed concrete, crushed brick.

It seems very likely that increasing levies will be imposed on aggregates obtained from land based sources and this would increase the commercial viability of aggregates obtained by recycling processes. The chief characteristics of recycled materials are:

1. Densities are in general lower and more variable than natural aggregates.
2. Aggregate absorption is likely to be higher depending on type.
3. Material variability may be a problem.
4. The strength of the product may have a ceiling value depending on source.
5. Shrinkage and moisture movement may be higher.

Provided a reliable source of material can be located recycled aggregates may well provide an economical solution for a number of applications. ( Taylor, 2002)

## **DENSE AGGREGATE MATERIALS**

In general, these materials must be non-porous and chemically stable in the cement environment. It is also advantageous if the cost of the material is low, hence the use of natural rocks and minerals, or waste materials. The four major classifications of dense aggregates are sands and gravels, rocks, blast furnace slag and broken bricks.

Sands and gravel consist of minerals that are resistant to weathering over long periods. Sands (with particle diameter < 5 mm) are normally quartz ( $\text{SiO}_2$ ), whereas gravels (with particle diameter > 5mm) may consist of quartz, quartzite, granite, sandstone, limestone etc. Some of the various types of crushed rock that can be used as aggregate are listed in Table 1.2.

Air-cooled blast furnace slag, which is obtained as a waste product from the manufacture of pig iron, can also be used as an aggregate but care must be taken in the preparation and selection of the slag. It must be crystalline and chemically stable. Dense blast furnace slag is produced by very slow cooling of the molten slag in air. The chemical

composition of the slag is important; it must not contain constituents which would cause problems with the set concrete. Examples of problem constituents are dicalcium silicate, sulphur compounds, high ferrous iron content or alkalis. Dicalcium silicate ( $C_2S$ ), can cause ‘dusting’ or ‘falling’ unsoundness in the aggregate because it undergoes phase changes at it is cooled.  $\alpha$ - $C_2S$  transforms to  $\acute{\alpha}$ - $C_2S$  at  $1400^\circ C$  which then transforms to either the stable  $\gamma$ - $C_2S$  at  $850^\circ C$  or the metastable  $\beta$ - $C_2S$  below  $675^\circ C$ . If the metastable  $\beta$ - $C_2S$  is formed then it can revert to the  $\gamma$ - $C_2S$  at ambient temperatures at some later time. This transformation is accompanied by a 12.5% increase in volume and can cause the aggregate to crumble in the set concrete. The other problem constituents react chemically with the set concrete, and can result in sulphate or alkali attack.

Broken bricks can be used as dense aggregate material, provided the calcium sulphate content is low. The presence of gypsum would cause the concrete to expand and crack due to sulphate attack after the concrete has set.

Rock	Comments
Granites	Well crystallized, fine to coarse grain
Dolerites	Very fine grain crystallized
Basalts	Very fine grain crystallized
Sandstones	Cemented quartz grains
Limestone ( $CaCO_3$ )	Must be dense and hard
Dolomite ( $CaCO_3, MgCO_3$ )	Must be dense and hard

**Table 1.2: Type of rock for use as dense aggregate material**

## LIGHTWEIGHT AGGREGATES

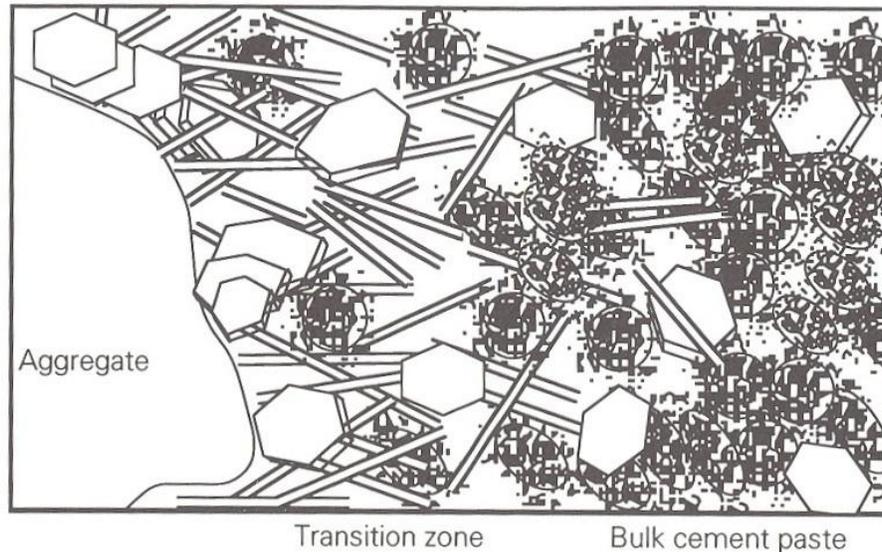
Natural and artificial porous materials are used to make lightweight concrete. These include pumice; clinker; expanded clay, shale and slate; exfoliated vermiculite and expanded volcanic glass (perlite). Foamed blast furnace slag can also be used as a lightweight aggregate. This is formed by foaming the molten slag with water sprays to generate steam, and then cooling slowly to ensure the slag has time to crystallize. A more detailed description of these porous materials is given in standards.

### 1.2.2 Aggregate and the aggregate/cement bond

Aggregate is much cheaper than cement, therefore as much as possible is put into the concrete mix, at least 75% of the volume of the concrete is composed of aggregate, so the aggregate can be regarded as a building material which is bonded together by the cement. This means that aggregates are not simply 'inert filler'; their physical, thermal and often also their chemical properties profoundly influence the durability and strength of concrete. The aggregate materials usually have a higher volume stability and better durability than the cement alone.

The cement serves to bond the aggregate particles together and the nature of the interface between the aggregate and the cement is of great importance. The interfacial region between the aggregate and the cement is thought to be very different from the bulk cement regions both in terms of morphology, density and composition. These regions are normally lower in density than the hydrated cement matrix and contain large orientated hexagonal crystals of CH and needles of  $AF_t$ . The structure is shown schematically in Figure 1.4

The thickness of this interfacial region is about  $50\mu\text{m}$ , with the weakest part of the zone lying about 5 to  $10\mu\text{m}$  away from the interface. The existence of this porous region can effect the fracture characteristics of the concrete and be a factor that limits the strength of the concrete.



**Figure 1.4: The interface between the aggregate and cement paste**

Some idea of the quality of the bond between the aggregate and cement can be obtained by inspecting a fractured sample of concrete. Ideally, there should be some fractures aggregate and some pull out. If all the aggregate has fractured, then the aggregate is too weak, and if all the aggregate has pulled out, then either the bond between the cement the cement paste and the aggregate is too weak or the cement paste itself is too weak. ( Gani, 1997)

### 1.3 WATER

In the production of concrete, water plays an important role. It is used to wash aggregates, as mixing water, during the curing process and to wash out mixers.

The use of an impure for aggregate washing may result in aggregate particles being coated with silt, salts, or organic materials. Aggregates that have been contaminated by such impure water may produce distressed concrete due to chemical reactions with the

cement paste or poor aggregate bonding. In most cases, comparative tests should be run on possible contaminated aggregates.

It is generally accepted that any portable water can be used as mixing water in the manufacture of concrete. Duff Abrams found sea water having 3.5 percent salt content adequate in producing concrete so that some waters used in concrete making are not potable.

Questionable water supplies may be used for concrete if mortar cubes made with the water meet C94 requirements shown in Table 1.3. Impurities in water may also affect volume stability and cause efflorescence (the leaching of free lime), discoloration, and excessive reinforcement corrosion.

	Limits	Test Method
Compressive strength, minimum percentage of control at 7 days	900	C109 or T106
Time of set, deviation from control, hour : min	From 1:00 earlier to 1:30 later	C191 or T131

**Table 1.3: Acceptance criteria for questionable water supplies (ASTM C94 or AASHTO M 157)**

Carbonate and bicarbonates of sodium and potassium affect the setting times of concrete. Sodium carbonate may cause rapid setting; bicarbonates may either accelerate or retard the set. In large concentrations these salts can materially reduce concrete strength. When the sum of these dissolved salts exceeds 1000 ppm (0.1 percent), tests for setting time and 28- day strength should be made.

Sodium chloride or sodium sulphate can be tolerated in large quantities; waters having concentrations of 20000 ppm of sodium chloride and 1000 ppm of sodium sulphate have been used successfully. Carbonates of calcium and magnesium are not very soluble in water and are seldom found in high enough concentrations to affect concrete properties. Bicarbonates of calcium and magnesium are present in some municipal water supplies, and concentrations of the bicarbonate of up to 400 ppm are not considered harmful.

Concentrations of magnesium sulphate and magnesium chloride up to 40000 ppm have been used without harmful effects on concrete strength. Calcium chloride is often used as an accelerator in concrete in quantities up to 2 percent by weight of the cement. It cannot be used in prestressed concrete or in concrete containing aluminium conduit or pipe.

Iron salts in concentrations of up to 40000 ppm have been used successfully; however, natural groundwater usually contains no more than 20 or 30 ppm.

The salts in concentrations, tin, zinc, copper, and lead may cause reductions in strength and variations in setting times. Salts that act as retarders include sodium iodate, sodium phosphate, sodium arsenate, and sodium borate, and when present in amounts as little as a few tenths of 1 percent by weight of cement, they can greatly retard set and strength development. Concentrations of sodium sulphide as low as 100 ppm warrant testing.

Generally, sea water containing 35000 ppm of salt can be used in nonreinforced concrete, which will exhibit higher early strength with a slight reduction in 28 –day strength. The reduction in 28-day strength is usually compensated for in the mix design. Sea water has been used in reinforced concrete; however, if the steel does not have sufficient cover or if the concrete is not watertight, the risk of corrosion is increased greatly. Sea water should never be used in prestressed concrete.

Aggregates from the sea may be used with fresh mixing water because the salt coating would amount to about 1 percent by weight of the mixing water.

Generally, mixing waters having common inorganic acid concentrations as high as 10000 ppm have no adverse effects on concrete strength. The acceptance of mixing waters

containing acid should be based on concentrations of acids in ppm rather than the pH value, as the latter is an intensity index.

Sodium hydroxide concentrations 0.5 percent by weight of cement do not greatly affect the concrete strength, providing quick set does not occur. Potassium hydroxide in concentrations up to 1.2 percent by weight of cement can reduce strengths of certain cements while not materially affecting strengths of others.

Industrial waste water and sanitary sewage can be used in concretes. After sewage passes through a good disposal system, the concentration of solids is usually too low to have any significant effect on concrete. Waste waters from tanneries, paint factories, coke plants, chemical plants, galvanizing plants, and so on may contain harmful impurities. As with all questionable water sources, it pays to run the comparative strength tests before using such waters in concrete manufacturing.

Sugar in concentrations of as little as 0.03 to 0.15 percent by weight of cement will usually retard the setting time of cement. There may be a reduction in 7 –day strength and an increase in 28-day strength. When the amount of sugar is raised to 0.20 percent by weight of cement, the set is accelerated. When the sugar exceeds 0.25 percent, there may be rapid setting and a reduction in 28-day strength. Water containing an excess of 500 ppm of sugar should be tested.

Clay or fine particles can be tolerated in concentrations of up to 2000 ppm. Though the clay may affect other properties of cement, the strength should not be affected at higher concentrations.

Silty water should settle in basins before use to reduce the suspended silts and clays. Mineral oils have less effect on strength development than vegetable or animal oils; however, when concentrations are greater than 2 percent by weight of cement, a strength loss of approximately 20 percent or more will occur.

Organic impurities such as algae in mixing water may cause excessive strength reductions by affecting bond or by excessive air entrainment.

As with all of the ingredients used in concrete production, if the water available is questionable, the comparative property tests should be run. Sometimes the concrete mix can be modified to compensate for water which produces low strength or exhibits other adverse characteristics.

The use of water containing acids or organic substances should be questioned because of the possibility of surface reactions or retardation. The other concern with curing water is the possibility of staining or discoloration due to impurities in the water.

The water used for concrete should be clean and free dirt or organic matter. Water containing even small quantities of acid can have a serious deleterious effect upon concrete. The presence of oil will result in slowing the set and reducing the strength. Generally speaking, if water is potable, it is satisfactory for the production of a good concrete.

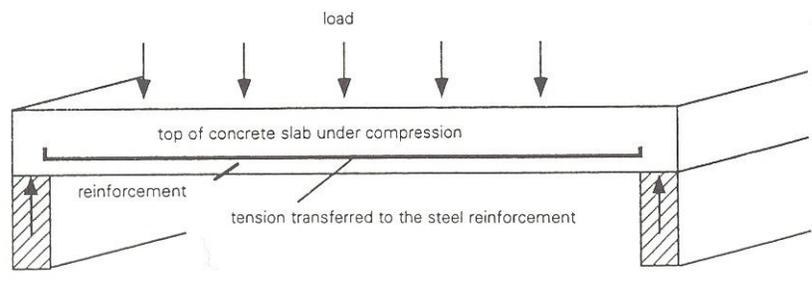
This is important, since contaminated water may lead to impaired performance of the hardened concrete. As a general rule, if water is suitable for drinking, then it is likely to be suitable for making concrete. If there is any doubt, it is advisable to carry out the setting time and strength test of the BS EN 176, using samples of the water in question and also distilled water for comparison. BS 3148 indicated that a strength reduction up to 20 per cent in the former is acceptable.

Sea water is generally suitable for ordinary concrete, since the effect of salt in the normal concentrations found is slight, but it is not recommended for reinforced or prestressed concretes. A further problem of sea water is the increased likelihood of efflorescence resulting in unsightly salt deposits, particularly if drying is concentrated at certain positions in the structure. Many salts are also hygroscopic and, therefore, tend to perpetuate dampness at positions where they build up. ( Marotta, 2005)

## 1.4 REINFORCED CONCRETE

For design purpose, the tensile strength of concrete is assumed to be zero. In order to obtain appreciable tensile strength in a concrete structure, reinforcement bars are embedded in the concrete. The rebars are normally made from mild steel. Tensile loads are supported by the rebars, as shown in the Figure 1.5

For efficient load transfer from the concrete to the steel, the strength of the bond between the concrete and the rebar is important. The bond arises primarily from friction and adhesion between the concrete and the steel, but it may also be affected by the shrinkage of the concrete during setting. The mechanical properties of the rebar and its location in the concrete member are also important.

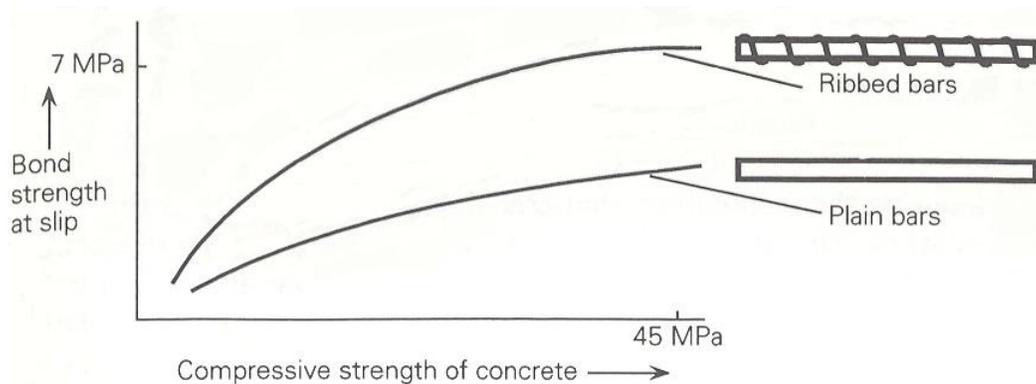


**Figure1.5: Transfer of tensile load to steel reinforcement.**

Generally the bond between steel and concrete is related to the quality of the concrete and the bond strength is approximately proportional to the compressive strength of the concrete. In order to obtain a better mechanical bond the rebars are normally ribbed (Figure 1.6). A thin layer of rust on the bars is also found to increase the bond between the concrete and the steel. This increase is probably due to the toughening of the surface of the steel by the rust formation.

If the steel rebar is surrounded with a sufficient coverage of good-quality concrete, the high pH of the concrete passivates the steel against corrosion. However continued corrosion of the rebar after placement sometimes takes place. This is normally due to

either insufficient coverage of the bars with concrete, which could arise from movement of the rebars during the pouring of the concrete, or the use of a porous concrete which could be the result of using too high a water/cement ratio in the production of the concrete. Both of these causes permit the ingress of chloride ions, water and carbon dioxide which can contribute to corrosion.



**Figure 1.6: Effect of ribs on bond strength of concrete to reinforcement bars**

### 1.4.1 Reinforcement

A wide range of steels are used for reinforcement ranging from low carbon steels (carbon content < 0.25 wt %), medium carbon steels (0.25-0.60 wt% C) to high carbon steel containing over 0.6wt % C. The rate of corrosion of the steel is dependent on a large number of factors which affect its microstructure, such as chemical composition (content of carbon, silicon, manganese, copper etc.), thermal processing of the steel (hot or cold rolling, thermal hardening etc.) and welding during fabrication. Galvanizing and other protective treatments to prevent corrosion of rebars are sometimes used, but these often result in a reduction of the bond strength, since the good bond which occurs when the surface is rusty has been lost.

The use of fusion bonded epoxy-coated rebars is described by Reed and Atkins. One of the arguments for the use of such coated rebars is that the poor quality of concrete used in

some constructions has made such treatment necessary, but there is the problem that if the quality control of the concrete is poor, then there is also likely to be a similar lack of quality control in the use of the coated rebars. Case histories are given which illustrate this point. In the first case, a bridge in the Florida Keys, there were areas of insufficient concrete coverage as well high concentrations of chloride in the concrete and these were combined with the use of coated rebars which had been bent to such an extent during the installation, that cracking and disbanding of the coating had occurred. The final result was corrosion at these coating defects. The second case, which occurred in the Middle East, was the use of coated rebars that had been laying on site for six months prior to use. During this time, the coating had degraded, and this led to corrosion of the reinforcement.

A detailed survey of the use of stainless steel instead of mild steel, epoxy-coated steel or even titanium, is presented by McDonald et al (1995). They conclude that stainless steel bars exhibit excellent resistance to corrosion even in severe chloride environments. In the many studies that are reviewed in the paper, no cracking of concrete was reported due to corrosion of the stainless steel and there was no evidence of stress corrosion cracking of the steel itself. The increased cost in the use of stainless steel was considered to be reasonable and the use of such steel is warranted in conditions where there must be a guaranteed long-term resistance to corrosion.

Although steel is still the most popular material for use as reinforcement in concrete, there is much active research being carried out into the possibility of using fibre-reinforced plastics as rebars. It is intended that those be used in concrete that would be subjected to corrosive agents such as would occur in marine environments, or because of the use of deicing salt or in the environs of chemical plants. The materials used range from hybrid fibre-reinforced plastic (FRP)/steel rebars, where the epoxy impregnated yarns of glass, aramid or carbon fibres are used to encase the steel wire fully, to glass-fibre-reinforced plastic(GFRP) rods made by a pultrusion process. Good adhesion to the concrete is achieved by bonding sand particles onto the surface of the rods. FRP fabricated into reinforcement grids have also been tested (Tao et al., 1992; Larralde, 1995; Schmeckpeper and Goodspeed, 1992). The articles refer to such advantages as corrosion resistance, light weight, high strength, good fatigue resistance ect. Erki and

Rizkalla list some of the disadvantage of the use of FRP for rebars as being the high cost (5 to 50 times that of steel), low modulus of elasticity and low failure strain. The low elastic modulus results in FRP-reinforced beams exhibiting much larger deflections than equivalent beams reinforced with steel rebars (Brown and Bartholomew, 1992). Pullout tests also indicate that the bond between the concrete and FRP is only about two-thirds that obtained between concrete and steel.

Continuous PAN-type carbon fibres which have been prefabricated into a three dimensional fabric impregnated with epoxy resin have been used by Zia et al. (1992) to reinforce concrete beams. The open weave fibre fabric reinforcement had a cross-sectional area of  $4.19 \text{ mm}^2$  and was made up from 48000 fibres. Concrete reinforced with this fabric exhibited the same ultimate strength and the same deflection at failure as a steel-reinforced beam, but in the post-cracking stage, the cracks were much smaller and more closely spaced in the carbon reinforcement beams. The bond between the epoxy coated carbon fibre reinforcement and the concrete was started to be excellent. ( Gani, 1997)

## **Chapter 2**

### **CORROSION OF STEEL IN CONCRETE**

This chapter discusses the basics of corrosion and how they apply to steel in concrete. The glossary of term at the beginning of the books gives some definitions of the terms used here s they apply to the corrosion of steel in concrete.

Why does steel corrode in concrete? A more sensible question is why steel does not corrode in concrete. We know from experience that mild steel and high strength reinforcing steel bars corrode (rust) when air and water are present. As concrete is porous and contains moisture why does steel in concrete not usually corrode?

The answer is that concrete is alkaline. Alkalinity is the opposite of acidity. Metals corrode in acids, whereas they are often protected from corrosion by alkalis.

When we say that concrete is alkaline we mean that it contains microscopic pores with high concentrations of soluble calcium, sodium and potassium oxides. These oxides form hydroxides, which are very alkaline, when water is added. This creates a very alkaline condition (pH 12-13). The composition of the pore water and the movement of ions and

gases through the pores are very important when analyzing the susceptibility of reinforced concrete structures to corrosion.

The alkaline condition leads to a 'passive' layer forming on the steel surface. A passive layer is a dense, impenetrable film which, if fully established and maintained, prevents further corrosion of the steel. The layer formed on steel in concrete is probably part metal oxide/hydroxide and part mineral from the cement. A true passive layer is a very dense, thin layer of oxide that leads to a very slow rate of oxidation (corrosion). There is some discussion whether or not the layer on the steel is a true passive layer as it seems to be thick compared with other passive layers and it consists of more than just metal oxides; but it behaves like a passive layer and it is therefore generally referred to as such.

Corrosion engineers spend much of their time trying to find ways of stopping corrosion of steel by applying protective coatings. Metals such as zinc or polymers such as acrylics or epoxies are used to stop corrosive conditions getting to steel surface. The passive layer is the corrosion engineer's dream coating as it forms itself and will maintain and repair itself as long as the passivating (alkaline) environment is there to regenerate it if it is damaged. If the passivating environment can be maintained, it is far better than any artificial coatings such as galvanizing or fusion bonded epoxy that can be consumed or damaged, allowing corrosion to proceed in damaged areas.

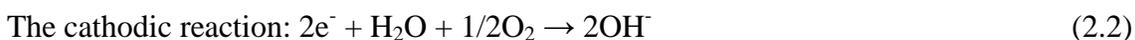
However, the passivating environment is not always maintained. Two processes can break down the passivating environment in concrete. One is carbonation and the other is chloride attack.

## **2.1 THE CORROSION PROCESS**

Once the passive layer breaks down then areas of rust will start appearing on the steel surface. The chemical reactions are the same whether corrosion occurs by chloride attack or carbonation. When steel in concrete corrodes it dissolves in the pore water and gives up electrons:



The two electrons ( $2\text{e}^-$ ) created in the anodic reaction must be consumed elsewhere on the steel surface to preserve electrical neutrality. In other words, it is not possible for large amounts of electrical charge to build up at one place on the steel; another chemical reaction must consume the electrons. This is a reaction that consumes water and oxygen:



This is illustrated in Figure 2.1. You will notice that hydroxyl ions ( $2\text{OH}^-$ ) are generated in the cathodic reaction. These ions increase the local alkalinity and will therefore strengthen the passive layer, warding off the effects of carbonation and chloride ions at the cathode. Note that water and oxygen are needed at the cathode for corrosion to occur.

The anodic and cathodic reactions (2.1 and 2.2) are only the first steps in the process of creating rust. However, this pair of reactions is critical to the understanding of corrosion and is widely quoted in any discussion on corrosion prevention for steel in concrete. The reactions will be referred to often in this book.

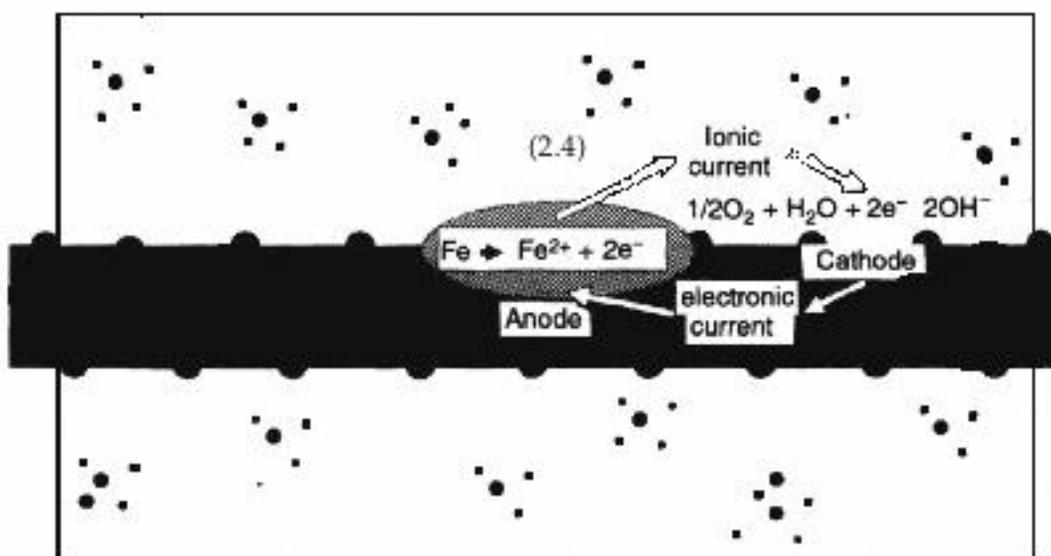


Figure 2.1: The anodic and cathodic reactions.

If the iron were just to dissolve in the pore water (the ferrous ion  $\text{Fe}^{2+}$  in equation 2.1 is soluble) we would not see cracking and spalling of the concrete. Several more stages must occur for ‘rust’ to form. This can be expressed in several ways; one is shown below where ferrous hydroxide becomes ferric hydroxide and then hydrated ferric oxide or rust:



Ferrous hydroxide



Ferric hydroxide



Hydrated ferric oxide (rust)

The full corrosion process is illustrated in Figure 2.2. Unhydrated ferric oxide  $\text{Fe}_2\text{O}_3$  has a volume of about twice that of the steel it replaced when fully dense. When it becomes hydrated it swells even more and becomes porous. This means that the volume increase at the steel/concrete interface is two to ten times. This leads to the cracking and spalling that we observe as the usual consequence of corrosion of steel in concrete and the red/brown brittle, flaky rust in the bar and the rust stains seen at cracks in the concrete.

The electrical current flow, and the generation and consumption of electrons in the anode and cathode reactions are used in half cell potential measurements and cathodic protection. The formation of protective, alkaline hydroxyl ions is used in cathodic protection, electrochemical chloride removal and realkalization. The fact that the cathodic and anodic reaction must balance each other for corrosion to proceed is used in epoxy coating protection of rebars.

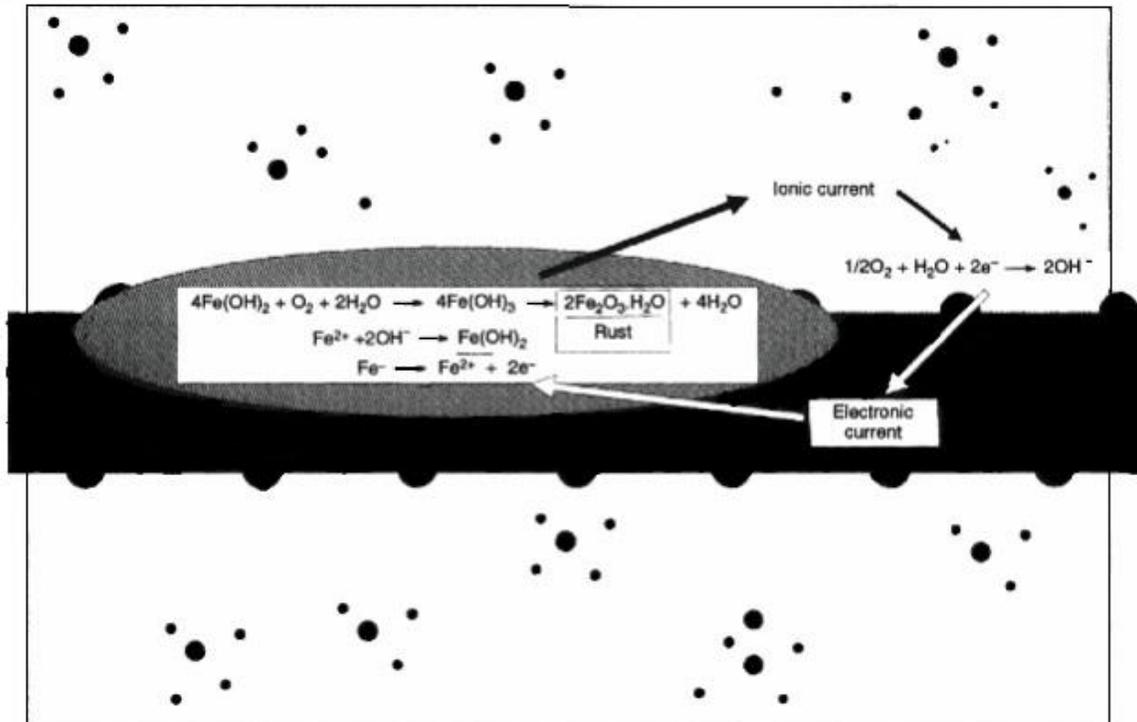
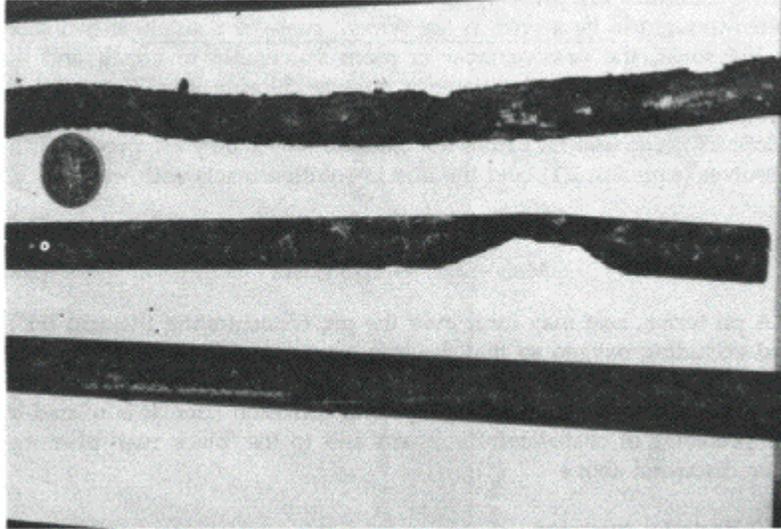


Figure 2.2: The corrosion reactions on steel.

## BLACK RUST

There is an alternative to the formation of 'normal' red rust described in reactions 2.3 to 2.5 above. If the anode and cathode are well separated (by several hundred millimeters) and the anode is starved of oxygen (say by being underwater) the iron as  $\text{Fe}^{2+}$  will stay in solution. This means that there will be no expansive forces to crack the concrete.

This type of corrosion (known as 'black' or 'green' rust due to the colour of the liquid seen on the rebar when first exposed to air after breakout) is found under damaged waterproof membranes and in some underwater saturated conditions. It is potentially as there is no indication of corrosion by cracking and spalling of the concrete and the reinforcing steel may be severely weakened before corrosion is detected. Rebars may be hollowed out in such deoxygenated conditions, particularly under membranes or when water is permanently ponded on the surface.



**Figure 2.3: Rebars taken from under the end of a waterproof membrane. They have been subjected to low oxygen conditions and therefore show local ‘wasting’ of bars with no expansive oxide growth.**

Examples of rebars attacked in this way are shown in Figure 2.3. These bars were taken from underneath damaged waterproof membranes. Rust staining on the concrete surface may be indicative of this type of attack, but obviously if water is getting under a membrane and excluding oxygen it is unlikely that the iron in solution will get to the concrete surface where it will then precipitate out to form rust stains.

## **2.2 CAUSES AND MECHANISMS OF CORROSION DAMAGE IN CONCRETE**

There are two main causes of corrosion of steel in concrete. This part will discuss how chloride attack and carbonation lead to corrosion and how the corrosion proceeds once it has started. The mechanism of corrosion damage is explained. There will also be discussion of the variations that can be found when carrying out investigations in the field.

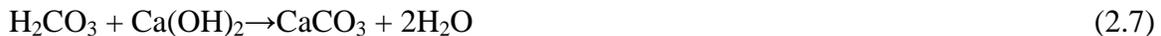
The main causes of corrosion of steel in concrete are chloride attack and carbonation. These two mechanisms are unusual in that they do not attack the integrity of the concrete. Instead, aggressive chemical species pass through the pores in the concrete and attack the steel. This is unlike normal deterioration processes due to chemical attack on concrete. Other acids and aggressive ions such as sulphate destroy the integrity of the concrete before the steel is affected. Most forms of chemical attack are therefore concrete problems before they are corrosion problems. Carbon dioxide and the chloride ion are very unusual in penetrating the concrete without significantly damaging it. Accounts of (for instance) acid rain causing corrosion of steel embedded in concrete have been shown to attack the steel and not the concrete.

### 2.2.1 Carbonation

Carbonation is the result of the interaction of carbon dioxide gas in the atmosphere with the alkaline hydroxides in the concrete. Like many other gases carbon dioxide dissolved in water to form an acid. Unlike most other acids the carbonic acid does not attack the cement paste, but just neutralizes the alkalis in the pore water, mainly forming calcium carbonate that lines the pores:



Gas Water Carbonic acid



Carbonic acid Pore solution

There is a lot more calcium hydroxide in the concrete pores than can be dissolved in the pore water. This helps maintain the pH at its usual level of around 12 or 13 as the carbonation reaction occurs. However, eventually all the locally available calcium hydroxide reacts, precipitating the calcium carbonate and allowing the pH to fall to a level where steel will corrode. This is illustrated in Figure 2.4.

Carbonation damage occurs most rapidly when there is little concrete cover over the reinforcing steel. Carbonation can occur even when the concrete cover depth to the reinforcing steel is high. This may be due to a very open pore structure where pores are well connected together and allow rapid CO<sub>2</sub> ingress. It may also happen when alkaline reserves in content, high water cement ratio and poor curing of the concrete.

A carbonation front proceeds into the concrete roughly following the laws of diffusion. These are most easily defined by the statement that the rate is inversely proportional to the thickness:

$$\frac{dx}{dt} = \frac{D_0}{x} \quad (2.8)$$

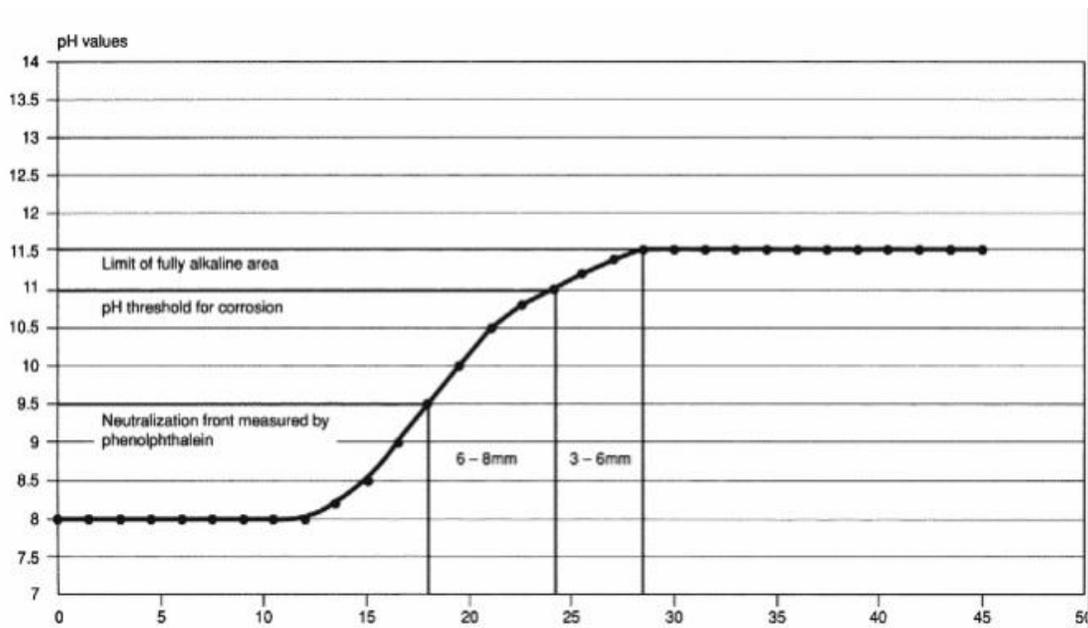
Where  $x$  is distance,  $t$  is time and  $D_0$  is the diffusion constant.

The diffusion constant  $D_0$  is determined by the concrete quality. At the carbonation front there is a sharp drop in alkalinity from pH 11-13 down to less than pH 8(Figure 2.4). At that level the passive layer, was created by the alkalinity, is no longer sustained so corrosion proceeds by the general corrosion mechanism as described.

Many factors influence the ability of reinforced concrete to resist carbonation induced corrosion. The carbonation rate, or rather the time to carbonation induced corrosion, is a function of cover thickness, a good cover is essential to resist carbonation. As the process is one of neutralizing the alkalinity of the concrete, good reserves of alkali are needed, i.e. a high cement content. The diffusion process is made easier if the concrete has an open pore structure. On the macroscopic scale this means that there should be good compaction. On a microscopic scale well cured concrete has small pores and lower connectivity of pores so the CO<sub>2</sub> has a harder job moving through the concrete. Microsilica and other additives can block pores or reduce pores sizes.

Carbonation is common in old structure, badly built structures (particularly building) and reconstituted stone elements containing reinforcement that often have low cement content and are very porous. Carbonation is rare in modern highway bridges and other civil engineering structures where water/cement ratios are low, cement contents are high with

good compaction and curing, and there is enough cover to prevent the Carbonation front advancing into the concrete to the depth of the steel within the lifetime of the structure. On those structures exposed to sea water or deicing salts, the chlorides usually penetrate to the reinforcement and cause corrosion long before carbonation becomes a problem. Wet/dry cycling on the concrete surface will accelerate carbonation by allowing carbon dioxide gas in during the dry cycle and then supplying the water to dissolve it in the wet cycle (equation 2.6). This gives problems in some countries in tropical or semi-tropical regions where the cycling between wet and dry seasons seems to favour carbonation, e.g. Hong Kong and some Pacific Rim countries.



**Figure 2.4: Schematic of the carbonation front and its relationship to the corrosion threshold and the colour change for phenolphthalein.**

When a repairer talks of repairing corrosion due to ‘low cover’ he usually means that the concrete has carbonated around the steel leading to corrosion. As the cover is low it was a quick process, perhaps within five year of construction. If the concrete were of the

highest quality carbonation may not have been possible and low cover might not have mattered.

Carbonation is easy to detect and measure. A pH indicator, usually phenolphthalein in a solution of water and alcohol, will detect the change in pH across a freshly exposed concrete face. Phenolphthalein changes from colourless of low pH (carbonated zone) to pink at high pH (uncarbonated concrete). Measurements can be taken on concrete cores, fragments and down drilled holes. Care must be taken to prevent dust or water from contaminating the surface, is cheap and simple. Figure 2.4 shows a typical carbonation front in concrete with the pH of the concrete before and after carbonation, the pH threshold of corrosion for steel and the pH change of phenolphthalein taken from Parrott (1987).

## **CARBONATION TRANSPORT THROUGH CONCRETE**

Carbon dioxide diffuses through the concrete and the rate of movement of the carbonation front approximates to Fick's law of diffusion. This states that the rate of movement is inversely proportional to the distance from the surface as in equation 2.8 above. However, as the carbonation process modifies the concrete pore structure as it proceeds, this is only an approximation. Cracks, changes in concrete composition and moisture levels with depth will also lead to deviation from the perfect diffusion equation. Integration of equation 2.8 gives a square root law that can be used to estimate the movement of the carbonation front.

### **2.2.2 Chloride attack**

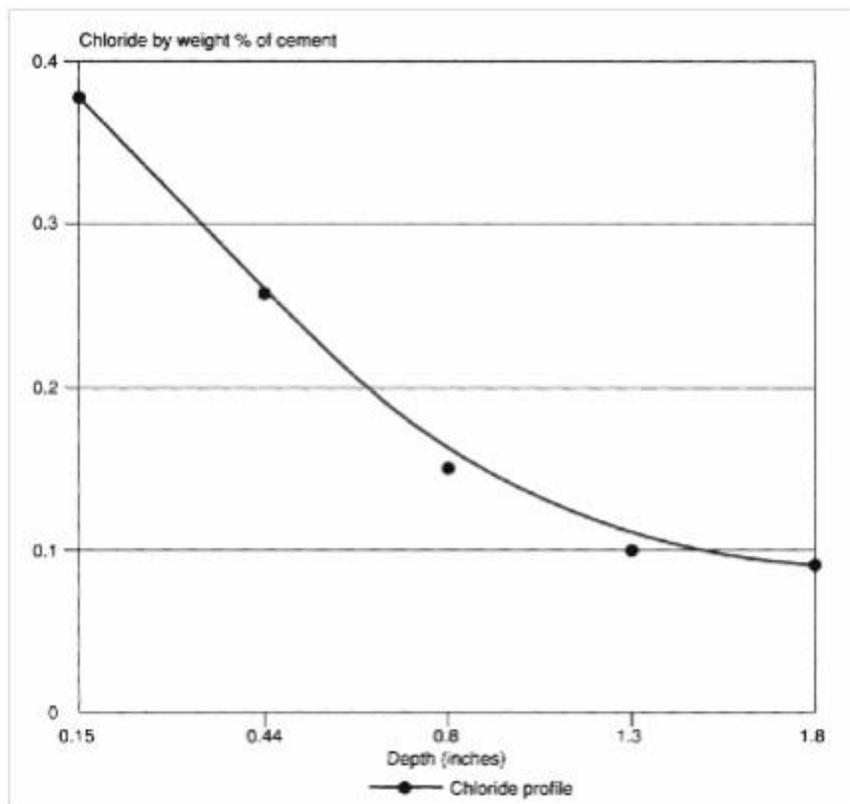
#### **Sources of chlorides**

Chlorides can come from several sources. They can be cast into the concrete or they can diffuse in from the outside. Chlorides cast into concrete can be due to:

- deliberate addition of chloride set accelerators (calcium chloride,  $\text{CaCl}_2$ , was widely used until the mid-1970s);

- use of sea water in the mix;
- Contaminated aggregates (usually sea dredged aggregates which were unwashed or inadequately washed).
- Chlorides can diffuse into concrete as a result of:
  - sea salt spray and direct sea water wetting;
  - deicing salts;
  - Use to chemicals (structure used for salt storage, brine tanks, aquaria, etc.).

Much of our discussion will centre in the diffusion of chlorides into concrete as that is the major problem in most parts of the world either due to marine salt spray or use of deicing salts. However, the cast-in chlorides must not be overlooked, especially when they are part of the problem. A low level of chloride cast in can lead to rapid onset of corrosion if further chlorides become available from the environment. This often happens in marine conditions where seawater contaminates the original concrete mix and then diffuses into hardened concrete.



**Figure 2.5: Chloride profiles of marine bridge substructure (Yaquina Bay bridge soffit)**

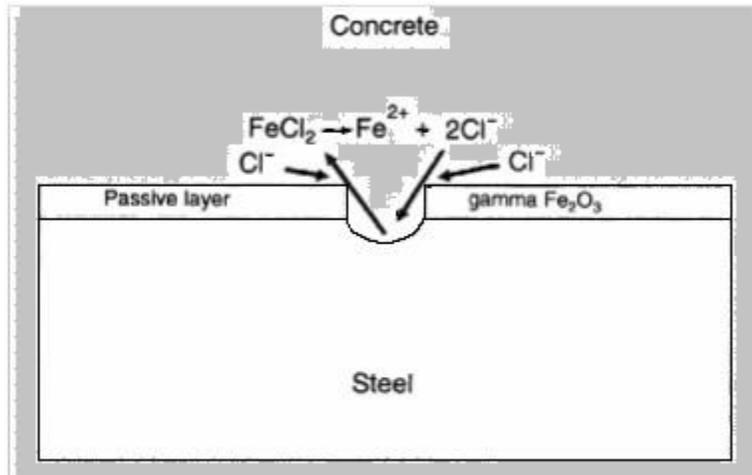
## CHLORIDE TRANSPORT THROUGH CONCRETE

Like carbonation, the rate of chloride ingress is often approximated to the laws of diffusion. There are further complications here. The initial mechanism appears to be suction, especially when the surface is dry. Salt water is rapidly absorbed by dry concrete. There is then some capillary movement of the salt-laden water through the pores followed by 'true' diffusion. There are other opposing mechanisms that slow the chlorides down. These include chemical reaction to form chloroaluminates and adsorption on to the pore surfaces.

The other problem with trying to predict the chloride penetration rate is defining the initial concentration, as chloride diffusion produces a concentration gradient not a 'front'. In other words we can use the square root relationship for the carbonation front as the concrete either is or is not carbonated, but we cannot use it so easily for chlorides as there is no chloride 'front', but a concentration profile in the concrete. A typical chloride profile is shown in Figure 2.5. This particular profile is a very convincing fit to a diffusion curve but show no error bars. Many profiles show far more scatter.

### *Chloride attack mechanism*

Previously we discussed the corrosion of steel in concrete and the effectiveness of the alkalinity in the concrete pores producing a passive layer of protective oxide on the steel surface which stops corrosion. In the previous section we observed that alkalinity in the concrete pores is neutralized by carbonation. The depassivation mechanism for chloride attack is somewhat different. The chloride ion attacks the passive layer but, unlike carbonation, there is no overall drop in pH. Chloride act as catalysts to corrosion when there is sufficient concentration at the rebar surface to break down the passive layer. They are not consumed in the process but help to break down the passive layer of oxide on the steel and allow the corrosion process to proceed quickly. This is illustrated in Figure 2.6. This makes chloride attack difficult to remedy as chloride are hard to eliminate.



**Figure 2.6: The breakdown of the passive layer and ‘recycling’ chlorides.**

Obviously a few chloride ions in the pore water will not break down the passive layer, especially if it is effectively re-establishing itself when damaged.

There is a ‘chloride threshold’ for corrosion given in terms of the chloride/hydroxyl ration. It has been measured in laboratory tests with calcium hydroxide solutions. When the chloride concentration exceeds 0.6 of the hydroxyl concentration, corrosion is observed (Hausmann 1967). This approximates to a concentration of 0.4% chloride by weight of cement of chlorides are cast into concrete and 0.2% they diffuse in.

In the USA a commonly quoted threshold is 1lb chloride per cubic yard of concrete. Although these figures are based on experimental evidence, the actual values are a function of practical observations of real structures.

All these thresholds are approximations because:

1. Concrete pH varies with the type of cement and the concrete mix. A tiny pH change represents a massive change in hydroxyl ion ( $\text{OH}^-$ ) concentration and therefore (theoretically) the threshold moves radically with pH.
2. Chlorides can be bound chemically (by aluminates in the concrete and physically (by absorption on the pore walls). This removes them (temporarily or

- permanently) from the corrosion reaction. Sulphate resisting cements have low aluminate ( $C_3A$ ) content which leads to more rapid diffusion and lower chloride thresholds.
3. In very dry concrete corrosion may not occur even at very high  $Cl^-$  concentration as the water is missing from the corrosion reaction.
  4. In sealed or polymer impregnated concrete, corrosion may not occur even at a very high  $Cl^-$  concentration if no oxygen or moisture is present to fuel the corrosion reaction.
  5. Corrosion can be suppressed when there is total water saturation due to oxygen starvation, but if some oxygen gets in, then the pitting corrosion can occur.

Therefore corrosion can be observed at a threshold level of 0.2% chloride by weight of cement if the concrete quality is poor and there are water and oxygen available. In different circumstances no corrosion may be seen at 1.0% chloride or more if oxygen and water are excluded. If the concrete is very dry or totally saturated (as in (3) or (5) above) then a change in conditions may lead to rapid corrosion.

### **2.2.3 Corrosion damage**

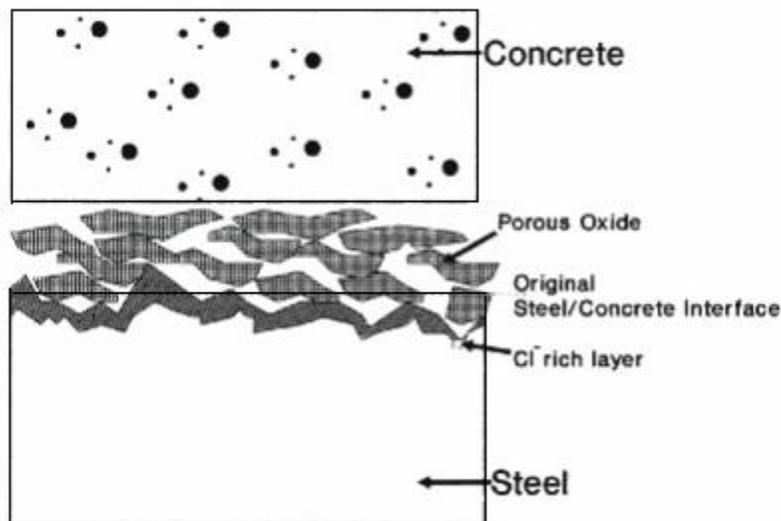
In most industries corrosion is a concern because of wastage of metal leading to structural damage such as a collapse, perforation of containers and pipes, etc. Most problems with corrosion of steel in concrete are not due to loss of steel but the growth of the oxide. This leads to cracking and spalling of the concrete cover.

Structural collapses of reinforced concrete structures due to corrosion are rare.. Concrete damage would usually have to be well advanced before a reinforced concrete structure is at risk.

Particular problems arise when the corrosion product is the black rust and in prestressed, post-tensioned structures where corrosion is difficult to detect as the tendons are enclosed in ducts. Tendon failure can be catastrophic as tendons are loaded to 50% or more of their ultimate tensile strength and modest section loss leads to failure under load.

The most common problem caused by corrosion is spalling of concrete cover. Special metal canopies have been built around the lower floors of high rise building where corrosion has led to risk of failing concrete. This enables the investigators to collect the fallen concrete at regular intervals and weigh it. In that way they can determine whether the corrosion rate is stable, increasing or decreasing.

The important factors in corrosion of steel in concrete compared with most other corrosion problems are the volume of oxide and where it is formed. A dense oxide formed at high temperatures (such as in a power station boiler) usually has twice the volume of the steel consumed. In most aqueous environments the excess volume of oxide is transported away and deposits on open surfaces within the structure. For steel in concrete two factors predominate. The main problem is that the pore water is static and there is no transport mechanism to move the oxide away from the steel surface. The second problem is that the oxide is not dense. It is very porous and takes up a very large volume, up to ten times that of the steel consumed. This is illustrated in Figure 2.7



**Figure 2.7: Rust growth forcing steel and concrete apart**

The thermodynamics of corrosion, coupled with the low tensile strength of concrete, means that the formation of oxide breaks up the concrete. It has been suggested that less

than 100µm of steel section loss are needed to start cracking and spalling the concrete. The actual amount needed will depend upon the geometry in terms of cover, proximity to corners, rebar spacing, bar diameter and the rate of corrosion.

Corners tend to crack first on corroding reinforced concrete structures. This is because the oxygen, water, chlorides and carbon dioxide have two faces as path ways to the steel. Delaminations occur as corrosion proceeds on neighbouring rebars and the horizontal cracks/join up as shown in Figure 2.8.

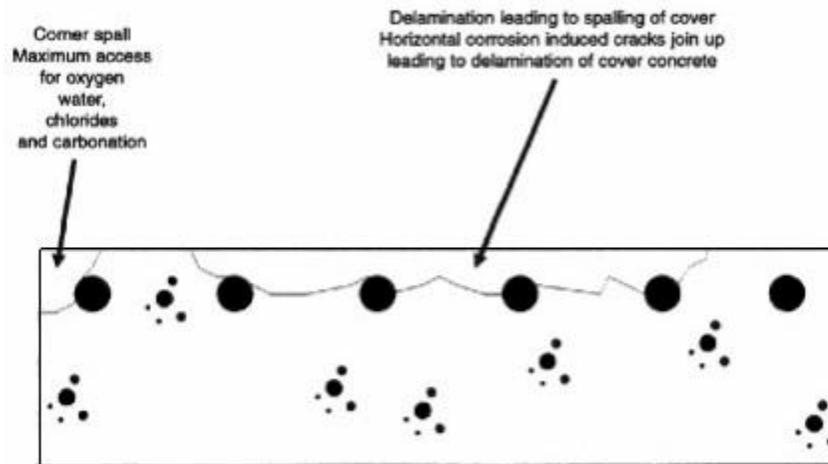


Figure 2.8: Corrosion induced cracking and spalling.

### VERTICAL CRACKS, HORIZONTAL CRACKS AND CORROSION

The importance of vertical cracks in accelerating corrosion by allowing access of corrosion agents to the steel surface has been widely discussed. If reinforcing steel is doing its job in areas of tension in structure, small cracks will occur as the tensile load exceeds the tensile reinforcing steel at right angles. They do not lead to corrosion of the steel as any local ingress of chlorides, moisture and carbonation is limited and contained by the local alkalinity. Obviously there is a limit to this ‘self-healing’ ability. If large cracks stay open (greater than 0.5mm), then corrosion can be accelerated. Such cracks may be due to plastic shrinkage, thermal expansion or other reasons. The relationship

between cracks in concrete and reinforcement corrosion is fully discussed in Concrete Society (1995) Technical Report No. 44.

Corrosion causes horizontal cracking long the plane of the rebar and the corner cracking around the end rebar. This leads to the loss of concrete cover as shown in Figure 2.8. This is the main consequence of reinforcement corrosion with its subsequent risk of failing concrete and unacceptable appearance.

### **2.3 CORROSION INHIBITORS**

The ability of nitrites to stop corrosion when added to concrete has been known for many years and a proprietary calcium nitrite additive has been used in a number of structures including bridges and car park. The principle of most inhibitors is to develop a very thin chemical layer usually one or two molecules thick, on the steel surface, that inhibits the corrosion attack. Inhibitors can prevent the cathodic reaction, the anodic reaction or both (cathodic, anodic and ambiodic inhibitors). They are consumed and will only work up to a given level of attack. The concern with inhibitors is that they will suppress the generalized corrosion; but if the amount available is inadequate due to low dosage or consumption, there could be localized, pitting attack. This phenomenon has not been clearly demonstrated in concrete but can occur in theory and has been observed in other corrosion environments.

There are now a number of inhibitors being offered to improve the effectiveness of concrete repairs. They can be applied as coatings on the surface or on to the exposed steel at patch repairs, incorporated into the patch repairs, applied in grooves or drilled holes in the concrete cover or incorporated into concrete overlays.

Calcium nitrite has the advantage that it will not affect the concrete significantly if added to a repair mix, or applied to a surface and the mix applied over it. However, calcium nitrite is a set accelerator so care must be taken that 'flash setting' does not occur.

Otherwise it is straightforward to use, other than some concern about the freeze-thaw resistance. Adequate air entrainment is advised for mixes including calcium nitrite.

Calcium nitrite is the principal corrosion inhibitor available to stop corrosion that is compatible with concrete in the casting process. Research shows that if sufficient nitrite is added to the concrete mix to ensure a chloride to nitrite ratio of less than 1.0 at rebar depth, then the nitrite will prevent corrosion. Obviously this is feasible in marine conditions where the chloride level is known but may be more difficult in other situations.

After their unfortunate problems with epoxy coated reinforcing steel, is being considering the use of calcium nitrite inhibitor against corrosion. This has the advantage that there is continuity of the reinforcing cage so electrochemical methods can be used to measure for corrosion and to treat for corrosion. Its major drawback is that with a good quality, dense concrete and good cover, the inhibitor should not be needed for at least 20 years.

The advantage of calcium nitrite is that it can be added to the mix and has no serious effect on the design, construction and performance of the structure other than its effect as a set accelerator. Mix design may require adjusting to include a retarder. Its disadvantage is that there must be enough to stop corrosion and it is consumed with its exposure to chlorides. It is therefore important to calculate the chloride exposure for the life of the structure and add sufficient inhibitor. It does not inhibit the application of cathodic protection or chloride extraction in later life of the structure if necessary.

Vapour phase inhibitors (VPIs) are volatile compounds that can be incorporated into a number of carriers such as waxes, gels and oils. They will diffuse through the air, or the concrete pores, to the steel surface. In principle their ability to diffuse as a vapour gives them an advantage over liquid inhibitors. However, they can also diffuse out of the concrete unless trapped in place. They may diffuse poorly through saturated concrete.

There are other materials on the market that have different effects on the steel or the concrete to enhance the alkalinity, block the chloride and reduce the corrosion rate. Some

are true corrosion inhibitors, some are hybrid inhibitors, pore blockers and alkali generators.

Although some field trials have been underway for several years, it is difficult to show how effective any of these systems are in suppressing corrosion in existing structures. Diffusion of the chloride ion into concrete is slow and most of the liquid inhibitor molecules are larger than the chloride ion so we would expect them to be even slower to reach the rebar from the surface. Many evaluations of inhibitors have been simplistic, not fully representing field concretes or conditions, or are in early stages with no results properly reported. The true effect of an inhibitor can only be assessed by corrosion rate measurement before and after application and with regular monitoring of a treated area and a control area. Such evaluations are in their earliest stages.

Several methods of speeding the inhibitor to the steel surface have been proposed. Drilling or grooving concrete to apply inhibitors is expensive and damaging. Simple spraying on to a dry surface will probably be very dependent upon the concrete quality and the moisture level in the concrete.

The advantage of inhibitor application is that they can reduce the incipient anode effect around patches if they incorporated into the repair mix and then diffuse into the concrete. Their disadvantage is the cost of materials, difficulty of application and unknown lifetime and effectiveness. However, with proper evaluation and monitoring, we may learn a lot more about these materials over the next few years. (P.Broomfield, 1997)

## **Chapter 3**

### **LIMESTONE IN CEMENTS**

The cement industry continues to introduce more sustainable practices and products for constructing and maintaining our concrete infrastructure and buildings. That sustainable development focus, proposed implementation of more restrictive environmental regulations on cement manufacturing, and potential global climate change legislation have prompted the US cement industry to propose provisions for Portland-limestone cements within specifications ASTM C595 and AASHTO M240. Such provisions are anticipated to be similar to those adopted by CSA A3000, with limestone contents greater than 5% and up to 15%. For many applications, Portland-limestone cements (PLC) can provide equivalent performance with reduced environmental impact.

Portland-limestone cements are in common use around the world. Similar cements have been produced in the US under ASTM C1157 for several years and have a history of satisfactory performance in field applications. However, C1157 is not widely specified. Therefore, provisions for Portland-limestone blended cements in ASTM C595 and AASHTO M240 are needed if a significant impact on sustainability is to be achieved.

The use of up to 5% ground limestone in Portland cement has been permitted by the Canadian cement standard since the early 1980s. The CSA standard (CSA 1998) for Portland cement, CAN/CSA-A5, defines Portland cement as:

***“The product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates to which calcium sulphate, limestone, water, and processing additions may be added at the option of the manufacturer.”***

Limestone is also provided for in the European standard EN 197-1 (CEN 2000) which allows cements to contain limestone in three different dosage levels. CEM I, “Portland cement,” may contain up to 5% minor additional constituents, of which limestone is one possible material. CEM II/A-L and CEM II/B-L, both called “Portland limestone cement,” contain 6% to 20% and 21% to 35% ground limestone, respectively. Roughly 19% of all cement sold in Europe contains between 6% and 35% limestone (CEMBUREAU 2001). The requirements specified for limestone use pertain to effects on performance only.

A review of *Cement Standards of the World* (CEMBUREAU 1991) shows that more than 25 countries allow the use of between 1% and 5% limestone in their P (“Portland”) cements. Many countries also allow up to 35% replacement in PB (“Portland composite”) cements. Since 1991, the latest edition of *Cement Standards of the World*, several countries have modified their standards to permit limestone in some amount, including Australia, Italy, New Zealand, and the United Kingdom.

### **3.1 LIMESTONE**

Sprung and Siebel (1991) point out that since pure dense limestone consisting primarily of calcite is not normally available for industrial grinding in cement plants, certain minimum requirements must be stipulated for its composition, and maximum limits put on its quantity in cement. Natural limestones contain clay minerals, which above a certain proportion can increase water demand and significantly reduce the frost resistance of

concrete. The CSA standard (CSA 1998) for Portland cement, CAN/CSA-A5, allows a maximum of 5% limestone in normal Portland cement, Type 10, and high-early-strength Portland cement, Type 30. Such limestone must be of a quality suitable for the manufacture of Portland cement clinker, but no specific limits on composition are given.

The European standard, EN 197-1, allows CEM I Portland cement to contain up to 5% minor additional constituents (MAC), of which limestone is one possible material. The requirements for minor additional constituents are only that they do not detract from performance: Fillers are specially selected, natural or artificial inorganic mineral materials which, after appropriate preparation, on account of their particle size distribution, improve the physical properties of the cement (such as workability or water retention). They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect.

Fillers shall be correctly prepared, i.e. selected, homogenized, dried and comminuted depending on their state of production or delivery. They shall not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar to deterioration in any way or reduce the corrosion protection of the reinforcement.

European Portland limestone cement can contain up to 35% ground limestone. In this case, with the limestone constituting a larger proportion of the cement, EN 197 specifies limits on the composition of the limestone:

CaCO<sub>3</sub> content             $\geq 75\%$  by mass

Clay content (EN 933-9)  $\leq 1.20$  g/100 g

Total organic carbon     $\leq 0.20\%$  by mass for class L

(prEN 13639)                 $\leq 0.50\%$  by mass for class LL

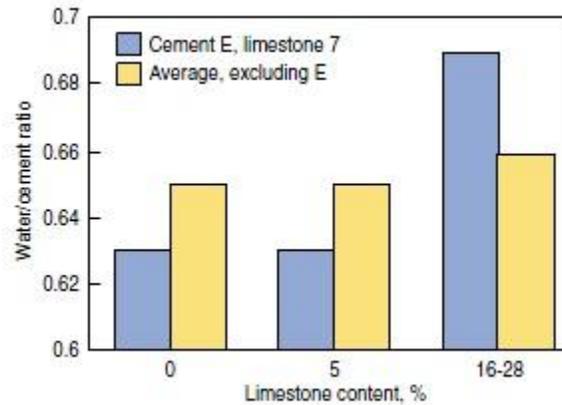
Schmidt (1992) adds that the MgO content should be limited to 5% by mass, although this restriction does not appear in the current version of EN 197-1. It is also to be noted that the MgO limit is intended to limit the amount of dolomite in the limestone.

The clay content is determined by prEN 933-9, “Test for geometrical properties of aggregates–Part 9: Assessment of fines–Methylene blue test” (CEN 1998). In this test a 10 g/l solution of methylene blue is injected in a series of 5 ml doses into the sample beaker. After each addition of methylene blue solution, the sample is mixed at least 1 minute and then a stain test is performed. The stain test consists of placing a drop of the sample onto filter paper. The test is considered positive when a halo of a persistent light blue ring of about 1 mm forms around the central deposit. The procedure is repeated until the end point is reached. The end point must be confirmed by repeating the stain test at 1-minute intervals for 5 minutes without adding more methylene blue solution, as the clay may adsorb more dye over time. The total volume of dye solution is used to calculate the methylene blue value to the nearest 0.1 g of dye per kilogram of sample.

Sprung and Siebel (1991) examined different limestones and their effects on the performance of cement. These limestones contained different proportions of clay minerals. They found that montmorillonite has about eight times the absorptive capacity of illite, while kaolinite has only about half that of illite. Thus the methylene blue test does not measure clay content per se, but the absorptive capacity of the clay component of the limestone. For the purposes of determining the suitability of a limestone for use in cement, this measure is actually more appropriate. In their studies of the frost resistance of concrete, they found that the EN 197 criteria for limestone composition are suitable for evaluating limestone for use in Portland limestone cement. However, they found a few borderline cases in which reliability would have been improved by raising the minimum  $\text{CaCO}_3$  content from 75% to 80% by mass.

In the Building Research Establishment study (1993), some testing was done with a limestone that did not meet the EN 197-1 criteria: Its methylene blue sorption value was 2.7 g/100 g (as opposed to the specified limit of 1.20), its total organic carbon content was 0.38% (specified limit 0.20%), and its  $\text{CaCO}_3$  concentration was lower than the minimum specified. Fig. 3.1 shows the water: cement ratio needed to achieve a given slump in concretes made with different cements, each made with or without its own limestone. Comparison of the water: cement ratios for 0% and 5% limestone contents shows that the poor quality limestone did not affect the water demand for the 5%

limestone cement even though it had a deleterious effect on the water demand when the limestone content exceeded 16%.



**Figure 3.1: Required water: cement ratio to achieve a slump of 60 to 70 mm in concretes made with different cements. Cement E contained a limestone not conforming to the EN 197-1 criteria. Comparison of the water: cement ratios for 0% and 5% limestone contents shows that the poor quality limestone did not affect the water demand for the 5% limestone cement, but had a deleterious effect on the water demand when the limestone content exceeded 16%.**

### 3.2 CEMENT WITH LIMESTONE

Livesey (1991) points out the need to consider the suitability of the limestone and the composition and fineness of the cement in order to achieve optimum performance. Sprung and Siebel (1991) determined that it is possible to make concretes with Portland limestone cement that have the same frost resistance as concrete made with Portland cement, provided that the limestone meets the EN 197 criteria, that the limestone content of the Portland limestone cement does not exceed 20% by mass of cement, and that the Portland limestone cement reaches the same strength as the Portland cement.

Yellepeddi et al. (1993) describe a test method that can be used to determine the limestone content of cement for the purposes of quality control. They consider X-ray fluorescence to be less than adequate because it is not directly correlated to a phase such

as  $\text{CaCO}_3$ . Instead it gives only the total carbon concentration. In addition, X-ray fluorescence analysis of carbon is subject to several difficulties:

- The fluorescence yield of light elements such as carbon is poor, and the carbon fluorescence escapes from only a very thin layer at the sample surface, the rest being absorbed by the sample matrix. Thus the measured value represents only a small part of the sample.
- Surface contamination and materials used in the preparation of the sample can affect the results because of their own carbon content.
- When carbon is measured by X-ray fluorescence, all errors are multiplied by a factor of eight when converting to limestone concentrations. However, quantitative X-ray diffraction can analyze the  $\text{CaCO}_3$  content directly. X-ray diffraction has the additional advantages of representing a larger portion of the sample (due to the high energy of the X-rays) and being insensitive to surface contamination or the presence of materials used in sample preparation. They developed calibration curves based on the  $\text{CaCO}_3$  peak intensities in sets of white and gray cement standards and found standard errors of estimate of 0.17% and 0.08%, respectively.

They also found that repeated analyses of the same standard over time were quite stable. Should peak positions and backgrounds change due to sensitivity to such parameters as grain size and matrix effects, peak search and peak integration can be used to provide an accurate analysis.

Particle size distribution can be monitored by sieving a sample of cement and analyzing the separate fractions in order to determine how much limestone and how much clinker are in each fraction. Ménérier-Sorrentino (1988) found such techniques to be useful in her studies. Since the compositions of the limestone and clinker are known, it is possible to do such a separation after the fact.

Hawthorn, reporting in the Building Research Establishment study (1993) on the experience with composite cements in France, addresses the concern that limestone-filled cements might be of less consistent quality than other cements. He maintains that the

quality of limestone cements is actually quite uniform over time, particularly in comparison to that of cements containing fly ash or slag. Selection of the parts of a quarry that provide consistent material, and a large supply of material in the quarry, allow a uniformity of raw material that is much greater than for industrial by products such as slag or fly ash. Moir (1995) also points out that the limestone content can be adjusted to give more uniform strengths.

Number of samples	Type I Cement 250+		Type 10 Cement with limestone 75	
	Mean	Standard deviation	Mean	Standard deviation
LOI	1.4	0.2	2.2	0.1
SiO <sub>2</sub>	20.03	0.23	19.98	0.22
Fe <sub>2</sub> O <sub>3</sub>	2.00	0.08	1.96	0.08
Al <sub>2</sub> O <sub>3</sub>	5.69	0.12	5.23	0.14
CaO	62.54	0.26	62.22	0.26
Free lime	1.17	0.30	1.05	0.29
MgO	2.62	0.08	2.62	0.08
SO <sub>3</sub>	4.10	0.15	4.13	0.17
K <sub>2</sub> O	1.08	0.03	1.09	0.02
Na <sub>2</sub> O	0.28	0.01	0.28	0.02
Blaine (m <sup>2</sup> /kg )	377	10	384	10
% Passing 45 µm	95.6	13	93.8	1.4
Flow	121	6	120	5
Compressive strength (MPa)				
3 days	27.1	1.5	27.4	1.4
7 days	34.2	1.5	34.1	1.4
28 days	42.1	1.8	42.0	1.8

**Table 3.1: Production Data for Cements With and Without Limestone (Helinski 1996)**

Although ASTM cement standards specify only minimum strength limits, cement companies could set their own targets for strengths and use limestone to maintain their cement strengths, producing a more uniform product than they can without the use of limestone. Indeed, data summarizing two years worth of grab samples shipped from a modern cement plant producing cements both with and without limestone from the same clinker (Table 3.1) shows that a similar level of quality control on both cements can be achieved, as evidenced by the similar spread in the chemical and physical data (Helinski 1996).

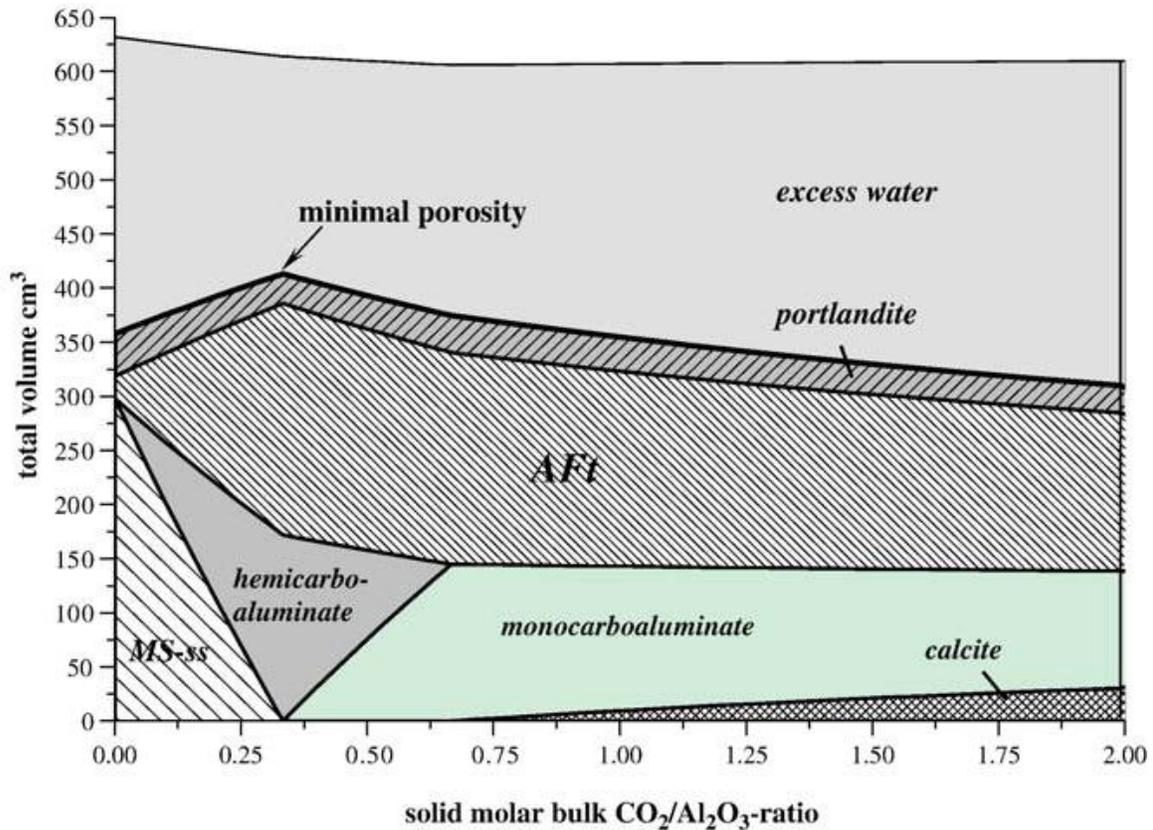
### 3.3 HYDRATION CHEMISTRY

In most early research it was believed that limestone acted as an inert filler; however more recent research has shown that limestone participates to some extent in hydration reactions. In addition, fine limestone particles may promote silicate hydration by providing nucleation sites for C-S-H precipitation.

Calcium carbonate has been reported to react with the tricalcium aluminate to form high and low forms of carboaluminates (Hooton et al. 2007). Matschei et al. (2007) observed that small amounts of limestone (calcite) reacted to form various carboaluminate phases. The unreacted calcite increased with an increase in the sulfate content. This work clearly showed the relative amounts of the phases that can be present. Lothenbach et al. (2008) coupled thermodynamic calculations with experimental observations to show that the formation of monocarboaluminate stabilized ettringite, increased the volume of hydrated products, and decreased porosity. These works provide quantitative calculations of the phases that may be present, providing a great step forward in understanding these systems.

Additionally, there may be a chemical effect that accelerates the hydration of tricalcium silicate in the presence of calcium carbonate. Pera et al. (1999) reported an acceleration of the C<sub>3</sub>S reaction in the presence of limestone.

Tsivilis et al. (2002) found that the addition of limestone as an interground material increased the reactivity of the clinker. Campitelli and Florindo (1990) found that the addition of limestone decreased the optimum SO<sub>3</sub> content. Production of CH appears to increase at early ages, which was attributed in part to the dissolution of limestone and in part to the role of the limestone in acting as a nucleation site (Turker and Erdoğan 2000).



**Figure 3.2:** Calculated volumes of hydrate phases for a model mixture consisting of C<sub>3</sub>A, portlandite and with fixed sulfate ratio (SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>=1) as a function of carbonate ratio (CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) at 25°C (constant total amount of solids, C<sub>3</sub>A+CaSO<sub>4</sub>+CH+Cc=3.25 mol, reacted with 500 g water) (Matschei et al. 2007).

Ye et al. (2007) reported that the limestone did not participate in chemical reactions; however it is important to note that in their study, the limestone was relatively coarse compared than the base cement.

## 3.4 DURABILITY

### 3.4.1 Permeability

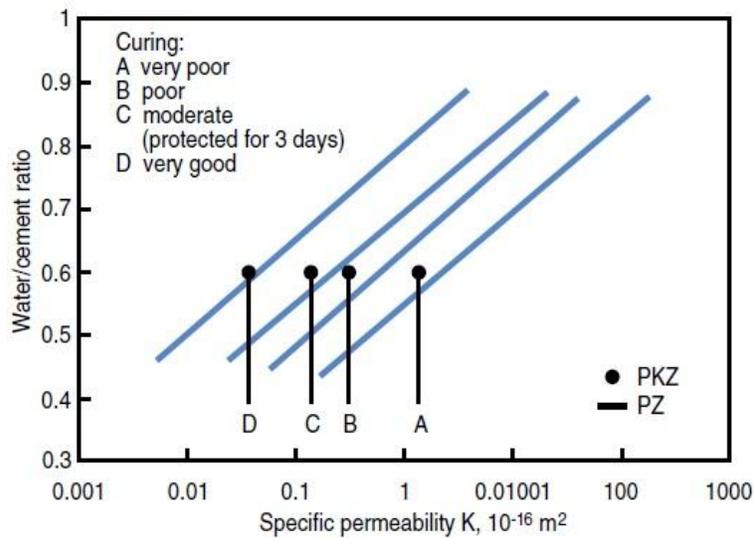
Permeability is the key to the durability of a porous material in all but the most protected environments. With the exceptions of abrasion and erosion, deterioration mechanisms involve the ingress of water and/or other harmful species (oxygen, carbon dioxide, chlorine ions, sulfate ions, acids, etc.). Frost damage does not occur in concrete unless it has reached a critical level of saturation. Corrosion requires water and oxygen, and is catalyzed by chlorine ions. Alkali-silica reaction requires water. While in some cases the water present in the original concrete mix -particularly if the concrete does not dry adequately after curing- is sufficient to allow deterioration to proceed, in general more water from the environment is needed. For deterioration of concrete in a hostile environment, low permeability reduces the rate of deterioration, allowing the concrete a longer service life. Unfortunately there are no simple, widely accepted test methods for the measurement of permeability. Thus, the data reported in this section are from a wide variety of test methods that are not directly comparable. Also, the permeability or diffusivity of concrete varies depending on what is moving through it—either because of interactions with the concrete components (for example, water will hydrate previously unhydrated cement, and chlorides can be bound by the hydration products of  $C_3A$ ) or because the size of ion, atom, or molecule affects its mobility.(Hawkins et al (2003))

Permeability is, of course, related to pore structure. Pore size is less important than the connectivity of the pore system. The improvement of pore structure attributed to the nucleation effect of the fine particles of  $CaCO_3$  was not due to the (slight) reduction in total pore volume, but to the refinement of the pore structure, which reduced its connectivity. ( Sellevold et al. (1982))

Moir and Kelham, reporting results from the Building Research Establishment study (1993), found that the permeability to oxygen for a series of concretes made with cements with or without 5% or 25% limestone was slightly reduced by the presence of limestone.

Not surprisingly, extended curing reduced the permeability significantly. Porosity was very similar for the control and 5% limestone cements. Water sorptivity was much the same for the control and 5% limestone cements.

Schmidt (1992b) tested the permeability of air entrained concretes made with Portland cement and Portland limestone cement by DIN 1048. In general the performance of the two types of cement was similar and well within specified limits (DIN 1045). He also determined the permeability coefficients for a series of concretes made from the two types of cement. In all cases the permeability coefficients for the Portland limestone concretes were slightly lower than for the comparable concretes made with Portland cement, as shown in Fig.3.3. Due to the limited number of tests, Schmidt was not sure whether the data indicated a trend of superior performance due to finer grinding and/or more efficient particle packing. However, it is clear that these cements perform at least as well as Portland cements in concrete having the same cement content and curing, even without taking advantage of the lower water demand to reduce the water: cement ratio.



**Figure 3.3: Permeability coefficient of concretes made with Portland cement (PZ) and Portland limestone cement (PKZ) containing 13 to 17% limestone and subjected to different curing regimes. In all cases the Portland limestone cements have lower permeabilities, but it is not clear from the small number of tests whether this is generally true.**

Alunno-Rosetti and Curcio (1997) presented data (Table 3.2) on water absorption of concretes made with cements with and without 20% limestone. The authors note that there are larger differences between cements from different plants than between cements from the same plant, irrespective of whether limestone is used.

	Plant B				Plant G			
	270		330		270		330	
Cement content, kg/m <sup>3</sup>								
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Water absorption, %	4.8	4.8	4.2	4.5	5.5	5.5	5.3	5.1

\* Italian national standard.

**Table 3.2: Water Absorption (UNI Standard 7699\*) of Concretes Made With Cements With or Without 20% Limestone (Alunno-Rosetti and Curcio, 1997).**

Tsivilis et al. (2003) measured the gas permeability,  $K_g$ , water permeability,  $K_w$ , sorptivity,  $S$ , and porosity,  $P$ , of concretes produced with 7 different cements. The cements were produced by intergrinding clinker (7.3%  $C_3A$ ), limestone of high purity (95.5%  $CaCO_3$ ) and gypsum (5% by mass of clinker) in a pilot plant ball mill. The cements differed in the quantity of limestone and the fineness of the finished cement. The cements were used to produce concrete samples which were cured for 28 days prior to conducting the tests. Details of the cements, the concrete mixtures and the results of the tests are shown in Table 3.3. In general, the concretes produced with PLC had higher gas permeability coefficients ( $K_g$ ) than the PC concrete, with the exception of the concrete produced with the PLC with 35% limestone, which recorded the lowest gas permeability value. On the other hand, the PLC concretes showed reduced permeability to water ( $K_w$ ) and lower water sorptivity values ( $S$ ). The porosity ( $P$ ) of the concrete was unaffected by the presence of up to 15% limestone in the cement, but increased with higher limestone contents. The authors concluded that overall the PLC concrete had “competitive properties” with the PC concrete (Tsivilis et al. 1999b). Earlier work at the same institute (Tsivilis et al. 1999a) reported that the quality and composition of both the clinker and the limestone had a significant impact on the permeability of concrete.

Cement Properties			Concrete Properties					
Lime-stone (%)	Blaine (m <sup>2</sup> /kg)	Strength at 28d (MPa)	W/CM	Strength at 28d (MPa)	$K_g$ (10 <sup>-17</sup> m <sup>2</sup> )	$K_w$ (10 <sup>-12</sup> m/s)	S (mm/min <sup>0.5</sup> )	P (%)
0	260	51.1	0.70	31.9	2.26	2.39	0.237	12.5
10	340	47.9	0.70	27.4	2.65	2.30	0.238	12.3
15	366	48.5	0.70	27.3	2.80	2.22	0.226	12.3
20	470	48.1	0.70	28.0	2.95	2.00	0.220	13.1
20	325	39.8	0.62	28.2	3.03	1.81	0.228	12.9
25	380	40.0	0.62	26.5	2.82	2.07	0.229	13.6
35	530	32.9	0.62	26.6	2.10	2.23	0.224	14.6

**Table 3.3: Permeability Test Results for Concretes Produced with PLC (Tsivilis et al. 2003)**

In a related study, Tsivilis et al. (2000) produced concretes with five cements with limestone contents ranging from 0% to 35%, and conducted the “Rapid Chloride Permeability Test” (RCPT) (ASTM C1202) after 28 days of moist curing. Table 3.4 shows details of the cements and concrete together with the results of the RCPT. The results show little significant impact due to increasing limestone content up to 15% to 20%. The mix with 35% limestone had a higher RCPT value despite being cast with a lower w/cm, indicating that permeability increased at this level of limestone.

Limestone, %	0	10	15	20	35
Fineness, m <sup>2</sup> /kg	260	340	366	470	530
Mortar: strength at 28 days (MPa)	51.1	47.9	48.5	48.1	32.9
Concrete: W/CM	0.70				0.62
Concrete: strength at 28 days (MPa)	31.9	27.4	27.3	28.0	26.6
Concrete: RCPT (Coulombs)	6100	5800	6000	6400	6600

**Table 3.4: Effect of Limestone Additions on the “Chloride Permeability” of Concrete (Tsivilis et al. 2000)**

### 3.4.2 Chlorides

Ramachandran et al. (1990) studied mortars containing 0%, 2.5%, 5%, and 15% precipitated  $\text{CaCO}_3$  (particle size 1 to 5  $\mu\text{m}$ ) or ground limestone – (particle size 1 to 40  $\mu\text{m}$ ) at water: cement ratios of 0.42 and 0.60. The specimens were hydrated in limewater or in laboratory prepared “seawater” (2.7%  $\text{NaCl}$ , 0.32%  $\text{MgCl}_2$ , 0.22%  $\text{MgSO}_4$ , and 0.13%  $\text{CaSO}_4$ ) for up to one year. They monitored length and modulus of elasticity periodically. They found that the strengths of the mortars were not affected by the ground limestone, but at 15% replacement, precipitated  $\text{CaCO}_3$  reduced the strength by about 50%. When the compressive strengths were similar, specimens at a water: cement ratio 0.60 or containing precipitated  $\text{CaCO}_3$  exhibited much higher expansions than the controls when exposed to seawater. Only those specimens with a water: cement ratio of 0.42 containing the ground limestone showed similar expansions to the controls. Moduli of expansion were similar to the control for the lower water: cement ratio mortars, except at the 15% replacement level by precipitated  $\text{CaCO}_3$ , which was much lower. Exposure to seawater generally lowered the moduli, with more reduction in the higher water: cement ratio mortars. The same authors (Feldman et al. 1992) also looked at limestone Portland cement mortars exposed to  $\text{NaCl}$  and  $\text{MgCl}_2$  solutions, concluding that the moduli are reduced and expansions increased compared to controls exposed to  $\text{Ca}(\text{OH})_2$  solution. The magnitude of the changes depended on the water: cement ratio, and the amount and fineness of the limestone used.

Deja et al. (1991) subjected mortar specimens containing 5% ground limestone to a low pressure steam treatment (maximum temperature 80°C) followed by immersion for up to one year in a mixed salt solution loosely based on the composition of seawater. Three types of specimens were tested: 25 × 25 × 100 mm prisms for strength tests, cylinders with steel bars along the axis for steel passivation studies, and 40 × 40 × 160 mm prisms with embedded steel plates for mass loss studies. Their data on the effect of chloride exposure on the compressive and flexural strength (Table 3.5) show that chloride exposure is equally deleterious to the strength of mortars with or without limestone. The mass loss of the steel plates for the control and 5% limestone specimens stored in water

for one year were 6.82 and 8.68 g/m<sup>2</sup>, respectively, while for the specimens stored in the salt solution they were 32.51 and 7.13 g/m<sup>2</sup>, respectively. Thus the limestone was effective in protecting the steel from corrosion. The passivation data lead to a similar conclusion.

Age	Compressive		Flexural	
	Control	5% Limestone	Control	5% Limestone
Initial	41.2	42.1	8.8	8.6
56 days: in water in solution	47.8	47.1	11.5	11.1
	45.4	42.3	11.3	12.1
365 days: in water in solution	49.2	47.6	11.0	11.3
	36.6	36.9	10.2	8.8

**Table 3.5: Strengths of Mortars Exposed to Mixed Salt Solution, MPa (Deja et al. 1991)**

Tezuka et al. (1992) determined the diffusion coefficient for chloride ions for a series of mortar specimens containing different quantities of limestone ground to 450m<sup>2</sup>/kg. They found that the diffusion coefficients for the control and the 10% limestone mortars were comparable ( $51.2 \times 10^{-9}$  cm<sup>2</sup>/s and  $53.1 \times 10^{-9}$  cm<sup>2</sup>/s, respectively), and that for the 5% limestone was lower ( $14.3 \times 10^{-9}$  cm<sup>2</sup>/s).

Moir, reporting the results of the Building Research Establishment study (1993), found no clear trend regarding the effect of 5% limestone on the resistance of concrete to chloride penetration. The best predictor of chloride ion penetration was compressive strength: The higher the strength, the more resistant the concrete to chloride ions. However, for concretes of the same strength class exposed to seawater for two years, chloride concentration 30 mm from the surface increases with cement C<sub>3</sub>A content.

Baron and Douvre (1987) state that for marine exposure, the limestone content should be limited to 10%, based on laboratory and field tests. They also recommend that the

limestone and clinker be tested for compatibility with each other and the environment in which the limestone Portland cement is to be used.

Alunno-Rosetti and Curcio (1997) presented data (Table 3.6) on chloride penetration of concretes made with cements with and without 20% limestone. The authors note that there are larger differences between cements from different plants than between cements from the same plant, irrespective of whether limestone is used.

Cement content, kg/m <sup>3</sup>	Plant B				Plant G			
	270		330		270		330	
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Chloride penetration, mm at 28 days	43	102	38	48	212	197	115	146
at 60 days	63	113	49	79	281	264	183	182

\* Italian national standard.

**Table 3.6: Chloride Penetration (UNI Standard 7928\*) of Concretes Made With Cements With or Without 20% Limestone (Alunno-Rosetti and Curcio, 1997)**

### 3.4.3 Carbonation

Sprung and Siebel (1991) found that in general concretes made with Portland limestone cement (6 to 20% limestone) showed increased rates of carbonation as compared with those made with Portland cements, even when the strengths were the same. Tezuka et al. (1992) found the depth of carbonation for mortars containing various quantities of limestone comparable to those for the control Portland cement mortars for limestone contents up to 10%. Baron (1988) found that the depth of carbonation for standard mortars made with 15% limestone cements was the same as for the control mortars.

Barker and Matthews (1994) studied the durability of two series of concretes: Series A made with constant cement content and water: cement ratio, and series B made with constant slump and 28-day strength. Their carbonation depth data for the Portland cement concretes and those made with various limestone contents are presented in Table 3.7. The concretes were stored at 20°C and 65% RH. They found that regardless of the

composition of the cement, the depth of carbonation correlated well with the strength of the concrete.

Cement	Moist curing	Series A 90 days	Series A 1 year	Series B 90 days	Series B 1 year
Portland	1 day	3.3	8.0	3.3	8.0
	3 days	2.4	6.6	2.4	6.6
9% Limestone	1 day	3.9	7.6	4.6	8.4
	3 days	3.1	6.2	3.3	6.6
15% Limestone	1 day	6.0	9.9	3.4	6.2
	3 days	5.3	9.0	2.7	5.0
24% Limestone	1 day	6.6	11.0	3.4	6.9
	3 days	6.9	9.7	2.6	6.3

**Table 3.7: Carbonation Depths at 90 days and 1 year, mm (Barker and Matthews, 1994).**

Schmidt (1992a) observed carbonation depths for concretes made with Portland limestone cement (13% to 17% limestone) that were higher than for comparable concretes made with Portland cement, but lower than for concretes made with slag cement. However, he maintains that since the field performance for slag cements has been good, this result should not be interpreted as disadvantageous to the durability of concrete. In any case the increases in carbonation depths measured after three years of exposure were minimal. Fig. 10 from Schmidt et al. (1993) shows the depth of carbonation for concretes cured in water for 6 days and then exposed to a standard atmosphere of 65% R.H. at 20°C for three years. These concretes were designed for constant water: cement ratio, so that the workabilities were different.

Moir and Kelham (1993), reporting the results of the Building Research Establishment study, found that carbonation depth is inversely related to concrete strength. Tests of concretes containing 5% or 25% limestone, as well as fly ash or slag, showed that carbonation depths have the same relationship to concrete strength regardless of cement type. Increasing the wet curing time from 1 to 3 days reduced the carbonation depths by approximately 40% for all cement types.

Alunno-Rosetti and Curcio (1997) presented data (Table 3.8) on carbonation depth in concretes made with cements with and without 20% limestone. Use of limestone in cement did not impact depth of carbonation.

	Plant B				Plant G			
	270		330		270		330	
Cement content, kg/m <sup>3</sup>	270		330		270		330	
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Carbonation depth, mm	20	10	18	13	19	21	15	16

\* Italian national standard.

**Table 3.8: Carbonation Depths (UNI Standard 9944\*) at 900 days in Concretes Made With Cements With or Without 20% Limestone (Alunno-Rosetti and Curcio, 1997)**

### 3.4.4 Sulfate Resistance

Soroka and Stern (1976) studied the effect of reagent-grade CaCO<sub>3</sub> and CaF<sub>2</sub> (used as an inert filler) on the sulfate resistance of Portland cement mortars having a water: cement ratio of 0.75. Specimens 25.4 × 25.4 × 158.7 mm in size were immersed in a 5% Na<sub>2</sub>SO<sub>4</sub> solution. Their time to cracking data is shown in Table 3.9. It can be seen that the CaCO<sub>3</sub> has a beneficial effect beyond the reduction of the C<sub>3</sub>A content of the cement.

Mortar	Time to cracking, weeks	28-day compressive strength, MPa
Reference	6	25.3
10% CaCO <sub>3</sub>	10	27.0
20% CaCO <sub>3</sub>	12	27.3
30% CaCO <sub>3</sub>	14	29.7
40% CaCO <sub>3</sub>	16	30.9
10% CaF <sub>2</sub>	6	23.7
20% CaF <sub>2</sub>	6	28.2
30% CaF <sub>2</sub>	6	32.6
40% CaF <sub>2</sub>	6	28.9

**Table 3.9: Time to Cracking for Mortar Prisms Exposed to 5% Na<sub>2</sub>SO<sub>4</sub> (Soroka and Stern, 1976)**

Soroka and Setter (1980) followed up this preliminary study by examining the expansion and deterioration of mortars containing various amounts of ground limestone, dolomite, or basalt and immersed in 5% Na<sub>2</sub>SO<sub>4</sub> solution for up to 11 months. The additive contents were 10%, 20%, 30%, and 40% by mass. They found that the limestone imparted some improvement in sulfate resistance as compared with the control. The fineness of the additive was also significant, as can be seen in Table 3.10. However, they found that after long periods of exposure the intensity of cracking of the limestone-filled mortars was essentially the same as for the others. Thus they conclude that the use of limestone improves the sulfate resistance of mortars, but not to such an extent as to produce sulfate resistant mortars.

Fineness, m <sup>2</sup> /kg	Limestone	Dolomite	Basalt
115-130	12	12(?)	4
370-300	10	6	4
660-710	10	6	4
960-1120	18	6	2
Reference		6 weeks	

**Table 3.10: Time to Cracking for Mortar Prisms Exposed to 5% Na<sub>2</sub>SO<sub>4</sub> with 30% Filler, Weeks (Soroka and Setter, 1980)**

Hooton (1990) tested pairs of commercially produced cements made from the same clinker with and without limestone. Both ASTM C 452 and C 1012 were used. In ASTM C 452, the SO<sub>3</sub> content is raised to 7.0% using gypsum and the mortar bars are stored in water while expansions due to the internal sulfate attack are measured. In ASTM C 150 the 14-day expansion limit for sulfate resistant cement is 0.040%, while in CSA/CAN-A5 the limit is 0.035% for sulfate resisting cement and 0.050% for moderate sulfate resisting cement. Hooton's data are shown in Table 3.11. There is no clear trend with regard to the effect of carbonate on sulfate resistance. Cements 2, 2c, 3, and 3c meet the CSA criterion for moderately sulfate resisting cement.

Cement	1	1c	2	2c	3	3c
%C <sub>3</sub> A	10.4	10.0	9.1	9.8	8.3	7.3
% CaCO <sub>3</sub> (by TGA)	0.3	4.1	0.8	4.7	0.3	2.6
Age, days						
14	0.054	0.058	0.036	0.041	0.039	0.036
28	0.071	0.092	0.053	0.054	0.051	0.043
56	0.084	0.126	0.066	0.058	0.058	0.050
91	0.086	0.142	0.075	0.058	0.061	0.054
105	0.088	0.144	0.077	0.059	0.062	0.055
119	0.088	0.145	0.079	0.059	0.062	0.056
170	0.087	0.146	0.079	0.059	0.064	0.056
261	0.088	0.148	0.079	0.059	0.065	0.057
365	0.090	0.150	0.080	0.060	0.068	0.060

**Table 3.11: ASTM C 452 Expansions, % (Hooton 1990)**

In ASTM C 1012, which was developed for the evaluation of blended cements, mortar bars are exposed to 5% Na<sub>2</sub>SO<sub>4</sub> solution once companion cubes have reached a compressive strength of 21 ± 1 MPa. Tentative expansion limits for this method are 0.10% at 6 months for moderate sulfate resisting cement and 0.05% at 6 months or 0.10% at 12 months for highly sulfate resisting cements. Hooton reported expansion data up to 365 days for the six cements. The time to reach 0.10% expansion is given in Table 3.12. Again, there is no clear trend as to the effect of carbonate use on sulfate resistance. Hooton concluded that sulfate resistance is not affected by carbonate and is primarily determined by C<sub>3</sub>A content.

Cement	1	1c	2	2c	3	3c
%C <sub>3</sub> A	10.4	10.0	9.1	9.8	8.3	7.3
% CaCO <sub>3</sub> (by TGA)	0.3	4.1	0.8	4.7	0.3	2.6
Time to 0.10% expansion, days	117	142	167	161	196	236

**Table 3.12: ASTM C 1012: Time to 0.10% Expansion (Hooton 1990)**

González and Irassar (1998) also evaluated effects on sulfate resistance (ASTM C 1012) of mortars made with Type II and Type V cements with 0%, 10%, and 20% limestone. Their results indicate no significant difference in sulfate resistance of low-C<sub>3</sub>A cements with or without 10% limestone; however, for 20% replacement levels, the sulfate resistance was lowered. Their results are summarized in Table 3.13.

Cement	Type V			Type V			Type II		
C <sub>3</sub> A content, % by mass	0			1			6		
C <sub>3</sub> S content, % by mass	40			74			51		
Limestone replacement	0	10	20	0	10	20	0	10	20
Time to 0.10% Expansion, days	1260	857	208	148	164	92	165	209	108
Reduction in compressive strength (1 year in sulfate solution). %	3	4	5	29	17	50	8	25	40

**Table 3.13: Sulfate Resistance in ASTM C 1012 Mortars (González and Irassar, 1998)**

Marsh and Joshi (1986) studied the effects of large quantities (30% and 50%) of limestone on the sulfate resistance of concrete. In their work limestone was added to cement paste rather than to the cement, since the Canadian standard limits the limestone content of cement to 5%, but allows additional amounts to be used in concrete. Specimens were cast and sealed in plastic molds 25×25×300 mm and were rotated until set. After 24 hours they were demolded and cured in saturated limewater for 28 days at either 20°C or 50°C. The specimens were cut to size at age 7 days. The resistance to sulfate attack was determined by measuring the length change of 125 mm cement paste prisms immersed in 0.35 M Na<sub>2</sub>SO<sub>4</sub> solution at 20°C. The pH of the solution was maintained at approximately 7 by the addition of 0.5 M H<sub>2</sub>SO<sub>4</sub> as needed. At these dosages the use of limestone resulted in increased expansions due to sulfate attack. However, in the specimens cured at 50°C all of the pastes were resistant to sulfate attack for exposure periods in excess of one year.

Matthews reports that in the Building Research Establishment study (1993) no relation was found between limestone content and sulfate resistance of concretes. The C<sub>3</sub>A content of the parent cement determined the sulfate resistance.

Taylor (2001a, b) studied effects of use of limestone in low-C<sub>3</sub>A content Portland cements on sulfate resistance. In one study (Taylor 2001a), a clinker with C<sub>3</sub>A content of 8% was interground with one of two limestones: One limestone was interground at either 2.5 or 3.5%, while another was interground in amounts of 3.0% and 5.0%. Both ASTM C 1012 and C 452 data indicated acceptable (per ASTM C 150, C 595, or C 1157) performance for all cements. Data are summarized in Figs. 3.4 and 3.5.

Skaropoulou (2013) investigate the use of mineral admixture improves the sulfate resistance of limestone cement, due to their beneficial effect on the permeability and pore structure. They use Portland cement (K) of industrial origin and limestone (L) of high calcite content (CaCO<sub>3</sub>: 95.7%). Portland limestone cement, containing 15% (w/w) limestone, was produced by intergrinding clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity. After 34 months of exposure, specimens with LC1-s presented the most severe deterioration. They also point out that the use of mineral

admixtures improved the resistance of the limestone cement concrete against sulfate attack at low temperature. Sand also play an important role, in the case of siliceous sand, the limestone cement concrete (LC1-s) presented the greatest mass loss (17%) after 35 months of exposure in the sulfate solution. In the case of calcareous sand, no mass loss was observed in the concrete specimens during the 35 months of storage in the 1.8%w/w  $MgSO_4$  solution at 5 °C. Mass measurements verify that the use of mineral admixtures improved the resistance of limestone cement concrete against TSA, especially in the case of siliceous sand when concrete seems to be more susceptible so TSA. Their experiments also showed that concrete containing exclusively limestone cement is susceptible to the thaumasite form of sulfate attack at low temperature. Deterioration is less severe when a certain amount of the Portland limestone cement is replaced by the studied mineral admixtures. Such minerals act chemically by reacting with calcium hydroxide (pozzolanic reaction) and forming C–S–H, which is the main cohesive phase in the cement paste. Some authors suggest that this silicon rich C–S–H, shows higher resistance against thaumasite formation.

In another study, Taylor (2001b) evaluated two cements with  $C_3A$  contents of 3% and 5% interground with limestone in amounts of 4.0% and 3.5%, respectively. Results of ASTM C 452 and C 1012 testing demonstrated acceptable performance according to cement specifications (ASTM C 150, C 595, or C 1157). Expansion data are plotted as a function of time in Figs. 3.6 and 3.7.

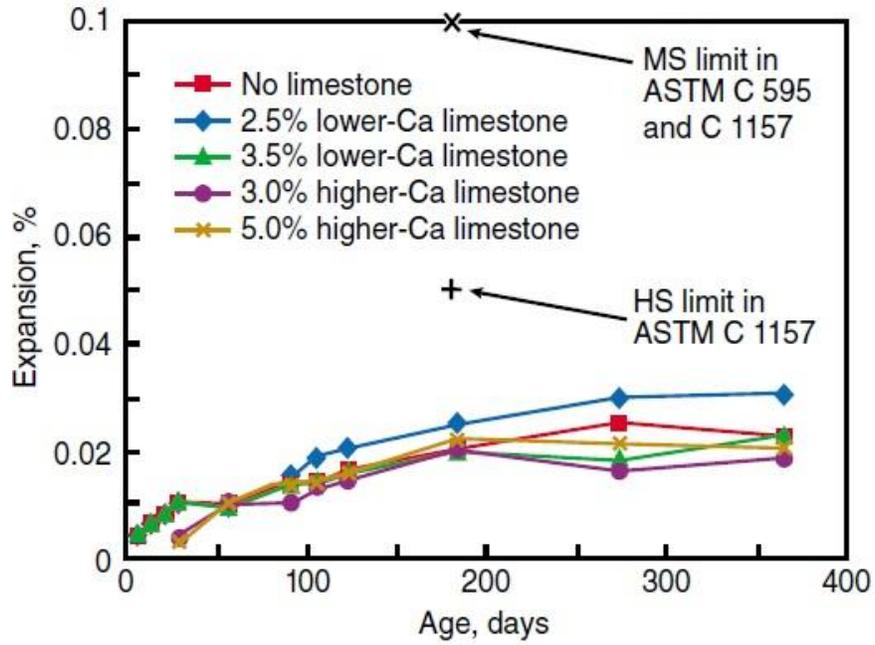


Figure 3.4: Expansion in test method ASTM C 1012 (after Taylor 2001a) for Type II cements with two levels of two different limestones.

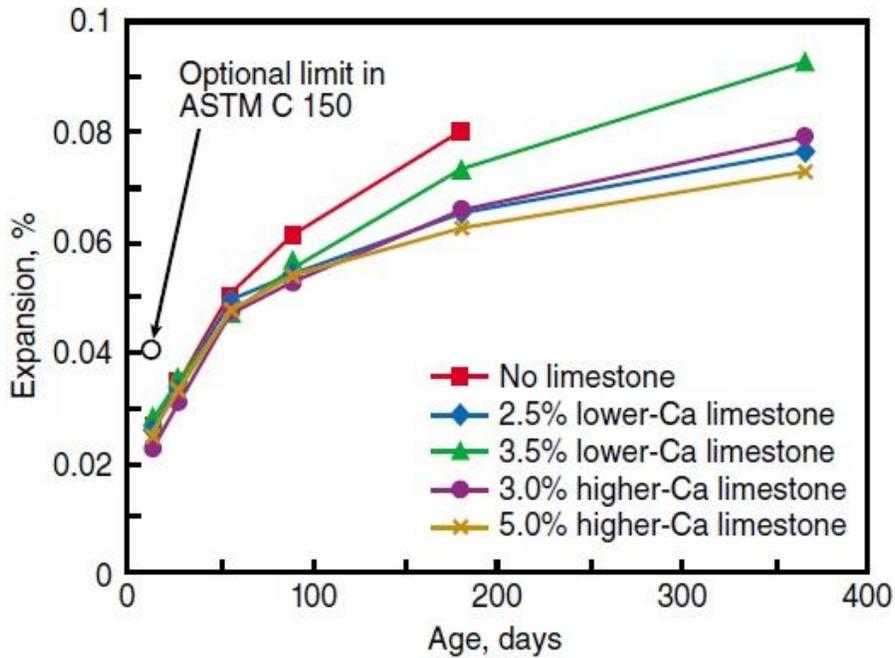


Figure 3.5: Expansion in test methods ASTM C 452 (after Taylor 2001a) for Type II cements with two levels of two different limestones.

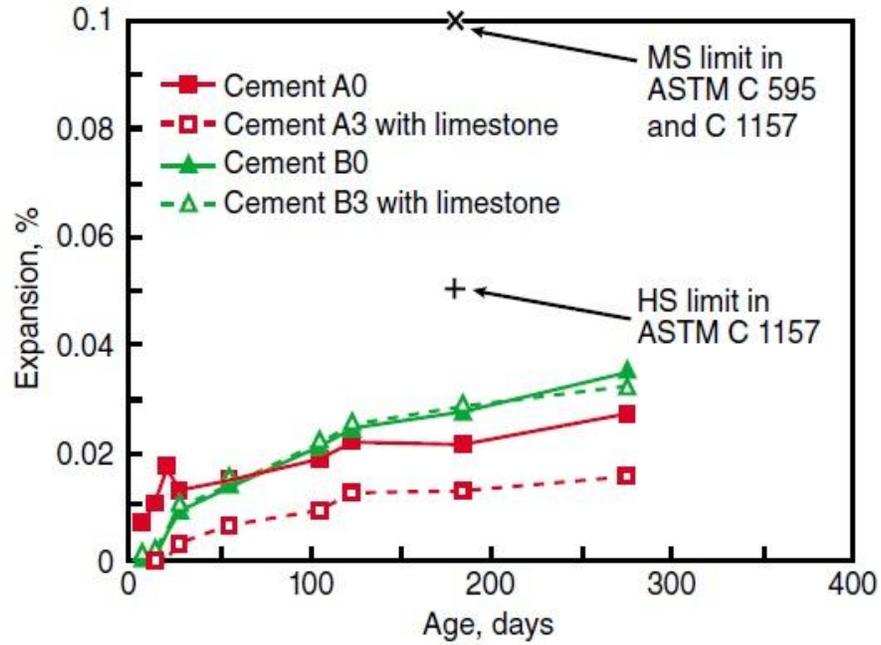


Figure 3.6: Expansion in test method ASTM C 1012 test for cements with C3A contents of 5% or less. Cements A3 and B3 were interground with 3% limestone (after Taylor 2001b).

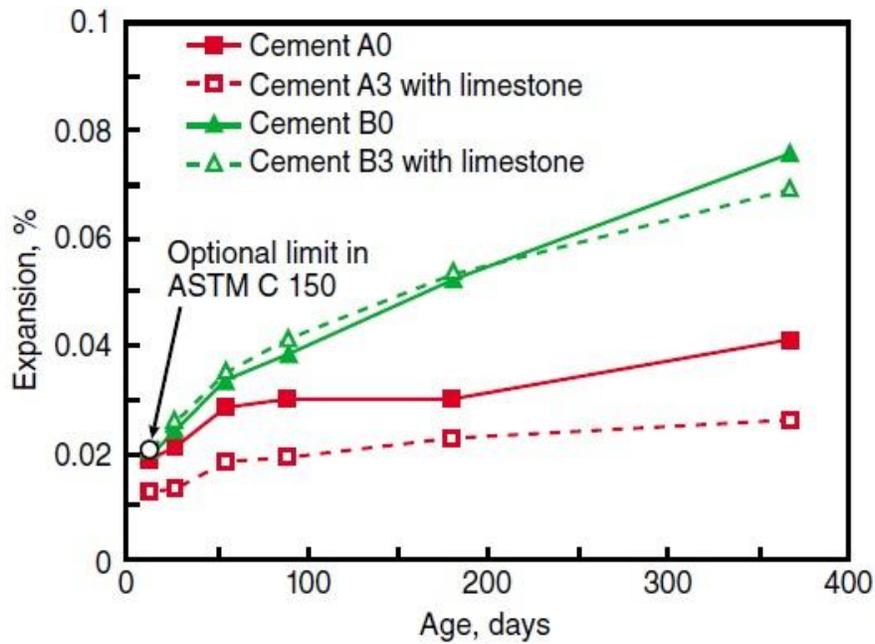


Figure 3.7: Expansion in test method ASTM C 452 for cements with C3A contents of 5% or less. Cements A3 and B3 were interground with 3% limestone (after Taylor 2001b).

### 3.4.5 Alkali-Silica Reactivity

Hobbs (1983) reported on the effects of 5% limestone on the expansion due to alkali-silica reactivity of  $25 \times 25 \times 250$  mm mortar bars made from Thames Valley sand and a Beltane opal rock having particles 150 to 300  $\mu\text{m}$  in size. The proportion of Beltane opal was adjusted to give the critical alkali-reactive silica ratio. The expansion at 200 days averaged 0.009% for the Portland cement specimens and 0.021% for the specimens with 5% limestone. Times to cracking were as shown in Table 3.14. Hobbs concluded that although there is some effect on the average expansion, the use of 5% limestone neither reduces the time to cracking below the minimum observed for Portland cement mortars nor increases the expansion at 200 days above the maximum observed for Portland cement mortars. He therefore concludes that it does not increase the likelihood of deleterious expansions due to alkali-silica reaction.

Water/solids	Cement alkalies	Portland cement	5% Limestone
0.41	1.00%	5, 6	8, 8
0.53	1.00%	28, 39	54, 54
0.53	0.79%	*	*

\*The bars had not cracked at age 250 days.

**Table 3.14: Time to Cracking Due to ASR, Days (Hobbs 1983)**

---

## **EXPERIMENTAL PART**

## **Chapter 4**

### **MATERIALS AND METHODOLOGY**

This chapter includes the details of experimental work of the present study. The target is to experimentally investigate the effect of different type of cement in corrosion of reinforcement in presents of corrosion inhibitors and without it. Three type of cement have been used: CEM II, LC 1 and LC 2. Electro chemical method will be consider investigating the mass loss. This thesis will investigate the use of corrosion inhibitor and effect of it on different type of cement.

#### **4.1 MATERIALS**

We prepared 18 cubic concrete specimens, 80×80×100 mm. A water to cement (w/c) ratio was 1/2, the cement to aggregate (c/a) ratio was 1/3 and the maximum aggregate size was 5 mm. To be more specific, for each type of cement 6 specimens were prepared, 3 of them with corrosion inhibitor and 3 without. In each specimen 4 reinforcement were

placed. The first 6 specimens were made with CEM II; the second 6 specimens were made with LC1 and the last 6 specimens made of LC2.

#### 4.1.1 Cements

In the present experiment 3 type of cement were used. CEMII, LC1 and LC 2. Portland limestone cements, contain 15%, 35% w/w limestone, were produced by intergrinding of clinker, limestone and gypsum in a pilot plant ball mill of 5 kg capacity. Preliminary tests with varying grinding time have been done in order to produce cements of appropriate compressive strength. The cements LC1, LC2 contain 15%, 35% limestone, respectively. The composition of the cement, as well as their 28 days compressive strength and specific surface are shown in Table 4.1 (Sotiridis et al, 2012)

Code	Cement composition	28-days compressive strength (MPa)	Specific surface (cm <sup>2</sup> /g)
LC1	Clinker: 85% w/w, limestone: 15% w/w	41.3	3980
LC2	Clinker: 65% w/w, limestone: 35% w/w	32.4	5040

**Table 4.1: Characteristic of the LC1 and LC2 cements**

Portland cement clinker of industrial origin and limestone of high calcite content (CaCO<sub>3</sub>:97.5%) were used. The chemical composition of the above materials is present in Table 4.2 and Table 4.3 respectively. The used clinker has a moderate C<sub>3</sub>A.

SiO <sub>2</sub>	AL <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cao	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI	Total
0.57	0.33	0.19	54.60	1.64	0.04	-	0.02	42.76	100.15

**Table 4.2: Chemical analysis of limestone (% w/w).**

Chemical composition (%)		Mineralogical composition (%)	
SiO <sub>2</sub>	21.92	C <sub>3</sub> S	48.4
Al <sub>2</sub> O <sub>3</sub>	5.68	C <sub>2</sub> S	26.3
Fe <sub>2</sub> O <sub>3</sub>	3.29	C <sub>3</sub> A	9.5
CaO	63.35	C <sub>4</sub> AF	10.00
MgO	1.44		
K <sub>2</sub> O	1.32		
Na <sub>2</sub> O	0.84		
SO <sub>3</sub>	1.25		
LOI	0.91		
fCaO	1.15		
<b>Moduli</b>			
		Lime Saturation Factor (LSF)	95.7
		Silica Ratio (SR)	2.5
		Alumina Ratio (AR)	1.43
		Hydraulic Modulus (HM)	2.18

**Table 4.3: Chemical and mineralogical composition of clinker**

The chemical composition of the CEMII cement is shown in Table 4.4. (Batis et al, 2005).

SiO <sub>2</sub>	AL <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cao	Mgo	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	CaO <sub>f</sub>	LOI	Specific surface (cm <sup>2</sup> /g)
27.38	9.1	5.65	45.39	2.73	0.94	0.56	2.71	2.67	5.04	3900

**Table 4.4: Chemical composition of CEMII cement**

### 4.1.2 Aggregates

The use of aggregates should be according to EN12620 for normal and heavyweight aggregates and according to EN13055-1 for lightweight aggregates.

In this thesis sand have been used as aggregate which confirm all required terms and conditions.

### 4.1.3 Reinforcement

Concrete reinforcement steel should be protected against corrosion, both before it is incorporated into concrete, and after. During its placement into the final position, steel should be relieved of all visible scaling alterations, or unwanted deformations and damage, which, besides other things, speed up the effects of corrosion.

In this experiment we use steels type of B500C EL0T. The marking for identifying the quality by a grad of concrete reinforcement steel is done with a different configuration of the transverse ribs on the surface of the bar. B500C grade steels have on their surface two rows of transverse consecutive ribs ar opposite direction. In each row, the consecutive ribs have alternating angle of gradient as to the longitudinal axis of bar as seen in Figure 4.1.

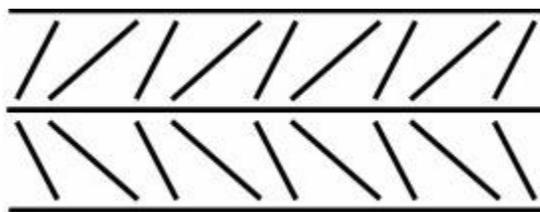


Figure 4.1: Rib configuration of B500C grade steel.

Steels with ribs are characterised by their surface geometry, which dictates their adhesion to the concrete. Concrete reinforcement steels with ribs have at least two rows of parallel transverse ribs uniformly distributed on each side of the steels surface and at equal distance throughout both rows. Longitudinal ribs may be added, but are not mandatory.

The tensile strength limits that the mechanical properties of concrete reinforcement steels must meet are given in Table 4.5.

The values of yield strength  $f_y$  and  $f_t$  are calculated according to the nominal cross-section.

Property	Technical Quality Grade
	B500C
Yield strength, $f_y$ (MPa)	$\geq 500$
Ratio of the actual to the nominal value of yield strength $f_{y,act}/f_{y,nom}$	$\leq 1.25$
Ratio of tensile to yield strength $f_t/f_y$	$\geq 1.15 \leq 1.35$
Total Strain (elongation) under maximum load $\epsilon_u$ (%)	$\geq 7.5$

**Table 4.5: The tensile strength limits of the mechanical properties of steel according to ELOT 1421-2 and ELOT 1421-3 (typical values).**

The common chemical composition, production methods, as well as the time-periods that the various categories of steel are display in Table 4.6.

Steel Grade	Common chemical composition (% of weight)				Production Method
	C	Mn	Si	S	
B500C	0.20-0.22	0.90-1.20	0.15-0.30	0.03-0.05	HRT (Hot Rolled Tempered steel)

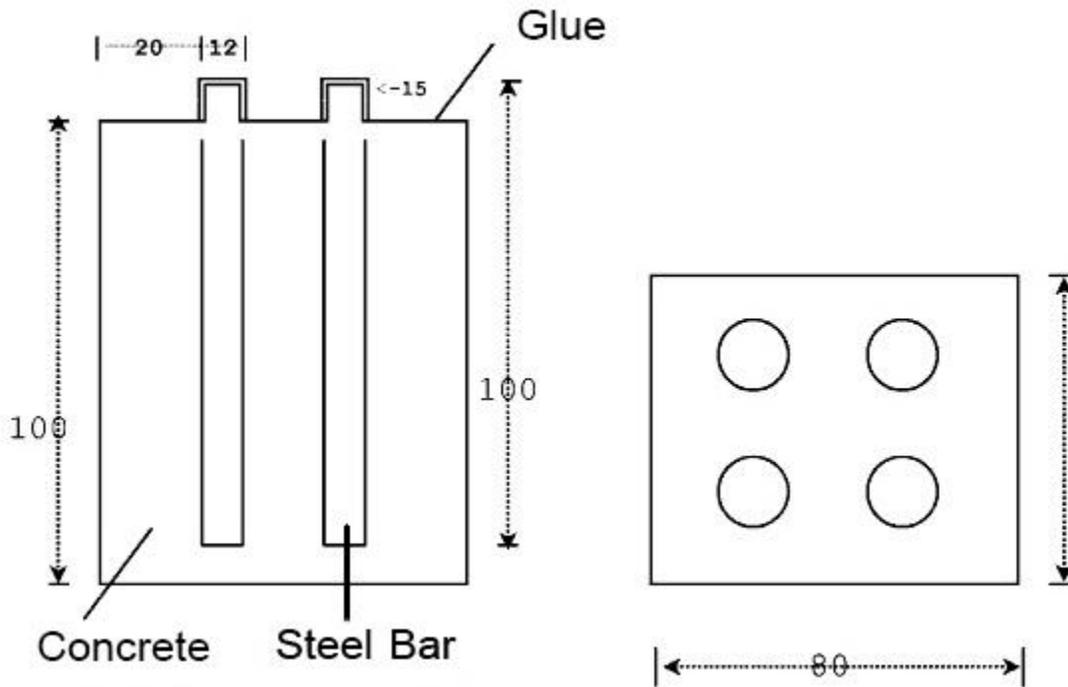
**Table 4.6: Common chemical composition, production methods**

During this project all Reinforcements were cleaned by immersing in acetone in order to removes rust and oxidation from steel. Steel bars were sunk in Acetone fore few seconds and afterwards they were weighted.

## **4.2 EXPERIMENTAL PROCEDURE**

### **4.2.1 Preparation**

The specimens were prepared using three different cement types CEMII, LC1, LC2. In all specimens the aggregate used was the same. Reinforcing steel bars of steel type B500c and tap water were used. Mix proportions aggregate/water/cement were kept constant and equal to 3/1/0.5. Each specimen was cast into a prismatic mould (80×80×100 mm), where four identical steel bars (100×12 mm) were embedded in position shown in Figure 4.2.



**Figure 4.2: Schematic representation and dimensions (mm) of specimens.**

Specimens were stored at ambient condition for 48 h, then cure in tap water for 7 days and then the part shown in Figure 4.2 was insulated with epoxy glue. Finally, all specimens were partially immersed up to  $\frac{2}{3}$  of their height in 3.5% NaCl.

### 4.3 METHODOLOGY

The corrosion potentials of steel in the specimens partially immersed in 3.5% NaCl solution were measured with 2 methods:

1. Monitoring the corrosion potentials
2. Linear polarization

### 4.3.1 Monitoring the corrosion potentials

The corrosion trend of the samples was estimated by monitoring the corrosion potential vs. exposure time. The corrosion potential of steels were measured according to ASTM C876-87, using a Ag/ AgCl/ KCl (3M) electrode as a reference electrode which was placed in 3.5% NaCl solution. A voltmeter is also needed.

As it's refer in ASTM C 876-87:

1. Potentials less negative than -0.2 volts generally indicate, 90% higher probability of no corrosion taking place at the time of measurement.
2. Potentials in the middle of -0.2 to 0.35 volts are inconclusive.
3. Potentials greater than -0.35 volts generally indicated, 90% or higher probability of active corrosion in the area at the time of testing.
4. Positive potentials, if obtained, generally indicate insufficient moisture in the concrete and should not be considered valid. However, stray DC currents may also cause potential measurements and therefore careful review analysis of the obtained data is required.

### 4.3.2 Linear polarization

The linear polarization technique requires us to polarize the steel with an electric current and monitor its effect on the half cell potential. It is carried out with a sophisticated development of the half cell incorporating an auxiliary electrode and a variable low voltage DC power supply. The half cell potential is measured and then a small current is passed from the auxiliary electrode to the reinforcement. The change in the half cell potential is simply related to the corrosion current by the equation:

$$I_{corr} = \frac{B}{R_p}$$

Where B is a constant (in concrete 26 to 52 mV) and it depend on type of cement, water cement ratio and the passivity or active condition of the steel. For steel in passivity condition B=52mV and for steel in active condition B=26mV. In this present thesis,

assuming that steel was in active condition,  $B=26\text{mV}$ .  $R_p$  is the polarization resistance (in ohms):

$$R_p = (\text{change in potential}) / (\text{applied current})$$

$R_p$  gives the technique its alternative name of polarization resistance. The change in potential must be kept to less than 20 mV or so for the equation to be valid and remain linear.

The change in potential must be kept to less than 20 mV or so for the equation to be valid and remain linear. The “iR drop” must also be removed. This is the voltage that exists because a current is flowing through concrete that has an electrical resistance. This is also referred to as the solution resistance. This means that the current is usually switched off during the measurement process so that the potential without the iR drop is measured. (P. Broomfield, 1997)

Corrosion is an electrochemical process whereby the amount of corrosion is related to the electrical energy consumed, which is a function of voltage, amperage, and time interval. The amount of corrosion can be estimated using an equation based on Faraday’s law :

$$\beta = \frac{t \cdot M \cdot I_{corr}}{z \cdot F}$$

Where: t is time (sec),  $I_{corr}$  is corrosion current (Amperes), M is atomic weight of iron (55.847 g/mol), z is ion charge (assumed 2 for  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ) and F is Faraday’s constant (96.487 Amp.sec).

## **Chapter 5**

# **MEASUREMENTS**

### **5.1 CORROSION POTENTIALS**

Corrosion potentials were measured for a period of 305 days for specimens.

#### **5.1.1 Specimens made from CEM II**

Measurement of corrosion potentials for specimens made from CEM II started after passing 12 days from immersing in 3.5% NaCl. The measurement for CEM II without corrosion inhibitor is shown in Table 5.1 while the measurement for CEM II with corrosion inhibitor is given in Table 5.2.

Specimen	E (mV)							
	12	57	74	125	142	156	173	187
1	-348.66	-310.15	-291.97	-269.37	-257.94	-285.28	-278.77	-285.42
2	-318.96	-450	-504.75	-440.55	-470.98	-483.91	-483	-495.24
3	-395.89	-330.25	-300.22	-298.21	-295.49	-305.39	-324.6	-338.35
Average	-354.5	-355.01	-365.64	-336.05	-341.47	-358.19	-362.12	-373

Specimen	204	218	228	243	256	264	277	305
1	-257.94	-285.28	-278.77	-285.42	-300.2	-312.25	-310.44	-330.16
2	-470.98	-483.91	-483	-495.24	-493.61	-499.66	-493.57	-494.64
3	-295.49	-305.39	-324.6	-338.35	-359.14	-441.66	-432.43	-367.42
Average	-384.32	-417.86	-412.14	-397.41	-394.85	-384.64	-395.32	-462.03

Table 5.1: Measurement of corrosion potentials for CEM II without corrosion inhibitor

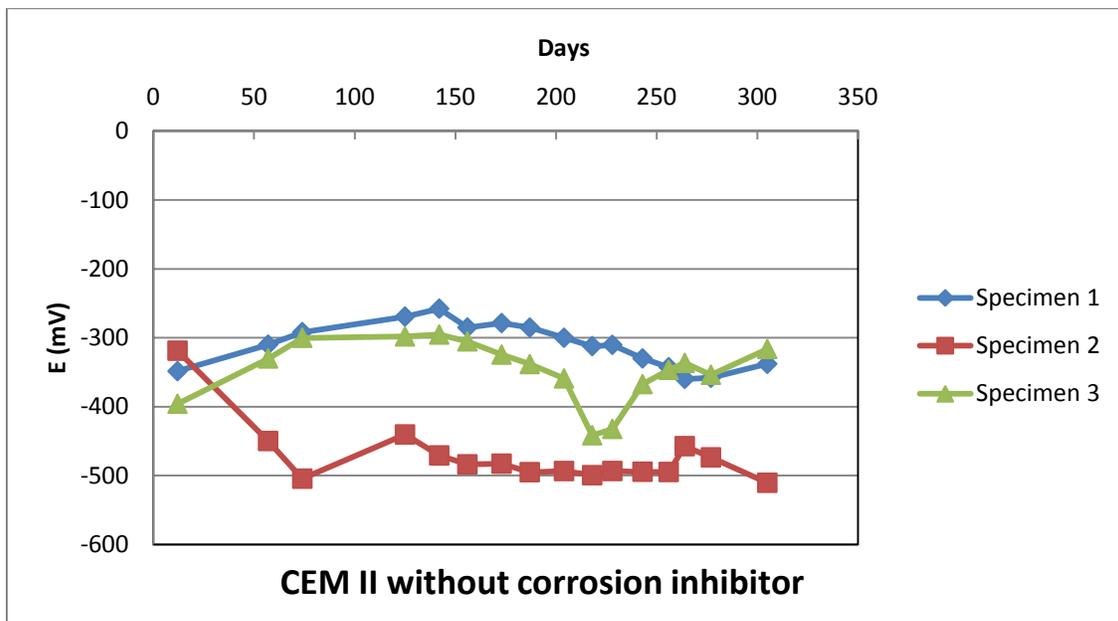


Figure 5.1: Diagram of corrosion potentials for CEM II without corrosion inhibitor

Specimen	E (mV)							
	Days							
Specimen	12	57	74	125	142	156	173	187
1	-456.52	-479.03	-445.4	-444.07	-451.29	-488.63	-487.87	-486.61
2	-330.15	-300	-266.54	-369.95	-356.72	-362.9	-330.71	-323.03
3	-404.14	-404	-405.11	-388.63	-335.61	-396.52	-402.86	-403.47
Average	-396.94	-380.01	-372.35	-400.88	-381.21	-416.01	-407.15	-404.37

Specimen	204	218	228	243	256	264	277	305
1	-466.28	-480.57	-458.29	-395.06	-455.04	-469.16	-417.39	-383.24
2	-343.36	-385.64	-432.73	-456.37	-334.05	-333.66	-319.72	-356.98
3	-415.72	-425.83	-422.38	-388.21	-382.11	-378.42	-375.68	-382.42
Average	-408.45	-430.68	-437.8	-413.21	-390.4	-393.75	-370.93	-374.21

Table 5.2: Measurement of corrosion potentials for CEM II with corrosion inhibitor

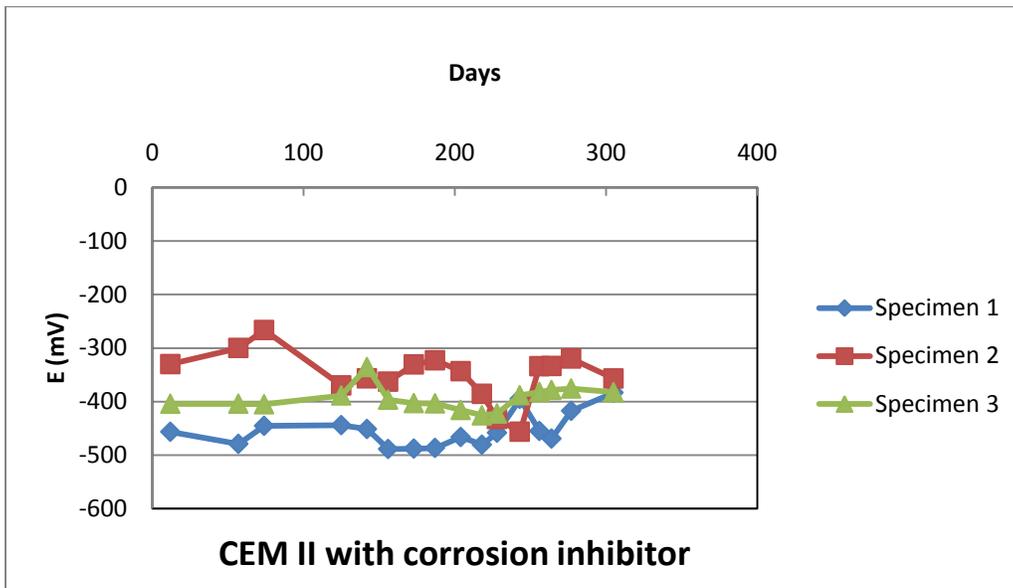


Figure 5.2: Diagram of corrosion potentials for CEM II with corrosion inhibitor

### 5.1.2 Specimens made from LC 1

The measurement for LC 1 without corrosion inhibitor is shown in Table 5.3 while the measurement for LC 1 with corrosion inhibitor is given in Table 5.4.

Specimen	E (mV)							
	Days							
	12	57	74	125	142	156	173	187
1	-387.16	-419	-400.95	-374.88	-367.83	-449.96	-491.18	-512.5
2	-443.4	-491.8	-451.87	-538.05	-573.24	-573.88	-597.52	-628.63
3	-370.58	-516.99	-459.15	-465.36	-469.91	-480.46	-531.83	-552.18
Average	-400.38	-420	-437.32	-459.43	-470.32	-501.17	-540.17	-564.44

Specimen	204	218	228	243	256	264	277	305
1	-504.52	-510.42	-501.12	-492.55	-473.9	-387.07	-413.64	-393.8
2	-631.83	-638.11	-637.92	-626.12	-629.13	-466.1	-526.5	-500.15
3	-566.58	-577.25	-548.63	-516.33	-512.3	-481.38	-468.75	-485.43
Average	-567.64	-575.26	-562.55	-545	-538.45	-444.85	-469.63	-459.79

**Table 5.3: Measurement of corrosion potentials for LC 1 without corrosion inhibitor**

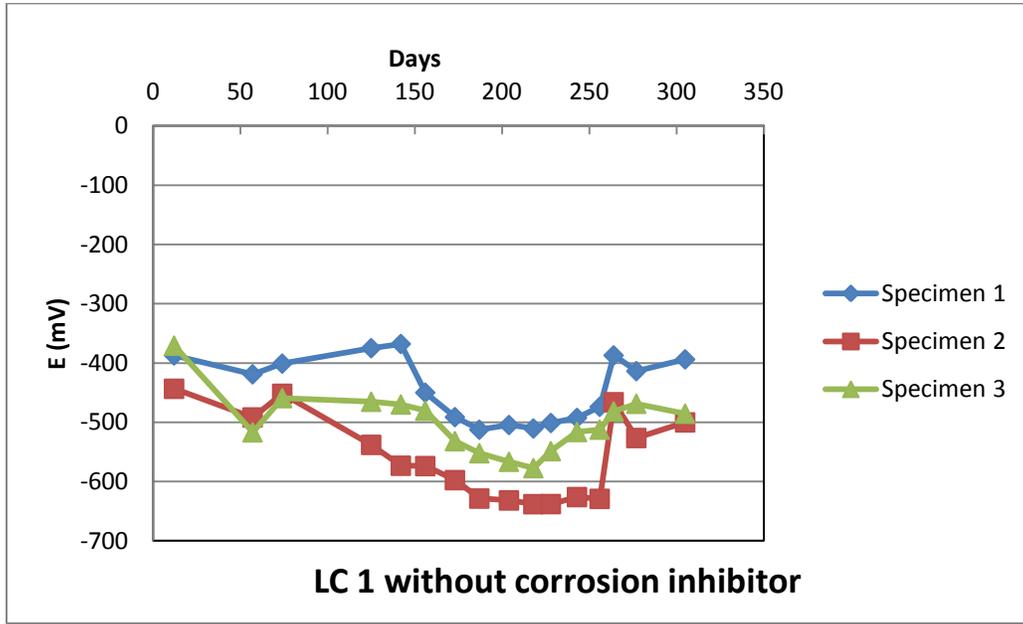


Figure 5.3: Diagram of corrosion potentials for LC 1 without corrosion inhibitor

Specimen	E (mV)							
	Days							
Specimen	12	57	74	125	142	156	173	187
1	-283.1	-467.27	-459.08	-674.62	-657.31	-635.02	-589.19	-584.26
2	-366.22	-450	-466.36	-500.73	-510.9	-525.29	-558.3	-548.97
3	-177.75	-400	-435.95	-461.34	-509.89	-508.24	-513.36	-504.39
Average	-275.69	-400	-453.8	-545.56	-559.37	-556.18	-553.62	-545.87

Specimen	204	218	228	243	256	264	277	305
1	-584.63	-559.96	-575.02	-547.44	-545.09	-540.25	-545.53	-454.91
2	-557.67	-558.19	-563.76	-530.88	-529.02	-485.73	-533.42	-470.5
3	-459.16	-459.32	-509.23	-462.14	-489.83	-508.95	-510.08	-485.72
Average	-533.82	-525.82	-549.33	-513.49	-521.31	-511.64	-529.68	-470.38

Table 5.4: Measurement of corrosion potentials for LC 1 with corrosion inhibitor

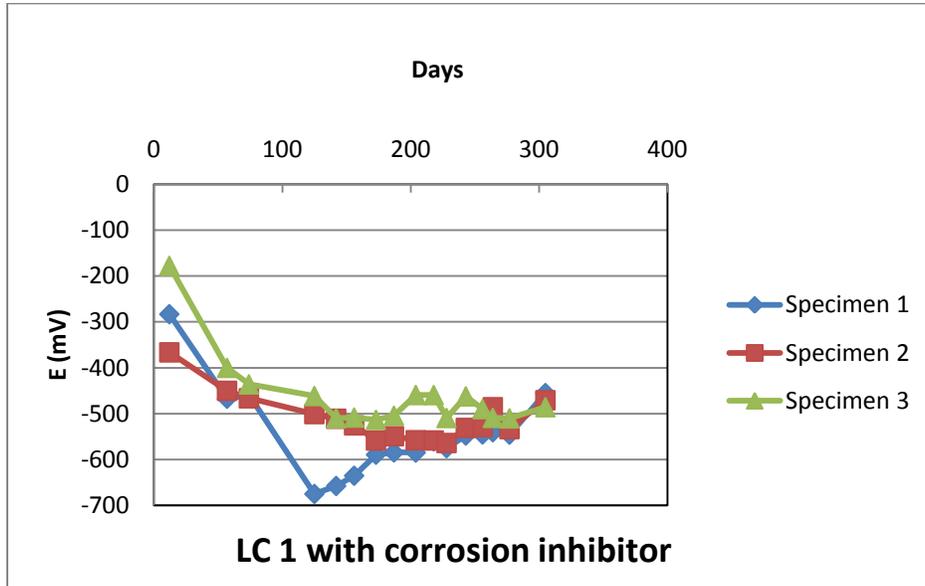


Figure 5.4: Diagram of corrosion potentials for LC 1 with corrosion inhibitor

### 5.1.3 Specimens made from LC 2

The measurement for specimens made from LC 2 without corrosion inhibitor is shown in Table 5.5 while the measurement for LC 2 with corrosion inhibitor is given in Table 5.6.

Specimen	E (mV)							
	Days							
Specimen	12	57	74	125	142	156	173	187
1	-440.99	-455.56	-439.94	-587.46	-565.65	-540.63	-584.3	-520.69
2	-331.23	-450	-394.25	-436.32	-422.59	-399.96	-407.62	-458.51
3	-430.08	-395.45	-540.68	-425.11	-408.8	-440.63	-429.64	-383.87
Average	-400.77	-443	-458.29	-482.96	-465.68	-460.41	-473.86	-454.36

Specimen	204	218	228	243	256	264	277	305
1	-533.75	-560.95	-557.21	-546.34	-526.4	-439.13	-466.35	-445.15
2	-416.94	-420.36	-444.59	-368.78	-388.9	-407.63	-414.05	-416.06
3	-388.75	-390.39	-431.34	-377.46	-357.55	-395.95	-378.11	-439.02
Average	-446.48	-457.23	-477.71	-430.86	-424.28	-414.24	-419.5	-433.41

Table 5.5: Measurement of corrosion potentials for LC 2 without corrosion inhibitor

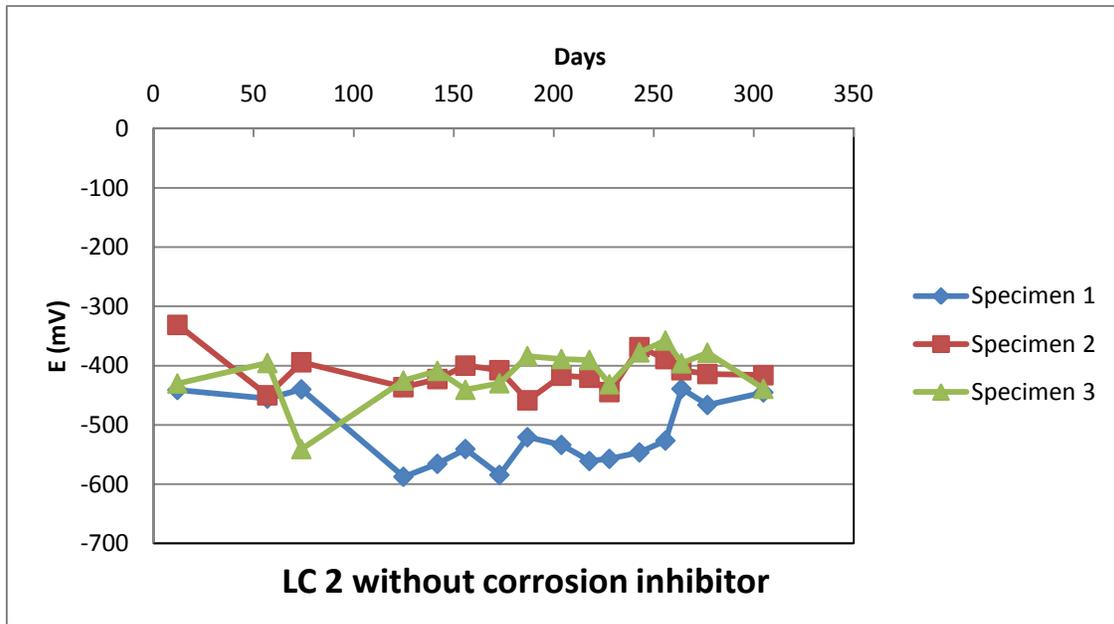
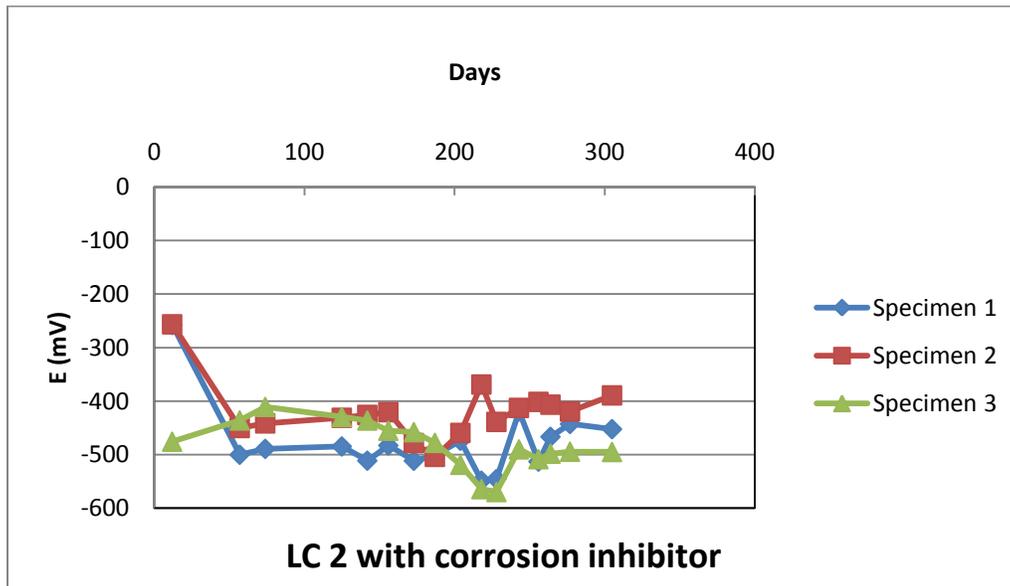


Figure 5.5: Diagram of corrosion potentials for LC 2 without corrosion inhibitor

Specimen	E (mV)							
	Days							
Specimen	12	57	74	125	142	156	173	187
1	-257.72	-500	-489.06	-484.53	-511.11	-482.67	-511.25	-500.93
2	-256.46	-450	-441.47	-431	-425.63	-420.52	-478.26	-503.91
3	-475.68	-435.98	-410.71	-429.44	-436.11	-455.16	-457.8	-477.82
Average	-329.95	-410	-447.08	-448.32	-457.62	-452.78	-482.44	-494.22

Specimen	204	218	228	243	256	264	277	305
1	-473.89	-548.43	-545.41	-419.25	-512.87	-466.48	-442.52	-452.2
2	-459.26	-368.85	-438.68	-412.53	-401.27	-406.51	-419.24	-389.17
3	-518.8	-564.27	-569.62	-489.9	-508.3	-498.04	-494.37	-494.85
Average	-483.98	-493.85	-517.9	-440.56	-474.15	-457.01	-452.04	-445.41

**Table 5.6: Measurement of corrosion potentials for LC 2 with corrosion inhibitor**



**Figure 5.6: Diagram of corrosion potentials for LC 2 with corrosion inhibitor**

As it is shown in diagrams and results with measurements of corrosion potentials we cannot come to conclusion clearly.

## 5.2 MASS LOSS

The corrosion rate of the bars was determined by measuring their mass losses at predetermined exposure time intervals in the corrosive environments. In order to find the mass loss the polarization resistance ( $R_p$ ) was measured and corrosion current ( $I_{corr}$ ) and mass loss were calculated.

The results are shown in the following Tables.

### 5.2.1 Corrosion current

#### CEM II

The measurement for CEM II without corrosion inhibitor is shown in Table 5.7 while the measurement for CEM II with corrosion inhibitor is given in Table 5.8.

Specimen	I(A)					
	12	57	74	125	142	156
1	0.00001829	0.00001776	0.00000721	0.00000766	0.00000841	0.00001067
2	0.00001403	0.00001197	0.00001184	0.00002013	0.00002314	0.00002042
3	0.00004635	0.00002146	0.00000824	0.00000889	0.00000625	0.00001142
Average	0.00002622	0.00001706	0.00000910	0.00001223	0.00001260	0.00001417

specimen	173	187	204	218	228	243
1	0.00000962	0.00001079	0.00001112	0.00000998	0.00000855	0.00000858
2	0.00001889	0.00002477	0.00002279	0.00002046	0.00001995	0.00002004
3	0.00001471	0.00001827	0.00001955	0.00002385	0.00002143	0.00001882
Average	0.00001441	0.00001794	0.00001782	0.00001810	0.00001664	0.00001582

specimen	256	264	277	305
1	0.00000883	0.00000872	0.00000839	0.00001115
2	0.00001997	0.00001808	0.00002083	0.00002659
3	0.00001793	0.00001705	0.00001681	0.00001619
Average	0.00001558	0.00001462	0.00001534	0.00001798

**Table 5.7: Measurement of corrosion current for CEM II without corrosion inhibitor**

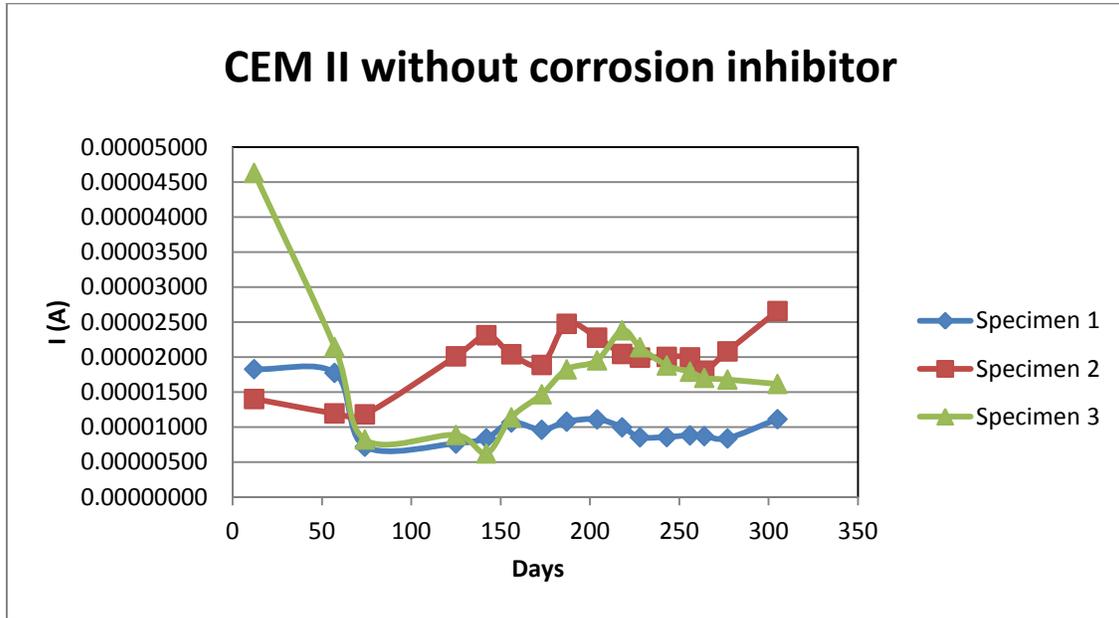


Figure 5.7: Diagram of corrosion current for CEM II without corrosion inhibitor

Specimen	I(A)					
	Days					
	12	57	74	125	142	156
1	0.0000493	0.0000196	0.0000146	0.0000184	0.0000171	0.0000225
2	0.0000125	0.0000096	0.0000125	0.0000128	0.0000117	0.0000123
3	0.0000330	0.0000151	0.0000113	0.0000104	0.0000099	0.0000106
Average	0.0000316	0.0000148	0.0000128	0.0000139	0.0000129	0.0000152

Specimen	173	187	204	218	228	243
1	0.0000200	0.0000242	0.0000182	0.0000184	0.0000130	0.0000051
2	0.0000103	0.0000122	0.0000126	0.0000122	0.0000131	0.0000139
3	0.0000091	0.0000109	0.0000105	0.0000096	0.0000094	0.0000093
Average	0.0000131	0.0000158	0.0000138	0.0000134	0.0000118	0.0000094

Specimen	256	264	277	305
----------	-----	-----	-----	-----

1	0.0000073	0.0000101	0.0000072	0.0000031
2	0.0000107	0.0000095	0.0000075	0.0000092
3	0.0000081	0.0000076	0.0000084	0.0000106
Average	0.0000087	0.0000091	0.0000077	0.0000076

Table 5.8: Measurement of corrosion current for CEM II with corrosion inhibitor

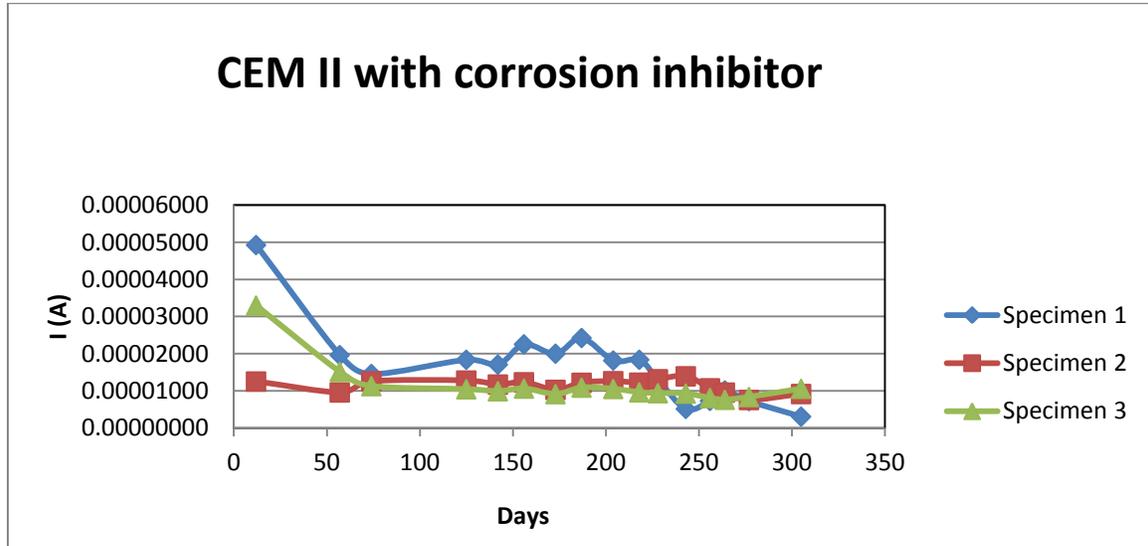


Figure 5.8: Diagram of corrosion current for CEM II with corrosion inhibitor

LC 1

Specimen	I(A)					
	Days					
	12	57	74	125	142	156
1	0.0000273	0.0000167	0.0000124	0.0000102	0.0000092	0.0000181
2	0.0000336	0.0000155	0.0000121	0.0000012	0.0000367	0.0000010
3	0.0000470	0.0000185	0.0000061	0.0000078	0.0000081	0.0000111
Average	0.0000360	0.0000310	0.0000280	0.0000330	0.0000340	0.0000265

Specimen	173	187	204	218	228	243
1	0.0000240	0.0000281	0.0000306	0.0000307	0.0000301	0.0000297
2	0.0000006	0.0000474	0.0000073	0.0000424	0.0000447	0.0000441
3	0.0000133	0.0000325	0.0000342	0.0000276	0.0000167	0.0000157
Average	0.0000350	0.0000360	0.0000400	0.0000336	0.0000305	0.0000299

Specimen	256	264	277	305
1	0.0000244	0.0000197	0.0000218	0.0000173
2	0.0000391	0.0000265	0.0000333	0.0000304
3	0.0000231	0.0000128	0.0000230	0.0000279
Average	0.0000289	0.0000196	0.0000261	0.0000252

Table 5.9: Measurement of corrosion current for LC 1 without corrosion inhibitor

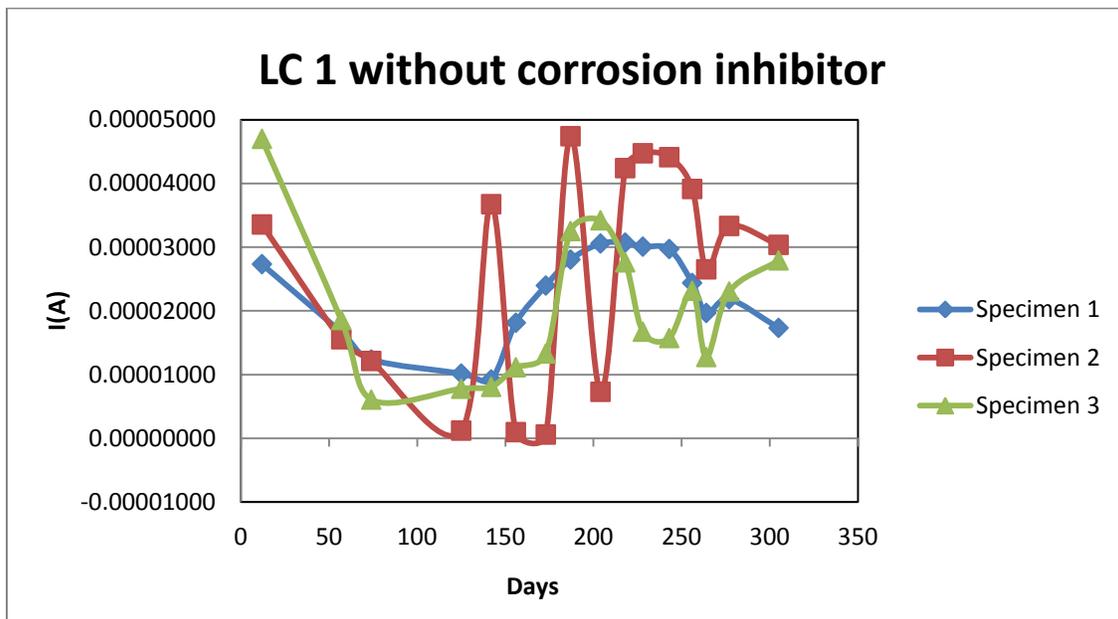


Figure 5.9: Diagram of corrosion current for LC 1 without corrosion inhibitor

Specimen	I(A)					
	Days					
	12	57	74	125	142	156
1	0.0000171	0.0000137	0.0000212	0.0000267	0.0000265	0.0000291
2	0.0000210	0.0000314	0.0000201	0.0000269	0.0000303	0.0000510
3	0.0000173	0.0000309	0.0000239	0.0000258	0.0000197	0.0000293
Average	0.0000185	0.0000253	0.0000217	0.0000265	0.0000255	0.0000365

Specimen	173	187	204	218	228	243
1	0.0000329	0.0000328	0.0000363	0.0000275	0.0000343	0.0000344
2	0.0000393	0.0000397	0.0000429	0.0000415	0.0000417	0.0000369
3	0.0000168	0.0000299	0.0000262	0.0000298	0.0000357	0.0000330
Average	0.0000297	0.0000341	0.0000351	0.0000329	0.0000372	0.0000348

Specimen	256	264	277	305
1	0.0000310	0.0000306	0.0000312	0.0000313
2	0.0000356	0.0000322	0.0000289	0.0000226
3	0.0000397	0.0000412	0.0000139	0.0000134
Average	0.0000354	0.0000346	0.0000246	0.0000224

**Table 5.10: Measurement of corrosion current for LC 1 with corrosion inhibitor**

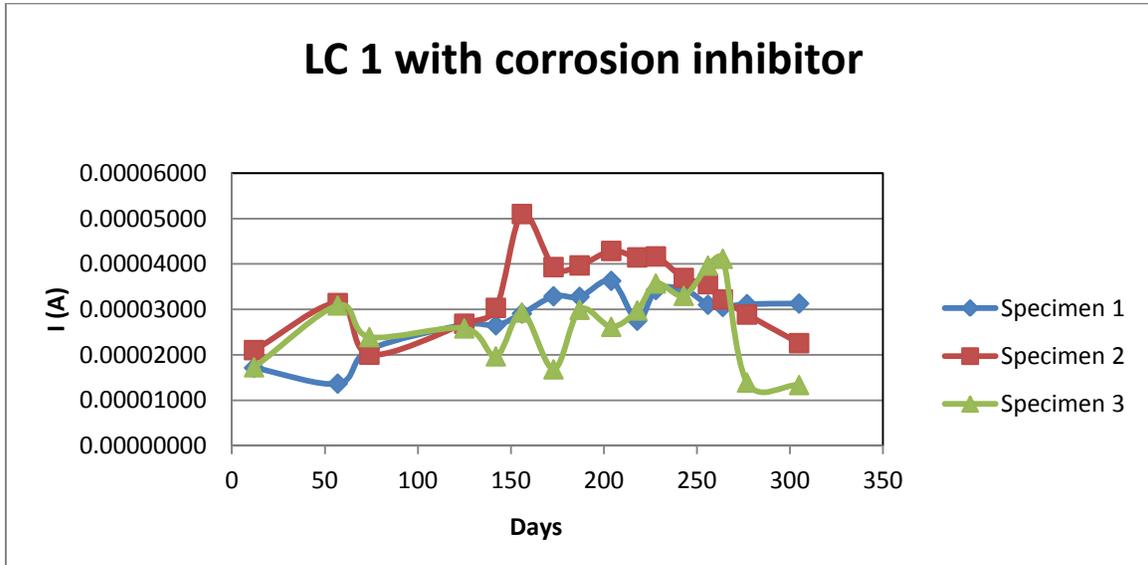


Figure 5.10: Diagram of corrosion current for LC 1 with corrosion inhibitor

LC 2

	I(A)					
	Days					
Specimen	12	57	74	125	142	156
1	0.0000607	0.0000147	0.0000137	0.0000238	0.0000233	0.0000270
2	0.0000274	0.0000063	0.0000171	0.0000184	0.0000235	0.0000302
3	0.0000269	0.0000187	0.0000069	0.0000096	0.0000077	0.0000142
Average	0.0000383	0.0000132	0.0000126	0.0000173	0.0000182	0.0000238

Specimen	173	187	204	218	228	243
1	0.0000208	0.0000336	0.0000492	0.0000530	0.0000497	0.0000483
2	0.0000212	0.0000311	0.0000237	0.0000026	0.0000212	0.0000086
3	0.0000109	0.0000130	0.0000154	0.0000152	0.0000153	0.0000164
Average	0.0000176	0.0000259	0.0000294	0.0000236	0.0000287	0.0000245

Specimen	256	264	277	305
1	0.0000475	0.0000360	0.0000315	0.0000429
2	0.0000166	0.0000148	0.0000158	0.0000089
3	0.0000144	0.0000140	0.0000165	0.0000188
Average	0.0000262	0.0000216	0.0000212	0.0000235

Table 5.11: Measurement of corrosion current for LC 2 without corrosion inhibitor

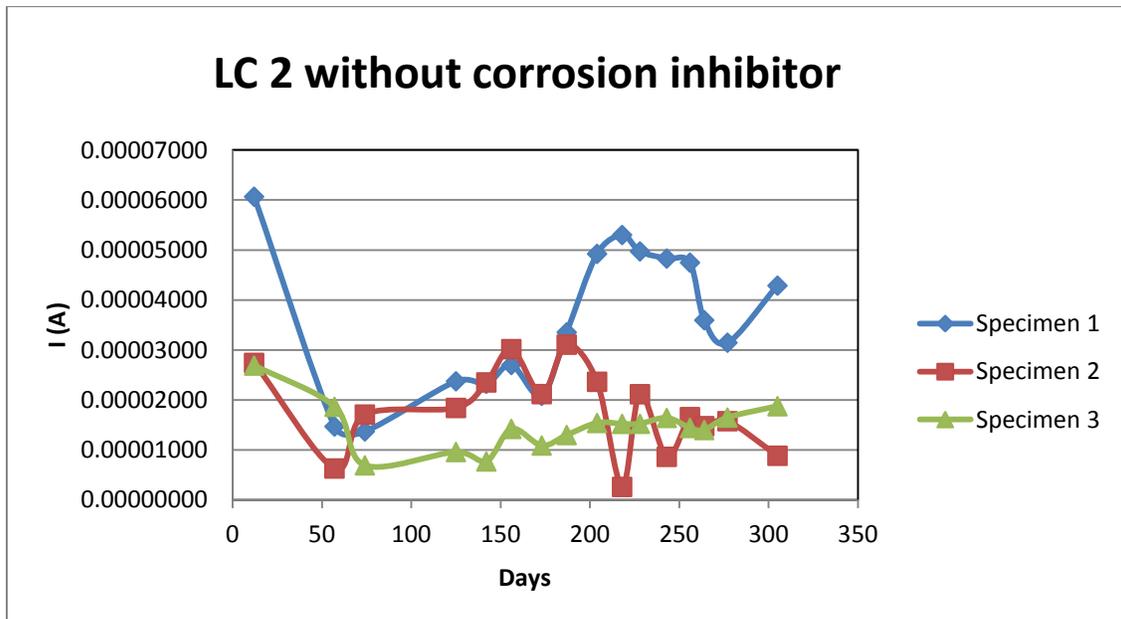


Figure 5.11: Diagram of corrosion current for LC 2 without corrosion inhibitor

Specimen	I(A)					
	12	57	74	125	142	156
1	0.0000147	0.0000267	0.0000123	0.0000153	0.0000144	0.0000291
2	0.0000201	0.0000179	0.0000189	0.0000303	0.0000100	0.0000385
3	0.0000693	0.0000138	0.0000003	0.0000065	0.0000076	0.0000089
Average	0.0000347	0.0000195	0.0000105	0.0000174	0.0000107	0.0000255

Specimen	173	187	204	218	228	243
1	0.0000298	0.0000329	0.0000171	0.0000328	0.0000291	0.0000176
2	0.0000252	0.0000395	0.0000149	0.0000116	0.0000141	0.0000139
3	0.0000092	0.0000114	0.0000133	0.0000127	0.0000152	0.0000145
Average	0.0000214	0.0000279	0.0000151	0.0000190	0.0000195	0.0000153

Specimen	256	264	277	305
1	0.0000305	0.0000265	0.0000002	0.0000029
2	0.0000128	0.0000120	0.0000123	0.0000125
3	0.0000078	0.0000080	0.0000090	0.0000158
Average	0.0000170	0.0000155	0.0000071	0.0000104

Table 5.12: Measurement of corrosion current for LC 2 with corrosion inhibitor

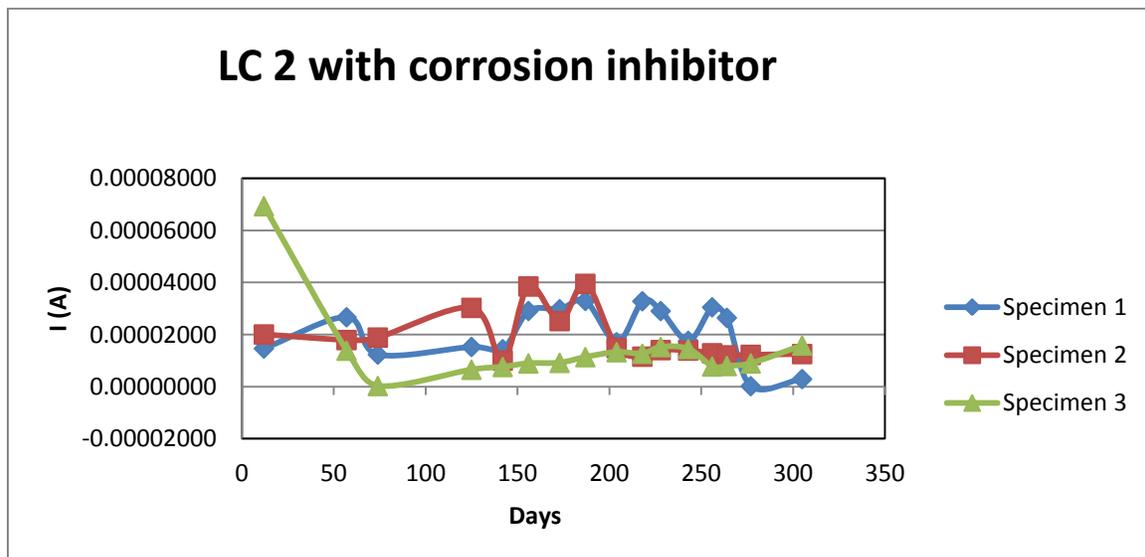


Figure 5.12: Diagram of corrosion current for LC 2 with corrosion inhibitor

### 5.2.2 Mass loss

CEM II

Specimen	Days							
	12	57	74	125	142	156	173	187
1	0.0055	0.03088	0.04427	0.06826	0.0982	0.13991	0.18166	0.23222
2	0.00422	0.02132	0.04328	0.10635	0.18874	0.26862	0.35056	0.46669
3	0.01394	0.04461	0.0599	0.08777	0.11002	0.15467	0.21845	0.30408
Average	0.00789	0.03227	0.04915	0.08746	0.13232	0.18773	0.25022	0.33433

Specimen	204	218	228	243	256	264	277	305
1	0.28907	0.34359	0.39248	0.44476	0.5014	0.55911	0.61736	0.70259
2	0.58325	0.69509	0.8091	0.9312	1.05937	1.17901	1.32366	1.527
3	0.40406	0.5344	0.65691	0.77159	0.88666	0.99954	1.11627	1.24003
Average	0.42546	0.52436	0.6195	0.71585	0.81581	0.91255	1.0191	1.15654

Table 5.13: Measurement of mass loss for CEM II without corrosion inhibitor

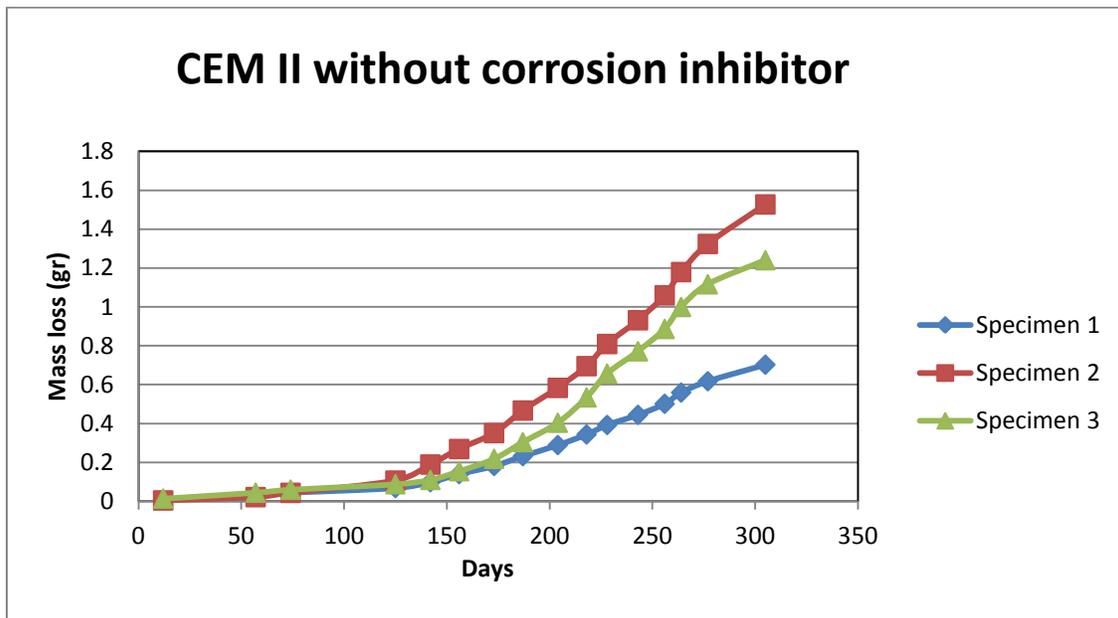


Figure 5.13: Diagram of mass loss for CEM II without corrosion inhibitor

	Days							
Specimen	12	57	74	125	142	156	173	187
1	0.01483	0.04288	0.06989	0.12749	0.18832	0.27645	0.36327	0.47696
2	0.00377	0.01745	0.04073	0.08076	0.12243	0.17057	0.21514	0.27223
3	0.00992	0.03152	0.05245	0.08518	0.12044	0.16195	0.20153	0.25252
Average	0.0095	0.03062	0.05436	0.09781	0.14373	0.20299	0.25998	0.3339

	Days							
Specimen	204	218	228	243	256	264	277	305
1	0.5699	0.67035	0.74477	0.77611	0.823	0.88993	0.94024	0.96368
2	0.3367	0.40343	0.47849	0.56326	0.63185	0.69497	0.74739	0.81739
3	0.30633	0.35884	0.41243	0.46889	0.52064	0.57095	0.62895	0.70976
Average	0.40431	0.47754	0.54523	0.60275	0.65849	0.71862	0.7722	0.83028

Table 5.14: Measurement of mass loss for CEM II with corrosion inhibitor

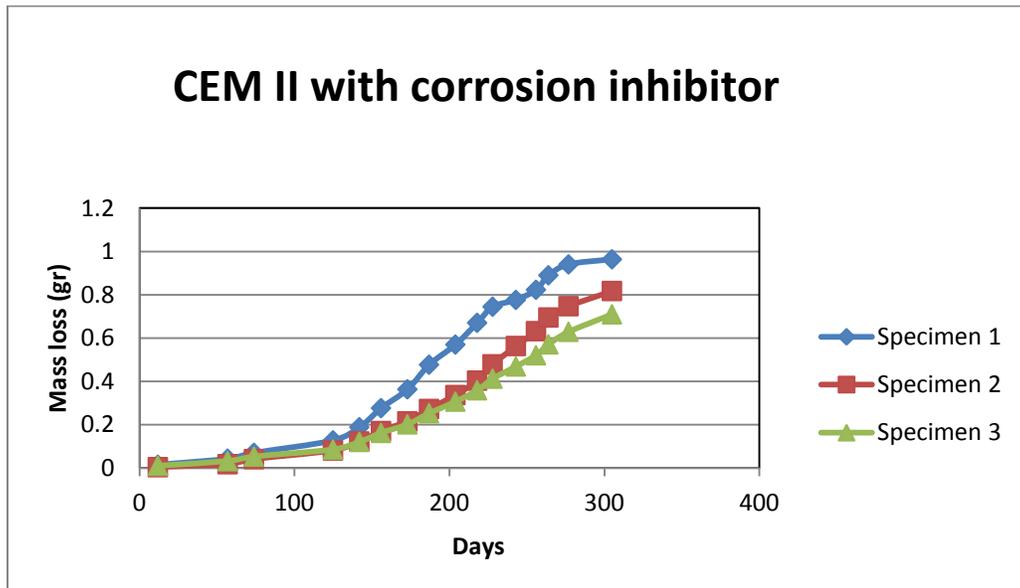


Figure 5.14: Diagram of mass loss for CEM II with corrosion inhibitor

LC 1

	Days							
Specimen	12	57	74	125	142	156	173	187
1	0.01483	0.04288	0.06989	0.12749	0.18832	0.27645	0.36327	0.47696
2	0.00377	0.01745	0.04073	0.08076	0.12243	0.17057	0.21514	0.27223
3	0.00992	0.03152	0.05245	0.08518	0.12044	0.16195	0.20153	0.25252
Average	0.0095	0.03062	0.05436	0.09781	0.14373	0.20299	0.25998	0.3339

1	0.00822	0.03201	0.05497	0.08678	0.11962	0.19051	0.29447	0.42599
2	0.01009	0.03229	0.05479	0.05855	0.18933	0.19307	0.19558	0.41783
3	0.01414	0.04064	0.05189	0.07624	0.10495	0.14849	0.20617	0.35861
Average	0.01082	0.05511	0.10706	0.21047	0.33151	0.43514	0.58694	0.75568

Specimen	204	218	228	243	256	264	277	305
1	0.58232	0.75014	0.92203	1.10298	1.25941	1.3896	1.54109	1.67352
2	0.4551	0.6868	0.94244	1.21119	1.46228	1.63774	1.86912	2.1012
3	0.53354	0.68443	0.78002	0.87586	1.02442	1.1088	1.26874	1.48216
Average	0.96024	1.14371	1.31809	1.49993	1.6853	1.8153	1.99624	2.1712

Table 5.15: Measurement of mass loss for LC1 without corrosion inhibitor

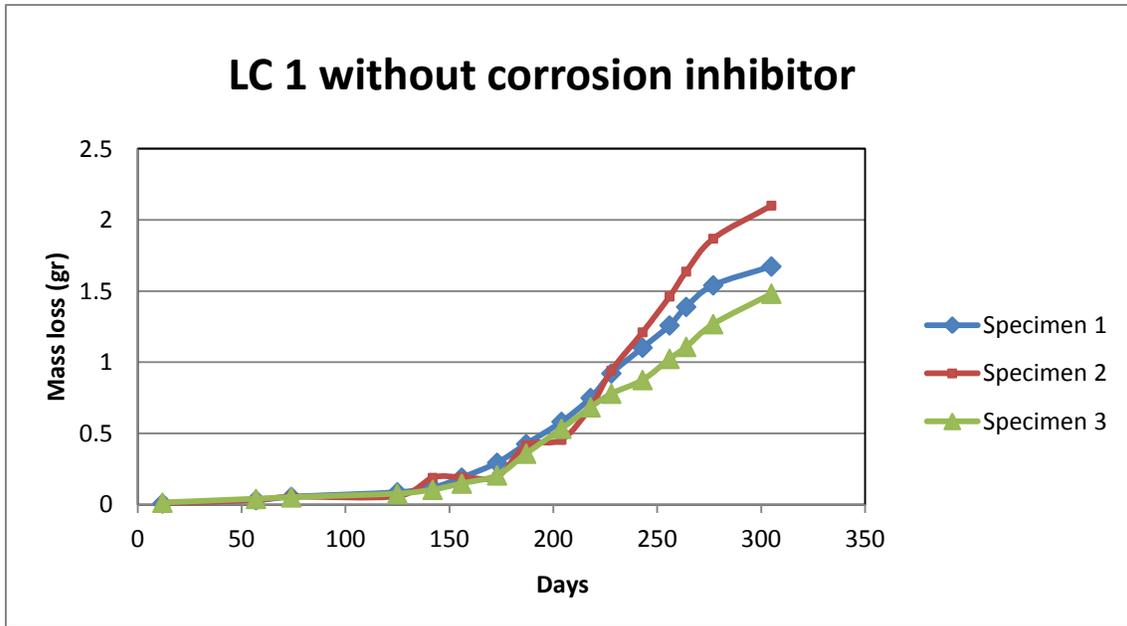


Figure 5.15: Diagram of mass loss for LC1 without corrosion inhibitor

	Days							
Specimen	12	57	74	125	142	156	173	187
1	0.00516	0.0247	0.06403	0.14763	0.242	0.3558	0.49852	0.65221

2	0.00633	0.0512	0.0884	0.17256	0.28058	0.48005	0.65062	0.8367
3	0.0052	0.04933	0.0937	0.17466	0.24472	0.35941	0.43236	0.57271
Average	0.00556	0.04174	0.08204	0.16495	0.25577	0.39842	0.52717	0.68721

Specimen	204	218	228	243	256	264	277	305
1	0.83782	0.98819	1.18408	1.39383	1.59303	1.79525	2.01166	2.25098
2	1.05602	1.2826	1.52079	1.74579	1.97404	2.18713	2.38767	2.56026
3	0.70661	0.86937	1.07352	1.27458	1.52905	1.80146	1.89803	2.0002
Average	0.86681	1.04672	1.25946	1.4714	1.69871	1.92794	2.09912	2.27048

Table 5.16: Measurement of mass loss for LC 1 with corrosion inhibitor

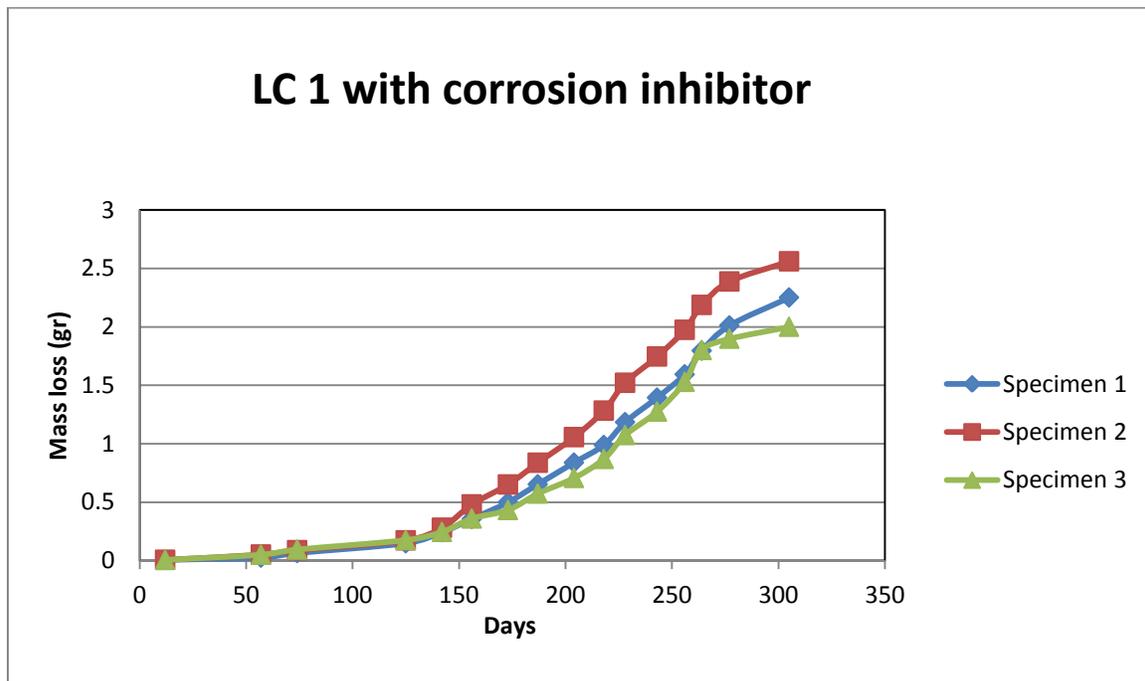


Figure 5.16: Diagram of mass loss for LC1 with corrosion inhibitor

LC 2

	Days							
Specimen	12	57	74	125	142	156	173	187
1	0.01825	0.03926	0.06471	0.13915	0.22195	0.32756	0.41795	0.57524

2	0.00825	0.01726	0.04897	0.1067	0.19044	0.30847	0.40038	0.54611
3	0.00039	0.03475	0.04763	0.07773	0.1052	0.16083	0.20812	0.26906
Average	0.00896	0.03042	0.05377	0.10786	0.17253	0.26562	0.34215	0.46347

Specimen	204	218	228	243	256	264	277	305
1	0.82709	1.11685	1.40112	1.69537	2.00016	2.23822	2.4568	2.78472
2	0.66706	0.68138	0.80237	0.85502	0.96144	1.05925	1.16877	1.23644
3	0.3479	0.43118	0.51835	0.61841	0.71093	0.80362	0.91822	1.0617
Average	0.61402	0.74314	0.90728	1.05627	1.22418	1.36703	1.5146	1.69429

Table 5.17: Measurement of mass loss for LC 2 without corrosion inhibitor

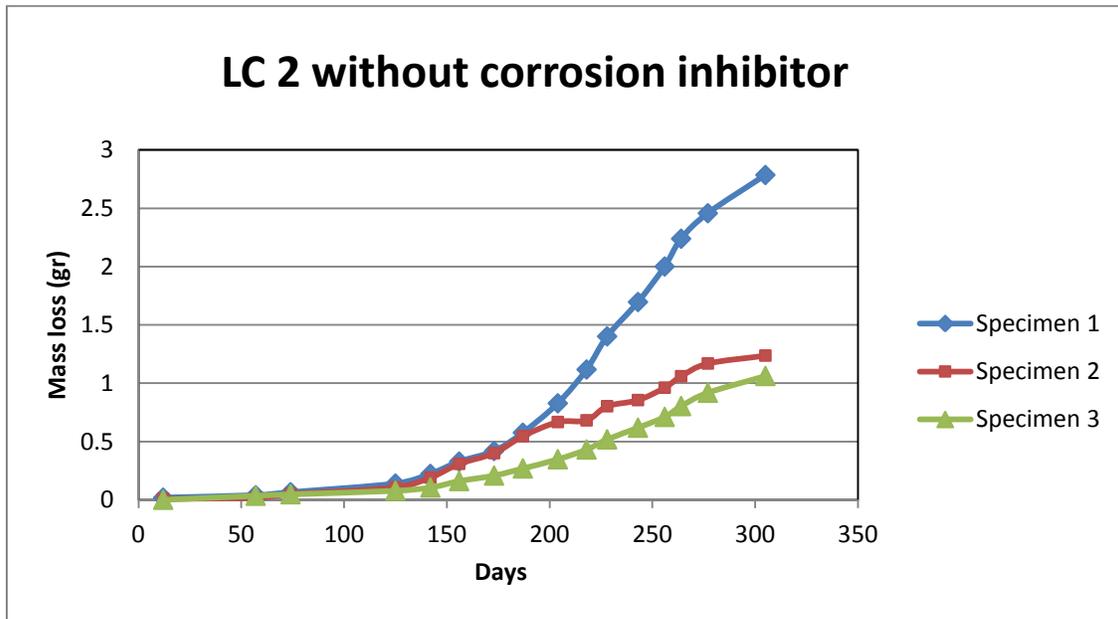


Figure 5.17: Diagram of mass loss for LC 2 without corrosion inhibitor

	Days							
Specimen	12	57	74	125	142	156	173	187
1	0.00442	0.04254	0.06545	0.11331	0.16462	0.27835	0.40744	0.56178
2	0.00603	0.03166	0.06669	0.16158	0.19726	0.3478	0.4571	0.64226

3	0.02085	0.04063	0.04113	0.06158	0.08859	0.12353	0.16331	0.2166
Average	0.01043	0.03828	0.05776	0.11216	0.15016	0.24989	0.34262	0.47354

Specimen	204	218	228	243	256	264	277	305
1	0.64918	0.82855	0.99461	1.10195	1.29768	1.47277	1.47431	1.49686
2	0.71851	0.78165	0.86207	0.94681	1.02927	1.10898	1.19405	1.28997
3	0.28448	0.35374	0.44088	0.52909	0.57891	0.63164	0.69383	0.81494
Average	0.55072	0.65465	0.76585	0.85929	0.96862	1.07113	1.12073	1.20059

Table 5.18: Measurement of mass loss for LC 2 with corrosion inhibitor

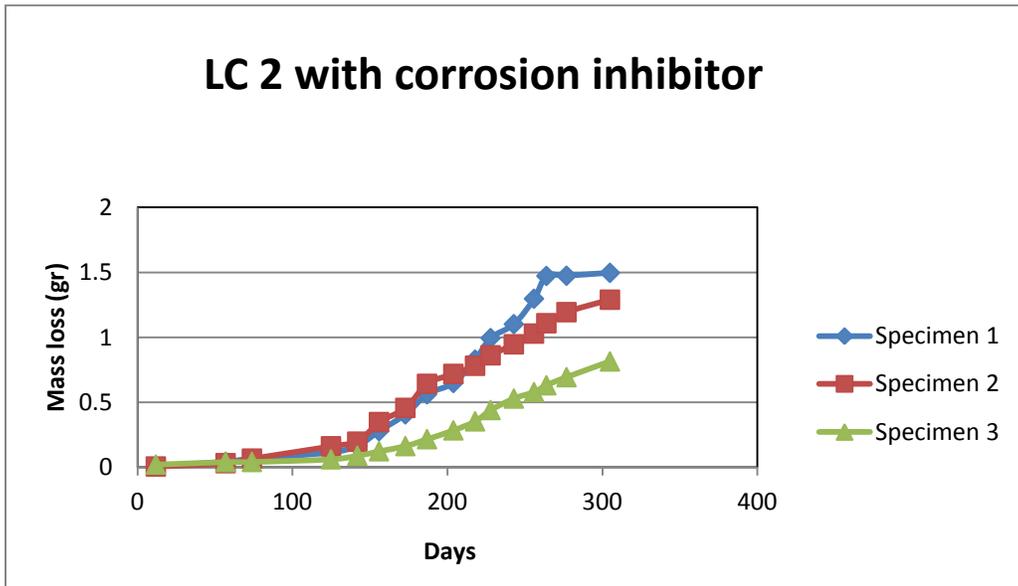


Figure 5.18: Diagram of mass loss for LC 2 with corrosion inhibitor

## Chapter 6

# RESULTS AND DISCUSSION

### 6.1 CORROSION POTENTIALS

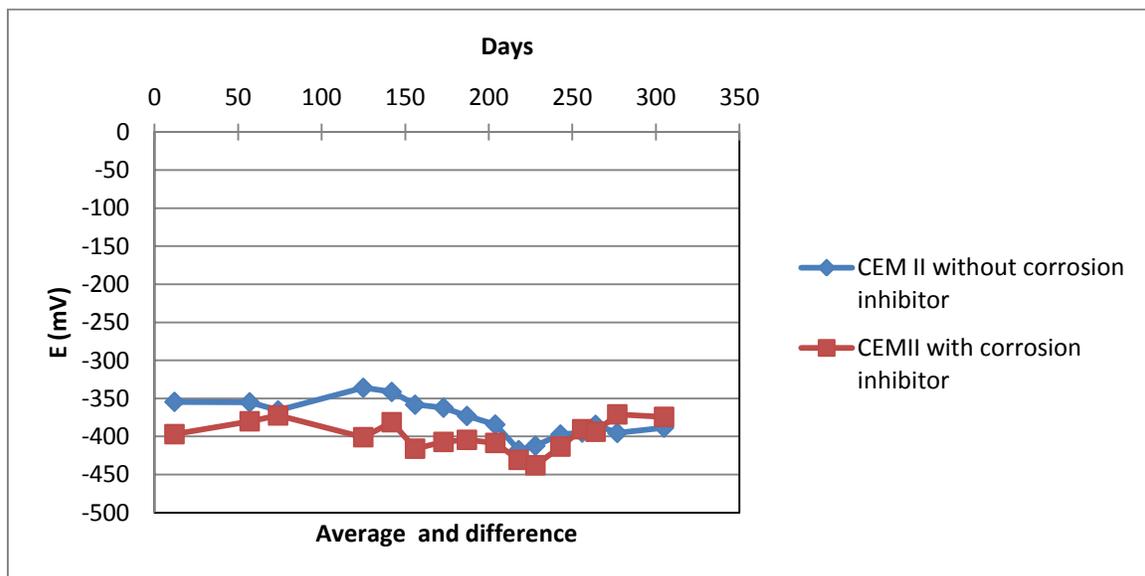
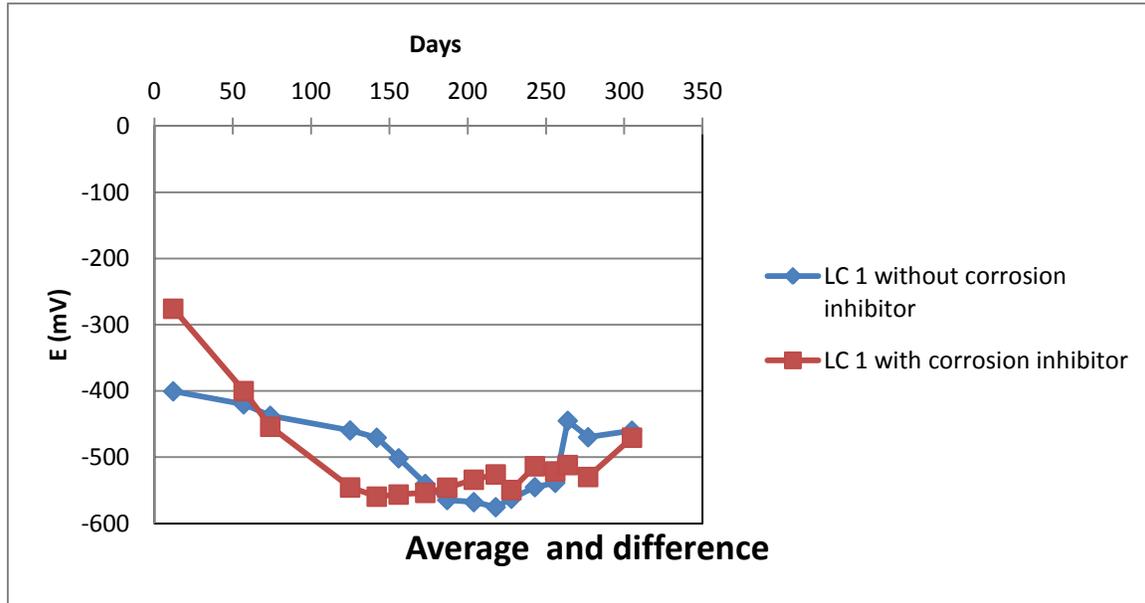
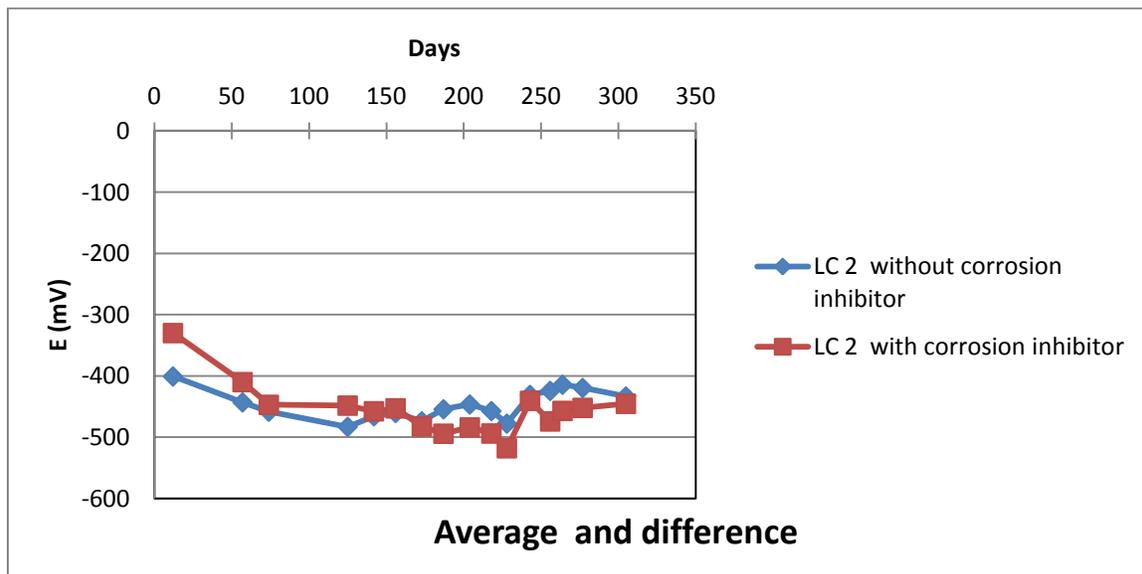


Figure 6.1: Average and differences of corrosion potentials of CEM II with and without corrosion inhibitor



**Figure 6.2: Average and differences of corrosion potentials of LC 1 with and without corrosion inhibitor**



**Figure 6.3: Average and differences of corrosion potentials of LC 2 with and without corrosion inhibitor**

The corrosion trend of the samples was estimated by monitoring the corrosion potential vs. exposure time. From procedure of corrosion potential vs. time it's difficult to come to conclusion because of continuous changing in corrosion potential vs. time.

## 6.2 MASS LOSS

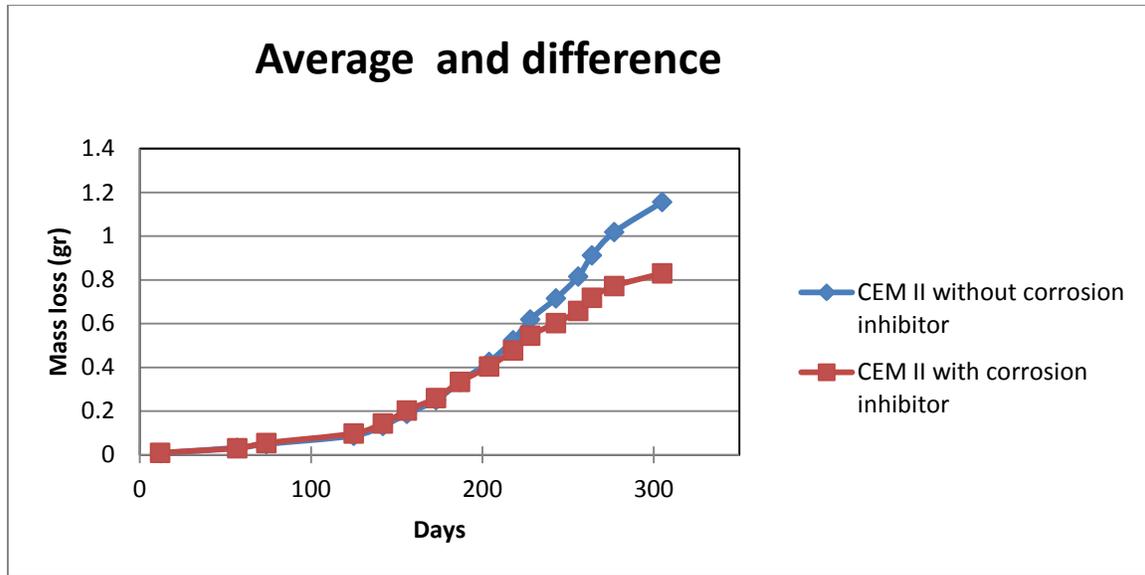
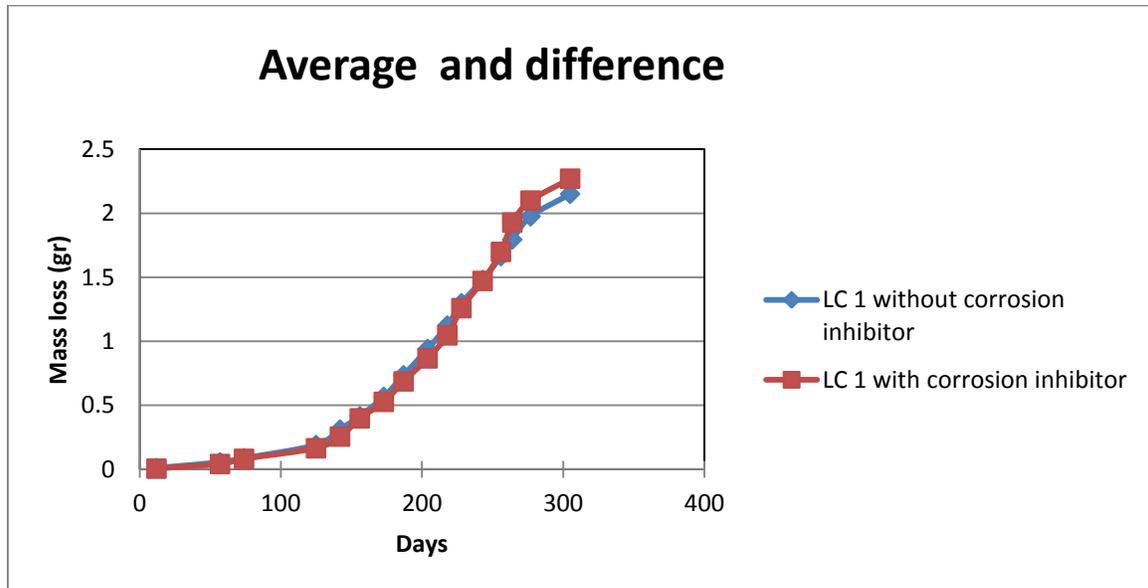
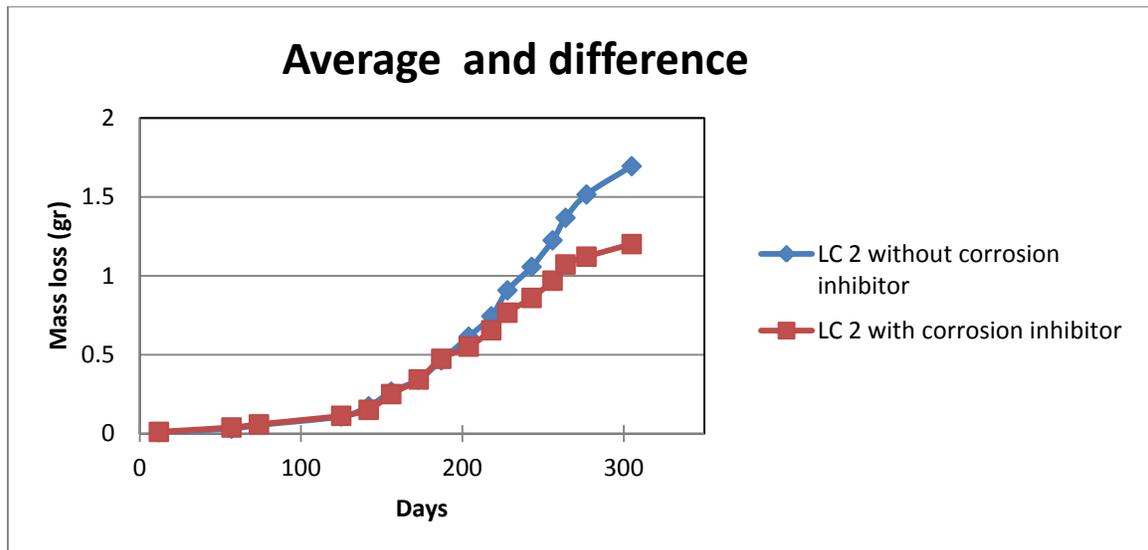


Figure 6.4: Average mass loss of CEM II with and without corrosion inhibitor



**Figure 6.5: Average mass loss of LC 1 with and without corrosion inhibitor**



**Figure 6.6: Average mass loss of LC 2 with and without corrosion inhibitor**

From the mass loss measurements vs. time as is shown in Figure 6.4, adding corrosion inhibitor improves the corrosion resistance of specimen. The time of corrosion protection for the specimen is about 200th days as well as specimen made from LC 2. (Figure 6.6).

In the opposite site as is shown in Figure 6.5, in specimens made from cement LC 1 adding corrosion inhibitor does not make any significant changes in corrosion of reinforcement.

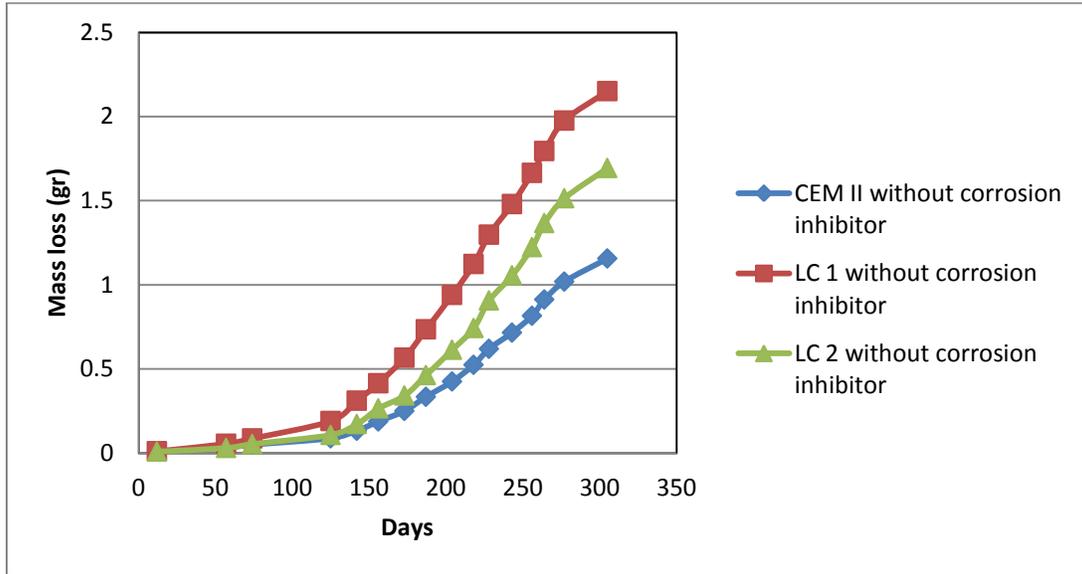


Figure 6.7: Comparison of different specimen without corrosion inhibitor

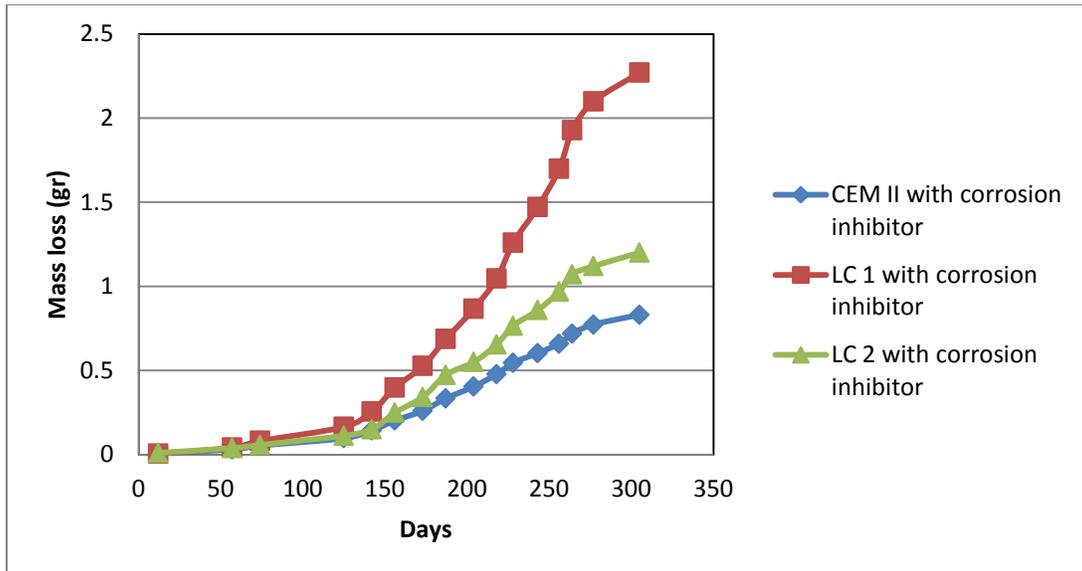


Figure 6.8: Comparison of different specimen with corrosion inhibitor

### 6.3 RESULTS AND DISCUSSION

From the mass loss measurements for three types of specimens (Fig 6.7) it is obvious that the specimens prepared with cement CEM II resisted better against corrosion than the other one prepared with LC1 and LC 2. Cement LC 1 has more corrosion than LC 2.

Knowing from previous measurements, we have found that LC 1 has more corrosion than LC 2. Also from Figure 6.4, 6.5, 6.6 comes out that adding corrosion inhibitor reduce significantly the corrosion of reinforcement in concrete based on cement type CEMII and LC 2. Unlikely in concrete based on LC 1 it has very small effect on corrosion of reinforcements. The difference between cements type LC 1 and LC 2 from CME II was predictable because the cements type CEM II are extensively investigated while lime stone cements are investigated less. Adding corrosion inhibitor had beneficial effect on CEM II and LC 2. In the case of cement LC 1, at least in present thesis period of time, had not any beneficial effects. That is probably because of high porosity of cement type LC 1 which facilitates the intrusion of chloride ions in comparison to CEM II and LC 2. Definitely these results should be checked from 2 sides. Firstly the porosity of specimen has to be measured and secondly the effect of corrosion inhibitor should be examined over extensive period of time. Also the corrosion rate of reinforcing steel should be determined by measuring their mass loss. The specimen should be smashed and the steel bars had to be cleaned from any corrosion products and be weighted. The mass loss is calculated from the difference between the initial and the final mass of each steel bar.

It is needed because the measurement of mass loss with electrochemical method has following uncertainty:

In Faraday's law, the performance of corrosion current should be added. The performance of corrosion current is a number less than one. Also the performance factor for each type of specimen is not the same. This determination could be measured electrochemical and gravimetric mass loss for the same period of time. From the results obtained in this thises it can be deduced following conclusions:

- The steel bars in cement type CEM II have less corrosion than bars in lime stone cements.
- Adding corrosion inhibitor in cement type CEM II and LC 2 decrease the mass loss of steel bars.
- Corrosion inhibitor in cement type LC 1 has not any significant effect on corrosion of steel bars.

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