CHAPTER 2

LITERATURE REVIEW

2.1 Introduction and Background

P.C. Aitcin (2000) stated that the concrete is the most widely used construction material, the annual global production of concrete is about 5 billion cubic yards, (Cement Association of Canada, 2008). This is twice as much concrete is used in construction around the world than the total of all other building materials, including wood, steel, plastic and aluminum. As reported by USGS Minerals (2008), the concrete production is 17 billion ton/year. Cement is still an essential material in making concrete. The annual production of the 1.56 billion tons of ordinary Portland cement (OPC) worldwide results an equivalent amount of carbon dioxide CO_2 gas release into the air. In a simple term, making one ton of cement produces approximately 1 ton of CO_2 gas.

Concrete is easy to make, technologically simple and inexpensive in production that turned it an ideal construction material. Wherever concrete has many advantages, there are some weaknesses for its application. Concrete is generally specified by the requirements of 28-days compressive strength without taking into account the environmental conditions to which it is to be subjected throughout the service life. As a result, many concrete structures are prematurely failing, giving a bad image of concrete to the public. Besides that, concrete is also mistreated during placement and curing.

According to P.C. Aitcin (2006), concrete definitely presents technological advantages where it can be made from local inexpensive materials and can be cast in any shape. Concrete also have good compressive strength, it does not rot, not much affected by humidity, it does not burn and it is not attacked by insects. When it is well proportioned, adequately mixed, transported, placed and cured, it becomes a durable construction material under most environmental conditions.

Concrete is weak in tension, heavy, not volumetrically stable because it shrinks and creeps or sometimes swells. Moreover, concrete must be properly cured to reach its full potential as a structural material and its durability can be applied in aggressive environmental conditions usually in the marine conditions. (J.L. Baron and M.N. Oliver, 1999).

2.1.1. Building 'Green' and Preservations

As mentioned by T.L. Ir. Chen (2009), building green in the future is a necessity and not an option. This is because buildings consume 40% of our planet's materials and 30% of its energy. The construction of a building uses 2 to 3 million tons of raw materials a year where it is mostly concrete and generates 20% of the solid waste stream.

Construction materials provide engineers with real opportunities to contribute to a project's sustainability. In using the traditional criteria for material selection such as economy and appropriateness to project structural requirements, has already been an active participant in sustainable design. This can also be done by considering and exploiting the efficiency, availability and the impact a material has on the environment. Taking for example if the material is concrete, concrete consists mostly of cement paste binder and aggregates.

Concrete is also an essential structural material for constructing structures. Cement production contributes approximately 1.5% of United States (US) annual CO_2 emissions and is about 7% of worldwide annual emissions. Cement production produces approximately one pound of CO_2 for each pound of cement. Reducing the amount of cement used in concrete will reduce CO_2 emissions.

2.2. Problems and Issues with Concrete

2.2.1. Towards Sustainable Concrete.

Continuous advances in technology development in every industry are very critical and the construction industry required such. According to the Portland Home Builders Association of Metropolitan (2009), concrete is one of the most environmental friendly construction products. It offers durability, design flexibility and stability for the residential marketplace. It also exerts great environmental advantages through every stage of manufacturing and use where it is created to conserve the availability of raw materials worldwide.

Concrete is durable as it can sustain weather conditions and withstand aggressive environment threats. It is because of that concrete does not rust or burn. It is also less susceptible to moisture damage and can generally ‘breathe’ and dry if the concrete structure is not too close to adjacent structures.

By simply outlasting other materials, concrete conserves energy and resources. The criteria mentioned above are obviously seen in the creation of High Performance Concrete (HPC). To have quality construction, quality materials are highly in demand and to cater for all required criteria, HPC is definitely the product that every practicing engineers, contractors and manufacturers are looking for.

2.2.2 Cement Consumption in Concrete Production.

According to the Portland Cement Association (PCA) (2005), concrete consists mostly of cement paste binder and aggregates; cement production contributes approximately 1.5% of US annual CO_2 emissions and is about 7% of the worldwide annual emissions. Cement production produces approximately one pound of CO_2 for each pound of cement. Therefore reducing the amount of cement in concrete production greatly results in reduction of CO_2 emissions.

P. Lassere (2007) mentioned that cement is a basic ingredient for the construction industry and is made from the 80% limestone, 3% shell and 17% clay that are mined from quarries close to the plant. The raw material is crushed, and then heated at temperature in excess of 1000 ºC in a rotating kiln to become clinker. The technology is a continuous process and is highly energy intensive. The cost of cement is derived as 29% energy, 27% raw materials, 32% labour and 12% depreciation which involved transfer of product to sites.

2.2.3. Cement Efficiency

M.L. Gambhir, (1997) reported that the compressive strength of the concrete increases with decreasing water to cementitious material ratio and with the increasing amount of SF. Thus, it is very important to understand the mechanism of the workability enhancement. The description is so as OPC and fine particles have a strong tendency to flocculate when mixed with water. The flocculation process leads to the formation of an open network of particles.

The network voids trap a part of the water, which is then unavailable for surface hydration of cement particles and for the fluidification of the mixture. These effects result in the stiffening or increase in apparent viscosity of the cementitious system. To achieve a homogeneous distribution of the water, and the optimal water cement contact, the cement particles must be properly deflocculated and kept in the state of high dispersion. Due to the dispersion effect, the fluidity in the cement mixture is increased.

The water reducing admixtures perform their function by deflocculating the lumps of the cement grain. In the normal stage, the surfaces of the cement grains contain negative and positive charges. As they bump into each other, they repel and attract. Superplasticizer on the other hand has very large molecules (colloidal size) which dissolve in water to give ions with a very high negative charge (anions).

These anions are absorbed into the surface of the cement particles in sufficient number to form a complete monolayer around them to become predominantly negative charged. Thus, they repel each other and flocs do not form. Because of that, the water trapped within the original flocs is released and it can contribute to mobility of the cement paste; hence, workability is improved. The representation of the superplasticizer molecule and its mode of absorption on cement grains are illustrated in Figure 2.1.

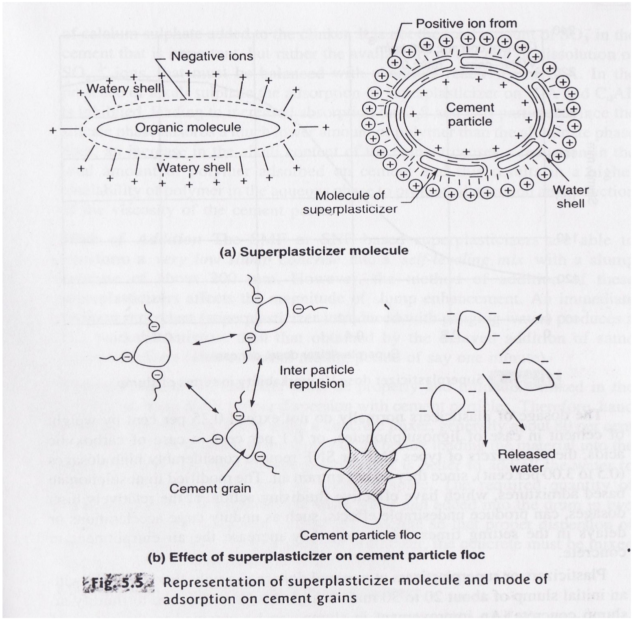

Figure 2.1: Representation of superplasticizer molecule and mode of adsorption on cement grains (M.L. Gambhir, 1997)

Thus, the amount of cement required within a mix is very important because it affects the strength of the concrete. The optimum amount is to be determined to ensure the quality of the concrete produced.

ACI (2005) estimated that for a 15% SF replacement of cement, there are approximately 2,000,000 particles of SF for each particle grain of OPC. A photomicrograph of the comparison of SF and OPC particles can be observed in Figure 2.2.

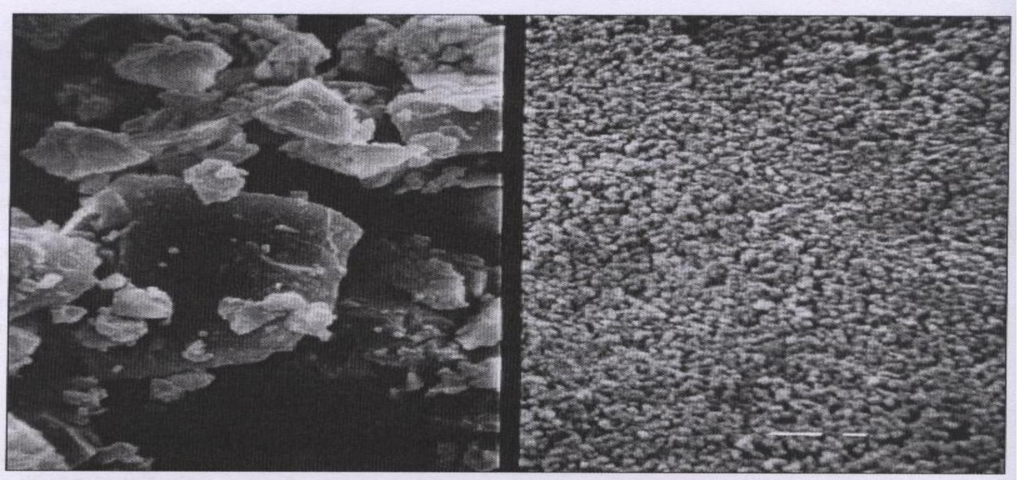

Figure 2.2: Comparison of OPC (left) and SF Particles (right) (ACI, 2005).

2.2.4. Environmental Impact of Concrete.

The amount of CO_2 embodied in a concrete depends primarily on the cement content of the mix designs. CO_2 produced during the manufacturing of cement is reabsorbed into the concrete during the product life-cycle. This particular process is called carbonation. Reabsorbtion of CO_2 also occurs over 100 year's life cycle and estimated absorption is to be in the range of 33% to 57%.

In terms of energy efficiency and energy consumption concerns, as defined by T.W. Bremner (2001), low energy consumption meant that the raw material to make both the cement and concrete is evenly distributed around the world and transportation is not the main consideration. The technology to make cement and concrete in many ways is similar to the technology used by the mining industry.

The advances in the mining industry have been adopted by the cement and concrete industry. In comparison with steel, aluminium, glass and plastic, the energy spent to create a concrete production facility in magnitude is less than what is required to create a comparable amount of competing material as can be seen from the cement kiln known to be a very energy efficient device. In addition, the energy to make concrete is mostly spent in making the cement.

The Environmental Council of Concrete Organizations (2006) mentioned that when evaluating the environmental aspects of building materials, concrete's overall impact is not harmful. Concrete is an ideal choice as a construction material as it actually helps to protect the natural resources and offers consumers benefits compared to other materials such as steel or timber. This can be observed in terms of resource efficiency, energy efficiency, waste minimization and prolonged structure lifespan.

However, the difference between cement and concrete have to be firstly understood. The two words which are concrete and cement are always being confused. Cement is actually one of the ingredients in concrete. It's in the form of fine greyish powder that when combined with water, binds sand and gravel or crushed stone into a rocklike mass known as concrete. Therefore even though cement is only 10%-15% by weight of the concrete's total mass, cement is the binding agent in concrete.

The severity of environmental impact is highlighted by K.P. Mehta (2001) as in the need for reducing the environmental impact of concrete is recognized in a recent report of the Strategic Development Council (2001). According to the report, 'Concrete technologists are faced with the challenge of leading future development in a way that protects the environmental quality while projecting concrete as a construction material of choice. Public concern will be responsibly addressed regarding climate change resulting from the increased concentration of global warming gasses.'

The Portland Cement Association, PCA (2005) reported that the cement production contributes approximately 1.5% of US annual CO2 emissions and is about 7% of worldwide annual emissions due to the demand of cement consumption during construction . Cement production produces approximately one pound of CO_2 for each pound of cement. Reducing the amount of cement used in concrete will reduce CO_2 emissions.

2.2.5. Natural Resources and Pre-Structural Deterioration

K.P. Mehta (2001) discovered that increasing the service life of structures is a long term and the fastest solution for preserving the Earth's natural resources. Thus, a new approach has been endorsed by the European Union known as the 'New Paradigm for Sustainable Development' suggests that minimization of materials use, maximization in product durability and reduction of maintenance cost will not only increase consumer's satisfaction and product value but also business profitability. When both manufacturers and consumers have achieved interest in improving the resource productivity, the world's ecosystem will be protected.

Ordinary concrete contains 12% cement and 80% aggregate by mass. Thus the annual global consumption of sand, gravel, and crushed rocks is at the rate of 10 to 11 billion tons. The mining, processing and transport operation involving large quantities affects the ecology of forested areas and riverbeds. Besides the three primary components; cement, aggregates and water, various chemical and mineral admixtures are also added into concrete mixtures not forgetting batching, mixing, transport, placement, consolidation and finishing of concrete.

Lack of durable materials causes pre-structural deterioration. Concrete structures are designed for a service life of 50 years, but experience shows that in urban and coastal environments many structures begin to deteriorate in 20 to 30 years or even less. This matter is not as wanted by many parties and is usually categorized as bad construction planning.

Considering funding constraints in high repair and maintenance works, it is suggested that in future structures are to be designed and built for a minimum service life of 100-120 years. The trend towards designing infrastructure based on life-cycle cost will not only maximize the return of available capital but also available natural resources.

S. Aiken and C.H. Leigh (1992); J.R. Vincent and R.M. Ali (1997) and World Bank (1987) mentioned that Malaysia is filled with natural resources especially minerals such as limestone and rocky mountains. Malaysia’s heavy reliance on its natural resources has been a salient feature from colonial days up until the 1970s.

2.2.6. Silica Fume Application – World and Malaysia.

In Malaysia the application of Silica Fume (SF) in the construction of structures is still in the preliminary stage. A step towards real understanding of SF and introductory to its application in the construction industry is greatly required. A.M. Neville (1995) and V.M. Malhotra and K.P. Mehta (1996) reported that since the development of Portland Cement by Joseph Aspdin in 1824, there have been some developments throughout the 20th century from the use of pozzolanic by-products such as SF in order to cut down the fuel cost and CO_2 emissions in the manufacturing process for example in cement and concrete productions.

At the same time turning waste to by-products, reusing of materials help reduce waste from industries, moving towards sustainable construction. Although its advantages are recognized more as compared to before, only a small percentage of the current supply of SF is being used as a mineral admixture in the cement and concrete industries.

M. Gary and J. Scanlon (2001) also mentioned that in the refractories world thirty five years ago, no one was working with SF and few knew what it was. Within a few years, it was being use as an additive in bricks. When the chemical is applied into the High Alumina Brick, mullite was formed in the matrix of the brick on firing, giving the brick good volume stability, strength and chemical resistance. At that time, it was only logical that silica fume would be used in brick and in no other construction materials. Silica fume is the pioneer in this transformation where SF has gone beyond having the brick-like properties too actually out performing brick in many applications.

2.2.7. Energy Consumption in Concrete

The cement industry is said to be an energy-intensive industry together with steel, paper and petrochemical industries. The percentage of energy cost in Portland cement production cost is 20% to 30%. If the energy cost is reduced, the manufacturing cost is lowered. Thus this results in increasing the company’s profits. UNIDO (2001)

Energy is crucial in all aspects of development from empowering manufacturing and modernization. Although new alternative, renewable, cleaner and more efficient technologies are being developed and implemented every year, the main strain by the rise in energy demand and global consumption outweigh the benefits brought by these improvements. The challenge lies in finding a way to reconcile the necessity and demand for energy supply with its impact on the natural energy resources in order to ensure a sustainable path for development (A.R. Mohamed and K.T. Lee, 2004).

As Malaysia's economy sector is developing, a recovery of energy in energy demand is very critical. According to J. Thaddeus (2002), the energy generating capacity within the last three years (increases according to energy demand) has increased almost 20% from 13000 MW to 15500 MW in the year 2003. The energy generating capacity is estimated to increase to 22000 MW by the year 2010. In order to meet the increasing demand, energy supply infrastructures have to be developed and be capital intensive. Consequently, this will impose tremendous pressure on natural resources.

At the same time, with the current pattern growth, resource used and environmental degradation cannot be ignored if looking to the future. Since the large demand has been placed on building material industry especially in the last decade, owing to the increasing population, which causes a chronic shortage of building materials the architects and civil engineers have been challenged to discover useful building and construction materials.

As mentioned by M.S.E. Sherif (2009), the increase in the popularity of using environmental friendly, low cost and lightweight construction materials in building industry has brought about the need to investigate how this can be achieved by benefiting to the environment as well as maintaining the material requirements affirmed in the standards. The standards can be obtained in Appendix E.

Therefore, it is logical to think that, in the immediate future, urban growth and its infrastructures will continue to produce maximum impact on the natural environment through the use of materials and the consumption of raw materials and energy. The number of construction works shall progressively increase however; these shall be undertaken by attempting to achieve the paradigm of sustainability, demanding an increasing durability of what is being built in order to minimize environmental impact. Thus as reported by B. Cazacliu and N. Roquet, 2009, to enhance production of HPC with low power consumption, new kinetic models using rheology and

2.2.8. Durability, Lifespan and Cost Consideration of Concrete

Touching the issue of durability and lifespan, concrete production continues to be a much debated issue in Malaysia. Often the Ready Mixed Industry is blamed for not being up to mark but the problem is much more complex than just poor performance at the batching plant (G.N. Kribanandan, 2000).

Today concrete is a complex material consisting not only of cement, aggregates and water but also admixtures and cement replacement materials. Concrete problems can arise from a few causes as stated below:

1. Inadequate specification
2. Batching Problems
3. Site Logistics and Long transport times
4. Poor placement
5. Lack of attention to finishing and curing

An inadequately prepared specification is the first problem. Problem structures were investigated where on occasion the specifications refer to CP110 a code which has not been in use for over two decades. In other cases the cutting and sticking of specifications from one project to another. This causes irrelevant code practices in projects especially when it comes to concrete testing before application in construction.

Problems at the batching plants do exist but increasingly the larger companies are much well organised, with internal training and many are ISO 9000 accredited. Site logistics and long transport times can be overcome by good planning and concrete designed for long setting times. Construction problems such as poor placement, finishing and curing are a function of poor training and lack of supervision. The issue of training and skills development in the construction industry clearly needs urgent attention.

During the design process it is normal to select a concrete strength requirement on the basis of 28 day strength of a cube (or in some countries a cylinder) tested in compression. The justification for this is the wealth of information that relates such an arbitrary test to observed structural performance. Even at this stage it is appreciated that the compressive strength as measured is only valid for the cube and in absolute terms shows only the potential for the concrete when used elsewhere in a structure itself. So we have a convenient assessment with which designers can work which is on a 28 day compressive strength requirement.

At this stage it should be remembered that in arriving at the quality (strength) of concrete, designers will have already incorporated some safeguards for uncertainty into the design process. Partial safety factors are used to increase material strength requirements to allow for some variability in the materials in a structure and in test specimens.

In selecting concrete type and mix, the need to provide concrete to a reliable standard involves an appreciation of the variability of the constituents that make up a concrete mix as well as its inherent non-uniformity. A statistical approach is taken to allow for variability. In this way the minimum strength requirement is increased so that a characteristic strength is selected and used as a target that within the scale of variability will mean that only some 5% of the test results will fall below the minimum specified level. While this provides a working platform for concrete production it should also mean that the majority of concrete used will be above or well above the limit.

To deal with concrete strength which is very much demanded in urban and offshore constructions, durability and service life issues are seldom considered except during remedial works. Concrete if it is understrength and has low cover provide the ideal conditions for the ingress of the environment to the level of reinforcement .

Possible initiation of corrosion mechanisms. If the buildings are away from the marine environment, the primary corrosion mechanism might be carbonation damage. A low strength cover concrete could reduce time to penetration considerably. This proves that quality ‘Green’ concrete mixes are very much required in the construction of urban and offshore structures.

2.3 Important Engineering Properties.

2.3.1 Ideal Concrete Mix Designs

Concrete mix design is the process of selecting suitable ingredients of concrete and determining their relative quantities with the objective of producing the most economical concrete while retaining the specified minimum properties such as strength, durability, and consistency (G. Akhras and H.C. Foo, 1994).

The easiest way to do mix design is to use proportions established for similar concrete using the same materials. Previous experience with concrete material is also of immense advantage in concrete mixture proportioning and adjustment. Where these are lacking the only possible option is to proportion the ingredient by a trial and error process. Several methods and codes are available to serve as guide for mix design of normal concrete (ACI Committee, 1991; R.E. Teychenne and W.A. Erntroy, 1988) and high performance concrete (P.C. Aitcin, 1998; ACI Comittee, 1995; G. de-Larrard, 1990 and K.P. Mehta and P.C. Aitcin, 1990). However, these are just guides to arrive at first trial mix.

Optimum mix proportions are obtained through testing of trial mixes and making adjustment accordingly (M. Kett, 2000). This is because these codes were developed based on experience with materials in certain parts of the world and may not be applicable to mix design in other parts of the world. Also, these codes do not address all issues regarding concrete mix design such as admixtures, transportation, and temperature effect (G. Akhras and H.C. Foo, 1993).

Concrete with several properties may be desired such as high workability, medium workability, high strength, lightweight, insulation etc. These challenges cannot be met by designing mix proportions based on existing codes and methods of concrete mix design. Concrete mix design and adjustment is complex and the correct way to perform this can be achieved with expert's advice and experience (M.F.M. Zain *et.al,* 2005).

2.3.2 Strength Consideration of Concrete in Construction Industry

The strength is one of the most important engineering properties of concrete. It reflects its mechanical quality and provides an indication of many other properties. The strength and durability of concrete are influenced by the use of cementing supplementary materials such as silica fume, rice husk ash, fly ash and etc. T. Brunauer and M. Copeland (1964) mentioned that the general factor affecting strength of concrete is water-cement ratio (w/c). The properties of concrete are largely governed by the cementatious matrix.

In particular, the strength of concrete is essentially dictated by the capillary porosity, which is a function of the w/c and degree of hydration of the cement particles. High w/c concrete contains a larger pore space than a lower one. This effect influences the strength of the hardened cement paste, which is the dominant factor in the strength of concrete. In other words, the strength of concrete resides in the solid part of the paste.

The knowledge of the 28 days compressive strength of a concrete is fundamental to be used in calculations that will allow the construction of a structure so that it is safe maintaining its mechanical strength during the whole life of the structure. The overwhelming importance of the compressive strength of concrete has been a constant preoccupation and links with the durability of the concrete. (P.C. Aitcin, 2000).

2.3.3 Mechanical Properties and Enhanced Durability of Concrete.

If discussed in terms of mechanical properties, K.C. Hover (1998) discovered that low water cement ratio (w/c) is responsible for improved mechanical properties and for enhanced durability. Water reducing admixtures can be used for the purpose of increasing the durability of e concrete, primarily by means of decreasing porosity, permeability and improving the mechanical properties. Such improvements do not only slows the rate of water but also oxygen, carbon dioxide and dissolved solids.

It will also provide increased resistance to stresses generated by external or internal loads. External loads include typical service loads, impact or abrasion while internal loads includes internal expansion of freezing water, alkali-silica gel, swelling aggregates, ettringite crystals or thermal stresses. If concrete is exposed to extreme temperatures (freezing for cold countries and extreme heat in hot countries), admixtures can be added to the concrete for specific resistance, another aspect of durability.

Durability of concrete structures is always a concern in aggressive environments. Factors to be considered in dealing with the durability of concrete includes concrete constituent materials, construction processes, physical properties of the concrete, type of loading and the nature of the environment to which the concrete structure is exposed.

The major durability problem such as the corrosion of steel reinforcement and cracking due to the reaction between alkalis released during the hydration of cement and certain types of aggregates, are caused by fluids penetrating the pore system of the concrete. Therefore as mentioned by A.S. El Dieb (1995), the porosity of concrete is critical to its durability in many service environments. Environmental conditions effects greatly the durability of concrete. One of the most aggressive environmental agents is chloride (found in soil, groundwater and seawater).

2.4 Concrete Properties and Material Performance

In this research, the properties of concrete were measured in the fresh and hardened conditions, Properties in fresh condition are very important as it controls the performance of concrete in the hardened condition.

2.4.1 Fresh Concrete Condition

2.4.1.1 Slump

Slump is measurement of the workability or fluidity of concrete. A stiffer mixture will have a low slump value. The higher slump values shows that the particular concrete mix has high workability. The decrease in the height of the slumped concrete is term as *slump* and it is measured to the nearest 3mm - 5mm. The decrease is measured to the highest point according BS1881: Part 102 (1983). There are three type of slumps which includes true, shear and collapse slump. (A.M. Neville, 1995)

Superplasticizer is commonly used to disperse cement particles. When added into cement paste, the value of the paste decreases close to zero. Then the paste and concrete will obtain good flowability without the segregation of raw materials. Naphthalene sulfonate Superplasticizer is often used to improve the rheology of fresh concrete.

When naphthalene sulfonate plasticizer is adsorbed to the surface of cement particles, it changes the sign of the zeta potential of the particle surface to the negative charge and increases the absolute value. Cement particles having the same sign of zeta potential cannot approach each other closely due to the electrostatic repulsion (P. Ternkhajornkit and T. Nawa, 2004).

2.4.2 Hardened Concrete Condition

2.4.2.1 X-ray Fluorescence Spectrometry (XRF)

XRF technology provides one of the simplest, accurate and economic analytic methods for the determination of the chemical composition of many types of materials. The strengths of this analytical method include easy sample preparation and are suitable for solid, liquid and powdered samples; analysis of non-conducting materials (notably oxides, glasses, ceramics and plastics) and exceptional precision, particularly for high concentration levels.

The XRF works when a primary x-ray excitation source from an x-ray tube or a radioactive source strikes a sample, the x-ray can either be absorbed by the atom or scattered through the material. The process which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is known as photoelectric effect.

During this process, if the primary x-ray had sufficient energy, electrons are ejected from the inner shells and in the process give off a characteristic x-ray whose energy is the difference between the two binding energies of the corresponding shells. Since each element has a unique set of energy levels, each element produces x-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. (Amptek Inc., 2002)

Thermo Fisher Scientific (2007) stated that the control and Research and Development (R&D) tasks can be undertaken and precision inside ±0.1% relative is routinely achieved whilst limits of detections are often at parts per million (ppm) or sub ppm levels. The XRF technique is also widely acceptable and used in the metals industry alongside Optical Emission (OE) spectrometers. This combination brings the optimum configuration for rapid and accurate analysis of both metals and the oxides associated with metal production such as ores and slag.

For sample preparation, in order to keep the geometry of the tube-sample –detector assembly constant, the sample is normally prepared as a flat disc, typically of diameter 20-50 mm. This is located at a standardized, small distance from the tube window. Since the X-Ray intensity follows an inverse square law, the tolerances for this placement and for the flatness of the surface must be very tight in order to maintain a reputable X-ray flux.

There are several ways to obtain sample discs depending on the materials that need to be tested; metals may be machined to shape, minerals can be finely ground and pressed into tablet ad glasses may be cast into required shape.

The purpose for obtaining a flat and representative sample surface is that the secondary X-rays from lighter elements often only emit from the top few micrometers of the sample. In order to further reduce the surface of the irregularities, the sample is usually spun at 5-20 rpm. It is important to ensure that the sample is sufficiently thick for absorption. For higher-Z materials, a few millimeters thickness is adequate, but for a light-element matrix such as coal, a thickness of 30-40mm is required.

2.4.2.2 X-Ray Diffraction Spectrometry (XRD)

According to the Limnological Research Centre Core Facility (2004), a routine XRD mineralogy profile can provide qualitative and semi-quantitative records of shifts in the source of sedimentary components to a lake sequence. XRD mainly displays information on autocthonous and authigenic minerals. But can give some indication of the abundance of amourphous silica phases. Set up with routine data collection, XRD is a rapid, accurate technique which can process 40 samples per-day using an automated sampler charger.

Each mineral is defined by a crystal lattice with characteristic diffraction properties resolved by x-rays. The Angstrom d-spacing of certain crystallographic lattice directions show up as relative peak (area) heights on the diffractogram (usually in mm) in a fixed relationship to the 2θ (two-theta) angle of the scintillator counter as defined by Bragg's Law of the diffraction. Using calibrated peak area intensities of the major peak, the proportion of mineral species in a profile can be given with about ±5% at least for minerals which constitutes more than 5% of the bulk sample.

Figure 2.3 shows that based on Bragg's Law, $n\lambda = 2d\sin\theta$, by controlling the wavelength with vary and continuously measure the incident angle, it will leave only the lattice plane spacing as variable. So whenever a constructive interference is observed, at a point a fundamental spacing parameter for the mineral of interest can be calculated (G. Arehart, 1999).

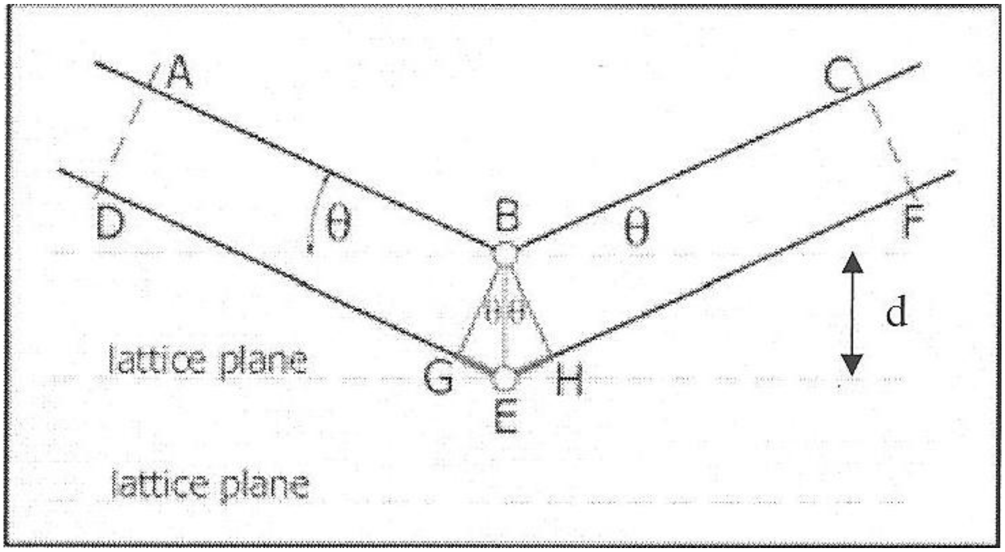

Figure 2.3: Geometry of X-Ray Reflection (G. Arehart, 1999)

2.4.2.3 Compressive Strength

The National Ready Mix Concrete Association, NRMCA (2000) reported that the compressive strength of concrete is a primary physical property and frequently used in design calculations for bridges, buildings and other structures. Conventional concretes have a compressive strength between 20 MPa to 35 MPa. For high strength concretes by definition has a compressive strength of at least 70 MPa. Compressive strengths up to 140 MPa have been used in special bridges and high-rise building applications.

Concrete mixes can be designed to provide a wide range of mechanical and durability properties to meet the required codes and standards of a structure. The compressive strength is measured by breaking concrete cube specimens in the universal testing machine for compression. The compressive strength is calculated from the failure load divided by the cross-sectional area resisting the load and reported in the units of pound-force per square inch (psi) in US customary units or Megapascal (MPa) in SI units.

The compressive strength test results are mainly used to determine if the concrete mix as delivered meets the requirements of the specific strength f'_{cr} in the job specification. A test result is the average of at least two or usually three standard cured strength specimens made from the same concrete sample and tested at the same age. In most cases, strength requirements for concrete are at the age of 28 days.

2.4.2.4 Porosity

Porosity is related to the original packing of the cement, mineral admixtures and the aggregate particles; the water-to-solids ratio; the rheology, which is related to the degree of dispersion of the solids originally present; and the conditions of curing.

The weight of the moisture and relative humidity in concrete with regards to the durability is highlighted. According to K.P. Mehta *et.al* (1993), permeability of concrete is influenced by two main factors: porosity and interconnectivity of pores in the cement paste and micro-cracks in the concrete, especially at the paste aggregate interface.

J. Berissi *et.al* (1986) proved that porosity and interconnectivity are controlled for most parts by the water cement (w/c) ratio, degree of hydration and the degree of compaction. On the other hand, density and location of interfacial micro-cracks are determined by the level of applied stress, external or internal which is experienced by the concrete.

Internal stresses in concrete occur as a result of shrinkage, thermal gradients, abrupt changes in the hydro-thermal environment and factors causing volumetric instability. In high performance concrete, it has been shown that the macroscopic property is related to the porosity. It is from this idea porosity is tested in this research.

2.4.2.5 Splitting Tensile Strength

Splitting tensile strength is obtained from split-cylinder test conducted on cylinder concrete samples. Tensile strength can also be obtained from an unreinforced concrete beam or slab to resist failure in bending. The general test includes the measurement done by loading 150 mm x 150 mm concrete beams with a span length at least three times of the depth. The flexural strength is expressed as *Modulus of Rupture* (MR) in psi or MPa. Standard tests methods are used such as ASTM C 78 (third point load) or ASTM C293 (center point loading) (The National Ready Mix Concrete Association, NRMCA, 2000).

Flexural MR is about 10%-20% of compressive strength depending on the type, size and volume of aggregates used. However the best correlations for specific materials are obtained by laboratory tests for some specific materials and mix design. The MR which is determined by three points loading is lower 15% than the MR determined by the center point loading.

As mentioned by Instron (2007), flexure testing is often done on relatively flexible materials such as polymers, wood and composites. There are two test types; 3 point bending and 4 point bending. In 3 point bending test, the area of uniform stress is quite small and concentrated under the center loading point. As in a 4 point, the area of uniform stress exists between the inner span loading points (typically half the outer span length).

2.4.2.6 Modulus of Elasticity (Flexural Tensile Strength)

As described in the ASTM C469 (1986), modulus of elasticity is the stress to strain ratio value of hardened concrete at whatever age and curing condition that may be designated. The standard also states that the modulus of elasticity is applicable with the customary working stress range of 0%-40% of the ultimate concrete strength. The modulus value is usually used in sizing reinforced and non-reinforced structural members, establishing the quantity of reinforcement, computing stress for observed strain and in the design of pre-stressed concrete members.

As reported by S. Bhanja and B. Sengupta, (2005), flexural tensile strength also known as the modulus of elasticity, plays a vital role in concrete making. In concrete, cracks can propagate very easily in tension and the cracking of concrete may cause serviceability and durability problems. The use of Silica Fume (SF) can improve the mechanical properties of concrete by replacement in different levels and percentages as well as strength improvement in the transition zone of cement paste.

Modulus of elasticity of concrete is expressed in terms of compressive strength. The mechanical properties of concrete are highly dependent on the properties and proportions of binders and aggregates. Modulus of elasticity is also known as the tensile strength of concrete and is a key factor to estimate the deformation of buildings and members. It is also a fundamental factor for determining the modular ratio, n which is used for the design of section members subjected to flexure (T. Fuminori and M. Noguchi, 1990).

L. Nawa and G. Horita (2004) described that the standard used for determining the Static Modulus of Elasticity of concrete in compression is the ASTM C 469. The standard describes modulus of elasticity as the stress to the corresponding strain ratio value for hardened concrete at whatever age and curing condition.

2.4.3. Durability of Concrete in Marine Condition

Concrete exposed to marine condition according to B.C. Gerwick (1986), may deteriorate due to effects of chemical action of the seawater constituents on cement hydration products, alkali aggregate expansion, crystallization pressure of salts within concrete if one face of the structure is subject to wetting and others to drying conditions, frost action in cold climates, corrosion embedded steel in reinforced or pre-stressed members and physical erosion due to wave action and floating objects. Attack on concrete by any of these causes will increase the permeability and porosity of the concrete.

As summarized by P.F. McGrath (1996) the causes of concrete deterioration are classified into two categories which are the physical and chemical causes as shown in Figure 2.4 and Figure 2.5.

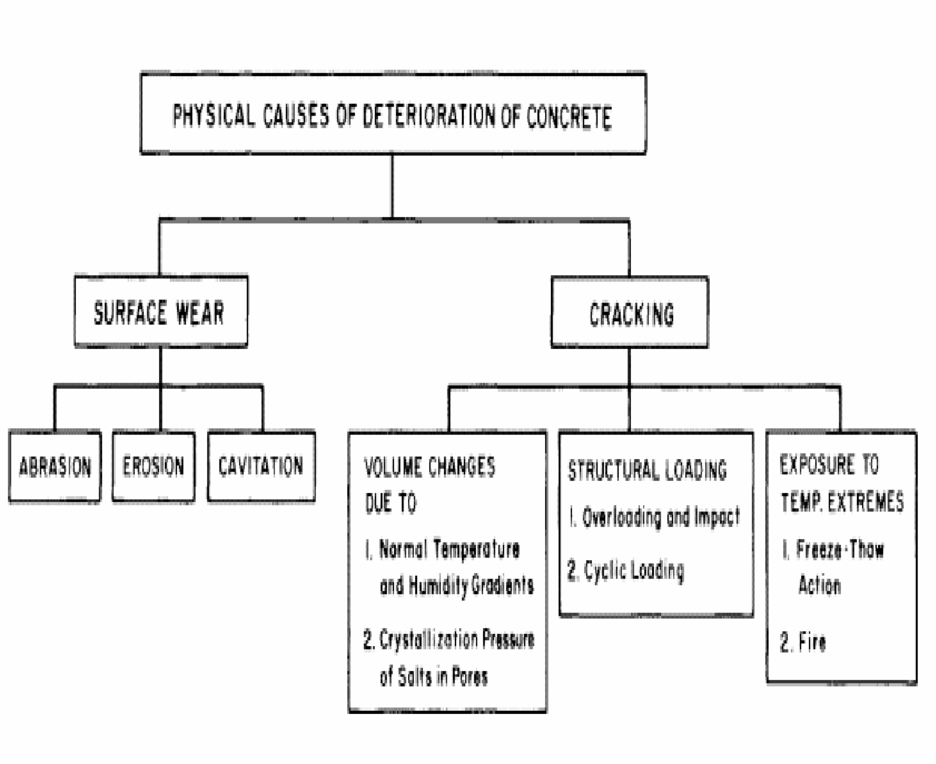

Figure 2.4: Physical Causes of Deterioration of Concrete (P.F. McGraft, 1996)

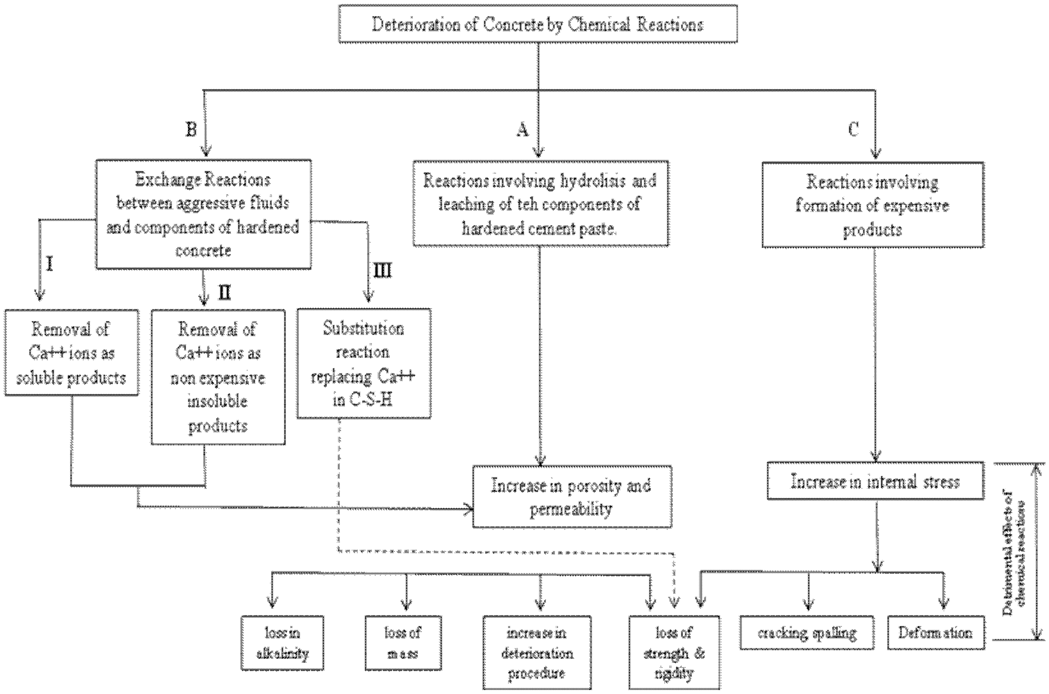

Figure 2.5: Corrosion of Concrete by Chemical Reactions (P.F. McGraft, 1996)

Expansion and micro cracking due to physical effects of pressure from salt crystallization in a permeable concrete will increase the permeability further and pave the way for deleterious chemical interactions between seawater and cement.

In terms of corrosion of reinforcing steel, G.C. Hoff (1986) and T. Mays *et.al* (1992) states that, when a concrete structure is exposed in deicing salts, salt splashes, salt sprays or seawater, chloride ions, those constituents will slowly penetrate into the concrete, mostly through pores in the hydrated cement paste. The chloride ions will eventually reach the steel and then accumulates to beyond a certain concentration level, the protective film is destroyed. This causes the steel to corrode when oxygen and moisture are present in the steel-concrete interface.

Once corrosion sets in on the reinforcing steel bars, it proceeds in electrochemical cells formed on the surface of the metal and the electrolyte or solution surrounding the metal. Each cell consists of a pair of electrodes (the anode and its counterpoint, the cathode) on the surface of the metal, a return circuit, and an electrolyte. Basically, on a relatively anodic spot on the metal, the metal undergoes oxidation (ionization), which is accompanied by production of electrons, and subsequent dissolution.

These electrons move through a return circuit, which is a path in the metal itself to reach a relatively cathodic spot on the metal, where these electrons are consumed through reactions involving substances found in the electrolyte. In a reinforced concrete structural element such as beams, columns or slabs, the anode and the cathode are located on the steel bars, which also serve as the return circuits, with the surrounding concrete acting as the electrolyte. This can be observed in Figure 2.6.

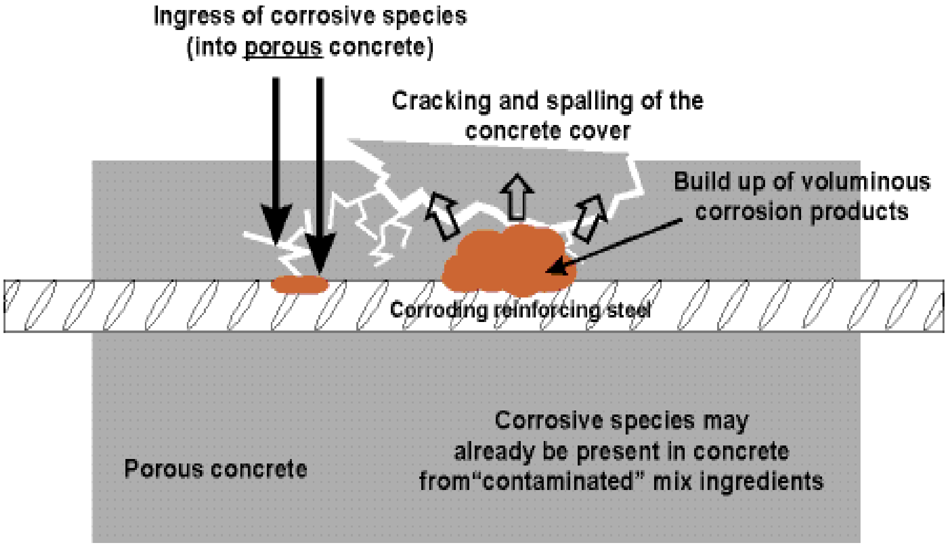

Figure 2.6: Corrosion of Reinforcing Steel (T. Mays *et.al*, 1992)

2.5. Modernization of Concrete

2.5.1. Modern Concrete Technology

As mentioned in P.C. Aitcin (2000), modern concrete is also known as the concrete of tomorrow. Modern concrete will be greener where it will have a low water cement (w/c) ratio; it will also be more durable and have various characteristics that will be quite different from one another for different applications. Concrete can now be designed as demanded. Concrete and cement producers have to realize that more profit can be made by selling small amounts of concrete 'customized' rather than a cheap commodity product. The cost of 1 MPa or 1 year of life cycle is more important if compared to the cost of 1 m³ of concrete.

Concrete producers in future will have to differentiate the types of concrete offered by the cement and admixture producers. This is to provide contractors concrete that is more high tech and economical. This will not only be in terms of cost of 1 m³ but in terms of performance. An example of the modern concrete technology is the High Performance Concrete (concrete with added admixtures).

2.5.2. Innovation in Concrete Technology

According to M. Ali (1997), in concrete construction, much of the technological changes were in the first half of the 20th century. Advances in formwork, mixing of concrete, techniques for pumping and types of admixtures to improve quality have all contributed to the ease of working with concrete in construction which also includes construction under aggressive conditions.

When transport began at 1913, it was executed using open trucks. Since segregation occurred on the way to the site, remixing was required. Actual means of transporting the quantities needed for enormous job as construction project entails by a transit-mix vehicle was not available until after 1920. In 1947, the first “hydraulically driven truck mixers” were introduced in the scene.

Delivery of concrete and material placements in large quantities has been an issue in urban and marine constructions. Technology remained primitive and stagnant in this area until 1960s when hydraulically powered and controlled pumps were first developed and mounted on a truck for mobile services. From here techniques improved continually until now when pumping of concrete is also considered in small construction projects.

Great thought must be considered to the properties of concrete during construction in effort to reduce consumption of energy through the usage of high-tech facilities such as pumps that requires high energy capacity.

2.5.3. Improvements in Concrete Technology

Along with advances in the ways that concrete is brought to the site, the types of formwork in which it is cured, and how it is placed at high levels, its mechanical and chemical properties have made great advances in the past century.

The most significant improvement is the application of High Performance Concrete (HPC) in urban and marine constructions. HPC truly began in 1927 when engineers were building a tunnel through the Rocky Mountains near Denver. The construction needed a quick way of supporting the loads on the tunnel. At that time, HPC, is under research stage and was not ready to enter the market. The engineer prevailed upon scientists to allow its use. Eventually, the tunnel was built using HPC. The builders were very interested in HPC as it has the ability to reach an adequate maturity in 24 hours rather than 7 days for regular concrete. HPC is also very different from conventional reinforced concrete and contains admixtures.

HPC is also an ideal choice among contractors. It encompasses more than just high-early performance. It is a mixture whose properties include increased strength and better performances in the areas of durability, ductility, density, mixture stability and chemical resistance. It also changes depending on the type of admixture combined with cement, aggregates and water for the final product. Building industry professionals are also very interested in increasing productivity by decreasing the amount of time for concrete to reach its strength and amount of material required to carry the loads of a structure as well as having improved stability and toughness.

HPC is very flexible with applications to many classifications of construction. It is well known that time, money and labour costs together are a matter of great concern in the building industry. With its low water cement (W/C) ratio, strength of 20 to 40

MPa can be developed within 24 hours of placing. This performance speeds the time for project completion and may reduce cost with the reduction of waiting time and more reuse periods for formwork. Higher strengths that can be achieved by HPC also add a few other beneficial effects to the structure. These features of HPC make it appropriate for applications to building constructions in urban and marine environment (M. Ali, 1997).

According to J. Hu and L. Larrard (1996), HPC has been widely used in the last decade. With superplasticizer added into concrete mixes, reduction of water happens in concrete mixes resulting in better compactness. The SF used in certain cases increases even more the concrete compactness by filling of some intergrain voids. Hence the HPC presents numerous advantages.

From G.N. Edward *et.al.* (2003), in order to cater to the world development and the increasing urbanization, HPC with high strength is highly needed so to sustain the capacity of a structure that is subjected to carry. This is so by reducing the size of the structural elements and maintaining the required strength of the concrete material. This saves cost for all parties and promotes technology development to the Concrete Industry.

2.6 Introduction to High Performance Concrete (HPC).

2.6.1. Background

‘All high performance concrete is high strength concretes but not all high strength concretes are high performance concretes’ (H.G. Russell, 1999)

HPC is not one product but a technology which includes a range of materials with special properties beyond conventional concrete and the routine construction methods. According to T.C. Holland (1997), ACI President, HPC is an ‘umbrella term for many exacting specifications for concrete construction’.

From S.C. McCraven (2002), HPC is relatively a new type of technology. HPC began in France in 1980 followed by Canada in 1990. In 1989, under the direction of Paul Zia from North Carolina University, a major effort in HPC technology began in the United States with the initiation of the Strategic Highway Research Program (SHRP). SHRP defined HPC in terms of strength, low water/cement (W/C) ratio and durability towards aggressive environments. These early efforts were in response to the critical deterioration rates of the nation's roads and bridges.

2.6.2. Global Development

M.L. Gambhir (1997) states that the Compressive Strength of HPC is much higher than those of the normal concrete of the same consistency. Strength of the normal concrete is achieved by concrete with reduced cement content. The use of superplasticizers generally improves the strength of HPC. The strength of concrete normally depends on a number of factors including the properties and proportions of the constituent materials, degree of hydration, rate of loading, method of testing and specimen geometry.

The properties of the constituent materials which affect the strength are: the quality of fine and coarse aggregates (well graded and have good distribution), the cement paste and the paste-aggregate bond properties of the interfacial transition zone. These, in turn, depend on the macro- and micro-scopic structural features including total porosity, pore size and shape, pore distribution and morphology of the hydration products as well as the bond between individual components.

As reported by H.G. Russell (1999), high strength is also known as high performance concrete and has been used in the columns in high rise buildings. The economic advantages of using HPC in the columns of high-rise buildings have been known for many years. The three major components contributing to the cost of a column are concrete, steel reinforcement and formwork. By utilizing HPC, the column size is reduced. Indirectly less concrete and less formwork are needed. At the same time, the amount of vertical reinforcement can be reduced to the minimum amount as long it is within the range specified by the code.

As a result, the least expensive column is achieved with the smallest size column, the least amount of reinforcement and the highest readily available concrete strength. Now, HPC has it all and is not only used widely in building constructions or bridges but also in carparks and marine structures (foundations and platforms).

2.6.3. Working with Silica-Fume Concrete

Aberdeen Group (1987) reported that, SF produces concrete that is stronger and more durable than conventional concrete. Field strengths of 80MPa have been achieved with this highly reactive pozzolan. Also, rebar corrosion is reduced because the reaction products of the extremely fine silica fume particles fills in the internal pores. This slows carbonation and helps keep chlorides out of the concrete. Because of these benefits, many engineers are now specifying silica-fume concrete for high-strength structural applications and abrasion-resistant surfaces.

This is modern concrete technology. Construction workers must be carefully trained to get the best results in handling concrete with SF. There is little or no bleeding in flatwork, so finishers must adjust the timing of finishing operations and structures exposed to de-icing agents or salt water. The addition of SF isn’t a substitute for good concreting practices, however, it is for best results. Concrete suppliers must pay close attention to several production details. Contractors must also need to know how placing, finishing, and curing procedures differ from those used for conventional concrete.

SF in concrete acts much like conventional concrete during transport, placement, and consolidation. However, depending on the amount of SF, the fresh concrete can be more cohesive and less prone to segregation than conventional concrete. For overall ease of placing and finishing, the slump is made as high as is practical. Concrete with SF can be transported in any equipment used to transport conventional concrete. After discharge, the equipment should be cleaned the same way as for conventional concrete.

Concrete with SF can be placed successfully using any placement device such as a bucket, pump, or tremie. During placing, water should not be added into the concrete to improve workability. Just as with conventional concrete, too much water reduces strength and durability. If a higher slump is needed, controlled amounts of a water-reducing admixture at the batch plant or at the jobsite is added. Consolidation by vibration is needed for silica-fume concrete even when a high-slump mixture is used. Concrete with a slump of 8 to 10 inches can be deceptive because it flows so well that workers may think vibration isn't needed. However, the increased cohesiveness caused by SF entraps air which must be removed by vibration, regardless of the slump.

The biggest difference between conventional concrete and concrete with SF shows up during finishing. Adding up to 5 percent silica fume by weight of cement makes little difference, but adding higher amounts of silica fume reduces bleeding and may eliminate it. This makes SF concrete more rapid to surface drying and has reduced plastic shrinkage cracking.

2.6.4. Silica Fume (SF) Concrete in Aggressive Environments

According to T.C. Well (2004), silica-fume concrete is gaining popularity as a corrosion-protection system for parking garages, bridge decks, and other structures because it reduces chloride penetrability. Twenty-two hundred parking areas were built between the years 1979 and 1984 in the United States. With more than 100 of the larger structures being constructed on an annual basis, it is important that precautions be taken to protect them against deicing salt-induced corrosion. The latest exciting product to enter the corrosion protection market is silica fume (microsilica).

Concrete in a non-aggressive environment is a very strong, durable, and long-lasting building material. In aggressive environments, some precautions may be needed to protect the concrete or embedded steel.

Bridges and parking garages are deteriorating at an alarming rate due to chloride-induced corrosion. Bridge decks have de-icing chemicals deposited directly on the surface where the chemicals affect not only the deck but also the supporting structural members due to leakage. Although de-icing chemicals are used only sporadically in parking garages, cars carry salt-infested snow into the garages. Much of this salt remains after the cars leave.

Unlike bridges, however, which are washed by rains, parking garages are rarely washed down. The salts deposited in the winter remain all year. Indeed, when comparing concrete chloride contents of bridge decks and parking garage decks in the same location, and all other parameters being equal, the garage decks usually show a higher chloride content at all slab depths. This chloride content is due to the presence of larger amounts of chlorides on the slab surface during hot weather. As ambient temperatures rise, chlorides are able to diffuse through the concrete pores at a greater rate of speed. This phenomenon is much applicable in the Malaysian context.

The highly alkaline environment of concrete creates a protective passivating layer on steel that inhibits the electrochemical reaction of corrosion under normal conditions. Chlorides will move through the concrete pores as well as through the transition zone between the paste and aggregate and eventually reach the embedded steel. Penetration of the passivating layer takes place, and corrosion of the steel begins.

As the chloride content around the rebar increases, so does the corrosion rate. The corrosion product will expand in size by roughly four times its original volume, creating tensile pressures on the concrete up to 50MPa. The concrete eventually ruptures, causing cracking and spalling which allows more chlorides to enter at an even faster rate. Eventually, the concrete will deteriorate, requiring expensive rehabilitation or causing structural failure.

2.6.5. HPC in Marine Environment

The degradation of concrete structures due to the ingress of salts like chlorides is of obvious importance in civil engineering. M. Mohamed and M. Hamid (2002) mentioned that, structures built in an aggressive environment like coastal regions will especially be subjected to chloride attack. The chloride attack is one of the most important aspects when the durability of concrete is considered. The chloride ion ingress is the primary cause for rebar corrosion. Statistics have indicated that over 40% of failure of structures is due to the corrosion of steel (M.S. Shetty, 2007). Thus, chloride induced corrosion of reinforcement is the most destructive form of damage affecting durability and serviceability of concrete.

G. Schutter (2004) discovered that chloride can be introduced into concrete via internal sources (from cement, aggregate, water and admixture system) and external sources (from environment). Due to chloride ingress the alkaline passive layer present around the rebar is destroyed and initiates corrosion.

Nowadays durability properties play an equal role as strength. The strength and durability of concrete was enhanced by adding mineral admixtures like fly ash, rice husk ash, in concrete. This enhancement of strength and durability is due to the improvement of micro-structure of cement paste like porosity, permeability and sorptivity (A.K. Tiwari, 2004). The development of concrete using silica fume improves the early age performance of concrete.

2.6.5. HPC – Service Life and Cost Consideration.

P.C. Aitcin (2000) mentioned that it is sufficient to look at the very poor appearance of many present infrastructures, and the numerous repair works that are consuming so much time and money. It is bad to have them demolished when they have only reached half of their intended life cycle. The enormous socioeconomic costs associated with various maintenance repairs (deviations, traffic jams, loss of time and pollutions) are also the major problems.

The price of 1 m³ of reactive powder concrete is very frightening to engineers who still compare this price to the price of 1 m³ of HPC. Logical comparisons should be applied and practiced. Thus HPC contributes to high early strength, with cost consideration and quote says;

2.7 Effects of HPC on chemicals

2.7.1. Admixtures

F.M. Lea (1971) states that, properties of concrete, in both the fresh and hardened states, can be modified by adding certain materials to concrete mixtures, those materials are known as admixtures. Admixtures vary widely in composition, from surfactants and soluble salts to polymers and insoluble minerals.

Generally, they are used in concrete to improve workability, accelerate or retard setting time, control strength development, and enhance the durability to frost action, thermal cracking, alkali-aggregate expansion, sulfate attack, and corrosion of the reinforcement.

Admixtures can be divided into two types as follows:

i. Chemical admixtures - Materials in from of powder or fluids that are added to concrete to give it certain characteristics not obtained with plain concrete mixes. in normal use, admixtures dosages are less than 5% by mass of cement and are added to concrete at the time of mixing .(i.e. $CaCl_2$, Plasticizers , Corrosion inhibitors etc).

ii. Mineral admixtures - Inorganic materials have pozzolanic or latent hydraulic properties. They can be added to improve the properties of concrete or as a replacement for OPC, such as silica fume and fly ash.

2.7.2 Cement Replacement Materials

From F. Edward and A.W. Charles (2001), there are a number of good reasons to replace a portion of the ordinary Portland cement (OPC) in high performance mixtures with pozzolans and alternative cements. From an economic standpoint, reducing the cost of the raw materials in a cubic yard of concrete by replacing cement with pozzolans and alternative cement is an attractive proposition because it will reduce the overall cost of the project.

In addition to the cost savings the use of alternative cementatious materials saves the energy that will be used in producing the cement replaced, reduces the production of carbon dioxide gas, CO_2 and maximizes the value and use of by-product materials.

The three most often used materials to replace OPC are silica fume, fly-ash and slag. All three of these materials are by-products of other material processes. There are even more attractive features of these replacement materials. They are better than OPC in improving some of the important properties of the finished concrete material.

One of the primary reasons to use HPC is to increase the strength of concrete. The most famous by-product used as replacement is still Silica Fume (SF) and has successfully proven itself to be a wonderful strength enhancer.

S.P. Shah and S.H. Ahmad (1994) mentioned that most modern high strength concrete contains one supplementary cementing materials. However, to cater for some unexpected and unavoidable incidents, a substitution of the cementing material has to be available. Here in this research the Microwave Incinerated Rice Husk Ash (MIRHA) suits the acceptance limits (chemical requirements of silica 85%) for silica fume (SF) as indicated in Table 2.1, 'Canadian Specifications for Silica Fume' taken from CSA Standard A23.5.

Table 2.1 - 'Canadian Specifications for Silica Fume' CSA Standard A23.5

Canadian Specifications on Silica Fume - CSA Standard A23.5	
Chemical Requirements	
SiO2, min (%)	85
SO3, max (%)	1
Loss in ignition, max (%)	6
Physical Requirements	
Accelerated pozzolanic activity index , min (%) in control	85
Fineness, max (%) retained on 45µm sieve	10
Soundness - autoclave expansion or contraction (%)	0.2
Relative density, max variation from average (%)	5
Fineness, max variation from average (%)	5
Optional Physical Requirements	
Increase in drying shrinkage, max (%) of control	0.03
Reactivity with cement alkalis, min reduction (%)	80

From K. Ismail and L. Waliuddin (1996), the color of the completely burned rice husk in the microwave is blackish. This product, the burnt rice husk is known as Microwave Incinerated Rice Husk Ash (MIRHA). Investigation on the chemical properties of the MIRHA shows that the silica content is about 80% - 90%. This matches the chemical requirements of Silica Fume (SF).

P. Pavlenko *et.al* (1998) states that if cement replacing materials such as Silica Fume (SF) from the metallurgical industry is to be added into a concrete mix of reduced cement content, there is normally little or no CO2 released into the atmosphere.

2.7.3. Silica Fume (SF) in HPC

2.7.3.1. Background

SF is also known as micro silica, a by-product resulting from the reduction of high-purity quartz with coal in electric arc furnaces in the production of silicon and ferrosilicon alloys. SF is a fine powder of spherical particles with an average diameter of about 0.1 μm, which are about 2 orders of magnitude finer than particles of ordinary Portland cement.

SF also contains more than 90% silicon dioxide; thus, they are highly effective pozzolanic material to be used in concrete. A pozzolanic material contains silica in a reactive form which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementatious properties (K.N. Yu *et.al,* 2000).

M.D. Luther; P.A. Smith (1991); V.M. Malhotra and K.P. Mehta (1996) reported that SF can contribute to the compressive strength development of concrete. This is because of the filler effect and excellent pozzolanic properties of the material that translate into a stronger transition zone at the paste-aggregate interface.

SF contribution to the development of compressive strength depends on various factors such as percentage of SF, water cement (w/c + SF) ratio, cement content and composition. Very fine particles of SF get absorbed on the top oppositely charged surface of cement particles and prevent them from flocculation. The cement particles are then effectively dispersed and will not trap large amounts of water, which means that the system will have a reduced water requirement for flow.

In addition to the mechanisms, particle packing effect is also responsible for water reduction. Note that OPC particles are mostly on the size of 1-50µm. Therefore physical effect of particle packing by the microfine particles of a mineral admixture will reduce the void space and correspondingly the requirement for plasticizing the system.

Microfine fillers which contain a very large proportion of very fine particles such as silica fume, it should be obvious that the filler particles themselves must be dispersed with the aid of a plasticizing agent before any benefit from the particle packing effect can materialize. The Figure 2.7 is the Mechanism of bleeding reduction in cement paste by silica fume addition.

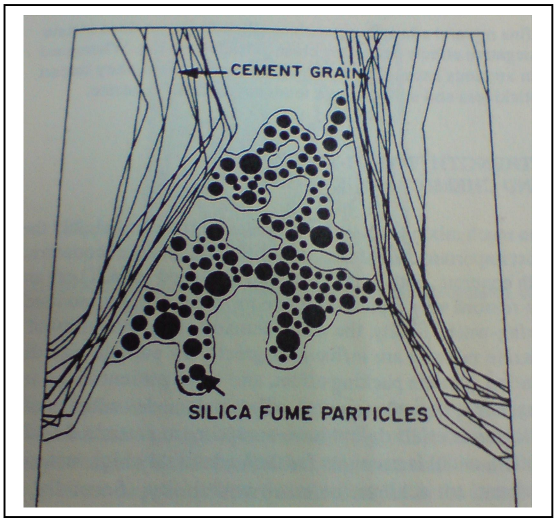

Figure 2.7: Mechanism of Bleeding Reduction in Cement Paste by Silica Fume Addition (V.M. Malhotra and K.P. Mehta, 1996).

From the research of materials conducted, the water demand of HPC with SF is directly proportional to the amount of SF used. The strength has shown very high increase as much as 15%, especially for high silica fume content at the early ages.

In general, the use of the superplasticizer is to achieve proper dispersion of the SF in concrete and to fully utilize its contribution to the strength potential. Superplasticizers are a must to be added in every HPC mixes. HPC containing SF has compressive strength development patterns which are different from those of Ordinary Portland Cement (OPC) Concretes.

If compared with those of fly-ash concretes, the effect of the pozzolanic reactions of the former is very evident in the earlier ages. This is because SF is a very fine material with very high amorphous silica content. The dosage of SF is obviously an important influence to the compressive strength of the concrete. For general construction, the optimum dosage generally varies between 7% and 10%, however, in specialized condition; up to 15% of the SF is incorporated successfully in concrete. The proper selection and proportion of cement also plays an important role in developing mixture proportions for high quality and improved HPC. The microscopic picture of the SF by A. Dunster (2009), can be observed in Figure 2.8.

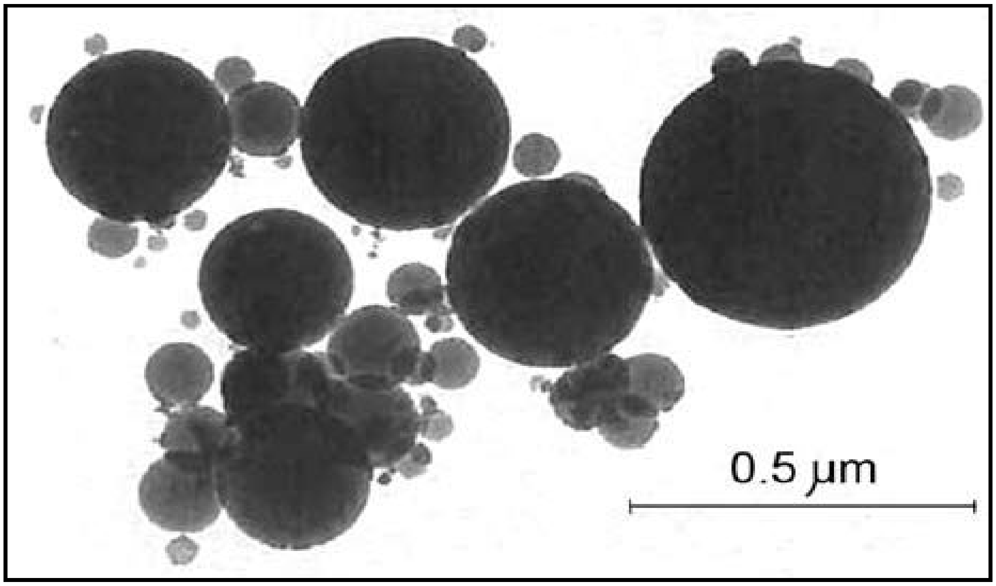

Figure 2.8 – Electron Micrograph of Silica Fume (SF), (A. Dunster, 2009)

2.7.3.1. Environmental Benefit of Silica Fume (SF)

According to D. Corning (2007), SF is aligned with the Eco-Design Principles which can be identified as below;

Principle 1: Minimize waste and consumables
Principle 2: Enable resources conservation by customers and end-use consumers
Principle 8: Create value from waste

In terms of health, environment and social benefits, SF extends construction life, resulting in resource savings and indirectly converting a waste product into a useful, marketable product. SF also increases the compression and abrasion resistance of HPC and protects it from the attack by other chemical elements. In the refractory business, SF increases high temperature strength and thermal conductivity in castables.

SF can also act as a Radon retardant. Radon is a radioactive gas that can be generated from concrete. Its concentration is enhanced in indoor environments and tracheobronchial deposition of radon progeny can lead to lung cancers. Aggregates particularly granites, are known to be the radon source in concrete (K.N. Yu *et.al*. 2000)

For building materials, such as concrete, the variation in moisture will not be very large. The main source of indoor radon for grounded houses is the soil underneath the building, while that for building constructions, it is the concrete used as a building material taking into consideration of the urban and marine environments as it was understood that radon from concrete effectively came from the aggregates mostly in granites.

When aggregates that contained mostly granites were used in concrete, improves the mechanical and chemical properties of concrete. First, due to its extreme fineness, it can effectively set the aggregate-cement paste interface, lower the porosity in the interfacial transition zone, and also effectively fill up the voids between cement grains. Second, because it is highly effective pozzolanic material, micro silica reacts with calcium hydroxide present in the hydrated Portland cement to produce additional calcium silicate hydrates.

As a result, the addition of micro silica is effective in improving the performance of concrete with a considerable improvement in ultimate strength in producing high-strength concrete and reduces the porosity of both the matrix and the aggregate-paste transition zone. The ability for the silica fume particles to lower the porosity of both the matrix and the aggregate-paste transition zone immediately suggests its ability to retard radon emission from the aggregates and radon exhalation from the concrete.

2.7.4. Superplasticizer in HPC

P. Bartow (1992) discovered that superplasticizers are based on two types of polymers, namely the salts of formaldehyde naphthalene sulphonate and formaldehyde melamine sulphonate. Superplasticizer increases the workability of the concrete without undesirable side effects compared to ordinary plasticizers. The fluidifying action of the super-plasticizer is similar to the ordinary plasticizers. It also involves the adsorption of the macromolecules of the polymer onto the grains of cement and changes the electrostatic charges on the particles.

The superplasticizer normally consists of long-chain polymer molecules of different molecular weight with a maximum of up to approximately 30 000. Investigations by M. Basile *et.al* (1999) suggested that within the range of molecular weights of the naphthalene sulphonate condensation products investigated the effectiveness of the admixture was governed by the content of the monomer and the fraction with the lower molecular weight. Increase in the molecular weight of the polymer increases the consistency of the paste measured by ‘slump’.

The amount of polymer absorbed on hydrated cement changes the electrical charges and decreases the air-entrainment up to the molecular weight of about 600. There was very little change for molecular weights greater than 600. The super-plasticizers also generate some air-entrainment which affects consistency of cement paste.

A high dosage of super-plasticizers permits greater water reduction. The amount of reduction can vary from 20% to 25% depending on the circumstances. The increase in workability can be so great that fresh mixes of moderate HPC can be converted into collapsed slump. The increment also shows increase in mobility and compactability. Stability (segregation, bleeding) tends to remain either the same or slightly reduced. Normal doses of the super-plasticizing admixture do not produce an unacceptable bleeding but overdoses and inappropriate grading of aggregates can lead to substantial bleeding. In such cases a layer of laitance forms on the surface of concrete and the mix stiffens very rapidly.

It is possible that the separation of water leaves behind cement particles with absorbed layers of polymer but little free water, thus increasing greatly the viscosity of the cement paste. The rapid stiffening can be so great that fresh concrete mixes will not become plastic even when vibrated with the vibrator apparatus.

The effects of the plasticizing and superplasticising agents are related for concrete of OPC (Type 1) as basis. P. Bartos (1992) have certainly met the purpose of this research in determining the efficiency of OPC Type 1 in HPC. The possibility of the reduction of water binder (W/B) ratio is to offer potential for producing better high quality HPC. A very high dose of ordinary lignosulphonate based plasticizer increases the slump thus increasing the workability of HPC thus producing high compressive strength in early period through the optimum amount of OPC Type 1.

S.P. Shah and S.H. Ahmad (1994) concludes that there is no a prior way of determining the required superplasticizer dosage but in the end, is it done by some sort of trial and error during the mixing procedure.

Basically if the strength is the priority criterion, as mentioned in this research, the lowest water cement ratio (w/c) ratio should be worked on with the highest superplasticizer rate that is to be adjusted during the concrete mixing process. In general, some intermediate position must be found so that the combination of strength can be optimized.

Aberdeen Group (1987) reported that using SF in concrete requires using another innovation in concrete technology: superplasticizers, or high-range water-reducing admixtures. SF has little use without them because its water demand is so high when used alone. This is because SF is about one hundred times finer than OPC. Just as with aggregates, decreasing particle size increases surface area and the water demand. Without a superplasticizer, silica fume dries up the mix. The extra water required to get a reasonable slump would increase the water-cement ratio, thus reducing strength and durability.

SF products are available with and without superplasticizers. If a product without a superplasticizer is used, addition must be made. Recommended admixtures to use must always be referred to SF supplier. If a product contains superplasticizer, it may be necessary to add more of the admixture or a standard water-reducing admixture to get the performance required. Always check with the silica fume supplier to ensure that the admixture required to use is compatible with that in the product.

During the addition of SP, the amount that are used in conventional concrete will be more as there is a huge surface area in the silica fume that must be wetted. For best results, the superplasticizer should be added at the batch plant. A 4- to 6-inch slump should be obtained at the batch plant to ensure adequate mixing of the silica fume into the concrete. If necessary, final slump adjustments can be made at the jobsite by adding more admixture and not water.

2.8. Marine Coastal Environment

W.S. Ha *et.al* (2008) discovered that it has become increasingly apparent that attack by aggressive agents such as chloride ions, leading to corrosion of embedded steel, may cause a structure to deteriorate. Thus, the corrosion of reinforcing steel in concrete structures due to chloride transport in marine environment has received increasing attention in recent years because of its widespread occurrence and the high cost of repair and maintenance.

In tropical countries such as Malaysia, the chloride content in the sea water is increasing due to factors such as climate temperature and the salinity. This phenomenon mainly takes place in jetties and offshore platform structures where corrosion in reinforcing steel happens due to the trend of the wide use of reinforced concrete in semi-permanent structures.

Marine concrete structures are subjected to very severe exposure conditions and their durability is directly related to the quality of concrete used. For these applications, the concrete mix must have low permeability/porosity characteristics and with proper mix compositions have good durability (R.S. Ravindrarajah *et.al*, 2002).

K.P. Mehta and P.C. Aitcin (1990) defined HPC as a material which is not only characterized by high strength but also having high dimensional stability. Dimensional stability means having reduced shrinkage and creep of concrete. This is obtained by limiting the total cement content in concrete and using good quality and well proportioned coarse aggregates. It is strongly suggested that SF is to replace and also to be added. This is to improve in achieving high early strength and long-term durability.

The Silica Fume Association (SFA, 2005) emphasized that the corrosion of reinforcing steel is very significant and costly and cause the concrete deterioration. It doesn’t matter whether the chloride comes from the ocean or from de-icing salts from the sea water the repair and maintenance is very expensive. Thus concrete with SF is used widely in applications where it is exposed to salts from any source. Reduced permeability/porosity prolongs the lifespan of the structure. A schematic process of the corrosion can be observed in Figure 2.9.

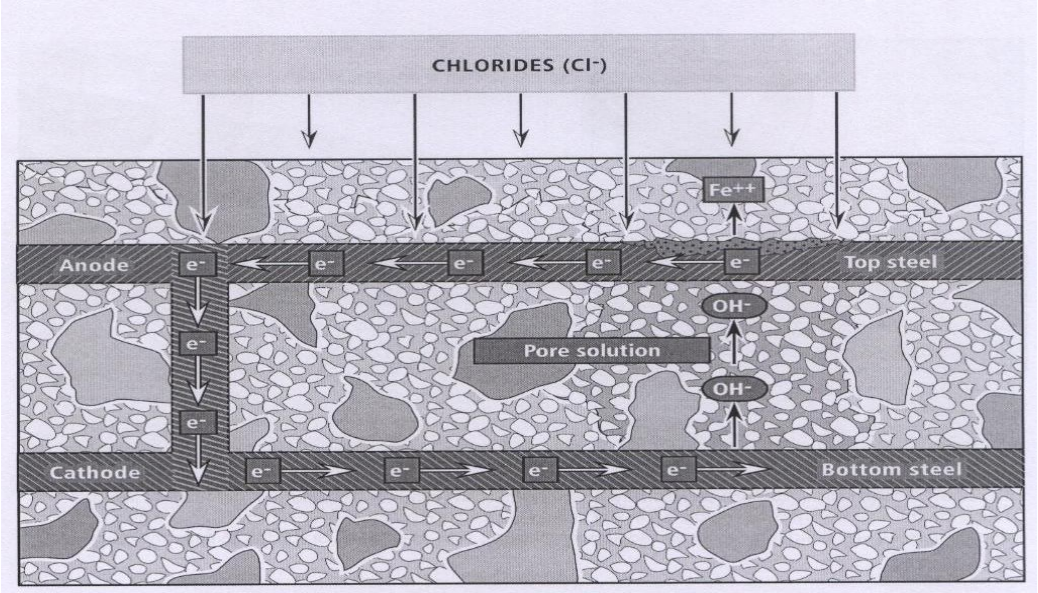

Figure 2.9: Schematic of Corrosion Process in Reinforced Concrete (Silica Fume User’s Manual, Silica Fume Association, SFA, 2005).

W.D. Callister Jr. (2003) mentioned that there are three environmental zones of marine exposure are summarized below.

1. Marine atmosphere, ATM concrete placed 3 m or more above the highest maximum water level. Concrete exposed to marine atmosphere can, if relevant, be subdivided into leeward and windward marine atmosphere.
2. Marine splash, SPL. Concrete placed between 3 m above the highest maximum water level and 3 m below the lowest minimum water level inclusive of waves.
3. Submerged in seawater, SUB. Concrete placed 3 m or more below the lowest minimum water level inclusive of waves.

The illustration of the zones are shown in Figure 2.10.

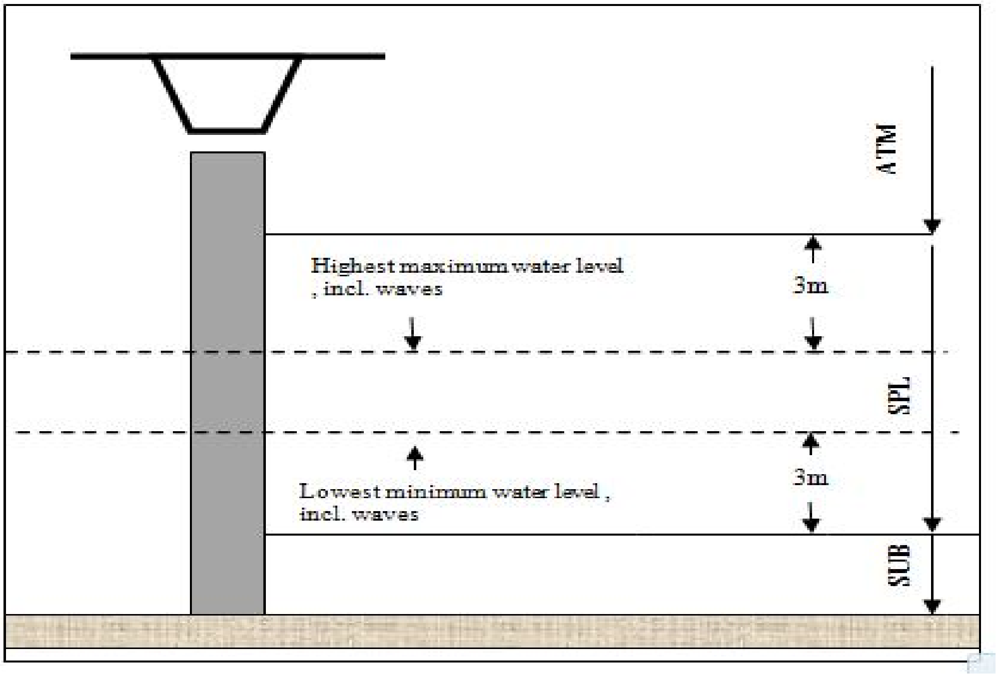

Figure 2.10: Various local marine environments. (W.D. Callister Jr., 2003)

2.8.1. Seawater

Most seawater is fairly uniform in chemical composition, which is characterized by the presence of about 3.5 percent soluble salts by weight. The ionic concentrations of Na+ and Cl− are the highest, typically 11.00 and 19.80 g/liter, respectively.Table 2.2 shows that seawater contains substances which are aggressive against concrete and its steel reinforcement (mainly chloride).

Table 2.2**:** Average Composition of Seawater, (H. Kejin, 1997)

Ions	**Concentration (g/liter)**
Na^+	11.00
K^+	0.40
Mg^{2+}	1.33
Ca^{2+}	0.43
Cl^-	19.80
So_4^{2-}	2.76

The presence of magnesium sulphate in the seawater may influence the diffusibility of the concrete by forming a coating of brucite; Mg $(OH)_2$.The presence of certain gases near the surface of seawater or in seawater plays an important role in the chemical and electrochemical phenomena influencing concrete durability.

Concrete exposed to sea water is susceptible to its corrosive effects. The effects are more pronounced above the tidal zone than where the concrete is permanently submerged. In the submerged zone, magnesium and hydrogen carbonate ions precipitate a layer of brucite, about 30 micrometers thick, on which a slower deposition of calcium carbonate as aragonite occurs. These layers somewhat protect the concrete from other processes, which include attack by magnesium, chloride and sulfate ions and carbonation (B.C. Gerwick, 1986)

Marine growth involving branches and mollusks is frequently found on the surface of porous concrete whose alkalinity has been greatly reduced by leaching. G.C. Hoff (1986) also mentioned that marine growth can also be a problem because it can produce increased leg diameter and displaced volume which would result in increased hydrodynamic loading.

B.C. Gerwick (1986) and G.C. Hoff (1986) also discovered that the additional surface roughness provided by the marine growth will increase the drag coefficient and will enhance the hydrodynamic loadings.

2.8.2. Temperature of Seawater

According to G.C. Hoff (1986), for concrete structures located in a warm climate, the heat may be an aggravating factor because heat is a driving energy source which accelerates both the onset and the progress of deterioration mechanisms. For each increase of 10 degrees Celsius in temperature, the rate of chemical reactions is doubled, which have a considerable impact on the rate of deterioration of concrete structures. The surface temperature of seawater varies widely from a low of $-2^{o}C$ in cold regions to a high of $30^{o}C$ in tropical areas. The temperature of seawater determines the rate of chemical and electrochemical reactions in concrete.

2.9. Concrete for the 21st Century

2.9.1. Concrete’s Carbon Footprint

Many scientists currently think at least 5 percent of humanity's carbon footprint comes from the concrete industry, both from energy use and the carbon dioxide (CO_2), the by-product from the production of cement, one of concrete's principal components.

Several studies have shown that small quantities of CO_2 are later reabsorbed into concrete, even decades after it is placed, when elements of the material combine with CO_2 to form calcite. The Environmental Engineering Committee, EEC (2009) suggests that the re-absorption may extend to products beyond calcite, increasing the total CO_2 removed from the atmosphere and lowering concrete's overall carbon footprint.

Researchers have known for decades that concrete absorbs CO_2 to form calcite (calcium carbonate, $CaCO_3$) during its lifetime, and even longer if the concrete is recycled into new construction--and because concrete is somewhat permeable, the effect extends beyond exposed surfaces. While such changes can be a structural concern for concrete containing rebar, where the change in acidity can damage the metal over many decades, the $CaCO_3$ is actually denser than some of the materials it replaces and can add strength.

"Understanding the complex chemistry of carbon dioxide absorption in concrete may help us develop processes to create the dream concrete of the 21st century. Perhaps this could help us achieve a nearly net-zero carbon footprint. Research relating to climate change is a priority." (H. Haselbach, 1997).

2.9.2. Admixtures of Tomorrow

As reported by P.C. Aitcin (2000), admixtures will be more numerous and will more often be made especially for concrete. They will be more pure, specific and precise in their action. It will be an essential component in concrete making with not a new constraint.

2.9.3. Binders of Tomorrow

The binders of tomorrow will contain less clinker where it will not be having such high C_3S content. They will have to fulfill tighter standard requirements and need to be consistent in their properties because the clinker will be having low cement content. It will also be more compatible with the complex admixtures that will result in more durable and stronger concrete. Thus quality and being inexpensive is very important to be in the consideration of various parties.

2.10. Overall Chapter Summary

The cement production and concrete consumption are increasing rapidly every year. The environmental impact delivered from the concrete industry has been a major debate. New eco- friendly concrete mixes are very high in demand. Research has shown that in order to produce good concrete mixes that caters for the building constructions in the urban and marine environment, ideal concrete mix designs need to be developed, mechanical properties in terms of aggregates need to be understood and demands from the construction industry for high strength building materials need to be fulfilled. Not only that the Earth's ecosystem needs critical consideration and balanced in effort to produce 'Eco-Friendly' concrete mixes; low cement consumption, low cost, low energy consumption and durable in various construction environments. To cater for such vision, in this research, waste chemical known as Silica Fume (SF) was used. It was known as the cement replacement material where it replaces OPC (Type 1) and is ideal in contributing in very high early age strength in design mixes. In addition, superplasticizer is used and is added into mixes through the trial and error method. The performance of the concrete mixes is to be investigated in fresh and hardened conditions. The engineering properties of the concrete mixes includes fresh properties; slump and hardened properties; compressive strength, total porosity, flexural capacity, tensile capability and chloride penetration ability in marine environment.

2.11. Design Development.

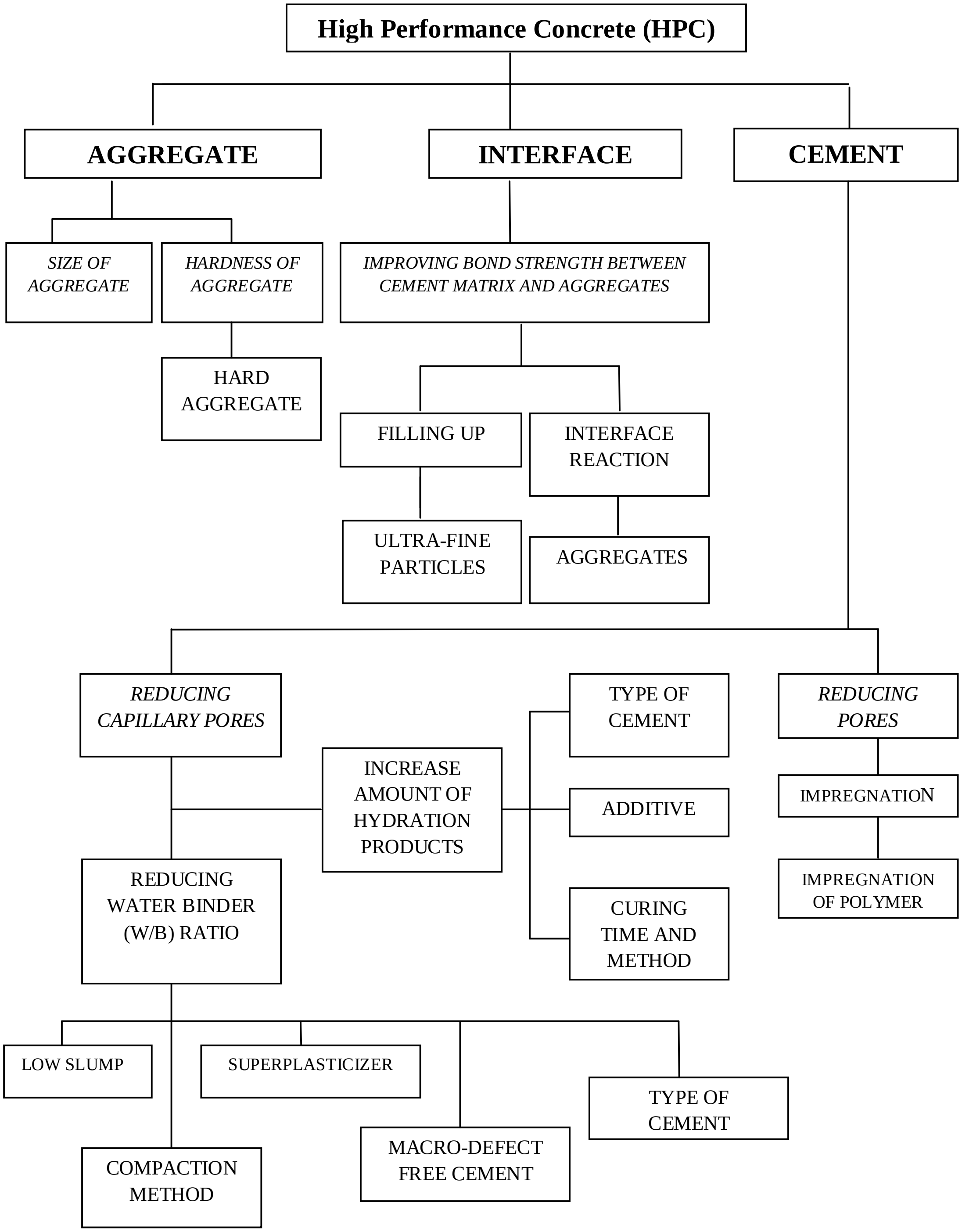

Figure 2.11: Design Development (HPC)