Degradation of Concrete Structures and Protective Measures

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Abstract— **Degradation of Concrete represents a topic of increasing significance, owing to the spread of damages of concrete structures in both urban and industrial areas. Type of cement being used in the structure is an important factor that affecting performance of cement constituents in an aggressive environment. This was adopted to examine cement based materials and impact of chemicals on cementization i.e., Aggressive action of CO_2, Attack by strong acids, Action of ammonia, Action of sulphates, Attack by strong alkalis, Bacterial corrosion with H_2S. The goal of this study is to find various possibilities of protecting cement based materials.**

Keywords—Concrete-structures ; Aggressive-action ; deterioration; Protective measures;

INTRODUCTION

Durability is an important engineering property of concrete, which determines the service life of concrete structures significantly. Due to the interactions of concrete with external influences, the mechanical and physical properties of concrete may be threatened and lost. Among the threatening factors like freezing and thawing, abrasion, corrosion of steel, chemical attack may also deteriorate concrete within time.ACI Committee Report 201 (2001) has classified chemical attacks into several types that include; acidic attack, alkali attack, carbonation, chloride attack, leaching and sulfate attack. It can be accepted as a general rule that acids are deleterious to concrete.

Acid attack generally occurs where the calcium hydroxide is attacked vigorously, although all the Portland cement compounds are susceptible to degradation. Acidic solutions both mineral (such as sulphuric, hydrochloric, nitric, and phosphoric acids) and organic (such as lactic, acetic, formic, tannic, and other acids produced in decomposing silage) are about the most aggressive agents to concrete. Depending on the type of acid, the attack can be mainly an acid attack, or a combination of acid followed by a salt attack. It cannot cause deterioration in the interior of the specimen without the cement paste on the outer portion being completely destroyed. The rate of penetration is thus inversely proportional to the quantity of acid neutralizing material, such as the calcium hydroxide, C-S-H gel, and limestone aggregates. In practice,

the degree of attack increases as acidity increases; attack occurs at values of pH below about 6.5, a pH of less than 4.5 leading to severe attack. The rate of attack also depends on the ability of hydrogen ions to be diffused through the cement gel (C-S-H) after calcium hydroxide (Ca $(OH)_2$) has been dissolved and leached out. Concretes made of Portland cement (OPC) are highly alkaline with pH values normally above 12.5 and are not easily attacked by acidic solutions. As the pH of the solution decreases the equilibrium in the cement matrix is being disturbed and the hydrated cement compounds are essentially altered by hydrolytic decomposition which leads to the severe degradation of the technical properties of the material. At pH values lower than 12.5 portlandite is the first constituent starting dissolution, if pH decreases to values lower than stability limits of cement hydrates, then the corresponding hydrate loses calcium and decomposes to amorphous hydrogel. The final reaction products of acid attack are the corresponding calcium salts of the acid as well as hydrogels of silicium, aluminum, and ferric oxides. Therefore, a strong aid having a high degree of dissociation may achieve very low values of pH, due to relatively small quantities of acid in the solution. The weak acids owing to their low degree if dissociation, achieve higher pH values.
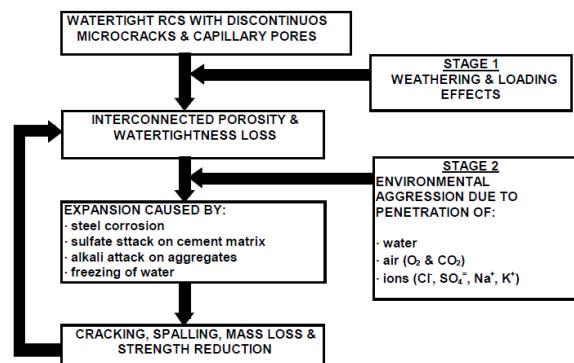

Fig: 1 A holistic model of concrete deterioration from environmental effects
Adapted from Mehta (1, 2).

2.0 Impact of Chemicals on Concrete Structures:

Chemical degradation of cement based structures can be caused in several ways:

Materials which are unfriendly to Concrete structures are presented in **Table-1:**

Table-1: Materials which are unfriendly to Concrete structures

Chemical substance	Effect on concrete
Acetic acid	Disintegrates slowly
Carbon dioxide	Harmless to mature concrete, but may dissolve in water to produce carbonic acid, which see. When freshly placed concrete is exposed to sufficient concentration of CO2 it will harden with chalky, dusting surface
Carbonic acid	Highly corrosive to lean, permeable concrete; causes slow disintegration of better concretes
Hydrobromic acid	Continued contact with solution destroys concrete weak solutions attack slowly
Hydrochloric acid	Continued contact with solution destroys concrete Weak solutions attack slowly
Hydrogen sulphide	Not harmful, except in moist, oxidizing environments where it produces sulfurous acid, causing slow disintegration
Magnesium sulfate	Solutions of 0.5% or more strongly attack concretes of inadequate sulfate resistance, producing disruptive expansion
Nitric acid	Continued contact with solution destroys concrete weak solutions attack slowly
Sewage	Usually not harmful to good concrete. If hydrogen sulfide gas is present and exposed to air, sulfuric acid may form and attack the concrete
Sodium hydroxide	Not harmful at ordinary concentrations except where concrete is made with alkali reactive aggregates. Above about 20% attacks concrete.
Sodium sulfate	Solutions of 0.5% or more strongly attack concrete of inadequate sulfate resistance, causing disruptive expansion
Sulfur dioxide	Dry gas has no effect on dry concrete. Combined with moisture, it forms acids which cause etching and long-term deterioration
Sulfuric acid	Continued contact with solution destroys concrete weak solutions attack slowly

2.1 Physical attack on concrete structures:

Soluble salts may be drawn into a sufficiently permeable concrete by capillary action and crystallize within the pore structure when evaporation occurs. Mechanical or thermal stress or drying shrinkage can all cause concrete to crack. Thermal stresses can cause damage at low temperatures even if the pores contain little or no water. Surface damage from abrasion depends markedly on w/c ratio and on the quality of the surface layer of the concrete at high w/c ratios it depends also on properties of the aggregate. Concrete may be damaged by frost, especially by repeated cycles of freezing and thawing .Damage usually begins with flaking at the surface and gradually extends inwards, through deep cracks may occur. Damage associated with freezing does not occur unless a sufficient quantity of water is present in the pores, and is minimal in dense concrete of low w/c ratio and low permeability. It can be much reduced by air entrainment. It is especially likely if freezing occurs before adequate hardening has occurred.

2.2 Aggressive Action of Gases:

2.2.1 Aggressive action of CO_2:

Structures are attacked by Carbon dioxide in the presence of soft water or when excess CO_2 goes above 15 mg/l.

However, there is a higher residue of lime alkalinity in the pores of the concrete and this allows the precipitation of a deposit of $CaCO_3$ and other salts, which temporarily slows down the destruction of the concrete by such water.This destruction can be tolerated if the calcium bicarbonate alkalinity of the water exceeds 5 to 6^0 TAC and pH is over 6.5, which is around $CaCO_3/ CO_2$ equilibrium.

2.2.2 Action by NH_3 :

Ammonia in waste water can contribute to destruction of concrete in two ways:

- ❖ By the development of nitrifying and therefore acidifying reactions, which can however develop only in an aerobic medium, as in the atmospheric coolers for example;
- ❖ By the release of ammonia displaced by the lime which accelerates solubilization of the latter and causes rapid degradation of cement.

The same process can be started by the salts of magnesium or any other base weaker than lime.

Excessive concentration of NH_4^+ and Mg^{+2} should be avoided therefore, particularly when sulphates are also present.

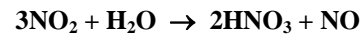### 2.2.3 Bacterial corrosion with H_2S:

This kind of corrosion occurs in sewers. The principle of corrosion in an anaerobic medium has already been described, but whereas the process follows and extendeds previous chemical corrosion in cooling systems, it is generally the result of the anaerobic fermentation of deposited solids in the case of domestic sewage or strong effluent.

There are two stages:

- ❖ Formation and release of H_2S
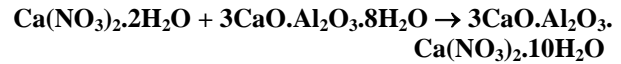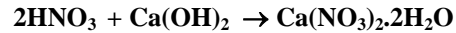- ❖ Oxidation of H_2S in the presence of water to form H_2SO_4.

These reactions are speeded up when pH falls below 6 as the temperature of the water rises.

In a sewer, the attack takes place above the liquid surface because of the deaeration and condensation of the water. Virtually the only way of preventing corrosion of this type is to maintain a high flow rate, after prior settling or preaeration of the water and to avoid turbulence and deaeration in the pipes.
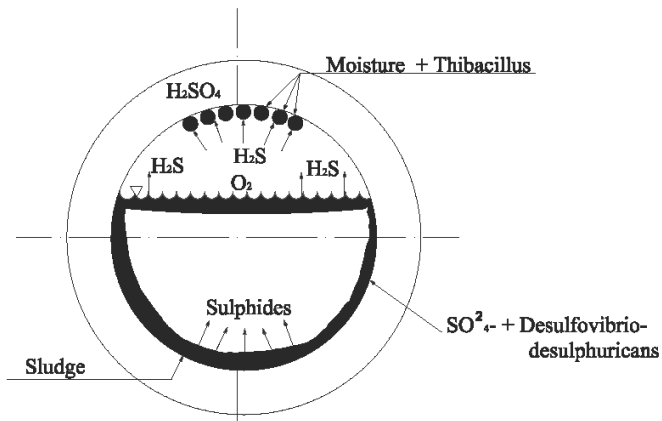
Attack mechanism by hydrogen sulphide on a sewer pipe

Fig: 2 Representation of the Bacterial Corrosion with H_2S
2.3 Aggressive action of acidic solutions:

2.3.1 Sulphuric acid attack:

Sulphuric acid attack causes extensive formation of gypsum in the regions close to the surfaces, and tends to cause disintegrating mechanical stresses which ultimately lead to spalling and exposure of the fresh surface. Owing to the poor penetration of sulphuric acid, the chemical changes of the cement matrix are restricted to the regions close to the surface. However, in some cases it is observed that deterioration process occurs accompanied by the scaling and softening of the matrix due to the early decomposition of calcium hydroxide and the subsequent formation of large amount of gypsum.

The chemical reactions involved in sulphuric acid attack on cement based materials can be given as follows:
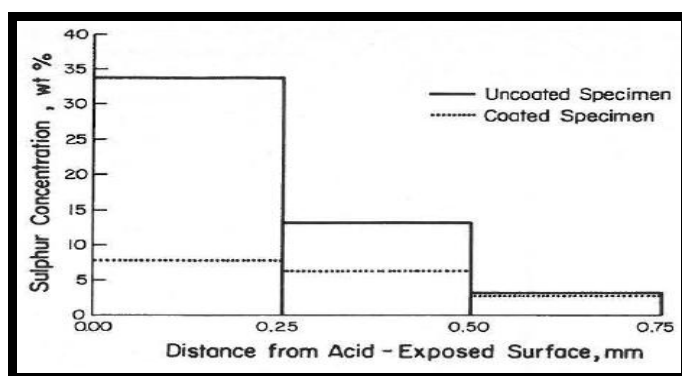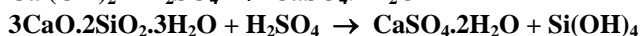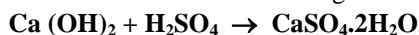
$$Ca\,(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$$
$$3CaO.2SiO_2.3H_2O + H_2SO_4 \rightarrow CaSO_4.2H_2O + Si(OH)_4$$

Fig: 3 Sulphur content versus distance from acid-exposed surface
Adopted from: Emmanuel etal, 1989

2.3.2 Nitric acid attack:

Nitric acid usually occurs in chemical plants producing explosives, artificial manure and similar products. Nitric acid can be formed from the compounds and radicals of nitrates in the presence of water
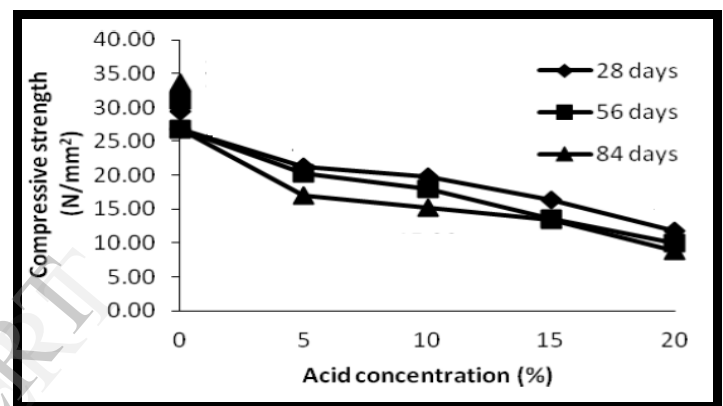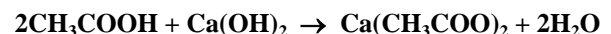
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Though HNO_3 is not as strong as H_2SO_4, its effect on concrete at brief exposure is more destructive since it transforms CH into highly soluble calcium nitrate salt and low soluble calcium nitro-aluminate hydrate

Nitric acid attack can be represented by the following equations;

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2.2H_2O$$
$$Ca(NO_3)_2.2H_2O + 3CaO.Al_2O_3.8H_2O \rightarrow 3CaO.Al_2O_3.Ca(NO_3)_2.10H_2O$$

Nitric acid attack is a typical acidic corrosion for shrinkage of the corroded layer due to leaching of highly soluble calcium nitrate. Such volume contractions of the corroded layer, especially for the case of nitric acid, can result in the formation of visually observable cracks across the corroded layer. The presence of cracks igniate the corrosion due to heavy mobilization of acid which gives birth to deterioration.

Fig:4 Variation of compressive strength with acid concentration (mix ratio 1:1.5:3, W/C = 0.65)
Adopted from: Olusola etal, 2012

2.3.3 Acetic acid attack:

Concrete use in agricultural applications may be attacked by the silage effluents containing mainly acetic and lactic acid.
Acetic acid reacts with cement hydration products to form calcium acetate

$$2CH_3COOH + Ca(OH)_2 \rightarrow Ca(CH_3COO)_2 + 2H_2O$$
$$2CH_3COOH + C\text{-}S\text{-}H \rightarrow SiO_2 + Ca(CH_3COO)_2 + 2H_2O$$

Attack by Acetic acid resembles the process of corrosion in nitric acid. However the growth of the corroded layer in solutions of acetic acid is relatively slower than that in the same concentrations of nitric acid solution. The chemical composition of the corroded layer is different from that in nitric acid solution of the same concentration due to higher pH values of the acetic acid solution, and due to its buffering effect in corroded layer. In lower concentrations of both acetic and nitric acid solutions, e.g. 0.025 mol l^{-1}, results in the formation of an additional zone, called as core-layer, which is relatively hard and located behind the corroded layer. Chemical compositions of the core layers in both acetic and nitric acid attacks are similar Core-layer originates due to portlandite dissolution in unaffected part of the cement paste and diffusion of Ca^{2+} and OH^- ions towards corrosion zone where they meet the acid diffusing from the opposite direction.

Formation of the core layer is noticeable only when the concentration of acid is low because in such a case the rate of diffusion of H^+ ions from the acidic solution is high enough to dissolve portlandite, but not sufficiently high to decalcify the other hydrates.
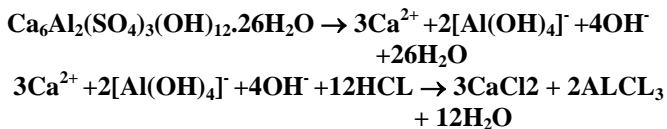
2.3.4 Hydrochloric acid attack:

The chemicals formed as the products of reaction between hydrochloric acid and hydrated cement phases are some soluble salts and some insoluble salts.Soluble salts, mostly with calcium, are subsequently leached out, whereas insoluble salts along with amorphous hydrogels, remain in the corroded layer. Besides dissolution, the interaction between hydrogels may also result in the formation of some Fe-Si, Al-Si, Ca-Al-Si complexes which appear to be stable in pH range above 3.5.

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$
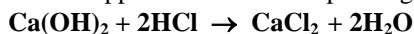
The reaction essentially causes leaching of $Ca(OH)_2$ from the set cement.

After leaching out of $Ca(OH)_2$, C-S-H and ettringite start to decompose, with release of Ca^{2+} to counter act the loss in $Ca(OH)_2$ and the set cement starts to disintegrate accelerating the dissolution.

$$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O \rightarrow 3Ca^{2+} +2[Al(OH)_4]^- +4OH^- +26H_2O$$

$$3Ca^{2+} +2[Al(OH)_4]^- +4OH^- +12HCL \rightarrow 3CaCl2 + 2ALCL_3 + 12H_2O$$

There are few indications through experiments about the formation of Friedel's salt, $C_3A.CaCl_2.10H_2O$, by the action of $CaCl_2$, formed due to reaction of HCL with CH and C_3A

2.3.5 Carbonic acid attack:

Carbonic acid attack usually occurs in the case of buried concrete structures exposed to acidic ground water for a long time.Atmospheric carbon dioxide absorbed by rain enters ground water as carbonic acid

❖ Factors affecting the rate of carbonic acid attack are:
- o Quality of concrete
- o Concentration of aggressive carbon dioxide
- o External exposure conditions

When concrete is exposed to carbonic acid, a reaction producing carbonates take place which is accompanied by shrinkage.Limited carbonation of surface layer of concrete is known to seal the pores by forming calcium carbonate, which reduces the permeability and increases the strength of the carbonated layer.

However, continued carbonation may cause a reduction in alkalinity of the cement paste which can be a serious problem not only in de-passivation and corrosion of steel bars but also in dissolution of cement hydrates.

2.4 Action of sulphates:

This action, which affects many cases, is complex; it is based on the conversion of calcium sulphate into expanding Candlotsalt, also known as ettringite.

Sulphatation of the free lime in the cement by the sulphates dissolved in the water:

$$Ca(OH)_2 +Na_2SO_4 + 2H_2O \rightarrow CaSO_4,2H_2O +NaOH$$
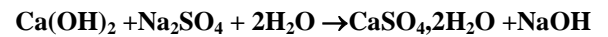
Conversion of the alluminates in the cement into Candoltsalt which expands very strongly (factor 2to 2.5)

$$3CaOAl_2O_3, 12H_2O+3CaSO_4, 2 H_2O +13 H_2O \rightarrow$$

$$3CaO, Al_2O_3, 3CaSO_4, 31 H_2O$$

If magnesia is present, decomposition of the alkaline silicates in the cement may be added to these two mechanisms.

ETTRINGITE FORMATION
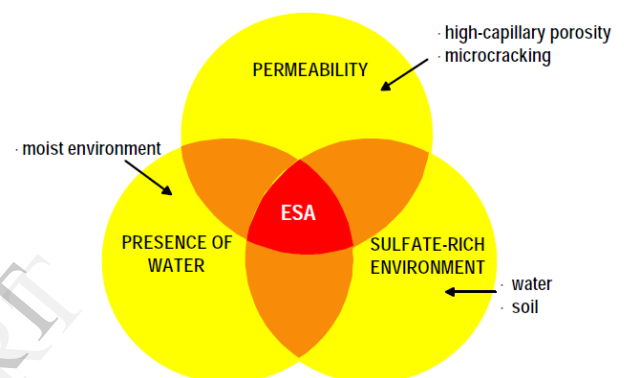**RELATED TO EXTERNAL SULPHATE ATTACK**

Fig: 5 Representation of the DEF related to ESA in RCS
Adopted from: M. Collepardi, ENCO, Engineering Concrete, Ponzano Veneto   (TV) Italy, 2005

ETTRINGITE FORMATION
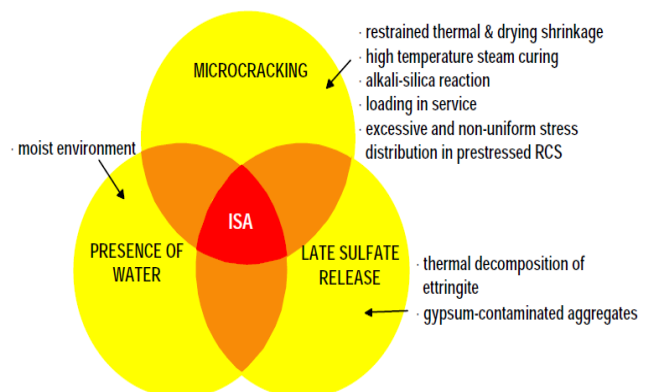**RELATED TO INTERNAL SULFATEATTACK**

Fig: 6 Representation of the DEF related to ISA in RCS
Adopted from: M. Collepardi, ENCO, Engineering Concrete, Ponzano Veneto (TV) Italy, 2005

2.5 Alkali silica reaction

Water with a strong alkali content is destructive to all cements because certain alumina-based constituents are liable to be solubilized if there is no coating, therefore, if it is advisable not to allow water with pH in excess of 12 with ordinary cements or in excess of 8.5 in the case of aluminous cements.
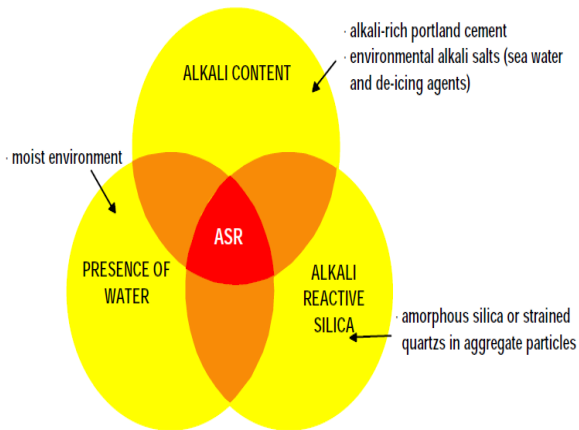
ALKALI-SILICA REACTION (ASR)

Fig: 7 Mechanism of alkali-silica reaction (ASR) for concrete damage

Adopted from: M. Collepardi, ENCO, Engineering Concrete, Ponzano Veneto (TV) Italy, 2005

2.6 Lime leaching:

Leaching of concrete by percolating or flowing water has sometimes caused severe damage and is potentially important for the long-term storage of nuclear wastes. Pure water may be expected to remove alkali hydroxides, dissolves CH and decompose the hydrated silicate and aluminium phases .reference to the equilibrium indicates that, for practical purposes, the ultimate residue will consist essentially of hydrous forms of silica, alumina and iron oxide, all the CaO having been lost. By this stage, the cement paste will have disintegrated. The equilibrium also suggests that CH will be dissolved before the other phases are attacked, but in practice attack is likely to be simultaneous, because of the greater specific surface area of the hydrated silicate and aluminate phases.

The rate of attack depends on the quality and shape of the concrete, the rate at which the water percolates through or flows over it, the temperature and the concentrations of solutes in the water. Attack is not most likely to be serious with soft water. The water in equilibrium with air and not containing any other solutes, the significant species present are CO_2 , HCO_3^- and H^+ ,$[CO_2]$ and pH is 5.6.In underground waters CO_2 maybe much higher and the pH correspondingly lower.

A solution of CO_2 can dissolve $CaCO_3$ with formation of additional HCO_3 and can similarly dissolve CH or Ca^{2+} and OH^- ions from C-S-H or hydrated calcium phases

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$
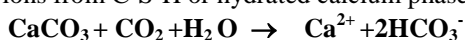
3.0 MECHANISM OF CONCRETE DETERIORATION:

The co-existence principle agents that initiate the concrete structure damage are
1. Inter connected porosity
2. Exposure to aggressive agents
3. Presence of water
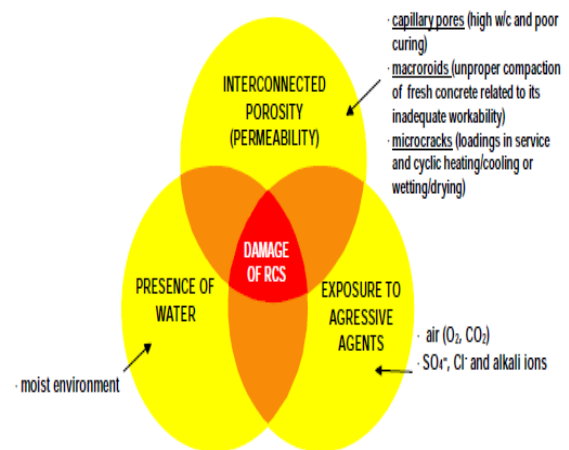A combination of all these factors initiate degradation of concrete structures, which was shown in fig: 9

Fig: 8 Process of degradation of concrete structures.

Adopted from: M. Collepardi, ENCO, Engineering Concrete, Ponzano Veneto (TV) Italy, 2005

4.0 PROTECTIVE MEASURES:

The principle of acid attack—dissolution of the cement matrix and its general alkaline nature—often makes the protection of concrete structures difficult task .In principle, there are two possibilities how to protect the concrete against acidic attack: TYPE-I.

Its possibilities are based on the fact that both the concrete and the structure built with it can be designed to afford desired protection.

In many instances the protection can take the form of self-protection through judicious selection of concreting materials, and the appropriate design of concrete mix and the structure, without a need to resort to special protective measures [8, 9&10].

The protective measures are based on the choice of the cement used, application of the admixtures, design of the suitable composition of the concrete mixtures, effective conditions of the consolidation of concrete mixture and curing of the hardening of fresh concrete. All these protective measurements are aimed at gaining maximal compactness and minimal porosity of the concrete [11, 12].

As it has been already mentioned, the application of modern super plasticizers is useful and effective. The super plasticizers used to give the possibility of a significant decrease of the w/c used, under the observing satisfied workability of the fresh concrete mixture [15, 16].

This last positive effect is very important for the high compactness and low porosity of concrete and in the end for its low water permeability and acidic resistance. The

mentioned measures may contribute to the acidic resistance of concrete. However, it should be stated that the concrete material remains of an alkaline nature willing to react with acids compounds and undergo acidic attack. Therefore, this property of concrete represents a durable threat for the concrete structures when exposed to the acidic attack.

- Use low water-cement ratio makes concrete dense and impermeable.
- Use surface hardeners such as magnesium or zincfluosilicate or apply an oil-insoluble resin.
- Use high quality concrete; cement-rich mixes with entrained air generally perform better.
- Use carbonate aggregates Design system to prevent conversion of hydrogen sulfide to sulfuric acid. If industrial wastes are present, use cement with less than 8% tricalciumaluminate.
- Exclude moisture by providing roof shelter over sulfur-bearing coal in cement based concrete storage bins.
- Cure concrete thoroughly. Then allow to dry at least 28 days in air. High alumina cement concrete has greater resistance, but may not provide a permanent remedy.

TYPE-II

Possibilities are based on the protection of concrete structures by the application of various coatings on their surface. Surface coatings have a significant role to play in protecting and preserving new and existing concrete structures. This protective measure has the unique advantage that it can be applied to protect existing concrete structures [17].

The choice and selection of the surface coating is most important depending on the specific requirements of the protected concrete structure.

The materials used are of an inorganic and organic nature, such as wide range of organic polymers, low viscosity organic materials silane, siloxane, and silica fluorides and as others. The protective effect is brought about mainly by providing a barrier film on the surface of concrete of varying thickness and blocking pores in the concrete. The hydrophobic character of the film can increase its protective effectiveness by repelling water or solutions containing aggressive species [13, 14].

Surface coatings seem to be less favorable than for protective measures of the first group, for many reasons, the causes are many. Used surface coatings are more vulnerable and inclined to decrease protective efficiency. The causes result in the possibilities of the failure of surface coatings. In a number of cases, it can be wholly attributable to non-existing concrete surface preparation, which is fundamental for the reliability of the coating. Other reasons are the occurrence of capillary and osmotic forces behind the coating causing blistering, then cracking evocated by temperature change and dynamic loading in the protected concrete structure. Moreover the protective measurements of the first group, as a rule, seem to be cheaper and more durable.

- Protective coatings may be ineffective where regular scraping with metal blade is necessary
- Bituminous, epoxy, rubber, and vinyl or neoprene many other coatings are effective. See ACI 515*
- Acid-resistant linings needed for concrete chimneys

- Storage tanks may require glass lining set in acid-resistant mortar. For coatings on other surfaces, see ACI 515*[19]

5.0 CONCLUSION:

In interest of the reliability of the study it has been shown that the rate of acidic attack of cement based materials is dependent on numerous factors conditioning the aggressivity of the acting medium and resistance of the attacked material. The resulting rate of the attack is a consequence of their mutual interaction. Therefore, this complexity should be taken into consideration at the evaluation of the service life of concrete structures in acidic media, and the choice of protective measures. The development and use of new generation binders enable the production of mineral binder composites compatible with an acidic environment seems to be a unique way for ensuring satisfied and reliable acidic resistance.

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