"Effect of Aggressive Environment on Durability of Metakaolin Based Cement Mortar"

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in

Civil Engineering

(Structures)

Submitted by

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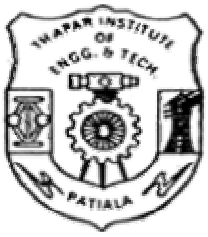

DEPARTMENT OF CIVIL ENGINEERING

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CERTIFICATE

This is to certify that the work presented in Thesis entitled **"Effect of Aggressive Environment on Durability of Metakaolin Based Cement Mortar"** submitted by **Amita Goel,** Roll No. **8042302** in partial fulfillment of the requirements for the award of degree of **Master of Engineering in Civil (Structures)** at **Thapar Institute of Engineering & Technology (Deemed University), Patiala,** is an authentic record of student's own work carried out under our supervision and guidance. The matter embodied in this thesis has not been submitted anywhere for award of any other degree.

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ABSTRACT

In all sectors of society there are growing demands for improvement in the quality of manufactured products and this demand is more so in construction industry. Concrete is the major product used in the construction industry. It has to constantly face challenges of aggressive environment either from within or from external sources during its service life.

Concrete immersed in a wet or moist aggressive medium tend to suffer damages; and exhibits so in the form of microcracks and spalling on its surface. This aggressive environment may be the acid content in surrounding environment that leads to reduction of pH of concrete i.e. during carbonation, or the acid attack due to the various gases present in the atmosphere which deteriorate the concrete. Even the marine structures are affected by the continuous salt crystallization and scaling damage.

In the present scenario, concrete is not only the mixture of cement, aggregates and water but now some smart materials i.e mineral admixtures like silica fume, fly ash, metakaolin, rice husk etc are also being used within the concrete to increase its durability and strength. These mineral admixtures due to their fineness not only increase the cohesiveness of mix but also improve the impermeability of concrete to various salt solutions.

Concrete subjected to repeated cycles of freezing and thawing may deteriorate rapidly, or it may remain in service far many years without showing signs of distress. Failure of the material be in the form of loss of strength, crumbling or a combination of the two. It is likely that due to varied behavior of climatic conditions in cold weather regions, the fresh concrete or hardened concrete gets subjected to freezing and thawing cycles. The durability of concrete gets greatly impaired due to this alternate freezing and thawing. It exerts fatigue in concrete.

Similarly, alternating cycles of wetting and drying during the curing process is also extremely harmful to the concrete surface and may result in surface crazing and cracking. Keeping in view the large coastal line of our country, the concrete used in coastal structures are also susceptible to distress due to several factors some of which are common and they affect the durability of concrete in general.

In the present study, the mortar specimens containing 0%, 5% and 10% metakaolin are cast at two water-cement ratios of 0.46 and 0.5. Then the detailed effect of various deicing solutions (3%) and corrosion inhibitors (1%) on the mortar samples subjected to freezing thawing cycles and wetting drying cycles have been studied.

Four salt solutions including sodium chloride with and without corrosion inhibitor and calcium chloride with and without corrosion inhibitor have been used. Triethanolamine is used as a corrosion inhibitor in the present research work. The samples are tested for compressive strength, scaling, and mass change after 14, 28 and 42 cycles of freezing and thawing and alternate wetting and drying cycles. Non destructive tests like ultrasonic pulse velocity test have also been conducted to check the quality of mortar samples.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL

Concrete is an important versatile construction material, used in wide variety of situations. When we talk of a building material, it is very important to consider its durability as it has indirect effect on economy, serviceability and maintenance. The concept of durability of concrete is contradictory to the misleading notion developed in the past that concrete is permanent and doesn't require any maintenance. Probability always exists that the best workmanship may not be achieved and hence concrete needs maintenance. The unfortunate trend in concrete construction is that people are bit over confident about the strength and durability of concrete. Concrete, however good it may be, deteriorates with the age. It is never possible to prevent deterioration completely. But if we understand the mechanics of deterioration we can retard the rate of and thus achieve the desired life of concrete.

Durability of concrete build by an average builder is of great concern today. Changes in manufacturing pattern of cement has brought emphasis on higher strength, low energy requirements, cost competition etc. With very rapid increase in the quantum of construction, the industry couldn't keep pace with the performance standards of structures. Large scale increase in the construction activity without commensurate increase in the manpower development, training and pressure to complete the job in time, has severely strained the achievable performance of concrete. So there is a need to understand the dependability and reliability of concrete construction.

There is a high potential for longevity of concrete as a material in different types of structures. Surprisingly overall performance of concrete in the past had been good, though little conscious effort was made with durability primarily in mind. However, experience indicates that this has to change and one must consciously design, detail, build and evaluate for durability with the design life in mind.

1.2 DURABILITY AND SERVICE LIFE

At present there is no definition of design life with consensus and wide acceptability. To facilitate communication and to develop proper understanding we have to define few terms and narrow down, the wider meaning in common use.

Life of concrete is a statistically variable quantity. It can not be assigned a particular value. Functional failures are likely to occur at different periods of time, with different probability of occurrence. Life of concrete is a period from the commissioning till the

structure serves its designed functional requirements satisfactorily with assigned system of maintenance, or till the earliest functional failure, if beyond the reasonable level of maintenance as was determined at the time of design.

Design life is the expected life to be achieved with the specified limit on probability of failure. Design life does not mean that the structure will remain serviceable till that time without any maintenance, nor does it mean that the structure will become redundant after that period.

Indian Concrete Institute, in general has suggested the limiting probabilities for different functions.

Collapse	- 1 in million
Achieving permeability	- 1 in 10,000
Internal factors affecting durability	- 1 in 10,000
External factors, aggressive (i.e. chloride, sulfates)	- 1 in 1000
Reinforcement corrosion	- 1 in 1000
Abrasion etc	- 1 in 100
Crack control	- 1 in 20

These limiting probabilities will change with the importance of the functions and the structure as a whole in particular case.

Durability is not to be considered in isolation nor can it be treated purely in material terms. It stems from every aspect of design, detailing and construction, and design life in practice will depend on the quality achieved in each of these aspects. An adequately durable structure is one which fulfills its serviceability, strength and stability functions without significant loss of utility or excessive unforeseen maintenance with in the designed life of the structure.

Zongjin Li et. al. (2005) shows in Fig 1.1 that durability of concrete can be defined as the period from the time of estimation to the time when the next major maintenance is needed. Defined so, concrete durability can be regarded as a key factor in maintenance and repair scheme planning for existing concrete structures.

1.3 FACTORS INFLUENCING DURABILITY OF CONCRETE

It will not be wrong to attribute the lack of durability to the reason of volume change. Volume change in concrete is caused by many factors. The aspect of the progressive hydration of cement is connected with the volume change of gel and consequently, the interior space (reduction in the volume of capillary cavities). The permeability aspects, leaching of calcium hydroxide in hydraulic structures, or the action of pozzolanic material, all deal with volume changes of solid products, which incidentally affect

durability. The unsoundness of constituent materials such as cement, reactive aggregates or aggregate containing unsound mineral fractions causes volume change and hence affects durability. The moisture movement in concrete, freezing and thawing, the thermal aspect of concrete and concrete aggregates all lead to a change in volume of concrete. Therefore, the study of durability is nothing but the study of volume change of concrete.

To study the mechanism of deterioration of concrete, durability influencing factors are classified as Internal and External.

1.3.1 Internal Factors

These include type of cement and aggregate, level of chemicals in the ingredients, alkali aggregate reaction, water cement ratio, cement content, volume changes, permeability of concrete, diffusion rates of ions, metals embedded in concrete, formwork etc.

The mechanics of deterioration is more affected by the characteristics of the microstructures and the chemical properties of constituent materials rather than their strength. The various internal factors are discussed below:

Permeability

Permeability is an indicator of the quality of concrete. Concrete with high permeability exposes its interior structure to the environmental parameters more readily which could lead to any combination of the following and this in turn affects the durability of concrete.

1. Leaching out of $Ca(OH)_2$ and thereby adding to the porosity.
2. Attack by aggressive chemicals, vapours and environmental constituents.
3. Aid corrosion of reinforcing and prestressing steel and other embedments.
4. Vulnerability to frost action.

Absorption

Another outcome of the construction practice is the absorption property of concrete. Absorption is the amount of water absorbed by standard specimen under standard test conditions. Absorption contributes to the formation and growth of sulphate and chloride deposits within the body of concrete which on cyclic wetting and drying cause adverse effects on the durability of concrete by expansion of the deposits.

Alkali Aggregate Reaction

The alkali silicate gel formed due to alkali aggregate reaction attracts water by absorption or by osmosis and thus tends to increase the volume. Therefore, due to internal pressure developed, it leads to expansion, cracking and disruption of cement paste and map cracking of concrete.

Water-Cement Ratio

The Water-cement ratio influences the permeability of concrete decisively. Particularly in cases where the w/c ratio exceeds 0.6, the permeability will increase considerably with w/c ratio, due to the increase in the capillary porosity. Increase in w/c ratio increases the rate of corrosion of reinforcing steel.

Cement Content

According to the investigations by *Thomas (1992)*, with increasing cement content, the binding capacity of concrete both for CO_2 and Cl^- will be increased. However over the normal range of cement contents, the penetration rates of carbonation and chlorides are influenced to a considerably lower extent by the cement content than by the w/c ratio, the quality of compaction and curing. Normally cement content in the range of 300 kg/m^3 is sufficient to achieve a sufficiently low permeability and sufficient durability if the w/c ratio is kept below 0.5 to 0.6, depending on the environmental conditions and provisions of adequate curing.

Curing Time

If the concrete is insufficiently cured (i.e. the concrete surface dries early) the permeability of the surface layer of concrete may be increase by five to ten folds and hence the rate of corrosion is also increased. Curing measures taken after the first drying out of concrete are useless, because the hardening will hardly continue after having been interrupted once. Therefore, curing measures must begin immediately after concreting and are not to be interrupted.

Hydrolysis and Leaching

Leaching process is the dissolution of ingredient of hardened cement by aqueous solution. Since calcium hydroxide is easily available soluble ingredient of hardened cement, the destruction is sometimes referred as lime leaching. It mainly depends on permeability of concrete. When the free lime is leached out, hydrolysis of calcium silicates and aluminates take place which releases more lime for the further leaching process. From the various silicate hydrates, dicalcium hydrosilicate ($2CaO.SiO_2$ aq), which is most unstable in the absence of saturated solution of calcium hydroxide, dissociates at a faster rate to liberate more lime. And from the aluminate hydrates, tetra-calcium aluminate hydrate ($4\ CaO.Al_2O_3.3H_2O$) is least stable in the absence of calcium hydroxide. Thus, when the concentration of lime inside the concrete is reduced on account of leaching action, more of it will dissociate to produce additional amount of lime.

According to *Biczok (1972)* leaching of a portion of hardened cement components, particularly of $Ca(OH)_2$,reduce the pH values; consequently, hydrolysis is resumed and produces eventually silica gel ($SiO_2.H_2O$), aluminium hydroxide gel ($Al_2O_3.nH_2O$) and ferroxide gel ($Fe_2O_3.nH_2O$). Due to the formation of these gels in the binding agent loss in strength is observed. The expansion caused by the aggressive action gives rise to disintegrating stresses in the concrete.

1.3.2 External Factors

These include climate, temperature, sulfate and chloride actions, freezing-thawing, chemically aggressive environment, electrolytic action, abrasion, erosion, cavitation, biological corrosion etc. a brief description of the above factors is provided below:

Climate

Climatic factors cover radiation, temperature and humidity etc. High temperature of fresh concrete and also during hardening, both increases the permeability of concrete. So the elevated curing temperature reduces long term strength. The effect of w/c ratio is such that at a given curing temperature, a lower w/c ratio results in reduced rate of Chloride ion diffusion. To an extent, lowering the w/c ratio can compensate the effect of elevated curing temperature.

Water

All deterioration processes require water; the important factor is the moisture state in the concrete rather than that of the surrounding atmosphere. Under steady conditions moisture state will be constant but under varying conditions concrete takes water more rapidly from environment than losing it. Pure water can wash out (leaching) concrete by dissolving some cement components and increase concrete porosity. Water of pH greater than or equal to 9 should not be used. The salt concentration increase as the water evaporates. The moisture penetration is the means whereby an exterior substance such as chloride salts, carbon dioxide and dissolved oxygen may gain access to reinforcement. Table 1.1 indicates the influence of effective humidity on corrosion of steel as per research of *Thomas (1992)*.

Sulfur Attack

When hardened concrete is exposed to soil or ground water containing sulfate compounds like magnesium and calcium sulfates, the sulfates in the solution are likely to react with hydrated C_3A in the hardened cement paste to form new chemical called ettringite. The products of reactions have a considerable greater volume than the

compounds they replace so the reaction with sulphates leads to the expansion and disruption of concrete and affects the durability of concrete.

Chloride Attack

Chlorides may enter in the concrete from several sources e.g. soluble chlorides, or from saline water, deicing salts, etc. Chloride salts are highly soluble in water. So, these ions are dissolved in water, and penetrate with it in concrete, either by the wetting of a non saturated concrete (convection), or by diffusion because the chloride content is higher in the environment than in the original concrete. The main part of chlorides coming from outside remain as dissolved ions, in the concrete pore solution. But they can also react with some components of the material.

The presence of these salts provides two opposing effects:

- It increases the conductivity of the electrolyte thus raising the corrosion rate and decreases its life.
- At high concentration, it diminishes the solubility of oxygen thereby lowering the corrosion rate. However there is a critical or threshold concentration of chloride ions which must be exceeded before the initiation of corrosion.

The process of deterioration of concrete due to chloride corrosion can be divided into 4 phases according to *Miyagawa (1991)* as shown in Fig 1.2 i.e. incubation stage, the development stage, the acceleration stage and the deterioration stage.

1. **Incubation Stage:** This is the process by which the chloride ions permeate into cover concrete and are accumulated around the reinforcing steel. Its duration is determined mainly by diffusion rate of chloride ion within concrete.
2. **Development Stage:** In this stage reinforcing steel begins to be corroded by chlorides. Corrosion products accumulate and cracks are generated in cover concrete due to the expansion pressure of the products.
3. **Acceleration Stage:** In this stage the rate of corrosion is accelerated by the generation of cracks along the reinforcing steel (longitudinal cracks). Delamination and peeling off of cover concrete start. While the static strength does not decrease even when longitudinal cracks have been generated, the strength and ductility begin to be reduced if repeated loading at high stresses are applied.
4. **Deterioration Stage**: Corrosion of reinforcing steel advances and the reduction in cross-sectional area and strength becomes conspicuous. The principal factors

in this stage are diffusion of chloride ion and of oxygen. The former dominates the generation of corrosion, while the latter dominates its rate.

Carbonation

The carbon dioxide gas in the atmosphere can be dissolved by the concrete pore solution, and react with some calcium compounds to form carbonates. This process is called carbonation. So, the pH value of concrete reduces from 13.5 to as low as 9 for the pore solution of a concrete deteriorated by carbonation. Carbon dioxide initiates reinforcement corrosion which leads to cracking of concrete.

Chloride diffusion and carbonation are the two diffusive processes which can not be examined separately, as they both depend on temperature and humidity. Temperature and humidity affects both physically on the diffusion processes by the change in their diffusivities and chemically on the rate of reaction in the chemical processes. Humidity and temperature, in turn, depend on the geographical location, and finally there is a coupling between carbonation and chloride diffusion through pore reductions.

Freeze Thaw Resistance

Concrete subjected to repeated cycles of freezing and thawing may deteriorate rapidly, or it may remain in service for many years without showing signs of distress. Failure of the material may take the form of loss of strength, crumbling or some combination of the two. To study the mechanism of freezing and thawing deterioration of concrete, we have to consider the two different aspects, i.e. hydraulic pressure and ice accretion as researched by *Detwiler et. al. (1989)*.

- **Hydraulic Pressure**

Water in the capillary pores of cement paste expands upon freezing. If the required volume is greater than the space available, the excess water is driven off by the pressure of expansion. The magnitude of this hydraulic pressure depends on the permeability of cement paste, the degree of saturation, the distance to the nearest unfilled void and the rate of freezing. If the pressure exceeds the tensile strength of the paste at any point, it will cause local cracking. In repeated cycles of freezing and thawing in wet environment, water will enter the cracks, during the thawing stage of the cycle only to freeze again later and there will be progressive deterioration with each cycle.

- **Ice Accretion**

Even when the hydraulic pressure is not great enough to damage the paste, pressure may built up due to ice accumulation in the capillary pores. Water in the gel pores is

under the influence of surface forces and thus doesn't freeze until the temperature drops to the point at which it can freeze with extremely fine redine of curvature associated with the gel pores. At 0^0 C, the ice in the capillaries is in equilibrium with the water in the gel pores. As the temperature drops, the gel water becomes super cool, but since it has a higher free energy than the ice in the capillaries, it can flow into the capillaries to freeze. In this manner, ice accumulates in the capillaries, eventually exerting pressure on the capillary walls. Near the bottom of the frozen zone of the concrete, water can be transported in the gel pores and then into the ice. This is similar to one of the mechanics of underlying "frost-heave" of soils, and it may play role in damaging concrete under certain conditions. The net effect on the concrete is a loss of volume due to loss of gel water and the potential increase of volumes in the capillary pores. When the concrete thaws, some of the melting water may return to the gel pores, but process is not completely reversible.

It is important to note that failure by the hydraulic pressure and failure by the ice accretion occur under different circumstances. Hydraulic pressure will be greatest when the rate of freezing is rapid. Ice accretion on the other hand, progresses with time and is more likely to cause damage if the concrete remains frozen for the extended period. Moreover, the effects are likely to be cumulative over a no. of winter seasons.

Acid Attack

No Portland cement can resist the acid attack. SO_2, CO_2 and many other fumes form acids which attack concrete by dissolving and removing the hydrated cement paste and leaving a soft and very weak mass. *Moulik (1990)* concluded that as the acidity increases, the degree of attack increases. The rate of attack also depends on the ability of hydrogen ions to be diffused through the cement gel, once the $Ca(OH)_2$ has been dissolved and leached out. Concrete is also attacked by the dissolved CO_2 in water. 60 ppm of CO_2 ions is very aggressive. The concrete is also attacked by domestic sewage which on oxidation by anaerobic bacteria forms H_2SO_4.

Acid first react with free lime of concrete forming calcium salts and later on attack the hydrosilicates and hydroaluminates forming the corresponding calcium salts, whose solubility govern the extent of deterioration of concrete. *Gambir (1992)* founded that the hydrochloric acid corrodes the concrete to a greater extent in comparison to the sulphuric acid at low concentration because H_2SO_4 forms a less soluble $CaSO_4$ on reacting with the lime of concrete, which seals the pores of concrete for further permeation and offers resistance to acid corrosion. But at higher concentration of H_2SO_4,

the concrete strength is reduced due to accumulation of $CaSO_4$ in the pores and the development of internal stresses. This can be observed in Fig. 1.3.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \quad \text{-------} \quad (1.1)$$

Part of $CaSO_4$ thus formed – about 1.2 gm is dissolved by ground water, the rest crystallizes in the form of gypsum. Concrete is destroyed soon by H_2SO_4 than HCl and HNO_3, because in the case of H_2SO_4, the aggressive effect of H^+ ions and the $(SO_4)^{2-}$ ions will combine.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2CO_3 \text{ (carbonic acid)} \quad \text{-------} \quad (1.2)$$

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2CO_3 \quad \text{-------} \quad (1.3)$$

$$CaCO_3 + 2H_2S \longrightarrow Ca(HS)_2 + H_2CO_3 \quad \text{-------} \quad (1.4)$$

$CaSO_4$,$CaCl_2$, Ca $(NO_3)_2$, $Ca(HS)_2$ etc. all are soluble calcium salts which are treated subsequently. $Al(OH)_3$ is transformed by strong acid, which are also leached out from the concrete.

1.4 BRIEF OUTLINE OF THE WORK

Concrete or cement mortar subjected to repeated cycles of freezing and thawing may deteriorate rapidly, or it may remain in service for many years without showing signs of distress. Failure of the material may take the form of loss of strength, crumbling or a combination of the two. It is likely that due to varied behavior of climatic conditions in cold weather regions, the fresh concrete or hardened concrete gets subjected to freezing and thawing cycles. The durability of concrete gets greatly impaired due to this alternate freezing and thawing which also exerts fatigue in concrete.

The behavior of normal concrete subjected to freezing thawing and wetting drying cycles is well established. However, now the concrete contains various mineral admixtures as well and the behavior of such concrete or cement mortar is not established.

In the present study, mortar specimens containing 0%, 5% and 10% metakaolin are cast at two water to cementitious material ratio of 0.46 and 0.5. Then the detailed effect of various deicing solutions (3%) and corrosion inhibitors (1%) on the mortar samples subjected to freezing thawing cycles and alternate wetting drying cycles is studied. Deicing solutions include sodium chloride, sodium chloride and corrosion inhibitor (triethanolamine), calcium chloride, calcium chloride and corrosion inhibitor (triethanolamine) are used. The samples are tested for compressive strength, scaling,

and mass change after 14, 28 and 42 cycles of freezing and thawing and wetting drying cycles. Ultrasonic pulse velocity test is also conducted to check the quality of mortar samples.

Table 1.1 Influence of Effective Humidity on Corrosion of Steel (*Thomas 1992*)

Effective Relative Humidity	Process				
	Carbonation	Corrosion of steel		Frost Attack	Chemical Attack
		In Carbonated Concrete	In Chloride Contaminated Concrete		
Very low (<45%)	1	0	0	0	0
Low (45-65%)	3	1	1	0	0
Medium (65- 85%)	2	3	3	0	0

High (85-95%)	1	2	3	2	1
Saturated (>98%)	0	1	1	3	3

*** 0 = insignificant risk; 1 = slight risk; 2 = medium risk; 3 = high risk**

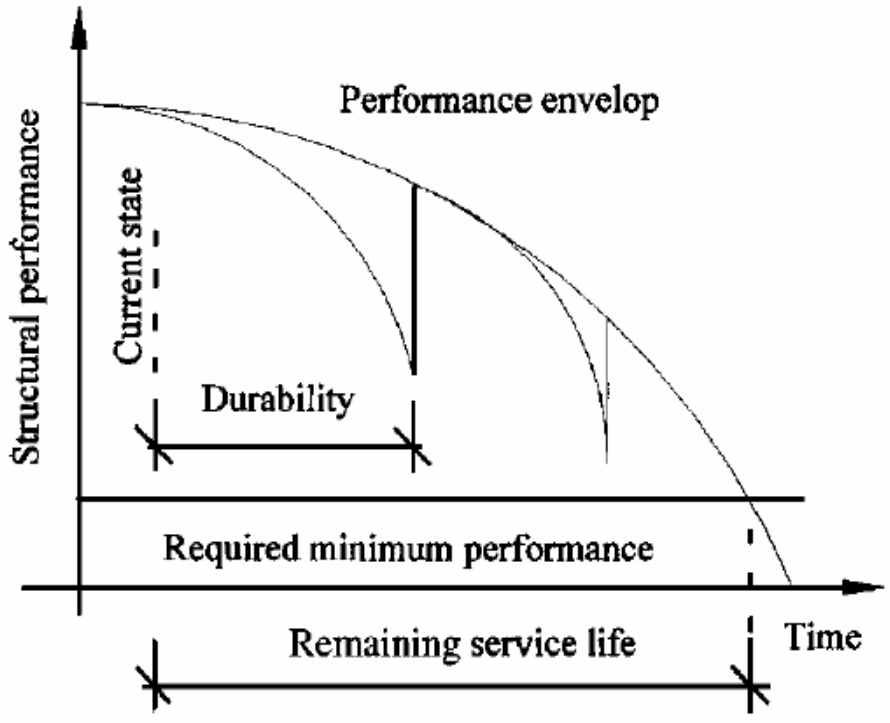


Fig.1.1 Graphical Representation of Durability and Remaining Service Life
(*Zongjin Li et. al., 2005)*

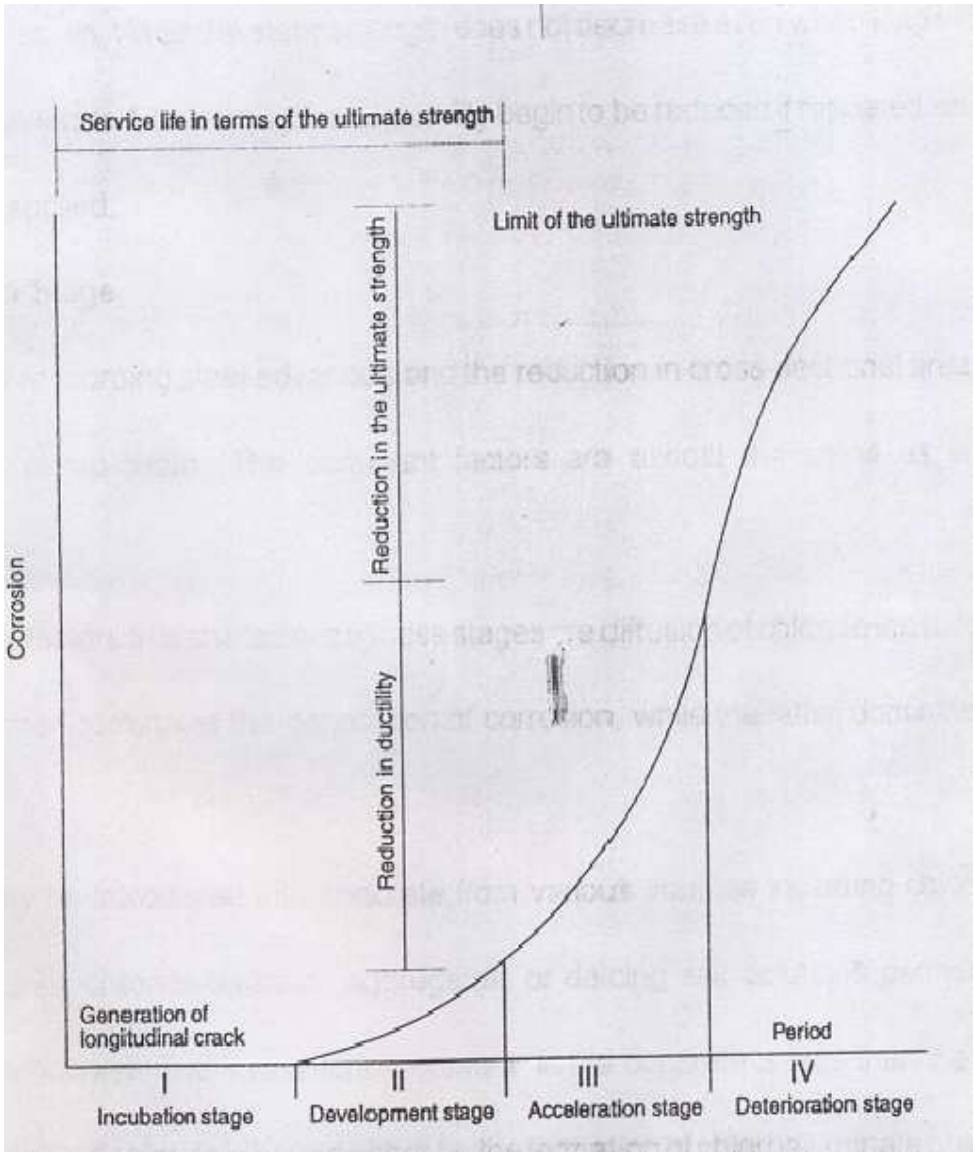


Fig 1.2: Process of Deterioration due to Chloride Corrosion (*Miyagawa, 1991)*

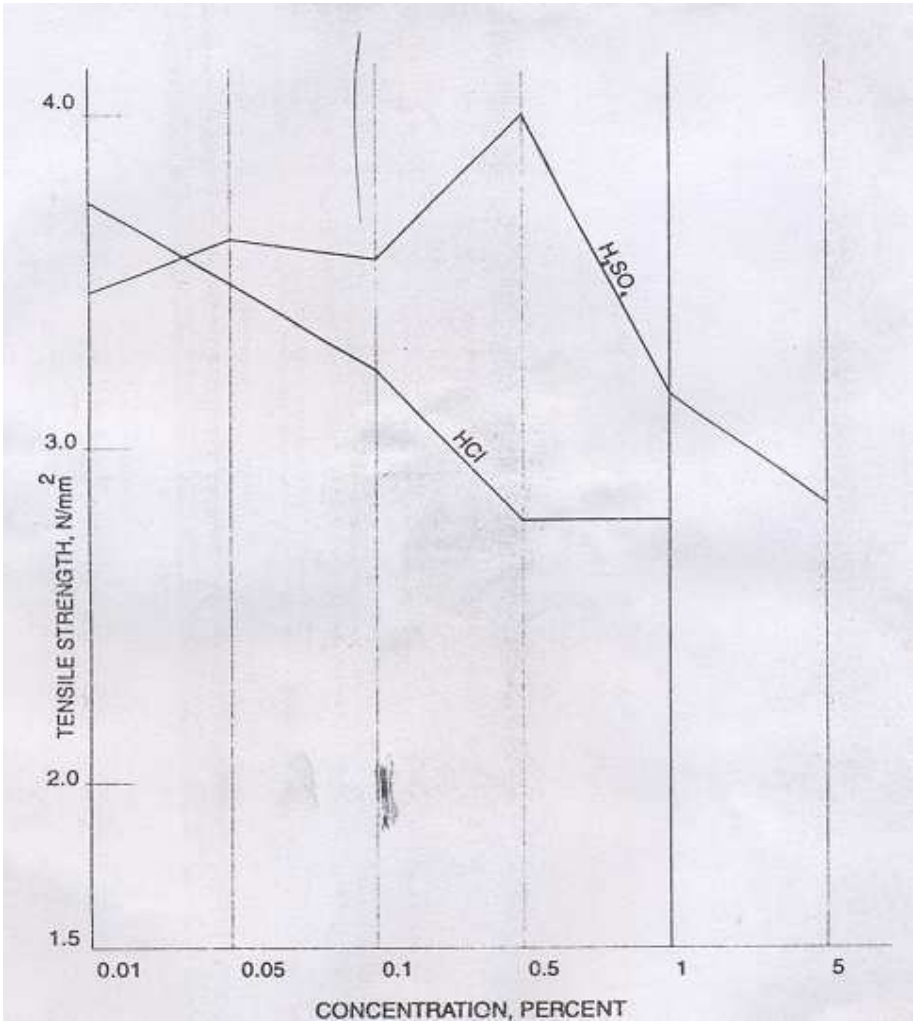


Fig: 1.3 Deterioration of Concrete Due to Acid Attack (*Gambir, 1992)*

CHAPTER 2
LITERATURE REVIEW

2.1 GENERAL

Insufficient long-term durability of civil engineering infrastructure, especially concrete structures, has been a major problem causing enormous economic loss to many countries. Concrete structures are plagued by reinforcement corrosion, cracking due to

drying shrinkage and non-uniform creep, alkali-silica reaction, sulfate attack, carbonation, leaching, freeze-thaw, etc.

Concrete immersed in a wet or moist aggressive medium tend to suffer damages; it will exhibit honey-combing and spalling on its surface. The extent of deterioration depends on the properties of aggressive medium, e.g. on the chemical composition of the ground water, on the type of rocks in contact with the water, on the depth of ground water table, climatic factors, microbiological condition, etc. Environmental damage of concrete is a complex multiphysics/ multiscale nonlinear-coupled problem. Whereas chemical intrusion in the concrete barely affects its performance, it is the detrimental effect of this intrusion in lowering the pH that is the primary concern, as it depassivates the steel, thus initiating the corrosion process. Hence, the global damage is really a two-part phenomenon: first chemical intrusion, and then corrosion-induced cracking of the concrete.

Short-term resistance of concrete structures exposed to fire has become a major question for high-strength concrete in recent years. At the same time, it would be highly beneficial to devise ways of incorporating certain industrial wastes into concrete, such as blast furnace slag and crushed bottle glass from curbside recycling. In the case of cement pastes containing rice husk or silica fume, or 70% of a granulated blast furnace slag, even at 28 days after hydration, the system was found to be almost impermeable. So depending on the individual characteristics of the mineral admixtures used, usually the combinations of a high-alkali Portland cement with 40 to 65% granulated blast furnace slag, or 30 to 40% low calcium flyash or 20 to 30% natural pozzolans have been found to be quite effective in limiting the alkali aggregate expansion to acceptable limits. Highly active pozzolans like rice husk, silica fume are effective in amounts as low as 10% and tend to increase rather than decrease, the strength at early ages.

The present chapter presents the point wise description of various factors mainly freezing-thawing and wetting drying affecting durability and the mechanism of their attack.

2.2 FREEZING AND THAWING

It is likely that due to varied behavior of climatic conditions in cold weather regions, the fresh concrete or hardened concrete gets subjected to freezing and thawing cycles. The durability of concrete gets greatly impaired due to this alternate freezing and thawing. Freezing and thawing also exert fatigue in concrete.

When the temperature drops below freezing point, the free water in the concrete freezes. Freezing of water not only prevents the hydration of cement but also makes the water in the concrete to expand. This expansion causes disruption of concrete due to which irreparable loss of strength and quality takes place. Also delay in hardening period does

not facilitate removal of formwork in a short period. Also the rate of progress of work will be very slow, all of which effects economy.

Achintya and Prasad (2003) studied the freezing and thawing environment on concrete, especially when placed under the submerged condition of sea water. They observed significant decrease in weight of concrete due to crumbling of exposed surfaces. Also there was reduction in volume and in compressive strength of concrete, placed in the freezing and thawing environment of sea water.

Following climatic conditions can occur while concreting in cold countries:

a) Low temperature, but above 0^0C at the time of concreting and later during hardening period: If the temperature is only low but always above the freezing point, it only retards the rate of development of strength. This leads to delay in removal of formwork and for putting the concrete into service.

b) Low temperature at the time of concreting but below 0^0C during hardening period: Many times it may happen that the concrete will have been mixed and placed when the ambient temperature is above freezing point. But before the concrete has attained the sufficient strength, the temperature of the air and also the temperature within the concrete may fall below freezing point, in which case the free water still available in the concrete freezes and forms ice lenses in the microscopic scale. These ice lenses formed in the capillary cavities may cause capillary suction of water from the ground, if the ground is saturated, and become bigger to disrupt the mass which disturbs the compaction of concrete. Ice formations may also appear as ice needles in the contact surfaces between aggregates and cement paste. After thawing these ice needles will melt forming cavities. Therefore, it can be concluded that freezing of freshly laid concrete seriously impair the structural integrity of concrete and results in considerable loss of strength.

On the other hand if the concrete is sufficiently hardened when freezing takes place, there will not be much harm to the structural integrity of the concrete. If the concrete has sufficiently hardened, the water that has been mixed for making concrete will have been lost either being used up in hydration process or lost by evaporation. Due to the formation of cement gels, the capillary cavities also will have been very much reduced, with the results that there exists very little of free water in the body of concrete to freeze. Therefore the magnitude of volume change due to the formation of microscopic lens is much less. Secondly, the concrete at this stage is strong enough to resist whatever

osmotic pressure resulting from the freezing. Therefore there is no immediate danger to the concrete.

c) Temperature below 0^0C at the time of concreting and during hardening period: Certain precautions are absolutely necessary for concreting when the temperature is below 0^0C, so that the fresh concrete does not get frozen. The consequences of freezing of fresh concrete and the effect of sub zero temperature on the hardened but not fully matured concrete is same as explained above.

d) Hardened concrete subjected to alternate freezing and thawing: Concrete pavements constructed at high altitude are normally subjected to alternate freezing and thawing. The interval of cycles may be between season to season or between day and night or even a couple of times in a day. It has been found that the durability of hardened concrete is reduced to 1/3 to 1/7 when it is subjected to alternate freezing and thawing depending on the quality of concrete. It is to be noted that concrete is a pervious material. Degree of porosity is depending upon the gel/space ratio. A concrete member is likely to get saturated due to the absorption of moisture from surface or from the bed. The free water that has filled the capillary cavities of concrete will get frozen with the fall of temperature. Subsequently when the temperature goes above 0^0C, the ice lens melts. Due to this alternate freezing and thawing, concrete is subjected to distress and surface scaling.

2.2.1 Factors Affecting the Freeze-Thaw Resistance of Concrete

a) **Water –cement ratio:** The primary influence of water-to-cement (w/c) ratio on the freeze–thaw durability of concrete is its effect on capillary pore volume, i.e., its permeability and ability to absorb freezable water. Using low water-to-cement ratios minimize the type of voids in which water typically freezes. Increase in w/c produces more capillary voids, both in volume and in size. It's pore size that determines if water can freeze within concrete.

Mehta (1986) showed that pore sizes in cement paste run from 0.02–10 μm for capillary pores to 0.0005–0.01 μm for gel pores. Clearly only capillary voids and some larger gel pores can freeze. Thus, capillary-size pores are critical to the frost resistance of concrete.

b) **Effect of Type of Cement:** *Janotka and Krajei (2000)* analyzed the resistance to freezing and thawing of mortar specimens made from sulphoaluminate–belite cement (M–SAB) with that of mortars made from Portland cement (M–PC). A more permeable

pore system of M–SAB enables faster transfer of the larger volume of water throughout SAB cement mortars relative to those of M–PC. A growth of formed ice crystals is then the source of internal expansive stresses which are responsible for mortar deterioration. The results suggest that larger median radius of the pores and total porosity of M–SAB compared to those of M–PC is primarily caused by the rapid setting of the SAB cement. The 'coarsening' of pore structure of mortar specimens under action of freezing and thawing is proved by the increase in the macro pores portion, median pore radius, and total porosity values. This process is more intense in M–SAB. The effect of the frost attack is confirmed by lower compressive strength and dynamic modulus of elasticity on the one hand and higher absorption capacity, expansion, and crack propagation of M–SAB compared with those of M–PC on the other hand.

c) **Cooling Rate:** It is generally accepted that the faster the cooling rate, the more damage will occur. *Pigeon et. al. (1985)* noted that changing the cooling rate from 2° to 6°C/hr has a significant detrimental influence on freeze–thaw durability. However, in some situations, cooling rate may not be so important. For example, *Fontenay and Sellevold (1980)* found in calorimetric studies of paste that the total amount of ice formed is independent of the cooling rate but also that the amount of ice formed per unit time is affected by the cooling rate.

d) **Degree of Saturation:** Partially dry concrete is extremely resistant to cycles of freezing and thawing. Some experts feel that below certain water content, concrete is immune to frost damage. *Whiteside and Sweet (1950)* showed that samples more than 91% saturated were easily damaged by freeze–thaw cycles but were difficult to damage when they contained less than 87% water, calculated as the percent of water absorbed during submersion in water.

e) **Air bubbles:** There are two kinds of air bubbles in the paste matrix of concrete: entrapped and entrained. Entrapped air bubbles are unintentionally included in the paste during the mixing process, and entrained air bubbles are purposely incorporated into the paste with the help of chemical admixtures. Incorporating entrained air into the concrete relieves pressures caused by freezing water *Powers (1958)* demonstrated the benefit of air for the frost resistance of concrete. In a series of experiments, he pointed out that de-aired paste elongated by 1600 microstrain during freezing to –24°C and retained a residual strain of 500 microstrain after thawing. When 2% air was entrained into the paste, it elongated 900 microstrain with a residual strain of 300 microstrain, but paste with 10% air showed no elongation on freezing and no residual strain on thawing. It has

since been established that when air is intentionally incorporated to around 4–8% of the volume of fresh concrete, the resulting hardened concrete will have good durability.

f) **Chemical admixtures:** *Kukko and Koskinen (1988)* described admixture as a substance added to fresh concrete in the range of 20% and above by weight of mixing water. These obviously are above the concentrations that exacerbate surface scaling, but not surprisingly scaling was not noted as a problem. In fact, freeze–thaw durability was usually reported as being superior to normal concrete. Fig 2.1 shows that only one of the six admixtures tested produced concrete that was less durable than control concrete. It may be that all or most of the admixtures stay in the pore water solution; they probably do not combine with the hydration products. If this is so, the admixtures may depress the freezing point of the concrete so that it experiences fewer, or no, freeze–thaw cycles compared to normal concrete exposed to outdoor conditions. It could also be that the admixtures somehow prevent the mixing water from fully expanding, even though it freezes, so that less internal pressure is generated inside the concrete.

2.2.2 Types of Freeze Thaw Damage:

Basic types of freeze thaw damage are:-

- D-cracking
- Surface Scaling
- Pop-outs
- Internal damage

a) **D-Cracking:** Cracking of concrete pavements caused by the freeze-thaw deterioration of the aggregate within concrete is called D-cracking. D-cracks are closely spaced crack formations parallel to transverse and longitudinal joints that later multiply outward from the joints toward the center of the pavement panel. D-cracking is a function of the pore properties of certain types of aggregate particles and the environment in which the pavement is placed. Due to the natural accumulation of water under pavements in the base and sub base layers, the aggregate may eventually become saturated. Then with freezing and thawing cycles, cracking of the concrete starts in the saturated aggregate at the bottom of the slab and progresses upward until it reaches the wearing surface. This problem can be reduced either by selecting aggregates that perform better in freeze-thaw cycles or, where marginal aggregates must be used, by reducing the maximum particle size. Also, installation of effective drainage systems for carrying free water out from under the pavement may be helpful.

b) **Surface Scaling:** Surface scaling is perhaps the most easily recognized result of frost damage; it occurs mainly on pavements, sidewalks and other horizontal surfaces, and is most severe if de-icing salts have been used. Scaling occurs to depths of an inch or more and is progressive. It is to be distinguished from peeling of the thin skin of laitance that forms on surfaces that have been made with concrete of excessively high slump or subjected to excessive compaction or trowelling.

There are many types of concrete structures that can be affected by saline environments like slabs on grade, footings, roads, concrete pipes, kerbs and gutters. Due to the different types of concrete used in these different applications, the extent and possible types of deterioration occurring could be different. The impacts of a saline environment manifest in different forms: efflorescence, scaling, progressive erosion of surface, cracking, crumbling and softening.

Scaling is considered to be the effect of salt crystallization. It will occur when the rate of evaporation of water from the concrete surface is faster than the rate of water entering the system. The deterioration is progressive and leads to surface damage, which could possibly lead to further salts penetration. Physical attack by salt crystallization could ultimately lead to crumbling of concrete.

Sea water contains many dissolved salts, some of which affect the durability of concrete. The salts which are present in significant amounts in most seas are sodium chloride, magnesium chloride, magnesium sulphate, calcium sulphate, potassium chloride and potassium sulphate. Concentrations vary from sea to sea, although the total salt content is commonly about 35 g/l. an exception to this is only Baltic which contains only 1/5 of this amount of dissolved salts.

The sea water also contains dissolved oxygen and carbon dioxide. The concentrations of these gases can be highly variable, depending on the local conditions.

Thomas (1992) classified several different types of marine exposure as summarized below:-

i. The marine atmospheric zone in which concrete is never directly in contact with the sea although it will receive salts from the blown spray and salt-laden mist. The various forms of deterioration in this zone are:

- Corrosion of reinforcement activated by chloride
- Frost damage

ii. The splash zone, which lies above high tide but is still subject to direct wetting by sea water from waves. The various forms of deterioration in this zone are same as of marine zone. Here abrasion due to wave action also takes place.

iii. The tidal zone, which lies high and low tide. Concrete will be submerged for periods each day. The various forms of deterioration in this zone besides marine zone are:

- Abrasion due to wave action, floating ice and other objects
- Biological fouling
- Chemical attack on concrete

iv. The submerged zone, which is below low tide and in which concrete is continuously submerged. The various forms of deterioration in this zone are same as above.

Physical Effect of Salts on the Concrete

ACI committee 201 on durability states that the mechanism by which the deicing salts damage concrete is physical rather than chemical. It involves the development of disruptive osmotic and hydraulic pressures during freezing, principally in the paste, similar to ordinary frost action. It is however more severe.

Kurdowski (2004) proposed two processes of the chloride corrosion of cement paste: decalcification of C-S-H and the formation of the skin on the paste surface. Decalcification is relatively quick in the magnesium chloride solution, and brucite as well as basic magnesium chloride are formed. A skin is formed on durable mortars immersed in the strong chloride solution. It is composed of brucite and basic magnesium chloride. The protective role of this skin was temporary, and sooner or later, the skin was destroyed. The alkali activated slag (AAS) mortar became then quickly destroyed. However, in high-alumina cement (HAC) paste, the dense layer was formed near the surface, which protected the paste, thus hindering the corrosion process.

McDonald and Perenchio (1997) researched on the effects of salt type on the concrete scaling. They observed that salts containing potassium are more likely to cause scaling damage to concrete. Deionised water did not cause significant scaling of the concrete.
The following 4% salt solutions were used to pond the concrete specimens which were slabs measuring 300 x 300 x 75 mm:

- 80% rock salt with 20% calcium chloride.
- 100% rock salt.
- Proprietary salt.
- 69% rock salt, 30% potassium chloride, 1% calcium chloride.
- 50% rock salt, 50% potassium chloride.

All solutions were made using deionized water. Control specimens were ponded with deionized water. *ASTM C 672* has given the visual grading of the specimens as shown in

Table 2.2. After 100 cycles of freezing and thawing they found that the most aggressive solutions with respect to scaling were the mixtures containing KCl. Scaling of grade 2 was observed in some of the specimens ponded with proprietary salt. After the cycles were completed, the solutions were vacuumed from each of the specimens. Upon drying it was observed that heavy white deposits formed on the surfaces of the concrete slabs that had been ponded with the proprietary salt. These deposits were identified as a mixture of calcium carbonate and a magnesium phosphate compound, possibly with a small amount of calcium phosphate.

The calcium carbonate is judged to be due to carbonation of calcium hydroxide from cement hydration. Magnesium phosphate is from soluble and insoluble phosphates present in the proprietary salt.

The proprietary salt and rock salt analyzed using spectroscopic techniques for water soluble orthophosphate, water soluble phosphate and total phosphates. The proprietary salt contains approximately 0.5% by weight of phosphate compounds, while the rock salt contains little or no phosphate. The results are shown in Table 2.3. The constituents of proprietary salt were determined using wet chemical and atomic absorption techniques which have been shown in the Table 2.4. A significant component of the proprietary salt is magnesium, which is absent from other samples.

They also found a dense front of Magnesium hydroxide crystals formed about 0.5 mm below the concrete surface. This crystallization of Magnesium hydroxide occurred when Magnesium chloride solution reached uncarbonated concrete below the surface region. Magnesium chloride will pass through carbonated concrete but when it comes in contact with hydroxyl ion from uncarbonated calcium hydroxide it precipitates as Magnesium hydroxide. This relatively dense formation of Magnesium hydroxide may act as a partial barrier to deeper penetration of the salt components. So magnesium chloride solutions cause the formation of a protective layer of $Mg(OH)_2$ on the surface of concrete. This film is very thin, but nevertheless is an efficient protection as long as water is stagnant. If the water containing the $MgCl_2$ flows or moves, the protective layer is washed away thus exposing the concrete surface to attack and finally destroying the concrete.

It was also found that the proprietary salt produced more damage to the higher strength concrete, low w/c concrete than to low strength, high w/c concrete. The possible reason they concluded was that lower w/c concrete cannot accommodate the crystallization of the magnesium hydroxide, either due to the decreased porosity of concrete or due to the different surface characteristics related to finishing or carbonation or both.

Effect of admixtures on scaling

Nehdi and Hayek (2005) prepared cement mortars with plain OPC or OPC incorporating either 8% silica fume, 25% slag, or 25%class F fly ash at w/cm of 0.30, 0.45, and 0.60. The specimens were submerged in both 10% Na_2SO_4 and 10% $MgSO_4$ solutions; their expansion and surface deterioration were monitored for up to 9 months of exposure. In addition, mortar cylinders were made from each mixture and tested under partial submersion in both 50-mm-deep 10% Na_2SO_4 and 10% $MgSO_4$ solutions that were maintained at either constant or cycling RH. The development of efflorescence due to salt hydration was monitored. They concluded that the addition of 8% silica fume was most efficient in reducing expansion followed by 25% slag and 25% class F fly ash, respectively. Surface deterioration of specimens exposed to Na_2SO_4 was not significant. Surface deterioration, likely due to decalcification of CSH, was significant in specimens subjected to $MgSO_4$. Again, the higher the w/cm, the higher the surface deterioration, but silica fume and fly ash did not exhibit any additional benefits in resisting surface deterioration and even lead to worse performance than pure OPC specimens at high water to cemetitious ratio.

c) Pop-outs: Pop-out is a small volume of concrete which has been separated from the body of concrete to leave a roughly conical depression. Examination of pop-out, or of the hole remaining, will usually indicate that the apex of the cone contains fragment of usually coarse aggregate. The most common cause is stress resulting from freeze thaw action within the coarse aggregate particle, whereby the stress is relieved through the cracking of the particle and simultaneous bursting of concrete between the particle and the nearest concrete surface. There is a close analogy between this effect and the partially destructive bursting test involving extraction of bolt cast in the concrete surface, which also results in a conical hole. Pop-outs rarely exceed 50mm diameter and 15mm depth but their occurrence can be unsightly and they can be dangerous on high walls, paths, roads and aircraft runways. When a pop-out is sensibly flat underneath and does not contain a fragment of the coarse aggregate at the apex it is more likely to be an example of scaling.

d) Internal damage: It is a cracking confined predominantly to the mortar rather than the coarse aggregate, and is associated with freeze-thaw damage of the fresh, young or mature cement paste which did not have pore structure capable of resisting stresses, due to the severity of the freeze- thaw action at the age at which it occurred. It is more likely to occur at the outer and the upper levels of the construction at the edges and corners and where water is more accessible.

2.2.3 Mechanism by Which Air Entrainment Improves Concrete Durability in Freezing and Thawing Exposures

The general mechanism by which air entrainment improves concrete durability in freezing and thawing exposures is as follows: When water in the concrete (generally resulting from precipitation or from contact with moist sub grade) freezes, it expands and this movement of water generates pressures that, when in excess of the tensile strength of concrete or mortar layer at a surface, can cause cracking and scaling. Concrete has to be critically saturated (>91%), which is generally true for concrete surfaces. Entrained air bubbles are microscopic in size (0.01 inches or less), evenly distributed in the paste fraction, and take on water in the form of ice during the freezing cycle to relieve pressure buildup. Generally, an air entrainment of 4 to 8% and, more importantly, an air bubble spacing factor of less than 0.01 inch provide satisfactory freeze-thaw performance under most conditions.

As opposed to conventional concrete, pervious concrete typically has a large volume of 15 to 35% of interconnected voids. This void structure is not the same as the entrained air in regular portland cement concrete. Pervious concrete that is partially saturated should have sufficient voids for the movement of water and thus demonstrate good-freeze thaw resistance.

2.2.4 Effect of Deicing Agents on Freeze-Thaw Resistance of Concrete

Deicing chemicals used for snow and ice removal, such as sodium chloride, can aggravate freeze-thaw deterioration. Moisture tends to move towards zones with higher salt concentrations (by osmosis). Therefore, if salts are present in the pore solution the osmotic pressure is increased. In addition, the application of deicing salts to pavements increases the rate of cooling, increasing the potential for freeze-thaw deterioration at the concrete surface. Chloride containing deicing materials such as calcium chloride, potassium chloride, and sodium chloride, can exacerbate a scaling problem as concrete goes through freeze-thaw cycles. Deicing salts reduce the temperature at which water freezes and their use maintains a high level of saturation of concrete and significantly increases the number of freeze-thaw cycles witnessed by the surface. With typical salts like sodium, potassium or calcium chloride, the mechanism that causes surface scaling is purely physical in nature and the chemical composition of the concrete surface is generally not modified. *Gillis et. al. (1994)* found that corrosion-inhibitor-added deicing salts caused degradation of concrete by both anions and cations. The following are the effects of deicing agents on concrete subjected to freeze thaw cycles.

i) **pH Change:** *Jang et. al. (1995)* researched on the precipitates resulting from chemical reactions between concrete and corrosion-inhibitor-added deicing salts. pH changes were also noted in the concrete-saturated solution mixed with the corrosion-inhibitor-added deicing salts. Precipitates were calcium and/or magnesium phosphates as a major component, and gypsum as a minor component.

ii)**Decalcification of Cement Paste:** *Lee et. al. (2000)* investigates the effects of different deicers on concrete deterioration. Laboratory simulations of environmental conditions (wet/dry and freeze/thaw cycling) were conducted on highway concrete samples with various deicer chemicals (NaCl, $CaCl_2$, $MgCl_2$, calcium magnesium acetate (CMA) of 5 different Ca/Mg ratios, Ca-acetate, and Mg-acetate). Each deicer produced characteristic effects on the concrete samples by physically and chemically altering the dolomite coarse aggregate, the dolomite coarse aggregate-paste interface, and cement paste. Chloride solutions commonly promoted decalcification of paste and altered ettringite to chloroaluminate. Magnesium-bearing deicer solutions (e.g., CMA, Mg-acetate and $MgCl_2$) caused severe paste deterioration by forming brucite and non cementitious magnesium silicate hydrate. For acetate solutions, the effects caused by Ca-acetate on concrete deterioration were much less severe than those caused by Mg-bearing acetates. For the experimental conditions utilized herein, NaCl solution was the least deleterious to the cement paste and aggregate.

iii) **Scaling:** *Wang et. al. (2006)* researched that Chloride-related deicing chemicals often brought about leaching of calcium hydroxide, as well as chemical alterations in concrete. Potassium acetate caused minor scaling, associated with alkali carbonation of the surface layer of concrete. Although producing a considerable number of micro-pores on the surface of the samples, the agricultural deicing product resulted in the least chemical penetration and scaling damage of paste and concrete.

iv) **Strength Change:** *Wang et. al. (2006)* researched the compressive strength of paste and concrete samples under freezing thawing cycling. They found that the water-immersed paste samples under freezing thawing cycling as shown in Fig 2.2 gained a smaller amount of strength with exposure time. This might result from the combined effect of frost damage and slow cement hydration at the low temperature. Paste samples immersed in $CaCl_2$ and $CaCl_2$ with inhibitor solutions displayed considerable strength loss, while the samples exposed to NaCl, K Acetate, and the Agr-deicing solutions had little strength loss with increasing freezing thawing cycles.

v) **Mass Change:** *Wang et. al.(2006)* found that the paste sample immersed in water and NaCl solution gained a minimal amount of mass under F–T cycling (0.5% for water-immersed samples and 1.0% for NaCl-immersed samples, respectively, at 60 cycles). The paste samples immersed in the Agr-deicing solution experienced the most but steady mass loss among all samples tested under F–T cycling. The paste samples immersed in the Agr-deicing solution experienced the most but steady mass loss among all samples tested under F–T cycling. $CaCl_2$ with corrosion inhibitor deicing chemical could only postpone, not eliminate, concrete damage. Once mass loss began, the rate in $CaCl_2$-inhib-immersed samples was significantly greater than the rate of mass loss in $CaCl_2$-immersed samples. This is shown in Fig. 2.3.

Sun et. al. (2002) show that the concrete specimens subjected to freeze-thaw cycling scaled more severely in chloride salt solution than those in water, and weight losses of the specimens tested in chloride salt solution were twice as much as those tested in water. However, dynamic modulus of elasticity of the concrete specimens decreased more slowly in chloride salt solution than in water due to the decline in the freezing point of the chloride salt solution compared with water. It is also shown that the performance deterioration in the concrete subjected to multidamaging processes was significantly accelerated. The larger the stress ratios, the fewer freeze–thaw cycles the concrete could bear. The results have been shown in Fig. 2.4 & 2.5. Various mix proportions are shown in Table 2.1.

2.2.5 Effect on the Dynamic Modulus of Elasticity Exposed to Freeze-Thaw Cycling in Water and in Sodium Chloride Solution

The relative dynamic modulus of elasticity is the ratio of the dynamic modulus of elasticity measured at certain freeze thaw cycles to that measured before the freeze thaw cycling. *Sun et. al. (2002)* concluded that NaCl lowers the freezing point of water which is beneficial to the improvement in the frost resistance of concrete. As shown in Fig. 2.5 the number of freeze - thaw cycles at failure in a NaCl solution were roughly 20% higher than those in fresh water.

Setzer (1996) introduced a method to calculate the total amount of scaled material (M_n) related to test surface after n^{th} cycle as:

$$M_n = ((\Sigma u_s)/A)* 10^6 \text{ g/m}^2 \qquad \text{------- (2.1)}$$

Where u_s = mass of scaled material after n cycles (g) with an accuracy of 0.01g. The sum is taken over all measurements until the nth cycle.

A = area of the test surface. It is calculated on the basis of linear dimensions. They are taken as the average of at least 2 measurements determined to the nearest 0.5mm.

The mean value and individual values of each specimen after 28 cycles are used for evaluating scaling resistance.

2.2.6 Consequences of Freeze-Thaw Damage

The consequences of freeze thaw damage on concrete include:

- Hazard for life, limb and property.
- Reduced protection against other forms of damage like reinforcement corrosion.
- Reduced service life.
- Remedial costs.
- Poor appearance.

2.3 WETTING AND DRYING

Alternating cycles of wetting and drying during the curing process is extremely harmful to the concrete surface and may result in surface crazing and cracking. In India we have a large coastal area we need to know that the concrete in coastal structures are also susceptible to distress due to several factors some of which are common which affect the durability of concrete in general.

The major factor in the durability of concrete in or near the sea is its degree of exposure. This influences the degree of saturation of concrete and the frequency and rate of wetting and drying. It is influenced by the structures location in relation to the climate, i.e. hot, temperature and cold zones and wet or arid, its exposure to the elements, i.e. exposed to or sheltered, and its position in relation to sea level, i.e. atmospheric, splash or submerged. Each of these factors affects the concrete in a different way and degree of distress also varies.

Concrete exposed to sea water can be subjected to various chemicals and physical actions. When concrete is repeatedly wetted by sea water, with alternating periods of drying during which pure water evaporates, some of the salts dissolved in the sea water are left behind in the form of crystals, mainly sulphates. These crystals re-hydrate and grow upon subsequent wetting and there by exert an expansive force on the surrounding hardened cement paste.

2.3.1 Effect of Wetting/Drying Cycles

1. **Corrosion:** Alternating cycles of wetting and drying leads to increase in capillary porosity due to leaching away of water soluble salts results in depletion of water soluble calcium hydroxide reducing the alkalinity which further allows the aggressive chemicals from its environment to penetrate easily resulting the concrete/reinforcement to get affected at accelerated rate and initiate the onset of corrosion.

2. **Carbonation:** Alternating cycles of wetting and drying i.e. intermittent exposure to water is the most favorable condition for accelerated carbonation of concrete. This tends to cause accelerated carbonation, more prominently in permeable concretes made with low cement content or with high water to cement ratio and/or are inadequately moist cured. Carbonation destroys the passive film over reinforcing steel, the affected depassivated portion is exposed to the action of oxygen and water, consequently corrosion in reinforcement steel is initiated.

2.3.2 Effect of Solutions on Concrete Placed in Wetting and Drying Cycle

1) Mass Change: *Trinder et. al*. studied the performance of various concrete blends exposed to ammonium sulfate environments by measuring weight loss and relative change in length of samples placed in a wetting and drying cycle. Mix proportions of various mixes are shown in Table 2.5. It has been found that the addition of catalytic crystalline waterproofing admixture substantially improves the performance of the concrete compared to GP mixes with the same cement content and approximate compressive strength. The level of performance being greater than which would be predicted from consideration of either concrete strength or water permeable void volume. The addition of silica fume in combination with a reduction in GP content, sufficient to achieve equivalent strengths, resulted in a smaller increase in performance to the addition of catalytic crystalline waterproofing admixture. Finally, the replacement of GP with blast furnace slag resulted in a significant reduction in performance. Fig 2.6 shows a graph of the average weight change with time (of 3 samples) for each of the trial mixes. The SR mix experienced the lowest level of weight loss for all samples tested. This is not surprising as the mix had strength 15 MPa higher than the average of all other mixes. It is considered likely that SR mixes with strengths equivalent to other mixes would have exhibited similar weight loss to that experienced by the SF and Admix mixes. The performance of the SF and Admix mixes were similar and only marginally worse than the SR mix. These three mixes exhibited significantly less weight loss than the GP mix, which in turn performed better than the GB80 mix. The low heat mix (LH) was by far the worst performing of all mixes.

Mbessa and Pera (2001) studied the durability of high strength concrete exposed to ammonium sulfate solution**.** The mineral admixtures were added at the rate of 10% of the cementitious material content**.** They concluded that high strength concrete (grade 100) is durable in a 20% ammonium sulphate solution due to its very low porosity and permeability. No swelling was observed during the durability cycles. Generally silica fume leads to best results.

Fig 2.7 represents the mass loss after 6 cycles of degradation i.e. each specimen was immersed in the 20% ammonium sulphate solution followed by 1 week of drying at 20^0C, in the range of 6-10%, depending on the nature of fine particles used. Silica fume led to the lowest mass loss, while metakaolin generated high values.

2) Strength Change: *Wang et al. (2006)* researched on the compressive strength of paste and concrete samples under wetting drying cycling exposed to different deicing chemicals. They found that the strength loss was associated with the scaling damage of the samples. The water-immersed paste samples increased strength with the exposure time due to continuous cement hydration. Paste samples exposed to all deicing solutions showed comparable strength to the water-immersed sample at 20 wetting drying cycles, but they all exhibited strength loss thereafter. The strength loss of the paste samples at 60 wetting drying cycles, from the highest to the lowest, was $CaCl_2$-inhib, $CaCl_2$, NaCl, Agr-deicing and K Acetate-immersed samples.

3) Ion Penetration: *Wang et al. (2006)* researched that the various deicing chemicals penetrated at different rates into a given paste and concrete, resulting in different degrees of damage. Among the deicing chemicals tested, two calcium chloride solutions caused the most damage. Addition of a corrosion inhibitor into the calcium chloride solution delayed the onset of damage, but it did not reduce the ultimate damage. Generally, for all samples immersed in deicing solutions, ion concentrations decreased with sample depth and increased with exposure time. However, ion concentrations of the water-immersed sample had a small variation with the sample depth and exposure time. The average chloride (Cl^-), sodium (Na^+), and potassium (K^+) ion concentrations within the layer 3.5 cm from the surface of the water-immersed concrete sample subjected to 60 wetting drying cycles were approximately 7, 580 and 490 ppm, respectively.

4) Scaling: *Wang et al.(2006)* paste samples submerged in distilled water and NaCl deicing solution showed no scaling damage (scale rating = 0). Paste samples submerged in K Acetate deicing solutions displayed minor damage (scale rating = 1.0) after 60 W–D cycles. Samples immersed in the Agr-deicing solution had a constant scaling value of 1.0 from 20 to 130 cycles due to the micro-pores observed on the

sample surfaces. Samples immersed in $CaCl_2$ and $CaCl_2$-inhib solutions demonstrated increasing scaling with wetting drying cycles.

5) Length variations: *Mbessa and Pera (2001)* studied the durability of high strength concrete containing mineral admixtures (silica fume, slag and metakaolin) exposed to ammonium sulfate solution**.** As shown in Fig 2.8, no swelling occurred after 6 cycles of degradation. Only shrinkage was recorded and its value was limited to (300-450 um/m).

6) Porosity: *Mbessa and Pera (2001)* studied the total porosity assessed by the mercury intrusion porosimetry of high strength concrete containing mineral admixtures (silica fume, slag and metakaolin) at the rate of 10% of the cementitious material content exposed to ammonium sulfate solution**.** The results are shown in Fig. 2.9, which shows a general decrease of porosity after 28 days. Generally silica fume leads to best results.

2.3.3 Effect of Admixtures on Durability of Concrete Exposed to Various Solutions

Montemor et. al.(2002) investigated the effect of fly ash addition on the corrosion process occurring in reinforced concrete exposed simultaneously to carbon dioxide and chloride. The corrosion process of steel rebars embedded in mortar with 15% and 30% of fly ash was tested under atmosphere containing 5% CO_2 (room temperature and 60–70% relative humidity) and spraying the blocks weekly with a 15% NaCl aqueous solution. They observed that under accelerated carbonation fly ash mortar shows higher corrosion rates. The chloride content in mortar exposed to accelerated carbonation increases with the amount of fly ash. However, under natural carbonation it decreases with the addition of fly ash.

Kayali and Zhu (2005) tested High-strength reinforced silica fume–cement concrete slabs with a compressive strength of 70 MPa for chloride diffusion and corrosion activity after partial immersion in a 2% chloride solution. Chloride diffusion in high-strength concrete was extremely low. They concluded that high-strength concrete containing 10% silica fume possesses exceedingly high corrosion resistance.

2.3.4 Effect of Corrosion Inhibitors on the Durability of Concrete

Sideris and Savva (2005) investigated that the addition of calcium nitrite as corrosion inhibitor increases the chloride-induced corrosion resistance of all mixtures, but the protection offered strongly depends on the type of cement used. They found that the best results were obtained under the combined use of calcium nitrite and high (30%) percent of natural pozzolan, flyash and 10% silica fume. Even the carbonation depth of all mixtures was reduced or remained the same when calcium nitrite was used.

2.4 NON DESTRUCTIVE TEST

Methods of non destructive testing are developed during the last four decades. Reliable equipment for such non destructive testing is manufactured only in recent times. Further various types of non destructive tests are available. Ultra sonic non-destructive testing has been accepted as a reliable method of testing. At the moment, rebound hammer test, ultrasonic test and core cutting tests are considered to be the dependable tests in concrete construction. Of these, ultrasonic test has its own advantage and considered being efficient in locating honeycomb and porous concrete.

2.4.1 Ultrasonic Pulse Velocity Test

Ultrasonic Pulse Velocity (USPV) is extensively used to assess the quality of concrete in existing structures. This test is generally used for the measurement of concrete uniformity, determination of cracking and honey-combing, strength, estimation and assessment of concrete deterioration.

The principle of USPV measurement involves sending electro acoustic pulse through a concrete path and measuring the transit time taken, for a known distance. Pulse velocity is then computed. This pulse velocity depends mainly on elastic modulus of concrete.
The UPV testing can be done as shown in Fig 2.10. The direct method of testing is the most reliable from the point of view of transit time measurement, as maximum pulse energy is transmitted at right angles to the face of transmitter. However semi-direct and surface to surface testing may be considered where direct testing is not possible.
Chellappan (2000), Bungey and Millard (1996), Stevens and Issa (1994) gave some of the important factors on which pulse velocity measurements depend, as described below:-

i) **Surface Condition:** It is difficult to obtain reliable reading if the concrete surface is rough or if there is a gap between the concrete surface and face of each transducer. For most concrete surfaces, the finish is usually sufficiently smooth and good acoustical contact can be assured by the use of coupling medium and by pressing the transducers against the concrete surface. Typical complaints are petroleum jelly, grease, liquid soap and glycerol paste. When the concrete surface is rough, it is necessary to smooth and level the surface before placing the transducer.

ii) **Moisture Content:** The moisture content of the concrete can have the small effect on the pulse velocity. For normal structure concrete in a saturated condition, the pulse velocity may be up to 2% higher than it is in the same concrete in a dry condition. The

moisture content has less influence on the velocity in high strength concrete than it does on the low strength concrete.

iii) **Temperature of Concrete:** Variations of the concrete temperature between 5^{o}C and 30^{o}C have been found to cause no significant change in the velocity values. Outside this range of temperature, pulse velocity may change without the occurrence of corresponding changes in the strength or elastic properties. At temperature between 30^{o}C and 60^{o}C, there is up to 5% reduction in pulse velocity. This is probably due to the initiation of micro cracking in the concrete.

iv) **Path Length:** The path length should be long enough to be significantly not influenced by the heterogeneous nature of concrete.

v) **Shape and Size of Specimen:** The velocity of short pulses of vibrations is independent of the shape and size of specimen in which they travel unless its lateral dimension is less than a certain minimum value. Below these values, the pulse velocity reduce is appreciable.

vi) **Reinforcement:** The pulse velocity measured in a reinforced concrete in the vicinity of reinforcing bars is usually higher than the plain concrete of the same composition. This is because the pulse velocity in the steel is 1.2 to 1.9 times the velocity in the plain concrete and under certain conditions, the first pulse to arrive at receiving transducer travels partly in concrete and partly in concrete. Wherever possible, measurements should be made in such a way that steel does not lie in the path of pulse. Correction factors should be applied if measurements are taken in the proximity of reinforcing bars.

Effect of Porosity, Permeability and Water Content on UPV

Zoubeir et. al. (2006) determined correlations between ultrasonic pulse velocity (UPV), porosity and permeability. The material investigated consists in seven mortar mixtures with water /cement ratio varying from 0.3 to 0.6. In addition, the samples were either dry, fully or partially saturated with water. Mortar was chosen instead of concrete, first, to limit excessive attenuation of ultrasonic waves due to scattering by large grains, and second, because mostly smaller grains are present in the first millimeters of the concrete cover.

The samples are cylinders of diameter 37 and 10 mm height. The thickness was chosen to be small enough so as to allow transmission of the ultrasonic wave with initial central frequency of 0.5 MHz.

Fig 2.11 displays the variation of longitudinal and shear wave velocity versus porosity, for dry, partially and fully saturated samples. It can be noticed that velocity is affected by both porosity and water content. For a given value of water content, a significant decrease of velocity with increasing porosity is observed for both waves.

They concluded that Pulse velocity decreases with porosity and permeability, and it increases with water content. Shear wave velocity is about half of the longitudinal wave velocity and seems to be less sensitive to the water content.
Yaman et. al. (2002) also confirmed velocity variation between the dry and the saturated state is due to the change of pore shape with moisture ingress into the material. They proposed a model which predicts a linear relationship between UPV, porosity and permeability.

Hernandez et. al. (2006) observed that an increase in porosity causes a decrease in the ultrasonic velocity and that an increase in the volume fraction or elastic constant of sand results in the opposite effect. To validate and contrast the predictions of the micromechanical model, destructive (porosity and density) and nondestructive tests (ultrasonic velocity measurements) were conducted on mortar samples with varying degrees of porosity, determined by the water/cement ratio of the sample, cement type and volume fraction of sand.

The application of the model of three phases to mortar samples suggests that an increase in water/cement ratio results in a reduction in the ultrasonic velocity, while an increase in the compressive strength of cement and the volume fraction of sand increases the ultrasonic velocity.

Effect of Compressive Strength on UPV

Demirboga et. al. (2004) evaluate the ultrasonic pulse velocity (UPV) and compressive strength of concrete with mineral admixtures. The relationship between UPV and compressive strength was exponential for Fly ash (FA), Blast Furnace Slag (BFS) and Fly ash+ Blast furnace slag. However, constants were different for each mineral admixture and each level replacement of Portland cement.

A determination coefficient (R^2) of 0.96 indicates a very good exponential relationship between UPV and compressive strength as shown in Fig 2.12, 2.13, 2.14.
Matusinovi et. al. (2004) prepared Calcium aluminate cement (CAC) mortars which were tested by nondestructive ultrasonic measurement in the through-transmission mode and compressive strength measurements. The detected profile of ultrasonic signal was fitted

as a sine wave modulated with the Gauss function. The linear relationship between compressive strength and the product of the amplitude and angular frequency of the signal was established.

Effect of Admixtures on UPV

Virendra et al. (2000) studied the development of pulse velocity at 7, 28 and 56 days in fly ash concrete mixes. The study shows a gradual increase in the pulse velocity with advancing age of the specimen irrespective of the percentage of fly ash content. Fig 2.15 shows that the velocity will decrease with increase of the percentage of fly ash content in the concrete mix. They concluded that the ultrasonic pulse velocity very much depends on the density of concrete. In case of high volume fly ash the density is slightly lower due to the presence of lighter particles of fly ash which replace heavier cement particles. Thus small decrease in ultrasonic pulse velocity is observed in case of fly ash concrete. At the age of 56 days, the structure of fly ash concrete becomes denser due to pozzolanic reaction and therefore shows increase in the pulse velocity.

Demirboga et. al. (2004) evaluates the ultrasonic pulse velocity and compressive strength of concrete with mineral admixtures. Ultrasonic pulse velocity (UPV) was determined at the 3, 7, 28 and 120-day curing period. UPV were very low for all the levels of mineral admixtures at an early age of curing, especially for samples containing FA. However, with the increase of curing period UPV of all the samples increased.

UPV values increased with the increasing curing period for fly ash (FA) samples. Maximum reductions occurred for 70% replacement of FA. The UPV of BFS for 3, 7, 28 and 120 days is shown in Fig. 2.16. UPV changed between 3330 and 4060 m/s at the 3-day curing period. Fifty percent, 60% and 70% BFS replacement for Portland cement were lower than that of control sample, but with the increasing curing period, the reduction due to BFS in UPV decreased. UPV values decreased with increase of BFS. However, after about the 28th day curing period, the UPV reached a certain value and thereafter increased only slightly. The UPV of FA+ BFS for 3, 7, 28 and 120 days is shown in Fig. 2.17. UPV values decreased with increasing FA+ BFS. With the increasing curing period, the reduction due to FA + BFS in UPV decreased, and at the 120-day curing period, UPV values of FA+ BFS was similar. At the 3-day curing period, UPV values were higher than those of FA and BFS separately. For the other curing periods, there was no significant gap in the UPV values of concretes made up of BFS and FA+ BFS.

Table 2.1: Proportions of the Concrete Mix *(Sun et. al., 2002)*

Series	w/c	V_f (%)	Cement (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m3)
C40NPC	0.44	0	409	180	658	1169
C60NPC	0.32	0	440	142	666	1237
C80NPC	0.26	0	477	124	622	1262

Table 2.2: Visual Grading of Specimens *(according to ASTM C 672)*

Grade	Condition of Surface
0	No scaling
1	Very slight scaling (1/8 in.) Depth maximum, no coarse aggregate visible
2	Slight to moderate scaling
3	Moderate scaling (some coarse aggregate visible)
4	Moderate to severe scaling
5	Severe scaling (coarse aggregate visible over the entire surface)

Table 2.3: Salt Analysis *(Mc Donald And Perenchio, 1997)*

Constituent	Proprietary Salt	Rock Salt
Water soluble orthophosphate, calculated as PO_4	0.072	< 0.001
Water soluble phosphates, calculated as PO_4	0.091	0.001
Total phosphate, calculated as PO_4	0.479	< 0.001

Table 2.4: Constituent of Proprietary Salt *(Mc Donald And Perenchio, 1997)*

Constituent	Percent by Weight on Dry Basis
Sodium	34.09
Chloride	53.97
Potassium	0.02
Magnesium	1.38
Calcium	0.3
Sulfate	1.07

Table 2.5: Composition of Various Mixes (*Trinder et. al.)*

Type GB80	20% Ground Granulated Blast Furnace Slag 80% General Purpose Cement
Type GP	General Purpose Cement
Type LH	70% Ground Granulated Blast Furnace Slag, 30% General Purpose Cement
Type SR	8% silica fume
Type (MGP)	92% General Purpose Cement

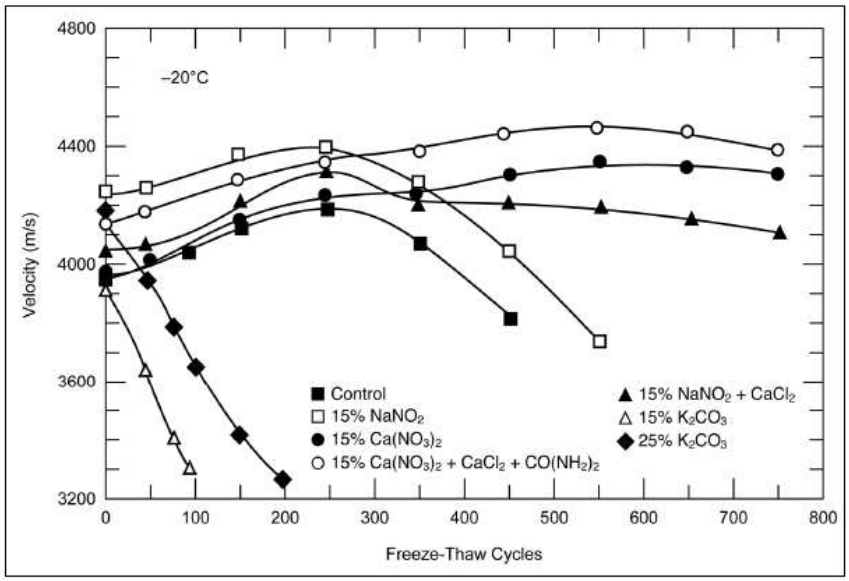


Fig. 2.1 Durability of non-air-entrained concretes made with various admixture concentrations given as percent by cement weight (*Kukko and Koskinen, 1988*)

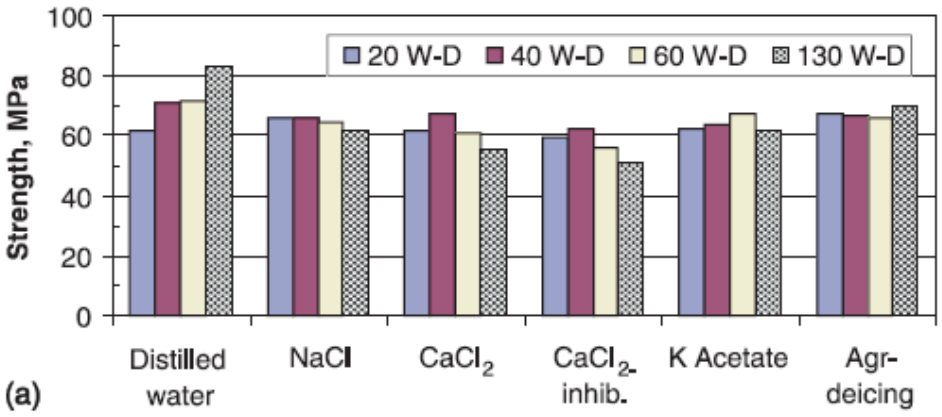


Fig. 2.2 Compressive Strength of Mortar Samples under Wetting Drying Cycling (*Wang et. al., 2006*)

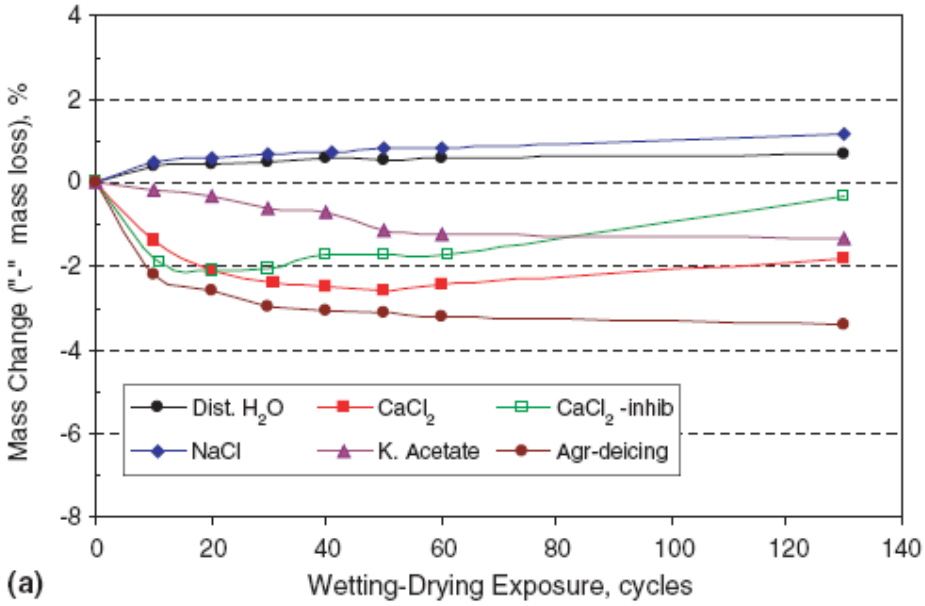
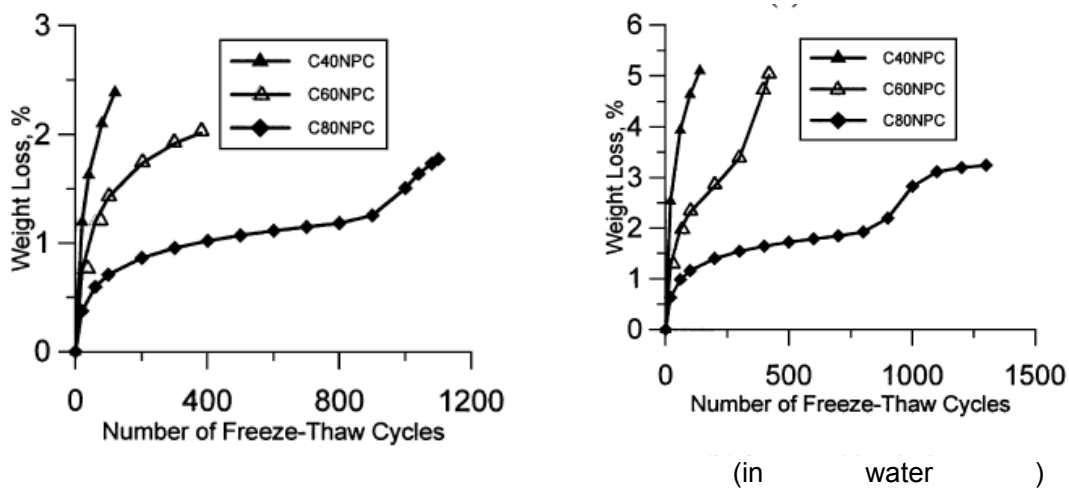
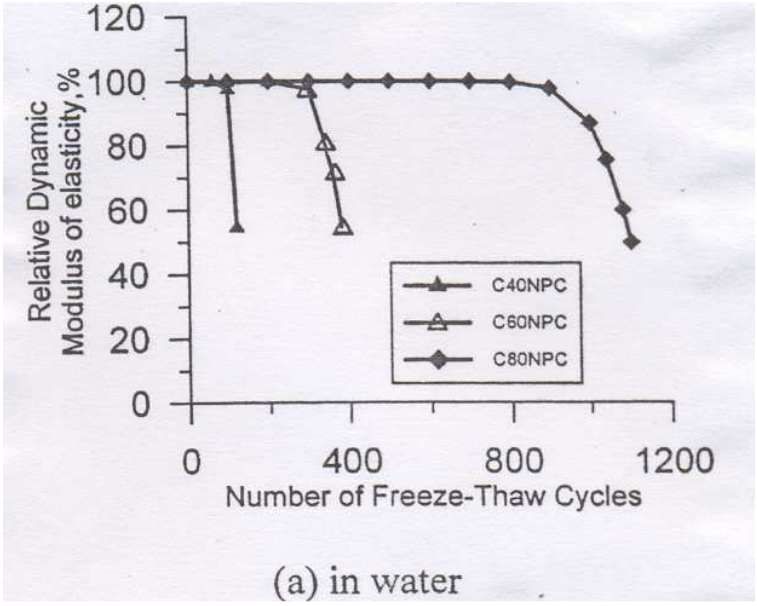


Fig. 2.3 Mass Change of Mortar Samples under Wetting Drying Cycling (*Wang et. al., 2006*)



(in NaCl) (in water)

Fig. 2.4 Weight Losses in Concrete Subjected To Freeze– Thaw Cycling a) in Water and b) in a NaCl Solution *(Sun et. al. ,2002)*



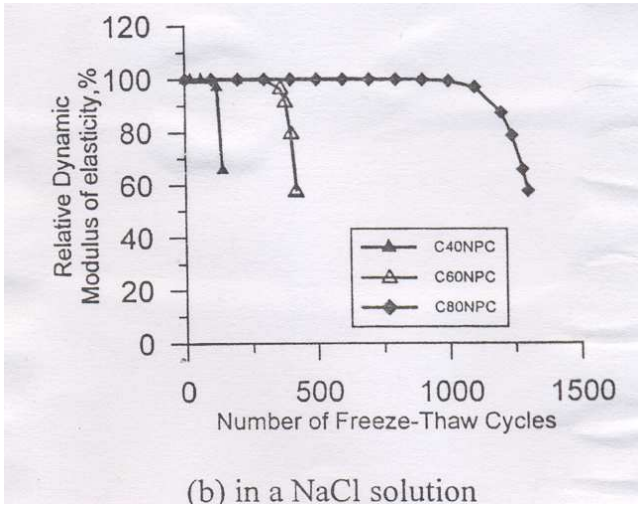


Fig: 2.5 Changes in the Relative Dynamic Modulus of Elasticity of Concrete Subjected to Freeze-Thaw Cycling in Water or in NaCl Solution *(Sun et. al., 2002)*

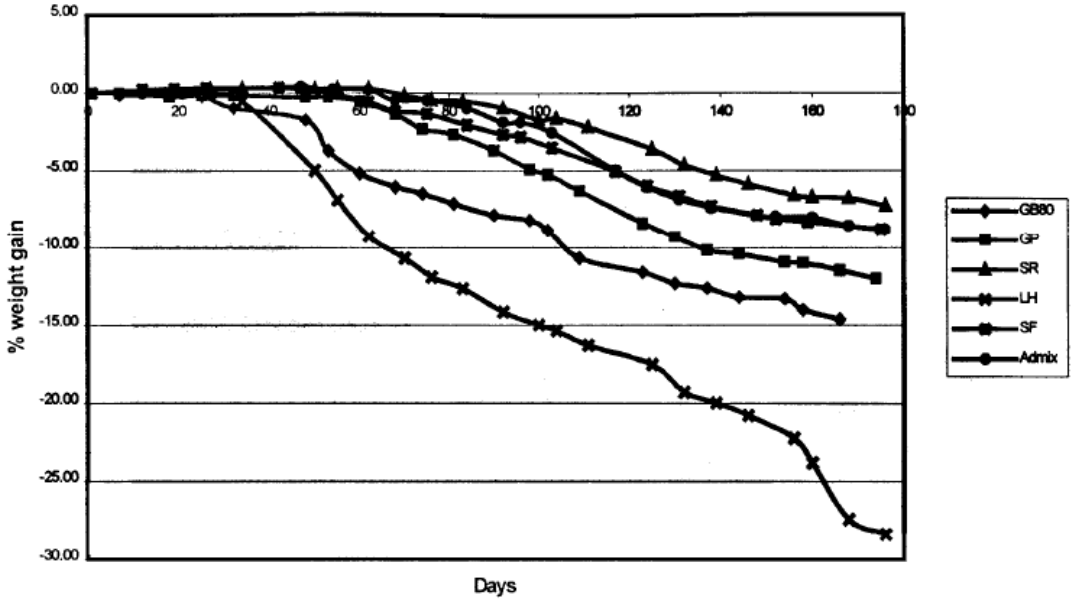


Fig. 2.6 Change in Weight with Time for Samples Exposed to Cycling in Ammonium Sulphate Exposure (*Trinder et. al)*

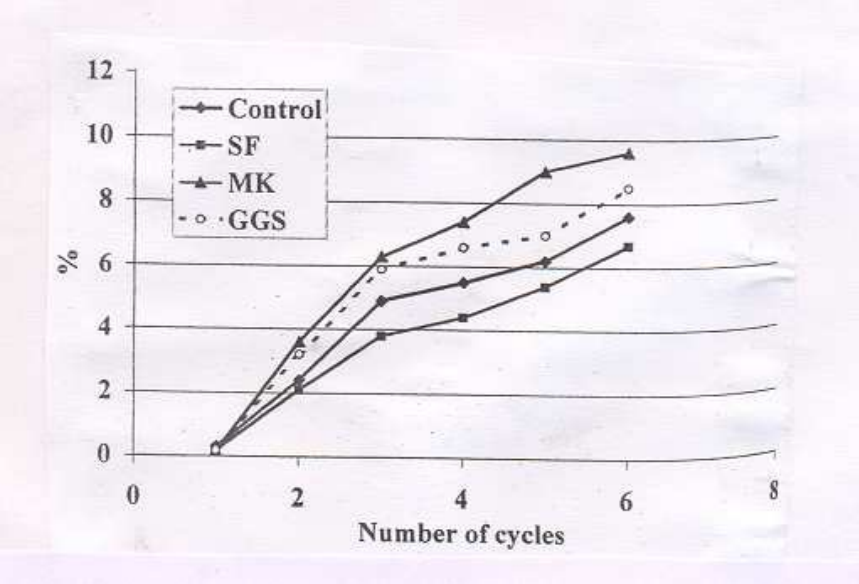


Fig. 2.7 Mass Loss after Six Cycles of Degradation (*Mbessa and Pera, 2001)*

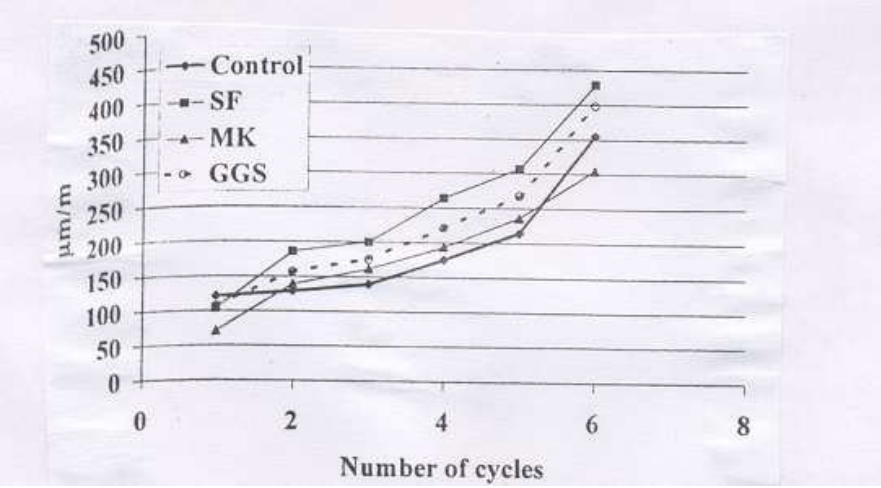


Fig. 2.8 Length Variations (Shrinkage) (*Mbessa and Pera ,2001*)

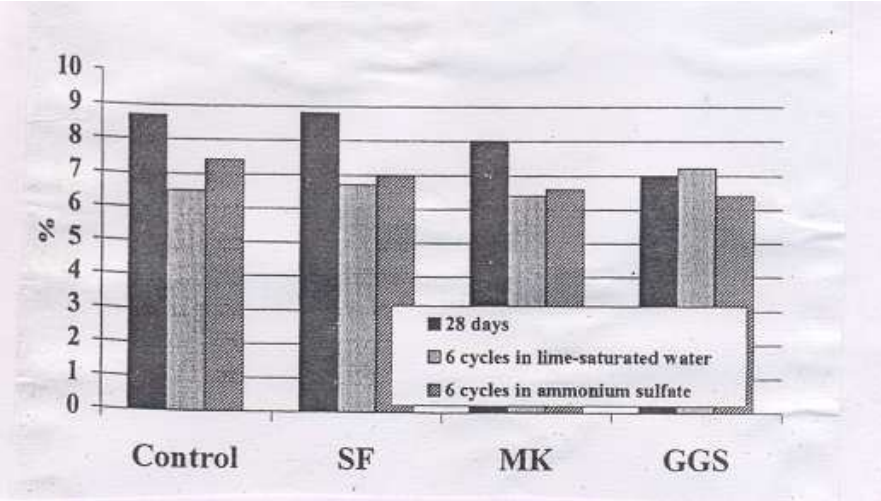
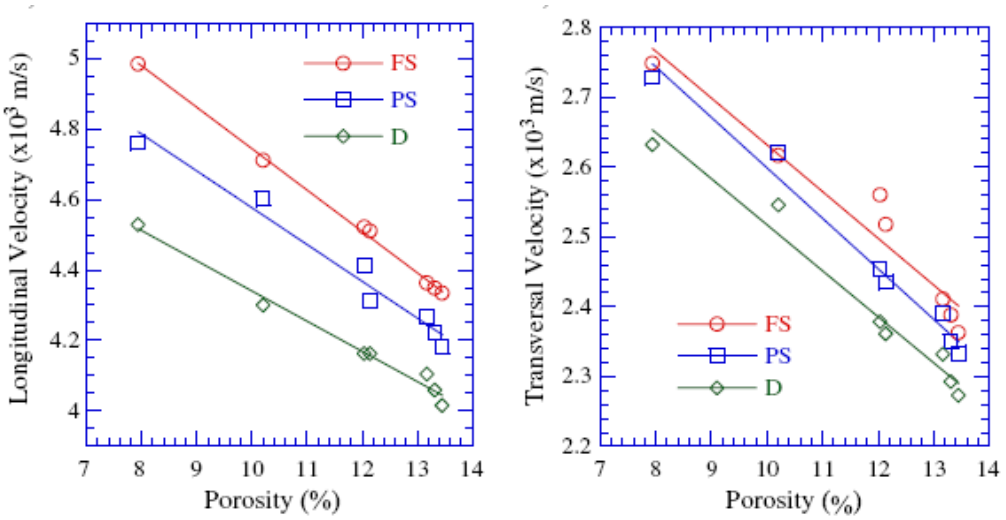


Fig .2.9 Total Porosity of Different Concretes (*Mbessa and Pera ,2001*)



FS – full saturation, PS-partial saturation, D-dry

Fig. 2.11 Variation of Ultrasonic Pulse Velocity versus Porosity. A) Longitudinal Wave; B) Shear Wave (*Zoubeir et. al., 2006)*

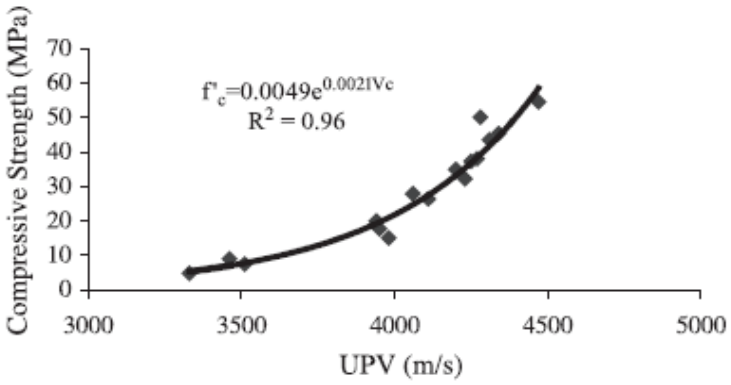


Fig. 2.12 Relationship between Compressive Strength and UPV for Samples Containing BFS (*Demirboga et. al. ,2004)*

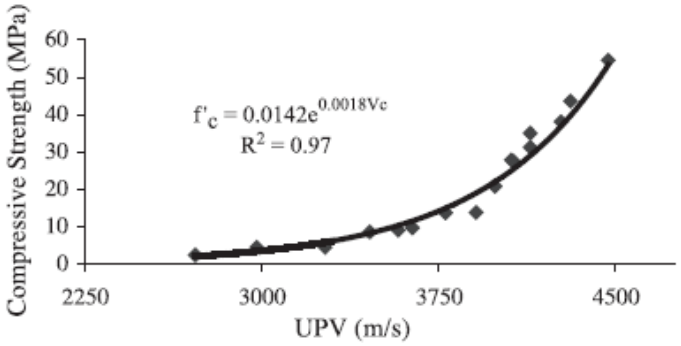


Fig. 2.13 Relationship between Compressive Strength and UPV for Samples Containing FA (*Demirboga et. al., 2004)*

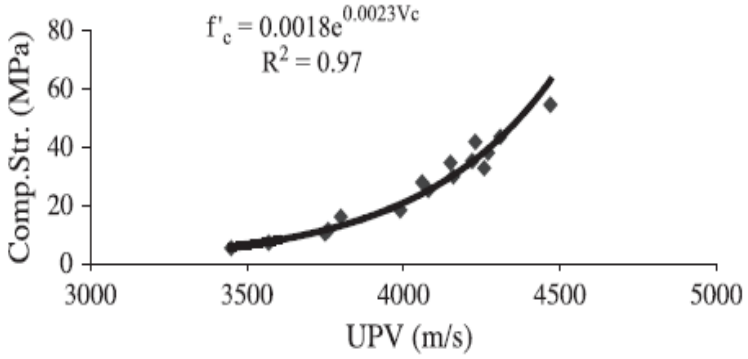


Fig. 2.14 Relationship between Compressive Strength and UPV for Samples Containing FA+ BFS (*Demirboga et. al., 2004)*

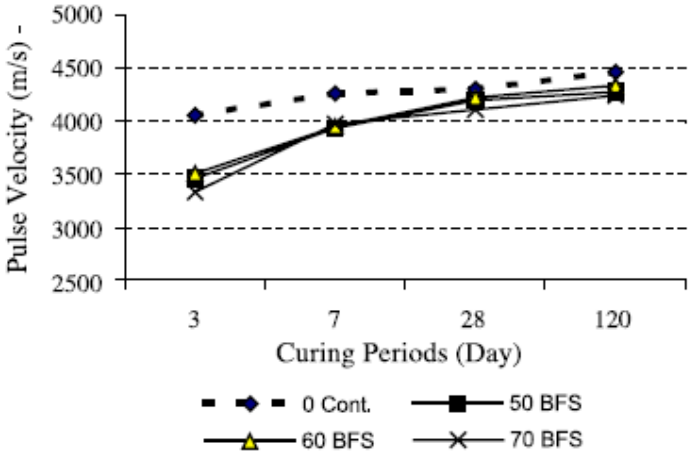


Fig. 2.16 Relationship between UPV (M/S) and Different Curing Periods (Day) for BFS (*Demirboga et. al., 2004)*

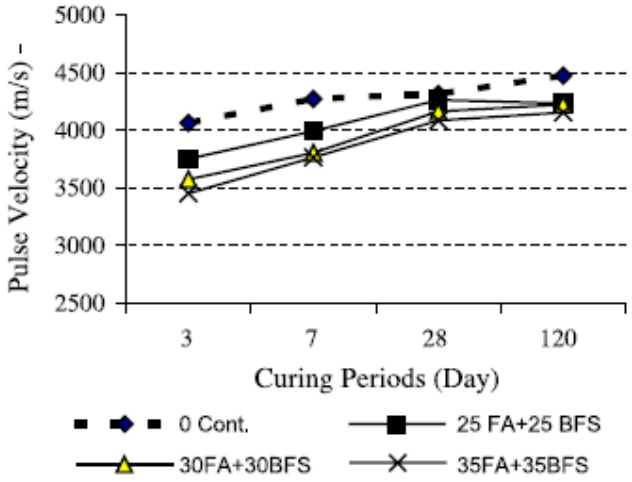


Fig. 2.17 Relationship between UPV (M/S) and Different Curing Periods (Day) for FA+ BFS (*Demirboga et. al., 2004)*

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 GENERAL

The details of various tests carried out on mortar samples are discussed in this chapter. In the present work the effect of metakaolin on the strength and durability of mortar samples cured for a short period of time was studied. Durability was checked in terms of its resistance to wetting–drying cycles and freezing-thawing environment. Mortar mixes containing 5% and 10% metakaolin as a replacement of cement are cast at each water cement ratio i.e. 0.46 and 0.50 and are compared to the control mix. Four salt solutions including sodium chloride with and without corrosion inhibitor and calcium chloride with and without corrosion inhibitor are considered. Mass change, ultrasonic pulse velocity and compressive strength of the paste subjected to the above salt solutions are evaluated.

3.2 MATERIALS

Same sets of materials have been used throughout for casting of cubes for the various mix proportions. Relevant tests in accordance with the Indian Standard codes of practice were conducted to determine the physical properties of the materials used in the study. The details of the materials along with their properties have been presented in the subsequent sections.

(a) Cement

Although the materials that go into cement mortar are essential, cement is very often the most important because it is usually the most delicate link in the chain. The function of cement is not only to bind the sand but also to fill up the voids in between sand and any coarse grained particles to form a compact mass. Although it constitutes only about 15 to 25 per cent of the volume, it is the active portion of binding medium and is the only scientifically controlled ingredient. Any variation in its quantity affects the compressive strength of the concrete mix also.

Pozzolana Portland Cement (PPC) of 43 grade (ACC Suraksha) has been used in the present work. The cement used was fresh and without any lumps. The cement content is fixed to 200kg/m^3 in the present study. Tests were conducted for cement as per *IS: 8112-1989*. The physical properties of cement used in the study are given in Table 3.1.

(b) Fine Aggregates

IS: 383 – 1970 defines the fine aggregate, as the one passing 4.75 mm IS sieve. The fine aggregate is often termed as a sand size aggregate. Locally available river bed sand was used in the present study.

Percentage passing 600 micron sieve = 62.35%

The sand conforms to grading Zone – III as per IS: 383 – 1970.

Sieve analysis was done to calculate the finesses modulus of sand. The results of the same are given in the Table 3.2 and the various other properties tested are tabulated in Table 3.3.

(c) Water

Generally, water that is suitable for drinking is satisfactory for use in concrete. Water from lakes and streams that contain marine life also usually is suitable. When water is obtained from sources mentioned above, no sampling is necessary. When it is suspected that water may contain sewage, mine water, or wastes from industrial plants or canneries, it should not be used unless tests indicate that it is satisfactory. Water from such sources should be avoided since the quality of the water could change due to intermittent discharge of harmful wastes into the stream.

(d) Metakaolin

Metakaolin which is obtained by the calcination of pure or refined kaolinitic clay at a temperature of between 650^0C and 850^0C, followed by grinding to achieve a fineness of 700-900 m^2/kg exhibits high pozzolanicity. When used in concrete it will fill the void

space between cement particles resulting in a more impermeable concrete. The metakaolin used in this study is Metacem of grade 85-C. The properties of metakaolin are given in Table 3.4.

3.3 CASTING OF MORTAR SPECIMENS

At each water to cementitious material ratio, twelve paste samples of size 70.5 x 70.5 x 70.5 mm were casted for each of the salt solution and three of each was tested after 14, 28 and 42 cycles from each of the solutions. For all these mix proportions, required quantities of materials were weighed to an accuracy of 0.5 grams. Cement and fine aggregates were mixed dry to get a uniform colour. The paste samples were prepared by hand mixing on a watertight platform. For mixes containing metakaolin due care was taken to have a uniform dispersion of metakaolin particles. It was blended with cement before mixing it with the remaining ingredients of the mortar mix. Water was added at the end and mixing was done till a uniform and homogeneous mix was achieved.

All the moulds were properly oiled before casting the specimens. To facilitate proper and uniform compaction, a vibration table with fixed revolutions per minute was used for the purpose. The cubes were filled in three layers. Vibrations were stopped as soon as the cement slurry appeared on the top surface of the mould. The specimens were removed from the moulds with care after 24 hours and then cured in a curing tank at the ambient temperature for seven days. The ambient temperature for curing was 27 ± 2^0 C.

3.4 MIX PROPORTIONS

Mortar specimens at two water-cement ratios (0.46 and 0.5) and with various percentage of metakaolin were prepared. These were exposed to different salt solutions under the effect of freezing-thawing cycles and wetting drying cycles. The details of various mix proportions for different replacement levels of cement by metakaolin (0, 5 and 10%) are shown in Table 3.5. Cement to sand ratio in all the mixes used is equal to 1:3.

3.5 SALT SOLUTIONS

The following salt solutions were used to pond the mortar specimens:

- Sodium chloride (3%)
- Sodium chloride (3%) and corrosion inhibitor (1%)
- Calcium chloride (3%)
- Calcium chloride (3%) and corrosion inhibitor (1%)

All the salt solutions were prepared using distilled water. Corrosion inhibitor used is triethanolamine in the present case.

3.6 EXPOSURE CONDITIONS

After seven days of initial curing, the samples were subjected to salt solutions in tin containers.

For wetting drying exposure, samples were immersed in all the four salt solutions explained above in a container and stored at normal room temperature for 16 hrs. Then the samples were taken out of the container and dried in air for 8 hrs. Thus one wetting drying cycles took a total of 24 hrs.

For freezing thawing cycling, samples were immersed in three salt solutions i.e. sodium chloride with corrosion inhibitor and calcium chloride with and without corrosion inhibitor in a container and stored in a freezer at -15 $\pm$ 1.0^0C for 16 hrs. The freezer used in the present study is shown in Plate 3.1. To facilitate thawing, the samples were taken out of the each container and were placed in different large tubs as shown in Plate 3.2 containing respective salt solution at normal room temperature for 8 hrs so that all the frozen samples were completely thawed. Thus one freezing thawing cycle took a total of 24 hrs- 16 hrs in a frozen state and 8 hrs in a thawed state.

The salt solutions in the containers were changed after every 14 cycles for wetting drying samples as well as freezing thawing samples.

3.7 TESTING OF SPECIMENS

The specimens, after the fixed curing period of 7 days were tested for mass change, ultrasonic pulse velocity and compressive strength.

3.7.1 Mass Change

After seven days of initial curing the specimens were taken out of curing tank and were dried in an oven. Then these oven dried samples were placed at the room temperature for some time and then rubbed with sand paper so as to remove all the loose particles on the samples. Then the samples were weighed to the nearest hundredth of a gram. The same process is followed after 14, 28 and 42 cycles under different exposure conditions, where in three specimens of each mix were taken out for the mass measurement.

The mass change of the specimens is determined as follows:

$$\text{Percentage mass change} = \frac{M_2 - M_1}{M_1} \times 100$$

Where M_1= mass (gm) of the specimens before immersing in the salt solution i.e. after seven days of initial curing.

M_2 = mass (gm) of the cleaned specimens after immersing in the salt solution for specified number of cycles.

3.7.2 Ultrasonic Pulse Velocity Test

This non destructive test method determines the velocity of the longitudinal waves. Its determination consists of the measurement of the time taken by the pulse to travel the measured distance. The test equipment consists of an arrangement for generating electronic pulse at regular intervals of time (usually between 10 to 50 s) transmitting these to specimens, receiving and amplifying the pulse, and measuring the time of transit between the transducers. Electronic timing device accurately measures the interval between the onset and reception of the pulse to accuracy better than $\pm$ 1 percent.

In the present study, the transducers used were having natural frequency of 56 kHz. Before starting the test, gel was applied on both the transducers as well as on the opposite faces of mortar specimens. This was done in order to make a proper contact and to reduce the friction between transducer and the mortar surface. The transducers are arranged on the opposite faces of the specimens i.e. direct transmission was used. It is so because the maximum pulse energy is transmitted at right angles to the face of the transmitter. The transit velocity was displayed as a digital readout. The test apparatus is shown in Plate 3.3. This test was performed to check the quality of various mortar samples. Mortar was chosen instead of concrete, first, to limit excessive attenuation of ultrasonic waves due to scattering by large grains, and second, because mostly smaller grains are present in the first millimeters of the concrete cover. The pulse velocity was compared with the velocity given in standard table in IS: 13311 (part-1) in which quality is estimated depending on its pulse velocity. This standard table is shown in Table 3.6.

3.7.3 Compressive Strength Test

The specimens, after the fixed curing period of 7 days and after 14, 28 and 42 cycles under wetting drying and freezing thawing were tested for compressive strength on an automatic compression testing machine (3000kN capacity) as per procedure laid down in *IS 516:1959*. A uniform pace rate of 3.33 kN/sec was maintained through out the testing of each specimen. The test apparatus have been shown in Plate 3.4.

Table 3.1: Results of Physical Properties of Cement

S.No.	Type of Testing	Requirements as per IS: 8112 - 1989	Results of 43-Grade Cement
1.	Fineness (% retain on 90 µm sieve)	Not more than 10%	3.5%
2.	Initial setting time	Not less than 30 min.	48 min.
3.	Final Setting Time	Not more than 600 min.	240 min.
4.	Specific Gravity	-	3.07

Table 3.2: Sieve Analysis of Fine Aggregate

Sieve size	Weight retained (gm)	Weight retained (%)	%age passing	Cumulative %age retained
4.75mm	95	9.5	90.5	9.5
2.36mm	42.5	4.25	86.25	13.75
1.18mm	110.5	11.05	75.2	24.8
600µm	128.5	12.85	62.35	37.65
300µm	308	30.8	31.55	68.45
150µm	281	28.1	3.45	96.55
Pan	34.5	3.45	-	-
SUM (ΣF) =				**250.7**

Fineness Modulus of fine aggregate = ΣF/100 = 250.7/100 = **2.507**

Table 3.3: Results of Tests on Fine Aggregates

S.No.	Property	Results
1.	Water absorption	1.02%
2.	Specific gravity (oven dry basis)	2.68
3.	Moisture content	0.16%
4.	Unit mass (compact)	1.63 kg/m^3
5.	% voids (compact)	20.72%
6.	% voids (loose)	44.65%
7.	Fineness modulus	2.507
8.	Grading zone	III

Table 3.4: Physical Properties of Metakaolin

S.No.	Properties	Results
1.	Brightness	76%
2.	Bulk density	308 gm/l
3.	Oil absorption	56.92 gm/100gm
4.	Moisture	0.23%
5.	Residue on 400 μm	0.6%
6.	pH	6.5

Table 3.5 Details of Mortar Mix Proportions

Mix	Metakaolin (%)	Water to Cementitious ratio	Mix Proportions (kg/m^3)			
			Cement	Metakaolin	Sand	Water
M-I-0	0	0.46	200	0	600	92
M-I-5	5	0.46	190	10	600	92
M-I-10	10	0.46	180	20	600	92
M-II-0	0	0.5	200	0	600	100
M-II-5	5	0.5	190	10	600	100
M-II-10	10	0.5	180	20	600	100

Table 3.6: Quality of Concrete and Cement Mortar Depending on the Pulse Velocity (*IS: 13311 (Part-1) 1992)*

S.No.	Pulse velocity(km/second)	Quality of concrete(Grading)
1.	>4.5	Excellent
2.	3.5 to 4.5	Good
3.	3.0 to 3.5	Medium
4.	Below 3.0	Doubtful

Plate 3.1 Photograph of Freezer used during Freezing Thawing Cycles

Plate 3.2 Photograph of Samples during Thawing Condition

Plate 3.3 Photograph of Ultrasonic Pulse Velocity Test Apparatus

Plate 3.4 Photograph of Automatic Compression Testing Machine (ACTM)

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 GENERAL

In this chapter, the results of the tests carried out on mortar specimens subjected to various salt solutions are presented and they are further discussed. The specimen sizes, material preparations and various salt solutions used are discussed in chapter 3. The test procedures are described in chapter 3.

4.2 DISCUSSION OF RESULTS

Different mixes were designed to see the effect of admixture i.e. metakaolin, water-cement ratio and various salt solutions on the durability of mortar samples which were subjected to wetting drying cycles and freezing thawing cycles. The details are discussed below:

4.3 EFFECT OF METAKAOLIN ON COMPRESSIVE STRENGTH OF MORTAR SAMPLES AFTER 7 DAYS OF INITIAL CURING

Fig 4.1 shows the effect of metakaolin on compressive strength of mortar samples. It is observed in general that with increase in the percentage of metakaolin from 5% to 10% there is marginal increase in the strength compared to the control mix containing 0% metakaolin. However, for the two w/c ratio's used the trend is different.

Control mix containing 0% metakaolin shows strength of 27.633 MPa at water to cementitious material ratio of 0.46. Although with 5% replacement of cement by metakaolin, the strength increases to 30.2 MPa, however with 10% replacement the strength decreases at 0.46 water-cementitious material ratio. This strength is even less than that which is obtained at w/cm ratio of 0.50.

It indicates that the optimum dosage of metakaolin at water to cementitious ratio of 0.46 is around 5%. With the increase in the dosage as the metakaolin particles are finer than cement, they have more surface area and hence require more water for proper hydration to take place. Thus at low water to cementitious material ratio there is a need to add superplasticizer so that due to its repelling effect, the water is properly utilized for wetting of all the particles.

On the contrary, at high water to cementitious material ratio of 0.5 there is increase in strength from 23.9 MPa of control mix having 0% metakaolin to 25 MPa for mix having 5% metakaolin and to 29 MPa when 10% cement is replaced with metakaolin.

This shows that at high water-cement ratio enough water is available for the wetting of metakaolin and hence the percentage of metakaolin can be increased to have better strength.

4.4 EFFECT OF WETTING DRYING CYCLES ON THE COMPRESSIVE STRENGTH OF VARIOUS MIXES

Fig 4.2 to 4.7 shows the effect of wetting drying cycles on the mortar samples exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles and solutions on the mortar samples is explained below.

4.4.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

For the control mix M-I-0, an increase in strength with the increase in the number of wetting drying cycles has been observed as shown in Fig 4.2 in all the mortar samples exposed to various salt solutions except in case of calcium chloride with corrosion inhibitor where the strength decreases after 28 cycles.

In sodium chloride solution, strength increases from 33.9 MPa after 14 cycles to 41 MPa at 42 cycles. The strength at 28 cycles is almost same to the strength at 42 cycles. This indicates that due to low water-cementitious material ratio, the paste has less pore volume i.e. its permeability is less to absorb salt ions. Cement hydration continues with less effect of salt solution on it. In sodium chloride and corrosion inhibitor (triethaonolamine) solution, same trend was observed as in sodium chloride alone, however the strength increase is higher at higher cycles. The strength increases from 32.8 MPa after 14 cycles to 43 MPa after 28 cycles and then it becomes 47MPa after 42 cycles. This shows that corrosion inhibitor further reduces the damaging effect of salt on the mortar samples. The possible reason could be that ions present in the corrosion inhibitor react with the salt ions and form a protective layer around mortar samples which prevent salt ions not the water to enter into the pores of cement paste till the hydration of cement gets completed. In calcium chloride solution strength increases from 33.6 MPa after 14 cycles to 44 MPa after 42 cycles which is higher than the trend shown for the sodium chloride solution. This indicates that due to low water-cementitious material ratio, the paste has less pore volume i.e. its permeability is less to absorb salt ions. Cement hydration continues with less effect of salt solution on it. However, in calcium chloride and corrosion inhibitor (triethaonolamine) solution, different trend was observed. The strength increases from 31.5 MPa after 14 cycles to 36.1MPa after 28 cycles and thereafter it decreases to 33 MPa after 42 cycles. The possible reason could be that corrosion inhibitor is not compatible with the calcium ions and hence not effective in controlling the damaging effect of salt on the mortar samples. It can be concluded that the effect of corrosion inhibitor depend on the salt type (cations in the salt) used. Like in the present study triethanolamine gave good results with sodium ions but not with calcium ions.

Fig 4.3 shows the effect of wetting drying cycles on the samples having 5% metakaolin. After seven days of curing the M-I-5 mortar samples with 5% metakaolin shows 30.2 MPa strength which is quite high compared to its control mix. But after 14 cycles of wetting and drying of decrease in strength was observed in all the solutions. Then after 28 cycles and 42 cycles a paste samples exposed to various solutions show comparable strength. In sodium chloride solution strength at 14 cycles decrease to 28 MPa as compared to the strength of 30.2 MPa at 7 days of initial curing. This decrease in strength could be due to the fact that though metakaolin is finer in size than cement particles and it fills up all the pores in the mortar specimen but when these samples are subjected to wetting drying cycles then during the drying stage, the outer environment has lesser water as compared to the inner environment so the steep gradient of water inside to outside develops. However, as the pores are very small and are not connected so the water will not be able to leach out of the mortar samples. Due to this pressure gradient, microcracks are formed that reduces the strength. Similar trend was observed in mortar samples exposed to sodium chloride and corrosion inhibitor solution as shown in Fig 4.3. The strength after 14, 28, 42 cycles are almost same as that of samples exposed to sodium chloride solution. This indicates that the addition of corrosion inhibitor along with metakaolin has not any advancing or retarding effect on the mortar samples. Even the mortar samples exposed to calcium chloride shows similar trend as above. The strength after 14, 28, 42 cycles are almost same as that of samples exposed to sodium chloride solution. This indicates that the action of metakaolin is same for sodium chloride salt as well as calcium chloride salt. Though the cations (Na^{+}, Ca^{++}) are different but metakaolin is able to resist their effects and maintain its strength. Even with the addition of corrosion inhibitor in calcium chloride mortar samples show almost similar strength at all the cycles of wetting and drying compared to samples in calcium chloride alone. This indicates that although the corrosion inhibitor was not compatible with calcium chloride, but due to the addition of metakaolin the negative effect of compatibility is arrested.

Fig 4.4 shows the effect of wetting drying cycles on the samples having 10% metakaolin. From the M-I-10 mortar samples containing 10% metakaolin exposed to sodium chloride solution tested after different number of cycles of wetting and drying, it is observed that there is decrease of strength from 25.1 MPa after 14 cycles to 24.1 MPa after 28 cycles. The continuous decrease in the strength can be due to two reasons. Firstly, the finer particle size of metakaolin fills the pores but pressure gradient is developed due to alternate cycles of wetting and drying. This pressure gradient leads to the development of microcracks in the mortar samples and hence its strength decreases. Secondly, due to the fineness of metakaolin particles enough water is not available for the hydration

reaction of cement, so secondary gel which is finer than primary CSH gel has not been formed. Even water is not available for the primary gel to form. It indicates that higher percentage of metakaolin retard the hydration reaction. But the hydration reaction does not stop as is indicated by the increase in strength after 42 cycles in all the cases. When samples exposed to calcium chloride solution are tested after different number of cycles of wetting and drying, it is observed that there is decrease of strength from 25.3 MPa after 14 cycles to 24 MPa after 28 cycles. Then after 42 cycles there is a considerable increase in the strength to 31.9 MPa. This trend is same is observed in case of sodium chloride solution. So it can be said that the effect of metakaolin when added at high dose is also independent of the cations present in the salt solutions. However, when corrosion inhibitor is added along with sodium chloride, an almost same strength was observed at 14, 28 and 42 cycles. This strength is almost comparable to that of strength after 7 days of initial curing. The possible reason for no change in strength is the formation of a protective layer around the specimen by triethanolamine that does not allow the salt ions to penetrate in the capillary pores of paste and hence helps in controlling the further loss of strength. On the other hand, due to the formation of protective layer even water is not available for proper hydration and hence there is no increase in strength as well. Almost similar trend is shown by the corrosion inhibitor in calcium chloride solution.

This indicates that with the increase in the percentage of metakaolin all the mortar specimens exposed to aggressive environment show decrease in the compressive strength. Highest gain of strength even with the increase in wetting drying cycles can be observed in control mixes (M-I-0) only. Even the addition of inhibitor in sodium chloride increases the strength of control mix but not of metakaolin mixes indicating that inhibitor is not compatible with the admixture used. On the other hand the addition of inhibitor in calcium chloride shows deteriorating effect and even decreases the strength of the control mix, but no change in strength was observed in metakaolin mixes.

4.4.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

Fig 4.5 shows the effect of wetting drying cycles on the control samples. M-II-0 mixes exposed to various salt solutions shows an increase in strength upto 28 cycles. Afterwards, the strength decreases regardless of the type of salt to which the specimen is subjected to. This indicates that due to high water-cementitious material ratio, enough water is available for the hydration reaction of cement and it continues to gain strength. But after the hydration is complete, the effect of salts and wetting drying becomes prominent. It clearly shows that higher water cementitious material ratio is detrimental to

concrete materials when it is exposed to aggressive environments. Therefore, water cementitious material ratio must be controlled in order to get better efficiency.

If the effect of salt type on the strength is compared it is clearly highlighted in the Fig 4.5 that calcium chloride is more detrimental than sodium chloride. The addition of corrosion inhibitor to sodium chloride, further arrests the deterioration and hence the strength does not decreases but attains a stable value. On the other hand addition of corrosion inhibitor to calcium chloride further accelerates the deterioration.

Fig 4.6 shows the effect of wetting drying cycles on the samples containing 5% metakaolin. In case of M-II-5 mixes, with the addition of metakaolin when the specimens are subjected to wetting drying solutions and aggressive chemicals, the strength increases continuously which indicates that the addition of metakaolin at high water to cementitious ratio compensates for the deterioration caused by the salts and the wetting drying cycles. The continuous increase of strength can be due to two reasons. Firstly, the finer particle size of metakaolin which fills the pores and make the mortar samples dense and cohesive. Secondly, as enough water is available for the hydration reaction of cement, so secondary gel due to the pozzolanic reaction has been formed. As it is finer than primary CSH gel so it makes the mortar samples dense and does not allow the salt ions to penetrate. Therefore, metakaolin is effective mineral admixture when the structures are subjected to aggressive environments. Even no change in trend was observed with the addition of corrosion inhibitor in both calcium chloride as well as sodium chloride solutions.

Fig 4.7 shows the effect of wetting drying cycles on the samples having 10% metakaolin. For mortar mixes M-II-10 containing 10% metakaolin when exposed to sodium chloride solution are tested after different number of cycles of wetting and drying, an increase of strength from 31.3 MPa after 14 cycles to 38.7 MPa after 28 cycles and then to 40 MPa after 42 cycles is observed. However, when corrosion inhibitor is added along with sodium chloride solution, an almost same strength was observed after 14, 28 and 42 cycles. But this strength is less compared to the strength of the mortar mixes exposed to sodium chloride only. Similar trend was observed on adding corrosion inhibitor to calcium chloride. In case of calcium chloride solution a continuous decrease of strength from 35.8 MPa after 14 cycles to 28.8 MPa after 42 cycles is observed.

This indicates that although initial strength of mortar specimens containing 10% metakaolin at water to cementitious material ratio of 0.5 is more than the corresponding strength at 5% addition of metakaolin, but when the mixes are subjected to wetting and

drying cycles, the mix with 5% metakaolin performs better than the mix with 10% metakaolin. Therefore even at water to cementitious ratio of 0.5, 5% metakaolin is the optimum dosage.

4.5 EFFECT OF WETTING DRYING CYCLES ON THE MASS CHANGE OF VARIOUS MIXES

Fig 4.8 to 4.13 shows the effect of wetting drying cycles on the mass change of mortar samples having 5% metakaolin and exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles on the mortar samples is explained below.

4.5.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

For the control mix M-I-0, with the increase in the number of wetting drying cycles, gain in mass of all the mortar samples exposed to various salt solutions is observed except for mortar samples exposed to corrosion inhibitor and calcium chloride solution. The results are shown in Fig 4.8.

In sodium chloride and calcium chloride solutions the continuous gain in mass by the mortar samples indicates that due to short initial curing period of 7 days, cement in the paste continue to hydrate. The continuous cement hydration consumes pore fluid, leaving the samples in an unsaturated state. It also produces more CSH gel, which has large surface area to absorb water. The samples therefore continue to gain mass until maximum saturation is reached. But when corrosion inhibitor was added to NaCl, gain in mass was more compared to samples exposed to NaCl only. The gain in mass in all the above solutions is also due to deposition of salt in the pores of the mortar samples as shown in the plate. However when corrosion inhibitor (triethaonolamine) is added to calcium chloride solution, continuous decrease in mass was observed with increase in the number of wetting and drying cycles. The possible reason could be that corrosion inhibitor is not compatible with the calcium ions and hence not effective in controlling the damaging effect of salt on the mortar samples. So due to scaling damage some material may fall from the samples which leads to decrease in the mass.

M-I-5 mixes exposed to sodium chloride with and without inhibitor show a large decrease in the mass i.e. 0.8% and 1.7% respectively after 14 cycles as shown in Fig 4.9 but this loss get compensated with increase in the number of cycles due to the continuous hydration reaction. After 28 cycles the hydrations gets completed so it does not absorb water and hence the mass decreases during 28-42 cycles. In case of calcium chloride with and without inhibitor, continuous increase in mass was observed during 14-42 cycles indicating that the salt deposition might take place which fills up the pores and

increases its mass. It is also observed from Plate 4.3 that after 28 cycles the no. of pores on the surface decreases. It may be metakaolin which fills up all the seen pores. But after 42 cycles some deterioration can be seen. Even the material loss is observed in case when inhibitor is added to NaCl.

When M-I-10 mortar samples containing 10% metakaolin exposed to various solutions is tested, it is observed that continuous mass loss occurs with increase in the number wetting and drying cycles. This may be due to the extreme fineness of metakaolin particles that fills the micropores between cement and sand particles. When such samples are subjected to wetting drying cycles, steep pressure gradient develop during drying cycles but water is not allowed to transfer from inside as no interconnected pores are present. Due to this pressure gradient microcracks develop. These microcracks deteriorate the specimens and hence the mass decreases. The addition of corrosion inhibitor shows the same results as shown by the salts alone. The same is also observed from Plate 4.4 that maximum deterioration in the form of loss of material from samples was observed after 28 cycles.

Thus it can be concluded that at low water to cementitious material ratio with the increase in the percentage of metakaolin the mass loss also increases. This is attributed to pressure gradient leading to scaling damage and subsequent mass loss.

4.5.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

At higher water to cementitious material ratio, M-II-0 mortar samples exposed to sodium chloride shows continuous gain in mass as shown in Fig 4.11. The reason for this gain is same as explained earlier. But the gain in mass is less as compared to the mixes at water to cementitious material ratio of 0.46. Here, in contrast, the mortar samples that were exposed to calcium chloride show a continuous mass loss with increase in the wetting drying cycles. This indicates that the type of cation also affect the nature of deterioration. Even the addition of corrosion inhibitor in calcium chloride increases the mass loss with time. This indicates that the porosity and hence the deterioration of mortar samples increases at high water to cementitious material ratio. The large number of pores on the surface of mortar samples is also observed in Plate 4.2.

Fig 4.12 shows that when 5% cement is replaced with metakaolin, the M-II-5 mortar samples show a continuous gain in mass with increase in the number of wetting drying cycles. After 28 cycles mass change almost becomes constant. It is due to the availability of enough water at higher water cementitious material ratio for hydration reaction and also finer particle size of metakaolin which increases the cohesiveness of

paste and hence increases the mass of the samples. Also addition of corrosion inhibitor in both the salts shows same results as shown by the salts independently, thus proving that metakaolin is an effective mineral admixture to be used in structures subjected to aggressive environments. From Plate 4.5, it is observed that diameter of pores is maximum after 14 cycles but as the number of cycles increases the diameter of pores decrease and almost same size pores are observed after 28 and 42 cycles.

Fig 4.13 shows the effect of wetting drying cycles on M-II-10 samples containing 10% metakaolin. When these samples are exposed to sodium chloride solution, a continuous mass gain is observed after different number of cycles of wetting and drying. But this mass gain is less when corrosion inhibitor is added to NaCl solution. This indicates that deteriorating effect of Na^+ ions on the samples having metakaolin reduces drastically. Even due to the continuous hydration reaction of cement, mortar samples continue to gain mass with time. Similar trend is observed for the samples exposed to calcium chloride salt with and without corrosion inhibitor. Thus it can be concluded that at higher water cementitious material ratio, high dose of metakaolin is effective in controlling the deterioration of samples exposed to various aggressive solutions. The visual changes in mortar samples exposed to aggressive environment are shown in Plate 4.6.

Thus, in control mixes a continuous mass loss is observed with increasing wetting drying cycles. But with the addition of metakaolin, the drastic mass loss after 14 cycles is compensated by the pozzolanic action of the metakaolin as well as the deposition of salts in the pores of the samples. Even the salt deposition takes place on the surface as can be observed in Plates 4.4 to 4.6.

4.6 EFFECT OF WETTING DRYING CYCLES ON THE ULTRASONIC PULSE VELOCITY OF VARIOUS MIXES

Fig 4.14 to 4.19 shows the effect of wetting drying cycles on the ultrasonic pulse velocity of mortar samples and exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles on the mortar samples is explained below.

4.6.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

Fig 4.14 shows the effect of wetting drying cycles on the pulse velocity of control mixes. In case of control mix M-I-0, paste samples immersed in sodium chloride solution shows almost constant ultrasonic pulse velocity of around 4000 m/s after 14 and 28 cycles but a slight decrease after 42 cycles but still it remains more than 3500 m/s, indicating that overall quality of mortar sample is good as per IS: 13311 (part-1). This trend indicates that control mix itself was able to resist alternating wetting drying cycles and kept its hydration reaction at the same rate and decreases its possibility of deterioration due to

salt ions attack. Similar trend is observed in the sodium chloride with corrosion inhibitor solution. However, for samples immersed in $CaCl_2$, initially an increase in velocity is observed but with increasing number of wetting drying cycles the velocity becomes constant whereas in calcium chloride and corrosion inhibitor (triethaonolamine) solution, an increase in the velocity is observed upto 28 cycles and a slight decrease is observed after 42 cycles.

When M-I-5 mortar mixes are immersed in sodium chloride solution, the pulse velocity increases from 3580 m/s after 14 cycles to 3846.67 m/s after 28 cycles as shown in Fig 4.15. But after 42 cycles the velocity decreases to 3800 m/s. However, this decrease is very marginal indicating good quality of mortar samples is maintained even with the increase of wetting drying cycles. A similar trend is observed in NaCl and inhibitor solution as well as for samples immersed in $CaCl_2$ solution. The addition of inhibitor in $CaCl_2$ shows a continuous increase in the pulse velocity with increasing number of cycles but the velocity after 42 cycles is less in all the cases when compared to the control mix.

Mortar mixes (M-I-10) exposed to sodium chloride solution shows that there is decrease of velocity from 3480 m/s after 14 cycles to 3370 m/s after 28 cycles as shown in Fig 4.16. Then after 28 cycles it almost becomes constant. This indicates that as enough water is not available for the hydration reaction of cement and for the pozzolanic reaction of metakaolin. Hence its quality decreases from ‘good’ to ‘medium’ range. The addition of corrosion inhibitor in NaCl helps in preventing the deterioration of samples. This is due to the formation of a protective layer of triethanolamine around mortar samples which prevent the salt ions to penetrate in the capillary pores of paste and helps in controlling its deterioration. Samples exposed to calcium chloride with and without corrosion inhibitor shows similar results as is observed from the samples immersed in sodium chloride with corrosion inhibitor.

Thus it can be observed that the quality of mortar samples without metakaolin is better as compared to metakaolin mixes. With the increase in the percentage of metakaolin the pulse velocity decreases. This indicates the formation of microcracks and scaling damage of mortar samples. Due to low water cementitious material ratio, metakaolin was unable to show its full effect and hence cracks were developed which diffract the ultrasonic pulse wave and hence it took more time to reach the receiving transducer. Thus it increases the transit time and hence pulse velocity decreases.

4.6.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

In case of M-II-0 mixes as shown in Fig 4.17, first an increase and then continuous decrease in pulse velocity is observed for all the mortar samples exposed to various salt solutions with increasing number of cycles. In sodium chloride solution, the velocity increases from 3980 m/s after 14 cycles to 4066.67 m/s after 28 cycles, thereafter it decreases. Even in calcium chloride solution, the velocity increases from 3956.67 m/s after 14 cycles to 3990 m/s after 28 cycles. After 42 cycles it decreases to 3860 m/s. The possible reason for this can be that due to high water-cementitious material ratio and alternate cycles of wetting and drying pressure gradient is developed which deteriorates the samples after 42 cycles. Hence the development of microcracks reduces the pulse velocity. The small microcracks are also seen in Plate 4.2. With the addition of corrosion inhibitor (triethanolamine) solution, decrease in quality is more as compared to the solutions without inhibitor in both the salt solutions. This shows that there is no effect of corrosion inhibitor in further reducing the damaging effect of salts on the mortar samples at higher water to cementitious material ratio.

Fig 4.14 shows the effect of wetting drying cycles on the pulse velocity of samples containing 5% metakaolin. In case of M-II-5 mortar mixes the pulse velocity first increases with increase in number of wetting drying cycles and then it becomes constant for all the solutions except $CaCl_2$ and inhibitor solution indicating that the addition of metakaolin helps in controlling the cracks which are developed due to the pressure gradient. It makes the cement paste cohesive and dense by filling its pores as can be observed from its rise in pulse velocity. But a decrease in velocity was observed after 42 cycles in case of corrosion inhibitor and calcium chloride solution. The possible reason could be that corrosion inhibitor is not compatible with the calcium ions and hence not effective in controlling the damaging effect of salt on the mortar samples as is also observed from the other performed tests.

M-II-10 mixes indicates that even with the further increase in the percentage of metakaolin a similar trend is observed as shown by 5% metakaolin mix. But the final pulse velocity attained after 42 cycles of wetting and drying is less as compared to the mix having low dosage of metakaolin. This indicates that there is some critical value with which if cement is replaced with metakaolin then mortar mix will show better quality. The mass change of M-II-10 mixes is shown in Fig 4.19.

From the above results it can be concluded that the best quality of mortar samples exposed to aggressive salts under wetting drying cycles is shown by the control mixes only upto 28 cycles. After that deterioration increases and that can be controlled by the addition of low dosage i.e. 5% metakaolin in the mix. Though it can be observed that the

velocity after 42 cycles in 5% mixes and control mixes is almost same but there is a tendency for 5% mixes to show an increasing trend after 42 cycles and it may happen that with further increase in wetting drying cycles the velocity may further increase as compared to the control mixes where a sharp decreasing trend is observed.

4.7 EFFECT OF FREEZING THAWING CYCLES ON THE COMPRESSIVE STRENGTH OF VARIOUS MIXES

Fig 4.20 to 4.31 shows the effect of freezing thawing cycles on the mortar samples exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles on the mortar samples is explained below.

4.7.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

as shown in Fig 4.20, for M-I-0 mortar mixes, with the increase in the number of freezing thawing cycles, an increase in strength is observed for all the mortar samples exposed to various salt solutions. In sodium chloride and triethanolamine solution, strength remains almost constant after 14 and 28 cycles. Thereafter there is increase in the strength after 42 cycles. In calcium chloride solution strength increases to 39.533 MPa after 28 cycles which almost remains constant even after 42 cycles but when corrosion inhibitor (triethaonolamine) solution was added to calcium chloride, the overall strength increases compared to mortars exposed only to $CaCl_2$. So this corrosion inhibitor is effective in controlling the damaging effect of freezing thawing cycles on the mortar samples. This indicates that triehanolamine maintains a high level of saturation in cement paste and significantly increases the resistance of mortar samples to withstand more number of freeze- thaw cycles.

In M-I-5 mortar samples decrease in strength is observed regardless of the type of deicing solutions as shown in Fig 4.21. The overall decrease in strength is 1.32% in sodium chloride with inhibitor, 7.3% in calcium chloride and 17.2% in calcium chloride with inhibitor. The possible reason can be the delayed hydration reaction due to lower temperature during freezing and due to the presence of metakaolin that reacts only when primary hydration has taken place. In samples exposed to calcium chloride, only a decrease in strength after 14 cycles of freeze thaw is observed. The strength after 14, 28, 42 cycles is almost the same. The possible reason is that the salts produce osmotic pressure and cause movement of water toward the top layer of mortar samples where freezing takes place and hydraulic pressure is developed. Due to this hydraulic pressure deterioration of mortar samples take place. With the addition of corrosion inhibitor in

calcium chloride mortar samples, a continuous decrease in the strength at all the cycles of freezing and thawing as compared to samples in calcium chloride alone was observed. This indicates that the addition of this corrosion inhibitor along with metakaolin is not able to control the deterioration caused by Cl^- ions. In sodium chloride and triethanolamine solution, an increase in strength after 14 cycles is observed but with increase in number of cycles the strength decreases and almost become constant after 28 cycles. Thus it indicates that corrosion inhibitor along with sodium chloride helps in delaying the damage caused by Cl- ions and freezing thawing cycles but once the damage starts, is not able to control it.

Fig 4.22 shows the effect of freezing thawing cycles on the samples having 10% metakaolin. M-I-10 mortar samples show similar behavior as shown by 5% metakaolin mortar samples, i.e. overall decrease in strength as compared to the strength at 7 days with the exception of calcium chloride in which the strength actually increased by 21.54%. However the decrease in strength is lower as compared to 5% metakaolin samples. The strength loss is arrested or even reversed in case of calcium chloride due to the combined effect of more number of metakaolin particles in paste and lower water cementitious material ratio. Due to more surface area of metakaolin particles, all the water given to mix was utilized in wetting the surface of particles. No water is available in the pores to freeze and expand during the freezing phase of freezing thawing cycles. So, frost damage could not take place. In sodium chloride with inhibitor solution, the strength decreased a bit due to the obvious reason. Similar behavior is shown by the samples exposed to calcium chloride with corrosion inhibitor solution indicating that at high dosage of metakaolin even the corrosion inhibitor shows the retarding effect on the mortar samples. When samples exposed to calcium chloride solution are tested after different number of freeze thaw cycles, an increase in strength was observed even with the increase in the number of cycles. The samples attain strength of 33.7 MPa after 42 cycles indicating that calcium chloride deicing chemical along with higher dose of metakaolin is highly effective in restraining the freeze thaw damage.

The variation of compressive strength of samples with increasing number of freeze thaw cycles and exposed to various deicing solutions are shown in Fig 4.23 to 4.25.

4.7.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

At water to cementitious material ratio of 0.5, all the specimen under any deicing chemical showed overall loss of strength after 42 cycles of freezing and thawing indicating that the freeze thaw damage is higher at higher water to cementitious material ratio. This is due to the fact that at higher water cementitious material ratio, excessive

water is available in the pores that freezes during freezing phase of the freeze thaw cycles and hence expands to cause frost damage in the form of microcracks.

M-II-0 mortar samples exposed to calcium chloride solution as shown in Fig 4.26 show a continuous increase in strength upto 28 freeze thaw cycles. But after 42 cycles a drastic decrease in strength by 16.72% is observed. A possible reason for this is that due to high water-cementitious material ratio and alternate cycles of freeze thaw, scaling damage reduces the strength after 42 cycles. Even with the addition of corrosion inhibitor (triethaonolamine) in it, a similar trend is observed. But the decrease of strength after 42 cycles is more at 25.24% with the addition of corrosion inhibitor. This indicates that the mortar samples are resistant to the effect of salt solutions upto 28 freeze thaw cycles, and also that calcium chloride helps in delaying the frost damage caused by the freeze thaw cycles but is not able to reduce the extent of same. Similarly when mortar samples are immersed in sodium chloride and triethanolamine solution, around 20% reduction in strength after 42 cycles is observed.

M-II-5 mortar samples containing 5% metakaolin immersed in various salt solutions also show a continuous increase in the strength till 28 cycles and after that strength either becomes constant or decreases a bit. As is observed from Fig 4.27 samples in sodium chloride with corrosion inhibitor solution show an increase in strength with increase in the number of freeze thaw cycles upto 28. But in case of calcium chloride a little decrease in the strength after 42 cycles is observed. With the addition of corrosion inhibitor in $CaCl_2$, this decrease in the strength after 42 cycles is reduced. This indicates that finer metakaolin reduces the capillary pore size for aggressive salt ions to attack. Also, finer metakaolin consumes more water thus leaving behind lesser amount of water in the pores to freeze. So addition of 5% metakaolin and triethanolamine in $CaCl_2$ mortars can effectively withstand the freeze thaw cycles. It can also be inferenced that deteriorating effect of calcium chloride is more as compared to sodium chloride.

When M-II-10 mortar samples containing 10% metakaolin are exposed to various salt solutions under freeze thaw cycling, a decrease in strength is observed in all the mixes except in calcium chloride. This indicates that there is some critical dose of metakaolin which when added can increase the freeze thaw resistance. As can be observed from Fig 4.28 corrosion inhibitor in calcium chloride further enhances the deterioration instead of controlling it. In case of calcium chloride, continuous increase in strength is observed with increase in the number of cycles at high dose of metakaolin upto 28 cycles.

Thus it can be concluded that at high water to cementitious ratio, there is an optimum dosage of metakaolin i.e. 5% at which the deterioration of mortar samples can be controlled in an aggressive environment containing sodium chloride. In case of calcium chloride the frost resistance increases with the increase in the dosage of metakaolin. But the inhibitor in calcium chloride does not show any positive effect and further enhances the frost damage.

The variation of compressive strength of samples with increasing number of freeze thaw cycles and exposed to various deicing solutions are shown in Fig 4.29 to 4.31.

4.8 EFFECT OF FREEZING THAWING CYCLES ON THE MASS CHANGE OF VARIOUS MIXES

Fig 4.32 to 4.37 shows the effect of freeze thaw cycles on the mass change of mortar samples exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles on the mortar samples is explained below.

4.8.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

For the M-I-0 mix, with the increase in the number of freezing thawing cycles, a continuous gain in mass was observed in all the mortar samples exposed to various salt solutions. This trend is almost similar to the mortar samples under wetting drying cycles exposed to various solutions. The variation is shown in Fig 4.32.

This indicates that due to short initial curing period of 7 days, cement in the mortar samples continue to hydrate to produce more CSH gel which occupies the voids and pores in the paste making it dense and compact. This mechanism is responsible for gain in mass by the control mix. Even the salt deposition on the surface of samples may be responsible for the gain in mass, this can be observed in Plate 4.7, no prominent pores or voids are observed on the samples. These pores may get filled with the salt deposits that lead to mass gain.

M-I-5 mortar samples exposed to calcium chloride first show a loss in mass upto 28 cycles then a continuous gain in mass during 28-42 cycles. As shown in Plate 4.9 a considerable amount of micropores are observed on the sample surface which corresponds to sample mass loss. But with increasing number of cycles though the number of pores increases but in these pores salt deposition takes place which leads to gain in mass by samples. Whereas, on the other hand, with addition of corrosion inhibitor in calcium chloride solution a continuous mass loss is observed. This shows that this corrosion inhibitor may not be compatible with calcium chloride and further enhances the deterioration. When samples are exposed to sodium chloride and corrosion inhibitor

solution, no mass change is observed upto 14 cycles as is observed from Fig 4.33. Then during 14-42 cycles a continuous sample mass loss is there indicating that with the addition of metakaolin water demand of paste increases but due to formation of protective layer around the samples water was not able to enter the paste and hence retards the hydration reaction. So the mass gain that could have taken place due to CSH gel formation (both primary and secondary) is not there. On the other hand due to freezing of water in the pores and the formation of microcracks the mass actually decreases.

A continuous loss in mass as shown in Fig 4.34 is also observed in M-I-10 mortar samples immersed in various salt solutions. Initially, after 14 cycles only around 1% mass gain is there but after 42 cycles there is around 3.5% mass loss. Thus, high dosage of metakaolin further increases the water demand but due to low water to cementitious material ratio, cement does not get enough water for the proper hydration reaction.

Thus it can be said that at low water cementitious material ratio with the increase in percentage of metakaolin the mass loss of mortar samples increases. Also only control mixes show gain in mass as compared to metakaolin mixes indicating that as percentage of metakaolin increases the water demand of samples also increases. So it attracts water from the salt solution and when this water freezes during freezing cycles it expands due to the higher volume of frozen ice. This expansion causes stresses in the samples and so during thawing cycle, ice melts and this leads to the development of pores and cracks. Even the scaling damage increases. Hence loss of mass is observed.

4.8.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

M-II-0 mortar samples exposed to calcium chloride solution with and without corrosion inhibitor show a continuous mass gain with increase in number of freeze thaw cycles. The possible reason for this is that due to high water-cementitious material ratio and alternate cycles of freeze thaw, salt deposition, crystal precipitation and fluid absorption occurs in the cracks. But the samples exposed to sodium chloride and corrosion inhibitor show a continuous gain in mass upto 28 cycles and thereafter mass loss is observed. This indicates that corrosion inhibitor can only delay the crystal precipitation which subsequently delays the onset of damage to the samples. However it is not able to reduce ultimate damage. So cement paste disintegration starts after 28 freeze thaw cycles. The results are shown in Fig 4.35.

M-II-5 Mortar samples containing 5% metakaolin immersed in various salt solutions also show a continuous gain in mass upto 28 cycles and thereafter mass loss is observed as shown in Fig 4.36. Samples in sodium chloride with corrosion inhibitor solution show a maximum mass gain of upto 1%. Finally, mass loss of the samples in all the solutions reaches 0.7% at 42 freezing thawing cycles which is almost close to the initial mass. There is a tendency that the rapid mass loss would continue if the freezing thawing cycles are extended. This indicates that at high water to cementitious ratio metakaolin gets enough water for its pozzolanic reaction and lead to the formation of secondary CSH gel which increases its mass.

When M-II-10 mortar samples containing 10% metakaolin are exposed to various salt solutions under freeze thaw cycling, mass loss is observed as shown in Fig 4.37 in all the mixes indicating that frost damage also increases with increase in the dose of metakaolin. Corrosion inhibitor in calcium chloride further enhances this loss instead of controlling it. The deterioration is seen from the surface scaling and the microcracks developed in the mortar samples as shown in Plate 4.12. It is observed that the samples undergo minor degree of scaling at 28 cycles, therefore some mass reduction through physical loss also occurs. But with increasing number of cycles, this mass loss might be offset by imbibed water and possible salt crystallization, thus increasing the mass of samples.

Thus it can be said that at high water to cementitious material ratio, there is some critical dose of metakaolin which can effectively decrease the pressure gradient developed in the samples. Also it is observed that triethanolamine is not favorable to add along with $CaCl_2$ to reduce the frost damage of mortar samples. But inhibitor is favorable if used in control mixes. In the present case high dose is not effective in controlling mass loss of mortar samples exposed to various salt solutions.

4.9EFFECT OF FREEZING THAWING CYCLES ON THE ULTRASONIC PULSE VELOCITY OF VARIOUS MIXES

Fig 4.38 to 4.43 shows the effect of freeze thaw cycles on the ultrasonic pulse velocity of mortar samples exposed to various salt solutions at different water cement ratio's. The detailed effect of cycles on the mortar samples is explained below.

4.9.1 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.46

As shown in Fig 4.38, it is observed that for M-I-0 mortar samples exposed to sodium chloride and triethanolamine solution, a continuous decrease in the velocity is observed with increase in the number of freeze thaw cycles. This indicates that some microcracks

may have been developed in the mortar samples and when pulse travels and strikes these cracks it get diffracted leading to increase of time in reaching the receiving transducer. But as the final velocity after 42 cycles is greater than 3500 m/s so the overall quality of mortar is good as per IS:13311 (part-1). Samples immersed in calcium chloride with and without inhibitor show a slight increase in velocity upto 28 cycles thereafter a continuous decrease is observed. Comparing it with the compressive strength it is observed that the strength also decreases after 28 cycles. But the decrease in the pulse velocity is much more as compared to the strength of the samples.

In case of M-I-5 mortar samples containing 5% metakaolin and exposed to various solutions show a similar behavior as shown by their control mixes. But the final velocity after 42 cycles in sodium chloride solution is more than its control mix showing that the metakaolin is effective in controlling deterioration due to frost attack and hence maintaining the quality of samples. But in case of $CaCl_2$ with and without inhibitor velocity increases during 14-28 cycles and after that a continuous decrease is observed. The pulse velocity after 42 cycles is less as compared to its control mix without metakaolin as shown in Fig 4.39.

Fig 4.40 shows the effect of freeze thaw cycles on the samples having 10% metakaolin exposed to sodium chloride solution. It is observed from the curves that the M-I-10 samples exposed to sodium chloride as well as calcium chloride with inhibitor show a continuous increase in the pulse velocity with increasing number of freeze thaw cycles. Even though there is salt crystallization and scaling damage on the above samples, but the continuity of the cement paste is maintained and hence no diffraction of waves take place. It may be due to the filling up of pores with metakaolin or with the salts. So its velocity increases. Thus it indicates that quality of samples increases with increase in percentage of metakaolin. But on comparing it with the compressive strength it is observed that the load carrying capacity of the above samples decreases. This indicates that although pulse velocity test indicates cohesiveness of the samples but it is opposite to the effect reflected by the strength behavior. This may be due to the deposition of aggressive salts in the pores which actually reduce the quality of samples but the same is not brought out by the UPV test.

4.9.2 Effect on Mortar Samples at Water to Cementitious Material Ratio of 0.5

M-II-0 mortar samples exposed to various solutions show a sharp decrease in the pulse velocity after 28 cycles. At high water cementitious material ratio though the hydration reaction is fast but due to alternating cycles of freeze thaw, the samples became more vulnerable to hydraulic, thermodynamic and osmotic pressures upon freezing. This

leads to increase in the porosity of the samples and hence the velocity decreases. The variation of results is shown in Fig 4.41.

As shown in Fig 4.42, M-II-5 mortar samples containing 5% metakaolin immersed in various salt solutions also show a continuously decrease in the velocity upto 28 freeze thaw cycles and thereafter an increase in the velocity is observed. But the gain in the velocity after 42 cycles is more as compared to the control mixes indicating that the low dosage of metakaolin is effective in controlling the loss due to frost damage upto some extent and hence the quality of the samples improved.

When M-II-10 mortar samples containing 10% metakaolin were exposed to various salt solutions under freeze thaw cycling, an increase in the pulse velocity was observed in all the mixes with the increase in the number of freeze thaw cycles. But as shown in Fig 4.43, these results do not match with the compressive strength of the mortar samples exposed to sodium chloride and calcium chloride with inhibitor where a continuous decrease in the strength is observed.

Thus it can be concluded that the ultrasonic pulse velocity test may not give the accurate results under freeze thaw cycles. There could be two possible reasons for its lesser reliability. Firstly, the size of the specimen is less i.e.70.5 mm in the present study. Secondly, though this test is the indication of the cracks and defects in the samples but when these samples are exposed to aggressive environment then the pores or cracks may get filled with the salts and hence the ultrasonic pulse wave will not get diffracted which results in higher velocity. Higher velocity will indicate a good quality of mortar samples but actually samples get deteriorated. It indicates that the pulse velocity test alone is not a reliable testing method unless some other destructive or non destructive test is done along with it to judge the quality of samples.

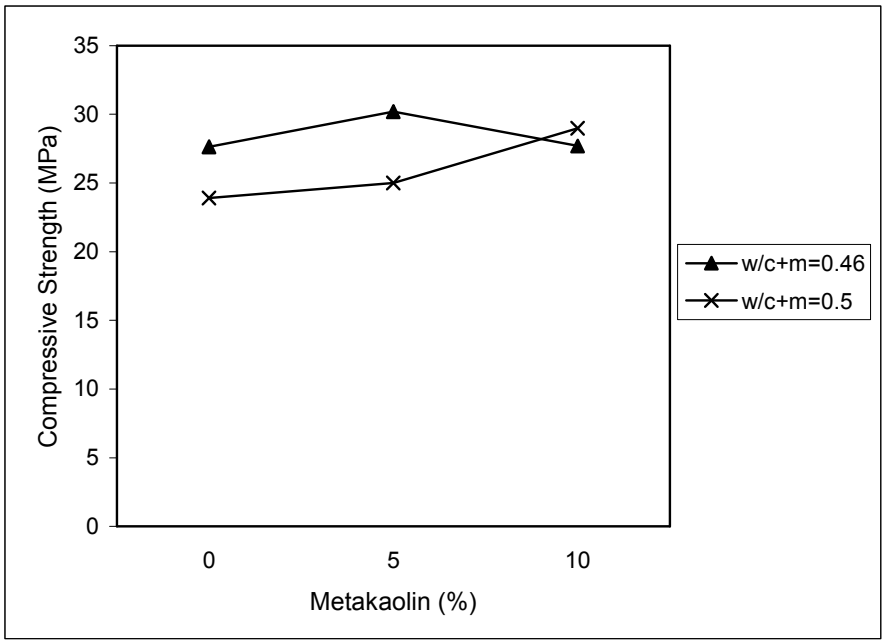


Fig 4.1: Variation of Compressive Strength of various Mortar Mixes after 7 Days of Initial Curing

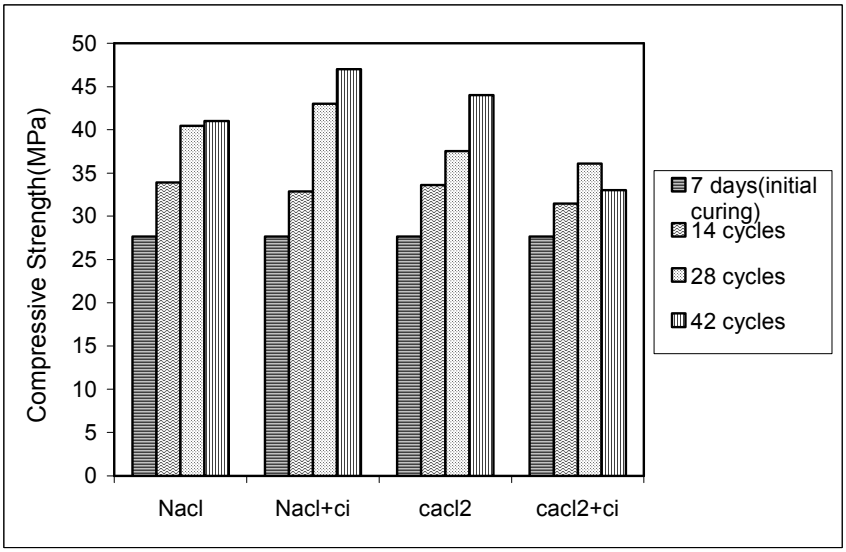


Fig 4.2: Variation of Compressive Strength of Control Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

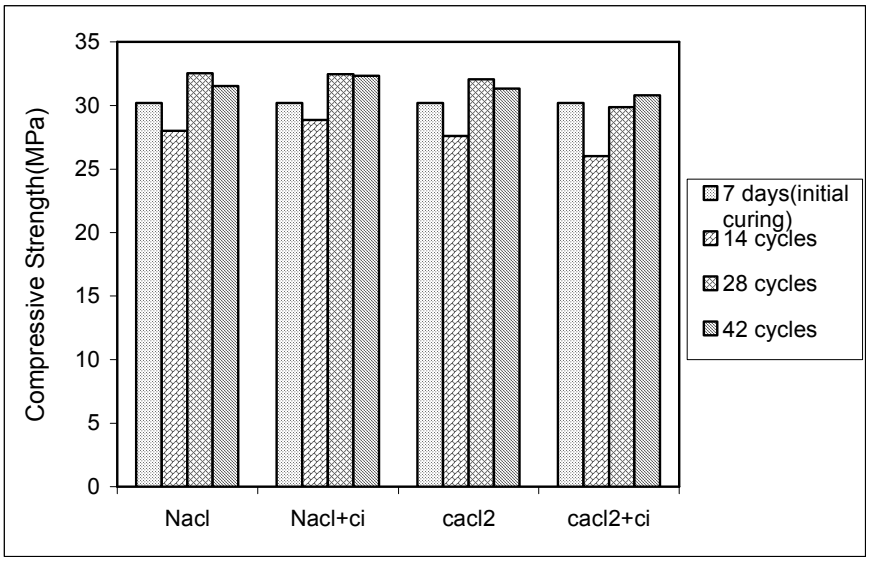


Fig 4.3: Variation of Compressive Strength of 5% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

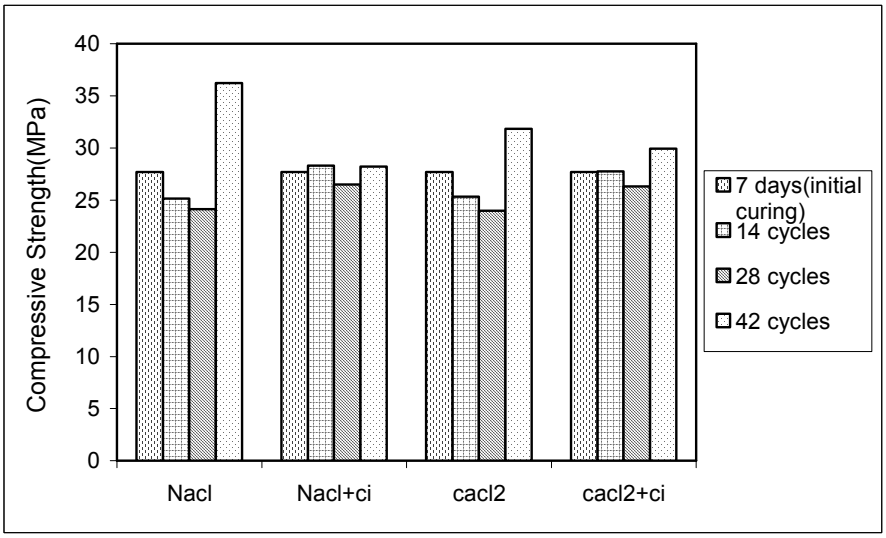


Fig 4.4: Variation of Compressive Strength of 10% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

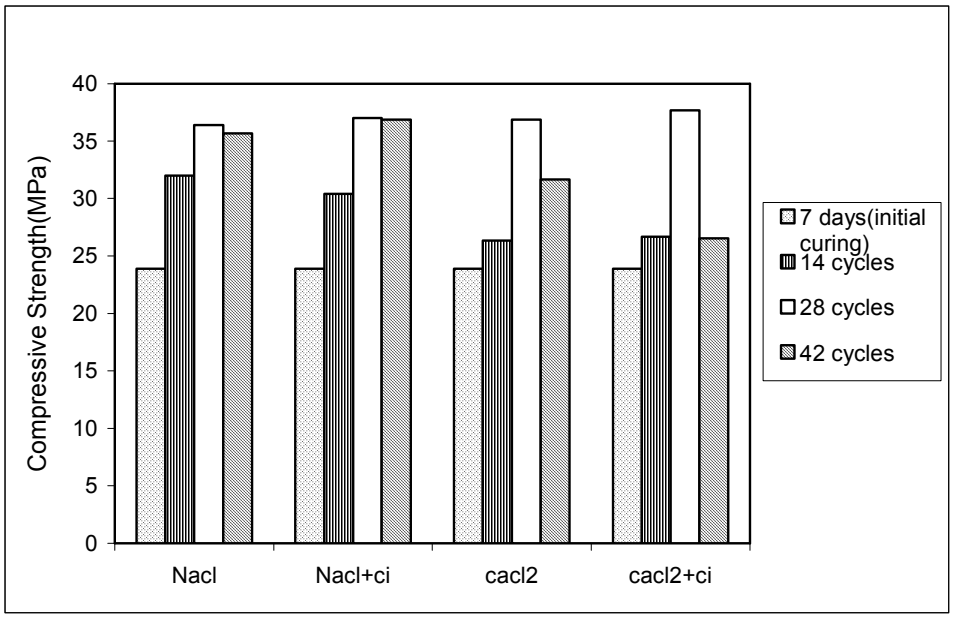


Fig 4.5: Variation of Compressive Strength of Control Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

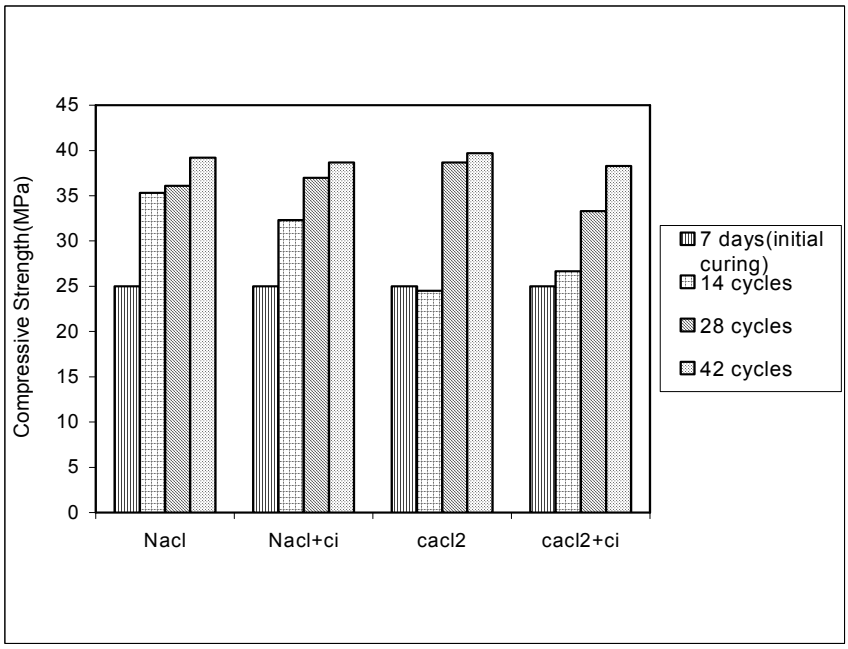


Fig 4.6: Variation of Compressive Strength of 5% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

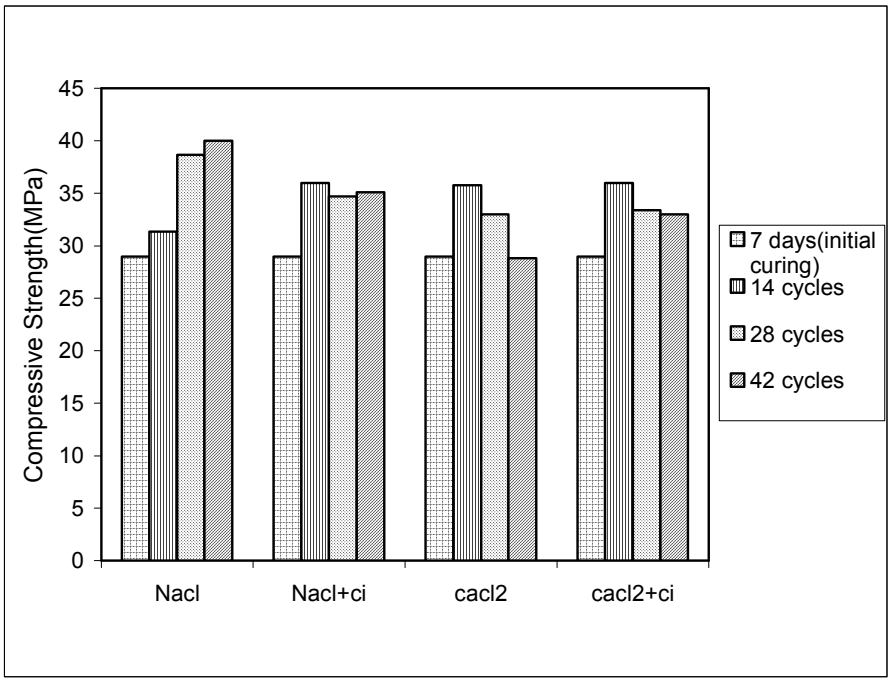


Fig 4.7: Variation of Compressive Strength of 10% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

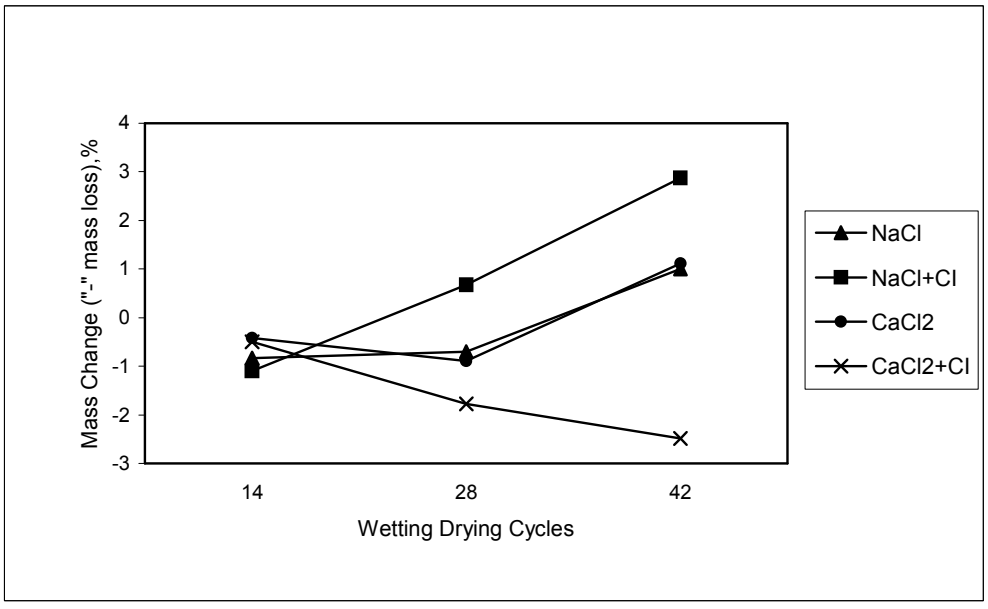


Fig 4.8: Mass Change of Control Mix under Wetting Drying Cycles at w/c=0.46

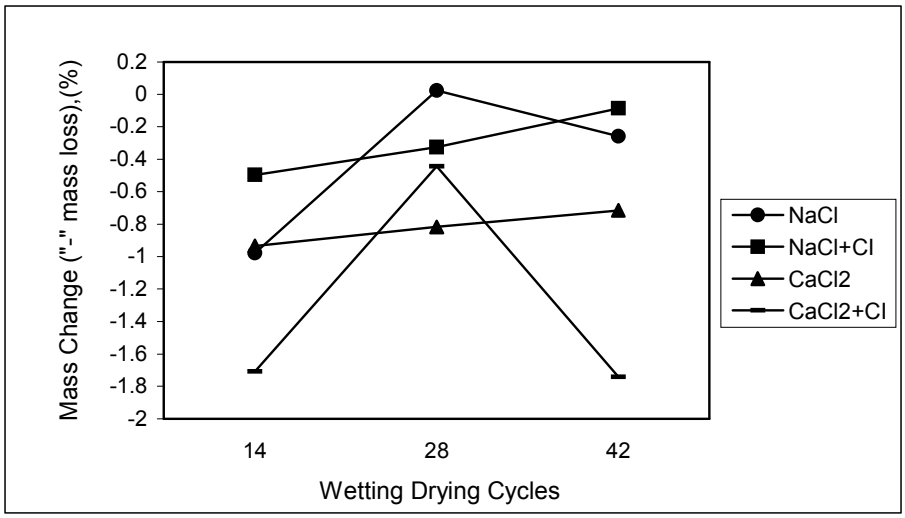


Fig 4.9: Mass Change of 5% Metakaolin Mix under Wetting Drying Cycles at w/c+m=0.46

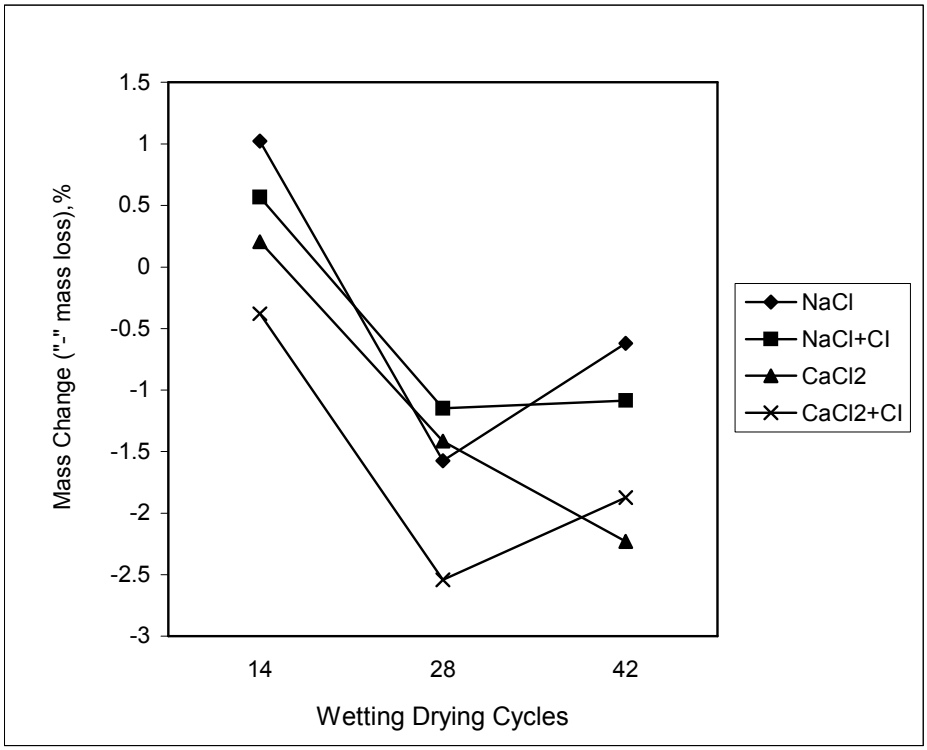


Fig 4.10: Mass Change of 10% Metakaolin Mix under Wetting Drying Cycles at w/c+m=0.46

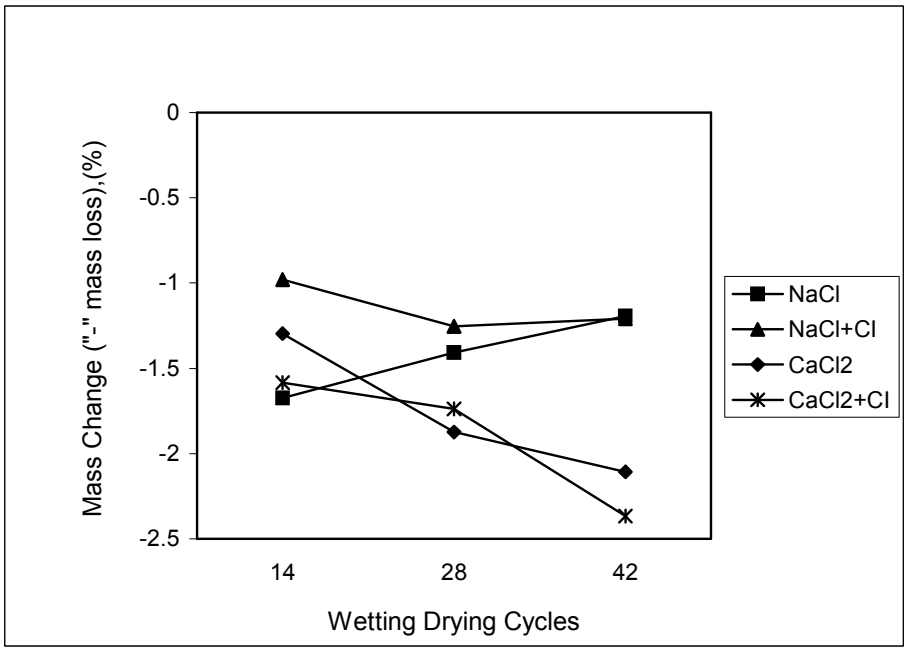


Fig 4.11: Mass Change of Control Mix under Wetting Drying Cycles at w/c=0.5

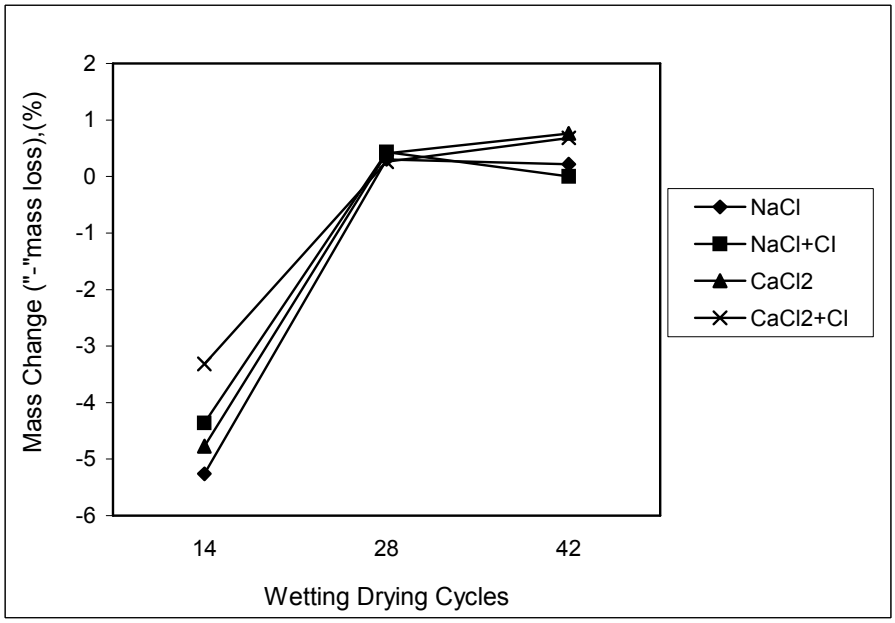


Fig 4.12: Mass Change of 5% Metakaolin Mix under Wetting Drying Cycles at w/c+m=0.5

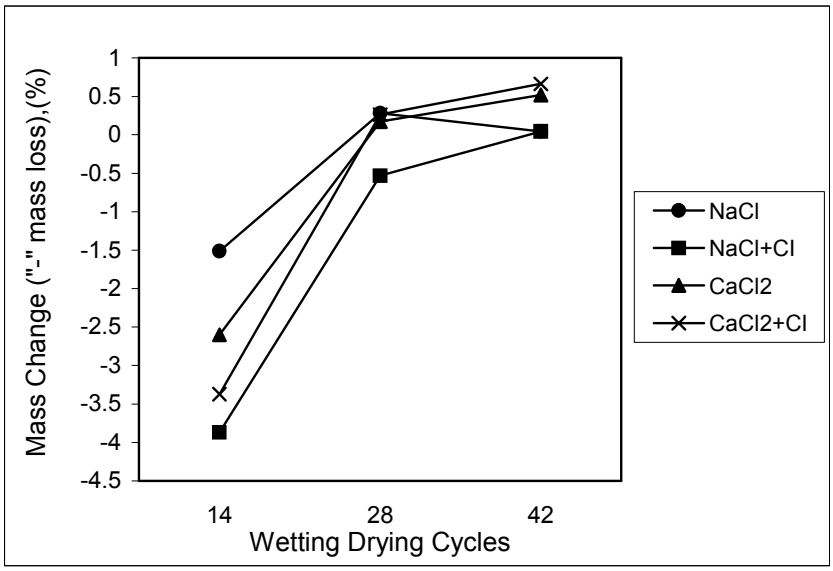


Fig 4.13: Mass Change of 10% Metakaolin Mix under Wetting Drying Cycles at w/c+m=0.5

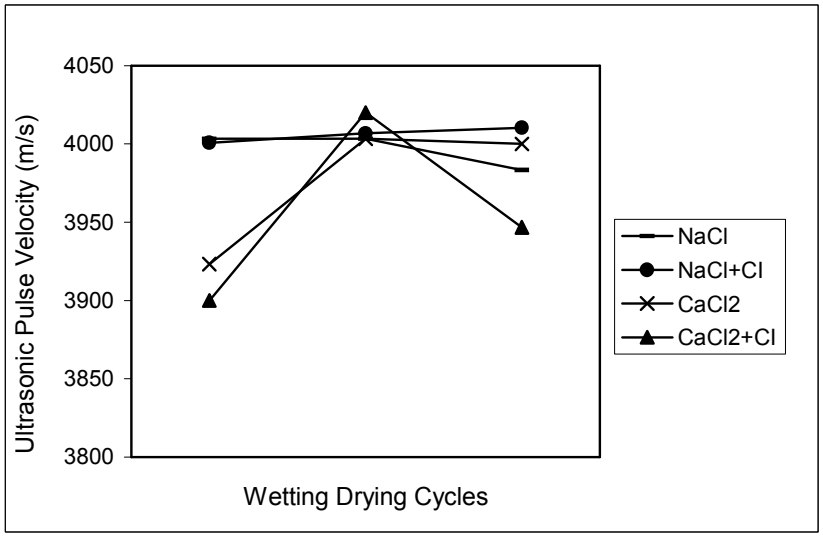


Fig 4.14: Variation of Ultrasonic Pulse Velocity of Control Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

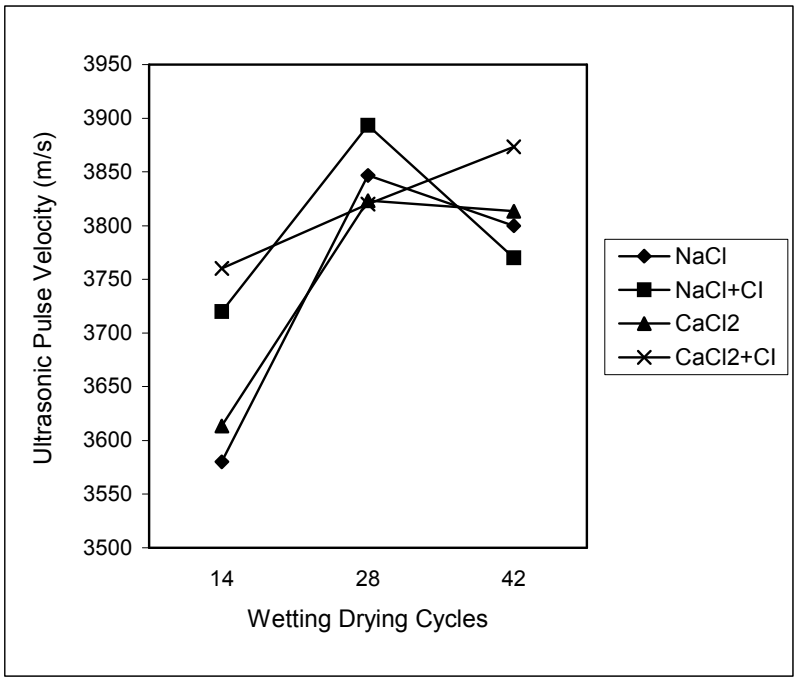


Fig 4.15: Variation of Ultrasonic Pulse Velocity of 5% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

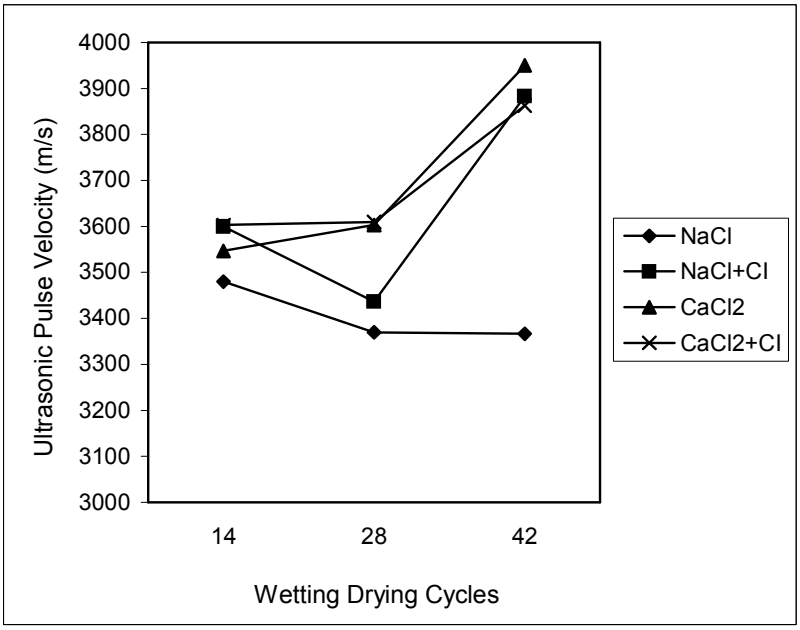


Fig 4.16: Variation of Ultrasonic Pulse Velocity of 10% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.46

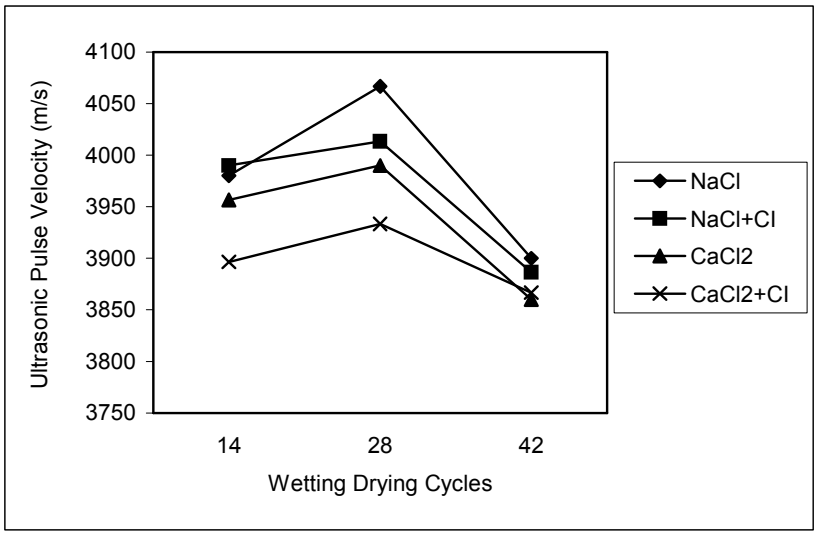


Fig 4.17: Variation of Ultrasonic Pulse Velocity of Control Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

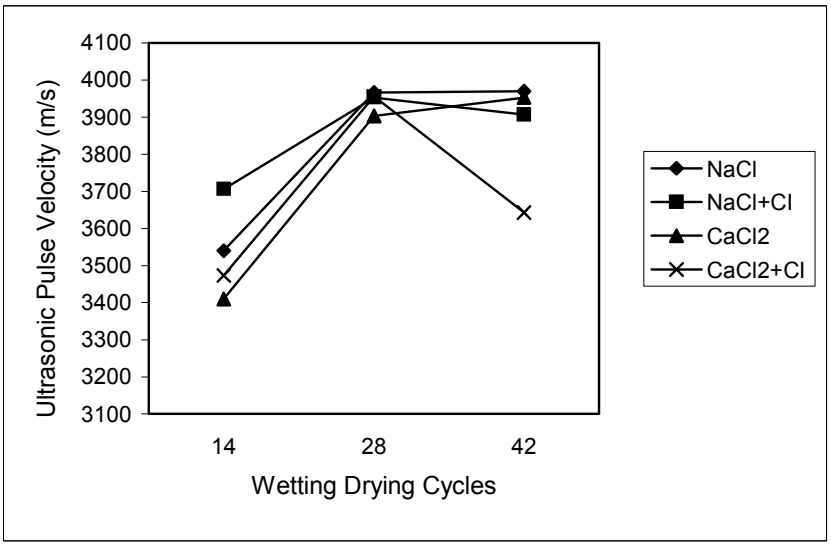


Fig 4.18: Variation of Ultrasonic Pulse Velocity of 5% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

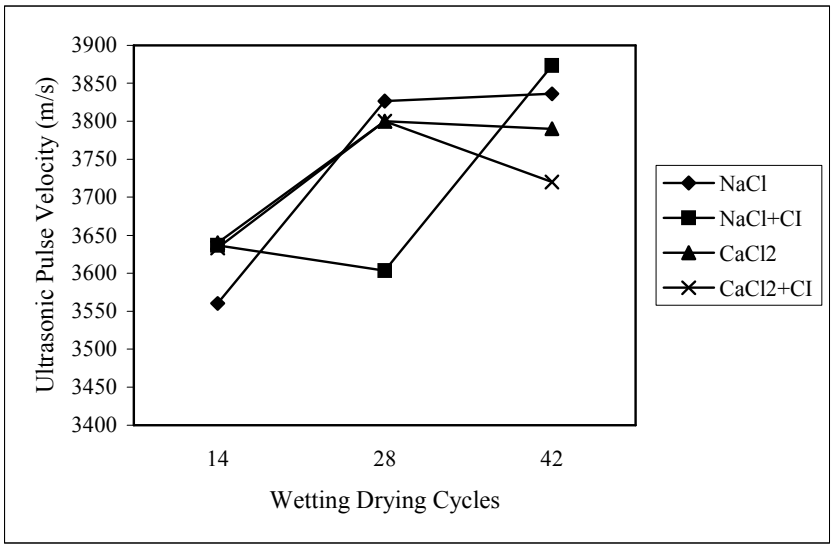


Fig 4.19: Variation of Ultrasonic Pulse Velocity of 10% Metakaolin Mix exposed to Various Solutions under Wetting Drying Cycles at w/c+m=0.5

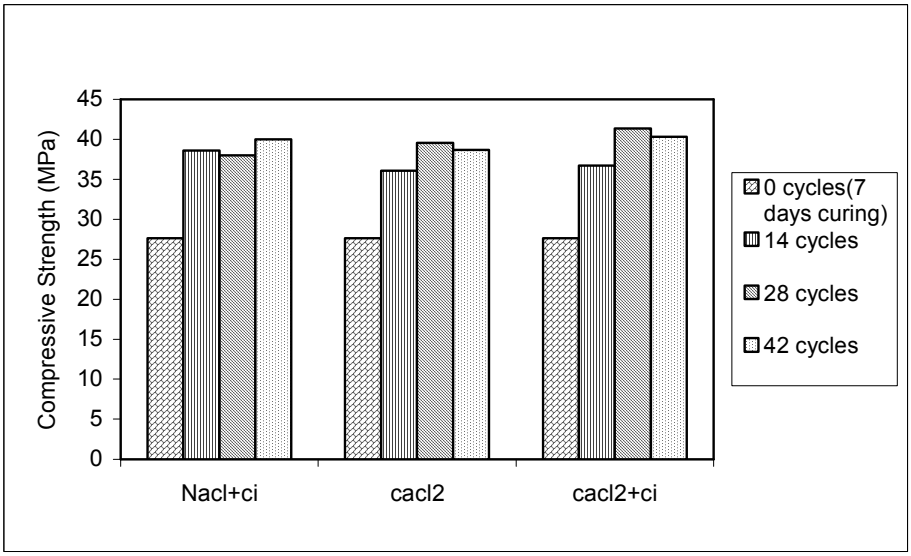


Fig 4.20: Variation of Compressive Strength of Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

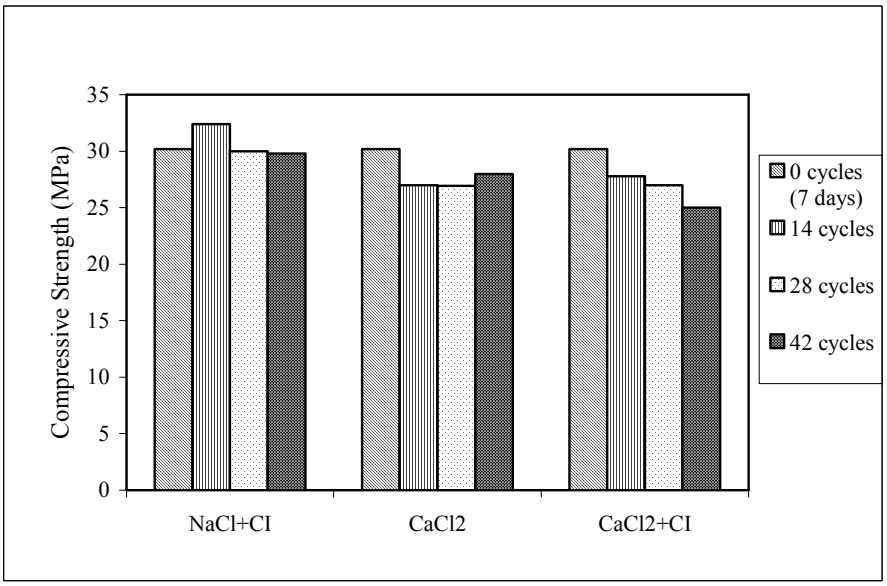


Fig 4.21: Variation of Compressive Strength of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

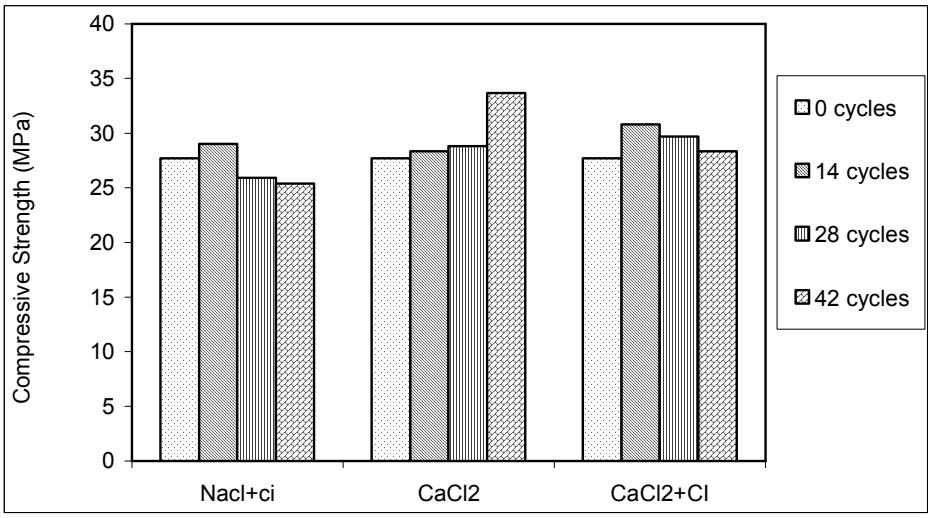


Fig 4.22: Variation of Compressive Strength of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

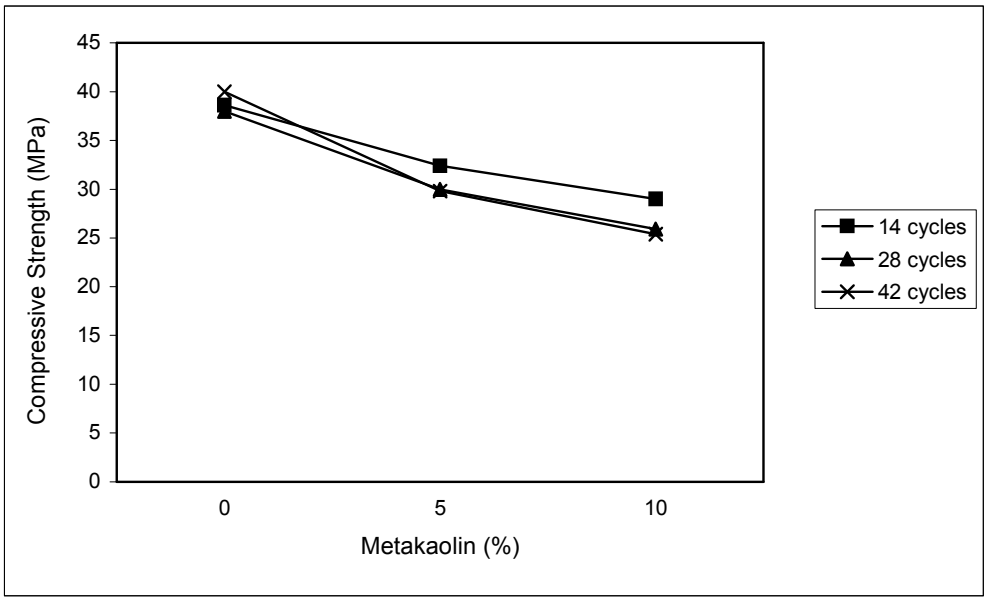


Fig 4.23: Variation of Compressive Strength of Mortar Samples exposed to Sodium Chloride with Inhibitor under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.46

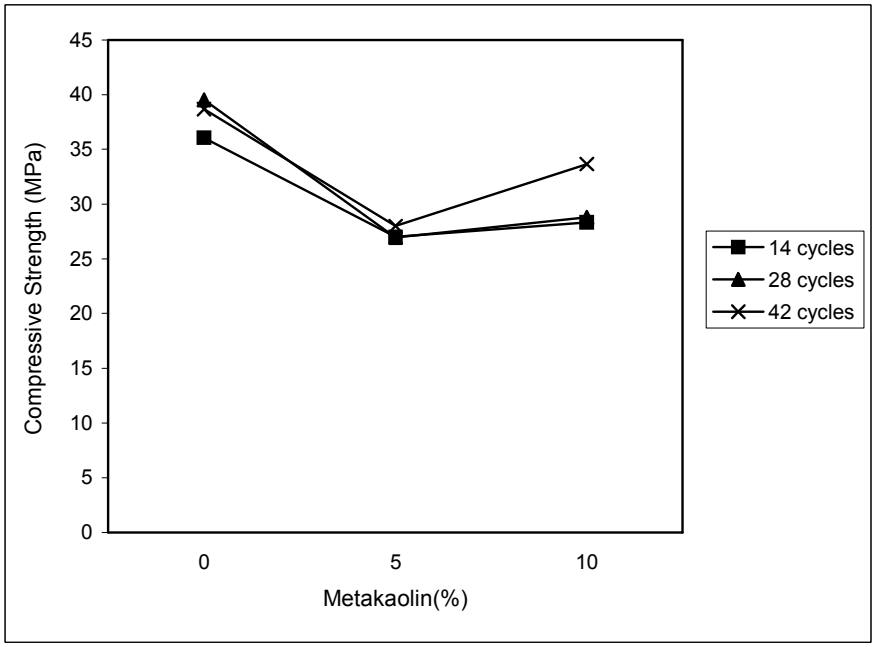


Fig 4.24: Variation of Compressive Strength of Mortar Samples exposed to Calcium chloride solution under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.46

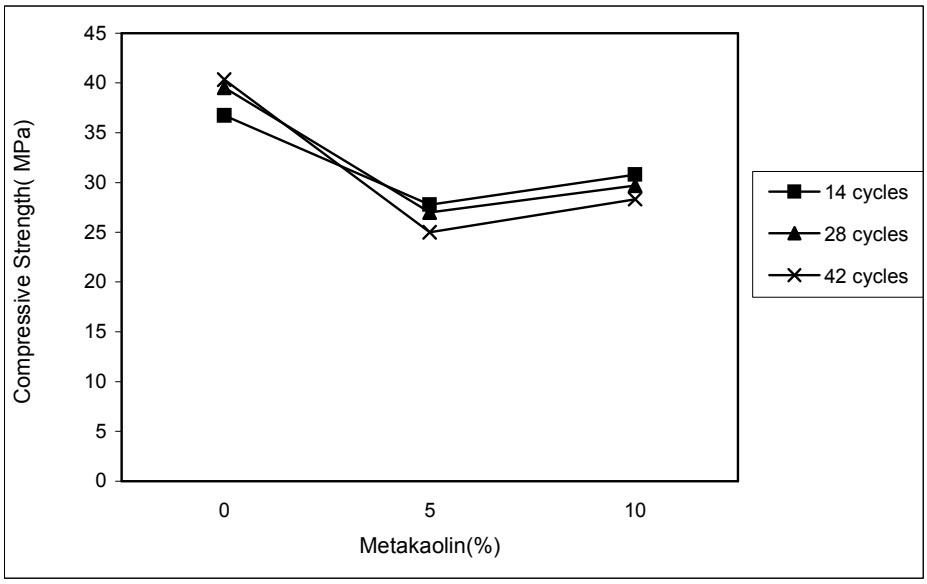


Fig 4.25: Variation of Compressive Strength of Mortar Samples exposed to Calcium chloride with inhibitor solution under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.46

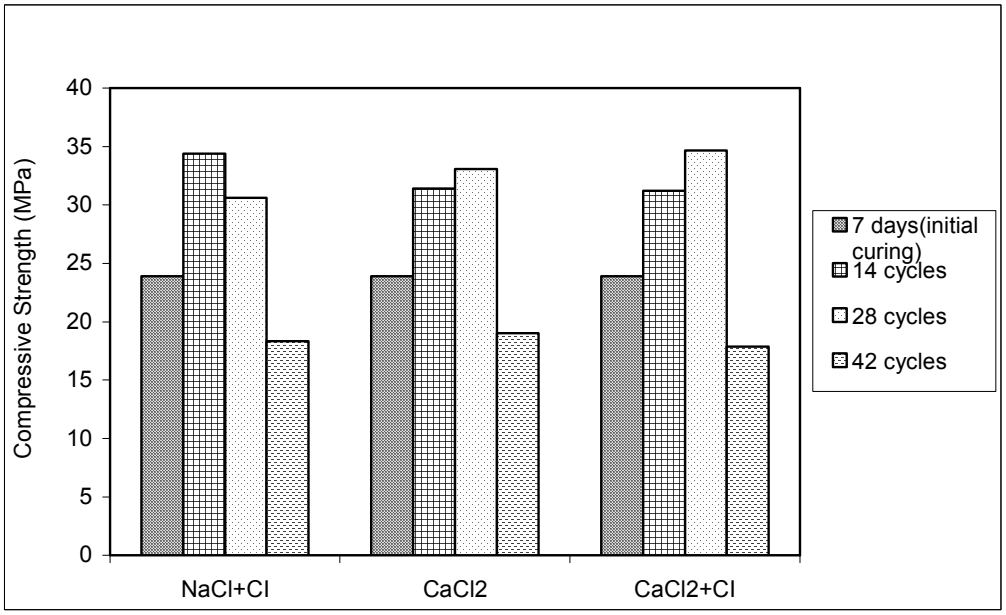


Fig 4.26: Variation of Compressive Strength of Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

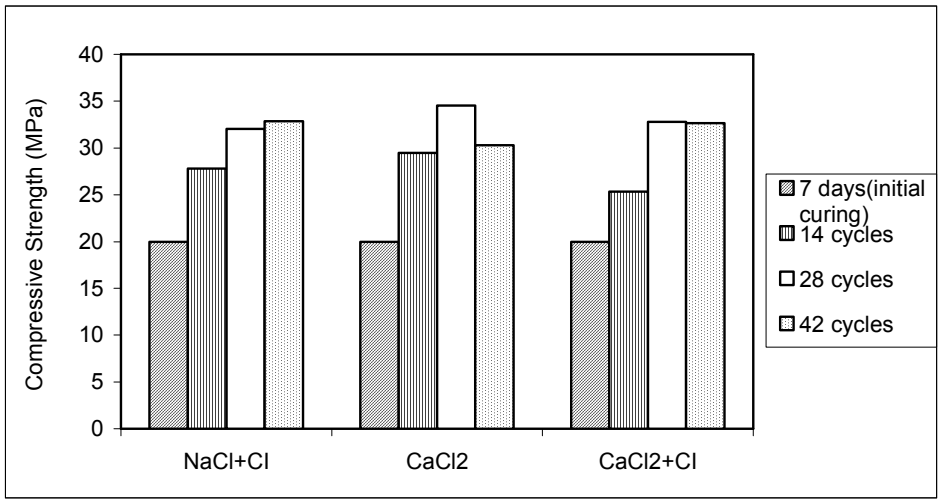


Fig 4.27: Variation of Compressive Strength of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

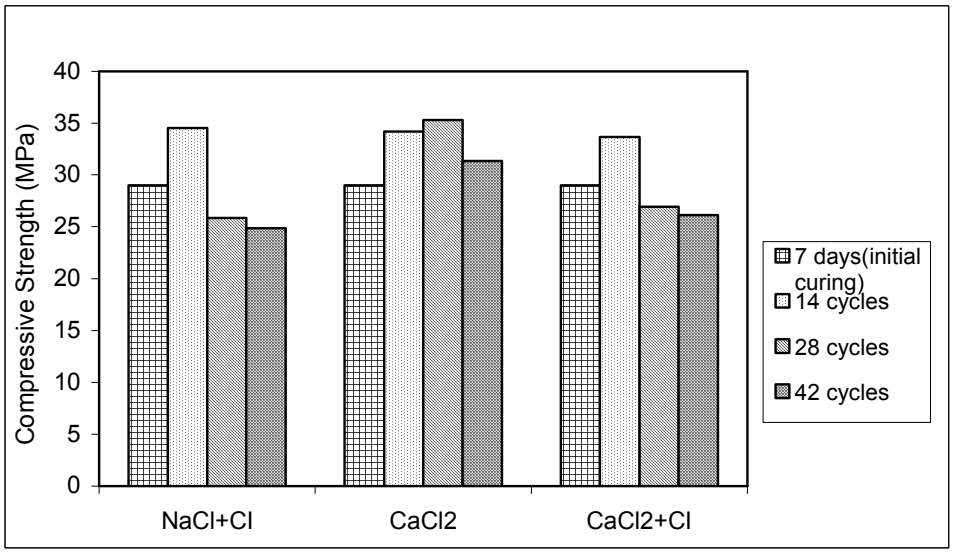


Fig 4.28: Variation of Compressive Strength of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

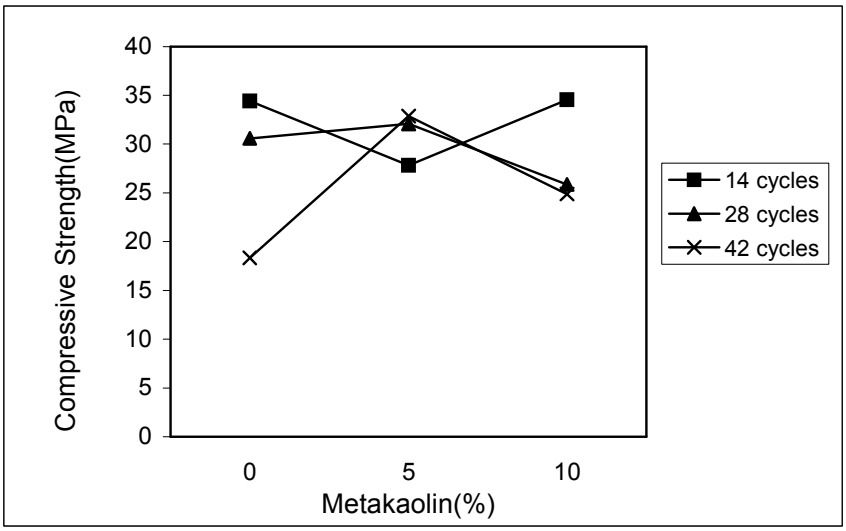


Fig 4.29: Variation of Compressive Strength of Mortar Samples exposed to Sodium chloride with inhibitor solution under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.5

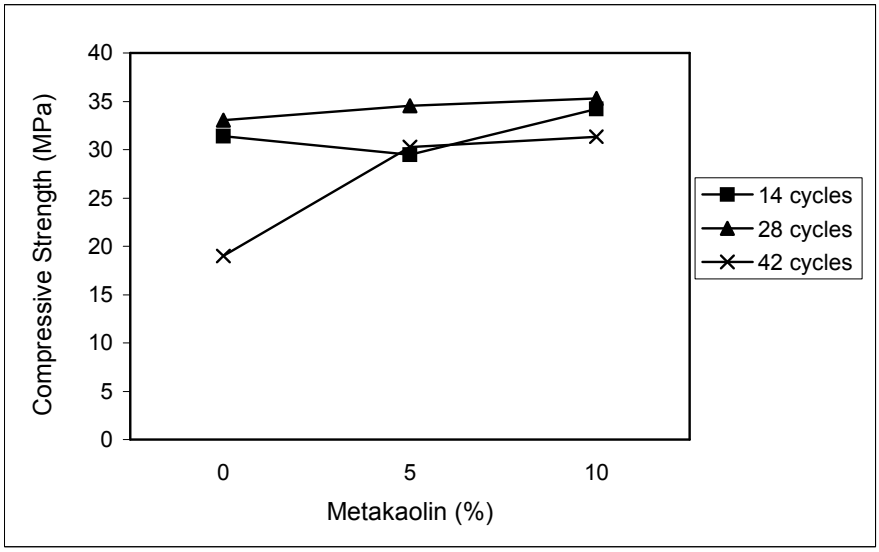


Fig 4.30: Variation of Compressive Strength of Mortar Samples exposed to Calcium Chloride Solution under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.5

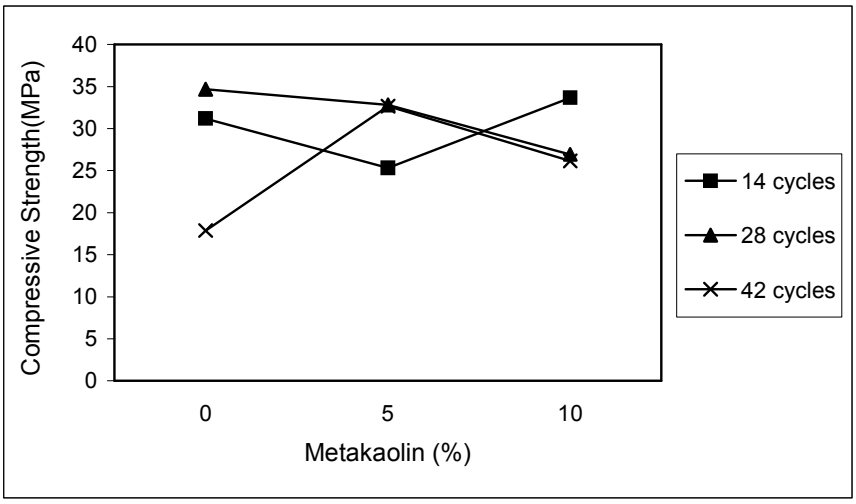


Fig 4.31: Variation of Compressive Strength of Mortar Samples exposed to Calcium Chloride with Inhibitor Solution under Freezing Thawing Cycles and with Varying Percentage of Metakaolin at w/c+m=0.5

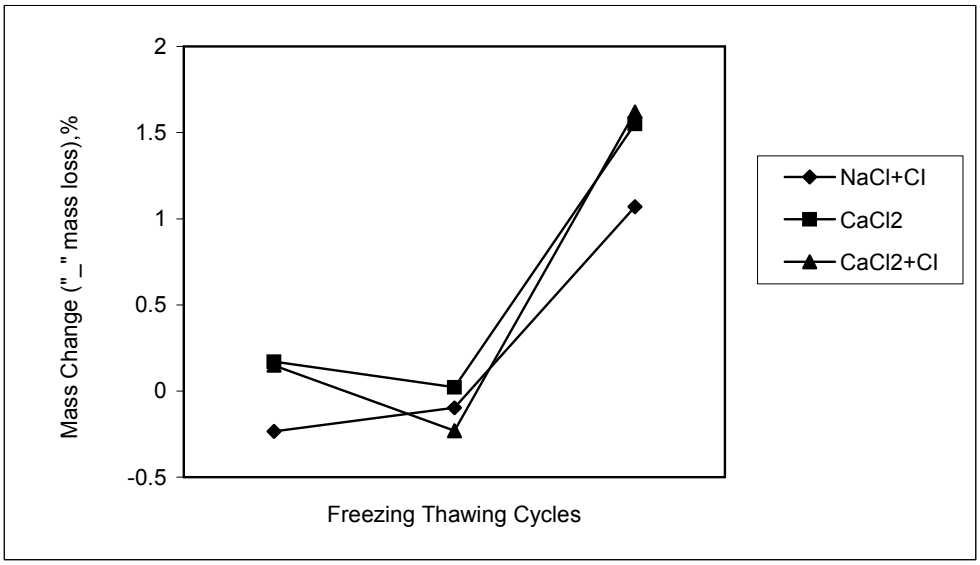


Fig 4.32: Variation of Mass Change of Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

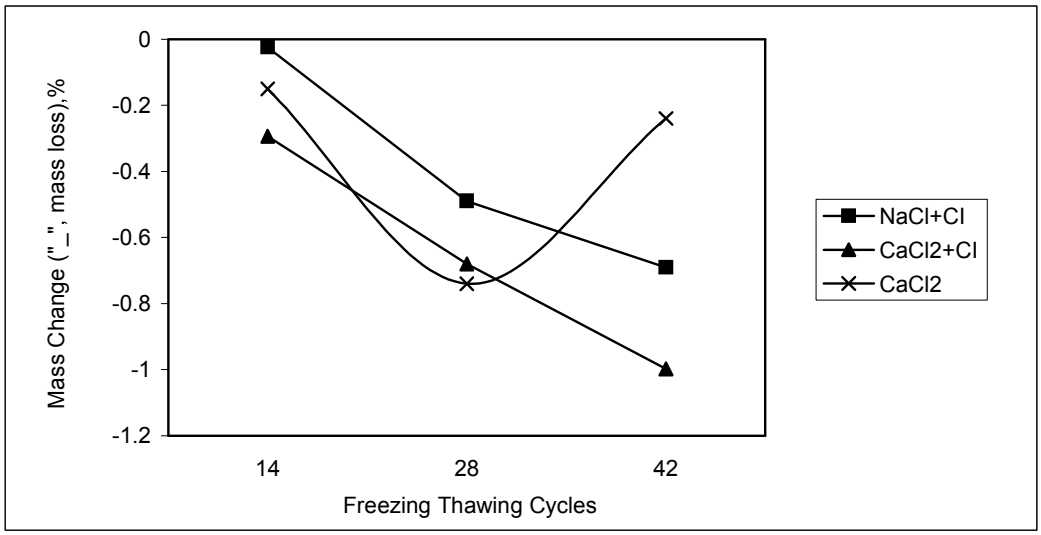


Fig 4.33: Variation of Mass Change of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

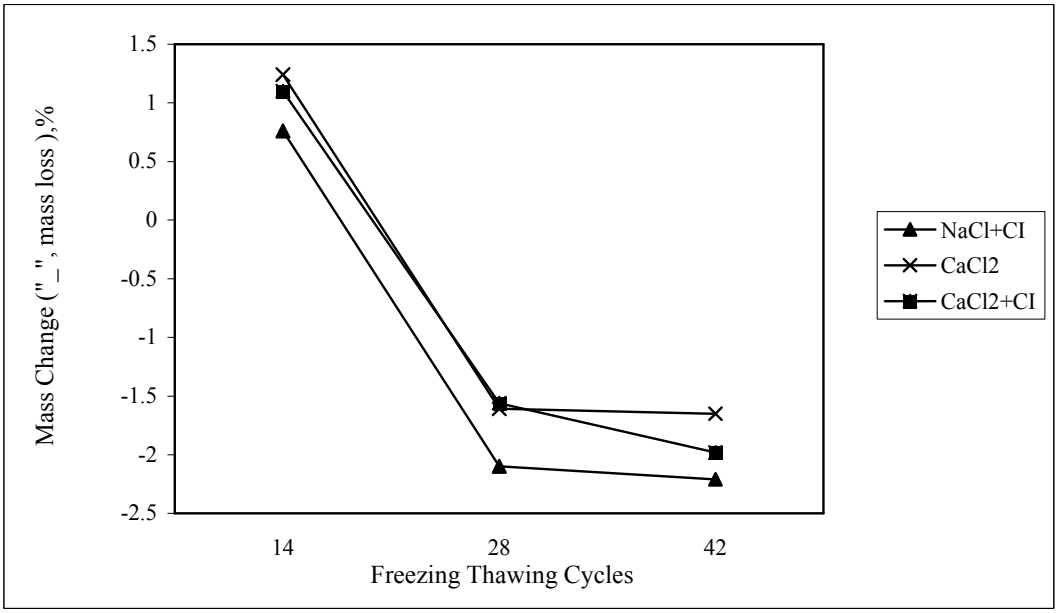


Fig 4.34: Variation of Mass Change of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

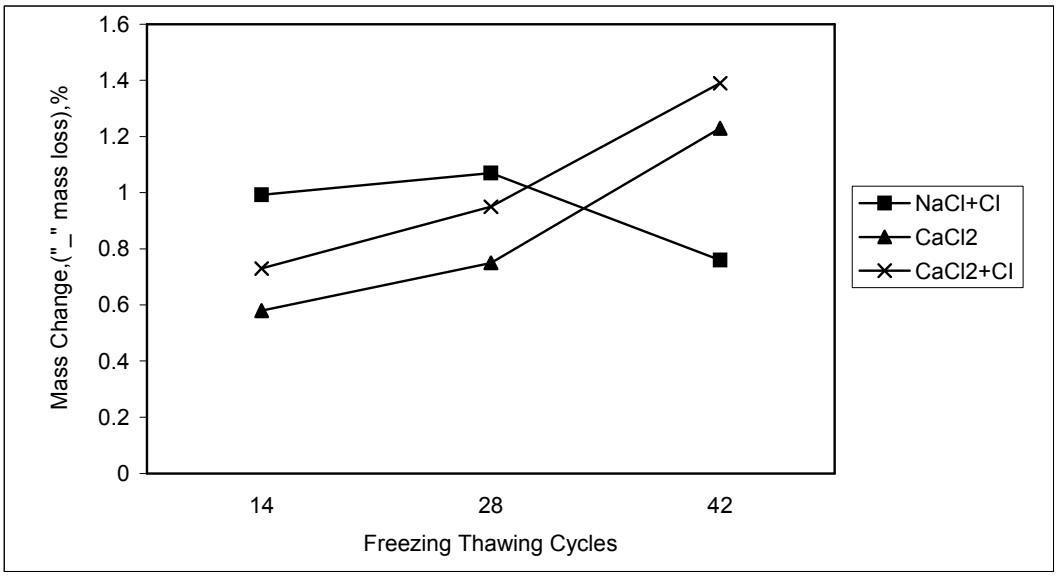


Fig 4.35: Variation of Mass Change of Mortar Samples under Freezing Thawing Cycles at w/c+m= 0.5

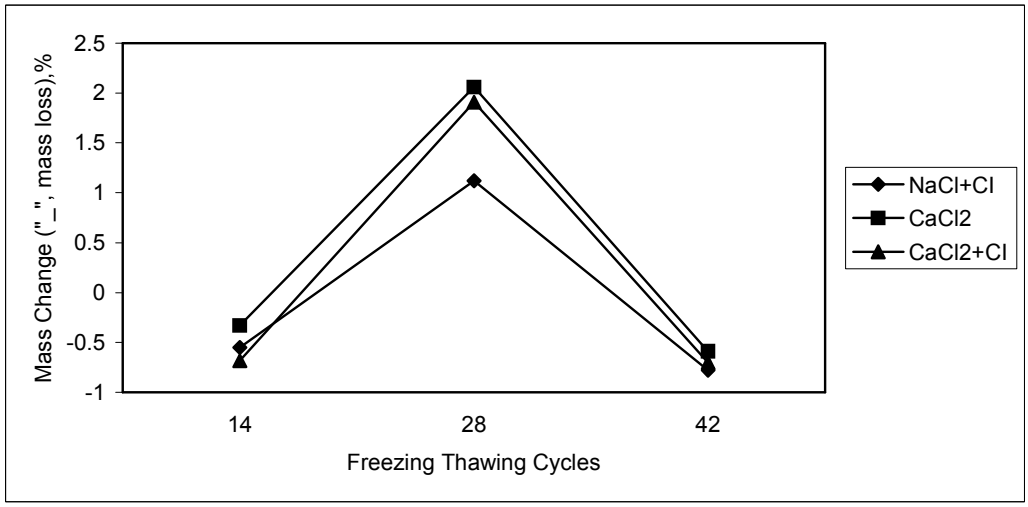


Fig 4.36: Variation of Mass Change of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

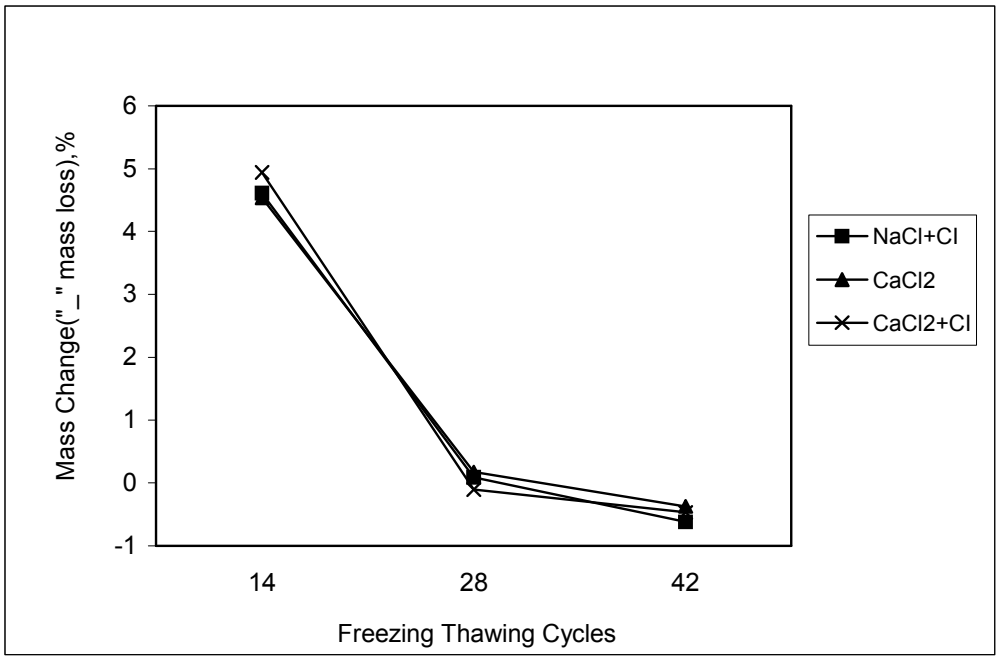


Fig 4.37: Variation of Mass Change of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

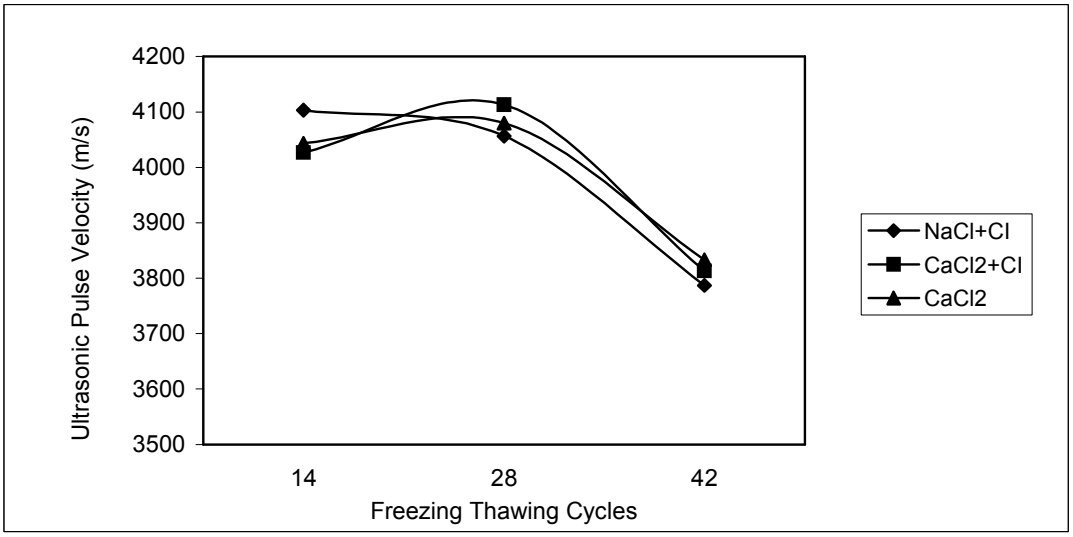


Fig 4.38: Variation of Ultrasonic Pulse Velocity of Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

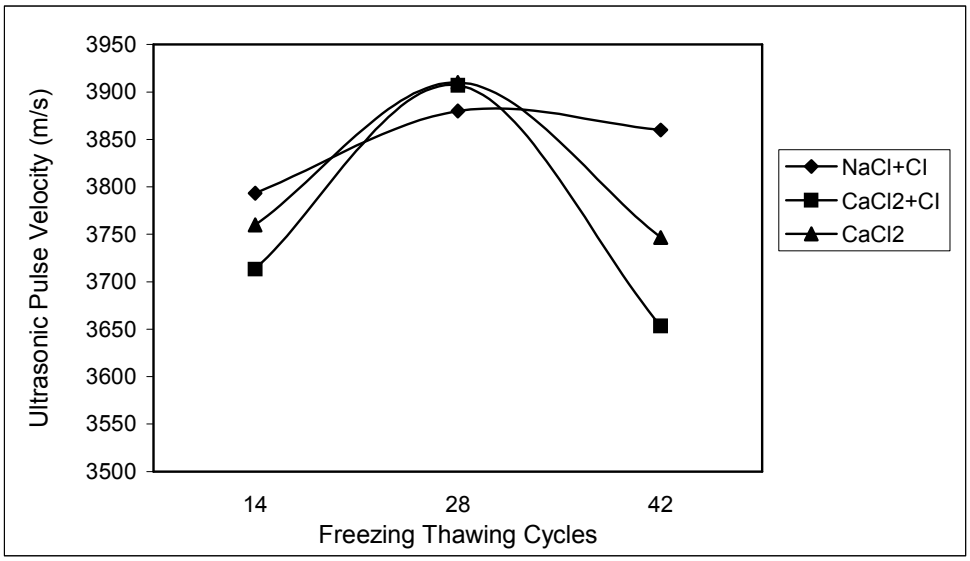


Fig 4.39: Variation of Ultrasonic Pulse Velocity of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

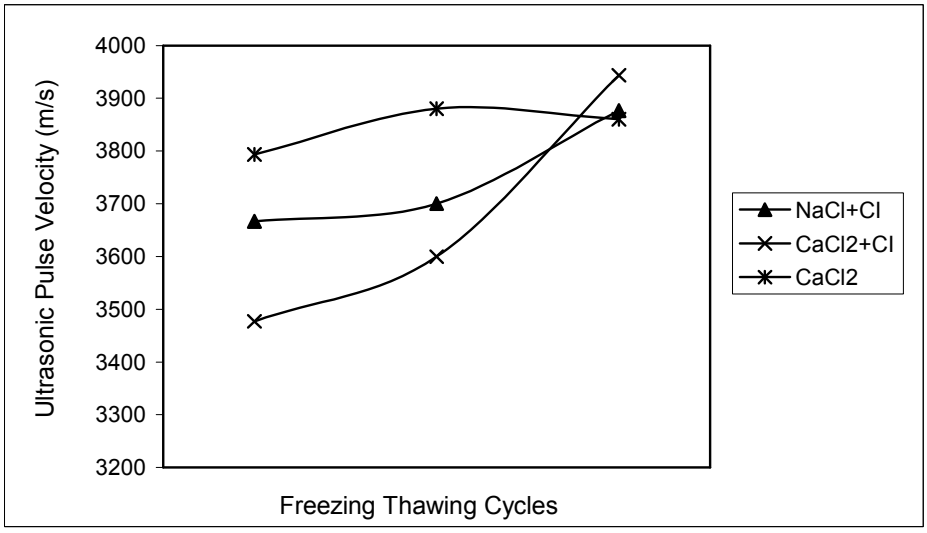


Fig 4.40: Variation of Ultrasonic Pulse Velocity of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.46

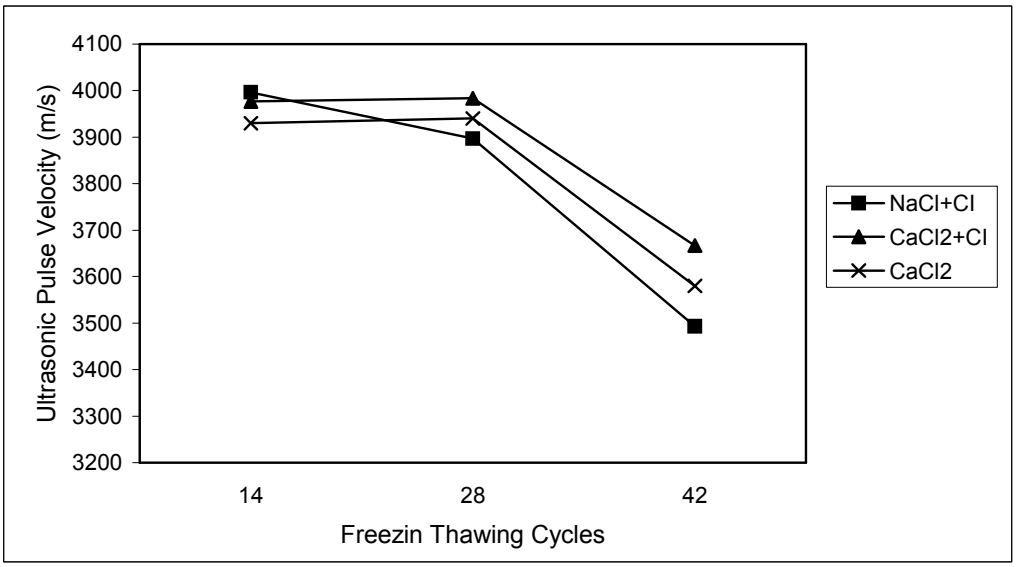


Fig 4.41: Variation of Ultrasonic Pulse Velocity of Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

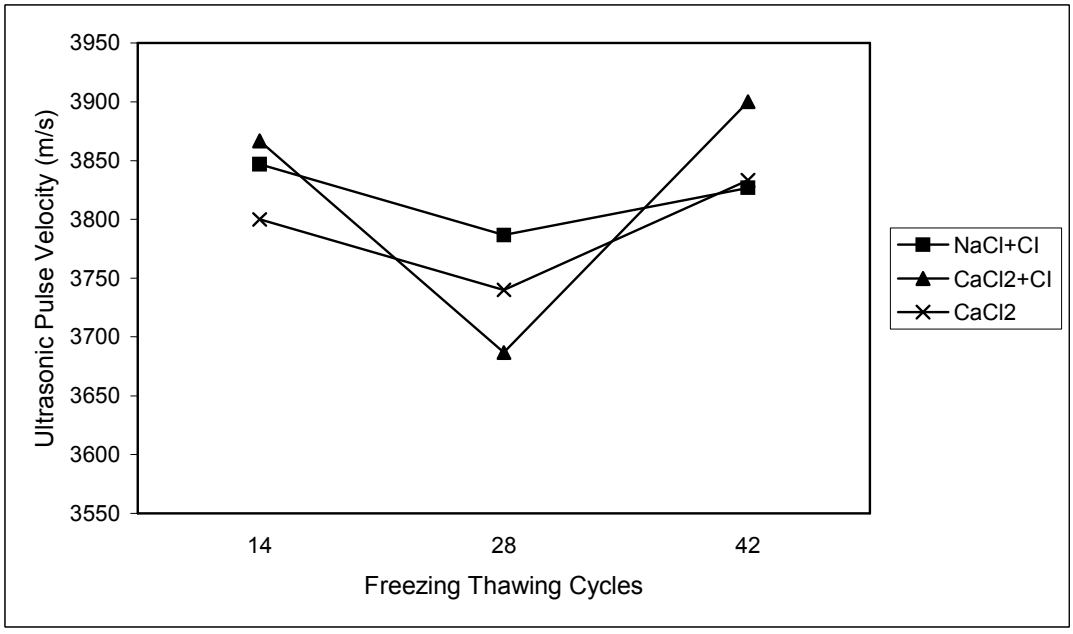


Fig 4.42: Variation of Ultrasonic Pulse Velocity of 5% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

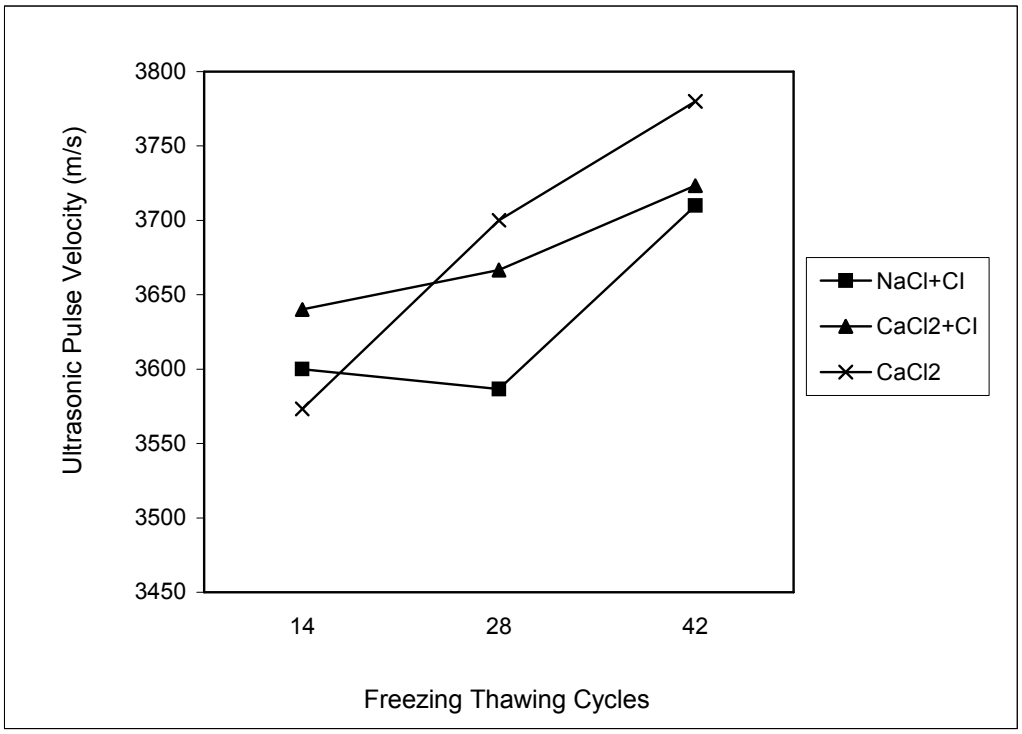


Fig 4.43: Variation of Ultrasonic Pulse Velocity of 10% Metakaolin Mortar Samples under Freezing Thawing Cycles at w/c+m=0.5

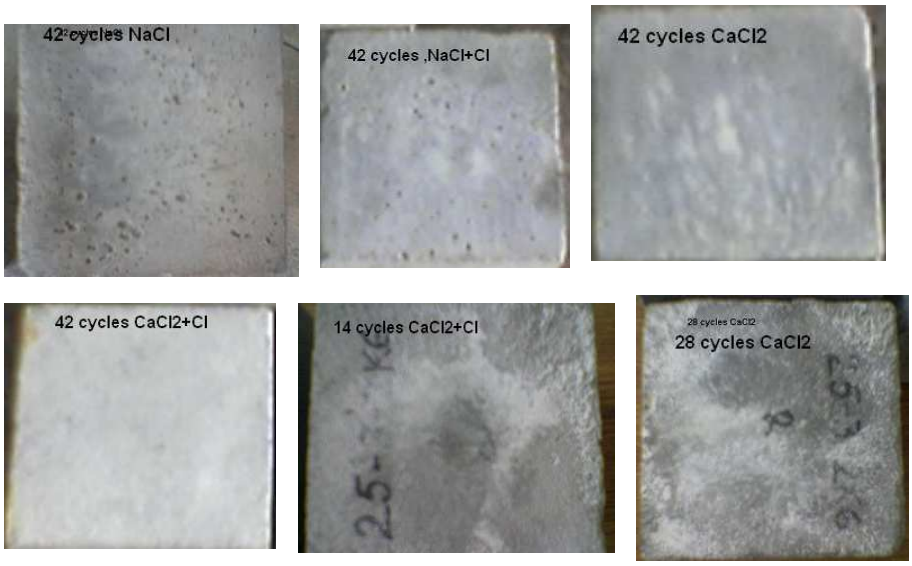


Plate 4.1: Conditions of Control Mix at w/c=0.46 Exposed to Various Solution at different Wetting Drying Cycles

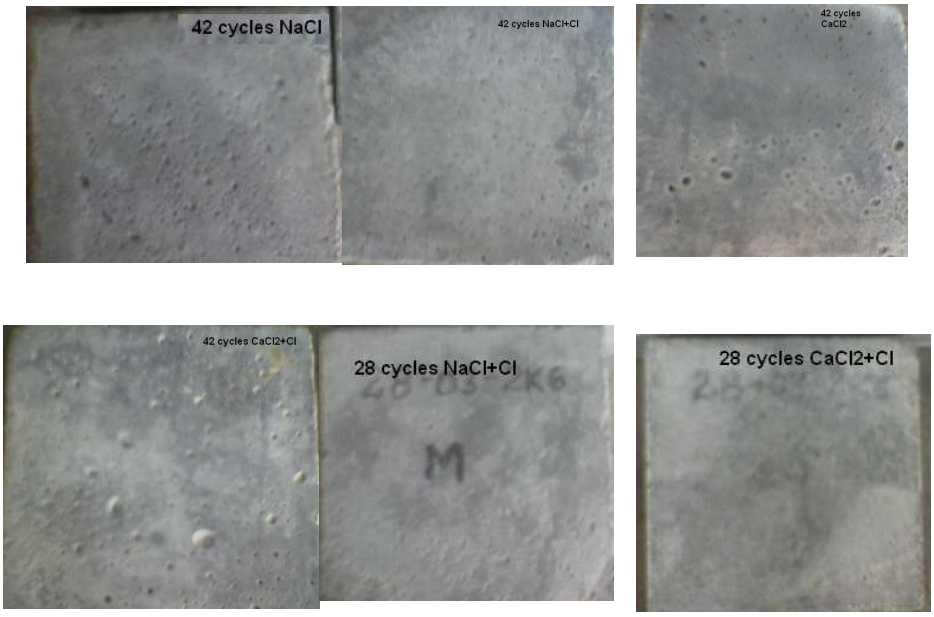
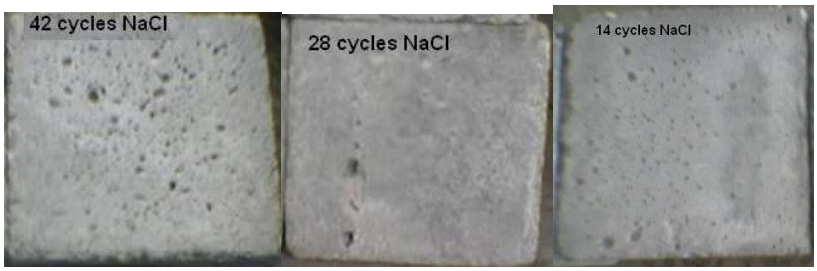
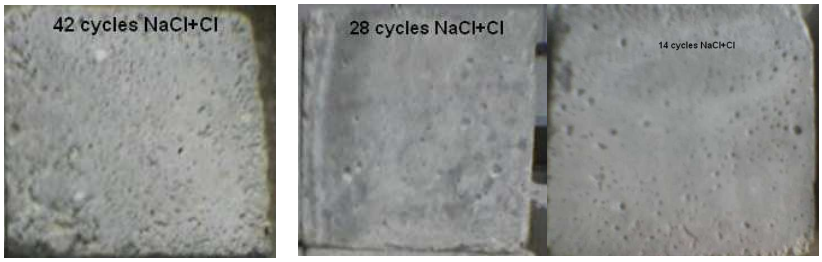


Plate 4.2: Conditions of Control Mix at w/c=0.5 Exposed to Various Solution at different Wetting Drying Cycles



(a)



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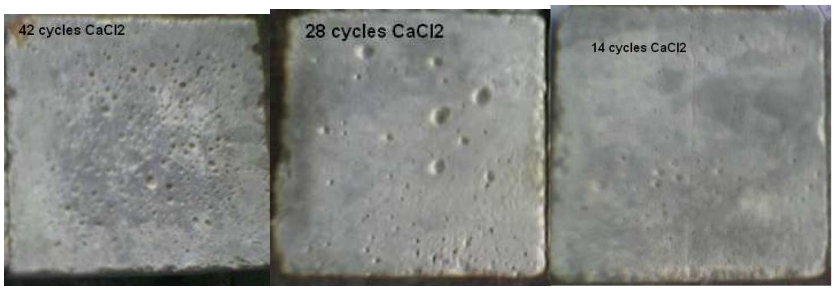

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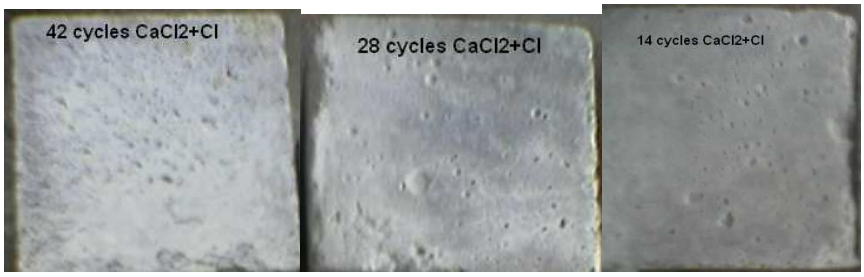


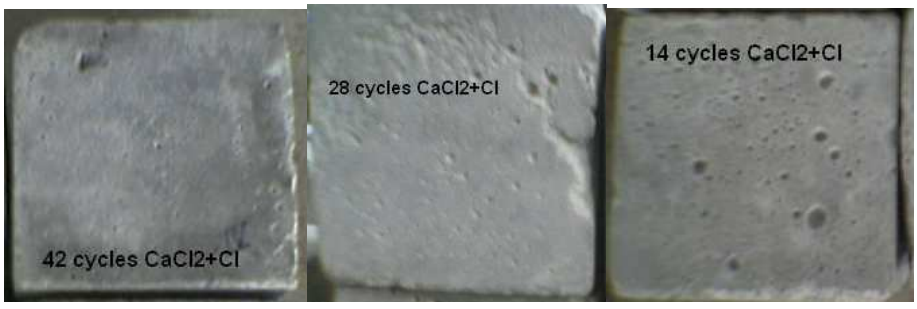
(d)

Plate 4.3: Conditions of 5% Metakaolin Mix at w/c+m=0.46 Exposed to (a)Sodium Chloride (b) Sodium Chloride with inhibitor (c) Calcium Chloride (d) Calcium Chloride with inhibitor at Different Wetting Drying

(a)

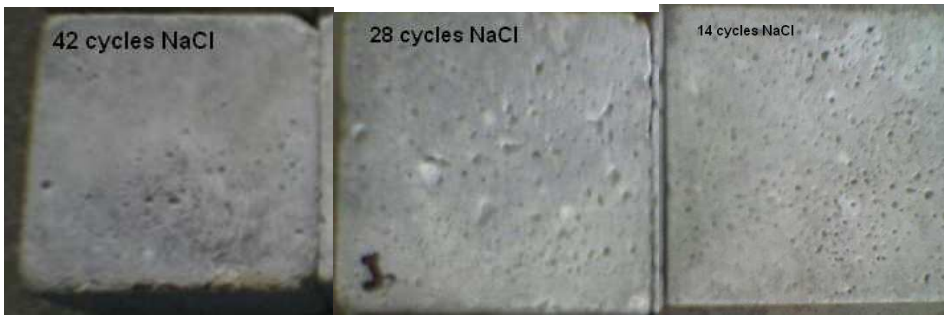
(b)

(c)

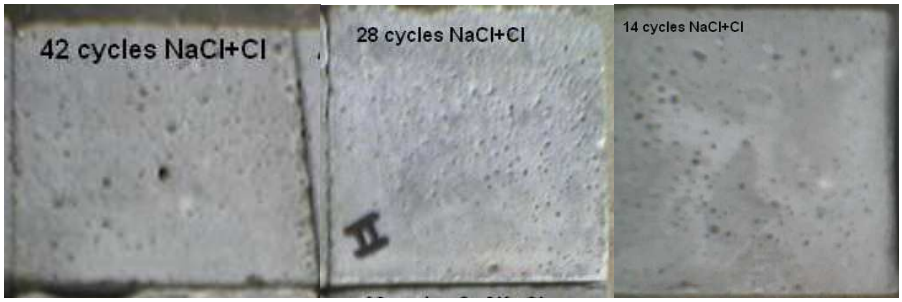


(d)

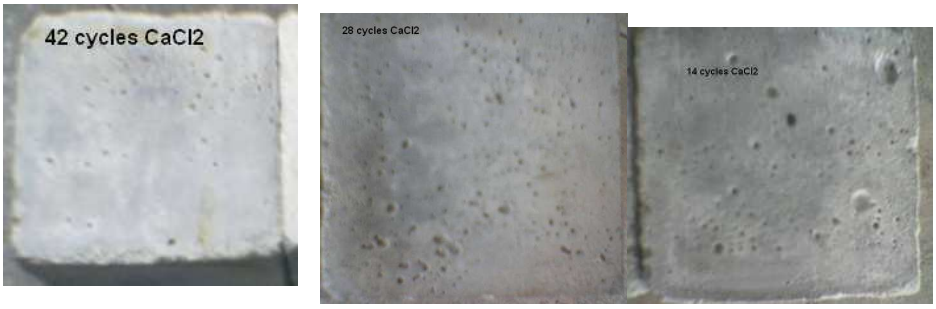
Plate 4.4: Conditions of 10% Metakaolin Mix at w/c+m=0.46 Exposed to (a)Sodium Chloride (b) Sodium Chloride with inhibitor (c) Calcium Chloride (d) Calcium Chloride with inhibitor at Different Wetting Drying Cycles



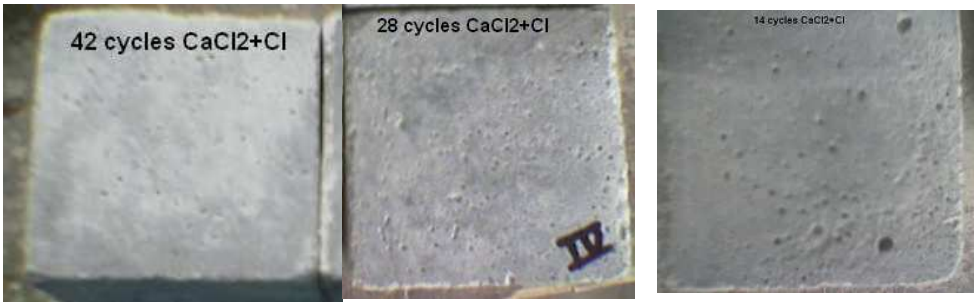
(a)



(b)

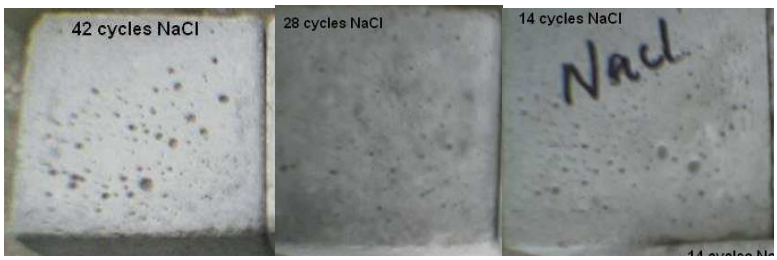


(c)

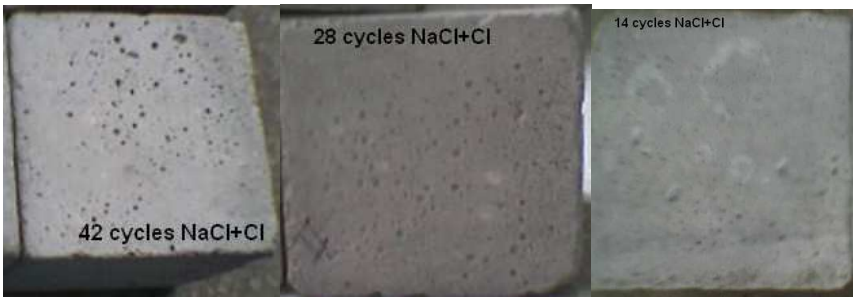


(d)

Plate 4.5: Conditions of 5% Metakaolin Mix at w/c+m=0.5 Exposed to (a)Sodium Chloride (b) Sodium Chloride with inhibitor (c) Calcium Chloride (d) Calcium Chloride with inhibitor at Different Wetting Drying Cycles

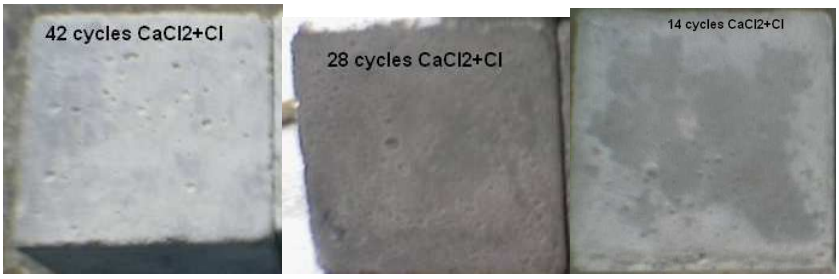


(a)



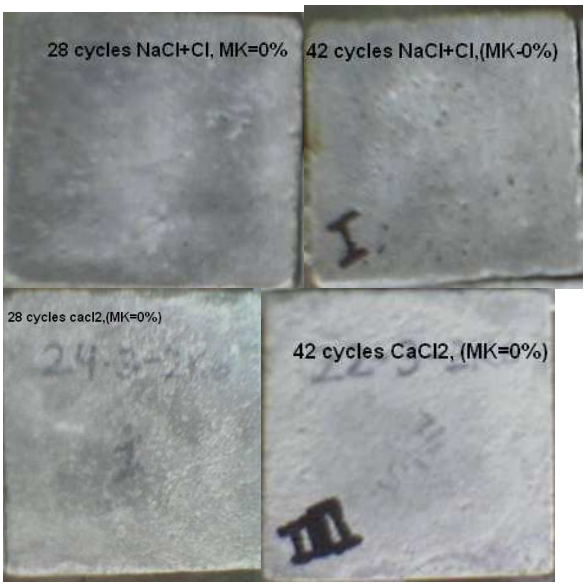
(b)

(c)



(d)

Plate 4.6: Conditions of 10% Metakaolin Mix at w/c+m=0.5 Exposed to (a)Sodium Chloride (b) Sodium Chloride with inhibitor (c) Calcium Chloride (d) Calcium Chloride with inhibitor at Different Wetting Drying Cycles



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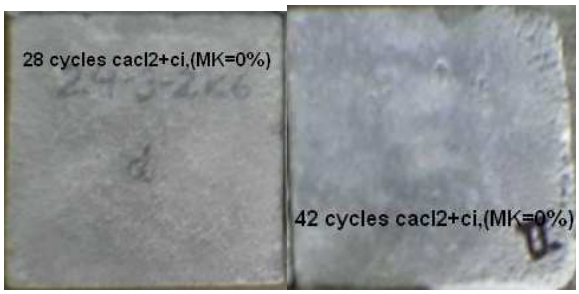
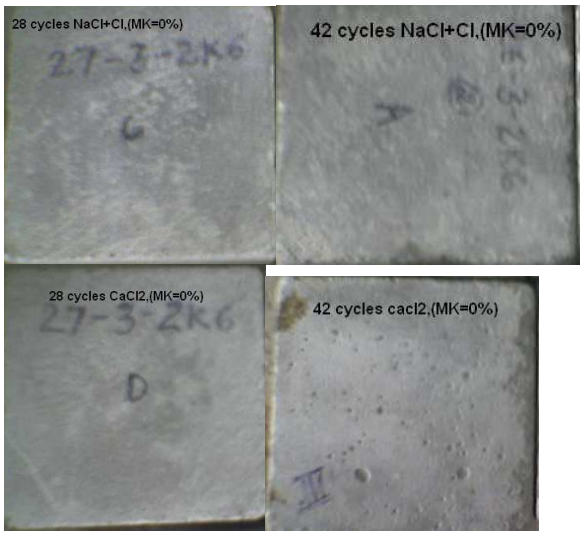


(c)

Plate 4.7: Conditions of Control Mix at w/c=0.46 Exposed to (a) Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles



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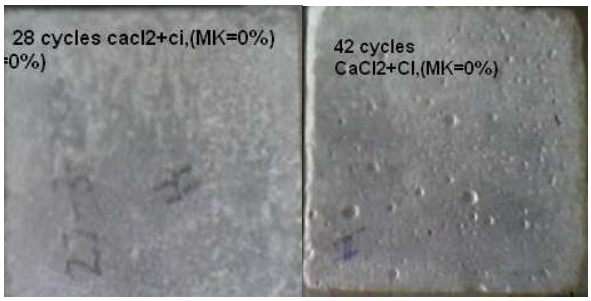
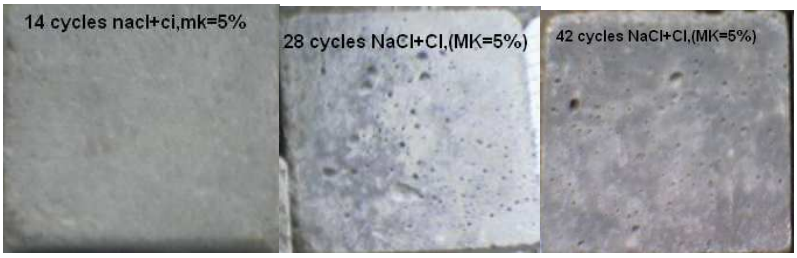
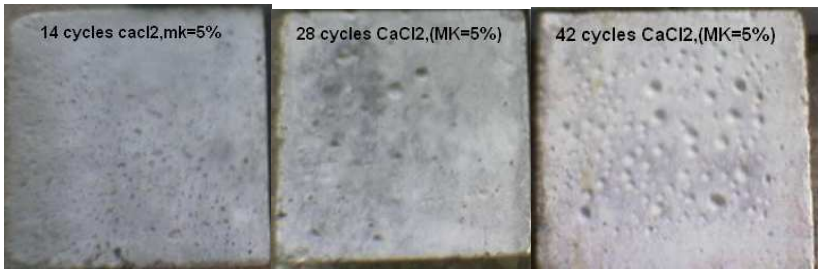


(c)

Plate 4.8: Conditions of Control Mix at w/c=0.5 Exposed to (a) Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles



(a)



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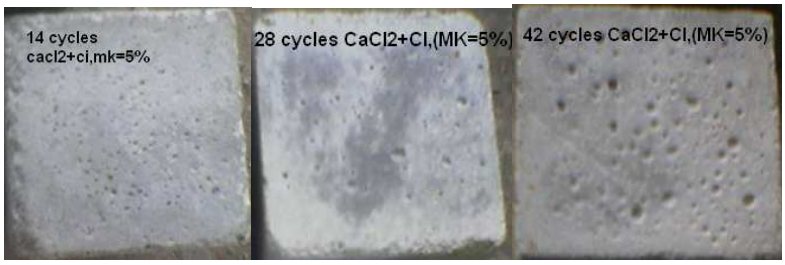
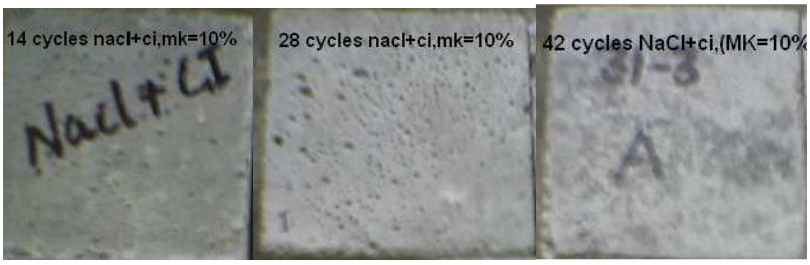
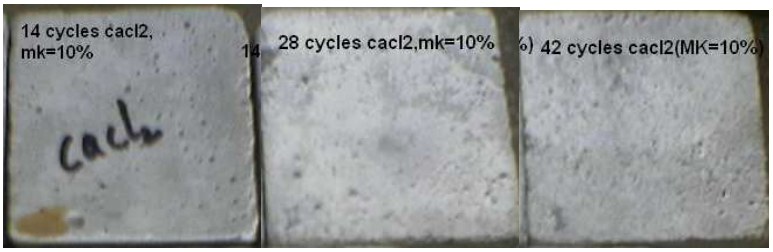


(c)

Plate 4.9: Conditions of 5% Metakaolin Mix at w/c+m=0.46 Exposed to (a) Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles



(a)



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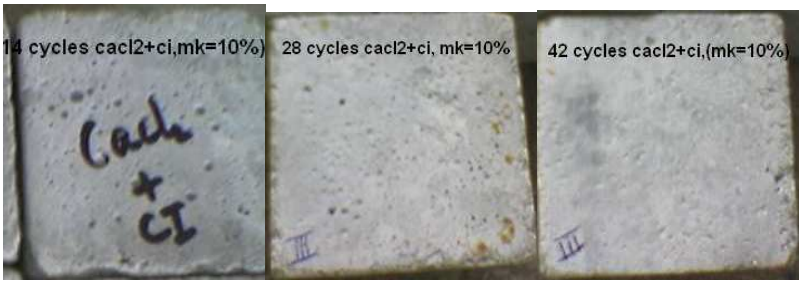
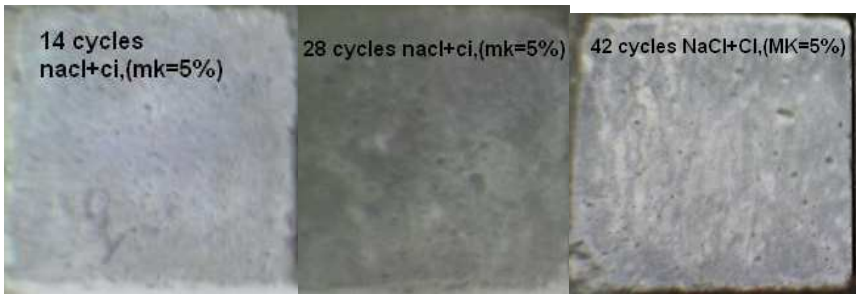
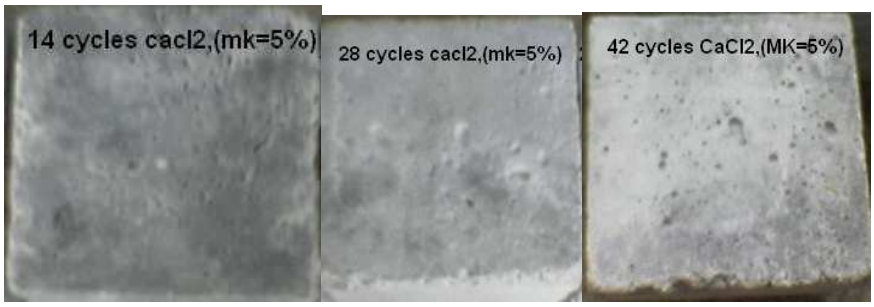


(c)

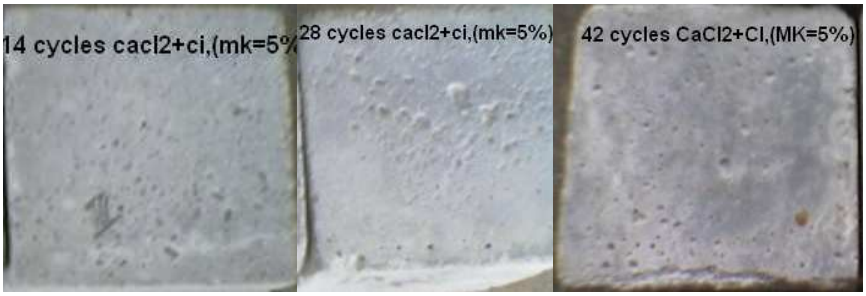
Plate 4.10: Conditions of 10% Metakaolin Mix at w/c+m=0.46 Exposed to (a) Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles



(a)



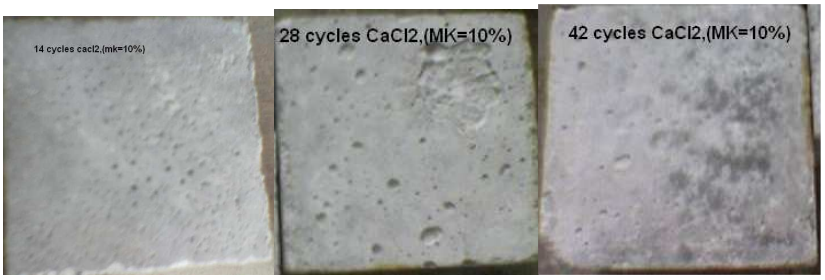
(b)



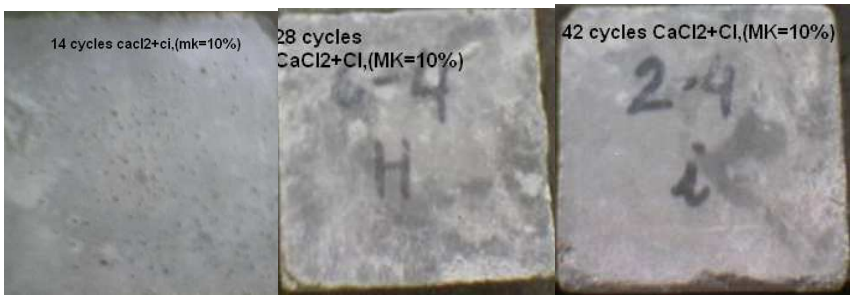
(c)

Plate 4.11: Conditions of 5% Metakaolin Mix at w/c+m=0.5 Exposed to (a) Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles

(a)



(b)



(c)

Plate 4.12: Conditions of 10% Metakaolin Mix at w/c+m=0.5 Exposed to Sodium Chloride with inhibitor (b) Calcium Chloride(c) Calcium chloride with inhibitor Solutions at different Freezing Thawing Cycles

CHAPTER 5

CONCLUSIONS

1. Metakaolin is a good admixture for samples cured in simple distilled water having no aggressive ions added to it.

2. Mortar samples without metakaolin when exposed to aggressive environment containing Na^{+}, Ca^{++}, Cl^{-} ions shows continuous increase in the strength with increase in the number of wetting drying as well as freeze thaw cycles at low water cementitious ratio, whereas, at high water cementitious ratio, mortar samples show poor resistance as the number of cycles increase.

3. Effect of freezing thawing cycles on the mortar samples exposed to various salt solutions is more detrimental as compared to wetting drying cycles. Scaling damage, salt deposition or material loss type of deterioration is aggravated in freeze thaw cycling as compared to wetting drying cycles.

4. Aggressive environment having Ca^{++} cause more reduction in load carrying capacity as compared to Na^{+} ions under both type of cycles. Corrosion inhibitor further enhances the deterioration in mineral admixtured samples.

5. Metakaolin is better suited in controlling the deterioration of mortar samples at higher water to cementitious material ratios. However, the optimum dosage of metakaolin at which its pozzolanic activity is maximum depends on the type of salt as well as the type of environmental conditions to which the mortar samples are exposed to.

6. The compatibility of corrosion inhibitor depends on the type of salt solution to which the mortar samples are to be exposed. As it is concluded from the study that triethanolamine is not compatible with calcium chloride but shows positive results with sodium chloride.

7. In case of samples under wetting drying cycles, 10% metakaolin is the optimum dose for samples exposed to sodium chloride and 5% is the optimum dosage for the calcium chloride immersed mortar samples.

8. Under freeze thaw conditions, 5% metakaolin is the optimum dose for samples immersed in sodium chloride with inhibitor and 10% metakaolin for samples immersed in calcium chloride solution.

9. Ultrasonic pulse velocity test method is not a reliable test method for samples subjected to freeze thaw cycling. Whereas, in case of wetting drying exposure conditions, the indication given by the pulse velocity about the quality of mortar samples matches with the load carrying capacity of samples. It is concluded that this test method should be used along with some other non destructive test to get accurate results regarding the quality of mortar specimens.

10. 5% metakaolin samples exposed to calcium chloride with and without inhibitor under freeze thaw cycling at low water cementitious ratio show significant mass loss as compared to the control mix.

11. This indicates that triethanolamine maintains a high level of saturation in cement paste and significantly increases the resistance of mortar samples to withstand more number of freeze- thaw cycles.

CHAPTER 6
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