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Improving Performance And Durability Of Concrete

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Ryerson University

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IMPROVING PERFORMANCE AND DURABILITY OF CONCRETE

by

Mohammad Reza Nazeran

(B.Sc., Azad University, Tehran, Iran, 2000)

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Presented to Ryerson University

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requirements for the degree of

Master of Engineering

in the program of

Civil Engineering

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Mohammad Reza Nazeran, Master of Engineering, 2009

Department of Civil Engineering

Ryerson University

ABSTRACT

Concrete is a porous material with different size of pores and cracks. Even the high quality concrete is a porous material which can pass the water through its cement paste. Porosity of the concrete can affect the natural performance of the concrete structure. Usually the water that comes from the environment contains the soluble contaminates which may initiate the reaction with the concrete materials and reduce the serviceability and design service life of the concrete.

Durable structures to withstand significant deterioration can help to reduce the maintenance problem and conserves energy, money, materials and resources. The purpose of this research is to determine the major durability problem of concrete structure. The effects of critical environment deterioration such as sulfate and chloride attack was studied. Also the use of recycle and new material that might offset the destructive effects of environment attack to improve the durability or reduce the permeability was investigated.

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1. CONCRETE DURABILITY AND PERMEABILITY

1.1. INTRODUCTION

Concrete has been recorded in existence as long ago as 7000BC. Concrete with the production of more than five trillion kilograms annually around the world recognizes as the largest production of all man-made materials. Each year around one cubic meter of concrete is produced for every person on the earth. The versatility, large production and huge usage of the concrete make it the most fundamental material for the construction industry.

Concrete may last forever when it is designed based on the given load and theoretical design method. But the materials cannot withstand forever and may lose their functions during the time according to the surrounding environment.

Concrete is a porous material with different size of pores and cracks. Even the high quality concrete with higher density is a porous material which can pass the water through its cement paste. Porosity of the concrete can affect the natural performance of the concrete structure. The paste-aggregate interfacial zone is known as the most porous part of the concrete that increase the risk of micro cracking in the concrete. The higher concentration of the calcium hydroxide (CH) at interfacial zone between the paste and aggregate is the main cause that increases the weakness of this zone and consequently makes it more susceptible for the cracking and path of the ingress of the aggressive agents.

Capillaries and pores inside the concrete can absorb the moisture from the environment and then transport it to the inner part of the concrete. Usually the water that comes from the environment contains the soluble contaminates which may initiate the reaction with the concrete materials and reduce the serviceability and design service life of the concrete. Deterioration of concrete may occur through chemical or physical reaction of aggressive material with cement paste, aggregate or even the reinforcing steel in the concrete. Durable

structures to withstand significant deterioration can help to reduce the maintenance problem and conserves energy, money, materials and resources. Design of durable concrete has the major effects on the reduction of waste material. In addition, it decreases the production of the building materials and has a grate impact on the environment.

Therefore, preventing deterioration by early planning can be very cost efficient. Evaluation of concrete and material to resist different environmental condition and prevent or delay the ingress of aggressive elements is necessary.

Focus of this study and literature review is in the major durability problem of concrete structure. The effects of critical environment deterioration such as sulfate and chloride attack will be discussed. Also the use of recycle and new material that might offset the destructive effects of environment attack and help the concrete to improve the durability and reduce the permeability will be introduced.

1.2. DURABILITY

Concrete life can be failed or ended before the ages that it is designed for it. In fact, a durable concrete will assure the owner and engineer of having a long life structures. It means that the durable concrete can last longer and tolerate the aggressive attacks without any significant defects on the performance of the structures.

Although all concrete structures should have the minimum strength, the strength of concrete cannot reveal the all means of durability. It has been well established that the durability is an independent factor to the strength and strength cannot ensure the durability of the concrete. In other word, the strength and durability are not linear to each other. The high strength concrete may be deteriorated in case of adverse mechanical, physical, or chemical causes and loose its stability, serviceability and performance. Higher strength of the concrete can

improve the strength against the cracking from the internal stresses but it does not necessary guaranty the durability of the concrete structures. The life extension of concrete structure basically depends on the quality control of the material selection, mix design method, production, transportation, placement, finishing and curing.

In principle, durability as it has been defined by the American Concrete Institute is the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining its desired engineering properties. Different concretes require different degrees of durability depending on the exposure environment and the properties desired. Durable concrete must have the ability to withstand the potentially deteriorative conditions. Ensuring the good durability is about minimizing the rate of penetration and deterioration. In severe exposure condition the use of high quality and low permeability concrete is recommended.

Important degradation mechanisms in concrete structures are categorized to the following items:

1. Freeze-thaw damage (physical effects, weathering)
2. Alkali-aggregate reactions (chemical effects)
3. Sulfate attack (chemical effects)
4. Corrosion of reinforcing steel embedded in concrete (chemical effects)
 - a) carbonation of concrete
 - b) chloride induced
5. Abrasion (physical effects)
6. Mechanical loads (physical effects)
7. Microbiological induced attack (chemical effects)

Controlling the transport properties of the concrete such as diffusivity, permeability, and sorptivity is the design issues for durability and service life of concrete structures in severe environments.

1.3. PERMEABILITY

Permeability is defined as the property that governs the rate of flow of a fluid into the porous solid. The difficulty of the migration of the liquid and gas through the concrete is described as the permeability of the concrete.

The permeability of concrete has a significant role in the durability of concrete since it controls the rate of penetration and ingress of the moisture. Increase in concrete permeability will allow the water and chemical ions penetrate to the concrete and facilitate the deterioration. Low porosity and permeability is the first line of defense against environment attack.

Low porosity controls the diffusion and movement of the moisture in the concrete. Since the pores of the aggregates are disconnected, the porosity of concrete usually refers to the porosity of the paste. It means that the paste controls the overall porosity of the concrete. In this case, the D'Arcy' law can be applied to the concrete paste to measure the coefficient of permeability based on the flow of water in the paste. The D'Arcy' law is presented as:

$$Dq/dt = K (\Delta H A)/(Lv)$$

Where: Dq/dt is the rate of fluid flow,

K is the coefficient of permeability

v is the viscosity of the fluid,

ΔH is the pressure gradient,

A is the surface area,

L is the thickness of the solid.

By using this formula the permeability or the ability of ingress of contaminated moisture can be determined. K parameter is not a constant value and it differs based on the age and w/c

ratio of the paste. K value is strongly depends on the porosity and the degree of hydration of cement paste.

At the later age of concrete hydration, the more C-S-H will be produced which decrease the connectivity of the pores inside the paste. Thus the mobility of the water in the concrete will be limited and consequently the K value decreases to the lower amount. The decrease in the K value will be continued by the age of the concrete. Even after full production of C-S-H, the calcium hydroxide (CH) can grow inside the capillary and reduce the coefficient of porosity. Also coefficient of porosity becomes higher in case of drying and rewetting. Rewetting of the concrete after drying will change the size of pores and partially connect the pores that results increases in the K value.

1.4. TRANSPORT MECHANISM

Since the sulfate and chloride are the two most aggressive agents for the concrete and will make lots of durability problem, we will discuss the formation and influences of these two deteriorative ions in following chapters. In addition, the role of different material and provision methods will be explained on those chapters.

But, first we should learn about the ingress or transport method of these two components into the concrete. The transport of deteriorated elements and aggressive ions can be occurred as following:

1. Diffusion (concentration difference)

In case of ions concentration in the surface of concrete, the driving forces will move the ions to the concrete. The significant concentration differences will cause this transportation. The diffusion coefficient of the concrete will control the rate of diffusion into the concrete. The w/c ratio, pore size, pore structure and material property will determine the diffusion coefficient and the speed of movement.

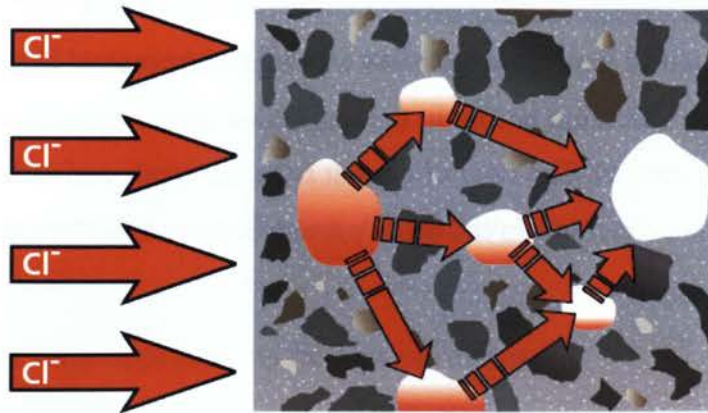


Fig.1.1 – Diffusion of ions based on concentration differences

2. Permeation (pressure difference)

When the contaminated water is facing the one side of the concrete structure, the water will flow to the opposite side of concrete due to water pressure. The water pressure at one side of concrete will cause that the water flow to the non-pressure surface. The movement of water through the concrete will accumulate the aggressive ions at the opposite side of the concrete.

3. Capillary rise (capillary suction)

Another way of ion movement in concrete is the capillary suction. Capillary pores exist between the partially hydrated cement particles. The interconnection network of the pores will cause that the bulk water flow in the capillary pores. The capillary pores will transport the water through the pores network and provide ionic diffusion. The rate of capillary suction will be controlled by the w/c ratio and pore structures of the paste.

4. Migration (voltage difference)

This kind of ionic transportation will happen in case of chloride corrosion. When the chloride corrosion occurs in the embedded steel reinforcement, the electrical current will be created. The flow of current between anode and cathode will transfer the ions in the concrete. In fact the dense pore structure will reduce the speed of ion migration.

1.5. ROLE OF WATER-CEMENT RATIO (W/C)

Water/Cement ratio (w/c) is a universally fundamental concept of concrete which is the oldest law in the concrete technology.

The water/cement ratio has the most significant effects on the durability of the concrete. The lower w/c ratio will decrease the porosity of the concrete and results in lower permeability and higher durability.

Generally, the capillary pores are depended on the w/c ratio and lower w/c ratio will decrease the capillary porosity of the concrete. In low w/c ratio, the concrete particles come closer to each other and reduce the free spaces inside the concrete (Figure 1.2). As a result, less outer products will be formed and therefore the capillary porosity of the paste will be reduced.

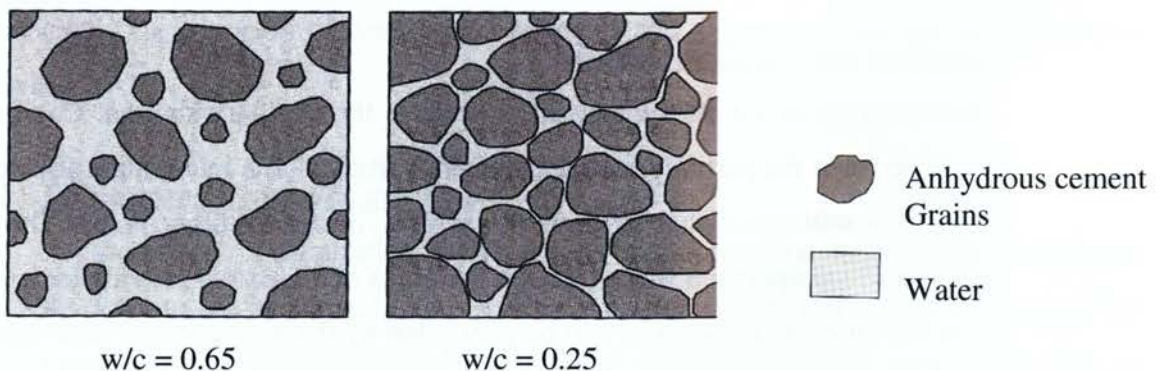


Fig.1.2 – Fresh cement pastes with different w/c ratio

In addition, the w/c ratio will affect the strength of the concrete. Based on Feret formula the strength of concrete will increase when the w/c ratio decreases.

$$f'c = k / (1 + (w/c)^2)$$

Where k is a constant value depending on the type of cement

Feret formula clearly shows the negative effects of water content on the compressive strength ($f'c$) of the concrete and also reveals that the reduction in w/c ratio causes an increase in compressive strength. The higher concrete strength will develop more resistance to the internal stresses and limit the cracking in the concrete that might be generated through expansive reaction of contaminated agents.

Moreover, it was observed from the researches that the reduction of the cement content for the fix w/c ratio has an effect in improving of the permeability. Also, it was concluded that the less amount of cement will improve the modulus of elasticity, shrinkage, creep and performance of the concrete.

2. SULFATE ATTACK IN CONCRETE

2.1. INTRODUCTION

One of the main causes that affect the long term durability and provide deterioration in the concrete is the ingress of aggressive components such as sulfate ions.

Sulfate attack is the most common type of chemical attack in the concrete and it was noted by the U. S. Bureau of Reclamation at 1936 with the limited use of sulfate in the concrete.

Ettringite, the most widespread kind of sulfate attack in the concrete, is an expansive material which causes expansion, crack, spalling, strength loss, weakening in mechanical properties, softening or loss of cohesiveness in cement paste, structural problem and etc.. All of these consequences increase the permeability of the concrete and accelerate the ingress and penetration of the contaminated water into the concrete.

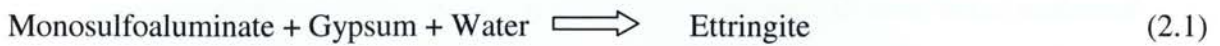
Sulfate attack can be divided into two different categories of “*external*” and “*internal*” based on the source of sulfate.

External sulfate attack happens when the source of the sulfate ions is environment. Contaminated soil, groundwater and seawater can supply enough sulfate ions which is required for the occurrence of sulfate attack in the concrete. Internal sulfate attack occurs when the source of sulfate is inside the concrete. Over sulfated cement or the source of gypsum in the aggregate can supply internal source of sulfate for the concrete.

2.2. MECHANISM OF SULFATE ATTACK

The hydration of C_3A with gypsum at early age of concrete hydration will create ettringite ($C_6AS_3H_{32}$, calcium sulfoaluminate hydrate). Dissolution of the gypsum supplies sulfate source for the hydration of C_3A inside the concrete. Since the hydration of C_3A and creation of ettringite occur at the plastic stage of hydration, it does not cause any damage (called

primary ettringite). Ettringite can grow around the cement particle inside the paste and retard the hydration of the cement without any expansion damage. Ettringite is a stable product as long as the ample supply of sulfate is provided to consume all C_3A content in the paste. The less amount of sulfate cannot completely hydrate the whole C_3A content. Hence, the remaining C_3A react with the ettringite and form another sulfoaluminate product with fewer sulfates in its composition. The new product is called monosulfoaluminate (C_4ASH_{12}) and can be turned to ettringite when subjected to the source of sulfate.



The reaction of monosulfoaluminate with gypsum usually takes place after hardening of concrete and when the concrete has gained its strength. Formation of expansive ettringite (secondary ettringite) after concrete hardening will cause cracks, spalling and concrete softening in the rigid concrete. In fact the cement with high C_3A content is more susceptible to deterioration when exposed to the source of sulfate. The code suggests to use of cement type V for the situation that the concrete structures are exposed to the of risk sulfate attack.

As mentioned, the presence of gypsum is critical for the conversion of monosulfoaluminate to ettringite. Gypsum provides enough sulfates to the solution and converts the monosulfoaluminate to an expansive product like ettringite. The formation of gypsum is also problematic and cause expansion in concrete. When the source of sulfate appears to the concrete, calcium hydroxide start to react with the sulfate and provides gypsum to the solution.



Gypsums that produce from this reaction can initiate the sulfoaluminate corrosion in the concrete.

Gypsum formation (gypsum corrosion) causes 120% expansions in solid volume whereas the ettringite formation increases the volume to about 55%. Lots of investigation in sulfate attack studies confirms that the formation of ettringite is predominate to the gypsum corrosion and that is why the gypsum formation is not the primary reaction in sulfate attack.

Besides the expansion, sulfate attack will cause softening and lose of cohesiveness in the paste. Attack of sulfate to the concrete will cause decalcification of C-S-H and reduce the bounding in the paste that may result in strength loss and softening in the concrete.

We can conclude that sulfate attack can cause two different corrosion in the concrete; sulfoaluminate corrosion and gypsum corrosion. The way to avoid these corrosions is the key to study the prevention method in case of sulfate attack.

Also it should be noted that the source of sulfate ions in this process is external which means that the environment (soil, groundwater and etc.) supplies the sulfate to the concrete. While the source of deterioration is external, the durability of concrete plays an important role to limit the influences of attack in the concrete. The diffusion of sulfate ions is easier in permeable concrete and hence the risk of attack is higher. On the other hand, the durable concrete with less capillary pores can mitigate the deterioration effects. High quality cement with low w/c ratio has significant effects on the durability of concrete. The lower w/c ratio provides fewer overall capillary pores in the concrete. In fact the low w/c ratio can reduce the rate of diffusion of sulfate ions and reduce the effects of sulfate attack in the concrete. It is agreed upon that effect of low w/c ratio is higher when the sulfate resistant cement is used. It appears that low w/c ratio does not have the same effects with the high C_3A cement and therefore it is not much effective. M. Sahmaran, O. Kasap, K. Duru, I.O. Yaman [2.6] concluded that the cement chemistry is more important than permeability of the concrete and thus the cement composition determines the rate of destructive effects in concrete.

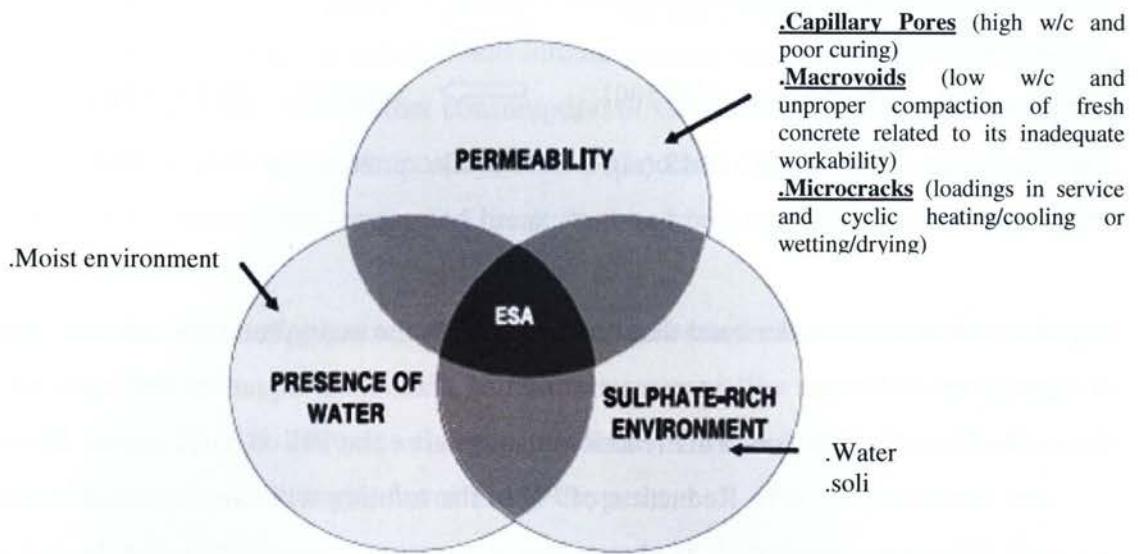
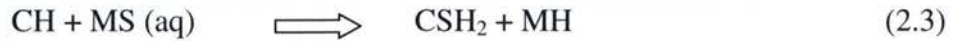


Fig.2.1 – ESA: External Sulfate Attack

2.3. MECHANISM OF MAGNESIUM SULFATE ATTACK

Sulfoaluminate and gypsum corrosion usually happens in the presence of sodium or potassium sulfate in the solution. The reaction of magnesium sulfate with concrete is more complicated and aggressive than other type of sulfate. In addition to sulfoaluminate corrosion and gypsum formation, the reaction of magnesium sulfate with concrete hydrated phases makes further corrosion in the concrete. The extra corrosive reaction of magnesium sulfate involves the decomposition of calcium silicate hydrate in the solution.

Magnesium sulfate reacts with the calcium in paste and substitute calcium with new product which is called brucite (MH or magnesium hydroxide). Both C-S-H and calcium sulfoaluminate phases in the solid paste will be decomposed to provide new components.



It is important to understand that brucite (MH) is the main product in all three equations. The presence of brucite will increase the rate of reaction in equation (2.3) and produces more gypsum in the solution. This reaction also reduces the PH of paste due to CH consumption and insolubility of MH. Reduction of PH in the solution will cause that Ca^{2+} leave the C-S-H gel. The new equation (2.5) shows that magnesium decalcificate C-S-H and replaces the calcium with brucite. Magnesium ions and low alkalinity both are responsible for the decomposition of C-S-H. Brucite in this equation can react with the silica gel and form the magnesium silicate hydrate (MSH) which does not have any cementitious properties.

2.4. ROLE OF C3S ON SULFATE ATTACK CONTROLLING

C_3A content is considered as the major methods of controlling sulfate attack in all standards and regulations all around the world. Recent studies show that C_3A content is not the only cement elements that determine whether the cement is sulfate resistance or not. Sulfate resistance cement with low C_3A and C_4AF generally has higher C_3S content. In another word, the $\text{C}_3\text{S} / \text{C}_2\text{S}$ ratio of this kind of cement is higher than other types of cements.

Investigation on the amount of C_3S is showing that high C_3S content (usually use for early strength) can modify the behavior of the concrete in exposure to the sulfate ions. The sulfate resistance (low C_3A) cements with high C_3S cannot tolerate the sulfate attack and may expand and lose strength. The reason is that the hydration of C_3S produces 2.2 times more CH in the paste than C_2S . As discussed in the mechanism of sulfate attack on the concrete,

there are two major corrosion in case of sulfate attack; sulfoaluminate corrosion and gypsum corrosion. The higher CH in the solution will initiate gypsum corrosion, expansion, spalling and cracks in the concrete. Also further consumption of CH with sulfate ions causes that the Ca^{2+} releases from C-S-H and decomposition of C-S-H occurs. Decalcification of C-S-H will reduce the cohesiveness of the mortar and break the bond between the paste and aggregates in the area of attack.

Moreover, the formation of gypsum could prepare the favored circumstances for ettringite formation. As it has been pointed out, the sulfoaluminate corrosion needs enough gypsum to be initiated. Since the CH increases the gypsum level of the solution, the sulfoaluminate corrosion can proceed and ettringite forms inside the paste.

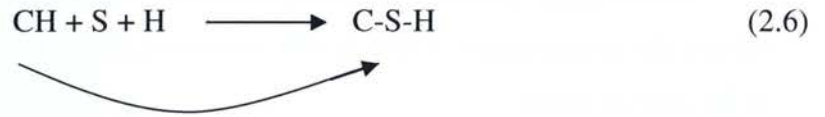
All of these consequences inform us that the rate of $\text{C}_3\text{S} / \text{C}_2\text{S}$ ratio in the cement composition shall be controlled. The high $\text{C}_3\text{S} / \text{C}_2\text{S}$ ratio cannot resist the sulfate attack and cannot be categorized under sulfate resistance cement. On the other hand, the low $\text{C}_3\text{S} / \text{C}_2\text{S}$ ratio shows a good strength in exposure to the sulfate and mitigate the deterioration effects of sulfate attack in concrete.

2.5. EFFECT OF POZZOLANIC MATERIAL AND LIMESTONE FILLER

To avoid or mitigate the sulfate attack consequences in the concrete, we have to control the formation of sulfoaluminate and gypsum corrosion inside the paste. Controlling these two corruptions is the main idea to prevent the sulfate attack for the concrete structures.

Mineral admixtures such as pozzolanic materials have a grate influence on controlling the effects of sulfate attack in the concrete. Firstly, because pozzolanic material has silica base

structure, it can convert the calcium hydroxide (CH) to C-S-H and reduce the crystalline phase inside the concrete. The depletion of CH results in the reduction of gypsum formation.



Formation of secondary C-S-H phases condenses the transitional zone and improves bounding between the paste and aggregate. In fact, it reduces the capillary pores and improves the main weakening area of fractures in the concrete and also enhances the total strength of the structures. Figure 2.2 indicates that the amount of CH is much less in the cement mix with fly ash and natural pozzolan.

Secondly, the addition of the pozzolan admixture to the cement will change the mix design of the concrete. In mix design, the admixture will substitute part of cement and results in reduction into C_3A and C_3S components in the concrete. This reduction is also favored for concrete to resist the sulfate attack.

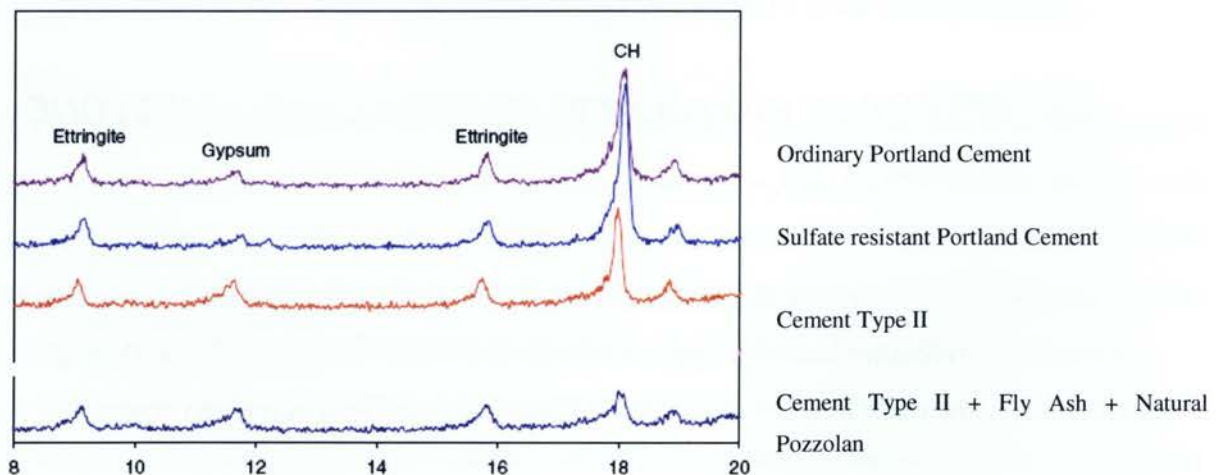


Fig.2.2 – XRD patterns of different cement mixtures

Thirdly, the pozzolanic admixtures reduce the pore size and total porosity of the paste. The very fine admixture acts like a lubricant between the cement particles in the paste and reduce the water demands which is needed for the workability of the concrete. In another word, the ability of packing between the cement particles will increase the workability of the paste and reduce the water demands. Decrease in w/c ratio will help to reduce the capillary pores and provide a less permeable concrete.

And finally, pozzolanic material can fill the gap between the cement particles and limit the connectivity of the capillaries and pores in the mortar.

The effects of limestone filler is reverse of using the natural pozzolan in the paste. It appears that the use of limestone filler is not helpful to prevent the sulfate attack and even in some cases accelerates the expansion and strength loss in the concrete. Limestone filler can accelerate the rate of hydration and provide more CH in the paste. As discussed, the higher level of CH make the cement susceptible to sulfate attack. In addition, because the use of limestone filler will not add any cementitious properties to the cement at later age, it cannot reduce the porosity of the mortar. This effect will cause that the CH crystals grows inside the pores and change the nature of the cement paste.

It is important to underline that the use of limestone filler in the concrete mixture also lead to another reaction in the paste. The carbonate ions which are embedded in the limestone fillers can start to react with the monosulfoaluminate and change it to monocarboaluminate. This reaction results to release of sulfate ions from AFm products which can be stored in the solution. At later age, these sulfate ions can be brought to the new reaction and form gypsum or ettringite. In order to prevent the sulfate attack in the concrete, we have to limit the use of limestone filler to avoid the release of more CH and sulfate ions in the pate. Controlled amount of limestone filler will reduce the risk of sulfate attack in the concrete.

2.6. DIFFERENT ROLE OF SILICA FUME IN PRESENCE OF DIFFERENT SULFATE IONS

It has been pointed out in section 2.5 that the replacement of the cement content with pozzolan admixture in concrete mix design is beneficial to offset the sulfate attack influences in the concrete. Use of silica fume (SF) (filler or replacement) can modify the chemistry of cement component and bring some advantages such as CH removal, C_3A dilution and pore refining to the concrete. Same as pozzolan reaction, very fine particle of silica fume can reduce the overall porosity and create secondary calcium silicate hydrate in the paste. All of these results will help to make a stronger concrete and reduce the effects of sulfate attack in the concrete.

Exposure of cement mortar containing the silica fume to different sulfate composition shows that the mortar reacts differently on each sulfate solution.

All effective parameters of using silica fume will appear in exposure to the sodium sulfate. Studies on different percentage of silica fume in the cement mix show that the 5-10 % replacement of silica fume in the paste brings the most effective performance to the concrete. It is therefore concluded that the 5-10% silica fume in the cement paste will decrease the expansion and strength loss in case of sodium sulfate attack to the concrete.

Different story happens for the same concrete in exposure to the magnesium sulfate. The destructive effects of magnesium sulfate attack are more severe for the concrete containing silica fume. Since the silica fume depletes the portlandite (CH), the less brucite will form on the surface of the concrete. The absence of brucite at the surface of concrete will remove the barrier around C-S-H and provides the situation for the direct attack of Mg^{2+} to the C-S-H gel. Direct attack of Mg^{2+} to C-S-H will decompose it more rapidly and decalcify the hydration products. This reaction causes that the non cementitious composition like the magnesium silicate hydrate (MSH) form in mortar that can result in the breakdown of the bonding between the concrete components. Also it should be pointed out that PH level of the

solution is decreased which means that ettringite becomes unstable. Reduction of PH is favored to provide more gypsum in the paste.

Formation of MSH and gypsum will have the negative effects on the concrete and reduce the overall compressive strength of the concrete.

In summary, the use of silica fume is effective to control the sodium sulfate attack in the concrete but it has negative effects when it is used at magnesium sulfate environment. Cement paste containing the silica fume cannot control the magnesium sulfate attack and accelerate the destructive effects of the attack.

2.7. USE OF CHEMICAL AGENTS TO PREVENT SULFATE ATTACK

The main idea of using the chemical agents in the concrete mix is;

1. to enhance the performance of concrete against sulfate attack
2. to not change the microstructure properties of the paste

The investigations on several chemical agents showed that the barium hydroxide has the most effective influences on mitigation of the sulfate attack consequences in the concrete. The barium hydroxide can be used as saturated water solution in the concrete mix. The main advantage of using of barium hydroxide in the concrete mixture is that this component will not affect the microstructures of the cement paste and thus the cementitious properties of the paste remain same as normal concrete [2.7]. Barium hydroxide has the chemical compatibility with concrete and will make the homogenous mixture with cement paste. This compatibility is the advantage of barium hydroxide since it does not affect the characteristics of the concrete. Barium hydroxide starts the reaction with sulfate ions in the solution and

forms the barite salt (BaSO_4). The BaSO_4 is an insoluble and non expandable salt in the paste. The formation of BaSO_4 reduces the concentration SO_4^{2-} in the solution. Hence the risk of sulfoaluminate and gypsum corrosion will be reduced. Also the lower concentrations of the sulfate ions will decompose the ettringite that may formed previously in the cement mortar and form the barite salts which dose not have any expansive effects on the concrete. In addition, the decalcification of ettringite will occur with the formation of another stable salt such as oxalate. In this case, the calcium will form the oxalate salt and reduce the concentration of the calcium in the solution. Because of this reason, the ettringite will be decomposed and consequently increase the durability of the concrete.

Besides lowering the concentration of SO_4^{2-} , the BaSO_4 acts as a barrier in the solution. BaSO_4 reduces the penetration of aggressive ions from the water into the solution. Moreover, the BaSO_4 barrier will reduce the dissolution of the calcite. Barite will surround the calcite and defend the dissolution of it in solution.

Another advantage of use of barium hydroxide in the cement paste mortar is that it will not affect the alkalinity of the solution. This phenomenon makes the PH level of the solution more stable.

All in one, the barium hydroxide can develop the durability of the concrete against sulfate attack and enhance the stability of hydration products without making any expansion or formation of any crystalline material.

3. THAUMASITE FORMATION IN CONCRETE

3.1. INTRODUCTION

Another form of sulfate attack in portland cement concrete is the formation of thaumasite. Early investigation of the sulfate attack damages on the concrete material was reported in the 19th century. It had been known that sulfate attack on the portland cement concrete could cause expansion, cracking and softening of concrete due to formation of ettringite and gypsum. Formation of ettringite and gypsum was found as the most phenomena in the deteriorated concrete and study of sulfate attack focused on the formation of these two components.

Recent studies on sulfate attack in concrete discovered that there is another form of crystal structure in the sulfate deteriorated concrete material. The new discovered crystal was named “*Thaumasite*”. Thaumasite crystals have a structure similar to the ettringite structure and can be formed in wet and cold environment.

It was concluded from the researches and experimental tests that the thaumasite form of sulfate attack requires the source of carbonate in addition to the source of sulfate. It means that thaumasite can only form when the sufficient supply of sulfates and carbonates are present at the mortar of concrete.

3.2. MECHANISM OF THAUMASITE FORMATION

Thaumasite is a form of sulfate attack that decomposes the C-S-H phase of hydrated concrete in presence of sulfate and carbonate at wet and cold environment. Four main required factors needed which are needed for the formation of thaumasite in concrete are:

1. Presence of “*Sulfate*” – generally from ground, ground water and etc.
2. Presence of “*carbonate*” – generally from aggregates in the mixed mortar, from the source of limestone in cement, from the CO₂ in the air and from the soils.

3. Presence of “*water*” – generally mobile water in the ground
4. Presence of “*cold temperature*” – generally temperature below 15 °C

It should be noticed that the formation of thaumasite is possible even in the absence of internal source of calcium carbonate. Carbon dioxide of the atmosphere may provide the enough amount of carbonate and facilitate the formation of thaumasite in the concrete without the internal source of calcium carbonate.

The threshold temperature which is indicated by the most of researcher for the formation of thaumasite is 15 °C or less. The temperature below 15°C may trigger the formation of a thaumasite.

When these four factors are present at the concrete environment, C-S-H structures will breakdown and new crystalline structure similar to the ettringite will be formed. Thaumasite has hexagonal needle shape structures which are growing into the capillary pores between the cement and grains. Fig. 3.1 shows the SEM image of the spicular crystal structures of the thaumasite.

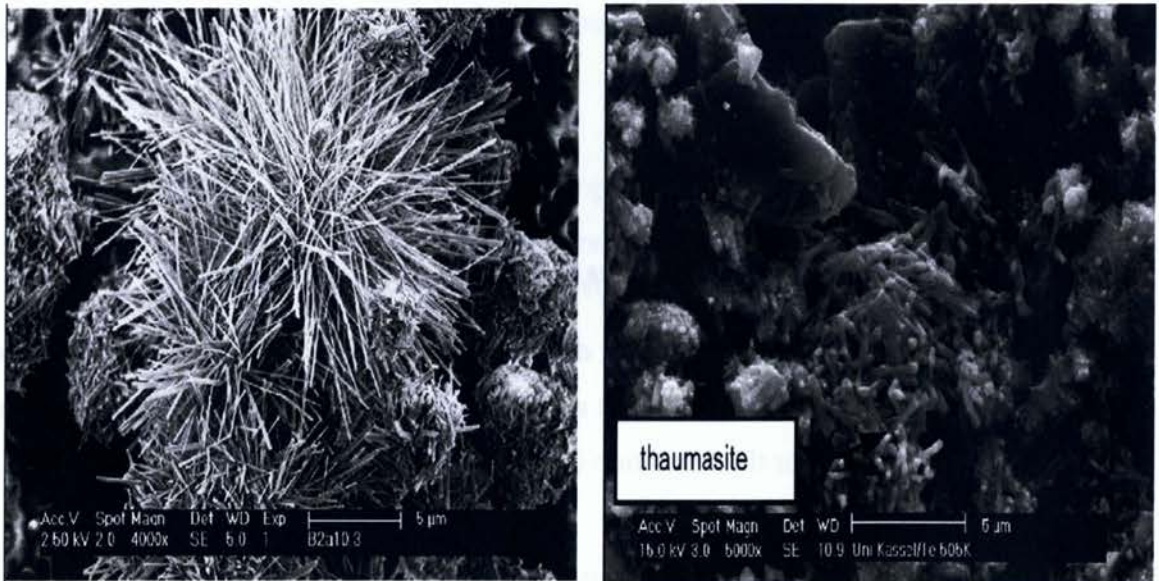


Fig.3.1 – SEM image of Thaumasite

The new crystal material, thaumasite, has two new phases of $[\text{Si}^{4+}]$ and $[(\text{SO}_4)^{2-} \cdot (\text{CO}_3)^{2-}]$ in its structure. In general, normal sulfate attack usually consumes the aluminums exist in the cement to form the ettringite. However, the thaumasite does not have the aluminums in its structure. Investigation on Formation of thaumasite shows that replacement of $[\text{Al}^{3+}]$ and $[(\text{SO}_4)^{2-} \cdot \text{H}_2\text{O}]$ by $[\text{Si}^{4+}]$ and $[(\text{SO}_4)^{2-} \cdot (\text{CO}_3)^{2-}]$ in the structure of ettringite occurs to form the thaumasite.

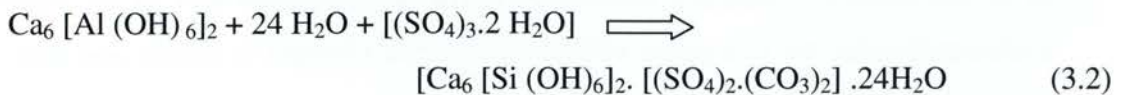


As it was discussed above and shown in the formula (3.1), thaumasite contains sulfate, carbonate and silicon. Silicon is derived from the decomposition of the C-S-H, thus the reduction of C-S-H in the concrete will decrease cohesiveness and turns the concrete to the white mushy mass.

Similar to formation of ettringite in regular sulfate attack, crystallization pressure will cause cracks and expansion during the formation of thaumasite.

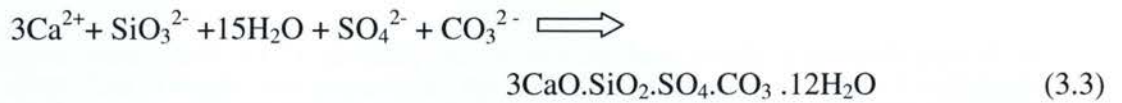
There are numbers of researchers that tried to find the formation route of thaumasite. Although the formation rout of thaumasite is not clear, there are two main mechanisms that explain the formation of thaumasite in the study of deteriorated portland cement concrete [3.2] [3.3] [3.4] [3.6]. These mechanisms can be summarized as:

- a) Mechanism of ettringite conversion: Decomposition of C-S-H and evolution of ettringite occur through the interchange of $[\text{Si}^{4+}]$ for $[\text{Al}^{3+}]$ and $[(\text{SO}_4)^{2-} \cdot (\text{CO}_3)^{2-}]$ for $[(\text{SO}_4)^{2-} \cdot \text{H}_2\text{O}]$. In this mechanism the secondary ettringite can be formed when the released aluminum $[\text{Al}^{3+}]$ start to react with the remaining sulfate and calcium $[(\text{SO}_4)^{2-}]$, $[\text{Ca}^{2+}]$ in the mix.



In this mechanism, the ettringite acts as a precursor of thaumasite and the amount of the ettringite which is available in the solution can control the rate of thaumasite formation.

- b) Mechanism of solution reaction: Through this mechanism sulfates consume the whole aluminums in the solution to form the ettringite. Then the carbonate and remaining sulfate interact with the ettringite to form the thaumasite. C-S-H can be decomposed in the solution since the solubility of thaumasite is lower than C-S-H.



Basically this mechanism occurs between the interaction of carbonate, sulfate and C-S-H in the solution.

As has been pointed out on both mechanisms, thaumasite formation depends on the presence of the ettringite and ettringite controls the thaumasite formation. Also it is obvious that silicate plays an important role in the formation of thaumasite. Since the external source of SiO_2 is not available in the mortar, it should be provided by the inner products of hydration. According to Kohler, Heinz and Urbonas [3.2], decomposition of C-S-H will provide enough amount of SiO_2 for the formation of thaumasite. Based on their research which is shown in Fig.3.2, the addition of the sulfates ions in the solution will breakdown and decompose the C-S-H. This breakdown reduces the amount of C-S-H and provides the required SiO_2 for the formation of thaumasite. This interactions increase the amount of thaumasite in the solution. In other words, it can be concluded that the formation of the thaumasite depends on the breakdown of C-S-H or thaumasite can not be formed without the decomposition of the C-S-H in the solution. Generally thaumasite forms at carbonated area of the concrete. At the carbonated zone, the CH phase of hydrated mortar changes to calcite and then sulfate ions decalcificate the C-S-H at the carbonated zone of the concrete to form the thaumasite.

According to the thaumasite formation mechanism, both decomposition of the C-S-H and crystallization pressure of the ettringite can deteriorate the concrete material.

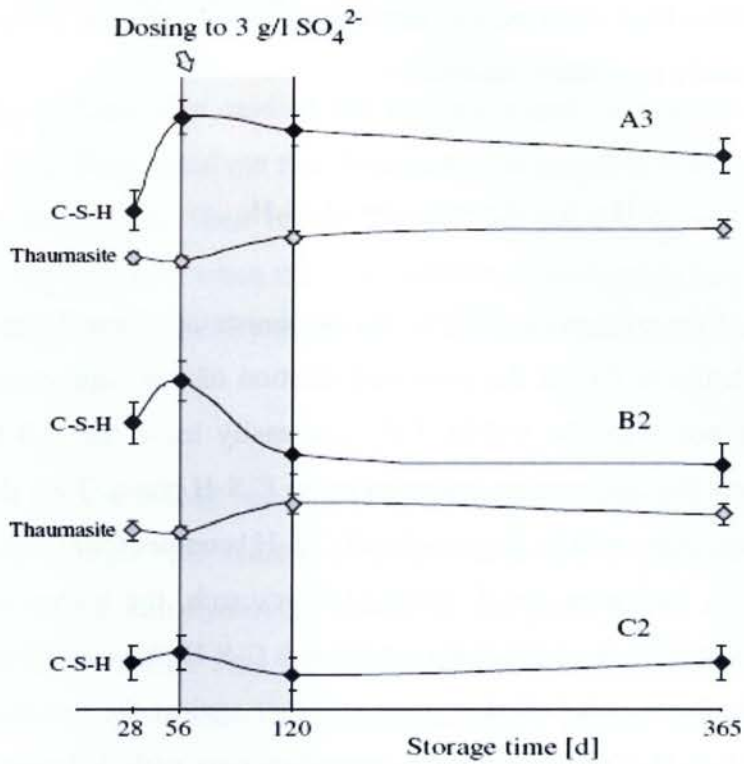
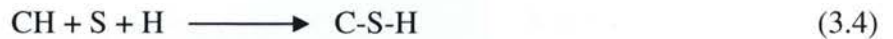


Fig.3.2 - XRD analysis for Thaumasite and C-S-H development

3.3. THE ROLE OF CALCIUM / SILICON RATIO

Calcium hydroxide (CH) with the crystalline structure and fixed composition is one of the hydration products in the concrete which occupies 20% to 25% of the volume of the hardened concrete. Pozzolanic and mineral admixture such as fly ash, slag and silica fume with amorphous silica base structure can turn the calcium hydroxide to the calcium silicate hydrate which is poorly crystalline material.



The consumption of the portlandite (CH) by the supplementary cementitious material (SCM) results in the depletion of CH in the paste and reaction of this admixture with the C-S-H. When the SCM reacts with the C-S-H, Ca^{2+} can easily leave the C-S-H phase into the solution and reduces the calcium concentration in the C-S-H phase. Thus the calcium silicon ratio (Ca / Si) of this phase will be decreased and C-S-H becomes the silicon rich phase.

According to the F. Bellmann and J. Stark [3.5] research, the higher amount of sulfate concentration is required to decompose the silicon rich C-S-H phase and form the thaumasite. They showed that silicon rich C-S-H is more resistant against the formation of thaumasite than calcium rich C-S-H. They investigated several mortars with different binder properties and concluded that the mortar with the mineral or pozzolanic admixture can withstand the moderate sulfate attack whereas the mortar without the admixture (higher portlandite concentration) is more susceptible to form the thaumasite in the exposure to sulfate attack.

Moreover, we can argue that the addition of supplementary cementitious material can reduce the size of pores and voids inside the hardened concrete. Because the permeability is reduced in this type of the concrete, the diffusion of external source of sulfate to the concrete will be difficult and the lower amount of sulfate can enter to the concrete. This situation reduces the risk of the sulfate attack at the concrete.

In another discussion we can also point out that reduction of the CH in the paste will mitigate the effects of the ettringite formation on the concrete. This fact can happen because the aluminum is more soluble in the absence of calcium hydroxide. Since the calcium hydroxides are consumed with the mineral admixture, aluminates can migrate to the pores and form the ettringite inside the voids and pores. Thus the destructive influence of expansive ettringite could be less harsh on the concrete.

F. Bellmann, J. Stark also studied the thermodynamic calculation for the formation of thaumasite [3.9]. They found out that hydroxide concentration (OH^-) plays a vital role in the formation of thaumasite. Their results showed that the C-S-H will not breakdown at the moderate sulfate exposure when the concentration of hydroxide ions are high enough. This means that OH^- can determine the amount of sulfate concentration which is needed for the decalcification of the C-S-H.

Fig.3.3 shows that the silicon rich C-S-H with the Ca/Si close to 1.1 needs higher amount of the sulfate ions at higher PH value to form the thaumasite. It was concluded that the calcium rich C-S-H with calcium hydroxide present at the paste ($\text{Ca/Si} = 1.7$) requires the lower concentration of the sulfate ions for this transformation. This investigation results that the silicon rich C-S-H is more resistant to decalcification at the low temperature and the presence of portlandite (CH) in the paste will reduce the threshold of sulfate resistance in the concrete and cause softening, spalling and strength loss.

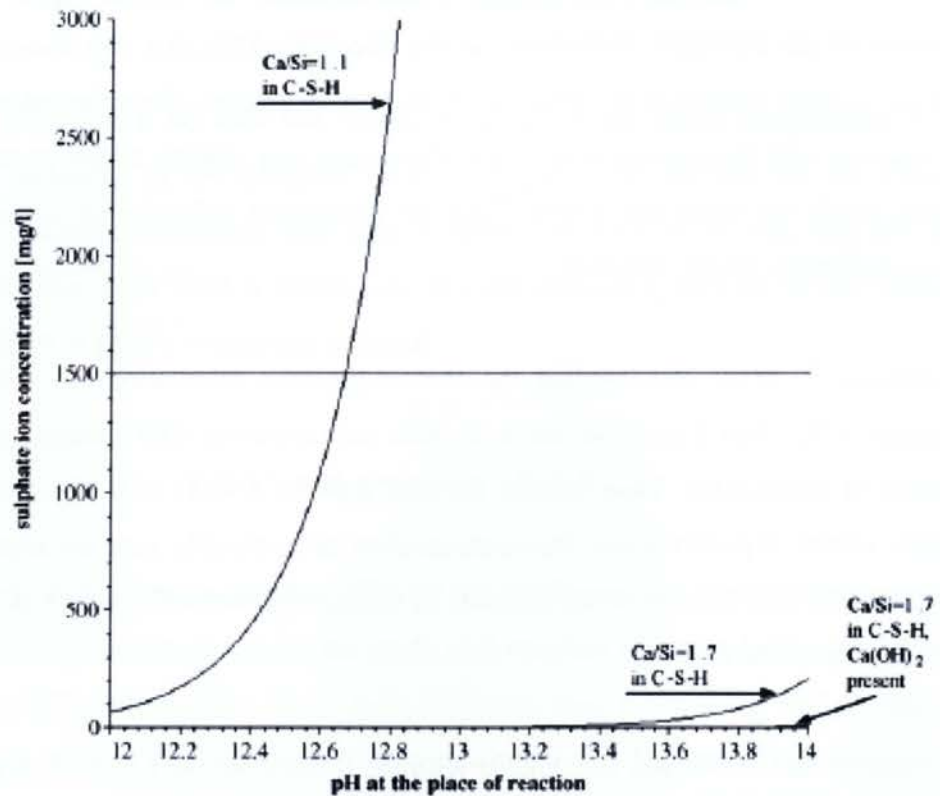


Fig.3.3 - Minimum sulfate ion concentration required for the transformation of C-S-H gel into thaumasite as obtained by thermodynamic calculation.

In conclusion for the role of calcium hydroxide or the effect of Ca / Si ratio on the formation of thaumasite we can indicate that the sufficient amount of mineral or pozzolanic admixture in the mixture can prevent the conversion of C-S-H to the thaumasite. Thus the addition of mineral admixture to the mortar can be excellent choice to delay or avoid the formation of the thaumasite in the concrete.

3.4. SULFATE RESISTANT CEMENT AND THAUMASITE

As it was explained at the sulfate attack chapter, the lower amount of the C_3A in the cement can reduce the harsh influences of the sulfate attack on the concrete. Using the low C_3A cement may result to the full conversion of C_3A to ettringite at the early life of the concrete hydration before gaining the full strength. But the formation of thaumasite is not related to the content of C_3A in the paste. Thaumasite generally occurs when the C-S-H phase decompose in presence of sulfate and carbonate ions at the wet and cold environment. Thaumasite usually use the inner phase of hydration product (C-S-H and ettringite) which are present at the hydrated cement and is not completely related to the outer component. Thus the formation of thaumasite is not C_3A depended and lowering the C_3A content in the cement will not avoid the formation of thaumasite.

The results of investigation in the effect of the C_3A content in the concrete shows that the only thaumasite can be formed in the concrete using low C_3A cement, but in the cement with the high content of the C_3A both ettringite and thaumasite can be seen. In high C_3A cement, the carbonation phase partially modifies the ettringite and develops the crystals similar to both ettringite and thaumasite. Either thaumasite and ettringite crystals or something between those can be recognized in the cement with the high C_3A content.

Generally the standards and regulations of all around the world limit the content of the C_3A in the cement for the concrete structure at the sulfate exposure. The standards usually suggests to use the cement type II for the low to moderate sulfate attack and type V for the higher sulfate attack risk to limit the amount of the aluminum in the mortar. But the standards and regulations do not indicate any limitation to avoid the thaumasite attack in the concrete. It is beneficial to regulate a topic in the standards for the prevention of thaumasite formation in the concrete. For example, we can specify the minimum percentage of the supplementary cementitious material that must be used when the engineers recognize the risk of the thaumasite formation in the structure which is exposed to the aggressive source of the sulfate and carbonate at the cold temperature (below 15 °C). This limitation

1. Will reduce the permeability and pore size of the mortar and decrease the ingress of the deteriorated materials
2. Cause to make the silicon rich C-S-H phase in the concrete that may withstand the decalcification and decomposition of the C-S-H in presence of the moderate sulfate attack.
3. and finally to deplete all CH products and prevent the gypsum formation in the concrete.

All in one, we have to consider the formation of the thaumasite as well as the ettringite in the cement and concrete standards.

3.5. THE ADDITION OF LIMESTONE

Mineral admixture or reactive filler such as limestone may be added to the cement paste in two different methods.

First, they may be added as the addition to the paste and improve the workability. They will replace the sand if they add as an addition to the concrete. In this case the minimum amount of the cement will be kept the same because the cement is responsible for the strength and durability.

In the second way, this material can substitute the particles of cement. At replacement method, they decrease the heat of the hydration and are responsible for the durability of the concrete.

When the limestone is used as a replacement of the cement in the paste, it will reduce the amount of the cement and consequently increase the water-cement (w/c) ratio. If we keep the w/c ratio constant with decreasing the amount of the water which is required for the workability, we will come up with the porous concrete. Increasing the w/c ratio will be resulted to the increase in the size and amount of the pores and voids and also will cause the

interconnectivity of the pores which is the favor of the aggressive ions to ingress. However, when the limestone is used as the filler or addition to the concrete, it will help the workability of the concrete and therefore reduce the amount of the water which is required for the same workability. Therefore the use of the limestone as filler can reduce the overall permeability and capillary porosity in the paste.

The use of the limestone in the cement although reduces the gravity segregation of the concrete materials but provides the calcium carbonates and increases the source of the carbonate. Ettringite will remain stable in the concrete in the absence of the carbonate. When the source of the carbonate is available in the concrete, the *monosulfoaluminate* phase changes to *monocarboaluminate* at the early age of the hydration. This conversion will result in the release of the sulfate ions from the monosulfoaluminate and formation of the additional ettringite in the paste. Secondary formation of the ettringite affects the porosity and permeability and provides the porous paste.

The use of specific mineral admixture such as fly ash and metakaolin in the limestone cement paste can retard the sulfate attack and mitigate the influence of the thaumasite formation. The addition of this material will improve the strength of the concrete to resist the thaumasite formation and retard the sulfate attack.

3.6. THE EFFECTS OF BARIUM HYDROXIDE, BARIUM NITRATE AND AMMONIUM OXALATE ON THAUMASITE PREVENTATION

Developing the issues that can help to prevent the formation of thaumasite and ettringite inside the mortar is the one the biggest concerns for the case sulfate attack in the concrete.

Finding the way that transform thaumasite and ettringite phases to the stable and non expansive phases is under investigation and researchers have tested several materials and the methods for this issue.

One thought to prevent the enormous deterioration effects of the ettringite and thaumasite is the conversion of these two phases to the less sulfate ions concentrated phases. Decomposition and releasing of the sulfate ions and making secondary phases with stable materials can help to avoid the ettringite and thaumasite inside the concrete.

Enrico Ciliberto, Salvatore Ioppolo b, Fabio Manuella[3.12] came up with this idea and tried to find the way to shift the expansive phases to the non- expansive, insoluble and stable phase. These researchers investigated the effects of the barium hydroxide, barium nitrate and ammonium oxalate on the concrete samples with the exposure to the sulfate attack. On their experiment they prepared three different concrete samples with the $\text{Ba}(\text{OH})_2$, $\text{Ba}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solutions.

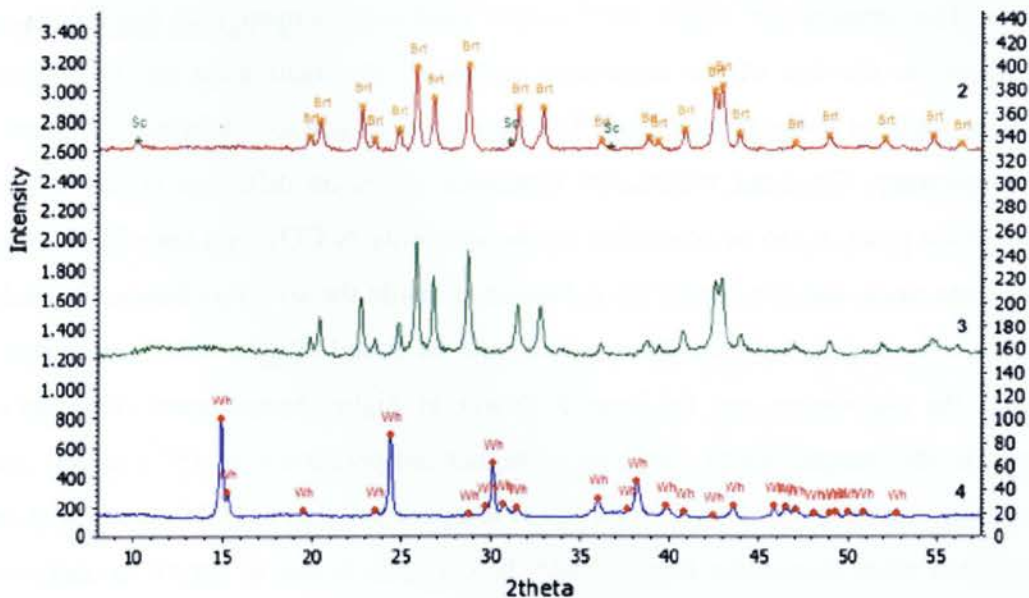
They tried to release the sulfate ions from the ettringite and thaumasite through the barium and ammonium reaction with the mortar and form the new salts such as BaSO_4 and BaCO_3 in the paste. In all three samples the trace of the decomposition of the ettringite and thaumasite with these solutions was observed.

The reactions of barium hydroxide and barium nitrate solutions with the mortar resulted in decomposition and decalcification of ettringite and thaumasite in order to form the BaSO_4 (barite) and the hydrated aluminum hydroxide (scarbroite). Barite is a preferable product because it reduces the concentration of the sulfate ions. The use of barium nitrate will also cause that the nitrate salts crystallize inside the pores and/or at the surface of the concrete. But the use of barium hydroxide will produce the insoluble slats which remain stable even at the PH and temperature differentiation inside the solution. Moreover, the use of barium hydroxide solution with the concrete mortar may produce the barium barrier wall with the remaining of the barium inside the solution and avoid penetration or ingress of the sulfate ions. This reaction will decrease the permeability and increase the durability of the concrete.

In addition, it should be mentioned that the barium hydroxide creates an alkaline environment compatible with the hydrated concrete environment which help the products to remain stable.

The same mechanism will occur in the term of ammonium oxalate solution reaction in the concrete mortar. In this case the whewellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$) will be formed but the released sulfate ions will remain free at the solution which may cause gypsum attack anytime later in the solution. Oxalate salt, the new product containing the calcium, can breakdown the destructive phases by lowering the calcium amount inside them.

All of these three new products are more stable than ettringite and thaumasite and do not cause any expansion in the concrete. However as it was pointed out, the use of saturated barium hydroxide water solution has is more beneficial to prevent the ettringite and thaumasite formation in the concrete. This solution can prevent thaumasite and ettringite formation without providing any expansion or destructive effects on the concrete.





2. Treatment with barium nitrate;
3. Treatment with barium hydroxide
4. Treatment with ammonium oxalate (whewhellite).

Fig.3.4 – XRD pattern of ettringite after three different chemical treatments

3.7. THE EFFECTS OF TEMPERATURE AND PH ON THAUMASITE FORMATION

The low temperature is one the four required factors which is needed for the formation of the thaumasite. The temperature below 15 °C is the ideal environment that thaumasite can be started. Based on the lots of the researches and tests, the thaumasite can be formed and remain more stable at lower temperature. This fact happens due to solubility of thaumasite at higher temperature. Since the thaumasite formation relies on diffusion of the sulfate and carbonate to the paste, it can be controlled by the solubility of CO₂. The gas of CO₂ is soluble at lower temperature and can create the carbonation inside the solution. Hence the carbonate phase that is required to form the thaumasite could be found at the lower temperature. This means that the thaumasite can be formed slower at higher temperature. The amount of thaumasite in the sample which was kept at higher temperature (i.e. 15°C) is less than the amount of thaumasite in the sample with lower temperature (i.e. 5°C). However it should be mentioned that when thaumasite forms inside the concrete, it can be stayed in concrete even at higher temperature close to 30°C [3.3], [3.10], [3.13].

The studies show that the stability of the thaumasite at higher temperature is directly related to the PH value of the paste. PH plays an important role in the formation of thaumasite.

C-S-H cannot be decomposed easily at alkali environment. Reducing the PH value will help Ca^{2+} leave the C-S-H in the solution which leads to decalcification of the C-S-H. At the concrete with high alkalinity environment, C-S-H is immune and Ca^{2+} cannot leave the hydrated phase easily. In contrast, the acidic environment depletes the calcium hydroxide (CH) of the paste and results in decomposition of the C-S-H. Mechanism such as leaching causes the reduction in the CH amount and consequently the reduction in the PH value. Hence the leaching will cause the C-S-H decomposition and thaumasite formation in the concrete.

Also as it was mentioned above (3.3), the higher amount of the sulfate ions is required to form the thaumasite at higher PH level in the solution. Fig 3.3 shows that the concentration of the sulfate ions which are required to form the thaumasite will decrease with the reduction in the PH level of the solution.

Based on all facts and researches we can conclude that the PH plays a vital role in the formation of thaumasite in the concrete. Controlling of PH will help us to mitigate the sulfate attack phases in the concrete.

4. DELAYED ETTRINGITE FORMATION (DEF)

4.1. INTRODUCTION

Delayed ettringite formation is another form of sulfate attack in the concrete. Delayed ettringite formation is kind of late formation of the ettringite that can be formed in several months or years after concrete casting. Since this type of sulfate attack happens after concrete hardening it can produce expansion, cracks, spalling, strength loss and other sulfate attack associated problems. DEF is called as the internal sulfate attack in the concrete and it does not need the environment or external source of sulfates. The internal mechanism that happens in presence of high temperature can supply the enough amounts of free sulfate ions to form ettringite at the hardening phase of concrete hydration. The moisture and high heat temperature are the main terms that are necessary for the deterioration mechanism of DEF.

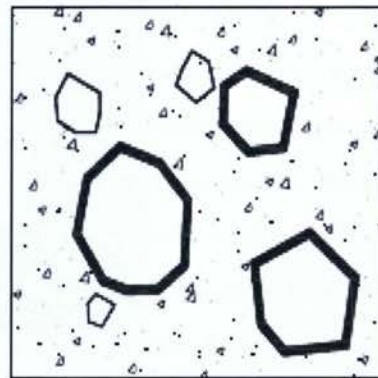
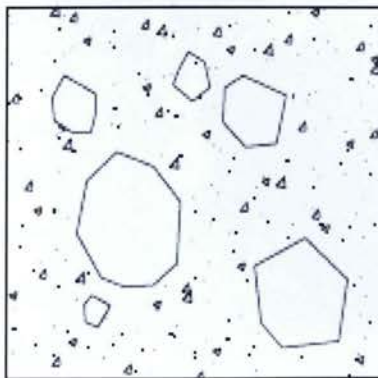
4.2. MECAHNIM OF DELAYED ETTRINGITE FORMATION

Delayed ettringite formation is the process of destruction of the ettringite at the presence of high temperature. The solubility of ettringite is more at the higher temperature. Thus it can be destroyed at the temperature close to 70°C or higher. This temperature can be provided during the cement hydration inside the paste or due to heat or steam curing of the concrete. The high temperature during the setting time of hydration in the concrete prevents the reaction of released sulfate from the cement and C₃A. Furthermore, aluminum and sulfate ions will be released to the solution due to breakdown of the ettringite at the high temperature. These ions can be absorbed by C-S-H at the high temperature and then released after cooling. When concrete hardens the temperature drop down and the sulfate ions leave the C-S-H to be available to reform another ettringite inside the concrete. The released sulfate ions which are coming from cement inside the concrete (no external source of the sulfate) create ettringite at

the presence of the aluminum (monosulfoaluminate) and moisture in the paste. This ettringite will be formed around the aggregates and make expansion in the concrete. Since the concrete is hardened it develops strength loss (reduction in tensile and compressive strength), cracks and reduction to Young's modulus in the concrete.

As discussed, delayed ettringite formation (DEF) is an *internal sulfate attack* and is not depended on the external or excess internal source of the sulfate in the concrete. DEF can be formed even at the normal sulfate content concrete when the heat of hydration or the heat of curing excesses the 70°C.

DEF usually forms at the interfacial zone of the aggregate and paste. Formation of ettringite causes the expansion at concrete. Since the aggregates do not expand, the paste carries the all expansion in the concrete. This expansion will create a gap around the aggregates at interfacial zone between the paste and aggregates. Separation between aggregate and paste cause that the aggregates do not contribute to the strength anymore and consequently reduce the strength of the concrete. The bigger surface area of the aggregate will create bigger gap around it and larger expansion in the concrete. The mechanisms of creating DEF around the aggregates are showing in the following figure.



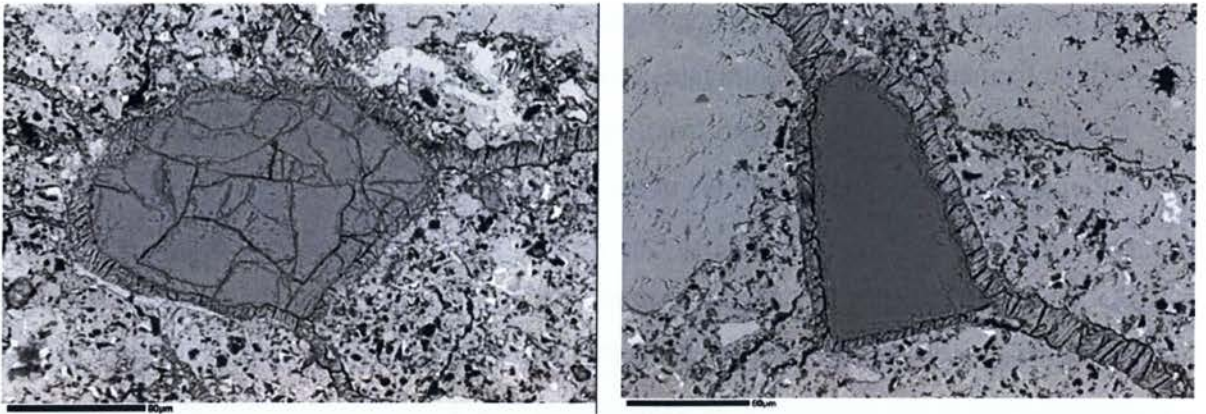


Fig.4.1 –BSE image showing the DEF at aggregate surrounding gap

Regarding the discussion and investigation on the delayed ettringite formation, the main factors which are vital for the formation of the delayed ettringite are summarized as following:

1. High temperature above 70°C: from the heat of hydration or steam curing in the concrete.
2. Mobile water: from surface exposed to water.
3. Internal source of sulfate ions: from cement inside the paste.

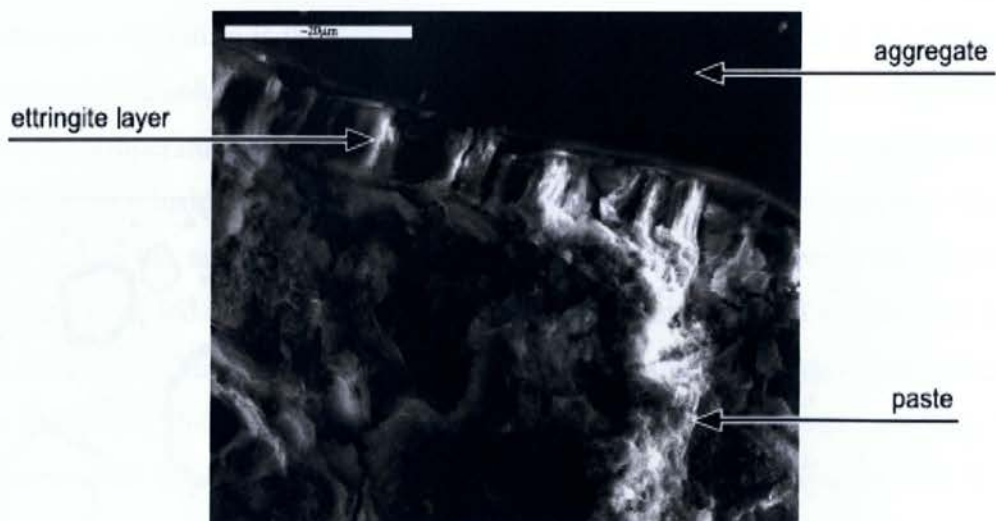


Fig.4.2 – Ettringite around the aggregate of steam-cured concrete

The most effective way to prevent the DEF in the concrete is the use of mineral or pozzolan admixture such as fly ash in mix design of the concrete. Pozzolanic admixtures are not the reactive material and can delay the early hydration of the cement. The reaction of this material is similar to slow reaction of C_2S that reduce the early heat of the hydration. Moreover, the pozzolanic material can be packed between the cement particles and reduce the capillary pores, pore size and overall porosity in the concrete.

4.3. RECOGNIZING OF DELAYED ETTRINGITE FORMATION AND SECONDARY ETTRINGITE FORMATION IN THE CONCRETE

Ettringite can be formed in the concrete via several mechanisms. The better understanding of the different deterioration routes in the concrete is necessary and helps to improve the durability and performance of the concrete. There is a distinction between the delayed ettringite formation (DEF) and secondary ettringite formation (SEF) in the concrete. To recognize different types of ettringite formation in the concrete, it is better to explain the definition and mechanisms of formation of these two types of ettringite in the concrete.

Delayed Ettringite Formation (DEF):

DEF is the process of absorbing sulfate ions by C-S-H at high curing temperature (above $70^{\circ}C$) and then slowly releasing these ions after cooling or at normal temperature. The released sulfates then can migrate to the solution and react with aluminum and moisture to create an ettringite. Since sulfate desorption from C-S-H gel is a slow process, the ettringite forms at later days after concrete hardening. Hence DEF creates cracks and reduces the ultimate strength of the concrete. High curing temperature is the most important factor for the formation of delayed ettringite in the concrete.

Secondary Ettringite Formation (SEF):

SEF is another form of ettringite attack in the concrete which can be formed in different situation from DEF. SEF can be seen in the normal concrete without moist or heat curing application. Decomposition of monosulfoaluminate in the AFm or Aft phases will provide free sulfates in the solution. The decomposition of the monosulfoaluminate can be the result of severe drying in the concrete. Re-wetting of the concrete will provide the mobile water to the concrete. This mobile water can move the sulfates from the solution to the nearest cracks. The sulfate ions can react with the local aluminates at the cracks and form the ettringite. In fact, the high temperature does not have any influence in the formation of secondary ettringite and this formation can be relatively quick.

As defined, SEF can be seen at any type of concrete whereas the DEF is usually seen at the precast concrete which cured with moist and high temperature. Understanding the rout of ettringite can help us to find the prevention method according to its mechanism or microstructures and improve the performance of the concrete structure.

4.4. THE EFFECT OF CEMENT TYPE ON DELAYED ETTRINGITE FORMATION

The studies on the different type of cements and their influence on creating the delayed ettringite have been performed by several researchers. The main factor for delayed ettringite formation is the excessive temperature in the concrete. This temperature can be supplied in two different ways; high heat of hydration or steam and moist curing.

Cement type III which is using for high early strength in the concrete structures, is containing more C_3A and C_3S . The higher C_3A content means the higher amount of sulfate (SO_3) is available in the cement to form ettringite. The higher content of C_3S is also available in

cement type III to create early strength in the concrete through higher degree of hydration and providing more C-S-H in the concrete. Since the higher C-S-H phases and higher sulfate contents are available, the risk of delayed ettringite formation in the concrete using type III cement is higher. If concrete is exposed to high curing temperature which arise the temperature of the concrete to above 70°C , the C-S-H phases can absorb higher amount of sulfates which are available in the solution or are released from the ettringite decomposition.

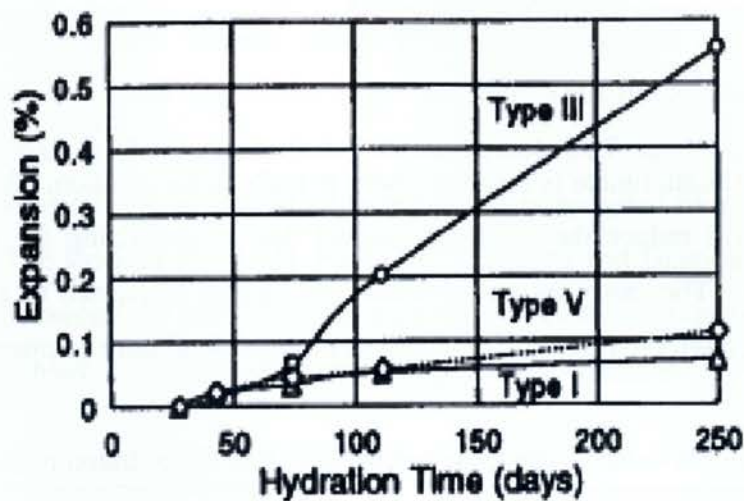


Fig.4.3 –Expansion and DEF comparison in different type of cements

After early hydration or rapid concrete hardening, the sulfates leave the C-S-H and become available to form the ettringite in the presence of the moisture and aluminum.

Figure 4.3 compare three different types of cement (type I, III and V) when the high heat moist curing is applying to all of them. It can be seen that ASTM type III cement expands almost five times more than other types of cement. Hence, it should be considered that do not apply high heat moist curing to the concrete with the ASTM type III cement.

4.5. THE INFLUENCE OF PH ON DELAYED ETTRINGITE FORMATION

Same as thaumasite, the PH value has a critical role on the formation of the delayed ettringite. There are several theories that confirm the high alkali contents increase the risk of delayed ettringite formation and consequently increase the expansion and decrease the strength in the concrete. The theories of the effect of PH in delayed ettringite formation were raised and developed by Taylor, Kelham, Randriambololona and Divet [4.2], [4.7], [4.8], and [4.9]. The main discussion and investigation on the role of high alkali on the DEF are as following:

- Monosulfoaluminate is a stable phase at high alkali solution. The increase in the PH value will reduce the ettringite content due to stabilizing the monosulfoaluminate content. The ready monosulfoaluminate can be converted to ettringite at the later days through the more sulfate contents of high alkali pore solution.
- The high PH value in the paste helps the C_3S to be hydrated more rapidly at early age of the concrete. The higher rate of C_3S hydration will create more C-S-H in the paste. The greater content of C-S-H in the paste can absorb more sulfates at higher temperature and then release them at lower temperature.
- Sidney Diamond [4.3] concluded from his experimental tests that the fluctuation of temperature causes the alkali hydroxide leaching from concrete to the surrounding water. Leaching of alkali hydroxide can reduce the PH of solution and provide the situation for desorption of the sulfate from the C-S-H phase. This condition will cause that ettringite forms due to temperature fluctuation and alkali leaching in the concrete. In the field, the alkali silicate reaction (ASR) or carbonation will reduce the alkalinity of the pores and produce ASR gel with high alkali concentration. Since the PH of

pore solution is reduced, encapsulated sulfates leave the C-S-H and form delayed ettringite in the concrete. Based on this discussion, it can be concluded that ASR and DEF are linked together and the ASR is the precursor for delayed ettringite formation. Presence of ASR and DEF at concrete makes it difficult to find the exact contribution of the DEF.

4.6. DEF INDEX

It has been pointed out that released sulfate from C-S-H can react with the aluminum and form an ettringite after hardening phase of the concrete. Thus the availability of sulfate and aluminates ions in the paste is a main factor for susceptible DEF samples.

$\text{SO}_3/\text{Al}_2\text{O}_3$ or molar ratio is an important factor which is accepted by numerous researchers for DEF study. The work of Fu [4.16], Famy [4.17], Zhang and Diamond [4.5] confirm that the molar ratio between 0.85 and 1.5 in the concrete can cause an expansion and molar ratio less than 0.85 or above 1.5 cannot make any changes in the concrete.

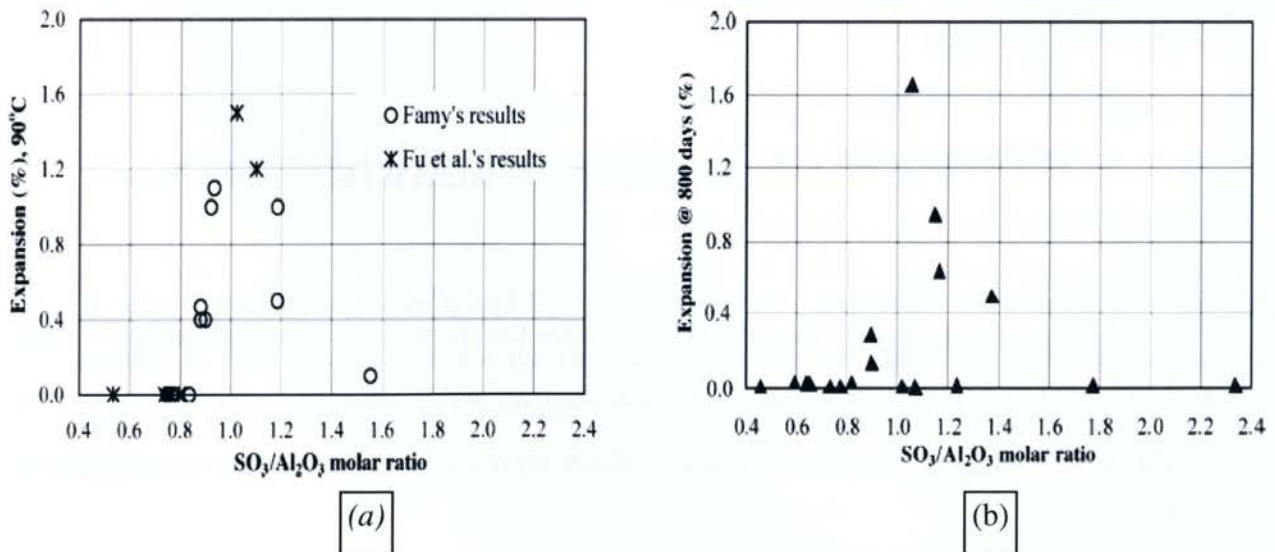


Fig.4.4 – (a) Expansion vs. $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio - results from Famy and Fu's study
(b) Expansion of 85°C treated mortar bars vs. $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio- Zhang study

Figure 4.4 (a) and (b) demonstrate the results of the work of Famy, Fum and zhang and confirm the $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio close to 1 has the biggest expansion effects on the concrete. As it can be seen in figure 4.4 (b), there are some specimens which do not show any expansion even when their molar ration is between 0.85 and 1.5. Zhang and Diamond concluded that there are some other factors beside the $\text{SO}_3/\text{Al}_2\text{O}_3$ molar ratio that affect the delayed ettringite formation in the concrete. Their investigations confirmed that the SO_3 and C_3A content play an important role in the formation of the ettringite. As discussed in section 4.4, the cement type III with higher SO_3 and C_3A content has more potential for the formation of the delayed ettringite in the concrete.

Also as defined in section 4.5, the stability of the ettringite depends on the alkalinity of the solution. In another words, the higher alkali content plays a significant role in the attack of sulfate to the concrete.

Thus all of these factors may affect the formation of delayed ettringite in the concrete. The new definition “*DEF Index*”, described by Zhang and Diamond, explains that the molar ratio is not the only parameter causing DEF in the concrete, but there is an integration of other factors such as SO_3 , C_3A content and PH level that influence the delayed ettringite formation in the concrete. DEF index defines as following and shows the involvement of all three factors in its definition.

$$\text{DEF Index} = (\text{SO}_3/\text{Al}_2\text{O}_3)_m \times [(\text{SO}_3 + \text{C}_3\text{A})_w / 10] \times (\sqrt{(\text{Na}_2\text{O})_{eq}})$$

$(\text{SO}_3/\text{Al}_2\text{O}_3)_m$ term represents the molar ratio, $(\text{SO}_3 + \text{C}_3\text{A})_w$ represents the percentage of total weight of SO_3 and Bogue-calculated C_3A in the content, and $(\sqrt{(\text{Na}_2\text{O})_{eq}})$ is the square root of the weight of alkali content in percent which represents the Na_2O equivalent alkali in cement.

Although the DEF index is not the %100 accurate formula but it proposes the possibility of DEF in concrete. Usually the calculated DEF index above 1.1 described as the possible index

for DEF in the concrete under certain conditions. The research by the Zhang and Diamond confirmed that 1.1 is the threshold number of DEF index for susceptible concrete as it was shown in following figure.

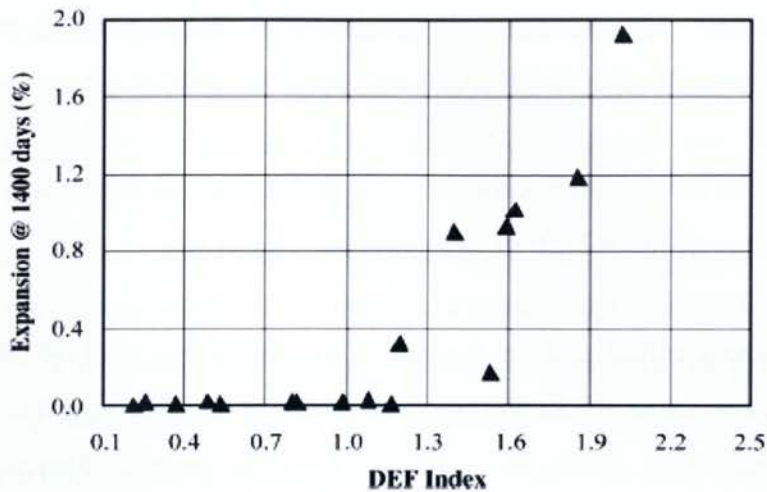


Fig.4.5 –DEF Index vs. Expansion

4.7. PREVENTATION METHODE

As described before, the SO_3 and C_3A content are very important and reduction in the C_3A content of cement will decrease the risk of DEF in the concrete. The high quality concrete with low C_3A content should be used for the concrete structures when there is the risk of DEF.

Low w/c ratio will reduce the overall porosity of concrete and can block the ingress of moisture and deteriorated ions to the concrete. Also the low w/c ratio will reduce the leaching

of hydroxide and alkali and prevent the reduction of PH in the paste. Reduction in alkali hydroxide from leaching can prevent DEF in the concrete.

Another way to mitigate or prevent the formation of delayed ettringite in the concrete is the use of pozzolanic material such as fly ash in the cement mixture. The use of pozzolanic material in the mixture will delay the early hydration and consequently reduce the high heat evolution at early age. Moreover, the replacement of this material will reduce the cement content and therefore decrease the C_3A content in the mixture.

In addition, the low w/c ratio concrete with the mineral admixture will avoid ASR formation which is the precursor of DEF in the concrete.

Cement fineness will also affect the risk of expansion due the DEF. The higher rate of fine cement particles cause the higher reaction occurs in the early age. In consequence, the more heat will be evolved during the setting time of the concrete. Hence the finer cement will increase the surface area and results in more expansion in susceptible DEF concrete structures.

5. CHLORIDE ATTACK AND STEEL CORROSION

5.1. INTRODUCTION

Corrosion of embedded steel is a world wide problem and major deficiency in concrete structures. The economic damage of the steel corrosion in concrete structure is quite large. the annual cost of repairs of concrete and reinforced concrete structures deteriorated due to chloride corrosion only in the Middle East, Japan, North Europe and North America, is estimated to be hundreds of billions of dollars.

The plain concrete without any reinforcement will not deteriorate in the case of chloride attack. The chloride ingress will have a corrosion effects on the reinforcing steels and leads to rust in the steels. The corrosion of reinforcing steels is expansive reaction that may result in cracking, spalling, delamination and concrete weakness.

Chloride can penetrate from several sources. Sea water, de-icing salts, contaminated aggregates, contaminated water, CaCl_2 of an acceleration admixture, airborne salts, salts in chemicals in contact with the concrete surface, salts in ground water and etc. can be the source of chloride ingress.

The porosity and permeability of concrete controls the rate of chloride diffusion. The penetrability of the surface of concrete will accelerate or slow down the ingress of chloride ions into the concrete. Concrete cover performs a significant role in protection of reinforcing steels corrosion. Thick cover over reinforcement will reduce the migration of chloride ions and protect the steels against corrosion.



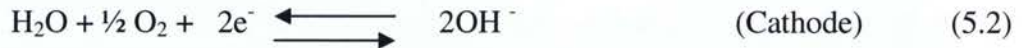
Fig.5.1 –Corrosion Ravaged Columns - Chicago, Illinois

5.2. GENERAL PRINCIPLE OF METAL CORROSION

As described, the chloride attack is one of the most destructive reactions in the concrete. It has been well established that the metal corrosion will happen when the moisture and oxygen are available in the concrete. In other words, the availability of water and oxygen are critical for steel corrosion. The presence of oxygen will initiate the metal oxidation in the concrete. The reaction of iron oxidation will release the electrons to the concrete and provide ferrous ion. The location where iron oxidization is happening is called the anode.



The free electrons of active site (anode) travel through the metal path to the less active sites of reinforcing bar through the flow of electrical current and convert the water to hydroxyl ions (OH^-) in presence of oxygen.



The process of anodic and cathodic reaction at steel bars depends on the movement of electrons from anode to cathode. In fact, the balance of the ionic current will cause that the OH^- transfer from the cathode to anode and start a reaction with the ferrous ion to form the hydrous iron oxide.

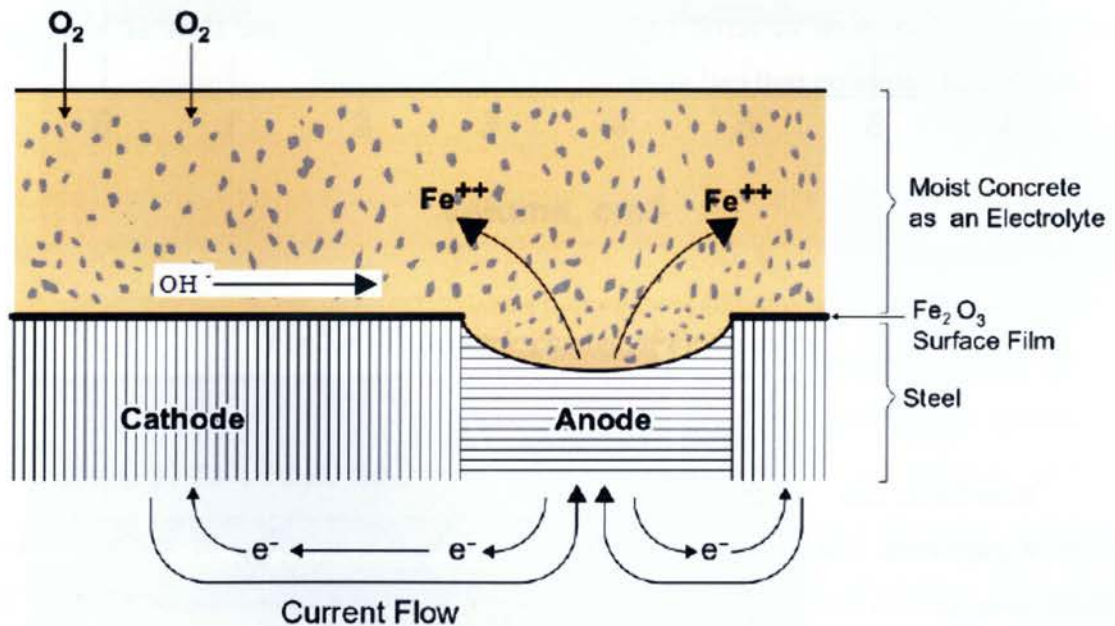
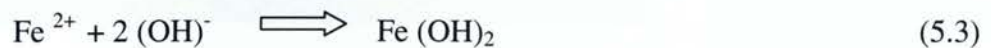
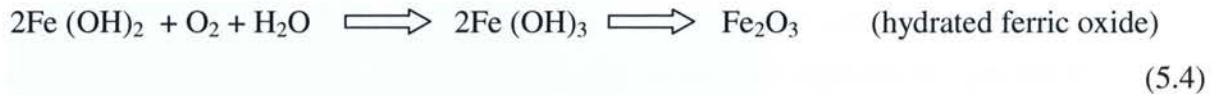


Fig.5.2 –Corrosion mechanism of steel bars



At the further reaction, the hydrous iron oxide suddenly converts to the hydrated ferric oxide.



It is important to underline that the formation of ferric oxide is accompanied by the expansive volume in the reinforcing bars and is called the rust. As a result, the rust in steel will cause the stress in concrete and results in internal cracks around the bars. As the corrosion continues, the volume expansion will occur and concrete spalls. The process of steel corrosion and formation of rust will increase the volume of iron 5 to 10 times higher than original one. Figure 5.4 shows that $\text{Fe}(\text{OH})_3$ and Fe_2O_3 occupy approximately 4-5 and 5-10 times respectively more volume than the Fe.

Since the formation of ferric oxide (rust) is depending on the flow of ionic current, the reaction of corrosion will call as an electrochemical reaction.

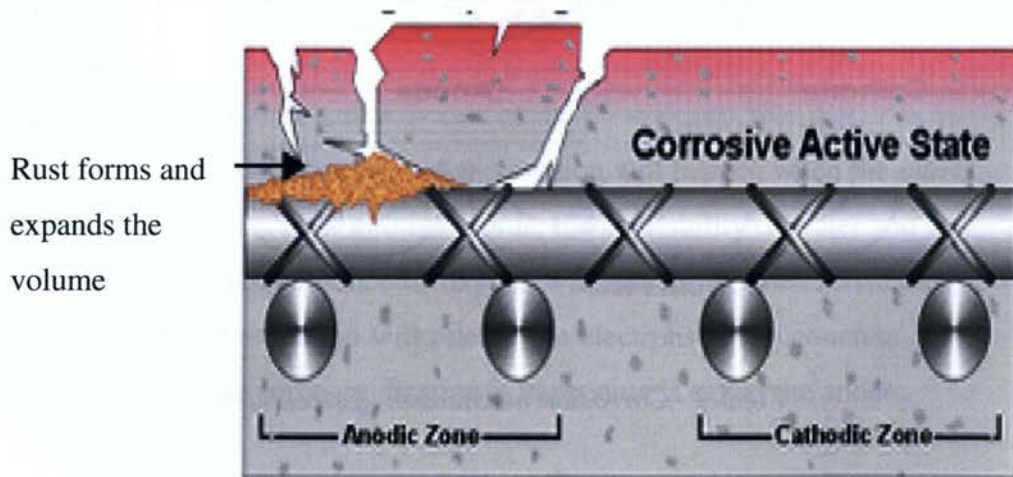


Fig.5.3 –Cracks and spalling around steel rusted area

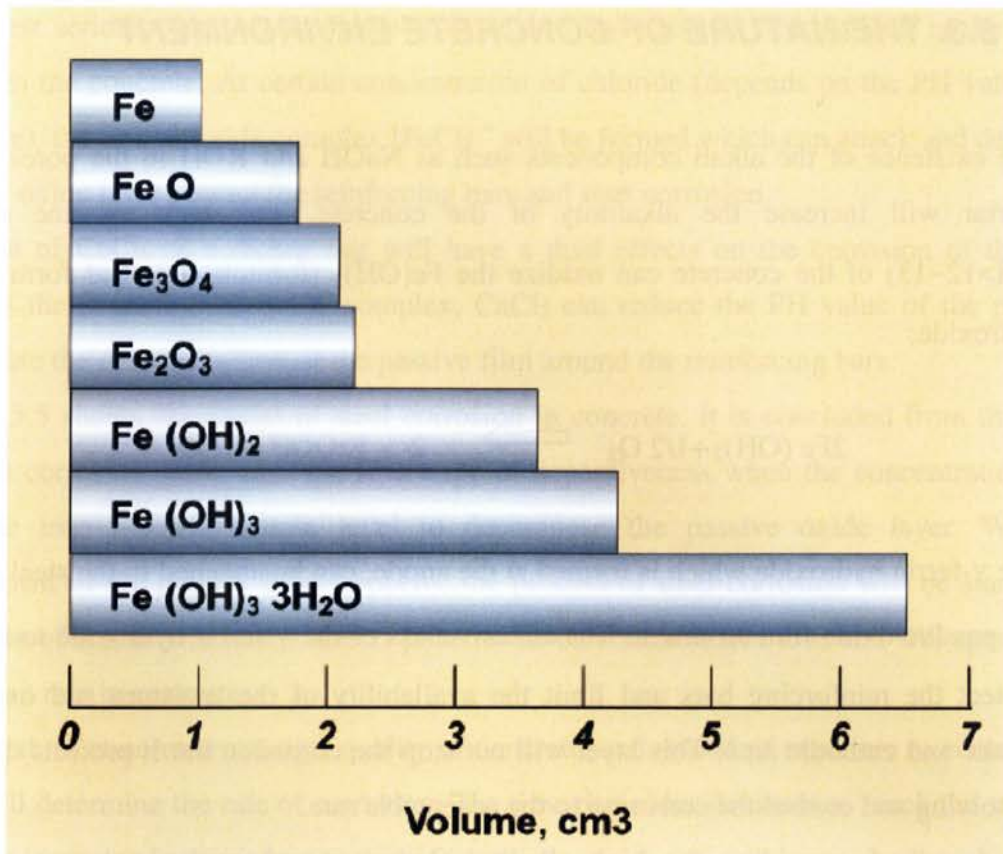


Fig.5.4 –Volumetric change of Fe products

Two different type of corrosion may occur in metal bars; microcell and macrocell. When the anode and cathode form at same bar, the reaction is called the microcell corrosion. In another vein, the macrocell corrosion is referred to the anodic and cathodic region at different bars. In this case, the whole bar or the whole layer of reinforcement acts as anode or cathode. It is obvious that the rate of corrosion and expansion is much higher at macrocell corrosion.

5.3. THE NATURE OF CONCRETE ENVIRONMENT

The existence of the alkali components such as NaOH and KOH in the pores of concrete mortar will increase the alkalinity of the concrete. The high alkaline environment (PH>12~13) of the concrete can oxidize the Fe(OH)₂ (formula 5.3) and form the γ-ferric hydroxide;



The γ-ferric hydroxide which is formed at the anode, can be attached to the steel and provide the passive oxide film around it. The adhesiveness of the γ-ferric hydroxide to the steel can protect the reinforcing bars and limit the availability of the moisture and oxygen to the anodic and cathodic area. This layer will not stop the corrosion but it protects the iron from dissolving and control the corrosion to the acceptable rate.

As described, providing the high alkaline environment is very important to resist the corrosion in the concrete. The protective passive layer forms at high alkaline environment and stays as long as the PH level is over 11.5. Thus the reduction of PH will destroy the passive layer and initiates the corrosion.

One case that may drop the PH value of the concrete is the carbonation. Carbonation occurs when carbon dioxide of the air penetrates into the concrete and reacts with calcium hydroxide to form carbonate. The reaction will decrease the alkalinity of the pore solution and reduce the PH of the solution. Therefore the carbonation in the concrete may result in corrosion at reinforcing steels.

Another case that may drop the PH of the concrete is the use of supplementary cementitious materials (SCM). Although SCM increases the durability of the concrete due to the reduction in the penetrate ability and permeability of the mortar, but it will reduce the PH value of the paste as well. Hence, the use of SCM should be controlled in case of iron corrosion in concrete.

The most serious case that the protective passive layer can be decomposed is the chloride attack in the concrete. At certain concentration of chloride (depends on the PH value of the concrete), the iron chloride complex $[\text{FeCl}]^+$ will be formed which can attack and destroy the passive oxide layer around the reinforcing bars and start corrosion.

The use of CaCl_2 as a dicing slat will have a dual effects on the corrosion of the steels. Besides the formation of FeCl^+ complex, CaCl_2 can reduce the PH value of the paste and accelerate the decomposition of the passive film around the reinforcing bars.

Figure 5.5 shows the model of steel corrosion in concrete. It is concluded from this model that the corrosion starts after the first stage of depassiveness when the concentration of the chloride ions reached certain level to decompose the passive oxide layer. When the breakdown of the passive layer happens, the process of steel corrosion will be started. The initiation of cracks will lead to easier penetration on contaminated ions and will speed up the corrosion rate in concrete.

The depth of concrete coverage, quality of concrete, and period of exposure to contaminated ions will determine the rate of corrosion. The time that chloride needs to reach the steels and start the corrosion is dependent to these factors.

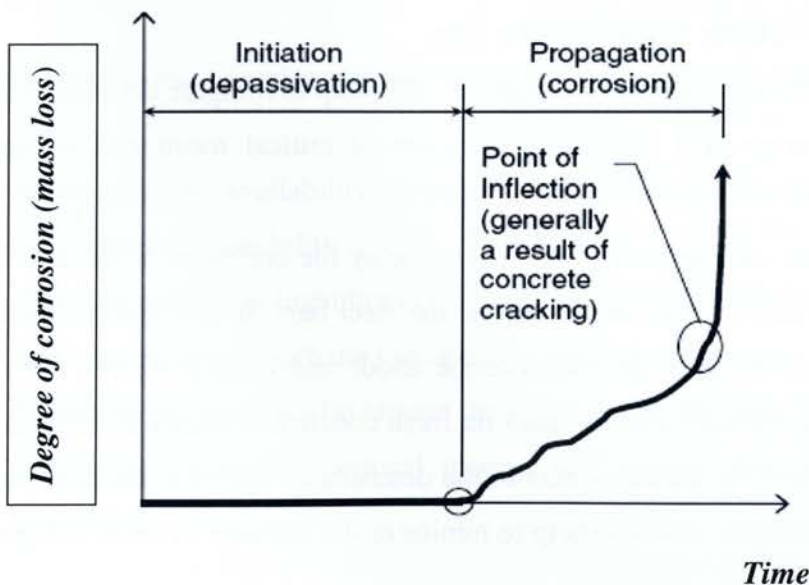


Fig.5.5 –Corrosion process for steel in concrete

5.4. PROTECTION METHODE

It has been widely accepted that the existence of following three parameters can results in rust formation in the reinforcing concrete; 1- moisture 2- oxygen and 3- electron flow.

Finding the way to limit these factors will help to mitigate the corrosion and protect the concrete against the crack and spalling.

It is agreed upon that impermeable concrete has a grate effects on controlling the rate of steel corrosion. The reduction in permeability will limit the penetration of moisture and chloride to the concrete. The low w/c ratio, high quality cement and proper curing help to reduce the permeability of the concrete. Moreover, the low w/c ratio will improve the strength of concrete and increase its strength against the cracks and spalling.

As mentioned before, the supplementary cementitious material (SCM) can improve the durability and reduce the permeability of the concrete. The use of SCM will decrease the overall porosity and size of capillary pores. As a result, the ingress of moisture and chloride will be limited to the controlled rate. When SCM is used for offsetting the destructive effects of corrosion, the engineer should be concerned about the amount of SCM in the mixture. The excessive amount of SCM can drop the PH of paste (explained in section 5.3) and decompose the protective passive layer around the steel bars.

Moreover, the additional concrete coverage can also help to mitigate the effects of corrosion. The adequate coverage will decrease the access of critical mentioned parameter to the reinforcing bars.

Another method that can be used to prevent or delay the corrosion is the use of protective material on the surface of concrete or around the steel bars. In this method the deteriorated factors cannot reach the iron and therefore the anode and cathode cannot form. In case of concrete protection, the use of membranes on fresh concrete or epoxy coating on the surface of concrete can ensure the limited access of the deteriorated agents to the concrete. The good drainage of the membrane will also help to minimize the entrance of these components to the surface of the concrete.

In case of steel coverage protection, the application of epoxy coating will be useful. The epoxy coating will attach to the steel bars and protect it against the formation of anode and cathode. The conclusion can be drawn that the epoxy coating can eliminate the current flow between the anode and cathode prevents the steel rusting in the concrete. One of the most popular industry used coating material is the galvanization or zinc coated material. Galvanizing provide dependable protection in concrete industry due to non reaction activities between the zinc coat and cement paste.

Protecting the passive oxide layer around the reinforcing bars could be another idea to mitigate the corrosion in the concrete. Some inhibitor components such as calcium nitrate can convert the ferrous oxide to γ -ferric hydroxide and protect steel against the chloride attack (details will be discussed in following next sections).

Finally, the last method that prevents the corrosion is the way that can cancel the electrochemical current. Supplying the current to overcome the existing current at the concrete is called the cathodic protection method. Cathodic protection is usually used in aggressive chloride environment (details will be discussed in section 5.6).

In conclusion, the most useable corrosion protection method will be summarized as:

- a) Minimizing the availability of oxygen, water and chloride through the improving of the concrete permeability
- b) Concrete protection (membrane, ...)
- c) Steel protection through the use of epoxy coating (zinc coat, ...)
- d) Protecting the passive film around the steel through the use of inhibitors
- e) Preventing the electrochemical process and current flow due to use of cathodic protection

Selecting of the appropriate method of protection is based on many factors such as the cost, design life, the expected service life of structure, level of chloride contamination, extent of chloride activity, existence of carbonation and

5.5. EPOXY CONCRETE COATING

Concrete coating, as defined in section 5.4, is one of the most beneficial method that is used in the aggressive environment. The epoxy coating can be applied to the fresh or existing concrete and develop the durability of the concrete.

The results of the research by the A. A. Almusallam, F. M. Khan, S. U. Dulaijan, and O. S. B. Al-Amoudi [5.4] revealed that the epoxy coated specimens are more durable against the chloride penetration and can resist the ingress of chloride ions more than conventional concrete. It means that epoxy coating can cover the surface of concrete and reduce the permeability of the concrete. The reduction in permeability implies on both the water and chloride permeability. In fact, the rate of diffusion will be decreased and thus the controlled corrosion will form with the long delay.

The study shows that the chloride diffusion coefficient of epoxy coated specimens is lower and its permeability diffusion is about one-tenth of the uncoated concrete specimens. Based on the same research, the polyurethane and epoxy coating reduce the electrical resistivity of the concrete and performs a better resistance against the chloride attack rather than other coating products such as acrylic, polymer and chlorinated rubber coating.

In addition, applying of epoxy coating on the surface of concrete will reduce the diffusion of carbon dioxide into the concrete and consequently eliminate the formation of carbonation. Since the carbon dioxide cannot reach the calcium hydroxide (CH), the carbonation will not occur (or just a limited can be formed). Hence, the PH of the paste will remain the same and passive oxide layers continue to protect the reinforcing bars.

In summary, the epoxy coating covers the surface of the concrete which is exposed to the harsh environment and limits the access of water and aggressive chemical components to the surface of concrete.

5.6. CATHODIC PROTECTION

Cathodic protection provides the highest level of protection to the steel. This method costs the project more than other method of protection. When there is an ongoing chloride attack into the concrete, the use of cathodic protection is recommended.

The electrical current which flow from anode to cathode in concrete will cause the corrosion problem. The way of supplying the current at the opposite direction to the corrosion current is referred to the cathodic protection. In this method the supply of external current will cancel the existing corrosion current and avoid the electron to be exchanged between the anode and cathode. Cathodic protection provides the opposite current to convert the anode to the cathode and prevent the electrochemical corrosion in concrete. Cathodic protection is usually applies in two different ways;

- external power source to impress the current
- use of dissimilar metal to provide localized current (galvanic systems)

Impress current system applied the DC voltage to the concrete to polarize the anode and overcome the corrosion. Electrons flow from the power (anode) to the steels (cathode) can cancel the electrochemical current in steel corrosion. Although this system is useful even at high chloride attack environment, the use of this technique will need the ongoing supply of

external current. The corrosion mitigation will stop as soon as the power disconnects from its source.

Galvanic protection method is the novel technique that extend the service life of the structures. This technique can be used for both the new and constructed structures.

The basic of this technique is based on the different corrosion potential of dissimilar materials. It has been suggested that the use of magnesium, aluminum or zinc materials are a good approach for this purpose. Since the magnesium, aluminum or zinc based material has the higher potential of corrosion, they will be corroded in favor of steel reinforcing bars. The preferred corrosion of galvanic based material will provide the electrical current against the corrosion current and therefore protects the steel corrosion. In principle, the magnesium, aluminum or zinc sacrifices themselves to protect the steel bars. That is why this method is also called the sacrificial system.

The recent development and ongoing research on galvanic protection approach provides the embedded galvanic anode system for cathodic protection. The embedded galvanic anode is made from the zinc core which encapsulated inside the cementitious materials. The galvanic anode has the cylindrical shape with diameter of about 64 mm and thickness of 27 mm.

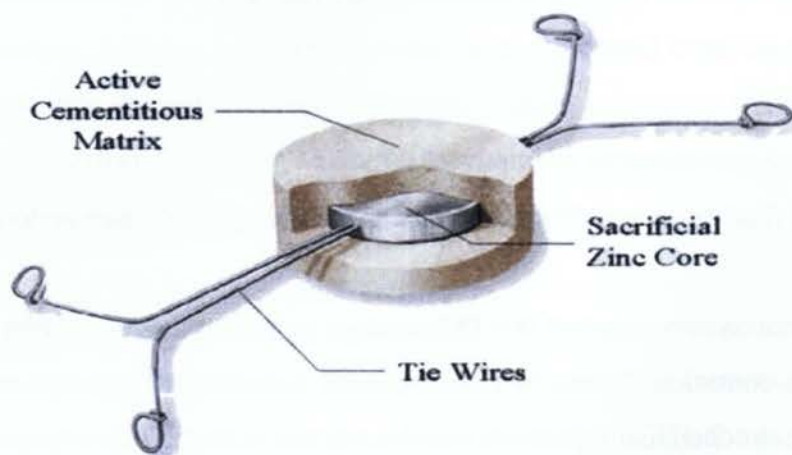
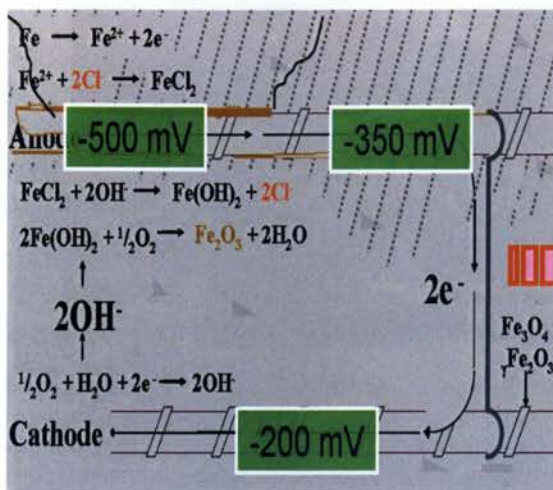


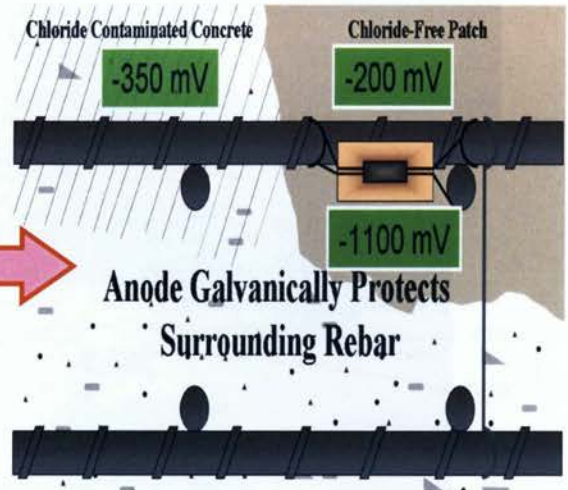
Fig.5.6 – Embedded Galvanic Anode

The zinc core material has the higher corrosion potential (potential of -1.10 volts) than the steel (potential of -0.2 to -0.35 volts), therefore the zinc device will be corroded before the steel. The galvanic anode method does not remove the chloride ions from the concrete, but it sacrifices itself to save the steel and reduce the rate of corrosion in the concrete.

As a result, the zinc device will perform the role of anode in electrochemical corrosion and release the electron to the attached reinforcing bars.



Corrosion in normal concrete



Concrete with Embedded Galvanic Anode

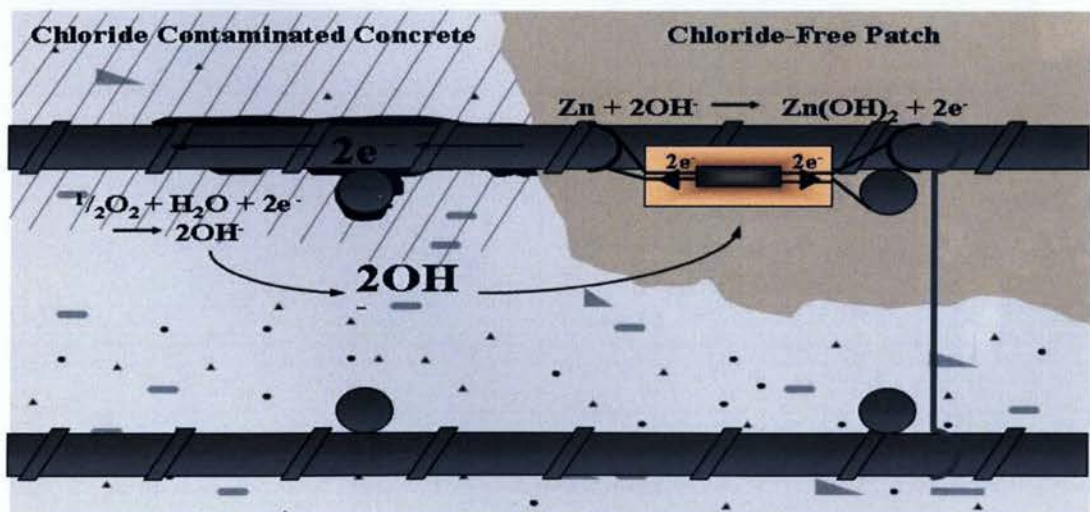


Fig.5.7 – Use of Embedded Galvanic Anode for Corrosion Prevention

As shown in figure 5.6, this device has the tie wires that can be easily fastened to the steel bars. The embedded galvanic anode is a light weight and cost effective device. Since the galvanic anode can be installed fast and easy, it does not need any special techniques, training or equipment for installation.

Also, the use of this device eliminates the needs of external source of power since it generates the current locally.



Fig.5.8 –installation of Embedded Galvanic Anode for bridge deck, Colorado



Fig.5.9 –installation of Embedded Galvanic Anode for beam

Another novel galvanic device which is usually using for the repair of corroded area in bridge and parking deck is “zincribbon”. The zincribbon uses the same technique of embedded galvanic anode but it provides more consistent current. The zincribbon is a thin and flexible tube that can be formed to any shape and used in targeted irregular shape area.





Fig.5.10 –installation of Zincribbon for bridge deck

5.7. ELECTROCHEMICAL CHLORIDE EXTRACTION METHOD

Corrosive environment with high degree of the undesirable chloride ions can accelerate the rate of failure. In regards of offsetting of destructive effects, the electrochemical chloride extraction is suggested for the long life protection.

The principal of this technique is based on the provision of the temporary anode outside of the concrete to attract the chloride ions to it. For this purpose, the metallic electrode mesh is installed outside of the concrete surface. The conductive media (fresh water with calcium hydroxide and cellulose fiber) is also added to the electrode mesh to play a role of an electrolyte. The external DC power supply the electric field between the electrode mesh (anode) and existing steel reinforcement inside the concrete (cathode). As a result, the negative chloride ions (Cl^-) will be extracted from the cathode toward the positive charge in anode. The transportation of chloride ions to anode will reduce the concentration of chloride ions in contaminated area and provide protection against further corrosion. At same time of

chloride migration to outside of concrete, the PH of concrete around the reinforcing steels will be increased. Therefore the passive oxide layer will be formed around iron and re-strength the passiveness of steels.

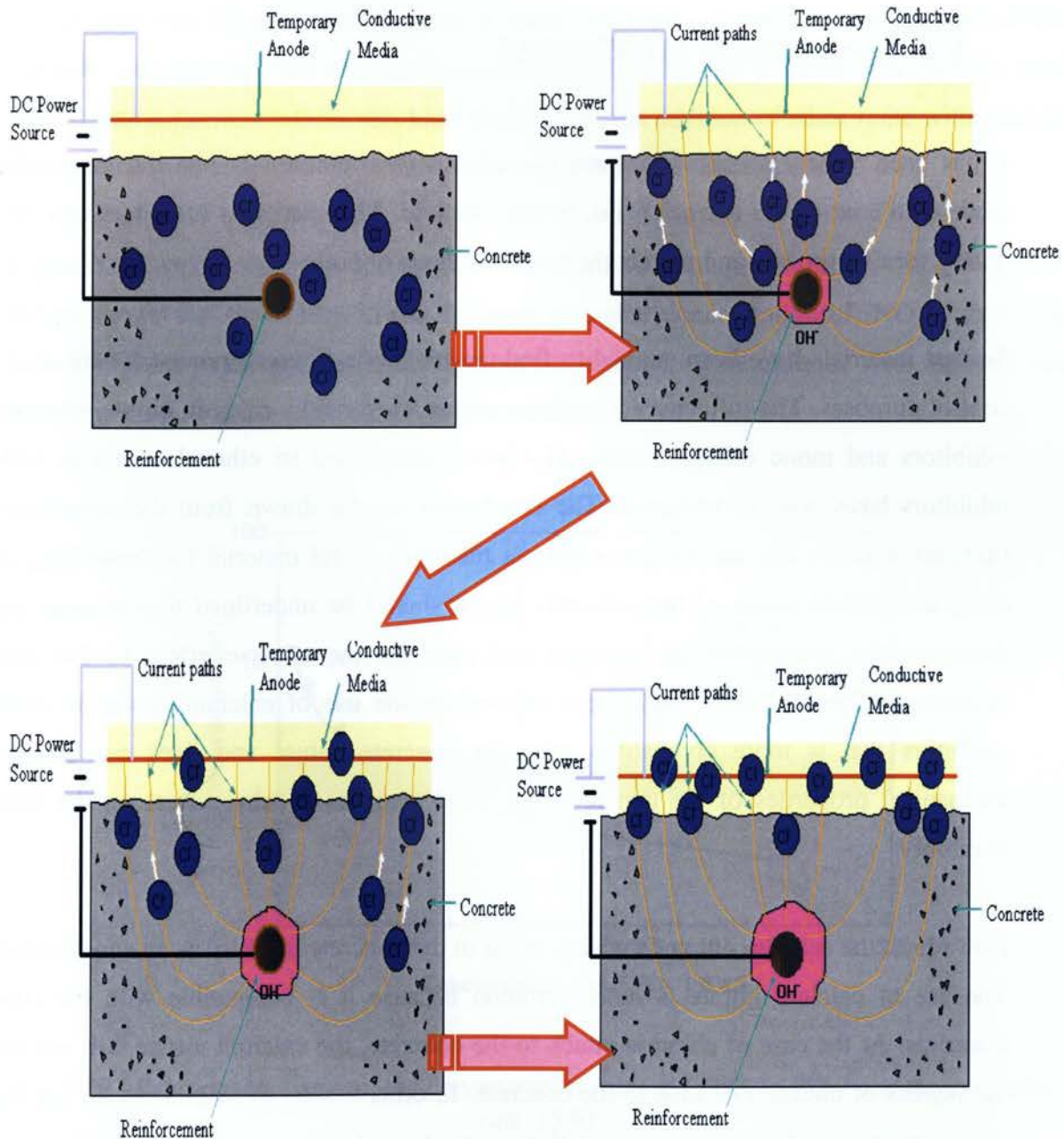


Fig.5.11 –Extraction of chloride ions to temporary anode outside of concrete

In conclusion, this method can reform the passive oxide layer around the reinforcing bars in addition to chloride removal from the concrete.

5.8. CORROSION INHIBITORE

It has been widely accepted that the use of concrete inhibitor is one the most effective method to control the corrosion inside the concrete. The corrosion inhibitors can be used during the mix process and protect the anode, cathode or both.

Several materials have been studied to find the most effective component for the corrosion control purposes. The influences of sodium nitrate, zinc oxide, calcium nitrate as an anodic inhibitors and mono ethanol amine, di ethanol amine and tri ethanol amine as cathodic inhibitors have been investigated. The conclusion can be drawn from the researches and literature reviews that the sodium nitrate is the most useful material for controlling of the corrosion control inside of the concrete. But it should be underlined that at same time it decreases the strength of the concrete and provides the adverse effect to the concrete properties. Thus the most researchers focused on the use of calcium nitrate as chemical inhibitors that is more compatible with the concrete nature and does not change the mechanical properties of the concrete that much and has a better effect on the concrete durability.

Nowadays, the calcium nitrate is widely using in the concrete industry as an anodic inhibitor. The use of calcium nitrate is more common because it is compatible with the concrete materials. At the case of chloride attack to the concrete, the calcium nitrate will not change the ingress of undesirable ions to the concrete. In other words, the inhibitors do not change the permeability of the concrete, but they compete with chloride ions for the ferrous ions (Fe^{2+}). Both nitrate and chloride ions tent to react with ferrous. At higher concentration of the

calcium nitrate, the nitrate will more tent to react with the ferrous ions. The calcium nitrate will react with ferrous ions to provide the passive oxide layer around the reinforcing bars and re-strength the passivity of the concrete. As a result, the calcium nitrate provides the stable passive layer and increases the threshold of chloride corrosion level in concrete.

It was observed from the studies that at harsh environment with higher exposure to the chloride ions, the calcium nitrate will accelerate the access of chloride ions into the steel bars. It was suggested that for this kind of situation, the addition of silica fume with calcium nitrate to be used to reduce the porosity and permeability of the concrete.

Figure 5.12 which was prepared by the K.Y. Ann, H.S. Jung, H.S. Kim, S.S. Kim, H.Y. Moon, shows that the corrosion rate is lower at higher concentration of $[NO_2^-]$ ions. The more inhibitors in the solution will suppress the reaction of the chloride with the steel and therefore mitigate the corrosion effects in the concrete.

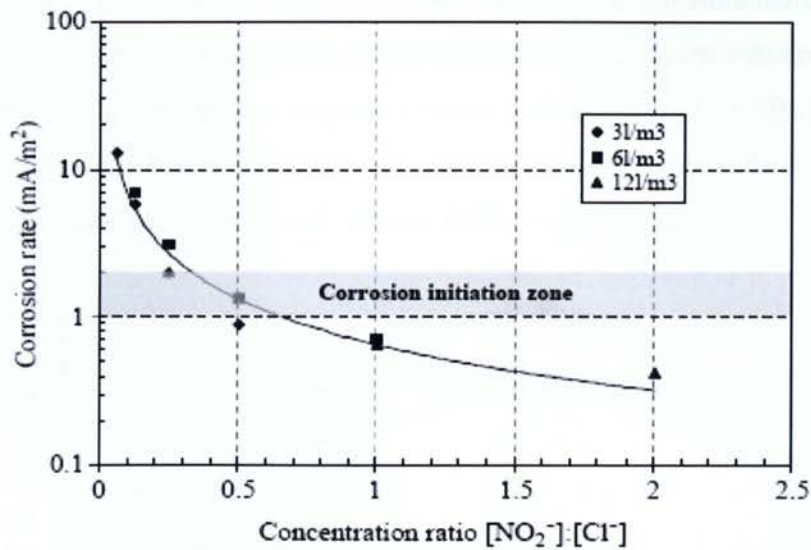


Fig.5.12 –Relationship between the concentration ratio of $[NO_2^-] : [Cl^-]$ and the corrosion rate. [5.9]

Also the use of the zinc oxide showed the grate effect on controlling of the corrosion in concrete. The addition of zinc oxide (ZnO) to concrete will produce the $(Ca (Zn(OH)_3)_2 \cdot 2H_2O)$ which increase the passivity of the concrete around the steel bars. Moreover, it has been seen that zinc oxide can reduce the porosity of the concrete beside the passive layer in concrete. The use of zinc oxide will help to maintain the lower porosity in the concrete which will suppress the penetration of contaminated ions to the concrete. It should be noted that the use of zinc oxide or the mix of zinc oxide with the calcium nitrate has the highest protection effect against corrosion in the concrete. The mix of zinc oxide and calcium nitrate also should be beneficial because the zinc oxide can reduce the chloride content which reduce the competition for ferrous ions that allows the calcium nitrate to react efficiently and provide the passive oxide layer around the reinforcement.

It is important to underline that the higher volume of inhibitors will have an adverse effect on the strength of the concrete.

Since the calcium nitrate or other inhibitors have the retarding effect on the concrete, the amount of this material that is used in concrete mix design should be optimized. The retarding effect of inhibitors will cause a delay in setting time and subsequently decrease the strength of the concrete. Furthermore, the retarding effect will evolve the higher heat of hydration at hardening stage which causes the cracks and strength loss at later age of concrete.

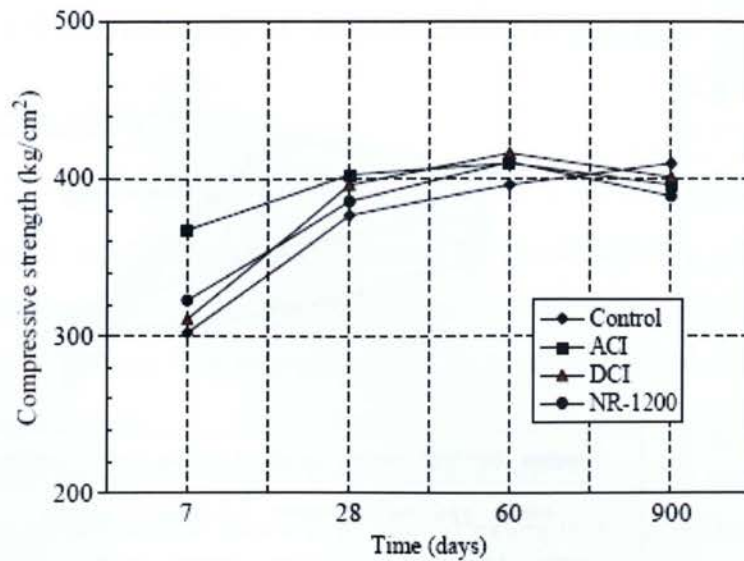
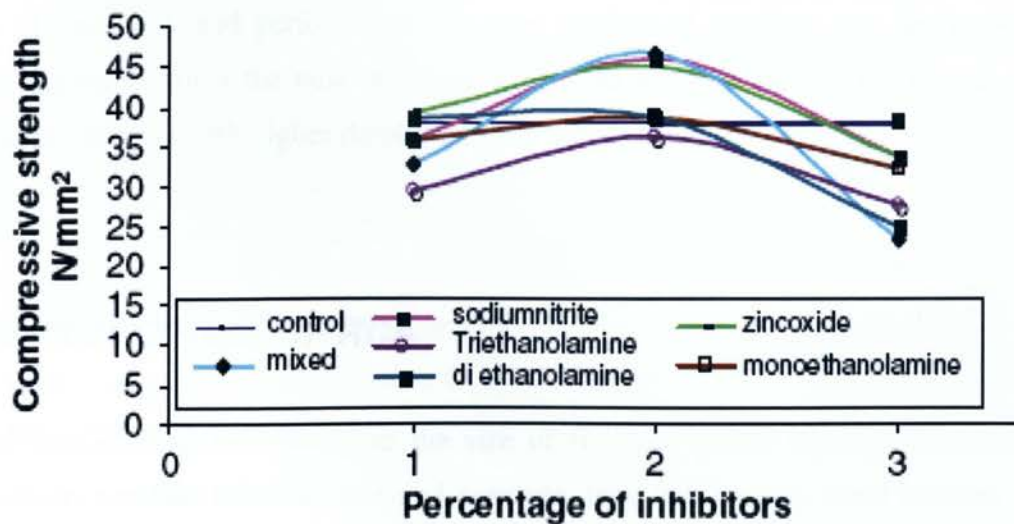


Fig.5.13 –Compressive strength for 3 types of inhibitors [5.9]

Based on several researches, the 2% addition of inhibitor is the most beneficial percentage in design mix of concrete for the harsh environment. Figure 5.14 indicates that concrete mix with 2% addition of inhibitors has the higher compressive and tensile strength.



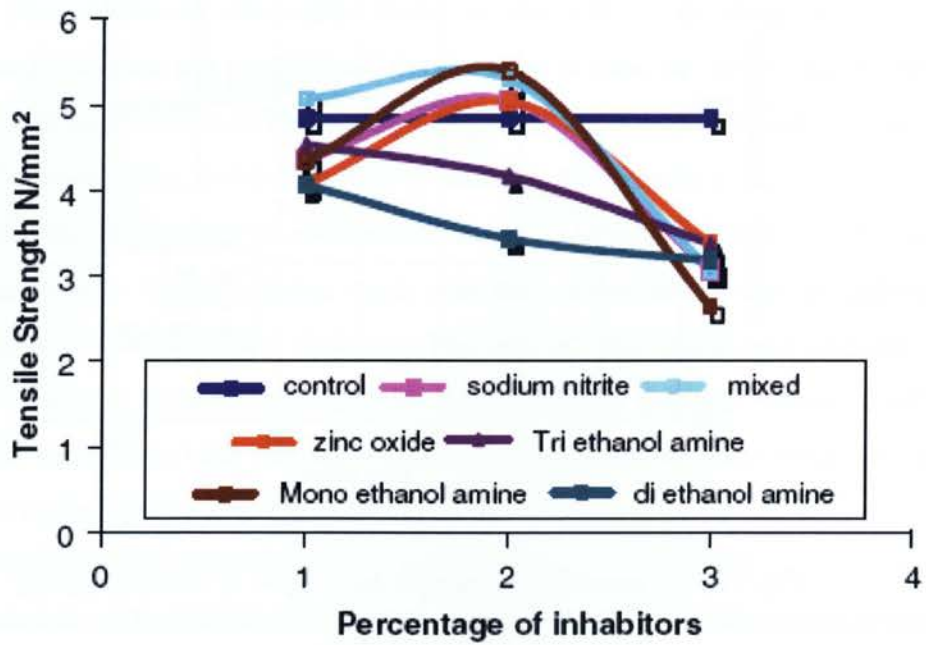


Fig.5.14 –Compressive 28 days strength and Splitting tensile strength of different percentages of inhibitors [5.8]

6. RECYCLED CONCRETE AGGREGATE (RCA)

6.1. INTRODUCTION

Concrete is the most widely used material around the world which is produced more than five trillion kilograms every year. The production of concrete is not considered as an environment friendly process. Concrete production uses the natural material and produces the pollution to the environment.

One way to produce the green concrete is to use the waste material in the production of the concrete. The use of pozzolanic material is a good example for producing the sustainable concrete. Use of this material helps to reduce the amount of the cement in the mix and consequently reduce the CO₂ evolution to the environment. Also because these materials are the waste product, employing of waste material in the production of the cement and concrete will reduce the pollution on the earth.

Another way to raise the sustainable process issues in the cement and concrete industry is the use of the recycled concrete aggregate in production of new concrete. The use of recycled concrete aggregate has been raised for environment friendly issue which reduces the depletion of the natural resources. Also this idea has solved the problem of unavailability of aggregates at the location of construction site.

In case of durability and performance, the new method of concrete mix design with the recycled aggregate offers the new materials which can even be used in the design of high performance concrete with higher durability to the same extends.

6.2. PROPERTIES OF RCA

Recycled concrete can be crushed to the size of fine and coarse aggregates. Since these aggregates are crushed from the recycled concrete, they will contain some residual mortar

which increase the impurity of the paste and affect the mechanical properties of the aggregates.

It is believed that there are 40% of the mortar in the recycled aggregate (RA) which results in lower mechanical properties in the concrete. The attached residual mortars have the lower specific gravity and thus reduce the specific gravity of the aggregates. This will decrease the unit weight of the new concrete and produce a light weight concrete.

Also the water absorption of the RCA is more than the regular aggregate and will change the workability of the concrete. Higher water absorption of the RCA will decrease the durability and strength of the concrete and provide the shrinkage problem to the concrete.

Recycled fine and coarse aggregates are categorized as following;

Type	C1	C2	C3
Recycled Coarse Aggregate			
Absorption (%)	3 or less	3 or less	5 or less
		40 or less	12 or less
Sulfate Soundness (%)	12 or less	40 or less (1)	-

(1) Where freezing and thawing resistance is not required.

Type	F1	F2
Recycled Fine aggregate		
Absorption (%)	5 or less	10 or less
Sulfate Soundness (%)	10 or less	-

Table 6.1 – Coarse and Fine Aggregate type

Type	Coarse aggregate	Fine aggregate	Suggested design strength (MPa)	Suggested use of recycled aggregate concrete
<i>Civil works applications</i>				
C1	Recycled coarse aggregate Type C1	Normal fine aggregate	18 to 24	Reinforced or plain concrete; lower structure of bridges, tunnel lining, retaining walls, etc.
CII	Recycled coarse aggregate Type C2	Normal or recycled fine aggregate Type F1	16 to 18	Plain concrete; masonry units, bases for road attachment, gutters, gravity type retaining walls, etc.
CIII	Recycled coarse aggregate Type C3	Recycled fine aggregate Type F2	Less than 16	Subslab concrete, back filling concrete, leveling concrete, etc.
<i>Building works applications</i>				
BI	Recycled coarse aggregate Type C1	Normal fine aggregate	18 or more	Ordinary reinforced concrete buildings
BII	Recycled coarse aggregate Type C2	Normal fine aggregate	18 or more	Concrete attached to ground; foundation, cast-in-place concrete piles, concrete slabs on steel decks, etc.
BIII	Recycled coarse aggregate Type C2	Recycled fine aggregate Type F1	18 or more	Foundation slabs, earthen floor slabs, subslab concrete, back filling concrete, leveling concrete, etc.
BIV	Recycled coarse aggregate Type C3	Recycled fine aggregate Type F2	18 or more	Subslab concrete, back filling concrete, leveling concrete, etc.

Table 6.2 – Suggested use of RCA in civil and building work

Result from the RCA testing revealed that foreign adhered materials are porous mortar with lower elastic modulus. The porous RCA with higher water absorption will adsorb the water of the new mix and reduce the w/c ratio in the concrete. The reduction of w/c ratio will affect the workability of concrete. Some engineer will add water or increase the w/c ratio of the mix to provide the same workability to the concrete. This increase in w/c ratio will decrease the compressive strength of the concrete.

Conclusion can be drawn from the investigation on RCA concrete that w/c ratio is lower in concrete containing the RCA (if do not change the mix design to provide the same workability) which results in higher compressive strength in the concrete.

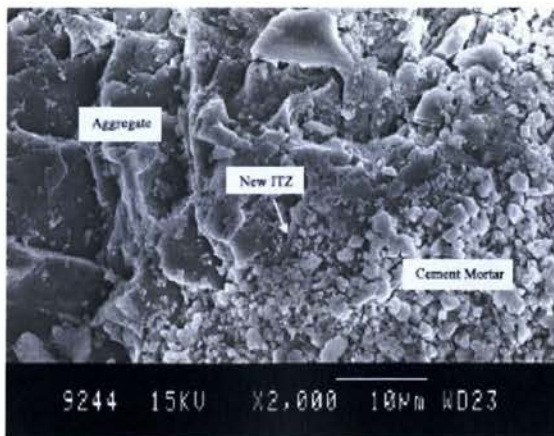
Quality control of concrete production with RCA is hard and use of RCA in new concrete causes variability in the hardened concrete. The low quality concrete is associated with the use of RCA in the new concrete.

6.3. TWO STAGE MIXING APPROACH (TSMA) METHOD

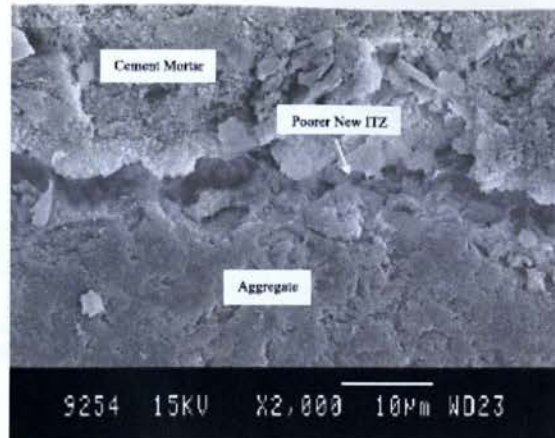
It has been well established that the weaken point of the concrete is the paste-aggregate interface or interfacial transition zone (ITZ). ITZ is the area with higher porosity and more unreacted cement that increase the risk of fracture in the concrete. That is the reason why the conventional concrete is always breaking at this point. In the purpose of providing high performance concrete or high durable concrete, ITZ should be improved.

In case of RCA concrete, it should be mentioned that two ITZs have been recognized in the concrete. One interface zone is between the RCA and new paste and the second one is located between the RCA and the old mortar attached to it. The old ITZ is more critical because it contains more cracks and pores that consume water in the paste. Hence to improve the durability and compressive strength in the RCA concrete, we have to find the way or method to overcome the old ITZ weakness in the concrete.

W. Y. Tam, X.F. Gao and C.M. Tam [6.9], have found the new practical mix design method for RCA concrete. The new method which is called two stage mixing approach (TSMA) can improve the quality of old ITZ and increase the strength of the new concrete. In the new mix design method, water is not applied to the material at one stage similar to conventional concrete mixing. They suggest that the water of the mix should be divided into two stages. The split of the water to half portion will cause that the RCA with higher water absorption premix with the water at the first stage. When the first half portion of water is added to the mix, cement reacts with the water around the recycled aggregates and provides the thin hydration layer around the recycled aggregate. The formation of this layer will cause the hydration products penetrate to the RCA mortar and fill the pores and cracks inside the RCA. This process will provide the denser material for the concrete. The second half of the water will be added at the second stage to complete the final hydration of the cement material to provide the final products of hydration.



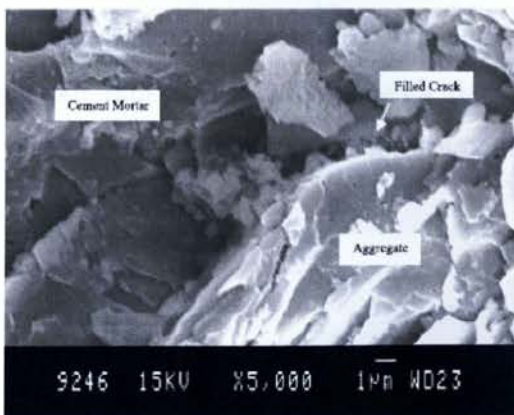
(a)



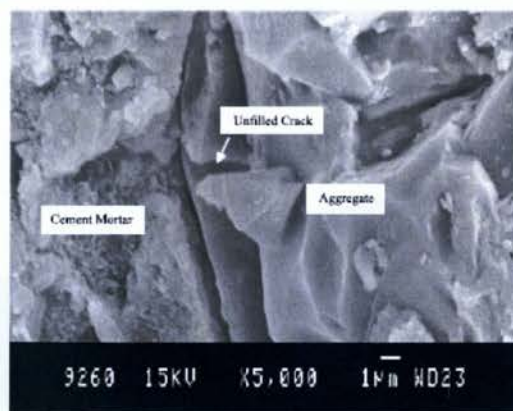
(b)

*Fig.6.1 – (a): Improved ITZ for TSMA concrete
(b): ITZ for normal mix concrete*

The experimental tests of the new method [6.9] shows that the TSMA mix design is more beneficial than the ordinary mix design and can improve the weak link of the concrete by filling the porosity of the RCA in the concrete (Fig.6.1 and 6.2). The scanning electron microscopy (SEM) of the concrete which used TSMA method is showing that the porosities of the RCA are filled up with the new cementitious material and the new paste is much denser than the normal mixed concrete.

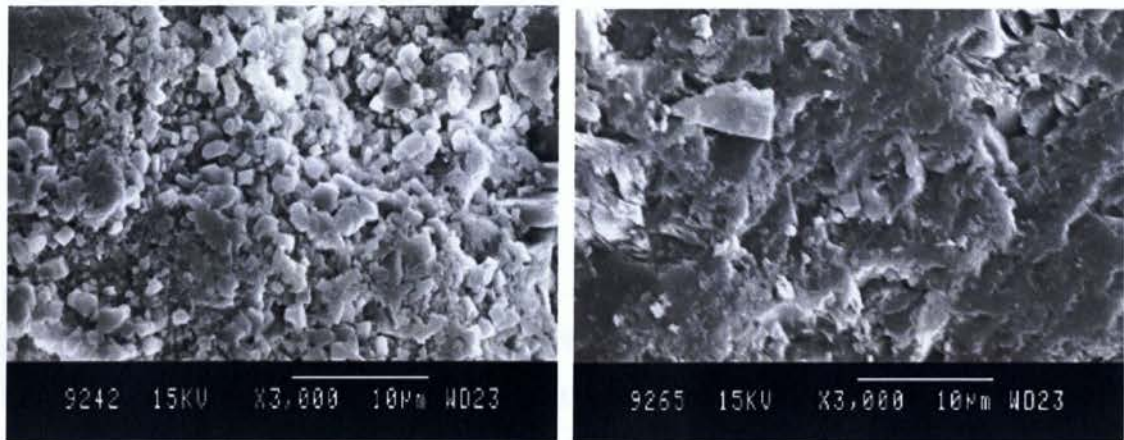


(a)



(b)

*Fig.6.2 – (a): cement paste for TSMA concrete
(b): cement paste for normal mix concrete*

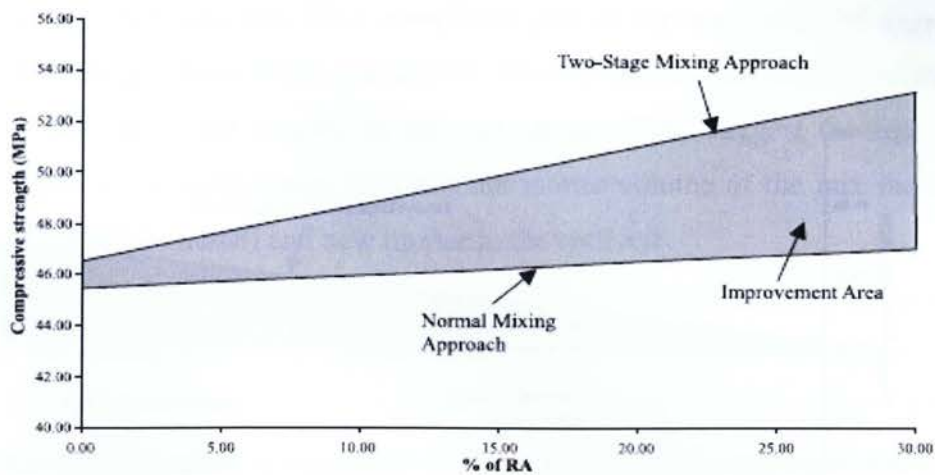


(a)

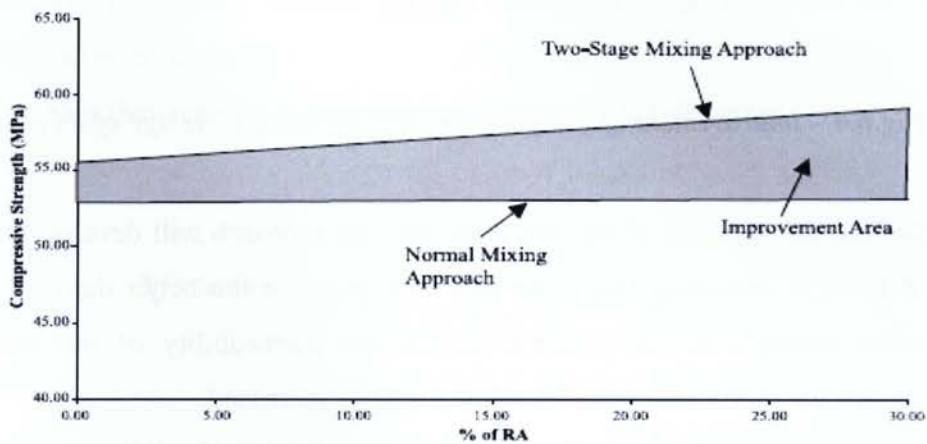
(b)

*Fig.6.3 – (a): Dense cement paste for TSMA concrete
(b): Loose cement paste for normal mix concrete*

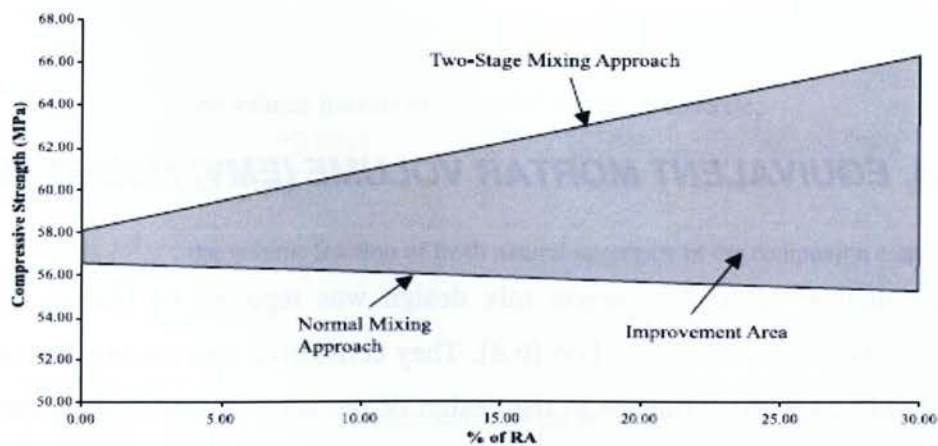
Moreover, the compressive strength of the concrete will be increased through the development of ITZ. The denser ITZ will develop the weak point of the concrete and consequently improve the strength. The compressive strength test of TSMA concrete indicates that the strength of the concrete can be improved by 20% and 10% after 28 and 56 days respectively. Figure 6.4 shows the improvement of compressive strength by applying the new mix method to the RCA concrete. Also these graphs define that the addition percentage of RCA up to 30% is effective and increase the compressive strength of concrete more rapidly.



7 days



14 days



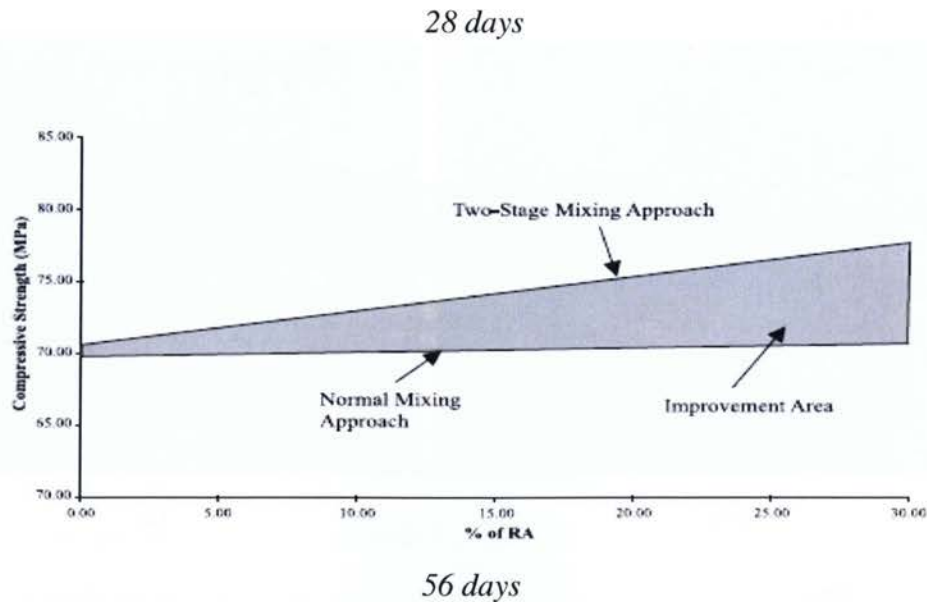


Fig.6.4 – improvement of compressive strength during the age of RCA concrete

In conclusion, the applying of the two stage mixing approach will develop both the old and new ITZ in RCA concrete. The better ITZ will result in the better density, durability and compressive strength in the concrete. Hence the permeability of the concrete will be decreased and the performance and durability will be increased.

The better quality of the material brings the idea of using the RCA in high performance concrete design.

6.4. EQUIVALENT MORTAR VOLUME (EMV) MIXING METHOD

Another method of RCA concrete mix design was reported by Abbas, Fathifazl, Isgor, Razaqpur, Fournier and Simon Foo [6.8]. They considered that the attached residual mortar in RCA will have the influence in the design of the concrete and consequently reduces the compressive strength and overall durability of the concrete.

They came up with idea that RCA should not just be replaced with the aggregates in the normal mix design. Since RCA contain the residual mortar, the amount of the old mortar should be calculated and counted in the mix design. They suggest the equivalent mortar volume (EMV) mix method that indicates the mortar volume of the mix includes the total volume of the old (residual) and new mortar in the concrete.

$$\text{Total mortar volume} = \text{Residual mortar} + \text{New mortar}$$

This method is equivalent to substitution of the RCA with the aggregate and portion of the total mortar in the conventional concrete mix. Since the amount of attached mortar in the RCA is considering in EMV method, the total volume of the concrete will not change due to extra mortar in the concrete.

The formula that they recommend for new mix design is as following:

$$V_{\text{RCA-concrete}}^{\text{RCA}} = \frac{V_{\text{NA}}^{\text{NAC}} \times (1-R)}{(1 - \text{RMC}) \times \frac{\text{SG}^{\text{RCA}}_{\text{b}}}{\text{SG}^{\text{OVA}}_{\text{b}}}}$$

$V_{\text{RCA-concrete}}^{\text{RCA}}$: the volume fraction of coarse RCA in RCA-concrete,

$V_{\text{NA}}^{\text{NAC}}$: the volume fraction of fresh natural aggregate in the companion conventional concrete,

RMC : is the residual mortar content of the RCA,

SG^{RCA}_b and SG^{OVA}_b : the experimentally determined bulk specific gravity values of RCA and original virgin aggregate respectively,

R: : the volume ratio of the fresh natural aggregate content of RCA-concrete to the fresh natural aggregate content of the companion conventional mix.

According to the formula, the correct amount of RCA (including aggregate and mortar) is calculated to provide the durable concrete. This calculation is based on the actual amount of the aggregates that is using in the conventional concrete mix design.

The experimental test results for the EMV method revealed that freeze and thaw resistance of the EMV samples are higher than the conventional mixed concrete samples. In fact, the less mortar in EMV method helps the concrete to resist the higher freeze and thaw cycles.

In addition, the EMV test samples showed that this method improves the durability of concrete against carbonation and chloride corrosion in the concrete. The results indicate that carbonation depth and chloride ingress is in the same range as the normal concrete. The addition of the SCM such as fly ash will even improve the chloride durability of concrete better than conventional concrete.

6.5. USE OF RCA IN HIGH PERFORMANE CONCRETE (HPC)

Section 6.2 described that the w/c ratio of the RCA is lower because of the water absorption of the attached mortars to the recycled aggregates.

The water absorption of the RCA will cause a reduction in the water content of the mix and results in higher resistivity to the concrete. Generally the lower water ratio in the paste

increases the resistivity of the concrete. In another words, the higher resistivity of the paste will reduce the ingress of the contaminated agents into the concrete. The durability of the concrete will increase when the penetration of chemical solution reduces by the lower water content.

According to this issue, the chloride penetration to the concrete will be decreased due to lower w/c ratio in the paste. The chloride attack can even be less if the higher portion of fine aggregates replaced the coarse aggregates in the design. The higher volume of fine aggregates will increase the durability of the concrete and develop the performance of the concrete against chloride corrosion in the concrete.

Since the durability of the concrete is increased in some cases, we can conclude that the RCA can be used in production of high performance concrete. However it should be noted that the use of RCA is limited in the high strength concrete since the RCA can not achieve high compressive strength in the concrete.

Use of pozzolanic material will help to develop the compressive strength in RCA concrete. The residual alkali in RCA can activate the pozzolanic reaction (formula 2.6) in the concrete and provide some strength into the concrete. The alkali from attached mortar to recycled aggregate will initiate the reaction between portlandite and pozzolan to develop the C-S-H phases inside the mortar [6.7]. Some pozzolan such as slag which has higher calcium content will improve the pozzolanic reaction and therefore produce more strength and durability for the concrete. Even the finer RCAs in the concrete mix can develop this idea through the higher surface area that they have.

7. NEW APPROACH TO CEMENT/CONCRETE INDUSTRY

7.1. USED AUTOMOBILE TIRE

The used automobile tires are the main problem for the environment. The worn tires are not capable of being decomposed by the bacteria and will remain for the long time on the earth. It is agreed upon that used automobile tires are not environment friendly and will provide the pollution to the earth.

Finding the way to reuse this material for the concrete industry will solve the lots of pollution and make the concrete a green material. Nowadays, used automobile tire is only using as a fuel in cement factories. Tires can be burned and provide enough energy in cement kilns. However the use of worn tires is not completely investigated in the cement paste mortar.

Some researchers worked on the effects of tire rubber products in the cement mixture. It was observed that the use of tire rubber will reduce the mechanical properties of the concrete. Results of investigation revealed that the use of granulated tire rubber as a replacement of sand in concrete mix design will reduce the workability, strength and mechanical properties of the concrete. The nature of rubber will cause that the elastic modulus of concrete decrease to smaller number. The smaller elastic modulus of the rubber makes the concrete more flexible material that can be used in specific situation.

Also the tire rubber will affect the workability of the concrete and reduce the place ability of the concrete.

Table 7.1 compares some mechanical properties of controlled mix with mixes of different tire rubber percentages.

From the numbers in table 7.1 can be concluded that flexural and compressive strength of the concrete will be decreased with increasing in the tire rubber percentages.

Characteristics \ Mixture	Mixture				
	Control mortar	5% tire rubber	10% tire rubber	12.5% tire rubber	15% tire rubber
Compressive Strength (Mpa)	40.75	21.33	11.12	9.75	8.60
Flexural Strength (Mpa)	9.00	5.75	4.30	3.50	2.90
Specific Weight	2.23	2.03	1.84	1.76	1.68

Characteristics \ Mixture	Mixture	
	Control mortar + 1% SP	12.5% tire rubber + 1% SP
Compressive Strength (Mpa)	43.70	13.86
Flexural Strength (Mpa)	10.26	4.5
Dynamic Modulus of Elasticity (GPa)	42.48	15.37

Table 7.1 – Mechanical properties of mixes with different tire rubber percentages

However, some researchers did not stop the investigation on the use of tire rubber and tried to expand the investigation on this material.

N. Oikonomou, S. Mavridoum [7.1], used the granulated tire rubber and replaces it with weight of sand in the mixture. Their investigation revealed that regardless of the decrease in mechanical properties of concrete, the use of worn automobile tires could be effective to offset the destructive effects of chloride attack in the concrete.

The result of test on different percentages of rubber in concrete mix shows that the addition of rubber can decrease the water absorption of concrete. Since the water absorption decreases in addition of the tire rubber in concrete, the ingress of chloride ions will become difficult in higher percentages of rubber.

They applied the rapid chloride permeability test (RCPT) to the specimen to measure the chloride permeability in case of tire rubber in concrete. The passage of electrical current to the specimens showed that the chloride ion penetration is decreased in the concrete which used the worn granulated tire in its mix. The chloride penetration can be reduced to 34-35% in case of using 15% tire rubber as a sand replacement.

Characteristics	Mixture						Control	12.5%
	Control mortar	5% tire rubber	10% tire rubber	12.5% tire rubber	15% tire rubber		mortar + 1% SP	tire rubber + 1% SP
Absorption of Water (%)	8.81	7.37	7.03	6.87	6.79		7.91	6.25
Chloride Penetrability Based on Charge Passed	6103	5080	4257	3956	3915		5910	3640

Table 7.2 – Chloride penetrability and water absorption of mixes with tire rubber

Based on different testes, the 12.5% and 15% of rubber replacement in concrete showed the similar protection against chloride ingress. Thus the 12.5 % replacement of the tire rubber with the sand was suggested by the researchers.

Moreover, it is noteworthy that the addition of superplasticizer which helps to improve the mechanical properties of the paste is also developing the chloride resistance of the concrete. The test of mortar with 12.5 % tire rubber and bitumen emulsion revealed the highest effects on the chloride penetration resistance. This mortar improved the chloride and corrosion resistance up to 55%. Therefore the use of 12.5% tire rubber substituted in the sand (by its weight) and addition of bitumen emulsion is suggested as a grate success in concrete industry against the corrosion.

It can be conclude that when the strength of concrete is not the matter and chloride attack is the main issue for the concrete structures, the worn automobile tires can be used up to 12.5% and mixed with the additive such as superplasticizer and bitumen emulsion to improve the chloride penetrability of concrete and protect the structure against the rust and corrosion.

7.2. CALCIUM NITRATE INHIBITOR

The effective use of calcium nitrate to control the rate of corrosion was discussed at chapter 5. It was explained that the calcium nitrate will increase the threshold level of chloride corrosion and also compete against the chloride ions for ferrous ions to provide the passive layer around the rebar.

Although the calcium nitrate has a beneficial influence in corrosion prevention, the use of this material will have the harmful effects in concrete at sulfate attack situation. It was observed from several tests that the calcium nitrate can decrease the sulfate resistance of concrete. Thus it is noteworthy that the use of corrosion inhibitors should be considered when the concrete structures are exposed to the sulfate as well as chloride attack.

The adverse effect of calcium nitrate on sulfate resistance can be explained by further formation of portlandite (calcium hydroxide – CH) and ettringite. In fact, the addition of calcium nitrate inhibitors in concrete will create more crystals. The crystal pressure from the excess of calcium hydroxide and ettringite will reduce the sulfate resistance of the concrete and results in cracks and spalling.

Research from Zongjin Li, Baoguo Ma, Jun Peng, Meng Qi [7.3] revealed the calcium nitrate inhibitor produces more ettringite and CH which are the main parameters for the sulfate deterioration and therefore weakens the sulfate resistance of concrete. The XRD spectrum analysis of specimens showed that the concentration of portlandite and ettringite is higher in mortar with the calcium nitrate inhibitors. The formation of these components will increase the crystal pressure in hardened concrete and induce the internal stress inside the concrete. The formation of calcium hydroxide and ettringite will have the following effects on the concrete:

- Providing the area which is favored for sulfate attack and expansion
- Increasing the overall porosity and pore size of concrete

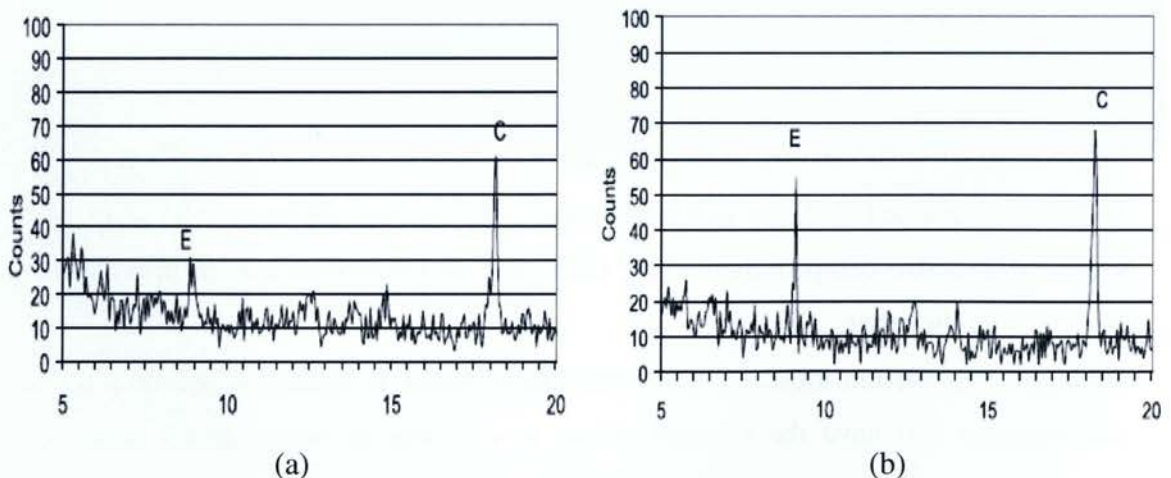


Fig.7.1 – XRD spectrum of: (a) HPC concrete, (b) HPC concrete + calcium nitrate

The work of this group showed that the expansion of concrete containing the calcium inhibitor is more than the non-inhibitors added concrete due to sulfate attack (figure 7.2). The existence of these two expansive components will accelerate the deterioration process of sulfate attack.

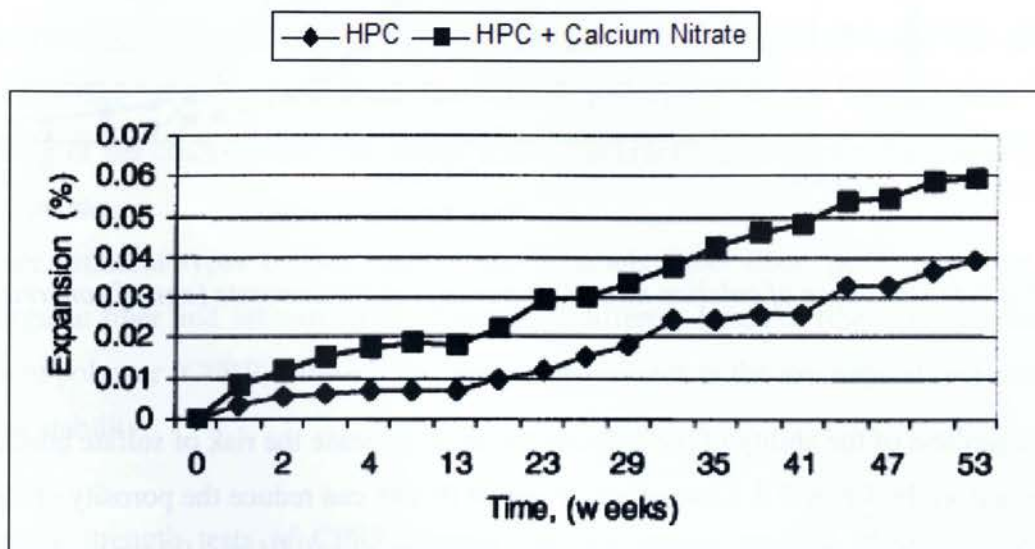


Fig.7.2 – Influence of calcium Nitrate Inhibitors on sulfate resistance of concrete

Furthermore, the formation of CH and ettringite will increase the pore size and pore volume of the concrete. As it can be seen in figure 7.3, the amount of larger pores (0.03 to 0.1 μm) is higher at the same cumulative pore volume. Also this figure represents that the cumulative pore volume in concrete using the calcium nitrate is higher than conventional and fly ash added concrete. It can be concluded from this study that the higher rate of porosity and pore size is due to formation of crystal materials.

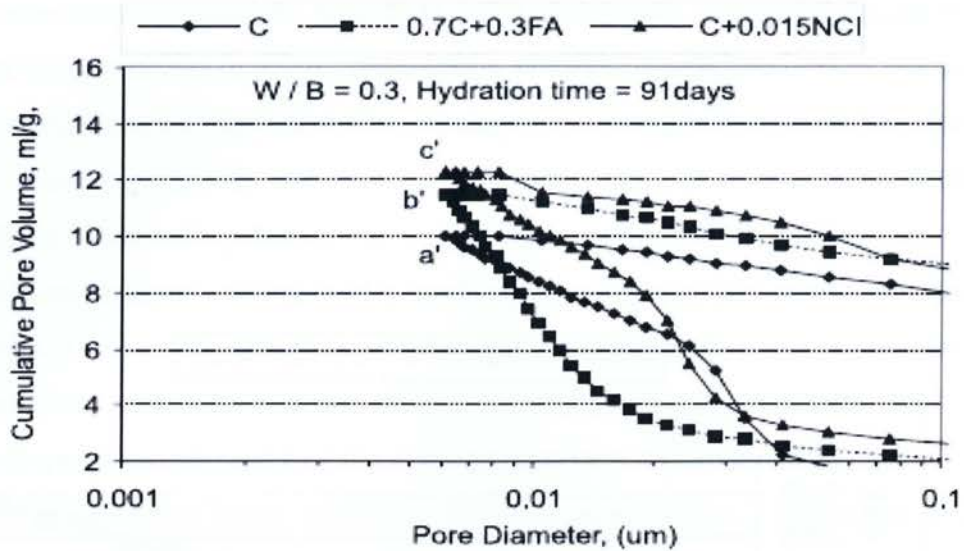


Fig.7.3 – Influence of calcium nitrate on porosity of the concrete (age of concrete = 91 days)

Regardless of the ability of the calcium nitrate to increase the risk of sulfate attack in the concrete, the figure 7.3, shows that the use of fly ash can reduce the porosity of the concrete. The use of fly ash will reduce the porosity and pore size (0.04 to 0.02 μm) at later age of the concrete hydration which confirms the formation of C-S-H through the reaction of fly ash with CH.

Overall, when the calcium nitrate is used to control the corrosion in the concrete, the sulfate resistance against sulfate attack will be decreased. Calcium nitrate can protect the steel against the corrosion and at same time accelerate the crystal formation and the risk of sulfate deterioration. Thus, the use of calcium nitrate inhibitors should be considered in harsh environment.

7.3. FIBER REINFORCED POLYMER (FRP)

The ongoing development of concrete industry finds the new material and techniques to develop the concrete structure under the extreme load and environmental effects. One approach of the new development is the use of fiber reinforced polymer (FRP) in the mix design of concrete.

It is believed that fiber can improve the strength and ductility of the concrete. However the main advantage of fiber reinforced concrete is underlined as the improvement in the controlling of the cracks. Fiber can bridge across the cracks and improve the crack ductility of the concrete.

There are different types of fiber reinforcing materials; steel fiber, polymeric fiber, glass fiber, organic fiber and asbestos fiber. Among all different kinds of fibers, the carbon fiber reinforced polymer (CFRP) showed the better improvement in the mechanical properties and chemical stability.

The tensile strength tests of CFRP express that the tensile strength of concrete will be increased with larger use of carbon fiber up to 5% of the volume. The tests provided the evidence that the concrete with 5% carbon fiber reinforcing polymer can increase the tensile strength to 3-4 times greater than conventional concrete.

Another investigation on the tensile strength of the CFRF showed that although the tensile strength is increased but the stress- strain curves is decreased. As figure 7.4 explains, the stress- strain curves will decrease with the increase in the amount of CFRP. However, this graph also indicates that the ultimate strength of CFRP concrete will be higher with the more percentage of CFRP.

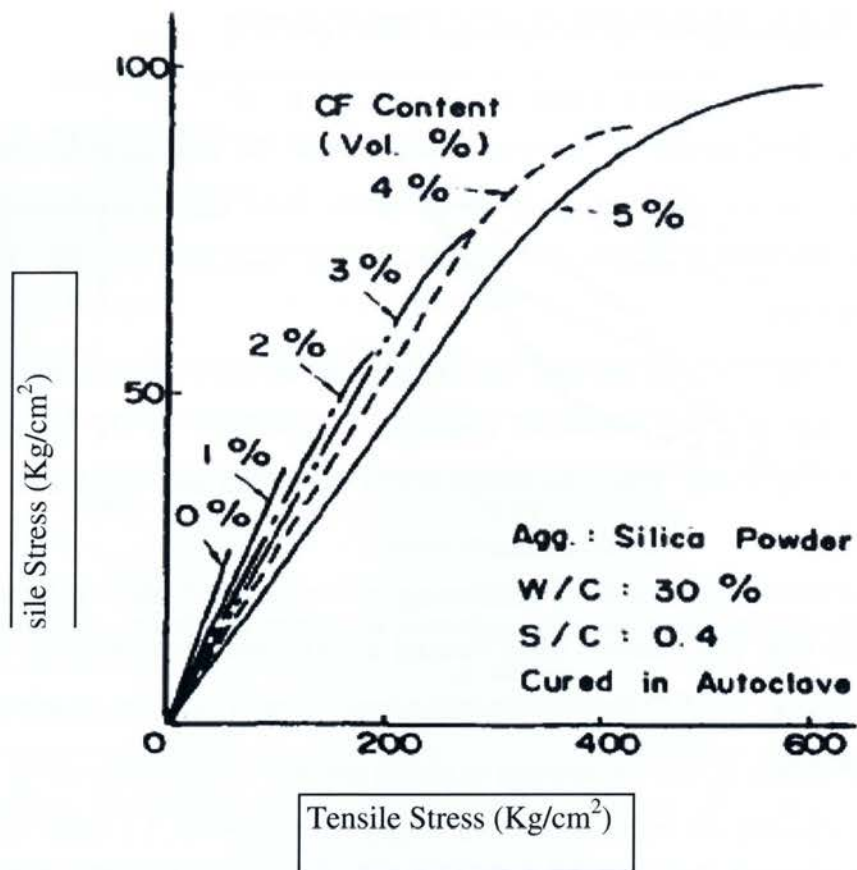


Fig.7.4 – Tensile stress- strain relationship of CFRP

7.3.1 STRESS STRAIN BEHAVIOUR OF FRP

The design of concrete structures in harsh environment could be based on FRP material as fully or partial wrapped systems. The FRP can be used as a layer or several layers in concrete structures.

The improvement of strength, ductility, seismic resistance and corrosion resistance of the FRP concrete has been investigated by several researches. FRP is usually used to increase the

strength of the concrete and improve the resistance against the corrosion in new construction industry.

The stress-strain model of FRP concrete was studied to find out the real improvement and increase in the strength and ductility of the concrete. Figure 7.5 compares the stress-strain distribution of conventional and FRP concrete. As it can be seen, the actual stress distribution of the FRP concrete is higher than the normal concrete. Since the FRP material helps to increase the ductility of the concrete, the strain development of specimen using this material is higher. It means that ultimate strain capacity of the FRP concrete passes the ultimate strain capacity of the normal concrete and goes beyond it. According to the increase in the ultimate strain, the compressive stress of the FRP concrete will be developed as well.

The area under the stress block of FRP concrete is divided into two areas; first area from the natural axis to f'_c , and second one from the f'_c to improved FRP concrete stress (f'_{cc}). The first area is parabolic similar to conventional concrete, but the second portion is linear. These studies demonstrate that the improvement of confined concrete has a linear relationship to the conventional concrete. The formula that was drawn from the material modeling is also representing the linear relationship between f'_{cc} and f'_c . The compressive stress and corresponding strain of confined concrete with FRB can be found from following formulas:

$$\begin{cases} f'_{cc} = f'_c (1 + 2.15 f_l / f'_c) & (7-1) \\ \epsilon_{cc} = \epsilon_{co} (2 + 15 f_l / f'_c) & (7-2) \end{cases}$$

The parameter of f_l in both formulas represents the effective lateral confining pressure of FRP and can be calculated from formula 7-3:

$$f_l = k_s [2f_{fr} t_{fe} / 0.5(b+h)] \quad (7-3)$$

Where the f_{fr} is rupture strength of the FRP and t_{fe} is the effective thickness of the FRP:

$$t_{fe} = \begin{cases} t_f & \text{full- wrapping} \\ (w_f/s_f) t_f & \text{Partial- wrapping} \end{cases}$$

$$K_s = \left[1 - [(b-2R_c)^2 + (h-2R_c)^2] / 3Ag - \rho_s \right] / (1 - \rho_s) \quad (\text{shape factor})$$

t_f : thickness of one layer of FRP

w_f : width of FRP

s_f : spacing between FRP (centre to centre)

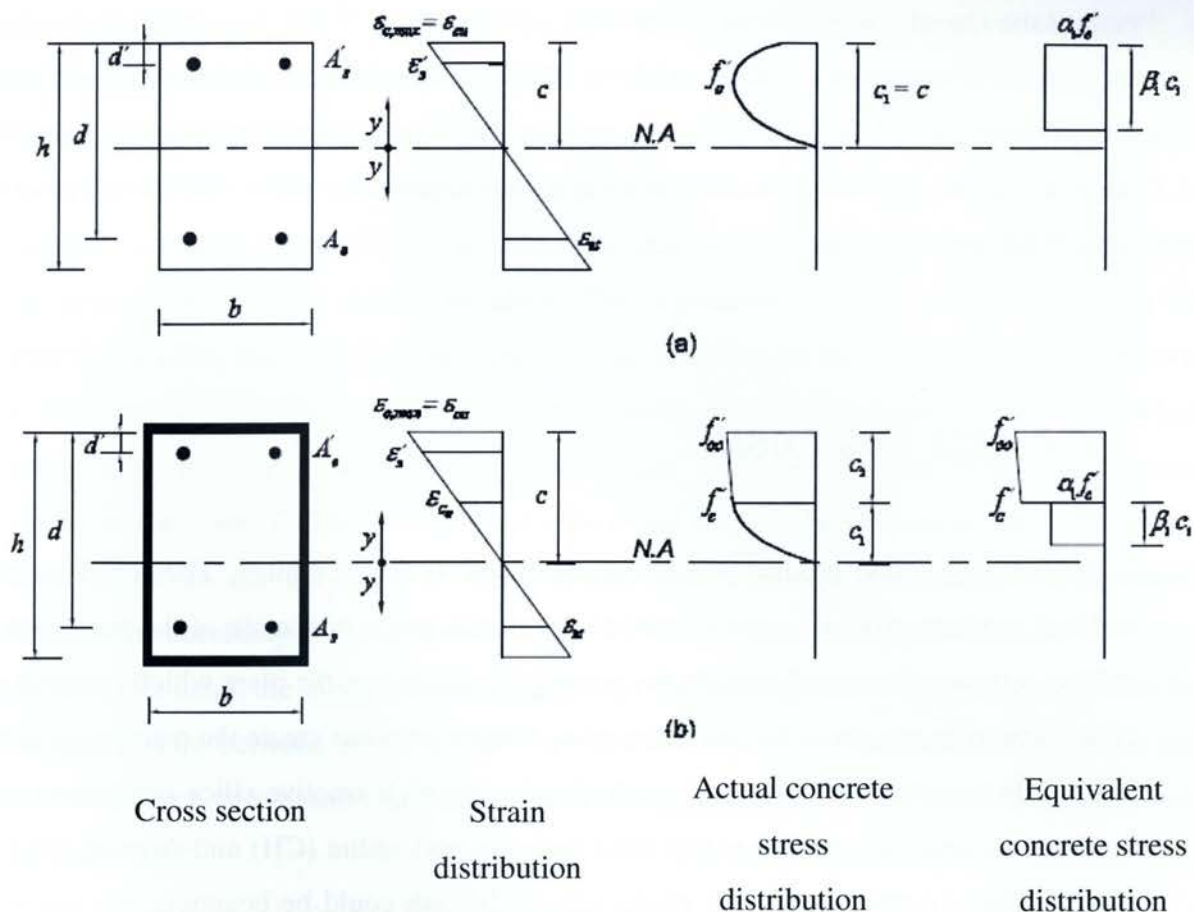


Fig.7.5 – stress and strain distribution of: (a) Conventional concrete
(b) FRP wrapped concrete

Beside the increase in ductility and strength of concrete, FRP provides the higher corrosion resistance to the concrete. The higher strength is one reason since it resists the higher internal stress and delays the formation of cracks. It was observed that FRP concrete can tolerate the high volume change of the rust formation.

The second reason is that the FRP inhibits the movement of chloride into the area of reinforcement in the concrete. In other words, the FRP changes the water absorption and reduces the ingress of chloride to the concrete. Reduction in the diffusion of chloride will

control the rate of corrosion and mitigate the rust formation in the concrete. It is obvious that the type and the numbers of layer of FRP will change the pathway of penetration and change the corrosion rate. The test of FRP showed that the confined concrete with fiber reinforced polymer can increase the corrosion resistance of concrete up to 40% depending on the water cement ration of the paste.

7.4. RICE HUSK ASH

Rice husk is a waste product which can be found at the rice plant. The rice husk ash is residual products from rice grain production process that will remain at the rice plant. The milling process of rice will provide the organic by-product in the plant which contains about 20% silica in its structure. The proper burning temperature can create the reactive amorphous silica in the residual product. The rice husk ash with high reactive silica component can be known as a pozzolanic material that react with the portlandite (CH) and develop the C-S-H phase in the concrete. Hence the proper use of this ash could be beneficial for concrete to improve the durability and decrease the permeability.

The use of rice husk ash not only helps to provide the high durable and low permeable concrete but also help the environment by reducing the waste material in earth. Moreover, since the ash is a by-product material, it could be categorized as a cost effective material that will replace the cement in the mortar and reduce the cost of construction.

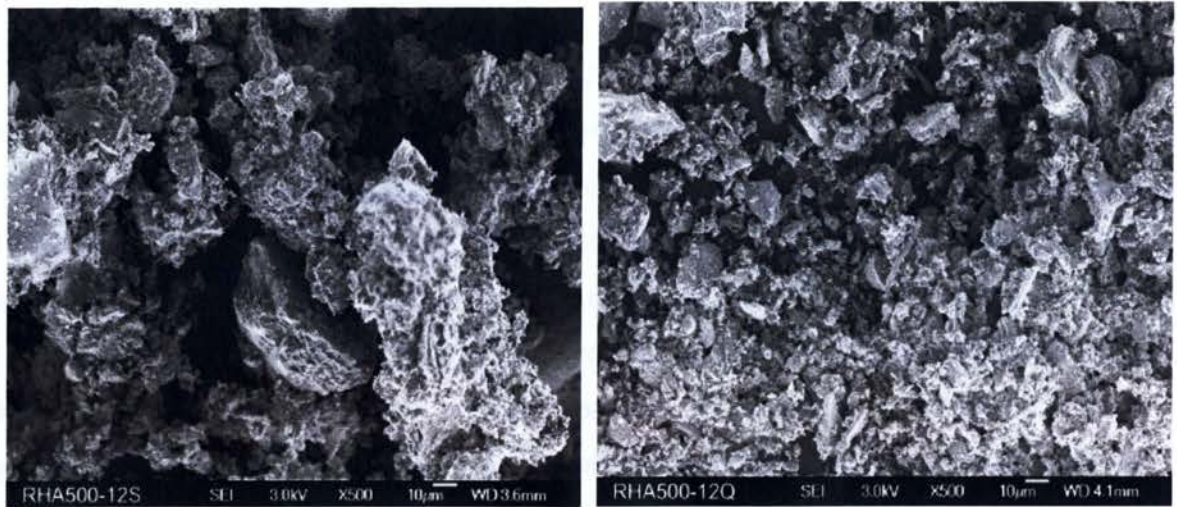
Rice husk is the most silicate based by-product among all plant waste products. The use of high silica material could improve the durability of the concrete. Beside the percentage of silica, the structure of silica is also very important and can be different from the plant to plant. The study of rice husk ash demonstrated that the structure of silica will be affected by the heat of combustion at the plant. To decompose the organic components and release the silica,

the temperature of 402°C is necessary. Although the minimum heat of the 420°C is mandatory, but the excess of heat will affect the structure of silica in the ash.

Finding the proper temperature to burn and prepare rice husk ash is the recent concerns of researchers. This study was started by Mehta and then continued by Deepa G. Nair, K.S. Jagadish, and Alex Fraaij [7.8]. They conclude that the temperature above 700°C will turns the amorphous silica to crystalline silica. The crystalline silica is less reactive than the amorphous silica and thus at cannot improve the durability of the concrete to the same level as non- crystal silica. The reason is that the crystalline silica has a higher surface area which makes it less reactive in the hydration of the cement. The lower reaction of silica in the paste results in the lower C-S-H formation. As discussed before, the amount of the C-S-H has a direct effect on the durability of the concrete. Therefore the less reactive silica cannot improve the durability of the concrete.

On the other hand, the investigation revealed that the burning time of more than 12 hours for the temperature between 500°C to 700°C can provide the more amorphous silica in the rice husk ash which can dissolve and react with calcium hydroxide quickly and form the C-S-H gel in the paste.

In addition the cooling method of the ash was studied by the same researchers. It was observed that cooling method also plays an important role in the structure of silica. Regardless of the burning temperature, the quick cooling method of the ashes will help to provide the smaller particle size of the silica. The SEM images from the samples which were burnt at 500°C and 700°C showed that quick cooling process will reduce the particle size and consequently increase the surface area. The higher surface area of the ashes will help to improve the reactivity of the ashes in the mix with cement paste materials.



(a)

(b)

Fig.7.6 – SEM image of samples burnt at 500°C _ (a): slowly cooling (b) quick cooling

The conclusion can be drawn from Nair, Jagadish and Fraaij's research (which was in accordance with other researchers such as; James and Rao, Yu et al, Chopra, and ...), that the combustion heat of the 500°C to 700°C and then the quick cooling is the perfect temperature to produce the most reactive rice husk ashes with the high surface area silica in their structures.

7.4.1 PROPERTIES OF RICE HUSK ASH

The grounded rice husk ash can be use as a replacement pozzolanic material with the cement in concrete mix and improve the properties of the concrete. The pozzolanic characteristics of the rice husk ashes can provide the higher amount of C-S-H gel to the cement pates mortar and develop the strength of the concrete.

Moreover, the formation of C-S-H gel will help to reduce the pore size and overall porosity of the concrete due to decrease in the crystalline components in the concrete. It has been well established that the pozzolanic material can pack between cement particles and reduces the inter particles friction. Therefore the lower the friction among the cement particles will improve the workability of the concrete and reduce the water demand in the mix. Providing the higher workability to the concrete, the lower w/c ratio concrete can be reached will is the most effective item to improve the properties of the concrete. As a result the high reactive percentage of silica in the rice husk material will make it a useful additive to improve the properties of the concrete.

In addition, the pozzolanic performance of the rice husk ash will develop the resistance of the concrete in destructive sulfate attack. The consumption of calcium hydroxide and formation of the C-S-H gel will decrease the concentration of portlandite and therefore reduce the risk of gypsum and monosulfoaluminate corrosion. Formation of C-S-h gel and reduction of CH, both have an influence in the reduction of the expansion through the sulfate attack.

Also the use of rice husk ash reduces the porosity which prohibits or limits the ingress of sulfate and chloride ions to the concrete. As a result rice husk ash cans provide the corrosion resistance and sulfate resistance concrete that can be constructed at harsh environmental condition. It is agreed upon the replacement of 30% of cement with rice husk ash will improve the durability and performance of the concrete without any adverse effect.

It is important to underline that the use of this by-product material cannot help the concrete to resist the magnesium sulfate attack. The studies showed that the rice husk ash will have an adverse effect in case of magnesium sulfate attack in concrete. It can be explained that the addition of rice husk ashes will consume the CH and reduce the concentration of CH in the paste. To balance the system in the paste, the calcium (Ca^{2+}) can be released from C-S-H and maintain the stability of the system. The release of calcium from the C-S-H gel makes it unstable component which is the favour of the magnesium to attack. In this case the magnesium can attack and decompose the calcium from the C-S-H gel and sits in its structure

instead of Ca^{2+} ions to form M-S-H. Since the valence of magnesium ion (Mg^{2+}) is twice the valence of sodium ion (Na^{+}), the ability of the magnesium to attack the C-S-H phase and substitute the calcium in its structure is almost double the ability of sodium to attack. In conclusion the rice husk ash could not be sued when there is the risk of magnesium sulfate attack in the concrete.

Figure 7.7 compares the same concrete mixes when they are immersed in the sodium and magnesium sulfate solutions. Obviously can be seen that compressive strength loss of the mortars with different percentages of rice husk ash is less than conventional concrete mixes when they exposed to the sodium sulfate. The higher replacement of the cement with ashes will increase the durability of the concrete against the sodium sulfate attack. But the story is reverse when they are exposed to magnesium sulfate solution and the expansion and strength loss will increase with the increase in the amount of rice husk ashes in the mix.

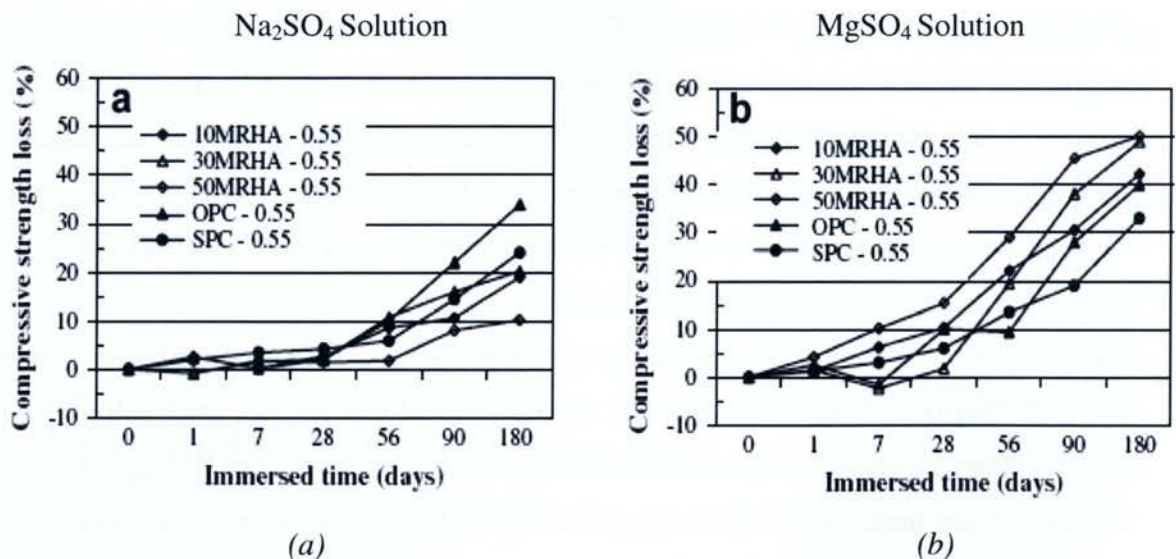


Fig.7.7 – Comparison of compressive strength loss of different concrete mix with the W/C ratio of 0.55 (a) immerse in Na_2SO_4 Solution, (b) immerse in MgSO_4 Solution

In order to find out the relation of rice husk ash blended concrete and rate of expansion when the concrete is attacked by the destructive sulfate environment, the expansion test was performed by B. Chatveera, and P. Lertwattanakul [7.9]. It was found from the test analysis that the rice husk ash blended concretes reduce the expansion since they have lower amount of calcium hydroxide in their composition. Less concentration of CH can reduce the amount of gypsum and ettringite formation which are the two most expansive components during and after hydration process in concrete. The use rice husk ashes up to 50% can produce the excellent sodium sulfate resistance concrete with the minor expansion and compressive strength loss.

Regardless of strength loss result (figure 7.7), the expansion test revealed that the rice husk ashes can help concrete to reduce the expansion of magnesium sulfate attack. Even the expansion of concrete which is blended with rice husk ashes can perform better and create less expansion when exposed to MgSO_4 solution. It can be discussed that the mechanism of expansion for Na_2SO_4 solution and MgSO_4 solution is different in concrete. Sodium sulfate will cause that the ettringite forms in concrete and therefore results in expansion in concrete but the deterioration of magnesium sulfate in concrete is due to decomposition of C-S-H gel. Hence, the expansion of magnesium sulfate is less than the expansion of the same concrete with sodium sulfate solution. Same as sodium sulfate expansion, the expansion of concrete will decrease with the higher replacement of cement with rice husk ash. Again, the cement can be replaced up to 50% to induce the better results against the expansion (figure 7.8).

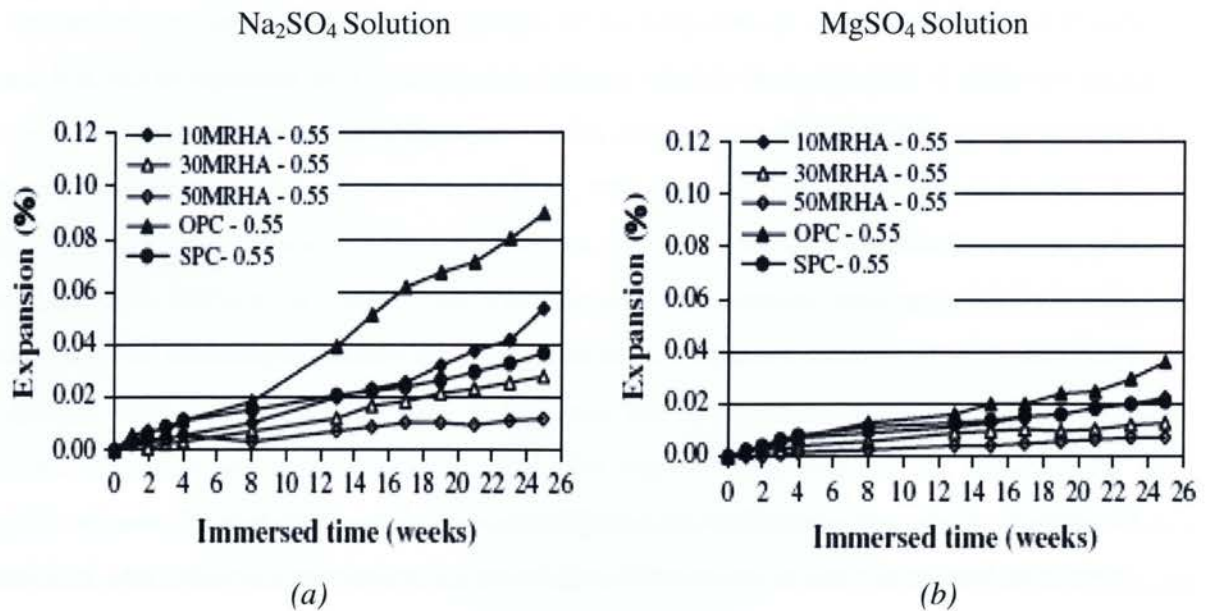


Fig.7.8 – Comparison of expansion of different concrete mix with the W/C ratio of 0.55
 (a) immerse in Na_2SO_4 Solution, (b) immerse in MgSO_4 Solution

In conclusion, the high amount of rice husk ash can be used in concrete in case of sulfate attack (Na_2SO_4). In other hand, the performance of concrete with cement type I blended with rice husk ashes is most likely the same as concrete with cement type V. with higher percentage of rice husk ashes, the performance of concrete is even better.

Special attention should be paid for the use of rice husk ashes in concrete when there is the risk of magnesium sulfate attack. Although these ashes can reduce the expansion but they will cause the higher rate of compressive strength loss in concrete.

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