# LITERATURE REVIEW:
# FLY ASH USAGE AT MARINE STRUCTURES TO RESIST CHLORIDE AND SULFATE ATTACKS

*Yasin Engin - Civil Engineer, MSc.*
*yasin.engin@gmail.com*

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The optimum cementitious materials for marine structures can be decided if the requirements and mechanisms of environmental effects are well-known. For this project, it is know that the dominant environmental effect is chloride ions attack and second important effect is sulfate attack coming from seawater and soil. Also there are some requirements for fresh concrete temperature and maximum core temperature. Sustainability should not be forgotten. So the main question is this: What type of concrete and cement (or binder) can satisfy all the requirements?

This can be answered by applying to standards and studies in literature. In this part it was aimed to show concrete produced with fly ash can resist chloride penetration and sulfate attack. It has to be told that the best and primary action to resist environmental effects is producing concrete with low water/cement(binder) ratio. In the project, the water/binder ratio should not exceed 0.38 for marine structures.

Durability of marine structures can be achieved by:

1) Low water/binder ratio
2) Proper cement and supplementary cementitious materials(SCMs)
3) Proper curing method

As BS 6349-1(Maritime Work) is reviewed, it can be seen that SRC(sulfate resisting cement) is not a must. In BS 6349-1, cement specifications are given as below:

- Where Portland cement is used, in UK waters, ***a maximum of 10 % $C_3A$***, when determined by the method described in BS 4027, is recommended. ***The $C_3A$ should not be less than 4 % for reinforced concrete in order to reduce the risk of attack of steel reinforcement by chlorides.*** This protection, though, applies mainly to any excess chlorides initially included in the mix, and has only a marginal effect when abundant chlorides are available from external exposure conditions. For this reason, sulfate resisting Portland cements with $C_3A$ less than 4 % are acceptable, provided that the chloride limits for the concrete constituents are properly specified and enforced. ***(It can be said if there is a combined effect (chloride + sulfate), SRC is not a good solution for durability. Because low $C_3A$ content cement does not include enough amount of alumina oxide to react with chloride ions.)***

- ***Alternative approaches, which combine sulfate resistance with chloride resistance, are to use combinations of Portland cement with at least 20 % pulverized-fuel ash (pfa) or 35 % ground granulated blast furnace slag (ggbs).*** Higher levels of replacement (e.g. 30 % pfa or 70 % ggbs can be expected to produce significantly reduced rates of chloride ingress. The choice of replacement proportion is affected by the ruling climatic and site conditions e.g. the lower range of replacement proportions are suitable for slender members and/or colder climatic conditions if early set and strength is required by construction logistics. ***(The best choice for resisting the combined effect is using SCMs like fly ash or slag).***

**The role of fly ash in concrete:**

As shown below, it can be understood that ***the fly ash reacts with the products of hydration and by this reaction more glue, so-called C-S-H gels, can be formed. This means less weak parts and more strong parts are generated in microstructure. Also by using fly ash a better adherence between paste and aggregates and steel bar can be obtained because*** $Ca(OH)_2$ ***mostly locates in interfacial zones.***

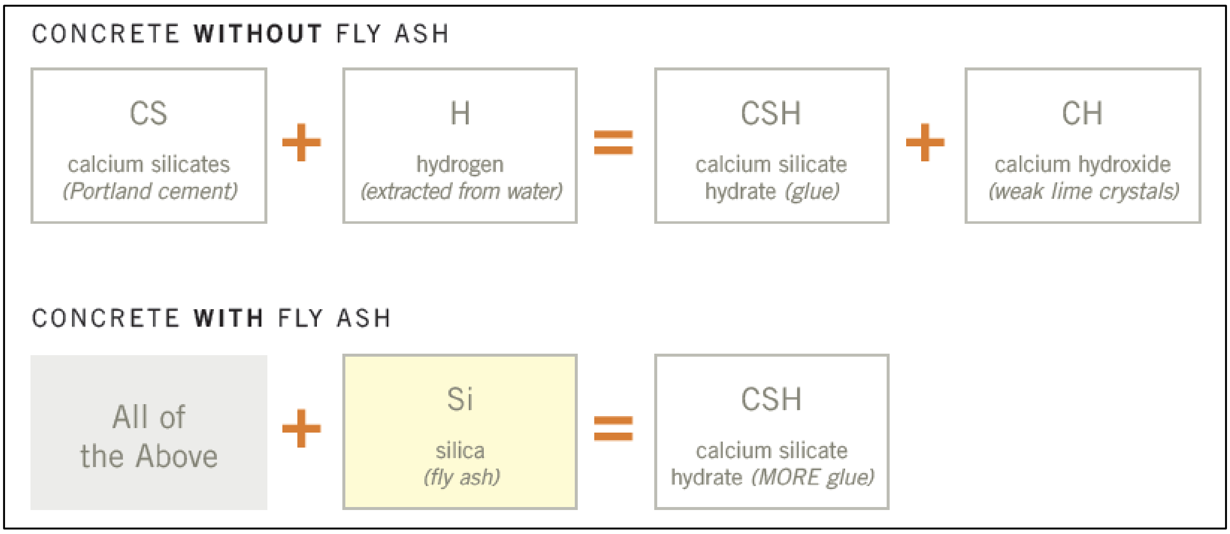



Figure 2.1. – Fly ash reaction with hydration products [13]

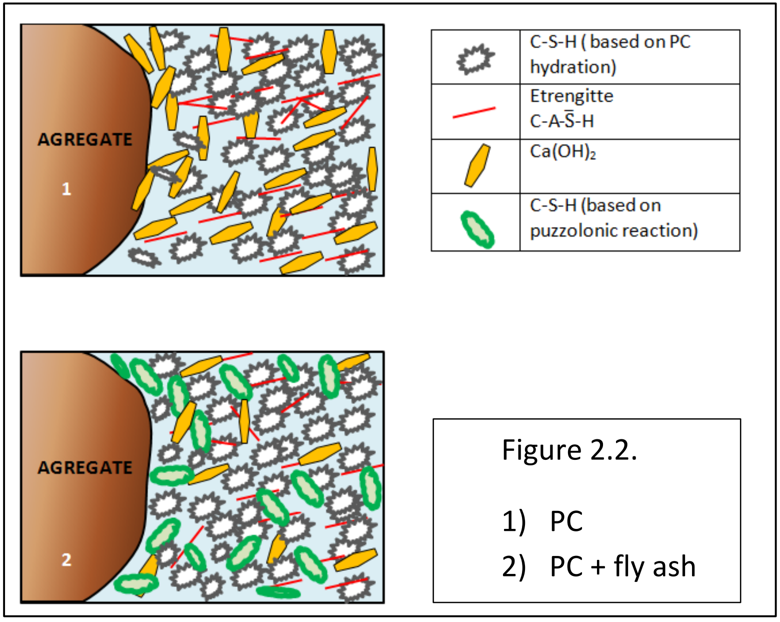



Figure 2.2.

1) PC
2) PC + fly ash

In Figure 2.2, it can be seen that if fly ash is used in concrete production more C-S-H gels come into existence. This can improve the strength of concrete and reduce the permeability. By getting less $Ca(OH)_2$ a better adherence can be obtained.

## *Fly Ash Helps in Five Ways*

1. Through pozzolanic activity, ***fly ash chemically combines with water and calcium hydroxide – forming additional cementitious compounds which result in denser, higher strength concrete***. The calcium hydroxide chemically combined with fly ash is not subject to leaching, thereby helping to maintain high density.

2. The conversion of soluble calcium hydroxide to cementitious compounds decreases bleed channels, capillary channels and void spaces and thereby reduces permeability.

3. Fly ash reduces the amount of calcium hydroxide susceptible to attack by weak acids, salts or other sulfates.

4. Concrete density is also increased by the small, finely divided particles of fly ash which act like micro-aggregates to help fill in the tiniest voids in the concrete.

5. Fly ash provides a dramatic lubricating effect which greatly reduces water demand (2% to 10%). This water reduction reduces internal voids and bleed channels and keeps harmful compounds out of the concrete.

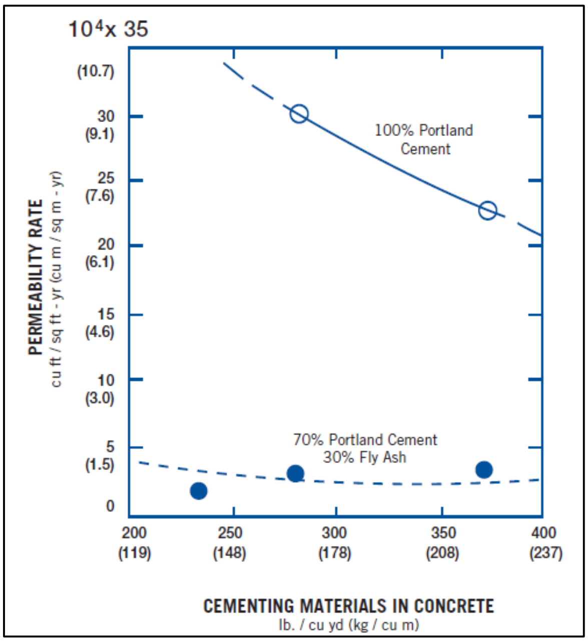



Figure 2.3. - Permeability of concrete with and without fly ash *[15]*

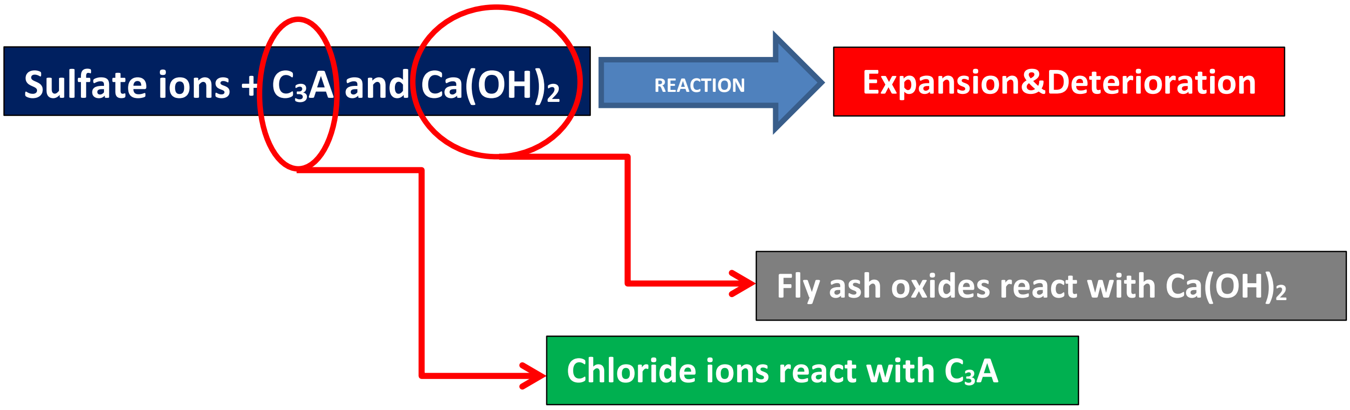
The other benefits of using fly ash in concrete are:

1) Less $CO_2$ emission
2) Less raw materials consumption
3) Lower heat of hydration
4) Lower fresh concrete temperature

**As known there are two chemical reactions involved in sulfate attack on concrete:**

1. Reaction of the sulfate with $Ca(OH)_2$ calcium hydroxide liberated during the hydration of the cement, forming calcium sulfate (gypsum).

2. Reaction of the calcium sulfate with the hydrated $C_3A$ (calcium aluminate) forming calcium sulphoaluminate (ettringite). Both of these reactions result in an increase in the volume of solids which is the cause of expansion and disruption of concretes exposed to sulfate solutions.




***Chloride ions and fly ash oxides react with $C_3A$ and this causes sulfate resistance. Fly ash oxides react with $Ca(OH)_2$ and this causes low permeability, better adherence and sulfate resistance.***

According to BS 6349-1 the limiting values for composition and properties of plain concrete with normal weight aggregates of 20mm nominal maximum size exposed to seawater condition for a required design working life in excess of 50 or 100 years is shown below Table 2.1:

Table 2.1. – Limiting values

| Exposure class and exposure conditions in the UK | | Submerged, intertidal and splash | |
|---|---|---|---|
| Min. strength class cylinder/cube[b,c] Mpa | | C30/37 | C25/30 |
| Max. w/c ratio[b,c,d] | | 0.55 | 0.55 |
| Min. cement content kg/m$^3$ [b,c] | | 320 | 320 |
| Permitted cements | | BS 12[e]<br>BS 4027<br>BS 6588<br>BS 146 | BS 4246<br>BS 6610 |
| Permitted properties for combinations % by mass | ggbs<br>pfa | ≤ 50<br>≤ 35 | 50 <ggbs< 80<br>35 <pfa< 55 |

NOTES
[a] The recommendations in this table are also appropriate for an intended design working life of 100 years.
[b] Minimum cement content depends on maximum aggregate size (see BS 5328). Water–cement ratio limits are the ruling parameters over minimum strength class and minimum cement content.
[c] Where there is difficulty in conforming to the strength recommendations at 28 days, because of the characteristics of the cement type or combination, then, provided that a systematic regime of checking is established to ensure conformity to the free water–cement ratio and cement content recommendations, the 28-day strength recommendations may be relaxed.
[d] Maximum free water–cement ratio, in accordance with BS 5328.
[e] $C_3A$ not greater than 10 %.

***So cement with a ratio of $C_3A$ lower than 10% and fly ash with a substitution ratio of ≤ 35% can be used for marine structure.***

## LITERATURE REVIEW

1. ***Sulfate resisting cement is not suitable where there is danger of chloride attack***. This will cause corrosion of rebar. ***If both chlorides and sulfates are present, Portland cement with $C_3A$ between 5 and 8 should be used [1]***. As $C_3A$ is important to trap chloride ions entering the concrete.

2. ***The sulfate resistance of fly ash and slag is recognized in BS 5328:1997 where it is allowed as an alternative to "low $C_3A$ sulfate resisting cement"[2].***

3. ***The use of Type V cement ($C_3A$<5%) provides adequate protection against sulfate attack but would fail to remove free chloride to any extent for the simple reason that up to 5% $C_3A$*** in the cement is preferentially consumed by 3% gypsum ($CaSO_4.2H_2$) typically added in all Portland cements to regulate the time of set [Mehta 1978, Rasheeduzzafar et al., 1990]. A possible approach to solve this problem of $Cl^-$ and SO4 is to use a high $C_3A$ cement modified with a suitable admixture to provide sulfate resistance equivalent to a low $C_3A$ (Type V). While high $C_3A$ would take care of free $Cl^-$ by complexing it, critical concentration admixture would lower down the $C_3A$ content equivalent to that present in type V cement. Such cement would be simultaneously resistant to sulfate attack and chloride induced reinforcement corrosion. ***Another approach to address chloride - sulfate problem is to formulate high***

***durability performance modified cements by blending Type I cement with pozzolanic materials such as fly ash.*** Results of the studies [Rasheeduzzafar et al.,1992] showed that concretes with fly ash performed 7 to 5 times better than plain Type V ($C_3A$ = 2%) and 3 to 2 times better than Type I ($C_3A$: 14%) cement concrete in terms of time of initiation of corrosion. ***A significant conclusion arrives from this study is that same blended high $C_3A$ cements performed 1.2 to 2 times better in terms of sulfate resistance than the plain Type V ($C_3A$=2%) cement[3].***

4. As described by Neville (1997), three approaches to mitigate sulfate attack are usually recommended. ***One is to use cement with low $C_3A$ content, the source of calcium aluminate hydrates.*** ASTM C 150 addresses the need for sulfate resistance in cement by limiting $C_3A$ content. Another is to reduce the $Ca(OH)_2$ in the hydrated cement paste by using cements that contain SCMs. ***The role of SCMs is to consume $Ca(OH)_2$ in the pozzolanic reaction and to dilute the $C_3A$ content of the system.*** SCMs with low lime contents also help mitigate sulfate attack by reducing the alumina content of the mixture. In addition, concrete be made as dense as possible in order to prevent the ingress of sulfate solutions. ***A combination of SCMs and low water /cementitious materials ratio (to reduce permeability) is regarded as the most useful means of increasing resistance to sulfate attack [4].***

5. In Figure 2.4, ***it can be seen that low water/cement ratio is more beneficial that low $C_3A$ content against sulfate attack.*** There is no guarantee for protection against sulfate attack when low $C_3A$ cement is used.

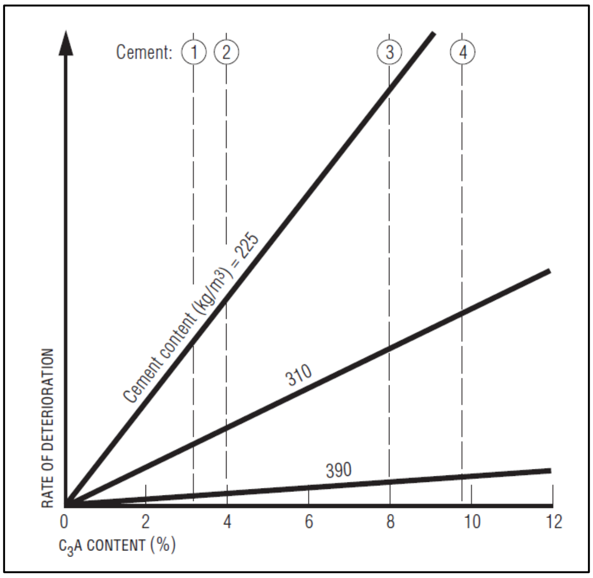



Figure 2.4. - Effect of different Portland cements and cement contents on rate of deterioration of concrete exposed to sulfate-bearing soils (after Verbeck) *[5,18]*

6. ***For marine concrete sulfate-resisting cement should not be used because tricalcium aluminate has high affinity for chloride ions. This is based on the possible reaction of chloride ions and tricalcium aluminate($C_3A$) to form calcium chloroaluminate hydrate as suggested by Prof. Kumar Mehta (1991) and the reduction of which may increase the rate of chloride attack to the concrete marine structure and result in faster corrosion of steel reinforcement in marine structures [6].***

7. ***Tri-calcium aluminate ($C_3A$), a compound found in Portland cement, is able to bind chloride ions forming calcium chloro-aluminate.*** Similarly, tetra calcium alumina ferrite ($C_4AF$) can also reduce the mobility of chloride ions forming calcium chloro ferrite. ***Fly ash also contains oxides of alumina, which are able to bind chloride ions.*** Fly ash concrete can increase the resistance to sulfate attack compared with a CEM I concrete of similar grade. Deterioration due to sulfate penetration results from the expansive pressures originated by the formation of secondary gypsum and ettringite. The beneficial effects of fly ash have been attributed to a reduction of pore size slowing penetration of sulfate ions. Less calcium hydroxide is also available for the formation of gypsum. The smaller pore size of fly ash concrete reduces the volume of ettringite that may be formed. One of the major constituents of cement that is prone to sulfate attack, tricalcium aluminate ($C_3A$), is diluted since a proportion of it will have reacted with the sulfates within the fly ash at an early age. Building Research Establishment Special Digest 1 (BRE, 1991) discusses the factors responsible for sulfate and acid attack on concrete below ground and recommends the type of cement and quality of curing to provide resistance. Concrete made with combinations of Portland cement and BS 3892: Part 1 PFA, where the fly ash content lies between 25 per cent and 40 per cent has good sulfate resisting properties ***[19]***.

8. The results of the study indicate that unreinforced concrete made with ASTM Type I normal Portland cement with $C_3A$ and $SO_3$ contents in the range of 8.5 to 11.8% and 3.9 to 4.6%, respectively, performed satisfactorily when exposed in seawater at mid-tide level. The performance of the concrete made with Type I cement is at least equal to or better than that of concrete made with ASTM Types II and V cements with $C_3A$ and $SO_3$ contents in the ranges of 2.0 to 5.0% and 1.9 to 3.0%, respectively. If significant surface deterioration is to be

avoided, the concrete should have a minimum cement content of 300 kg/m$^3$ and a water-to-cement ratio of 0.50 or less ***[20]***.

9. In Figure 2.5, ***the least expansion resulted from sulfate attack was seen when 20% fly ash was used.*** The difference between FA1 and FA2 is CaO content. FA1 is Class F type fly ash. ***It can be said that Class F fly ash is better for sulfate resistance.***

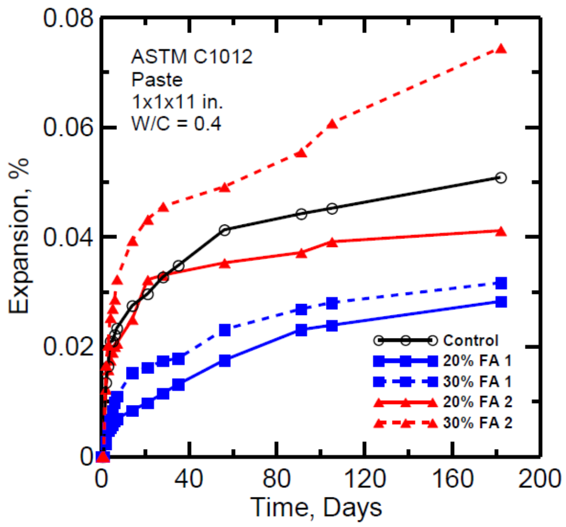



Figure 2.5. – Expansion due to different mixes *[7]*

10. In seawater, chlorides usually pose a greater threat to steel in concrete than sulfates do to concrete as calcium sulphoaluminate or ettringite (the expansive reaction product of sulfate and tricalcium aluminate in the cement) is more soluble in the presence of chloride and hence does not cause the disruptive expansion. ***Portland cement reacts with sodium chloride to form chloroaluminates or Friedel's salt (*** $3\,CaO\,.\,Al_2O_3\,.\,CaCl_2\,.10\,H_2O$ ***), thus immobilizing the chloride and reducing the free chloride ions available to depassivate the steel [8].***

11. In Figure 2.6, ***it can be seen that when 28-30% fly ash is used in concrete there can be a better improvement for chloride permeability.***

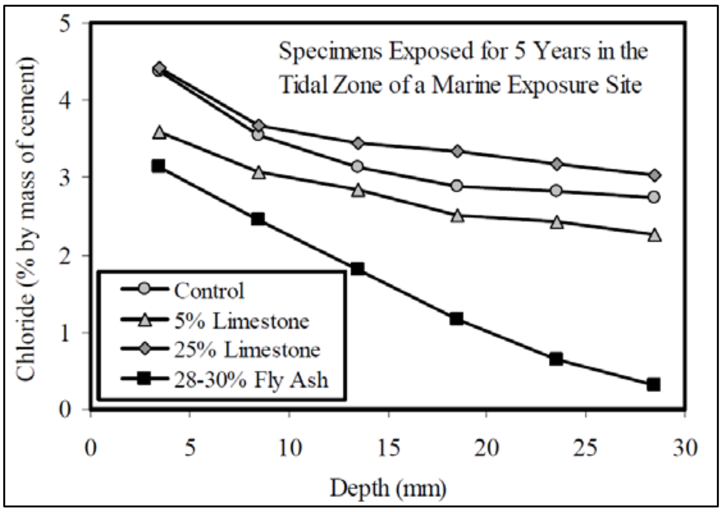



Figure 2.6. – Chloride content in concrete due to different mixes [10]

12. According to Figure 2.7, ***it can be said that low $C_3A$ cement cannot trap chloride diffusion. Fly ash with higher $C_3A$ cement can retard corrosion initiation time.***

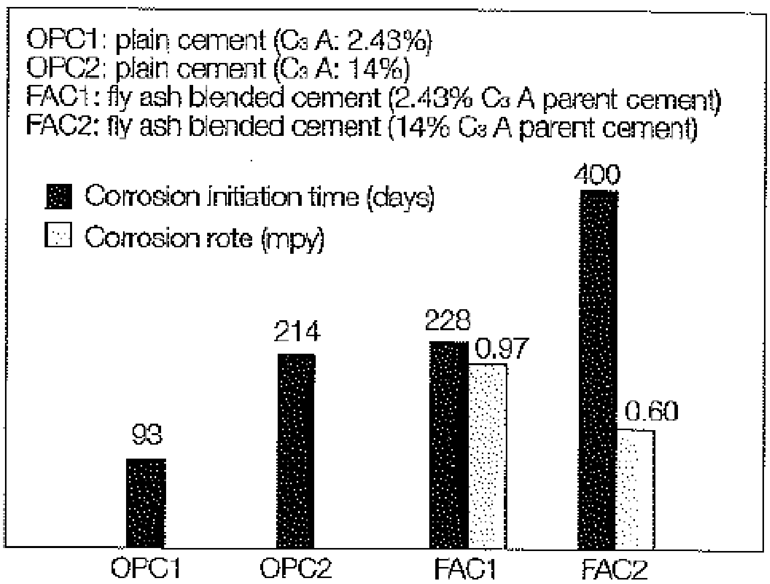



Figure 2.7. – Corrosion time due to different mixes [11]

13. A comparative study on the sulfate resistance of concrete made with an ASTM Type V cement (high sulfate resisting cement), and with cements incorporating slag or fly ash was commenced at CANMET in 1993. ***Concrete specimens of similar w/cm after 28 days moist curing were immersed in 5 % Na2SO4. The condition after 10 years showed no significant length change. The high volume fly ash concrete visually looked better than the slag and the control concrete. They think this is due to low permeability.***

**Fly ash reduces sulfate deterioration in three important ways:**

1) ***Fly ash chemically binds the CH in calcium silicate hydrate (CSH) rendering it unavailable for sulfate reaction to gypsum (calcium sulfate) and ettringite (calcium sulfoaluminate).***
2) ***Fly ash reduced the concrete permeability, keeping sulfate from penetrating concrete.***
3) ***By replacing a part of the cement content with fly ash, the amount of reactive aluminates is reduced, and the reaction with sulfate to ettringite is reduced.***

United States Bureau of Reclamation (USBR) show that properly proportioned concrete utilizing up to ***35 % Class F fly ash will withstand sulfate attack far better than conventional Portland cement***. Plain and fly ash concrete mixes using Type I (normal Portland cement), Type II (moderate sulfate resisting and cement with heat) and Type V (high sulfate resisting cement) were tested in sodium s sulfate under standardized conditions. In all instances, Class F fly ash concrete was better than conventional Portland cement concrete. The test demonstrated that Type II cement with Class F fly ash was more resistant to sulfate attack than Type V cement alone. ***The Portland Cement Association (PCA) reports the use of Class F fly ash improves sulfate resistance, while Class C fly ash is less effective and may even accelerate deterioration.*** They also mention that further United States Bureau of Reclamation (USBR) work correlates the chemistry of a given fly ash with its ability to resist sulfate attack through a mathematical equation called the R-factor formulated below:

$$R = \frac{CaO - 5}{Fe2O3}$$

The limits established by the USBR requiring progressively lower values as sulfate attack severity increases are as follow:

Table 2.2.

| R Limits | Sulfate resistance |
|---|---|
| <0.75 | Greatly improved |
| 0.75-1.5 | Moderately improved |
| 1.5-3 | No significant change |
| >3.0 | Reduced |

***ACI reports that fly ash with CaO content less than 15 % will generally improve sulfate resistance [12]***.

***Important Note:* *The fly ash which can be used at the project is Class F. CaO content of fly ash is below 20% as seen in Table 2.3.***

Table 2.3. – Properties of fly ash that can be used for the project

| Analysis | Unit | Method | Limits | Results |
|---|---|---|---|---|
| LOI | % | EN 196-2 | < 5 | 2 |
| Fineness | % | EN 451-2 | < 40 (over 45 μ) | 21,1 |
| Activity Index (28-day/90-day) | % | EN 196-1 | > 70 / > 80 | 76,7 / 93,5[a] |
| Free CaO | % | EN 451-1 | < 2,6 | < 0,1 |
| $SiO_2 + Al_2O_3 + Fe_2O_3$ | % | EN 196-2 | > 65 | 90,47 |
| Total Alkali Content | % | EN 196-2 | < 5,5 | 2,484 |
| Reactive $SiO_2$ | % | EN 197-1 | > 22 | 62,4 |
| $Cl^-$ | % | EN 196-2 | < 0,1 | 0,01 |
| MgO | % | EN 196-2 | < 4,5 | 1,7 |
| Density | $kg/m^3$ | EN 196-6 | 2,015 < value < 2,465 | 2,2 |
| Setting Time(initial/final) | min. | EN 196-3 | | 205 / 255 (fly ash)<br>145 / 220 (cement) |
| Reactive CaO | % | EN 197-1 | < 11 | 2,04 |

14. In Figure 2.8, MS means marine structure. I refers to Type I cement, V refers to Type V($C_3A$<5%) and IF refers to Type I cement + 20% fly ash. ***It can be seen that the length change is lower at MSIF. It is a clear proof that concrete with fly ash can resist sulfate ions better than concrete produced with low $C_3A$ content cement.***

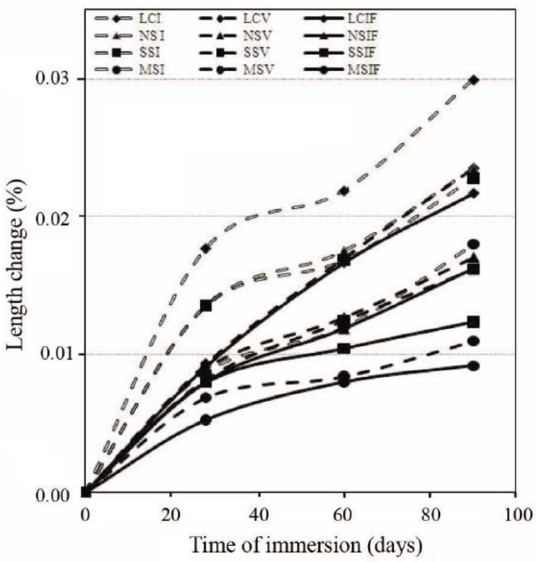



Figure 2.8. – Expansion resulted from sulfate attack *[14]*

***The chloride attack resistance increases with the use of fly ash because of the pore structure tightening and water permeability reduction resulting from the pozzolanic reaction. The chloride attack resistance of the specimen that used Type V cement is the weakest because it contains a smaller amount of $C_3A$, which is related to the production of Friedel's salt in comparison with Type I cement. In addition, the chloride penetration speed decreases as the strength increases regardless of cement type or fly ash replacement, because the microstructure becomes denser and deters the chloride ion penetration [13]***.

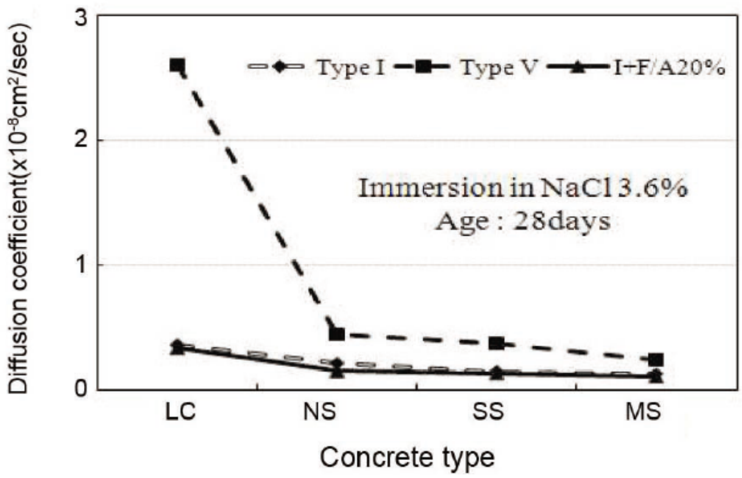



Figure 2.9. – Chloride diffusion *[14]*

15. The use of Type V cement (high sulfate resisting cement $C_3A<5\%$) , which is low in $C_3A$ (tricalcium aluminate), as a replacement for a higher $C_3A$ Type I cement, greatly increases sulfate resistance. ***However, the availability of Type V can be a problem. In addition, chloride resistance may be sacrificed when Type V cement is used. $C_3A$ chemically binds chloride ions leaving fewer ions available to attack embedded steel. In a concrete produced with Type V cement, less $C_3A$ is present to bind chloride ions than in Type I cement, and the potential for corrosion of reinforcing steel is increased [16]***.

16. According to ACI 201.2R-08(Guide to Durable Concrete):

**Clause 6.4.2.** - The presence of chloride ions, however, alters the extent and nature of the chemical reaction so that less expansion is produced by a cement of a given $C_3A$ content than would be expected of the same cement in a freshwater exposure where the water has the same sulfate ion content. ***Concrete made with Portland cement having $C_3A$ contents as high as 10% may have proven satisfactory for continuous immersion in seawater, provided that the permeability of the concrete is low*** (Browne 1980). The U.S. Army Corps of Engineers (1984) permits and the Portland Cement Concrete Association recommends up to 10% calculated $C_3A$ for concrete that will be permanently submerged in seawater if the w/cm is kept below 0.45 by mass.

**Clause 7.4.1.** - ***The presence of $C_3A$ in the cement appears to be beneficial to the reduction of chloride ingress.*** This was first established by Verbeck (1968) and has since been confirmed by several other researchers, such as Rasheeduzzafar et al. (1992). The main conclusion of this work is that the use of very low $C_3A$ (Type V) cements in a strong chloride environment is generally not recommended.

17. According to ACI 357R-84 (Guide for the Design and Construction of Fixed Offshore Concrete Structures):

**Clause 2.5.2.** - ***The tricalcium aluminate content ($C_3A$) should not be less than 4 percent to provide protection for the reinforcement. Based on past experience, the maximum tricalcium aluminate content should generally be 10 percent to obtain concrete that is resistant to sulfate attack. The above limits apply to all exposure zones.***

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