

PERFORMANCE OF PCC CONCRETE IN NaCl ENVIRONMENT- A REVIEW

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Abstract- : Concrete is the most widely used construction material all over the world. Since the past century it is difficult to find out alternate material for construction which is as suitable as that of such material from durability and economic point of view. Cement is the most important constituent of concrete construction. Presently various reasons exist for an increasing interest in “blended cements” that incorporate supplementary cementing materials with Portland clinker; usage of industrial by-products and waste materials (ground granulated blast furnace slag, pulverized fuel ash or fly ash from powder coal fired power stations and some pozzolanic materials) thus saving precious raw materials; reduction of Portland clinker usage in order to reduce CO₂ emission and increased durability in aggressive environment including chloride environment. In this paper, a review of the results of the experimental investigations are reported with the objective to compare the resistance against chloride penetration of different types of PCC concrete being used for concrete structures in chloride containing environment.

Keywords: Blended cement, cementing material, durability, PCC concrete.

1. INTRODUCTION

Concrete generally performs well under loads and have shown robustness as far as the strength is concerned; however, durability is the factor which has to be considered if the structures are to serve for their design life span. Concrete structures exposed to the severe conditions of marine environments can be affected by three types of deterioration mechanisms: 1) physical, such as freezing and thawing, wetting and drying, and abrasion, 2) chemical attack and 3) chloride induced corrosion [1]. Corrosion, one of the main causes of deterioration in concrete structures, initiates due to its exposure to harmful chemicals that may be found in nature such as in some ground waters, industrial effluents and sea waters. The most aggressive chemicals that affect the long term durability of concrete structures are the chlorides and sulfates [2]. The dissolved chloride in waters reacts with chemical constituents of concrete and results in leaching and thus increases the porosity of concrete, and leads to loss of stiffness and strength. In recent years, however, more optimized, high-performance portland cements and combinations of portland cements with pozzolanic materials such as fly ash, slag and silica fume have been introduced for concrete structures in severe environment [3]. Extensive experience shows that blastfurnace slag, fly ash, silica fume based cements generally provide better durability and long-term performance of concrete

in severe environment compared to that of pure portland cement [4]. The blended cements affect both the chemical and physical characteristics of the concrete in such a way that the resistance both against chloride penetration, alkali-aggregate reaction and chemical deterioration may be substantially increased [5]. In countries where pure portland cements have typically been used for concrete structures in chloride containing environments, both extensive and very severe durability problems due to chloride-induced corrosion is found to exist. In order to investigate the resistance against chloride penetration of different types of cements currently being used for concrete structures in chloride-containing environment a concern literature overview has been undertaken and reported. Moreover since the end of 20th century, concern towards preservation of clean environment has initiated research on these material leading to discover pozzolanic material suitable to be used as constituent in concrete production [6]. From that time onwards, efforts taken to produce concrete using these pozzolanic materials has result in several types of concrete such as normal concrete and high strength concrete that exhibits enhanced strength and durability upon utilization of these materials as partial cement replacement material.

2. DIFFERENT TYPES OF BLENDED CEMENTS

The cements which are produced by using supplementary cementing material including various pozzolanic

material like slag or some other material such as lime stone powder or fly ash or silica fume are known as blended cements or composite cements [7]. Blended cements are mainly manufactured as follows:

- a) Fly ash based
- b) Slag based
- c) Silica fume based
- d) Rice husk based

Among these, most widely used pozzolanic material is Slag. Slag based cement consists of an intimate mixture of Portland cement clinker and ground granulated blastfurnace slag.

2.1 Slag – It is a waste product in the manufacture of pig iron. Chemically, slag is a mixture of 42% lime, 30% silica, 19% alumina, 5% magnesia, and 1% alkalis, that is, the same oxides that make up Portland cement but not in the same proportions [8]. Table 1 shows the chemical composition of Slag & OPC.

Table 1: Chemical composition of Slag & OPC.

| SI No. | Constituents | Percentage (%) in (Slag) | Percentage (%) in (OPC) |
|--------|--------------------------------|--------------------------|-------------------------|
| 1. | CaO | 43 | 61-67 |
| 2. | SiO ₂ | 36 | 19-23 |
| 3. | Al ₂ O ₃ | 14 | 2.5-6 |
| 4. | Fe ₂ O ₃ | 1 | 0-6 |
| 5. | MgO | 4 | 0.7-1.5 |
| 6. | SO ₃ | 0.5 | 1.5-4.5 |
| 7. | Free Lime | 1.5 | 2-3 |

2.1.1 Property of Slag Blended Cement:

- The early strength of Slag cement is lower than that of ordinary cement, but their strength is equal at late ages (about 2 months).
- The requirements for fineness and setting time and soundness are similar for those of ordinary cement (although in reality its fineness is higher than that of ordinary cement) [9].
- The workability is higher than that of ordinary cement.
- Heat of hydration is lower that of ordinary cement.

2.2 Fly ash- Fly ash is a by-product of burning pulverized coal in an electrical generating station. Specifically, it is the unburned residue that is carried away from the burning zone in the boiler by the flue gases and then collected by either mechanical or electrostatic separators.

2.2.1 Property of Fly ash cement:

- Workability is improved and water demand is reduced for most fly ashes.
- Long-term strength Increased.
- Resistance to carbonation decreases.
- Permeability & chloride penetration decrease significantly (especially at later age) [10].

2.3 Silica Fume-By product from silicon & ferrosilicon industry.

2.4 Binary cement: The binary cement, e.g. Portland cement blends with slag or fly ash or limestone, has gained great popularity in many countries. However, each kind of binary cement has its own shortfalls, e.g. the addition limestone can reduce the later strength due to its dilution effect, while the reaction of slag is relatively slow in the early ages [11].

2.5 Ternary Cement: To utilize materials more effectively and reduce the cost in construction industry, ternary cement that made with Portland clinkers and other two admixtures may be a better option because it presents several advantages over binary cements. With the development of separate grinding and mixing technology in cement industry, it is becoming more convenient to produce these so-called market-oriented cement. The combination of limestone and slag with Portland cement can help to produce a new cement-based material which has advantage over binary blended cement. An obvious advantage is that limestone contributes to the early strength while slag increases the long-term strength, this leads to an adequate development of strength compared with either slag cement or limestone cement [12].

3. NaCl ENVIRONMENT

The main source of NaCl is the marine environment. According to Osei and Water encyclopedia³, great bodies of water covers about five seventh of the earth's surface. The average salt concentration of sea water is about 3.5% [13] although it varies from sea to sea depending upon geological location. The primary chemical constituents of seawater are the ions of chloride, sodium, magnesium, calcium and potassium. The concentration of major salt constituents of seawater are given in weight % of salt as 78% NaCl, 10.5% MgCl₂, 5% MgSO₄, 3.9% CaSO₄, 2.3% K₂SO₄, and 0.3% KBr [14]. It is evident from above that sodium chloride is by far the predominant salt component of seawater. Sea water has a total salinity of about 3.5% (78% of the dissolved solids being NaCl and 15% MgCl₂ and MgSO₄), and produces a slightly higher early strength but a lower long-term strength [14]. Table 2 shows the salt concentrations of different seas.

Table 2: Average Salt Concentration in Different Seas.

| Seas | Salt concentration (%) |
|------------------------|------------------------|
| Mediterranean | 3.8 |
| Baltic | 0.7 |
| North Sea and Atlantic | 3.5 |
| Black Sea | 1.8 |
| Dead Sea | 5.3 |
| Indian Sea | 3.55 |

3.1 Different zones of Seas:

Depending on the tidal range, nature, extent and mechanism of deterioration process, a reinforced

concrete structure exposed to a marine environment can be divided into different zones like Atmospheric zone, Splash zone, Tidal zone and sub[15] merged zone

3.1.1 Atmospheric Zone:The atmospheric zone is the upper most part extending upwards from the splash zone. In this zone, the air is heavily laden with moisture containing substantial quantities of salts and gases. Due to temperature variation and waveaction, freeze-thaw cycles may occur in some oceans.

3.1.2 Splash Zone: The splashzone extends upwards from the tidal zone and is the most critical area for offshore structures due to erosive effect of continuous salt water spray and wave action in presence of atmospheric O₂ and CO₂.

3.1.3 Tidal Zone:The tidal zone experiences alternate wetting and drying action in seawater and is considered as the second most corrosive area.

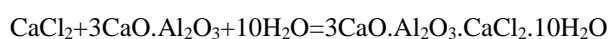
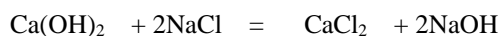
3.1.4 Submerged Zone:The submerged zone is defined as that lying between low water level and above the bed. The hydrostatic pressure increasing with depth can cause rapid penetration of harmful salt ions into the concrete and is regarded as the least corrosive zone due to non-availability of O₂ and CO₂.

3.2 DETERIORATION PROCESS OF CHLORIDE ATTACK

In most of the concrete structures, seawater, soil containing sulfate, fertilizer, industrial effluents, acid rain, and ground water may cause chloride and sulfate attack on reinforced concrete. In aqueous environments, chloride and sulfate ions penetrate into the interior of concrete structure and start chemical reaction. As a result, many complex reactions occur which leads to physical and chemical changes within the concrete. In these consequences, the deterioration of concrete takes place in the form of discrete surface cracks, concrete spalling and corrosion of reinforcement. Permeability is another important property for durability of concrete. Improper mix proportioning may lead to permeable concrete that tends to deteriorate in marine environment. This is due to the fact that the hydration products of Portland cement becomes unstable in certain aggressive salt ion component present in sea water [16]. Complete understanding of the mechanism of salt attack in concrete matrix and embedded rebar is therefore bears great importance for research activities in marine constructions.

Chloride ions may cause adverse effect on hardened concrete in variety of ways.

The process of chloride attack on concrete may be explained by the following series of chemical reaction [17].



According to Metha, MgCl₂ after reacting with Ca(OH)₂ of

hydrated cement forms calcium chloride, which being soluble, gets leached out leading to material loss and weakening[18]. Possible reaction is given below:
 $\text{Ca(OH)}_2 + \text{MgCl}_2 = \text{CaCl}_2 + \text{Mg(OH)}_2$

4. EFFECTS OF USING BLENDED CEMENTS IN CONCRETE

The effect of the addition of blended cement is that the concrete pore structure becomes finer, according to Larbimost importantly of the bulk paste possibly the chloride binding capacity is higher.

4.1 Positive effects: The main positive effects of these additions are:

- slower chloride penetration by 3 to 10 times as compared to Portland cement concrete;
- similar or higher critical chloride content value (which starts corrosion);
- similar or lower corrosion rate (once corrosion has started).

These positive effects have been demonstrated by numerous field and laboratory studies [19].

4.2 Possible negative effects are:

- lower strength at early age.
- more sensitive to poor curing.
- more critical mix design for workability.

The negative effects can be minimized by proper mix design, making mix trials and applying quality control of raw materials and concrete on site. Further developments of composite cements are in progress (like rapid hardening blast furnace slag cement).

5. RESEARCH ON PCC CONCRETE

A lot of independent research has been devoted to blended cement in concrete and its durability over the last 40 years, both in the field and in the laboratory level. Although a large amount of positive experience exists on the use of blended cements, it is not easy to evaluate. There are only a limited number of field surveys of concrete made with blended cements. Wiebenga described 50 years of experience with slag cement in coastal construction in The Netherlands [20]. The amount of corrosion damage in blast furnace slag cement structures was low (one case with much corrosion, one with moderate corrosion, and both after 45 years, out of 48 inspected structures with slag cement). There is relatively little comparative testing under practical conditions. Polder & Larbi described tests of OPC and BFSC concrete after submersion in the North Sea for 16 years [21]. They have shown that chloride penetration is much less in slag cement concrete than in OPC concrete. In a recent monograph, Bijen has reviewed the experience with slag cement concrete. In addition to reinforcement corrosion, other durability aspects are included, such as resistance against carbonation, sea water and salt attack, alkali-silica reaction and freeze-thaw (deicing salt) action. The durability of the slag cement used in the King Fahd Causeway, Saudi Arabia is described in detail. Overall, the durability of slag cement concrete is shown to be excellent. Bamforth and co-workers have published on splash zone exposure of various concrete mixes since 1987, including fly ash, slag and silica fume. The results have shown that chloride penetration is less in blended cement concrete as

compared to various OPC concretes [22]. The British Building Research Establishment has exposed concrete with various fly ash contents to marine environment. Thomas has reported that the critical chloride content decreases with higher fly ash contents in particular over 30%. For fly ash dosages less than or equal to 30%, corrosion initiates later [23]. From these findings and despite the possibly lower chloride threshold, he states that fly ash concrete provides better protection.

Rob B. Polder [24], carried out an investigation on five concrete mixes included three mixes with additional cementing materials and one plain Portland cement, all with river sand and gravel, one with lightweight (sintered fly ash) aggregate and river sand mix. All mixes had a low w/c of 0.43, such as specified by the Dutch concrete technology standard for marine environments. The main compositional features and the mix codes are given in Table 3.

Table 3. Concrete composition.

| Concrete Type | Mix S | Mix L | Mix F | Mix P | Mix B |
|-------------------------------------|----------------------|----------------|------------------------------|-------|-----------------------|
| Cement Type | OPC | OPC | OPC | OPC | BFSC (CEM III/B 42.5) |
| Specific features | 5% silica fume | - | 5% silica fume & 10% fly ash | - | 70% slag |
| Coarse Aggregate | River gravel D 16 mm | Lyttag D 12 mm | River gravel D 16 mm | same | same |
| Sand | Silicious river sand | same | same | same | same |
| Cement Content (kg/m ³) | 340 | 353 | 337 | 339 | 338 |
| Water content (kg/m ³) | 146 | 152 | 145 | 146 | 145 |

For each mix, compressive and tensile strength of three 150 mm cubes and density of six cubes were determined after 28 days storage in a fog room according to the relevant Dutch concrete testing standards.

The results of the mechanical testing and the densities at 28 days are given in Table 4. The mixes S and F have higher strengths (by about 30%) than mix P, apparently due to the addition of silica fume. Regarding strength, mix B is completely equivalent to mix P. Mix L has a

normal compressive strength but a slightly lower tensile strength and expectedly, a lower density. All other mixes had similar densities.

Table 4. Mechanical properties and densities of concrete after 28 days curing in a fog room.

| Concrete type | Mix S | Mix L | Mix F | Mix P | Mix B |
|---|-------|-------|-------|-------|-------|
| Compressive strength (N/mm ²) | 64.1 | 49.1 | 68.2 | 50.4 | 51.2 |
| Tensile strength (N/mm ²) | 5.2 | 3.5 | 4.9 | 3.9 | 3.9 |
| Density (kg/m ³) | 2412 | 2037 | 2413 | 2431 | 2415 |

The fitted chloride penetration profiles after 1.5 years of exposure to salt solution of 30°C are given in Figure 1. The differences between the five mixes are large. The OPC mixes P and L have a relatively high chloride diffusion coefficient. On the other hand, the composite (blended) cement mixes B (blast furnace slag) and F (silica fume and fly ash) have a diffusion coefficient which is about three times lower than for mix P. Only the silica fume mix S, which is a blended mix, does not fit into this pattern.

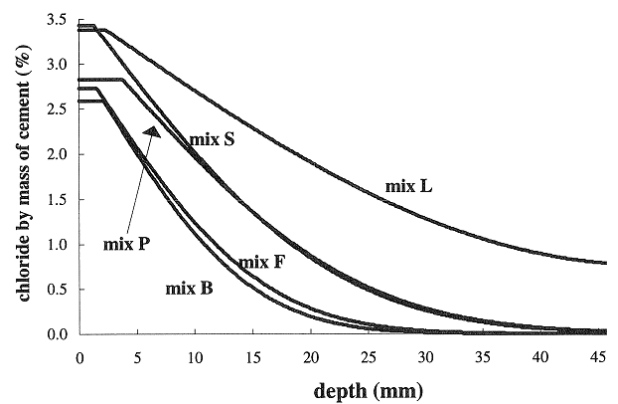


Fig.1: Fitted chloride diffusion profiles for five mixes after 1.5 year submersion in 3.5% NaCl solution at 30°C.

M. Ferreira et.al [19] used six different types of cement for making concrete specimen including two blast furnace slag cements (CEM III/B 42.5 LH HS and CEM III/A 52.5) with 70 % and 53 % slag, respectively, one portland cement blended with 20 % fly ash (CEM IV/A), one high performance portland cement (CEM 1 52.5R LA) and one high performance portland cement blended with silica fume (ArmitBinder 10A). The ArmitBinder type of cement has been specially developed for very aggressive environments, but it is a non-standardized cement. As a reference, an ordinary portland cement of type CEM I 42.5R was also used.

Table 5 shows the cement type & compressive strength of concrete.

Table 5. Cement types & Compressive strength.

| Symbol | Cement type | Compressive strength | |
|--------|---------------------|----------------------|------|
| | | 28d | 180d |
| GGBS1 | CEM III/B42.5 LH HS | 57.1 | 62.9 |
| GGBS2 | CEM III/A 52.5 | 64.0 | 81.2 |
| PFA | CEM IV/A | 53.9 | 61.0 |
| HPC1 | CEM III//A 52.5 | 55.1 | 78.6 |
| HPC2 | ArmitBinder 10A | 78.7 | 88.2 |
| OPC | CEM I 42.5R | 55.1 | 72.3 |

From Table 5 it can be seen that the Armit Binder type of cement (HPC1) gave a considerably higher compressive strength compared to that of the other types of cement. For Concrete Mix I, this cement gave a 28 day strength of 78.7 MPa, while the other cements gave strengths varying from 53.9 to 64.0 MPa.

From Fig. 2 which demonstrates the development of chloride diffusivity for both concrete mixtures, it can be seen that the two slag cements (GGBS1 and GGBS2) gave a distinctly lower chloride diffusivity at an early age compared to all the other types of cement, thus demonstrating a very high early age resistance against chloride penetration. At 180 days, both the high performance portland cements (HPC1) and the ordinary portland cement (OPC) still showed relatively low resistance against chloride penetration.

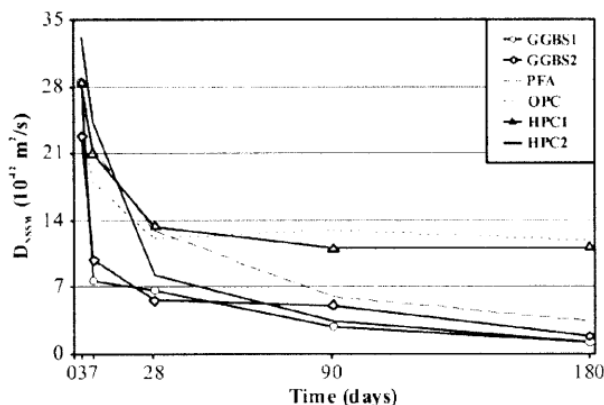
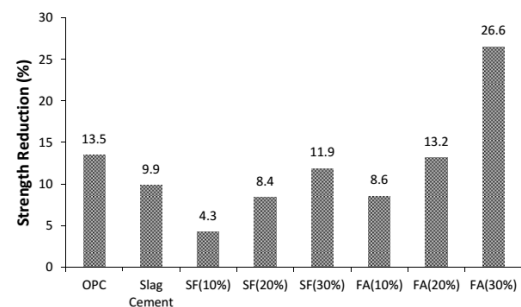


Fig.2. Chloride diffusivity for Concrete.

A.R. Khan [1] aimed to compare the performance of different types of blended cements in marine environment. A testing programme was conducted for this purpose. Mortar samples for OPC, Slag cement, OPC with 10%, 20%, 30% fly ash and silica fume were cast. Compressive strengths of mortar samples were determined at seven (07) and twenty eight (28) days to be used as reference for comparison with compressive strengths after exposure to marine environment. Here strength reduction for all types of cements used in the study is shown in Fig.3. Maximum reduction (26.6%) was found to be in Fly ash (30%) samples while least

reduction (4.3%) was observed in Silica fume (10%) samples. It can be seen from the figure that as the percentage of Silica fume and Fly ash is increasing resistance to chemical attack is decreasing and is more pronounced in Fly ash samples. Performance of Silica fume (10%) and (20%) samples is better than Fly ash (10%) samples as well as Slag samples. It can be noticed that almost all the blended cements have performed better or close to OPC except for Fly ash (30%) samples where maximum deterioration is observed indicating that blended cements are a better option in marine environment.



Type of cement

Figure 3. Percentage change in compressive strength of mortar samples.

6. CONCLUSION

The paper presents the research outcomes of the various experimental investigation carried out at laboratory and field levels. Most of the investigations were based on a limited number of variables and the testing was only based on accelerated test methods, which may not reflect the complete resistance of concrete against chloride penetration. However, based on the previous study results, the following conclusions can be made:

1. Concrete mixes made with blended (composite) cements containing (50- 70%) blast furnace slag or (20-30)% fly ash or fly ash plus 5% silica fume have improved durability properties in marine (NaCl) environment.
2. The development of compressive strength for slag concrete is not significant at the early age of curing. The gain in strength occurs at relatively rapid rate at later ages of curing.
3. Service lives of structure made with blended cements (PCC) can be ensured several times longer than with plain Portland cement (OPC) concrete.
4. The substitution of Portland cement by silica fume in the granulated slag-Portland cement pastes improves the physico-mechanical properties of the hardened cement pastes especially at early ages as well as gives a better resistance of cement to sea water attack.
6. In terms of strength, performance of slag blended cement was found to be better than other cement types including OPC, Silica fume and Fly ash blended.
7. In terms of resistance to aggressive chemical attack, performance of Silica blended cement

was found to be better than other types of cement.

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