

**A CRITICAL EXPERIMENTAL INVESTIGATION ON HIGH PERFORMANCE
BEHAVIOR OF HIGH VOLUME SLAG ADMIXTURED
CONCRETE TOWARDS CORROSION**

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CANDIDATE'S DECLARATION

I hereby certify that the work, being presented in this dissertation, entitled "**A Critical Experimental Investigation on High Performance Behavior of High Volume Slag Admixture Concrete Towards Corrosion**", in partial fulfillment of the requirements for the award of Master of Technology in Civil Engineering, with specialization in Structural Engineering, submitted to Jawaharlal Nehru University, New Delhi, is an authentic record of my own work carried out for a period of six months from June 1999 to November 1999, under the supervision of **Dr S.C.Pal**, of Civil Engineering Department, College of Military Engineering, Pune.

I have not submitted the matter embodied in this dissertation report for the award of any degree or diploma.

Dated: 30 Nov. 1999



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CERTIFICATE

This is to certify that the above statement made by Maj. Deepak Sharma is true, to the best of my knowledge and belief, hence recommended for acceptance and approval.



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EXAMINER'S CERTIFICATE OF APPROVAL

This dissertation, entitled "**A Critical Experimental Investigation on High Performance Behavior of High Volume Slag Admixture Concrete Towards Corrosion**", submitted by **Maj. Deepak Sharma** in partial fulfillment of the requirements for the award of Master of Technology in Civil Engineering, with specialization in Structural Engineering, submitted to Jawaharlal Nehru University, New Delhi, is hereby approved for the award of degree

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*Ik zarra-e-naa cheez ko anjum samjha,
Ik mauj-e-khafif ko talaatum samjha,
Is ilam-e-qalil ko ke hai siraf ek boond,
Afsos ke jaahalon ne qulzum samjha.*

- Josh malihabadi

(A tiny speck is deemed a star,
A ripple confused with tempest large,
A little knowledge, no more than a drop,
By the ignorant, alas, is ocean called)

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DEEPAK SHARMA

MAJOR

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ABBREVIATIONS / NOTATIONS

ASR	Alkali silica reaction
ASTM	American society for testing and materials
CA	Coarse aggregate
CC	Constant current
CE	Counter electrode
CV	Constant voltage
CSE	Copper sulfate electrode
ECORR	Corrosion potential
FA	Fine aggregate
GGBS	Ground granulated blast furnace slag
HPC	High performance concrete
ICORR	Corrosion current
MTPA	Million tones per annum
OCP	Open circuit potential
OPC	Ordinary Portland cement
RE	Reference electrode
SEM	Scan electron microscope
SHE	Standard hydrogen electrode
SCE	Standard calomel electrode
U.S.	United States of America
WE	Working electrode
XRD	X-ray diffraction studies
W/C	Water - cement ratio

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SYNOPSIS

At the threshold of the *new millenium*, the human population has reached the six billion mark. Increased industrialization and urbanization, has led to an exponential growth in the world's demand for residential and industrial buildings and mass transit facilities for people. Of all the construction materials used since antiquity, reinforced concrete has emerged, as the material of choice for infrastructure needs.

The reinforced concrete has two major components, the energy intensive cement and the steel. Each tonne of Portland cement, besides other raw material requires approximately 1.5 tonnes of limestone, and considerable amount of fuel / electrical energy. Also, a tonne of Portland cement clinker when produced releases approximately one tonne of carbon dioxide, which is one of the gases responsible for the greenhouse effect and global warming.

Second important component of reinforced concrete structure; the steel, when corroded has been the primary cause of deterioration leading to structural collapse. This problem is particularly serious in tropical countries because the rate of corrosion increases greatly with temperature. It is reported that in India, about one ton of steel is lost every 14 seconds due to corrosion.

On these issues, there is a growing concern that we can no longer ignore the environmental pollution problems and the unrestricted depletion of natural resources. To move toward the goal of sustainable development, a judicious balance needs to be struck between the two equally important needs of society,

namely the infrastructure build up and the protection of the environment/resources.

One of the means to make an '*ideal*' construction material would be to use blended cements that could enhance durability properties into concrete. *This would fulfill the overall environmental concerns without putting extra pressure on the existing resources of the country.* However in this study, of all the blended materials only slag admixed concrete has been discussed.

It is because blast furnace slag has the largest potential to replace cement by higher percentage because of its inbuilt cementitious property. Further, blast furnace slag is produced in phenomenal quantities at the rate of 0.3 to 0.4 tons per ton of iron / steel produced, depending upon the type of ore.

However, the properties of industrial slags vary significantly depending upon the type of raw material used, the method and rate of cooling, etc. *Thus there is a need to investigate characterization of slags, mix design methodologies and corrosion resistance parameters for production of high performance slag admixed concrete.*

CHAPTER 1

INTRODUCTION

1.1 NEED

At the threshold of the *new millenium*, the human population has reached the six billion mark^(ref:1). Increased industrialization and urbanization, has led to an exponential growth in the world's demand for residential and industrial buildings and mass transit facilities for people. Of all the construction materials used since antiquity, reinforced concrete has emerged, as the material of choice for infrastructure needs.

1.2 ENERGY AND ENVIRONMENTAL CONCERNS

The reinforced concrete has two major components, the energy intensive cement and the steel. Each tonne of Portland cement, besides other raw material requires approximately 1.5 tonnes of limestone, and considerable amount of fuel / electrical energy. Also, a tonne of Portland cement clinker when produced releases approximately one tonne of carbon dioxide, which is one of the gases responsible for the greenhouse effect and global warming^(ref:1).

There is a growing concern that we can no longer continue to ignore the environmental pollution problems and the unrestricted depletion of natural resources. To move toward the goal of sustainable development, a judicious balance needs to be struck between the two

equally important needs of society, namely the infrastructure build up and the protection of the environment.

1.3 PRESSURE ON EXISTING RESOURCES

The world consumption of Portland cement has risen from less than two million tonnes in 1880 to 1.3 billion tonnes in 1996^(ref:1). The Indian consumption is estimated to be around 100 MTPA, which works out to be 50 to 60 kg per capita per year; a very low figure considering, 300 to 350 kg per capita per year consumption in some of the developing countries. *This leaves a lot of scope for meeting the requirements of the country without putting extra pressure on the existing resources of the country.*

1.4 HUNT FOR AN IDEAL MATERIAL

Second important component of reinforced concrete structure; the steel, when corroded has been the primary cause of deterioration leading to structural collapse. This problem is particularly serious in tropical countries because the rate of corrosion increases greatly with temperature. It is reported that in India, about one ton of steel is lost every 14 seconds due to corrosion. So these problems have led to a hunt for an 'ideal' material which could meet these conflicting requirements.

1.5 USE OF SLAG ADMIXTURED CONCRETE- A Solution

One of the means to make an 'ideal' material, resistant to corrosion would be to use mineral admixtures as cement replacement

material. It has been observed that out of these materials blast furnace slag has the largest potential to replace cement by higher percentage because of its inbuilt cementitious property. Further, blast furnace slag is produced in phenomenal quantities at the rate of 0.3 to 0.4 tons per ton of iron / steel produced, depending upon the type of ore.

The replacement of cement by such slag could ideally aim at development of concrete which utilizing the industrial wastes, save natural resources and energy^(ref:Table1), in turn reducing the consumption of cement by 60 to 70 per cent. The research carried out so far reveals that the GGBS can effectively be used as cement replacement materials to achieve durable concrete.

Its utilization would also meet the environmental concerns as, the disposal of slag even as a waste fill is a serious environmental hazard.

However, the properties of industrial slags vary significantly depending upon the type of raw material used, the method and rate of cooling, etc. *Thus there is a need to investigate characterization of industrial slags as well as mix design methodologies towards production of high performance slag admixed concrete optimized for corrosion resistance.*

1.6 MEDLEY OF THEMES

The word corrosion comes from the Latin '*corrodere*' i.e. to gnaw away. The phenomenon of corrosion is associated with the

disintegration and oxidation of the consumed metal and most often, with its irrecoverable loss.

Of all types of destruction of structural materials, corrosion of metals attracts the greatest amount of attention. The importance of the study of corrosion process leading to development of effective practical methods for protection against corrosion of structures thus can not be over emphasized.

For reinforced concrete structures, the corrosion of embedded steel has generally been the primary cause of deterioration and even structural collapse in some cases. This problem is particularly serious in tropical countries because the rate of corrosion increases greatly with temperature. Corrosion of ordinary steel is inevitable. However, under certain conditions process is slow enough for practical purposes.

To address the issue of corrosion of reinforcement in concrete, many methods and materials are being promoted. However in this study, slag admixed Concrete is only being mentioned.

1.7 SCOPE OF THIS STUDY

This study plans to investigate the effect of high volume, slag admixed concrete (based on IS code mix design) on corrosion of embedded steel. The test results thus obtained will be correlated to predict characteristics of high performance concrete composites developed with such slags with reference to corrosion aspects.

1.8 AIM

1. To develop an experimental setup to study the high performance behavior of slag admixed concrete in comparison with reference concrete
2. To establish the corrosion pattern in slag admixed concrete within the preview of the experimental setup so developed.

1.9 SCHEME OF STUDIES

The studies intended to be carried out can be classified based on following test procedures, which were developed:

1.9.1 Direct studies

1. Potentio-dynamic polarization study
2. Accelerated electrolytic corrosion study
3. Copper-copper sulfates half-cell potential study- A qualitative study

1.9.2 Indirect studies

1. Accelerated carbonation test.
2. Micrographic (SEM) study
3. XRD study

Misc. - Acid test

1.10 PHILOSOPHY OF THIS STUDY

Even amongst the engineering community in India, there are grave reservations regarding use of blended cements / concrete.

Reasons vary, from bad past experiences to total lack of information. Bringing out even a thought of reconsideration from existing mindset would be a big achievement of this study. It is sincerely hoped that the results of this study would corroborate usefulness of slag cements leading to 'Grey revolution' in the country.

The experiments as planned are described in Chapter 3, followed by their observations in the next Chapter. A brief discussion is given in the Chapter 5. While Chapter 2 reflects on the growing importance of the subject by covering most of the important studies and reports in the form of a literature survey including a review of similar work on related / contemporary topics across the globe, Chapter 3,4 and 5 cover the details of the studies carried out and the discussion on the results obtained. Chapter 6, covers the conclusions arrived at. Scope for further studies have been given in Chapter 7, and lastly Chapter 8 gives the list of references.

TABLE 1

Energy Consumption for Portland Slag Cement Manufacture

Existing plant

Cement	Energy Consumption	
	Thermal	Electrical
OPC	100%	100%
PSC	47%	86%

New plant

Cement	Energy Consumption	
	Thermal	Electrical
OPC	100%	100%
PSC	47%	79%

Assuming 50% slag addition.

Source: Indian cement industry-Emerging trends

P.Parthasarthy and SM. Chakravarty

CHAPTER 2

LITERATURE SURVEY

2.1 IMPORTANCE OF CORROSION

Huge investments are made to obtain metallic materials from the forms in which these exist in nature such as oxides, sulfides and carbonates. After recovery from their ores, the metals undergo infinite type of deformations such as alloying with other elements, purification heat treatment, cold working, annealing, and conversion into wires, rods, sheets and many other shapes so as to become useful industrial products. In the course of such transformation, investments smaller or larger than what was made in the recovery of the metals from their ores is also made. After recovery the metals and alloys get exposed to various environments and tend to revert to the forms in which they existed in nature with decrease of free energy - *hence spontaneously metals corrode.*

2.1.1 CORROSION AND ECONOMY

The gradual destruction of material by electrochemical reaction with environment has a very grave consequence for the industrial world. When the useful products undergo corrosion by exposure to environment, all investments into them are affected. More than the wasting away of investments, relevant

to us is deterioration and collapse of structures- such as bridges, roofing, towers, jetties etc.

2.1.2 COST OF CORROSION

Various individual scientists and organizations belonging to several countries have attempted to make estimates of the cost of corrosion in the respective countries. In U.S., the National Bureau of Standards embarked upon a study of the economic effects of corrosion in 1976^(ref:2). The study was conducted jointly by National Bureau of Standards and Battelle Columbus Laboratories. Direct costs were obtained from the reduction in the requirements or inputs for production, if the phenomenon of corrosion did not exist. Differences between existing economy and economy, in which best corrosion control measures are implemented, gives the avoidable cost of corrosion.

The information obtained was reduced to industry indicators in the form of coefficients for the 130 sectors. The coefficient for direct cost varies from 0.001 to 0.2 and for avoidable direct cost from 0.000 to 0.023. By multiplying the respective coefficients by the dollar value of production, they obtained direct and avoidable costs of corrosion for all the sectors for the year 1975 as 70 billion U.S. dollars and at 13 million U.S. dollars respectively^(ref:3).

On the same lines, the direct and avoidable costs of corrosion obtained by Rajagopalan ^(ref:3) for the Indian economy specific to construction sector (including highways) for 1984-85 was 300 and 100 crores respectively. Though applicability of the US coefficients to the Indian economy is questionable, the analysis does indicate the magnitude of the problems in the various sectors of the economy.

2.2 CORROSION IN METALS

2.2.1 THERMODYNAMIC INTERPRETATION

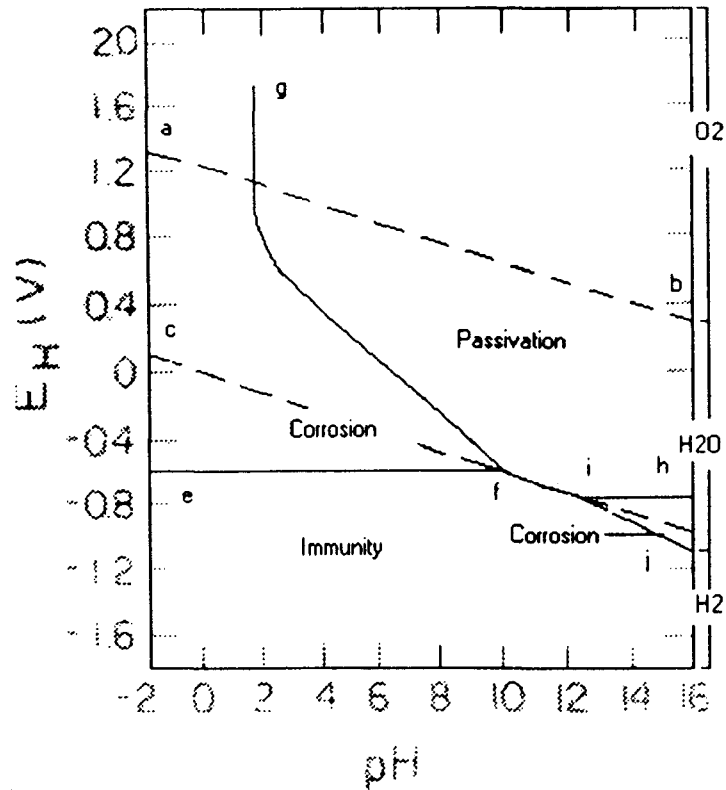
Compounds of metals except for noble metals like gold, platinum etc have lower energy as compared to metal it self. By spending energy the ore is converted into metal, which is then processed to yield a component or a structure. It is unstable, because it is energy rich and tends to revert back to more stable lower form, namely a compound like oxide or carbonate. *This process is what we call corrosion.*

The above viewpoint is a thermodynamic way of looking at corrosion. Pourbaix developed the thermodynamic interpretation of corrosion in a systematic way and presented his result in the form of Pourbaix diagrams, which is shown in the next page.

It depicts the stability of iron and water as a function of pH and potential. Hence the name Potential-pH diagram.

Looking at water, one finds that it is stable in the region bounded by the two dotted lines. Above the upper dotted line, oxygen is stable, while hydrogen is the stable species below the lower dotted line

Viewing the stability regions of Fe, one notices that the metallic iron is stable below the line, e f i j. Within the triangle e f g, the stable species are ferrous and ferric, while the triangle h i g represents the *region of stability* of ferrite.



Potential-pH diagram

Using this diagram, it is possible to infer the conditions that will lead to corrosion of iron. Since corrosion converts Fe into ions which form hydroxide / oxide, the triangular regions representing stable species as ions of iron would be the regions of corrosion of iron. Thus the larger triangle, e f g, represents corrosion of iron with the formation of ferrous and ferric ions while the smaller triangle, h i j, indicates corrosion of iron with the formation of the anion ferrite.

In the region below the line e f i j, metallic iron and hydrogen are stable. In this region iron cannot get corroded and hence it is called the *region of immunity*. In the region

above the line g f i h, the various oxides and hydroxides of iron are stable. Consequently iron getting corroded in this region would be covered with a film of one or more of these compounds, as they are insoluble in water^(ref:4). If this film is non-porous and acts as an efficient barrier between iron and the environment, the metal will be protected from corrosion. However, if the film does not have good barrier property the metal will corrode forming solid corrosion products. This region is known as *passive region*.

Thus from the consideration of stability of metal one is able to recognize three regions from Pourbaix diagram; *the region of corrosion, where metal can corrode, the immunity region, where metal cannot get corroded and the passivity region, where metal may or may not get corroded.*

Besides the broad conclusions indicated above, it is possible to get more pointed information too. For example, consider the region between the bottom dotted line and e f i j, in this region, hydrogen is stable and iron is not stable. Therefore this area represents region, where iron can get corroded in aqueous environment, with the formation of hydrogen. Similarly one can infer that within the area of the large triangle, e f g, lying between the two dotted lines, dissolved oxygen can corrode iron.

2.2.2 ELECTROCHEMICAL THEORY FOR CORRODING METALS.

The thermodynamic approach discussed above has its limitations. It does not indicate the rate at which corrosion

takes place, which is necessary for planning appropriate strategy for combating corrosion. *The electrochemical theory on the other hand is able to provide information on rate.*

2.2.2.1 Local Cell Theory

The electrochemical theory considers a corroding metal to consist of anodic and cathodic areas. At the anodic area, metal dissolves forming metal ions and thus generates electrons.



They travel to the cathodic areas through the bulk of the metal, where they are consumed by a reduction reaction. This reaction in acid solution leads to formation of hydrogen or reduction of O₂ to Water and in alkaline solution to reduction of O₂ to OH.

Migrations of negative ions, in solution phase, from cathodic site to anodic site completes the circuit. Thus the electrochemical theory considers corrosion to be the result of short-circuited galvanic cell or battery. *This is also known as local cell theory.*

Here, one can consider the corroding metal to be represented by a battery which is externally shorted, its voltage, V will then be zero and can be represented by equation^(ref:4).

$$V = 0 = E_c - E_a + IR,$$

Where E_c and E_a are respectively the potential of cathode and anode, while IR represents the potential drop, when the solution resistance is not large (As is the case with metals corroding by immersion)

then $IR \cong 0$ and one finds,

$$E_c \cong E_a$$

This condition is also true when a homogeneous metal is corroding, because in that case, the cathodic and anodic sites are not spatially separated to any significant extent. Consequently under conditions of immersion in electrolytic solution, the entire surface of both homogeneous and heterogeneous corroding metals is at one potential, E_{corr} .

Ultra-pure metals are free from heterogeneities that contribute to the formation of spatially divided cathodes and anodes. As per the local-cell theory they would be expected to resist corrosion, but they also undergo corrosion. Such corrosion has been explained by Rajagopalan^(ref:4) by assuming that cathodic and anodic sites are not spatially separated but shift randomly over the surface of the corroding in respect of time and space. Thus the entire surface supports cathodic and anodic reactions. *This may be considered as homogeneous theory of corrosion, while the local -cell theory may be regarded as heterogeneous theory of corrosion.*

2.2.2.2 Open Circuit Potential

The electrochemical behavior of corroding metal implies the existence of potential difference between local anodic and cathodic sites and consequent current flow. The potential drop across the electrical double layer, namely, metal and the solution is known as the *electrode potential*. In a corrosion couple, the electrode potential is lower at a local anode than at a cathode. The quantum of difference varies depending upon the spacing of anode and cathodes and the resistance of separating medium. Absolute values of electrode potentials are indeterminate. Relative values are expressed in a scale on which the zero-point is arbitrarily defined by the fixed electrode potential of a *reference half-cell*. For the purpose of electrochemical studies, the Standard Hydrogen Electrode (SHE) has been chosen as zero-point reference cell. The reference half-cells are reversible electrodes having equilibrium reactions under defined conditions of concentration and temperature. Their relationship to zero point reference is as shown in the table 2.2.1.

The measurement of corrosion potential of reinforcement with respect to a standard reference electrode, such as saturated calomel electrode, copper/copper-sulphate electrode, silver/silver chloride electrode is referred to as *open circuit potential or corrosion potential*.

2.2.3 Corrosion Of Metals In Atmosphere

This can also be explained by the electrochemical theory of corrosion^(ref:4). In this case the electrolyte is provided by the moisture/ film condensing on the metal which contains dissolved O₂ and CO₂. In addition it may contain NaCl (derived from droplets of sea water carried by wind) in marine environment and H₂ / SO₂ gases in industrial atmosphere. The pollutants and CO₂ impart ionic conductivity, to the condensed moisture film and thus provide the ionic path, needed for the corrosion current. However, resistivity of such condensed moisture film is bound to be high. The corrosion current being small and distance between local cathode and anode also not being large, the system resistance IR drop is in the range of a few millivolts.

2.2.4 Illustration for Corroding Metals

Thus one can compare corroding metal under conditions of immersion in electrolyte, with a battery, which has zero internal resistance and is externally shorted. And metal corroding in atmosphere can be represented as short-circuited galvanic cell, with low internal resistance. However, in both cases the potential over the entire surface is virtually uniform^(ref:4).

Table 2.2.1

Reference Cells and Electrode Potentials on SHE scale at 25 deg C

REFERENCE HALF CELL	REVERSIBLE REACTION	E _{SHE} (V)
Standard hydrogen electrode (SHE) Unit Activity H ⁺ 1.2 M HCl, 1 atm H ₂	$2\text{H}^+ + 2\text{e} \Rightarrow \text{H}_2$	0.0
Copper sulfate electrode(CSE) (Aq. Saturated CuSO ₄)	$\text{Cu}^{2+} + 2\text{e} \Rightarrow \text{Cu}$	+0.32
Saturated calomel electrode(SCE) (Aq. Saturated KCl)	$\text{Hg}_2\text{Cl}_2 + 2\text{e} \Rightarrow 2\text{Hg} + 2\text{Cl}$	+0.25
Silver silver chloride (Ag/AgCl) (Aq. Saturated KCl)	$\text{AgCl}_2 + 2\text{e} \Rightarrow \text{Ag} + 2\text{Cl}$	+0.22

2.3 CORROSION OF STEEL IN CONCRETE

2.3.1 COMPLEX NATURE OF THE PROBLEM

Reinforced concrete is a composite material of active metal namely mild steel and equally active non-metal namely concrete. Concrete is again a heterogeneous material composed of cement, sand and stone aggregate. Heterogeneity is mainly due to the differed orientation of aggregates. Thus concrete behaves like an unpredictable electrolyte, its resistivity varying from *a few hundred ohms to many hundred-kilo ohms*. The active metal reinforcement lies surrounded by this unpredictable electrolyte and is inaccessible.

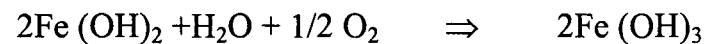
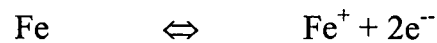
The first evidence of distress of any structure may be brown staining on the member around the embedded steel. This brown staining takes place due to corrosion of steel and it makes the concrete permeable even with out cracking. The volume of corrosion products i.e. *rust* or $\text{Fe}(\text{OH})_3$ being two to three times more than that of corresponding metal leads to development of tension forces in concrete, which finally results in cracks. These later on, are manifested as spalling of concrete and failure of member. Roger ^(ref.5) reports that *a growth of only 0.1 mm to 0.2 mm sized cracks may be sufficient to damage the concrete cover.*

Cement forms an important constituent responsible for corrosion protection in concrete, as it develops alkalinity by way of releasing calcium hydroxide. The effect of blending cements is claimed to further

increase chemical resistance of the concrete. However *many of the Indian Pozzolana cements are interestingly found to offer lesser protection to steel reinforcements* ^(ref:6). There is a school of thought that *the chemical reaction in certain blended pozzolana cements may lead to increased porosity* ^(ref:7).

2.3.2 CHEMISTRY OF CORROSION

For a local area on a steel bar in concrete (say, because of an attached air bubble that doesn't allow penetration of the alkaline paste)



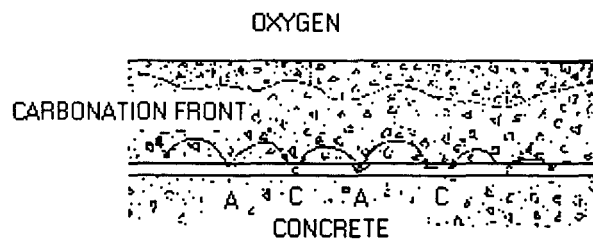
Chemical reaction $\text{Fe} \Rightarrow \text{Fe}^+ + 2\text{e}^-$ occurs on anode and is known as *anodic reaction* or *anodic half-cell reaction*. Since the iron is ionized, it is also termed as *Oxidation of iron*.

Chemical reaction $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 4(\text{OH})^-$ occurs on cathodes and is known as *cathodic reaction*. As the electrons are consumed, it is also known as *reduction reaction*. In an electrochemical

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reaction, oxidation and reduction takes place simultaneously and with the same velocity.

In reaction $2\text{Fe}^{++} + 4(\text{OH}) \Rightarrow 2\text{Fe}(\text{OH})_2$, ferrous hydroxide $\text{Fe}(\text{OH})_2$ precipitates from solution. However, this compound is unstable in oxygenated solution and is oxidized to the ferric hydroxide (*rust*) which is the final product of corrosion.



CORROSION INITIATED BY CARBONATION OF CONCRETE FIG 2.3.1

From the fig 2.3.1, it is clear that on the surface of the steel local anodic and cathodic regions are developed and the electron flow from anodic areas to cathodic areas, consequently the metal (iron) is ionized.

There can be so many reasons behind formation of these local anodes and cathodes however two general causes are as follows:

(a) **Differences in pH values of two areas**. The area where pH value is less, obviously has higher hydrogen ions concentration and hence attracts the electrons. Consequently electrons begin flowing from higher pH areas towards the low pH regions. Thus, an area with comparatively higher pH value will turn into an anode.

(b) **Dissimilarities**. It is not possible to manufacture steel with no dissimilarities for instance, the surface smoothness may differ and there may be slag and sulfide inclusions. Ragagopalan^(ref:8) indicates *that each of crystalline defects can produce highly localized differences in electrochemical behavior of the metal*. Therefore, despite being having same pH value at the paste steel interface, the electron flow may be setup leading to corrosion.

2.3.3 MECHANISM OF CORROSION

2.3.3.1 Break Down Of Passivity

Tendency for the steel reinforcement to corrode depends on the potential developed by it in its environment. It depends on the surrounding environment. In an acid medium, steel reinforcements tend to corrode freely, whereas in an alkaline medium corrosion is found to be almost negligible. As stated by Rengaswamy^(ref: 9), *This is due to the formation of a stable corrosion product [r-Fe₂O₃] on the surface and this is termed as passivity.* However this stable passive layer can be locally broken and corrosion can be initiated whenever there is a decrease in pH and increase in salt contamination in the surrounding concrete medium. The major individual constituent of cement is CaO (*free lime*) and during setting and hardening of concrete, CaO reacts with the mixing water to form calcium hydroxide. Actually the steel reinforcements is reported to be *surrounded by such a lime rich layer.* pH of a saturated solution of Ca(OH)₂ is around 12.6 (0.04N Ca(OH)₂ when expressed in normality). Even though other alkalies like Na₂O and K₂O also contributes to the pH, because of carbonation affect on Ca(OH)₂, the normal alkalinity one can expect in a good quality concrete is around 0.04N^(ref: 9).

The modified Pourbaix diagram for corrosion in the presence of chlorides is shown in fig 2.3.2. It can be seen that the passivity break down is followed by an electrochemical process of corrosion in which the moist concrete serves as the electrolyte.

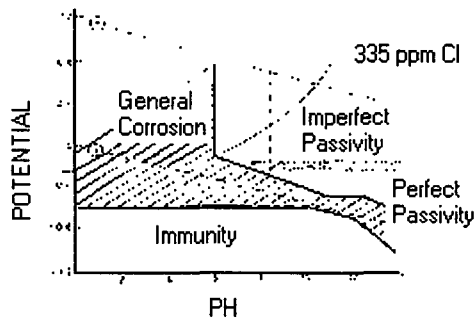


Fig 2.3.2: Modified Pourbaix diagram for concrete

It is interesting to note that penetration of chloride to the steel surfaces does not necessarily destroy passivity. A zone of perfect passivity can exist even at high levels of chloride concentration, and it is possible to control the corrosion by maintaining a potential corresponding to this zone indicated by the Pourbaix diagram.

There are two general mechanisms by which highly alkaline environment and accompanying passivating effect may be distorted: (a) *Reduction of alkalinity of the cement slurry by atmospheric carbon dioxide i.e. carbonation*, (b) *By electrochemical action involving chloride ions in presence of oxygen*.

2.3.3.2 Corrosion Initiated by Carbonation of Concrete

The basic principle of corrosion by this mechanism is the neutralization or leaching out of alkaline substances of the concrete, which is generally called as the Carbonation. The water available in concrete reacts with calcium oxide (CaO), which is the predominating constituent of cement, to form Ca (OH)₂. Depending upon the

concentration of OH ions $\text{Ca}(\text{OH})_2$ has a limited solubility. A highly alkaline environment is imparted to the concrete surrounding the steel by $\text{Ca}(\text{OH})_2$, which results in the formation of a tightly adhering film of oxide, which passivates the steel and protects it from corrosion. As already mentioned, the initial pH value of pore solution is reported to be from 12.5 to 13.0 ^(ref:10). Also it has been indicated that completely hydrated paste of pure Portland cement contains about 24%, $\text{Ca}(\text{OH})_2$ by weight ^(ref:11).

Carbonation of concrete is the formation of calcium carbonate and calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$. As Calcium bicarbonate is soluble in water, it gets dissolved reducing the pH value of the concrete.

2.3.3.2.1 Carbonation Front Propagation

The concentration of CO_2 in the atmosphere as reported by Tuutti ^(ref:12,13) to be 0.032%, which may go upto 0.1% in large urban areas. The gas first attacks $\text{Ca}(\text{OH})_2$ formed on the surfaces of the concrete member, forming CaCO_3 . This CaCO_3 further, reacts with CO_2 and moisture of the atmosphere and forms $\text{Ca}(\text{HCO}_3)_2$, which gets dissolved in the water. This process opens the micro-cracks for the further entry of O_2 , CO_2 and moisture etc. Hence, the corrosion inducing contaminants propagate deeper inside the concrete making it more permeable and more porous. The above process of movement of carbonation towards the paste-steel interface is known as *carbonation front propagation*.

2.3.3.2.2 Carbonation Depth

An approximate idea can be drawn about the depth of penetration of carbonation by the following expression^(ref:13).

$$X = k \star t,$$

Where

X = Penetration depth,

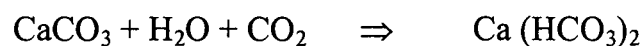
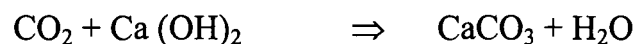
t = Exposure time,

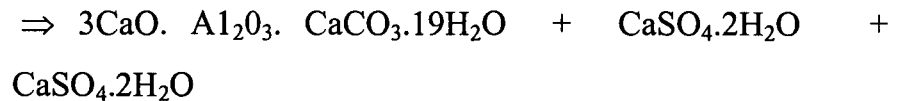
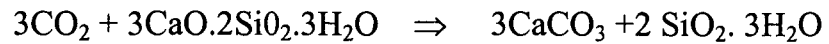
k = A constant which is dependent on the effective diffusivity for CO₂ through concrete, the concentration difference and the quantity of bound CO₂.

Tuutti^(ref:13) has reconfirmed in his work that, *in the process of carbonation the pH value of concrete reduces from 13.0 to 9.0, which is enough to initiate the corrosion of reinforcing bars*. It is obvious, that as the pH value of pore solution decreases, the concentration of H⁺ increases and at pH value 9.0 the hydrogen ion H⁺ concentration is such that they are capable of destroying the passive film of oxide around the steel.

2.3.3.2.3 Chemical Reactions

Following are the possible chemical reactions illustrating the process of carbonation:





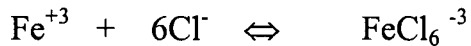
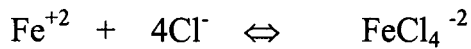
2.3.3.2.4 Physical Effects Associated With Carbonation Process

Both $\text{Ca}(\text{HCO}_3)_2$ and CaSO_4 produced in chemical reaction are soluble in water^(ref:11). Loss of Material and weakening of hardened cement paste can therefore be associated with the formation of these compounds. Since all the hydration products of Portland cement, including the calcium silicate hydrate, can be decomposed by carbonation reactions, permeable concrete when exposed to larger concentration of CO_2 is likely to deteriorate.

Carbon dioxide (CO_2) is chemically just $1/10^{\text{th}}$ as corrosive as oxygen (O_2). But due to its greater solubility and high chemical activity in water, it is dangerous to the concrete from the durability point of view. At 20°C , the solubility of CO_2 in water is 900-ml/l ^(ref:14), which is very high when compared to concentration of dissolved oxygen in seawater, which is less than 10 ml/l .

2.3.3.3 Corrosion Initiated By Chloride Ions

One of the mechanism, which possibly explains the chloride depassivation of steel is '*Complex Ion Formation*', the theory attributed to Hoar and Folley^(ref:15). The theory says that *chloride ion 'complex' the ferrous ion in the passive film, breaking down the film.* To expand on this, a mechanism proposed by William Hime^(ref:15), explains the process of Corrosion of steel as follows:



The chloride complex ion product of first equation being unstable reacts:



Freeing the chloride ion to move back to the steel causing more corrosion.

2.3.3.3.1 Availability of chloride Ions in concrete

Chlorides occur in concrete in three forms. Chemically bound, physically absorbed and as free chlorides. Chloride ions may be introduced in to concrete in a variety of ways. Some are intentional inclusion as an accelerating admixture; accidental inclusion as contaminants on aggregates or by penetration in concrete from the

surroundings like industrial brines, marine spray, deicing salts, fog or mist. Chlorides can reach at paste- Steel interface by following two ways:

a) **Incorporation in Concrete during Mixing.** In areas where fresh water is scarcely available contaminated or seawater is used as the mixing water, which increases the chloride ions concentration. Or even if aggregate is exposed to seawater, it absorbs the chlorides. In some important constructions, where rapid strength is required, 1½% to 2% calcium chloride $\text{CaCl}_2 \times \text{H}_2\text{O}$ may be added as an accelerator and this way chlorides mixing becomes unavoidable.

b) **Diffusion in to Mature Concrete.** Chlorides can permeate through the sound concrete i.e. cracks are not required for chlorides to enter the concrete^(ref:19).

2.3.3.3.1 Admixed chloride vs. 'alien 'chloride

William Hime^(ref:19), has tried to argue against apparent success of chloride containing structures. He cautions against the explanation that *chloride present in the original mix is rendered non-corrosive through reaction with cement aluminates to calcium chloro aluminate hydrates (Friedel's salt)*. He goes on to prove that chloroaluminate is unstable in the presence of sulfate and carbon dioxide that leads to freeing of chloride ion.

2.3.3.3.2 Electrochemical Process Involving Chloride Ions

Heterogeneities of reinforced concrete as already covered leads to building up of electrochemical corrosion cells . Two types of corrosion cells may exist corresponding to the prevailing conditions. The first type,

called the *Micro cell*, is characterized by microscopic distance separating the anode and cathode. In the second type, called the *Macro cell*, both the anodic and cathodic reactions frequently take place together at some distance^(ref:16). The potential difference between the anode and the cathode of a Macrocell is larger than that of Microcell. Therefore the corrosion reaction is more rapid in former than in later. In concrete, Microcell corrosion is important and takes places frequently; it is shown diagrammatically.

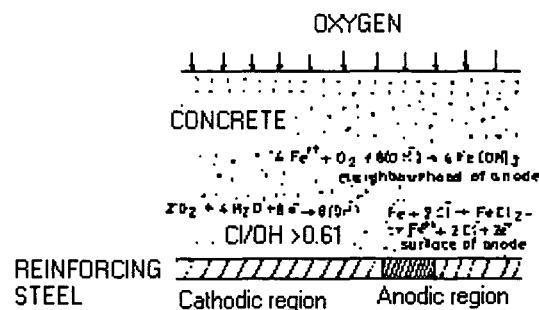
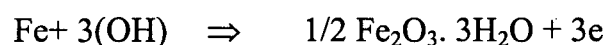


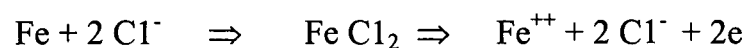
Fig 2.3.3:Macrocell Corrosion initiated by Chloride Ions

Following are the electrochemical reactions involved in chloride initiated corrosion Mechanism:

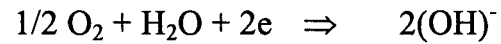
a) Anodic reaction, assuming high $(OH)^-$ concentration:



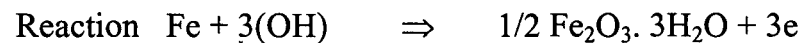
b) Anodic reaction, assuming high Cl^- concentration:



c) Cathodic reaction, if oxygen is present:

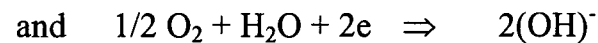
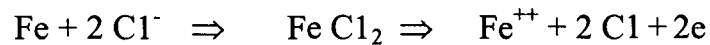


2.3.3.3.3 Physical Effects Associated With Chloride Induced Corrosion Process



Shows that if a high alkaline environment (high OH^- ions concentration) is available in concrete then an insoluble passive film of hydrated iron-oxide is formed on the steel surface making the steel noble thus preventing further loss of material.

It is obvious from reactions



That high concentration of chloride ions and oxygen would favor the corrosion of steel. The threshold value of ($\text{Cl}^- / \text{OH}^-$) to initiate the corrosion is 0.63^(ref:11,13).

2.3.4 STATES OF CORROSION

Mani^(ref:17) reiterates that the passivity of steel requires a minimum pH value of about 11.5 to be maintained. General loss of passivity can, therefore, arise if the pH value of pore-water at the depth of the reinforcement becomes substantially reduced from its initial, high level^(ref:17). This can happen as a result of carbonation, which involves penetration into the material of acidic gases (CO₂ etc) from the surrounding air. Thus reinforced concrete, contaminated with excessive level of chloride ions, leads to cause complete destruction of the passive film. This gives rise to general corrosion of the steel.

The corrosion potential of reinforcement, which is undergoing general corrosion, is usually in the range – 450mV to 600mV (SCE scale), i.e. similar to that of uncoated steel undergoing corrosion in a nearly neutral aqueous environment.

2.3.4.1 Pitting Corrosion

The passivity of steel in an alkaline environment may be destroyed by the presence of chloride ions. Pitting corrosion is therefore, likely to occur in reinforced concrete containing significant levels of chloride salts. *This corrosion state is characterized by galvanic action between relatively large areas of passive steel acting as cathode and small anodic pits where the local environment, within the pits, develops a high chloride concentration and a depressed pH value.* For sustained pitting, it

is necessary that a sufficient concentration of oxygen should be available to cause polarization of the anodes. The formation of pitting corrosion product involving the various reacting materials as illustrated in Fig 2.3.4.

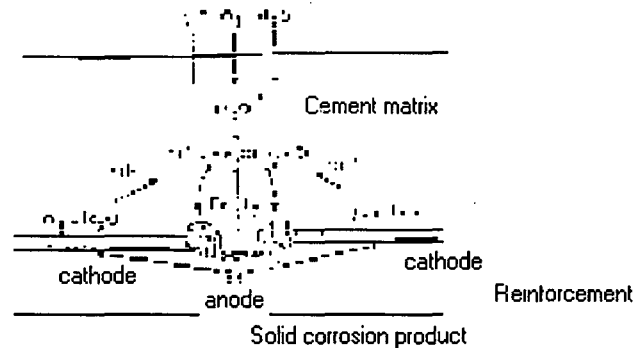


Fig 2.3.4: Corrosion product with various reactions

The average corrosion potential of steel reinforcement undergoing pitting ^(ref:17) is likely to vary between that of the passive state and that of the anodic pitting areas, being typically in the range- 200mV to 500mV (SC scale). Anodic sites, which may be identified by corrosion potential mapping as the most negative regions within a structure, are generally surrounded by areas of high potential gradient.

2.3.4.2 Low-potential Active Corrosion

In environments where the availability of oxygen is extremely limited, as is sometimes the case for fully submerged or buried reinforced concrete, the limiting cathodic current density may eventually become insufficient to maintain the passive film on steel.

Under these circumstances, the metal behaves ‘actively’ in the highly alkaline environment, undergoing uniform dissolution to form soluble $\text{FeO} \cdot \text{OH}^-$ ions, as represented in the Pourbaix diagram for the Fe- H_2O system ^(ref:17). The corrosion potential is depressed and the rate of metal dissolution is extremely low owing to the restricted availability of the cathodic reactant.

2.3.4.3 Time-dependence

The state of corrosion of steel in concrete when modeled as a function of time forms distinct stages. The *initiation period*, during which the metal, remains passive whilst, within the concrete, environmental changes are taking place that may ultimately terminate passivity. The *corrosion period*, which begins at the moment of depassivation and involves the propagation of corrosion at a significant rate. A *final state* is reached when the structure is no longer considered acceptable on grounds of structural integrity, serviceability or appearance.

The service life may thus be represented in terms of these components ^(ref:17).

2.3.5 FACTORS INFLUENCING CORROSION OF STEEL IN CONCRETE

Factors, that affect the process of corrosion of steel in concrete are enumerated and described below.

2.3.5.1 Chemical Environment

2.3.5.1.1 Alkalinity and Chloride concentrations: Chloride ions appear to be a specific and unique destroyer of the protective oxide film. The work of Varback ^(ref.10) indicates that a cement compound, Hydrated tricalcium chloroaluminate is mainly responsible for reducing the Cl^- concentration in the concrete by reacting chemically and forming tricalcium aluminate. Actually, 75% to 90% of chlorides present in cement paste, exist as chloroaluminate compound. Therefore the total amount of chlorides depends upon C_3A (tricalcium Aluminate) content of cement, degree of hydration of cement, etc. As mentioned earlier, the threshold value of ratio of Cl^- / OH^- (0.6 to 0.63), if exceeded, then there is 90% probability of active corrosion taking place.

2.3.5.1.2 Oxygen and Carbon dioxide Contents

Despite having different roles in corrosion process and different solubility both the gases perform critical reactions in water. *Oxygen remains an essential factor to sustain the cathodic reaction in corrosion of reinforcement in concrete In case oxygen is not available at steel-paste interface, the cathodic reaction stops and consequently by law of electrochemical reactions the complete corrosion process will stop.* Oxygen penetrates inside the concrete by slow diffusion process. This is what explains comparatively lesser instances of corrosion in submerged structures than less partly submerged structures.

The effect of CO₂ on corrosion process is limited to carbonation or neutralization of alkaline environment in concrete, thereby making concrete more permeable and more porous.

2.3.5.1.3 Cement.

The important constituents of the cement affecting the corrosion process are tricalcium aluminate C₃A (3CaO. Al₂O₃) and Pozzolona .

Some reports suggest that the cements containing high tricalcium aluminate (C₃A) have the tendency to retard the corrosion because the formation of tricalcium chloroaluminate (C₃A.CaCl₂.11H₂O) reduces the chlorides by chemical reaction .It is reported ^(ref:6) that the test piles of reinforced concrete made with high C₃A (8-11%) cement showed less cracking in sea water at St. Augusta, Florida than Similar piles made with low C₃A (2-5%) cement after an exposure duration of 25 years. However as stated in 2.3.3.3.1.1(*Admixed chloride vs. 'alien' chloride*), this contention stands challenged as on date.

As per ASTM Specification C 618–78, a Pozzolona is siliceous and aluminous material which in itself possess little cementitious value but will, in the presence of moisture, chemically react with calcium hydroxide Ca (OH)₂ at ordinary temperature to form compounds possessing cementitious properties ^(ref:18). It is obvious from above that pozzolona drives the cementitious properties from

the reaction with $\text{Ca}(\text{OH})_2$ which implies that *pozzolana*^(ref:19) reduces the alkalinity with in the concrete. The pH is reported to have been reduced to 8.5 or 8.7 by the use of pozzolana, which is not a good sign for concrete.

2.3.5.1.4 Aggregates and Admixtures. Aggregates generally have little effect on the corrosion of reinforcement concrete. The only exception being, the porous aggregate, which may absorb chloride, salts. This can happen when the sand is dragged from seaside. A common admixture, CaCl_2 when added to concrete mix to accelerate the rate of development of strength may prove to be harmful by adding the extra chlorides.

2.3.5.2 Physical Environment

For corrosion to occur besides depassivation, potential differences also plays a major role. Differences in electrochemical potential with in the concrete may arise in various ways.

2.3.5.2.1 Use of different Metals in construction.

All the metals can be graded as per their electrochemical potential and arranged in an order of their decreasing potentials or activity. List of such metals is known as EMF series. If two metals in this series A and B ('A' is more reactive, 'B' less reactive) are coupled together in a electrolyte, then a Corrosion current is set

up, flowing from A to B. This is called a *galvanic action of metals*. Thus corrosion may occur by galvanic action, if different metals are used in R.C.C work or if galvanized steel ruptures, bringing two metals into galvanic action.

2.3.5.2.2 When single metal is Used in construction

Differences in potential on the same metal may be due to:

Presence of inclusions.

Difference in surface conditions.

Imperfections in crystalline structure of metal.

Differences in alkalinity.

Differences in temperature.

2.4 IMPORTANCE OF CORROSION TOWARDS DEVELOPMENT OF SLAG ADMIXTURED HPC

2.4.1 GENERAL

Corrosion of reinforcing steel is the major factor affecting the durability of concrete. Because of the high alkalinity of the concrete pore fluid, steel in concrete remains in a passive state. As already covered initiation of corrosion occurs either due to a reduction in alkalinity arising from carbonation or the breakdown of the passive layer by chloride ions. Corrosion initiation time is determined by the permeability of the concrete. Once depassivation occurs, corrosion propagation is governed by the anodic, cathodic and electrolytic properties of the corrosion cell^(ref:40) i.e. the oxygen availability and resistivity.

Chloride-induced corrosion of steel bars embedded in concrete is related to the chloride permeability of the concrete. Examination of published data shows^(ref:20-24) that *the slag concrete possesses much lower chloride permeability than the corresponding OPC concrete*. The pore structure of the slag concrete prevents the chloride ions from intruding into concrete, and concentrates the chloride ions near the surfaces of concrete specimens.

2.4.2 PORE STRUCTURE AND PERMEABILITY

Many studies have shown *that the incorporation of slag produces concrete with a much more refined pore structure than OPC concrete*^(ref:25-27). Pore structure is mostly influenced by water curing and a continuous humid environment is known to reduce the pore sizes. It is this unique reduction in pore size which refines the pore structure giving slag concrete its superior durability properties, as compared to OPC concrete.

With insufficient curing, pores larger than 1 μm remain, and it is these pores, rather than the total porosity, that govern the chloride permeability of concrete^(ref:21,22).

2.4.3 CARBONATION

There is considerable contradiction in literature on the rate of carbonation in slag compared to OPC concretes. *Many tests appear to show*^(ref:28-32) *that carbonation proceeds more rapidly in slag concrete than in OPC concrete specimens of equal age.* Concretes containing low amounts of slag appear to perform better in this respect than concretes with high replacement levels. *The overall conclusion appears to be that the higher content of carbonation in slag concrete is related to the high content of micro-pores at early ages in slag incorporated concretes.*

The progress of the carbonation front in slag concrete depends on the mix proportioning method adopted for the slag concrete. The complex inter-relationship between carbonation depth and compressive strength is shown in Table 2.4.1 and 2.4.2 for concrete containing 50% and 65% slag replacements respectively. *The data show that concretes with 65% slag carbonate more than concretes with 50% slag when exposed to a drying environment.*

The results shown in tables 2.4.1 and 2.4.2 are interesting and more research needs to be carried out to clarify the effects of slag on carbonation.

2.4.4 SO WHAT IS GGBS !

Ground granulated blast-furnace slag, derived as a by-product from pig iron production is a unique cementitious material. It possesses inherent ability to provide strength, stiffness and durability to concrete materials.

2.4.5 STRUCTURE OF SLAG

Slags are by-products of the metallurgical industry. Their chemical composition structure and properties vary depending on whether they are ferrous or non-ferrous slags. The slag results from the fusion of the raw materials used in the blast furnace forming the production of pig iron. Fusion temperature ranges between 1400 degree C and 1600 degree C when the molten slag floats on top of the molten iron.

A slow cooling of slag melts result in the formation of crystalline mineral compounds, which have little or no cementitious value. If however, they are quenched from its molten state the granulated slags retain their disorganized liquid structure and remain in a meta-stable, amorphous, vitreous or glassy state and possess latent hydraulic qualities.

Rapid cooling is necessary to impart glassy structure and the most commonly employed method of quenching slag is by water granulation.

2.4.6 FACTORS INFLUENCING SLAG HYDRAULICITY

There are four major factors that influence the hydraulic activity of slags, (a) *The Glass Content (i.e. Degree of Vitrification)* (b) *Chemical Composition*, (c) *Mineralogical Composition and* (d) *Fineness*.

2.4.6.1 Glass Content

Several factors influence the degree of vitrification achieved during quenching but the biggest variable remains the temperature at which the furnace is tapped. *The rate of quenching and the glass content are thus the predominant factors affecting strength of slag cements.* Increasing crystalline contents reduce hydraulicity but there is no well-defined or single relationship between strength and glass content^(ref:34). Although a glassy structure is essential to

reactivity research shows that *there is no exact correlation and therefore, there is no guarantee that a high glass content will produce a highly reactive slag*. Research data also show that *slags with as little as 30-65% glass contents are still suitable but no specific minimum glass content appears to arise from these tests*^(ref:34,35,36).

2.4.6.2 Chemical Composition

Chemical composition of slag determines its basicity and in general, the hydraulicity of slag increases with increasing contents of lime and alumina, and with decreasing contents of silica and manganese oxide. All the research indicates that *consistency of chemical composition is more important than the actual composition to produce cement with uniform properties*^(ref:36).

2.4.6.3 Mineralogical Composition

It is the mineralogical composition, rather than the chemical composition that determines the hydraulic properties of cementitious materials. However, much research shows that, *the hydraulic properties of slag cannot be evaluated by calculation of the minerals present at equilibrium*^(ref:37).

2.4.6.4 Fineness

As with all cementing materials, the reactivity of slag is determined by its surface area. Increased fineness results in better strength development, but then it is limited by economic

and performance considerations and factors such as setting time and shrinkage^(ref:38). In the UK, GGBS is marketed at a surface area of 375-425 m²/kg, whereas some slags in the USA have surface area in the range 450-550 m²/kg and Canadian slags are about 450 m²/kg. In India the GGBS commonly available is at 330 m²/kg.

2.4.7 ACTIVATION OF SLAGS

Because of their nature slags react more slowly with water than Portland cement, but they can be activated chemically. Activators are generally of two kinds - alkaline activators such as sodium hydroxide, lime and sodium carbonate, or sulfate activators such as calcium sulfates or phospho-gypsum. From a practical point of view, Portland cement (OPC) is the best activator, as it contains two slag hydration activators i.e. gypsum (sulfate activation) and portlandite, Ca(OH)₂ liberated by the hydration of clinker silicates (lime activation). Research data show that *there are contradictory views as to whether hydration reactions of slag activated with hydrated lime and Portland cement are similar or different*. However the mineralogical composition and in particular, the total alkali content of the portland cement clinker, are the most critical factors affecting strength development.

In spite of having hydration products similar to those of Portland cement^(ref:39), there is difference in development of strength in Portland slag cement.

2.4.8 INTERNATIONAL STANDARDS FOR SLAG ADMIXTURED CEMENTS

Following are some of the International codes, which lay down standards for slag cements.

BRITISH CODES - BS-146 Part 2 1973 gives specification for Portland Blast Furnace Cement and BS-4246(1974) gives specification for Low Heat Blast Furnace Cement and BS-4248(1974). The use of Air Cooled Slag in concrete is covered in BS-1047(1974). The use of Foamed Slag Aggregate is covered in BS-877(1973).

AMERICAN STANDARDS Manufacture of Blast Furnace Slag Cement is covered in ASTM C- 205 (1946). An ASTM specification covering separate Ground Granulated Slag was issued in 1982, only a few months after the USA product was marketed the specification is under jurisdiction of ASTM sub committee C-09.03.10 and is titled 'Ground Iron Blast Furnace Slag for use of Concrete and Mortar', with the designation ASTM C - 989.

NETHERLANDS STANDARDS Netherlands standards for cement are given in NEN-3550.

THE GERMAN DIN 1164 part -1 'Portland Eisenportland Hochofen and Trabzement', Portland Blast Furnace and

Pozzolanic cement (November 1978) gives the details followed in Germany.

INDIAN STANDARD CODE IS-12098 (1987) Refer Table 5 for prescribed quality of granulated slag as above code. In India, although there have been many studies, on the behavior of concrete containing Mineral Admixtures like Fly Ash, Silica fumes and Granulated Blast Furnace Slag, the useful information relevant to the Indian scenario remains very scanty.

TABLE 2.4.1**Carbonation properties of concrete with 50% slag replacement**

CURING REGIME	AGE (MONTHS)	COMP STR (Mpa)	CARBONATION DEPTH (mm)
Lab	3	45.8	4.6
	6	51.3	9.8
7 Fog + Lab	3	65.8	3.5
	6	71.3	5.1
Fog	3	70.9	0
	6	71.3	0

TABLE 2.4.2**Carbonation properties of concrete with 65% slag replacement**

CURING REGIME	AGE (MONTHS)	COMP STR (Mpa)	CARBONATION DEPTH (mm)
Lab	3	36.1	5.1
	6	33.9	11.6
7 Fog + Lab	3	57.8	4.5
	6	59.7	7.8
Fog	3	64.5	0
	6	67.6	0

TABLE 2.4.3
SPECIFICATIONS OF GRANULATED SLAG AS PER IS 12089

CONSTITUENTS

PERCENTAGE OF	MAX. PERCENTAGE
MANGANESE OXIDE	5.5
MAGNESIUM OXIDE	17.0
SULPHIDE SULPHUR	2.0
GLASS CONTENT	85.0 (MIN)

OXIDE RATIOS

$\frac{\text{CaO} + \text{MgO} + \frac{1}{3} \text{Al}_2\text{O}_3}{\text{SiO}_2 + \frac{2}{3} \text{Al}_2\text{O}_3}$	≥1.0
$\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}$	≥1.0
$\frac{\text{CaO} + \text{C}_2\text{S} + \frac{1}{2}\text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + 2\text{MnO}}$	≥1.5

2.5 METHODOLOGIES TO DETERMINE REINFORCEMENT CORROSION

To be able to quantify the status of deterioration of a reinforced concrete during its lifetime or to assess the need for repair, an array of methods to study the corrosion behavior of reinforcement are available; *mundane to the highly sophisticated*. They can be broadly classified under tests related to concrete and reinforcements

2.5.1 TEST RELATED TO CONCRETE

The factors affecting the durability of concrete also influence the corrosion of steel in concrete and many of them are interrelated. The important tests on concrete relating to the corrosion of reinforcements are *alkalinity* (pH), *resistivity*, *diffusion* (for chlorides), and *permeability* (for sulfates and oxygen).

2.5.1.1 Alkalinity Tests

The alkalinity (Ph) of concrete is a parameter influencing the passivation film on steel. It is primarily dependent upon the cement content and its interaction with the environment. Penetration of salt solutions and carbonation form the two important factors .The basic methodology is to prepare an extract of the concrete and measure the pH directly.

2.5.1.2 Permeability Tests

The permeability and diffusion characteristics of concrete have a great influence on the corrosion behavior of steel in concrete. Both these parameters are highly interrelated as both of them depend on the

pore structures and pore size distribution. Permeability is a parameter, to be mainly considered in case of submerged or marine structures wherein the depth of water has a profound influence. Apart from permeability, the diffusion of the salts like chlorides, sulfates and others have to be considered for any design against corrosion. Regarding diffusion tests, most of the research has concentrated on the diffusion of chlorides into concrete. *While most permeability results are established by applying a differential pressure between two boundaries, the diffusion tests can either be through natural diffusion or by diffusion by applying a potential difference between two boundaries.*

2.5.1.3 Carbonation Tests

The depth of the carbonation layer in a concrete component can be assessed by several different methods; X-ray or chemical analysis of suitable samples, collected from different depths, to determine their content of calcium hydroxide and calcium carbonate. To assess the potential hazards of corrosion of embedded metal, simple procedure of making the reduction in alkalinity visible by spraying freshly broken surfaces of the concrete sample with Phenolphthalein solution sufficiently indicates color change according to the alkalinity or pH value.

Tests with these indicator compounds distinguish between the zones where the alkalinity of the concrete has been maintained to a high level and the zone where the alkalinity has become reduced. (PH-value of 8 or below).

2.5.1.4 Tests For Chloride Ion Penetration

Because of the clear role of chloride ion in initiating corrosion of the steel, the techniques to determine chlorides are important. Most of the techniques involve sampling of the concrete around the reinforcing steel and then conducting either an electrometric or a conventional titration against silver nitrate solution to determine the chloride level. ASTM also gives out specifications of RCPT (*rapid chlorine penetration test*). Some research has recently been undertaken using portable neutron activation analysis techniques to conduct scans of the structure for chloride content.

2.5.1.5 Resistivity Mapping

The corrosion of a specific length of reinforcement is dependent on the algebraic summation of the electrical currents originating from the corroding sites on the steel and flowing through the moist surrounding concrete to non-corroding sites. Hence the electrical resistance of the concrete plays an important role in determining the magnitude of corrosion at any specific location. *Resistivity, thus as a parameter, influences the conductivity of the medium which in turn allows the galvanic currents to set up in the structure.* This parameter is expressed in terms of ohm centimeters. The factors which govern the resistivity values are:

Constituents of concrete.

Chemical contents of concrete such as moisture, chloride level, and other ions.

Type of pore structure of concrete.

In view of the many influencing factors as given above, it is possible that resistivity values vary quite significantly over a structure. Therefore, it is necessary that a systematic survey over well-defined grid points be done and a map of the resistivity values plotted to assess the most potentially corroding areas. Table below indicates the general guidelines of resistivity values based on which areas having probable corrosion risk can be identified in concrete structures.

<u>Resistivity</u> (ohm.cm)	<u>Corrosion</u> Probability
Greater than 20,000	Negligible
10,000 to 20,000	Low
5,000 to 10,000	High
Less than 5,000	Very high

2.5.2 TESTS RELATED TO STEEL REINFORCEMENT

Although it is desired that techniques be developed for monitoring reinforcement corrosion in actual structures, laboratory studies simulating various field conditions are essential for fundamental investigations. Studies of reinforcement corrosion in concrete can be carried out in following ways.

2.5.2.1 Qualitative Assessment (NDT methods)

2.5.2.1.1 Visual And Sonic Techniques

The first sign of reinforcing steel distress in a conventional reinforced concrete structure is frequently the appearance of rust standing on the surface. Obviously, this only occurs where the surface can be visually examined. At a later stage, cracks which may have developed subsurface reaches the surface and spalling of the concrete ultimately takes place. At the earlier stage, it is possible to assess damage due to internal cracking by using a “*sounding*” technique involving chain drag or striking of the surface with hammer, or alternatively by using an ultrasonic reflective method to determine the presence of subsurface delaminations .

2.5.2.1.2 Half Cell potential and mapping

During the corrosion process, the rest potential of the corroding bar with reference to reference electrode changes and the potential become more and more negative as the process continues. The potential measurement in concrete surfaces essentially consists of making a metallic contact with the reinforcement and measuring the voltage difference between the steel and a reference electrode in contact with concrete surface .A few common standard electrodes as reference cells are copper/copper sulfate, silver/silver chloride, and calomel electrodes.

An ASTM Standard (C-876) has been published on this method, which indicates the potential ranges in relation to be probability of corrosion. Even though, this method has serious limitations and liability to yield erroneous inferences, the method is still recognized to

be useful with the availability of more and more authoritative reports and data. The general guidelines for identifying the probability of corrosion based on half-cell potential values as suggested in ASTM C-876 are given below:

Probability of corrosion	E_{corr} (Vs Cu/CuSO₄)
Greater than 95%	More negative than -350 mV
Less than 5%	More positive than -200mV.
Approx 50%	Between -200 and -350 mV.

It is important to realize that *the potential of any metal in cement concrete environment is a function of a large number of variables such as concrete composition, pore liquid, concrete resistivity, cover thickness, degree of polarization, etc. Hence, no quantitative conclusion can be drawn from it.*

However, a systematic “*Potential Mapping Survey*” is considered to be more useful for on-site identification of the Corrosion State of the reinforcements. This facilitates setting up potential profile or potential contour. For assessment, potential values should be taken as a group and not in isolation, i.e. the interrelationship of the potentials within that group should form the basis for interpretation.

Analysis of potential contour will generally consist of (a) *Identifying the locations with accumulated potential lines indicating a clue to the corroding areas beneath.* (b) *Locating the anodic areas*

identified by the gathering of is potential lines having more severe potential gradient. (c) Ascertaining whether or not a structure is actively corroding.

Certain important parameters, which influence the measured potentials of the reinforcements, are follows.

1. *The potentials of reinforcement measured on the surface of, or within concrete may not be a true representation of the value at the surface of the steel.*
2. *The physical and chemical state of concrete can result in wide variation.*
3. *The ohmic drop due to electrical resistance of the concrete also can induce variations.*

2.5.2.1.3 Studies by alternate wetting and drying /Accelerated salt spray test.

Accelerated salt spray tests involving alternate drying and wetting are used to create field exposure in a relatively shorter period of time. However the IS: 9844-1981(Methods of Testing Corrosion Resistance of Electroplated and Anodized Aluminum Coatings by Neutral Salt Spray Test) states that '*there is seldom a direct relation between resistance to the action of salt spray and the resistance to corrosion in other media because several factors influencing the progress of corrosion vary greatly with the actual conditions encountered*'.

2.5.2.2 Quantitative Assessment (Electrochemical / Polarization Methods)

Polarization generally means a disturbance or a perturbation given to a system from its natural state. In the case of corrosion studies, it is controlled perturbation given to the existing state of the metal in an electrolyte through an external force.

Principle

The best known technique for evaluation of instantaneous corrosion rate in the laboratory is the resistance polarization method. This technique was developed by Stern and Geary in 1957 . The principle involved in this technique is that a linear relationship exists between potential and applied current, at potentials only slightly shifted from the corrosion potential. Based on the kinetics of electrochemical reactions and the concept of mixed potential theory postulated by Wagner and Traud, the equation was derived, which relates quantitatively the slope of the polarization curve in the vicinity of the corrosion potential to the corrosion current density (I_{corr}) as follows:

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p} = \frac{k}{R_p}$$

Here,

b_a = Anodic Tafel slope constant

b_c = Cathodic Tafel slope constant
 R_p = Polarisation resistance

This principle can be applied for estimating the corrosion rate (I_{corr}) of reinforcements embedded in concrete. This technique, a small amount of D.C. current is applied to the embedded reinforcement and the corresponding potential is monitored. This polarization can be carried out from -10 mV to $+10$ mV in the vicinity of open circuit potential (OCP).

Concrete being a heterogeneous material composed of cement, sand and stone aggregate behaves like an unpredictable electrolyte. As on date, there is no foolproof non-destructive technique to quantify corrosion of embedded steel at various locations. However, In an attempt to do so, polarization studies are conducted in two ways:

- 1. Reinforcement in solution simulating pore's liquid environment of concrete.*
- 2. Reinforcement embedded in concrete.*

In normal situation, the reinforcement acts as both anode and cathode and both anodic and cathodic currents occur on the specimen surface. Any corrosion process that occurs is usually a result of anodic current. But, for fundamental studies, it is advantageous to make the specimen to act separately as either an anode or cathode but not simultaneously. *By separating the functions in this manner and*

studying anodic and cathodic processes separately behavior in a particular medium can be better understood.

The test set up for polarization studies of reinforcement consists of an electrochemical cell, having a three electrode system, namely, a **Working Electrode (WE)** which is the reinforcement under investigation, a **Counter Electrode (CE)** and a **Reference Electrode (RE)** kept in the solution simulating pore liquid of concrete.

Polarization studies can be done in three different ways, *Potential-dynamic, Potentio-static or Galvano-static*. Each method gives different information and results, which are useful in understanding the corrosion behavior.

2.5.2.2.1 Potentio Dynamic Polarization

A specimen, in contact with corrosive liquid and unconnected to any instrumentation, exhibits a potential (relative to a reference electrode) and it is termed as "*Corrosion Potential*" or Rest Potential or **Open Circuit Potential (E_{corr})**. A specimen of E_{corr} has both anodic and cathodic currents existing on its surface and it is considered to be in equilibrium with the environment having both anodic and cathodic currents exactly equal in magnitude. Thus there is no net measurable current (even though it may be visibly corroding). Therefore, E_{corr} can be defined *as the potential at which, rate of oxidation is exactly equal to the rate of reduction.*

The polarisation consists of shifting the E_{corr} slightly in a desired direction by using an external source. If the E_{corr} is shifted

to the positive direction (less negative direction), that is, made to function more as an anode than it would be at E_{corr} , the anodic current predominates at the expense of the cathodic current. Alternatively, if the specimen is polarized for more negative potential, the cathodic current predominates and anodic current becomes negligible. Experimentally, this is achieved by using a highly sensitive potentiostat having facilities for shifting the potential at a predetermined rate in an electrochemical cell. *Shifting the potential at a definite rate is known as potentiodynamic polarization and the measurements consist of the shifted potential and the current response to the shifted potential.* The polarization characteristic is expressed in a termed as a **potentio dynamic polarization plot**.

A potentiodynamic polarization plot such can yield important information such as:

1. *The ability of the material to spontaneously passivate in the particular medium.*
2. *The potential region over which the specimen remains passive; and*
3. *The corrosion rate in the passive region.*

2.5.2.2.2 Potentiostatic Polarization

The theory of polarization remaining the same, the potentiostatic polarization involves a test setup of a similar type. The experiment consists of monitoring the current with time under *constant* applied

potential with reference to a reference electrode. *A potentiostatic polarization curve will relate time and change in current density for a given constant potential and it can also be used to derive curves relating current densities and potentials by conducting several experiments.* Where as in potentiodynamic method, in which the potential is increased at a predetermined rate, it is the scan rate that influences the final results of the polarization curve.

2.5.2.2.3 Galvanostatic Method

In the galvanostatic method, *a constant current is applied to the specimen in the cell and the potential with reference to a standard electrode is monitored with time.* Different combinations of current densities and time can be applied and the results are useful in determining **threshold chloride concentration, depassivation time and initiation of corrosion.**

In this method, it is also possible to apply current incrementally by keeping each current value for a specified duration. Such method is termed as “*Galvano staircase*” method. The application of this method is described for aluminium in ASTM G 100 and its applicability and data for steel reinforcements are yet to be established.

The results contained in polarization experiments for steel reinforcements are useful only *to study the corrosion tendency of the metals in different environments and it will be erroneous to apply the results to actual conditions, especially to actual concrete structures.* Steel embedded in concrete is influenced by several other factors such

as, cement content in concrete, pore structure, permeability characteristics, cover thickness, resistivity of concrete etc. Such parameters are non-existent in experiments of metal/solution electrolytic cell.

2.5.2.3 Misc. methods

2.5.2.3.1 Impedance Technique

Difficulties with the polarization resistance technique involve the high resistance of the concrete. One solution to this problem is to use electrical impedance measurements. This method can be used as a research tool (for example for studying the initial passivation or possible time to breakdown of the passive film) as distinct from practically monitoring the deterioration onset and severity with time in an actual reinforced concrete structure.

2.5.2.3.2 Electrochemical noise

This consists of the analysis of the very small voltage perturbations (in the range of microvolts) measured at the corrosion potential. After recording the fluctuations with a very sensitive and accurate voltmeter, the noise signal is transformed from the time domain into the frequency domain through a Fast Fourier Transform spectrum Analyzer and plotted in the form of amplitude versus frequency. The equipment needed for the measurements consists of a micro-voltmeter, a spectrum analyzer and a microcomputer. Its

application to steel embedded in concrete has very recently been published and only a few experiments have been carried out

2.6 SIMILAR RESEARCH ACROSS THE GLOBE

A glimpse on similar work on related and contemporary topics is being presented below:

2.6.1. NON-DESTRUCTIVE TECHNIQUES TO ASSESS CORROSION RATE OF STEEL IN CONCRETE. (A ETHZ RESEARCH PROJECT)

Principal investigator: Dr Prof. Hans bohni, Dept of Civil and Environmental Eng., Institute of Building Material, Geneva

Supported by: Swiss Federal High Way Agency.

Maintenance, planning of the restoration work, quality control and the evaluation of structure live cycle-cost need rapid, non-destructive field test methods for locating corroding zones as well as for measuring the corrosion rate of reinforcing steel in concrete structures. A few commercial devices based on electrochemical linear polarization technique are available today. During this research work a very rapid new technique, galvanostatic pulse measurements (GPM), has been developed and tested successfully in the laboratory and on site.

Experimental data from on-site measurements have shown that in the frequent case of chloride induced, localized corrosion attacks the average corrosion rates determined from electrochemical measurements under-estimate the real, local penetration rates by a factor of five to ten. From an engineering point of view such local reduction in cross section of the reinforcements are dangerous for the safety of structures. In this project a new approach to measure experimentally localized and not average corrosion rates has been

tested in the laboratory on artificial macro-cells and compared to the traditional techniques. Numerical simulations with a network have helped to develop the algorithm for calculation of the local corrosion rates.

2.6.2 CHLORIDE IN CONCRETE: CRITICAL CONTENT FOR THE INITIATION OF CORROSION

Principal Investigator: Dr Prof. L Zimmerman, Dept of Civil and Environmental Eng., Institute of Building Material, Geneva

Supported By: Research Foundation of Swiss Cement Industry

Chloride induced localized corrosion attacks are the main cause for failure and deterioration of reinforced concrete structures. The '*critical chloride*' frequently cited in literature can not be considered a constant value, it depends on pH of the pore solution, environmental conditions (especially oxygen availability and concrete humidity). In simulated pore solutions the influence of pH and reinforcement quality on the critical chloride content is studied with electrochemical methods. Mortar samples with reinforcements, chloride and pH sensors are exposed to alternate wetting / drying cycles in chloride containing solutions. With these experiments the critical chloride activity in the pore solution for the onset of corrosion can be obtained. With the same experimental setup the influence of different cement types on the critical chloride content for corrosion initiation is studied. A further goal of the project is to study the behavior and durability of a novel chloride sensor.

2.6.3 ELECTRICAL RESISTIVITY OF CEMENT BASED MATERIALS

Principal Investigator: Dr Prof. S.Jaggi, B Elsener, Corrosion and Protection Centre, UK

Supported By: Swiss Federal High Way Agency

Corrosion of the reinforcement in concrete is associated with ionic current flow in the '*electrolyte*' concrete; thus the electrical resistivity of the concrete governs to a great extent the corrosion rate. Non-destructive methods as galvanostatic pulse technique or polarization resistance measurements have shown good correlation of corrosion rate to concrete resistivity.

On site measurements of the concrete resistivity might thus give an indication of the corrosion risk. In the first part of the research the dielectric properties and the resistivity of cement paste and mortar have been studied systematically as a function of porosity (water / cement ratio, curing, age) and humidity (100% to 60%). Weight change, H.F. impedance spectra (10 kHz to 200 MHz), MIP porosity and pore water expression and analysis were performed. The huge set of experimental data allowed to model the resistivity of cement based materials on the basis of the percolation theory. Two parameters of this model; conductivity and volume fraction filled with pore solution are related to the pore solution. The Other two parameters, the percolation threshold and the percolation exponent, are related to the distribution of the pore solution in the cement paste matrix.

In the second part of the research the application of resistivity measurements as a method for assessing the durability of the

reinforcement and the relation to corrosion rate is studied in the laboratory and on site.

Special attention is given to the influence of temperature on resistivity and on corrosion rate. The anodic and cathodic partial reactions of the corrosion process are studied. The research work has great impact for several fields in the corrosion of steel in concrete, the resistivity as a function of total porosity, pore size distribution and pore water composition is a key factor in the corrosion of the reinforcement in concrete. It may be used as non-destructive technique to assess the corrosion risk of structures.

2.6.4 CORROSION MODELING AND COMPUTER TECHNIQUES IN LIFE ASSESSMENT OF HIGHWAY STRUCTURES

Principal investigator: Dr Campbell Middletown, Dr Victoria Hogg, University of Cambridge CUED, and Bridge Institute

Funded By: The Highways Agency in the UK

The applications of computers in modeling of corrosion mechanisms and in the acquisition and processing of corrosion data are rapidly expanding.

A study of the effects of corrosion on the deterioration of steel and concrete highway structures is currently underway. The study aims to provide a practical tool for use in the assessment of highway structures such that indications of future performance can be obtained for a number of different bridges. The methodology allows comparisons of the future repair and maintenance needs of a bridge

stock to be made and thus aids in the decision making process of fund allocation.

Corrosion of Highway Structures Steel and concrete structures are both affected by corrosion. The main cause of corrosion in structures around the UK is the application of de-icing salts to roads. Chloride ingress results from leaking expansion joints and from vehicle spray.

Theoretical models exist for the prediction of corrosion in both concrete and steel structures. These can be used to predict the onset of corrosion and also the rate of corrosion loss. Once corrosion has initiated the effects of loss of cross-sectional area on the section capacity of a bridge element can be calculated.

2.6.4.1 APPLICATIONS OF CORROSION MODELING

The corrosion modeling has been applied in both deterministic and probabilistic analyses of bridges. The resultant has been a number of "*whole life profiles*" showing the effects on corrosion on the load capacity factor and the reliability index over a period of time.

2.6.5 NEURAL NETWORK APPLICATIONS IN CORROSION ENGINEERING

Principal Investigators: Dr R.A. Cottis, Dr M. Turega, Corrosion and Protection Centre and Department of Computation, UMIST.

Supported by: EPSRC (The Engineering and Physical Sciences Research Council).

The objective of the project was to develop methods for the reduction of corrosion data to a readily useable form using artificial neural network techniques.

The first part of the work was concerned with the examination of the problems associated with the use of neural networks for the reduction of corrosion information. It identified several problems associated with the inherent variability of corrosion data, together with the poor quality of much corrosion data, including missing or uncertain parameters, the poor coverage of the multi-dimensional input space and the relatively limited quantity of data available. It then went on to develop solutions to these problems.

These solutions are considered to be general advances in neural network technology for use with noisy, poor-quality or otherwise restricted data. In essence they depend on the production of two further output parameters in addition to the corrosion rate. The first of these is the variance, and is essentially the same as the conventional statistical parameter. The second has been termed the confidence, and is an indicator of the reliability of the prediction for a given set of input parameters.

These two parameters are essentially independent, and it is perfectly possible to have both a high variance (implying that the behavior in these conditions is inherently variable) and a high confidence (implying that the behavior is well defined).

blocks are cast with reinforcements inside, along with any appropriate corrosion inhibitor(s). Holes are drilled into the blocks for measurement of electrical potentials at interior locations; other holes are drilled to promote intrusion of saltwater. During exposure of a block to a saltwater or other corrosive environment, electrical potentials are measured at reinforcements as well as in holes. Corrosion currents are also measured, and polarization resistances are determined. Optionally, potentials can be applied to accelerate corrosion. At the end of a test, the blocks are broken for visual examination of the reinforcements.

CHAPTER 3
EXPERIMENTAL WORK

3.1 GENERAL

A study was planned to investigate the effect of high volume, slag admixed concrete (based on IS code mix design) on corrosion of embedded steel, so as to predict characteristics of high performance concrete composites developed with such slags with reference to corrosion aspects.

In this direction various fresh and hardened concrete parameters were taken into account, namely:

1. *Water / cement ratio.*
2. *Mix proportions.*
3. *Different proportions of high volume replacement of slag.*
4. *Efficacy of slags of different origins.*
5. *Efficacy of different curing methods.*

Considering the limitations of time, it was aimed that an experimental setup be established so as to study the corrosion parameter of high performance behavior of slag admixed concrete in comparison with reference concrete.

A parametric study was carried out on slag admixed concrete to establish its corrosion pattern. The experimental results showed a trend that could easily be examined against existing work available in the literature.

3.2 STUDIES ENVISAGED

The studies intended to be carried out can be classified based on following test procedures, which were developed:

3.2.1 Direct studies

1. Potentio-dynamic polarization study
2. Accelerated electrolytic corrosion study
3. Copper-copper sulfates half-cell potential study- *A qualitative study*

3.2.2 Indirect studies

1. Accelerated carbonation test.
2. Micrographic (SEM) study
3. XRD study

3.2.3 Misc. - Acid test

3.3 MATERIALS USED

3.3.1 Coarse aggregate: Locally available 12.5 mm downgraded. The grading conformed to IS-383 (1970) Specific gravity - 2.67

3.3.2 Fine aggregate: Locally available river sand was used. The fine aggregate was sieved thoroughly to conform to zone II of IS-383 (1970).

The physical properties of the fine aggregate are as follows:

Fineness Modulus - 2.7

Uniform coefficient - 1.9

Specific Gravity - 2.65

Percentage Bulking - 29 %

3.3.3. Cement: OPC 53 grade of Larsen and Tubro was used conforming to IS-269 (1976)

3.3.4 Steel: MS Bars of 8 mm ϕ were used as reinforcement for corrosion studies.

3.3.5 Slag (GGBS) ex steel plants: Conforming to BS 6699: 1992

(a) Andhra (Duncan GGBS ex Vizag) referred as **slag A**

(b) Bhilai (sample courtesy M/s ACC) referred as **slag B**

3.4 CHARACTERIZATION OF THE SLAG SAMPLES

3.41 Physical

		A	B
1.	Glass Content %	85	95
2.	Fineness M ² /Kg	330	325

3.42 Chemical %

1.	SiO ₂	29.88	32.88
2.	Al ₂ O ₃ + Fe ₂ O ₃	28.92	25.98
3.	CaO	34.72	36.4
4.	MgO	3.77	3.34
5.	Ignition loss	Nil	Nil

3.5 REPLACEMENT DOSES (CONSIDERING HIGH VOLUME REPLACEMENT)

1. 50%
2. 70 %

3.6 WATER/CEMENT RATIOS

1. 0.4
2. 0.55

3.7 MIX PROPORTIONS USING GRADE 53 CEMENT

At present there are no specific mix proportioning methods developed for slag admixtured concrete. The method of incorporating slag in concrete by replacing cement by mass results in higher volume of paste with the consequent advantage of improving the workability of the mix. Taking advantage of this, the mix design was developed based on various codes by altering the aggregate / binder ratio, so as to optimize the mix proportion for higher dosage of slag replacement.

<u>W/C</u>	<u>MIX PROPORTION</u>	<u>CORRESPONDING STR</u>
0.40	1:1.14:2.59	36.38
0.55	1:1.83:3.62	22.12

3.8 PREPARATION OF SAMPLES

3.8.1 SELECTION OF SAMPLES

Two types of samples were selected for direct studies. The cylinders of size 100-mm diameter x 200-mm ht and Tetragonal of 132-mm square

x 200-mm ht were chosen for reinforced concrete sample. The moulds for making cylinders were made of cast iron with inner surface accurately machined, and watertight. The interior surfaces of moulds were lightly oiled before pouring the concrete. The Tetragonals were cast in wooden moulds made of waterproof ply. All joints were carefully sealed to avoid any loss of water / paste. Adequate and consistent vibrations were given depending upon the amount of slag dosage. For indirect studies only cylinders as mentioned above were cast. And these were cast without reinforcing bars.

3.8.2 SURFACE PREPARATION OF STEEL BARS

Ideally the surface of steel bars, should be identical with the surface of the actual steel to be used in the construction. However, this is usually impossible because the surface of the commercial steel vary. Because of this, a clean metal surface is recommended. Also a standard surface condition facilitates comparison and correct interpretation of results.

As per 5.1 G-1 of ASTM 1981, the surface finish was produced by polishing with no 120 abrasive paper. The polishing operation was performed in such a way that there was no excessive heating of the specimen.

As the steel available, already had signs of pitting and rust, it was pickled in an acid solution containing 5% HCl of commercial grade. Then it was polished for 15.0 minutes to remove the pitted and rusted parts. Polishing was done till a good shine was obtained.

3.8.3 POSITIONING OF BARS AND CASTING

3.8.3.1 Potentio-Dynamic Polarization Test / half cell studies

3.8.3.1.1 Cylinder: A 230 mm long 8 mm ϕ reinforcement was centrally placed in 100 mm ϕ x200mm ht cement mould. The bar was exposed only in the middle 100 mm by selective painting, along the length. The bar was centrally held at the bottom by using 3-mm acrylic sheet. The exposed part of the bar at the bottom was later on capped using M-seal cap. The details are as shown in the fig 3.1

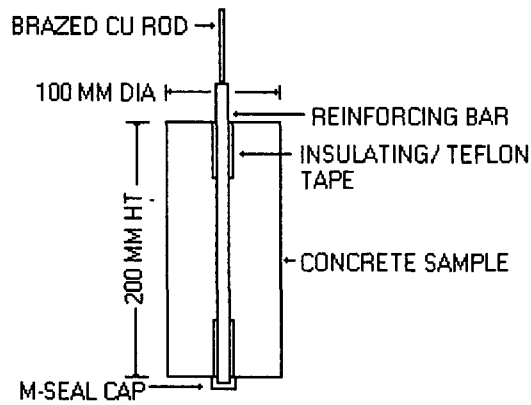


FIG 3.1

3.8.1.1.2 Tetragonal: A 132x132x200 Tetragonals were cast in which again 230 mm long 8 mm reinforcement bars were placed at 21 mm / 66 mm / 30 mm / 38 mm from two adjacent sides. The bar was again centrally held at the bottom by using 3-mm acrylic sheet.

3.8.3.2 Accelerated Electrolytic Corrosion Test: For this test only cylinders were cast. A 140-mm long 8-mm ϕ reinforcement was centrally placed in 100-mm ϕ x200mm ht cement mould. The bar was exposed only in the middle 100 mm by selective painting, along the length. The top

edge of bar which is at 30 mm from the top surface was brazed to an electric conductor.

3.8.3.3 Accelerated carbonation /SEM / XRD/Acid Test: Cylinders of size 100 mm ϕ x 200-mm ht were cast.

3.8.3.4 SUMMARY OF SAMPLES CASTED

Test	Sample	NUMBERS OF SAMPLES						
		Slag	W/C	Dosage = 0 %	Curing Types	Curing Days	Sets	Total
P.D.P And C.C.S	CYL	2	2	2 + R	1	(7+45/28)	2	20
	CUBE	2	2	2 + R	1	(7+45/28)	2	20
A.E.C	CYL	1	1(0.4)	2 + R	2	14	(C.C.) (C.V.)	6 3
A.C.T	CYL	2	1(0.4)	2 + R	1	1(56)	3x3	45
SEM/ XRD	CYL	2	1(0.4)	2+R	1	1(56)	3	15

3.8.3.5 SAMPLE CODING (IN THE ORDER OF PRIORITY)

1. Type of slag A- Andhra, B- Bhilai, R- Reference
2. W/C ratio X-0.40, Y-0.55
3. Slag replacement 5-50%, 7-70%.

3.9 TEST PROCEDURES

3.9.1 POTENTIO-DYNAMIC POLARIZATION/ HALF CELL TEST:

(a) **Accelerated Corrosion:** After demoulding, one set of samples were placed in environmental chamber after 7 days of curing. The temperature of the chamber was maintained at 35 degree C. Wetting cycle of 8 hrs per day was maintained using 5% NaCl solution. To ensure the consistency of the mist in the environmental chamber, the salt solution was replaced every week with a fresh solution. This cycle was repeated for only 28 days. The other set of sample was directly taken for Potentio-Dynamic polarization Tests after 28 days of wet curing followed by 60 days of dry curing.

(b) **Setup:** Prior to the main test copper-copper sulfate half-cell potential was measured. Then the test was carried out in 3% NaCl solution (sample dipped for one day) by using the embedded steel bar as a working electrode, a 10 x 15-cm stainless steel of grade 316 as counter electrode and standard calomel electrode as a reference electrode.

3.9.2 ACCELERATED ELECTROLYTIC CORROSION TEST (CONSTANT VOLTAGE / CONSTANT CURRENT)

(a) **Measuring and weighing of bars:** After surface preparation, the bars were brazed to 22 gauge copper wire. The centrally exposed area was rechecked to be 5026.54 mm² (10-cm length being exposed). The bars were then coded and individually weighed to the accuracy of 0.1 mg.

(b) Casting as already explained.

(c) **Curing:** Two sets of samples were prepared for CC studies out of which one set was given seawater curing. The composition of Sea water was taken as (28.9g) NaCl + (2.7g) MgCl₂+ (2.3 g) MgSO₄ + (0.2 g) KHCO₃in 1 lit water. For CV studies only one set was used. All samples were wet cured for 14 days.

(d) **Setup for CC Studies:** Test was carried out in 3% NaCl solution by providing constant DC of 80 mA .A circular 5-cm wide stainless steel rim of grade 316 was used as cathode electrode.

(e) **Setup for CV Studies:** Test was carried out in 3% NaCl solution by providing constant voltage of 60 V .A circular 5-cm wide stainless steel

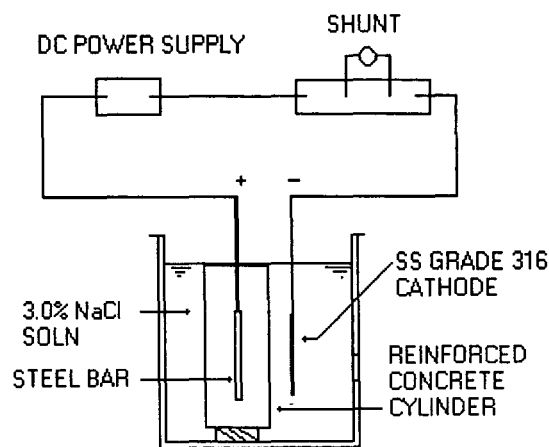


FIG 3.2

rim of grade 316 was used as cathode electrode.

(f) **Measurements:** For both kinds of tests, the variable parameter (i.e. Voltage / current) was monitored at every 15 min interval

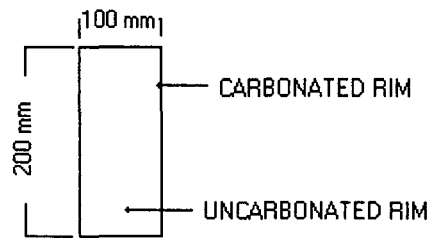
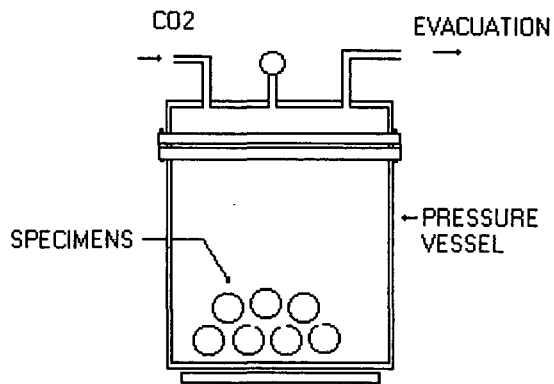
1. For CC studies the test samples were taken out after the duration of the test i.e. 6 hrs. The specimens were visually inspected and thereafter carefully split open to access the corroded steel bar. The bars were cleaned as ASTM G1 of 1981 by dipping in Clark's solution (HCl SP gravity 1.19 - 1 lit + antimony trioxide 20g + stannous chloride 50 g) for 25 minutes. Then the bars were weighed again to the accuracy of 0.1 mg to find out the net weight loss.

2. For CV studies, only the varying current was recorded at the interval of every 15 minutes.

3.9.3 ACCELERATED CARBONATION TEST:

(a) **Curing of cylindrical samples:** Concrete specimens 100 mm ϕ x 200 mm ht were molded as per the designed mix proportion and then given combined air and water cure (28 days-water, 28 days-dry) at 20 degree C.

(b) **Setup:** The concrete specimens were placed in a specially designed pressure chamber and evacuated to 5mm Hg or less at ambient temperature for 10 minutes, then exposed to CO₂ gas with the pressure of 1,3,and 6 kg/ cm² for 6 hrs.



MEASURED AND AVERAGED FOR CARBONATION DEPTH

FIG 3.3

After accelerated carbonation the concrete specimens were split and surfaces of X-sections were sprayed with 1-% phenolphthalein solution.

Thereafter depth of the rim of each X-section without color change was measured as carbonation depth.

3.9.4 SCAN ELECTRON MICROSCOPE STUDY

These studies were carried out with a view to study the pore structure of the slag admixed cement matrix as compared to the reference matrix after 10 weeks of hydration and for few cases accelerated carbonation. The samples selected were of design mix 1:1.14:2.59 with w/c ratio 0.40 (IS code mix design for target strength of 36.38 Mpa). High volume slag replacement levels of 50% and 70% were taken. These samples were water cured for 28 days followed by 6 weeks of air curing. Carbonated samples were taken after the accelerated carbonation test.

Small representative pieces of the samples were carefully selected. To make these samples conductive, they were coated with carbon film in a sputter-coater. Mounting on the stubs was done, using silver adhesive. Thereafter micrographs of various magnifications and EDAXing was of these samples was carried out.

3.9.5 X-RAY DIFFRACTION STUDIES

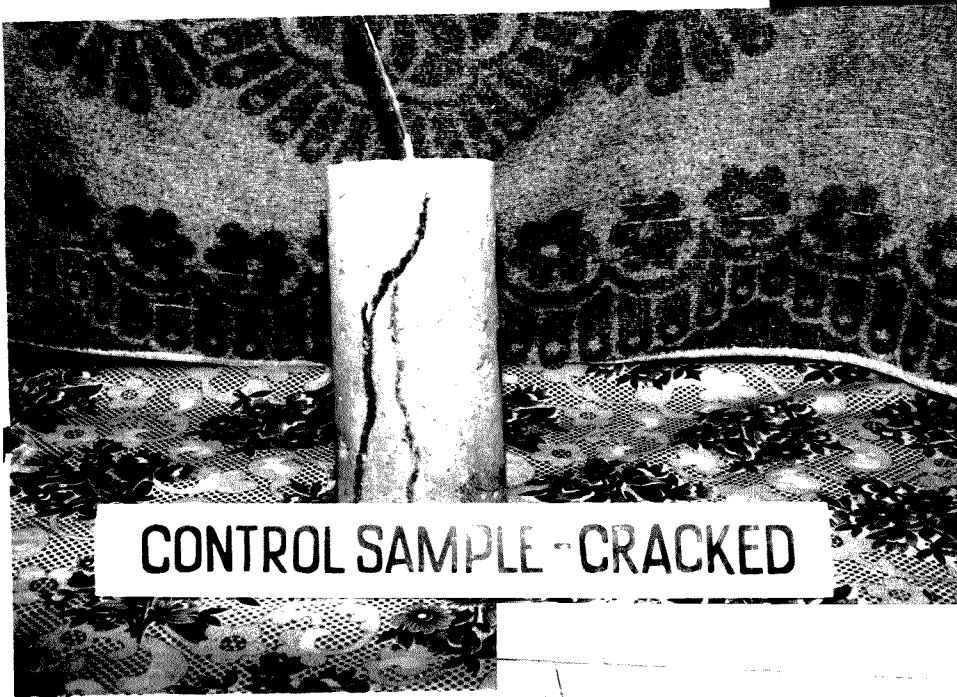
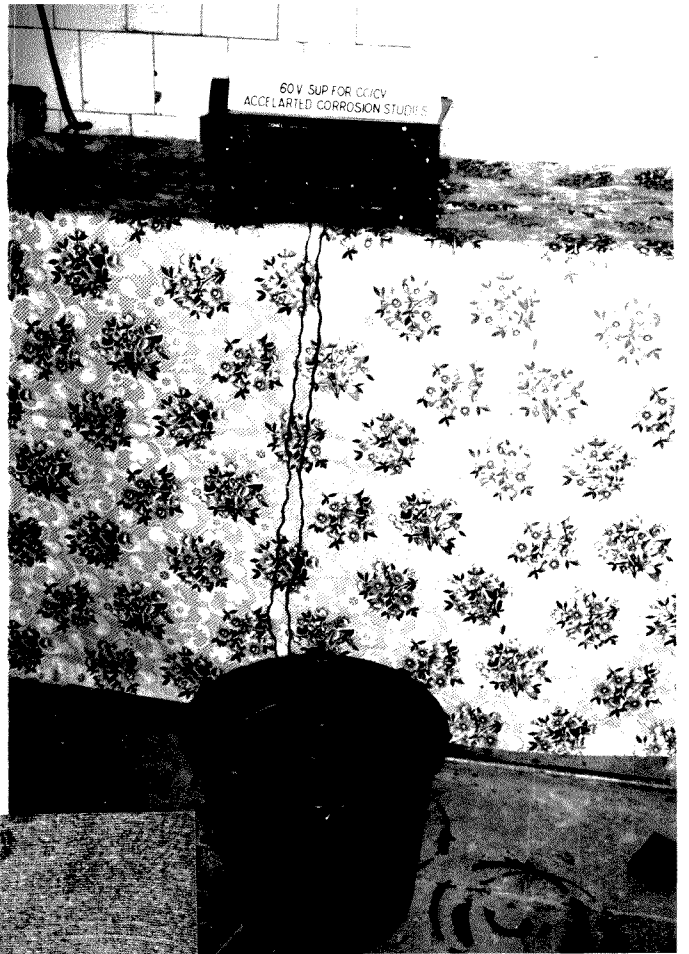
This study was carried out to study the presence and growth of various compounds in the reference and slag admixed concrete after 10 weeks of hydration and for a few cases accelerated carbonation. The samples selected were of design mix 1:1.14 with w/c ratio 0.40. High

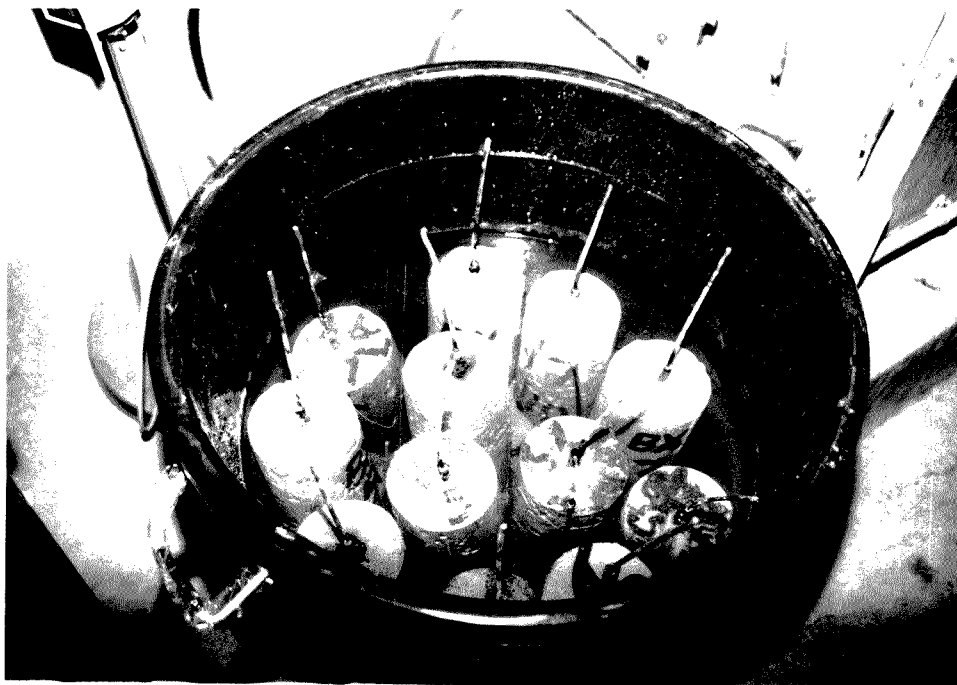
volume slag replacement levels of 50% and 70% were taken. These samples were water cured for 28 days followed by 6 weeks of air curing. Carbonated samples were taken after the accelerated carbonation test.

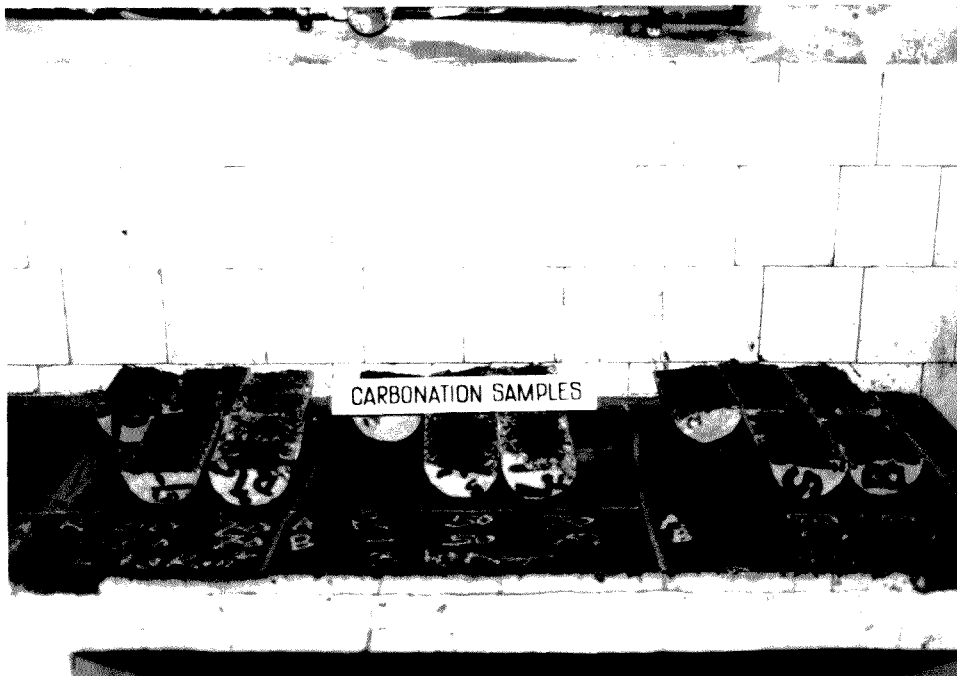
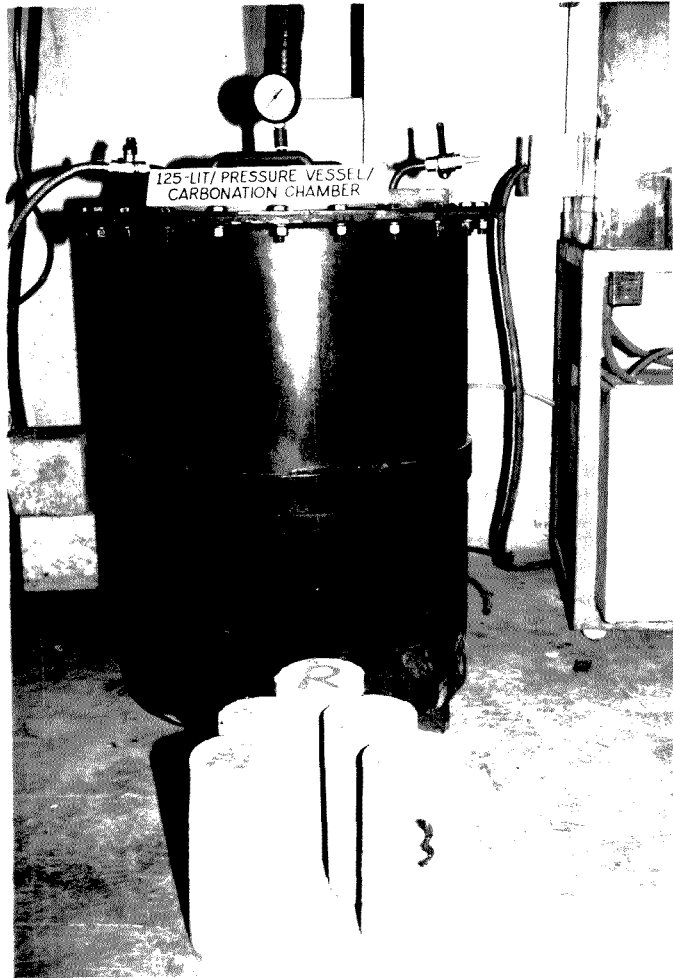
A fine powder of the samples was made and then they were mounted on the slide. The powder was exposed to copper $K\alpha$ X-rays of wavelength 1.542 \AA . The angle of exposure was kept at 4° to 30° . The voltage was kept at 30KV and current was 30 mA. Graphs were obtained for the products for intensity Vs 2θ . A comparison was also made with similar graphs of dry cement and slag samples individually and in mixed proportions of 50% and 70%. This was done to assess the hydration process.

3.9.6 ACID TEST

To check and comment on the chemical resistance of slag admixed concrete as compared to the control concrete, one set of cylindrical samples, wet cured for 28 days followed by dry cured for 28 days were put into 10 % HCl solution after being accurately weighed. These samples were taken out after 30 days and then dried at room temperature for 24 hrs. They were then weighed again to compare the percentage weight loss in the mass of the concrete.







CHAPTER 4

OBSERVATIONS AND RESULTS OBTAINED

4.1 VISUAL EXAMINATION

A set of 100 mm ϕ x200mm ht cylindrical samples with 230 mm long 8 mm ϕ reinforcement bar exposed only in the middle 100 mm by selective painting, put under accelerated curing were cut open to check the corrosion of reinforcing steel. This set had been placed in environmental chamber after 7 days of curing. The temperature of the chamber was maintained at 35 degree C. Wetting cycle of 8 hrs per day was maintained using 5% NaCl solution. To ensure the consistency of the mist in the environmental chamber, the salt solution was replaced every week with a fresh solution. This cycle was repeated for 28 days. The observations were as follows:

TABLE 4.1

<u>S.No</u>	<u>SAMPLE</u>	<u>OBSERVATION</u>
1	R	VERY MILD
2	A-5	NO CHANGE
3	A-7	NO CHANGE
4	B-5	NO CHANGE
5	B-7	NO CHANGE

4.2 HALF CELL POTENTIALS

Half cell potential measure the electrical activity of the corrosion process. Corrosion occurs at the anode areas on the steel releasing iron ions into the concrete. At the same time, cathodic areas accept ions from the concrete to react and form deposits. This energy exchange results in a flow of current from the anode to the cathode areas of the steel. This magnitude of the current is proportional to the corrosion activity.

Corrosion can be due to any of the chemical reasons, low pH, adverse permeability etc., but generally it starts as an Electro-chemical process around the reinforcement which can easily be read and predicted well in advance by CSE readings. The general guidelines for identifying the probability of corrosion based on half-cell potential values as suggested in ASTM C-876 are given below:

Probability of corrosion	E_{corr} (Vs Cu/CuSO₄)
Greater than 95%	More negative than -350 mV
Less than 5%	More positive than -200mV.
Approx 50%	Between -200 and -350 mV.

These studies were carried out on cylindrical samples prepared for potentiodynamic polarization studies. The results obtained are tabulated from table 4.2 to table 4.21.

4.3 POTENTIO-DYNAMIC POLARISATION STUDY

The final tests for this study were held up due to non-commissioning of potentiodynamic testing equipment. Notwithstanding this delay, it will be endeavored to add the results and discussion of these tests as an Annexure, in case this equipment gets operationalised well before the termination of the course of study.

4.4 ACCELERATED ELECTROLYTIC CORROSION STUDY

For this test 100-mm ϕ x200mm ht concrete cylindrical sample with 140-mm long 8-mm ϕ reinforcement bar exposed in the middle 100 mm with area of 5026.54 mm², were used.

4.4.1 CC Studies: The bars were then coded and individually weighed to the accuracy of 0.1 mg. Tests were carried out in 3% NaCl solution by providing constant DC of 80 mA .A circular 5-cm wide stainless steel rim of grade 316 was used as cathode electrode. Two sets of samples were tested, one with normal curing and other with seawater curing.

TABLE 4.2

COMPOSITION OF SEAWATER

S.No	SALT	g/lt.
1.	Sodium chloride	28.9
2.	Magnesium chloride	2.7
3.	Magnesium sulfate	2.3
4.	Calcium sulfate	1.2
5.	Potassium bicarbonate	0.2

The test samples were taken out after the duration of the test i.e. 6 hrs. The specimens were visually inspected and thereafter carefully split open to access the corroded steel bar. The bars were cleaned as per ASTM G1 of 1981 by dipping in Clark's solution for 25 minutes. Then the bars were weighed again to the accuracy of 0.1 mg to find out the net weight loss. Table 4.22 and table 4.23 gives the potential variation as monitored at every 15-min interval for the duration of the test. Based on these the tables, graphical descriptions are given in graphs 4.1 and 4.2. Also, the observed weight loss in reinforcing steel is mentioned in tables 4.24 and 4.25.

4.4.2 CV Studies: Test was carried out on a set of samples, in 3% NaCl solution by providing constant voltage of 60 V .A circular 5-cm wide stainless steel rim of grade 316 was used as cathode electrode. The varying current was recorded at the interval of every 15 minutes for 8 hrs and is shown in table 4.26. Same data has been graphically shown in graph 4.3.

4.5 ACCELERATED CARBONATION TEST

Molded Concrete specimens 100 mm ϕ x 200 mm ht after being given combined air and water curing (28 days-water, 28 days-dry) were put in a specially designed pressure chamber and then exposed to CO₂ gas with the pressure of 1,3,and 6 kg/ cm² for 6 hrs. After the test, the concrete specimens were split and surfaces of X-sections were sprayed with 1-% phenolphthalein solution. The depth of the rim of each X-section without color change was measured (carbonation depth) at six

places and averaged. The record is presented in table 4.27. The graphical representation is given in graphs 4.4 and 4.5.

4.6 SCAN ELECTRON MICROSCOPE STUDY

The SEM was used to extract additional information from the samples at the microscopic level. The only requirement being that specimen should withstand the vacuum of the chamber and the electron bombardment. The Philips model XL20 was used. It accepts specimens up to 2 Cms in diameter and can move them 20 mm in X and Y directions. As concrete specimens are non-conducting, they were given a fine carbon coating in a sputter coater to ensure formation of conducting layer.

These studies were carried out to verify changes at microscopic level. Also the adhesion of cement paste with the aggregate was studied. The micrographs obtained are shown in figures 4.1 to 4.4.

4.7 X-RAY DIFFRACTION STUDY

The tests were carried out to study the process of hydration and accelerated carbonation. The samples selected were of design mix 1:1.14 with w/c ratio 0.40. High volume slag replacement levels of 50% and 70% were taken. These samples were water cured for 28 days followed by 6 weeks of air curing. Carbonated samples were taken after the accelerated carbonation test.

A fine powder of the samples was made and then they were mounted on the slide. The powder was exposed to copper $K\alpha$ X-rays of wavelength 1.542 \AA . The angle of exposure was kept at 4° to 30° . The

voltage was kept at 30KV and current was 30 mA. Graphs were obtained for the products for intensity Vs 2θ . The compounds were then identified using the JCPDS tables of International Centre for Diffraction Data. The formula used was

$$2d \sin \theta = n\lambda$$

Where,

θ is the angle at which the peak is found

λ is the wavelength of the radiation. In this case, $\lambda = 1.542 \text{ \AA}$

d is the distance between the two planes of atoms

n is an integer i.e. 1,2,3 etc.

A comparison was also made with similar graphs of dry cement and slag samples individually and in mixed proportions of 50% and 70%.

TABLE 4.2

HALF CELL POTENTIAL OF TEST SAMPLE: RX

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 0 %

-151	-161	-168	-169
-158	-167	-168	-170
-165	-163	-168	-166
-164	-175	-173	-178

TABLE4.3

HALF CELL POTENTIAL OF TEST SAMPLE: RY

DATE OF CASTING: 02 SEP 99
DATE OF TESTING: 30 OCT 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 0 %

-152	-160	-162	-165
-157	-159	-161	-160
-154	-137	-169	-161
-162	-165	-161	-164

TABLE 4.4

**HALF CELL POTENTIAL OF TEST SAMPLE: RX KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 0 %

-251	-257	-259	-261
-250	-260	-258	-254
-255	-265	-267	-258
-276	-263	-281	-268

TABLE 4.5

**HALF CELL POTENTIAL OF TEST SAMPLE: RY KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 02 SEP 99
DATE OF TESTING: 30 OCT 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 0 %

-578	-570	-572	-576
-572	-563	-580	-579
-586	-586	-584	-575
-560	-570	-586	-578

TABLE 4.6

HALF CELL POTENTIAL OF TEST SAMPLE: AX-5

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 50 %

-103	-111	-118	-125
-123	-115	-135	-141
-109	-121	-135	-148
-135	-130	-144	-154

TABLE 4.7

HALF CELL POTENTIAL OF TEST SAMPLE: AX-7

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 70 %

-105	-108	-112	-120
-109	-111	-104	-106
-95	-105	-113	-108
-103	-110	-120	-135

TABLE 4.8

**HALF CELL POTENTIAL OF TEST SAMPLE: AX-5 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 50 %

-115	-120	-135	-151
-125	-135	-140	-158
-128	-135	-143	-153
-138	-149	-156	-170

TABLE 4.9

**HALF CELL POTENTIAL OF TEST SAMPLE: AX-7 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 08 SEP 99
DATE OF TESTING: 05 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 70 %

-105	-115	-135	-145
-103	-118	-123	-135
-107	-128	-139	-145
-94	-108	-115	-137

TABLE 4.10

HALF CELL POTENTIAL OF TEST SAMPLE: BX-5

DATE OF CASTING: 30 SEP 99
DATE OF TESTING: 27 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 50 %

-54	-62	-52	-49
-89	-67	-92	-88
-85	-106	-104	-84
-67	-96	-94	-34

TABLE 4.11

HALF CELL POTENTIAL OF TEST SAMPLE: BX-7

DATE OF CASTING: 01 OCT 99
DATE OF TESTING: 28 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 70 %

-92	-102	-108	-61
-64	-98	-77	-79
-72	-94	-96	-86
-83	-104	-108	-105

TABLE 4.12

**HALF CELL POTENTIAL OF TEST SAMPLE: BX-5 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 30 SEP 99
DATE OF TESTING: 27 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 50 %

-111	-105	-107	-101
-114	-107	-110	-103
-105	-111	-121	-113
-120	-120	-121	-93

TABLE 4.13

**HALF CELL POTENTIAL OF TEST SAMPLE: BX-7 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 01 OCT 99
DATE OF TESTING: 28 NOV 99
MIX PROPORTION: 1:1.14:2.59
SLAG REPLACEMENT: 70 %

-132	-125	-101	-131
-145	-138	-149	-153
-139	-125	-130	-137
-147	-160	-161	-151

TABLE 4.14

HALF CELL POTENTIAL OF TEST SAMPLE: AY-5

DATE OF CASTING: 10 SEP 99
DATE OF TESTING: 08 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 50 %

-67	-72	-80	-89
-87	-85	-81	-110
-71	-85	-105	-115
-80	-87	-97	-114

TABLE 4.15

HALF CELL POTENTIAL OF TEST SAMPLE: AY-7

DATE OF CASTING: 03 SEP 99
DATE OF TESTING: 01 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 70 %

-71	-84	-71	-91
-95	-98	-110	-115
-120	-114	-102	-117
-93	-101	-118	-120

TABLE 4.16

**HALF CELL POTENTIAL OF TEST SAMPLE: AY-5 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 10 SEP 99
DATE OF TESTING: 08 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 50 %

-85	-121	-114	-125
-81	-114	-117	-120
-74	-115	-127	-131
-128	-121	-115	-121

TABLE 4.15

**HALF CELL POTENTIAL OF TEST SAMPLE: AY-7 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 03 SEP 99
DATE OF TESTING: 01 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 70 %

-105	-78	-120	-135
-85	-115	-120	-130
-120	-127	-130	-85
-105	-110	-121	-128

TABLE 4.18

HALF CELL POTENTIAL OF TEST SAMPLE : BY-5

DATE OF CASTING: 16 SEP 99
DATE OF TESTING: 13 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 50 %

-147	-145	-140	-148
-147	-146	-139	-137
-135	-142	-150	-157
-161	-150	-143	-149

TABLE 4.19

HALF CELL POTENTIAL OF TEST SAMPLE: BY-7

DATE OF CASTING: 16 SEP 99
DATE OF TESTING: 13 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 70 %

-129	-135	-142	-160
-150	-142	-136	-159
-161	-130	-140	-148
-151	-130	-136	-149

TABLE 4.20

**HALF CELL POTENTIAL OF TEST SAMPLE : BY-5 KEPT IN
DOCTORED ENVIRON MENT**

DATE OF CASTING: 16 SEP 99
DATE OF TESTING: 13 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 50 %

-151	-146	-136	-149
-152	-149	-152	-134
-154	-147	-143	-138
-157	-151	-153	-131

TABLE 4.21

**HALF CELL POTENTIAL OF TEST SAMPLE: BY-7 KEPT IN
DOCTORED ENVIRONMENT**

DATE OF CASTING: 16 SEP 99
DATE OF TESTING: 13 NOV 99
MIX PROPORTION: 1:1.83:3.62
SLAG REPLACEMENT: 70 %

-149	-147	-138	-135
-141	-139	-145	-136
-142	-140	-122	-138
-110	-105	-121	-135

TABLE 4.22

POTENTIAL VARIATION FOR 'CC' STUDIES

CONSTANT CURRENT SUPPLIED: 80 mA

CURING: NORMAL

TIME	REF	A5	A7
0.15	16.2	22.3	38.4
0.30	16.5	21.9	39.7
0.45	17.0	21.6	40.3
1.00	17.6	20.9	40.6
1.15	18.1	21.2	41.7
1.30	18.8	21.6	42.3
1.45	19.5	22.3	43.0
2.00	20.1	23.0	43.8
2.15	20.7	23.9	44.1
2.30	21.3	24.7	45.6
2.45	21.8	26.1	46.7
3.00	22.4	26.6	47.2
3.15	22.8	27.6	48.4
3.30	23.6	28.6	48.8
3.45	23.8	29.3	49.6
4.00	24.1	31.2	51.3
4.15	24.4	32.6	52.2
4.30	24.7	33.4	52.7
4.45	25.1	33.5	53.1
5.00	25.4	33.6	53.8
5.15	25.8	34.1	54.5
5.30	26.2	34.3	55.1
5.45	26.5	34.7	55.8
6.00	27.0	35.2	66.1

TABLE 4.23

POTENTIAL VARIATION FOR 'CC' STUDIES

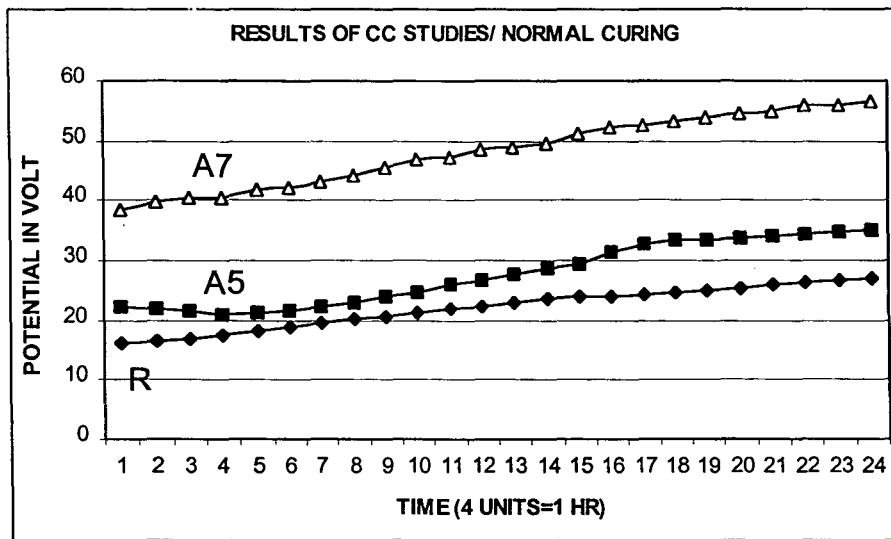
CONSTANT CURRENT SUPPLIED: 80 mA

CURING: SEAWATER

TIME	REF	A5	A7
0.15	22.2	24.2	43.0
0.30	22.7	23.6	43.5
0.45	23.5	23.9	44.1
1.00	24.5	24.9	44.9
1.15	24.9	25.6	46.0
1.30	25.3	26.1	47.1
1.45	25.8	27.2	47.9
2.00	26.4	27.3	48.7
2.15	26.9	27.4	50.1
2.30	27.3	29.9	50.6
2.45	27.5	30.7	51.4
3.00	28.1	31.3	51.8
3.15	28.6	31.7	52.4
3.30	28.8	32.2	52.7
3.45	29.3	32.5	53.8
4.00	29.7	32.8	54.2
4.15	30.1	33.1	55.5
4.30	30.6	33.3	56.4
4.45	31.1	33.7	57.2
5.00	31.3	34.1	57.4
5.15	31.5	34.5	58.2
5.30	31.7	34.9	58.9
5.45	32.2	39.1	59.1
6.00	33.2	39.5	59.8

GRAPH 4.1

POTENTIAL VARIATION FOR CONSTANT CURRENT OF 80 mA



GRAPH 4.2

POTENTIAL VARIATION FOR CONSTANT CURRENT OF 80 mA

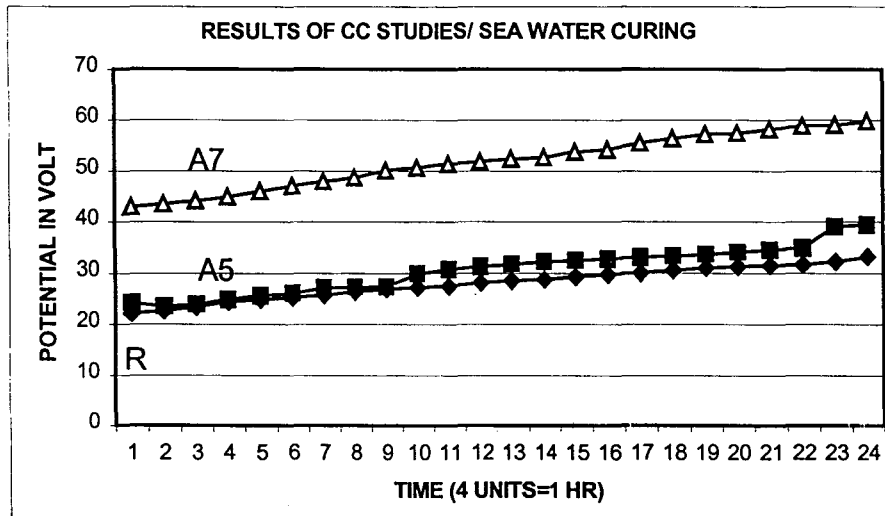


TABLE 4.24

**WEIGHT LOSS IN STEEL REINFORCEMENT OBSERVED
DURING 'CC' STUDIES**

CONSTANT CURRENT SUPPLIED: 80 mA
CURING: NORMAL

Samples	Weight before the test	Weight after the test	Loss of weight
REF	84.3405 g	84.0932 g	0.2473 g
A5	84.0642 g	83.8740 g	0.1902 g
A7	86.0449 g	85.9001 g	0.1448 g

TABLE 4.25

**WEIGHT LOSS IN STEEL REINFORCEMENT OBSERVED
DURING 'CC' STUDIES**

CONSTANT CURRENT SUPPLIED: 80 mA
CURING: SEAWATER

Samples	Weight before the test	Weight after the test	Loss of weight
REF	87.0213 g	86.7089 g	0.3124 g
A5	86.4299 g	86.2050 g	0.2249 g
A7	87.2278 g	87.0245 g	0.1448 g

TABLE 4.26
CURRENT VARIATION FOR 'CV' STUDIES
 CONSTANT POTENTIAL: 60 V

TIME	REF	A5	A7
0.15	334	226	145
0.30	333	229	148
0.45	331	232	151
1.00	330	239	155
1.15	328	241	158
1.30	322	234	163
1.45	319	227	168
2.00	314	224	170
2.15	310	218	175
2.30	305	214	180
2.45	301	210	184
3.00	296	207	188
3.15	290	204	191
3.30	284	201	195
3.45	276	198	198
4.00	272	194	203
4.15	268	190	196
4.30	265	186	190
4.45	261	181	187
5.00	258	177	181
5.15	256	173	178
5.30	250	168	174
5.45	248	164	165
6.00	245	160	150
6.15	251	155	155
6.30	256	150	160
6.45	262	146	165
7.00	268	151	170
7.15	272	156	175
7.30	278	160	179
7.45	284	162	183

GRAPH 4.3

CURRENT VARIATION FOR CONSTANT POTENTIAL OF 60 V

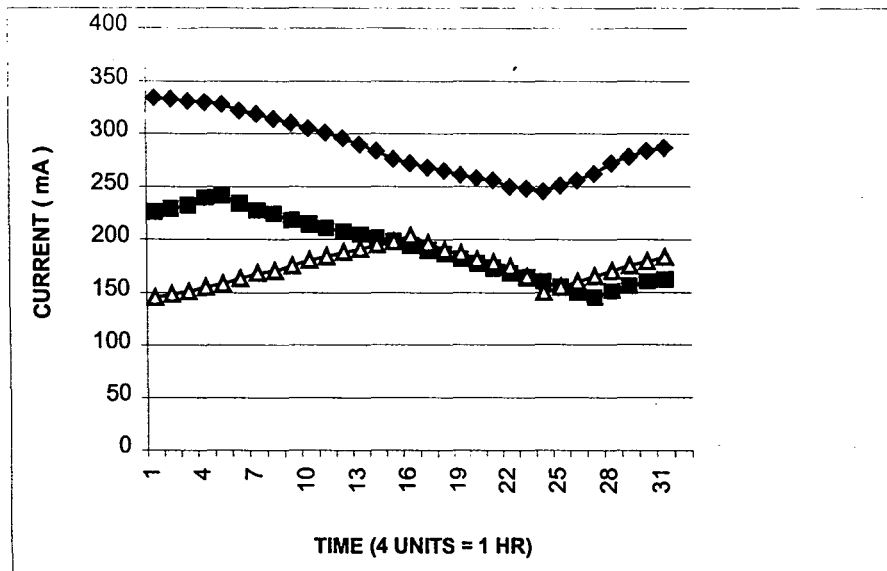


TABLE 4.27

ACCELERATED CARBONATION TEST

SUMMARY OF RESULTS

MIX PROPORTION: 1: 1.14: 2.59

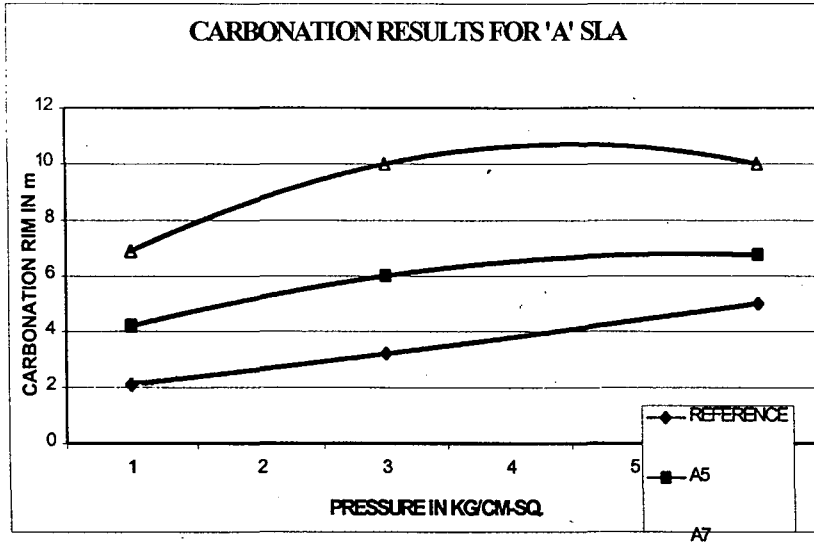
WATER CEMENT RATIO: 0.4

CURING: 28 DAYS WET CURING FOLLOWED BY 28 DAYS AIR CURING

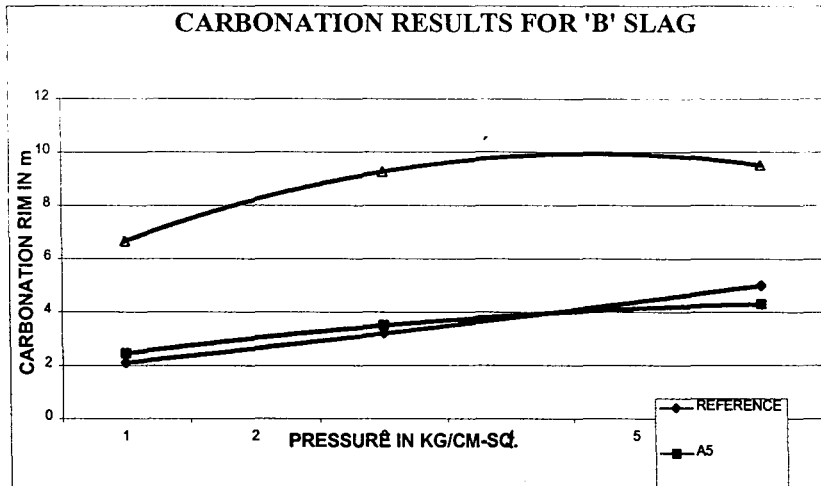
AVERAGE CARBONATION DEPTH IN MM

PRESSURE (KG/CM²)	REF 0 %	SLAG 50 %		SLAG 70 %	
		A	B	A	B
1	2.1	4.2	2.45	6.9	6.65
3	3.2	6	3.5	10	9.25
6	5	6.75	4.3	10	9.5

GRAPH 4.4



GRAPH 4.5



MICROGRAPHS

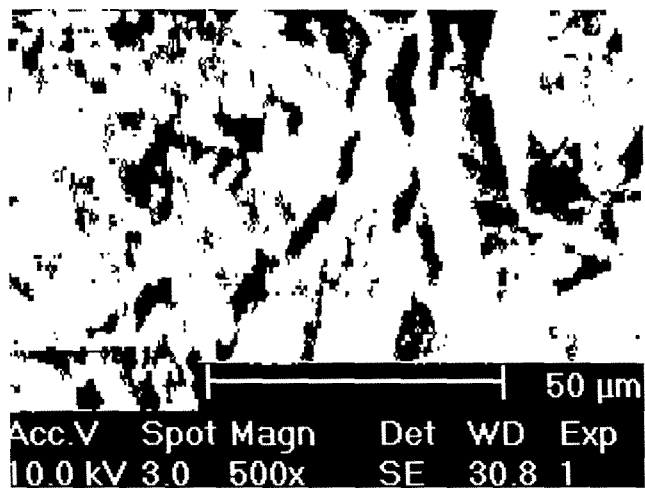


FIG 4.1

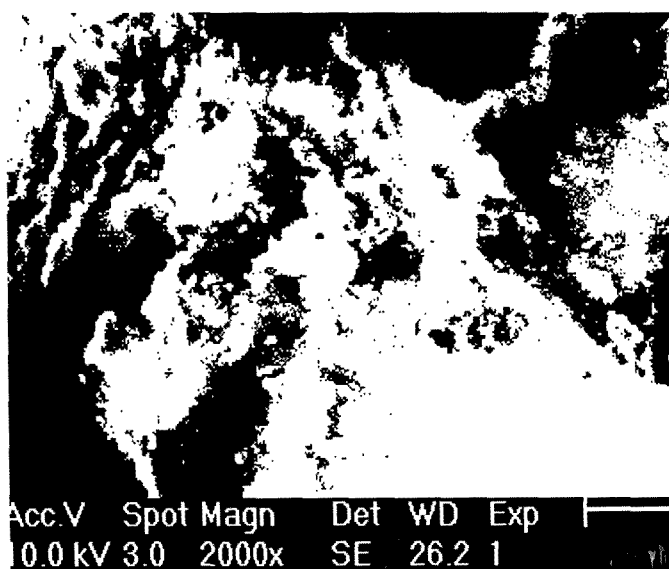


FIG 4.2

MICROGRAPHS

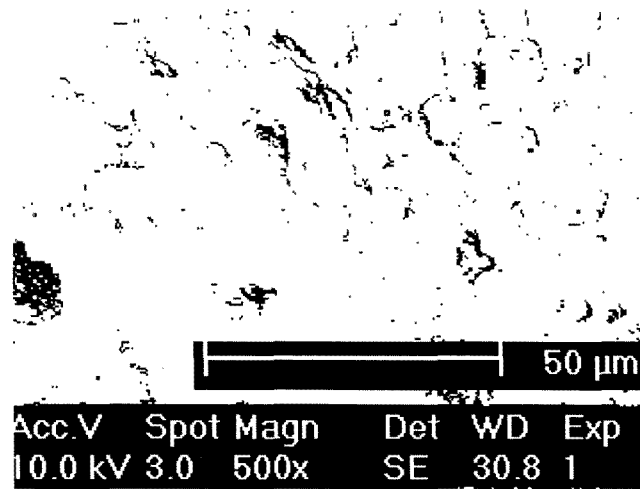


FIG 4.3

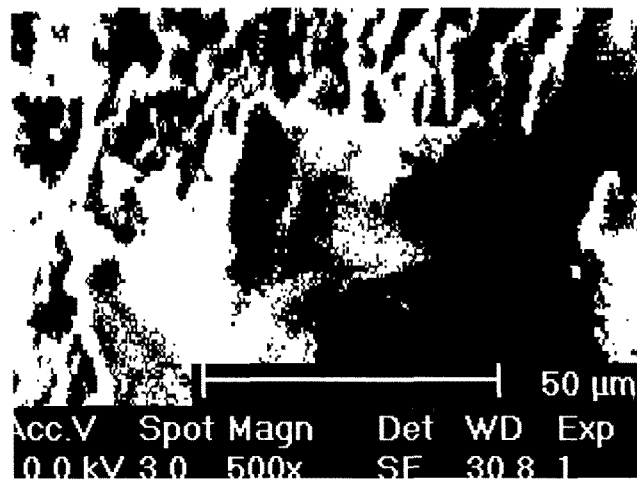
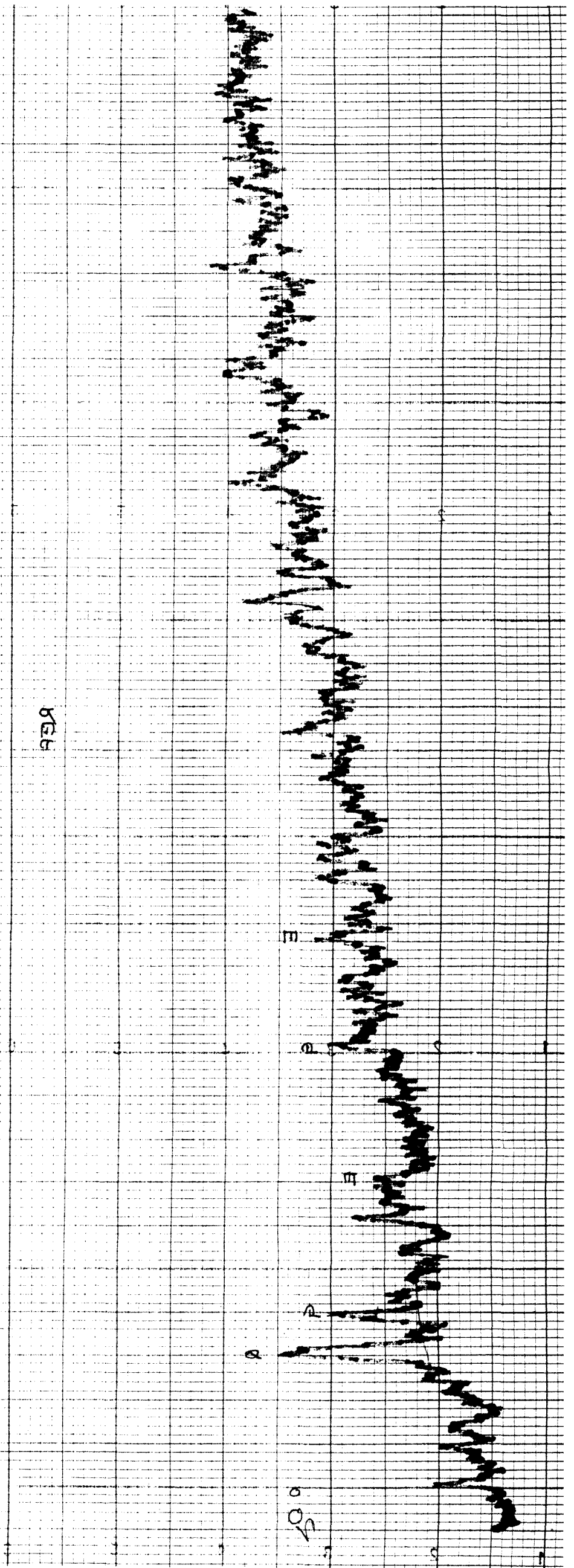
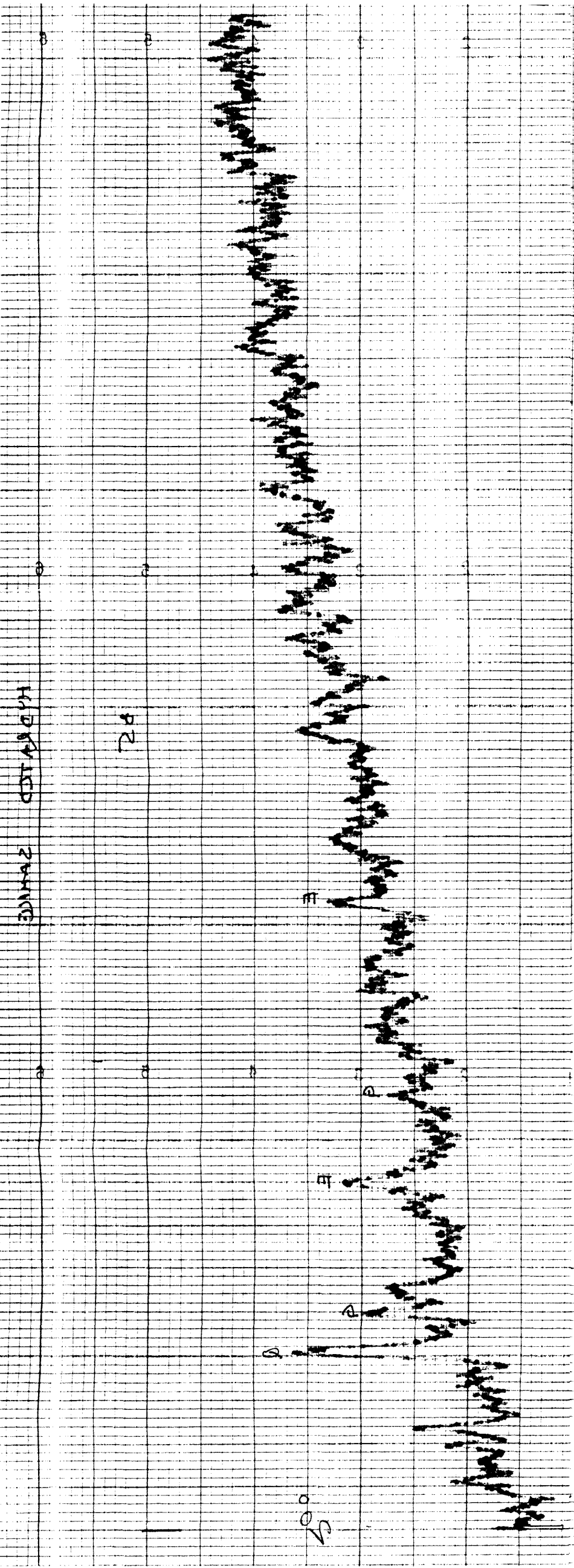
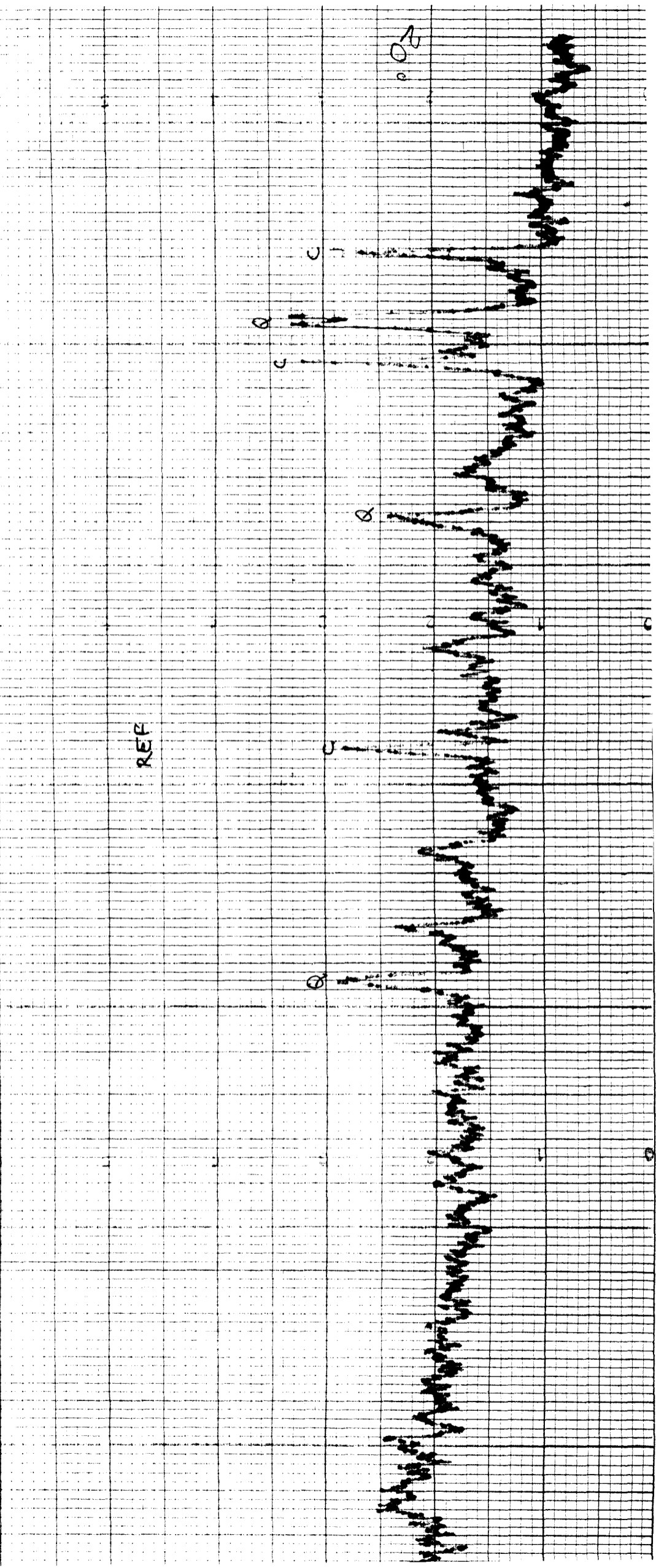
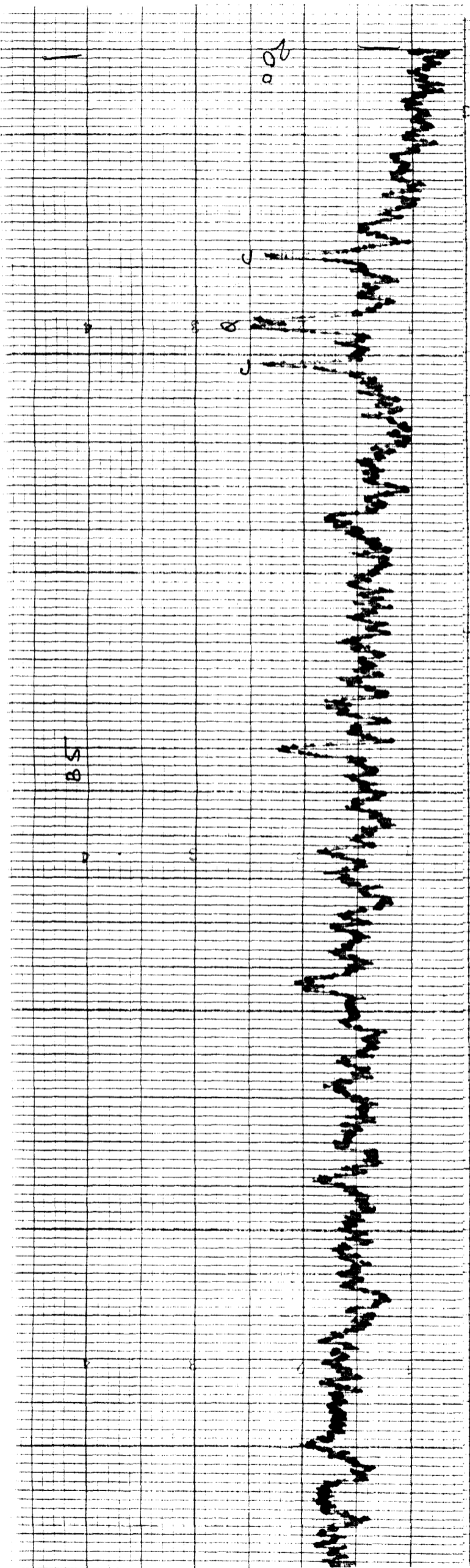
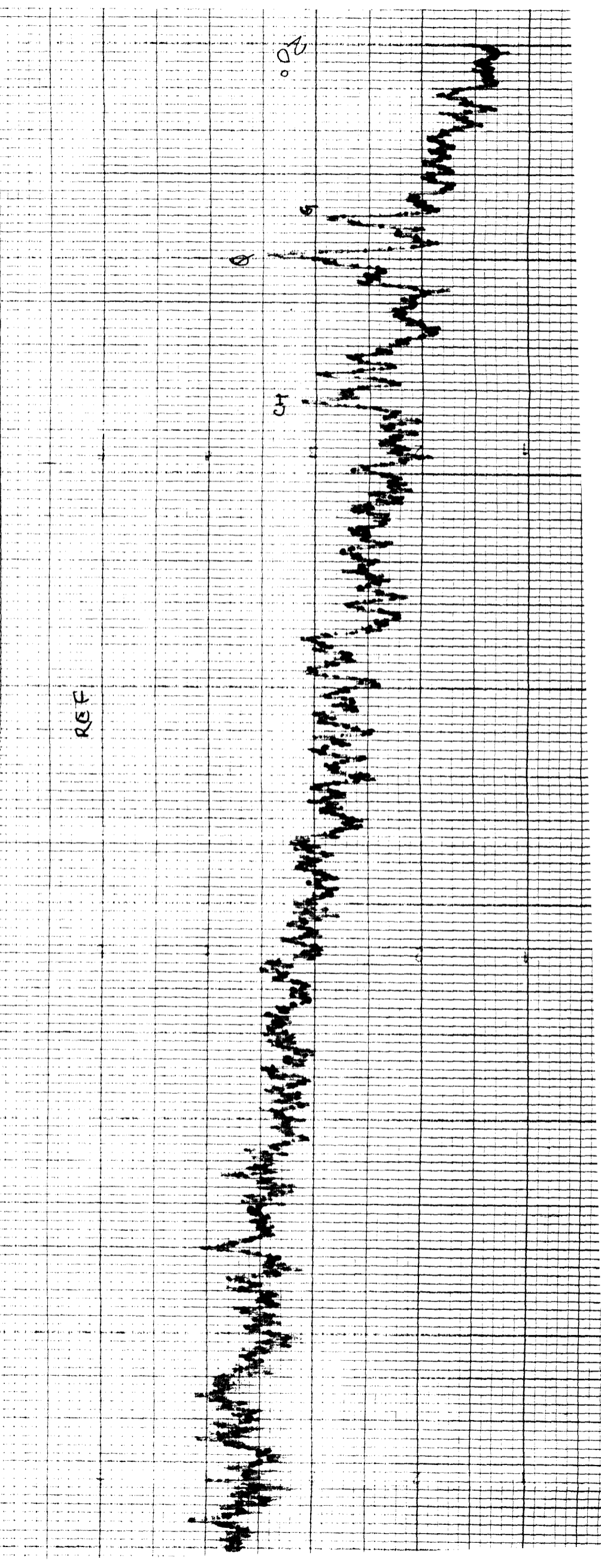
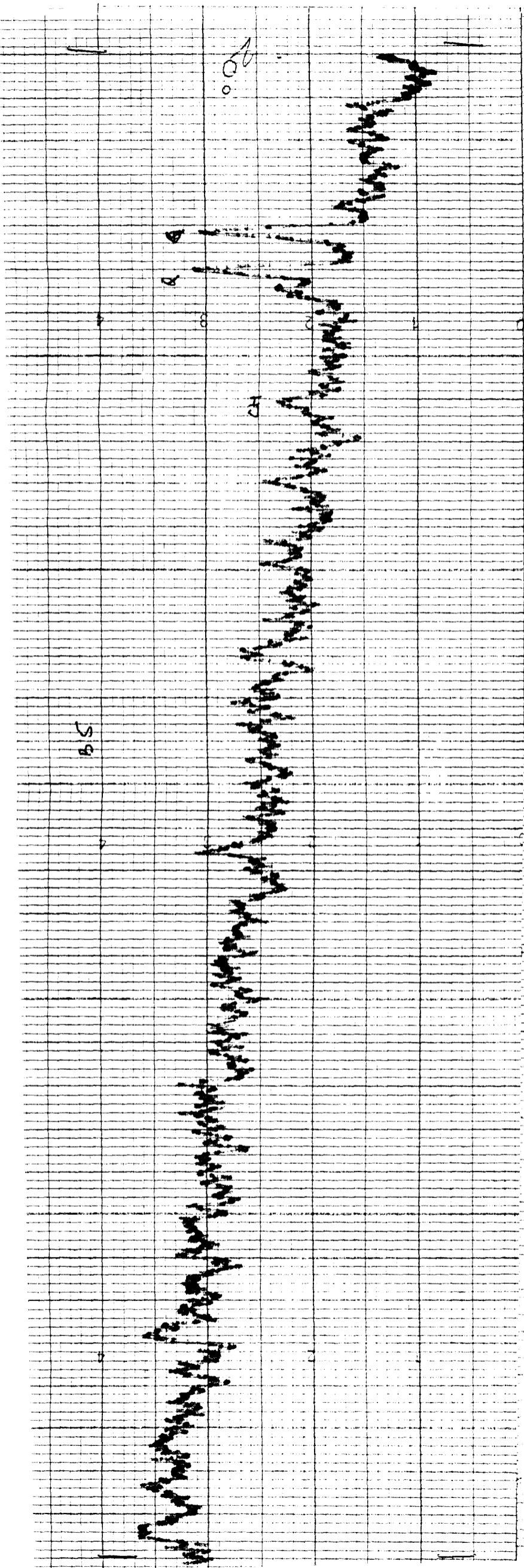


FIG 4.4







CHAPTER 5

DISCUSSION

5.1 VISUAL ASSESSMENT

The steel bars of the cylindrical samples were examined for corrosion. These samples had been exposed to the doctored environment for 28 days only due to limited time available for studies. The stain marks on the reference samples made with OPC were quite distinct, where as all other samples with slag dosages of 50% and 70% did not show any changes. This was in agreement with the other tests conducted. These results clearly indicate that corrosion of steel in mature concrete decreases as the content of slag increases.

5.2 HALF CELL POTENTIALS

Based on the general guidelines for identifying the probability of corrosion as suggested in ASTM C-876, the examination of the results from table 4.2 to table 4.21, for 8 weeks old samples resulted in following:

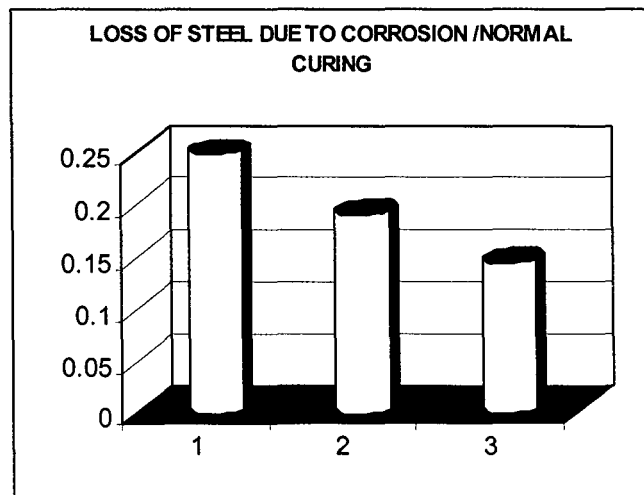
Type of sample	Normal curing	Environmental chamber
Reference	Low	Med
A5	Low	Low
A7	Low	Low
B5	Low	Low
B7	Low	Low

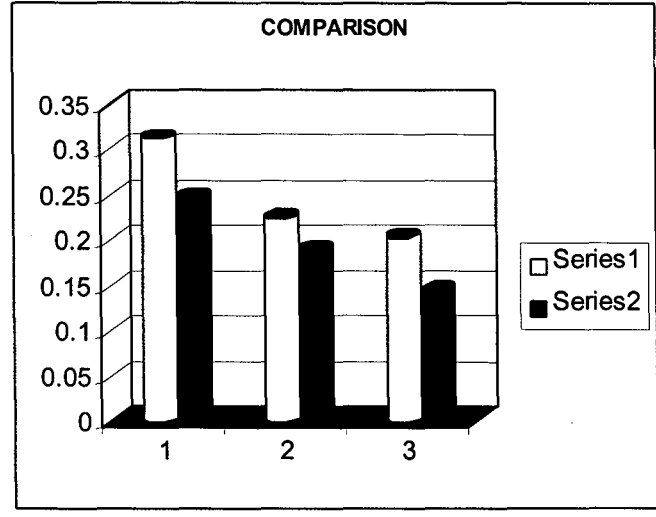
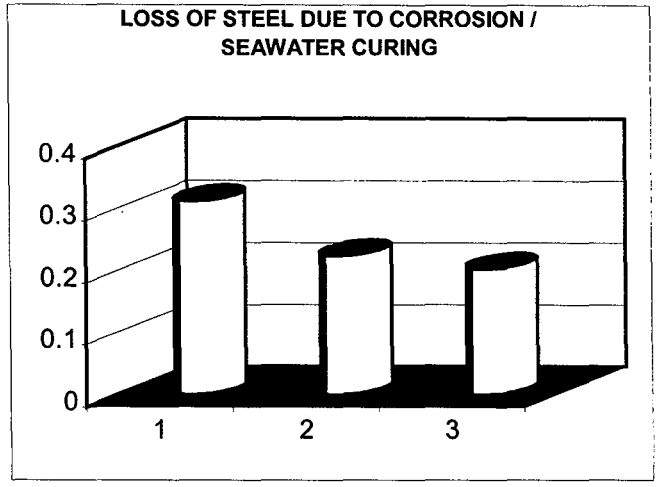
5.3 ACCELERATED ELECTROLYTIC CORROSION STUDY

5.3.1 CC Studies:

1. The area under the respective curves as given in graphs 4.1 and 4.2. indicate the amount of energy spent for the corresponding amount of corrosion. The 70% slag admixed samples consumed more energy as compared to 50 % slag admixed samples and reference samples required the least amount of energy to initiate corrosion. Similar trends were also observed for seawater curing, implying greater resistance to corrosion of slag admixtures concrete.

2. The loss of steel due to corrosion is as shown in following diagrams. Reference is depicted by serial no 1 followed by A5 and A7.





3. The corrosion rate as per para 8 of ASTM G1-81, equals $78W$ (in mm / year) considering the density of steel as 7.45 g / cm^3 and a 6 hrs accelerated model equal to one year in normal course. Here 'W' is the wt loss in grams nearest to 1 mg. Taking above inputs; it can be further deduced that the corrosion rates for the given tests were as follows.

Corrosion rates in mm / year

Type of sample	Normal curing	Seawater curing
Reference	19.20	24.37
A5	14.83	17.54
A7	11.29	15.85

5.3.2 CV Studies: Considering the test results as shown in table 4.26 followed by its graphical representation, it can be seen that:

1. The resistance offered by the reference concrete is the least, whereas the 70 % slag admixed concrete sample offered the maximum resistance.
2. A threshold limit was observed in slag admixed samples when the process of polarization could have started. For 50% slag admixed concrete it was observed to be 1 hr 15 min and for 70% slag admixed concrete samples, it was seen to be 4 hrs.
3. On similar lines, the threshold limit for the process of depolarization for 50% slag admixed concrete was observed to be 6 hr 45 min and for 70% slag admixed concrete samples, it was seen to be at 6 hrs only.

5.4 ACCELERATED CARBONATION TEST

Subject to further studies and ramification, the conclusion that can be drawn from the records presented in table 4.27 and its graphical representation in graphs 4.4 and 4.5, are as follows:

1. In a cement and slag comparison, cement hydrates immediately filling its pores where as slag hydrates slowly and hence the pores remain unfilled for a long time, leading to a greater penetration of CO₂.
2. However, B slag samples with glass content of 95% showed less carbonation than A slag samples with glass content of 85%. Apparently higher the glass content, higher the resistance of the concrete against carbonation.
3. The results obtained for the pressure of 6 kg / cm² showed lowering trends as compared to trends seen for reference concrete. Roughly this phenomenon was started at 41/2 kg / cm². From this it can be concluded that although for a recently cast slag admixed concrete under accelerated conditions the carbonation may be more, in the long run the carbonation in slag admixed concrete is likely to reduce.

5.5 SCAN ELECTRON MICROSCOPE STUDY

Fig 4.4 shows the gel formation (hydration mechanism) in 70 % slag admixed concrete. Though a reaction rim can be seen around the slag particle, the slag reaction remains incomplete even at twenty-eight days. In fig 4.1 dense pore structure of 50% slag admixed can be seen. For 70 % slag dosage, the pore structure further gets refined as seen in fig 4.2. The heavily carbonated pore structure for 70 % slag admixed concrete can be seen in fig 4.3.

5.6 X-RAY DIFFRACTION STUDY

A fine powder of the samples was made and then they were mounted on the slide. The powder was exposed to copper K α X-rays of wavelength 1.542 Å. The angle of exposure was kept at 4° to 30°. The voltage was kept at 30KV and current was 30 mA. Graphs were obtained for the products for intensity Vs 2 θ . The compounds were then identified using the JCPDS tables of International Centre for Diffraction Data. The formula used was

$$2d \sin \theta = n\lambda$$

Where,

θ is the angle at which the peak is found

λ is the wavelength of the radiation. In this case, $\lambda = 1.542 \text{ Å}$

d is the distance between the two planes of atoms

n is an integer i.e. 1,2,3 etc.

A comparison was also made with similar graphs of dry cement and slag samples individually and in mixed proportions of 50% and 70%.

CHAPTER 6

CONCLUSION

From the experimental investigations carried out, following conclusions are drawn:

1. The corrosion of steel in mature concrete decreases as the content of slag increases. The maximum resistance to corrosion is observed in 70% slag admixed concrete. Thus slag has a great role to play in environmental friendly high performance concrete.
2. As compared to reference concrete, 50 % slag (Andhra) admixed concrete showed improved corrosion resistance of 22.76 % under normal circumstances and up to 28 % improved resistance, when cured with seawater. Similarly comparing to reference concrete, 70 % slag dosage showed improved corrosion resistance of 28.8 % in normal circumstances and up to 34 % improved resistance, when cured with seawater.
3. In comparing cement and slag hydration, cement hydrates immediately filling its pores where as slag hydrates slowly and hence the pores remain unfilled for a long time, leading to a greater penetration of CO_2 . This process continues till the pore structure in slag admixed concrete gets refined. As the exact process of transportation of CO_2 ion in slag admixed concrete is not clearly understood, it is proposed that this topic be further taken up for research. However seeing the trends of the

results, it can be established that, in the long run the carbonation in slag admixed concrete is likely to reduce.

4. Higher the glass content in the slag, higher the resistance of the concrete against carbonation. Slag 'B' (Bhilai) at 50% dosage showed resistance to accelerated carbonation almost equal or better to reference concrete, hence proving that it is better than slag 'A'. Further studies are being recommended to establish this pattern.

5. It was clearly evident, from the microscopic study that when properly cured, the bond between aggregate and cement is stronger in slag cement. In normal strength concrete the transition zone comprising of calcium hydroxide formed due to a higher local concentration of water, plays a major role in paste-aggregate bonding. The formation of calcium hydroxide in the transition zone remains a source of weakness in concrete, as the cracks are liable to be generated along this cleavage without any significant resistance. However, In slag admixed concrete, the consumption of calcium hydroxide by the pozzolonic reaction of slag precludes its formation at the paste aggregate interface.

CHAPTER 7

SCOPE FOR FURTHER STUDY

The present work was initiated as a part of a collaborative project with IIT Chennai, the research project, "**Utilization of Industrial slags for High Performance Concrete Composites**" sanctioned under the aegis of Ministry of Water Resources. The scope was intended to be exhaustive; so as to form a basis for continued research as per the overall requirements of the mother project.

The following studies appear to be worthy of attention for furthering this study.

1. Development of codified mix design methodology for slag admixed high performance concrete.
2. Characterization and the action mechanisms of the additives in the improvement of the early strength of the slag admixed concrete.
3. Investigation in the carbonation mechanics of the slag admixed concrete.
4. Studies are being recommended to establish the correlation between carbonation resistance and glass content.
5. Modeling of corrosion pattern in slag admixed concrete having known its chemical and mineralogical composition, fineness and glass content.
6. Role of calcium hydroxide at various stages of hydration in the life cycle of slag admixed concrete

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