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Impact of Sulphates on Binding of Chlorides Associated with Different Cations

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ABSTRACT

Chloride Binding has a significant effect on the chloride transport process. It retards chloride ion penetration into concrete and prolongs the corrosion initiation time. Chloride deprives embedded steel of the corrosion protection normally developed in chloride-free cement environment. The current findings evaluates the chloride binding capacity of various cementitious materials namely OPC, Zeolite, Metakaolin Shale Power etc,.The binding of chlorides in hydration phases can lower the chloride concentration in the pore solution and reduce the rate of chloride diffusion as well as lower the free chloride concentration near the steel. This study helps to know the value of diffusion of chloride into cement paste which does not damage the protective layer of steel. In addition, it can help to analyse the risk of corrosion, thereby improving service life of Reinforced Concrete Structures.

1. INTRODUCTION

Reinforced concrete structures exposed to marine environments are highly susceptible to durability issues due to corrosion of embedded steel reinforcement. This degradation is primarily driven by aggressive ions such as chloride (Cl^-) and sodium (Na^+), commonly simulated using sodium chloride (NaCl) in laboratory studies. However, seawater also contains significant concentrations of magnesium (Mg^{2+}) and sulfate (SO_4^{2-}) ions, which influence pore solution chemistry and may interact with chloride ions to exacerbate corrosion and sulfate attack. Despite extensive research, the combined effect of chloride and sulfate ions remains a subject of ongoing debate. Given the substantial economic implications for marine infrastructure—including bridges, tunnels, wharfs, and piers—accurate assessment of corrosion mechanisms under realistic exposure conditions is essential for reliable service life modeling of reinforced concrete systems.

In general, there are two major factors, which cause corrosion of reinforcement in concrete to proceed to an unacceptable degree. They are: (i) carbonation, and (ii) presence of chloride ions, which may either have been present in the concrete constituents right from the beginning or are introduced into the concrete through ingress during the service life.

The quality of concrete, mainly the permeability, nature and intensity of cracks, and the cover thickness, have also a great bearing upon the initiation and sustenance of reinforcement corrosion.

Once reinforcement corrosion is initiated, it progresses almost at a steady rate and shortens the service life of the structure, by causing surface cracking and subsequently spalling of the cover concrete due to expansion of the corroding steel. The rate of corrosion directly affects the extent of the remaining service life of a corroding RC structure.

A wide range of techniques have been reported in the literature that may be suitably employed for the monitoring of corrosion of steel in concrete structures for the purpose of diagnosing the cause and extent of the reinforcement corrosion.

The prediction of the remaining service life of a corroding structure may be carried out with the help of various available prediction models or experimental techniques, using the data obtained through monitoring.

In this paper a review of the following aspects of reinforcement corrosion are presented:

- mechanism of reinforcement corrosion,
- factors affecting reinforcement corrosion,
- initiation and progress of reinforcement corrosion,
- effects of reinforcement corrosion on performance of the structure,
- monitoring techniques,
- prediction of the remaining service life.

The concrete industry is estimated to accountable for at least 7% of global carbon dioxide emissions. Annually, the world uses more than 10 billion tons of concrete for construction.

As the cement is the main ingredient of concrete, the cement production causes a huge environmental problem. It is estimated that the concrete consumption may reach 18 billion tons per year by 2050. Therefore, the concern among the researchers is raised on the utilization of industrial waste and by-products or other supplementary cementitious materials (SCMs) as the replacement of cement.

2. LITERATURE

Chloride Binding and Corrosion Mechanisms:

C. Arya and Y. Xu et al. investigated chloride binding and its influence on reinforcement corrosion using pore solution analysis and galvanic current measurements. They found chloride binding followed the order GGBS > PFA > OPC > SF, while corrosion rates varied with chloride concentration. At 1% chloride, corrosion followed PFA > SF > GGBS > OPC, and at 3% chloride, PFA > OPC > GGBS > SF. Higher corrosion in PFA and GGBS concretes was attributed to reduced OH^- concentration from pozzolanic reactions, while SF showed relatively low corrosion due to its dense matrix.

Chunyu Qiao, Prannoy Suraneni, Nathalene Wei Ying Then, Antara Choudhary, and Jason Weiss et al. studied chloride binding in cement pastes. They highlighted binding through Friedel's salt and calcium oxychloride formation. Fly ash increased chloride binding, while temperature significantly influenced binding capacity. Chloride binding by C-S-H was shown to vary with pH, exposure solution, and fly ash content.

Mulbah Gbozee, Keren Zheng, Fuqiang He, and Xiaohui Zeng et al. explored chloride binding in Portland cement with 10–30% metakaolin. They found binding depended on phase assemblage, with monosulfoaluminate converting to Friedel's salt under NaCl exposure, making it the main contributor to chloride binding.

Jian Zhang, Caijun Shi, and Zuhua Zhang et al. analyzed chloride binding in alkali-activated slag/fly ash cements (AACs). They found chloride adsorption followed Langmuir isotherm, with binding capacity influenced by slag/fly ash ratio, Na_2O content, and water/binder ratio. Friedel's salt formed only in slag-rich systems.

Effect of Deicing Salts:

A. Poursaee, A. Laurent, and C.M. Hansson studied the effect of deicing salts (NaCl, $MgCl_2$, $CaCl_2$) on rebar corrosion in Canada. They reported $CaCl_2$ had the most severe effect on both steel and mortar integrity, $MgCl_2$ deteriorated mortar at high concentrations, while NaCl had minimal impact on mortar durability even at high levels.

Yaghoob Farnam, Bochen Zhang, and Jason Weiss et al. investigated supplementary cementitious materials (SCMs) in mitigating calcium oxychloride formation caused by $CaCl_2$ ingress. They found SCMs reduced damage by lowering calcium hydroxide content through pozzolanic reactions, thus improving durability against deicing salts.

Sulfate Attack and Combined Chloride–Sulfate Exposure:

A.A. Ramezanianpour and E. Riahi Dehkordi et al. reviewed chloride-sulfate interactions in concrete. They noted contradictory results: some studies showed chloride ions mitigated sulfate attack, while others reported acceleration. The outcome depended on C_3A content, w/c ratio, ion concentration, pozzolan type, and exposure duration.

Raghu Babu U. and Kondraivendhan B et al. analyzed the combined effects of chloride and sulfate ions along with Mg^{2+} in seawater. Using half-cell potential and corrosion current density (Icorr), they reported statistical distributions of corrosion data and developed regression models linking resistivity to material type, salt exposure, and w/cm ratio.

U. Raghu Babu and B. Kondraivendhan et al. studied combined effects of NaCl and $MgSO_4$ on rebar corrosion in OPC, OPC+MK, and OPC+red mud concretes. Using guard ring and IR-compensated polarization, they found MK blends showed superior performance with lower Icorr and higher resistivity, while combined chloride-sulfate exposure increased corrosion.

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3. METHODOLOGY

Materials:

Ordinary Portland Cement (OPC) was used as the base material. Cementitious materials such as Metakaolin (MK), Shale Powder (SP), Silica Fume (SF), Fly Ash (FA), and Rice Husk Ash (RHA) were incorporated at 10% replacement of OPC by weight. Chemical solutions of sodium chloride (NaCl), magnesium sulfate ($MgSO_4$), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$) were used at 0.1M concentration. Distilled water was used for mixing, and silver nitrate ($AgNO_3$) solution was applied for potentiometric titration and pH determination.

Preparation of Test Specimens:

Concrete pastes were prepared using OPC blended with 10% SCMs at a water–cement ratio of 0.42. Each mix included 0.1M solutions of NaCl, $CaCl_2$, $MgSO_4$, or $MgCl_2$. After mixing, the pastes were sealed in airtight covers and cured at 20°C for 14, 28, and 56 days. After curing, samples were demoulded, ground into powder (<45 µm), and stored in double plastic bags to prevent carbonation.

Experimental Procedure:

From each sample, 5 g of powdered paste was mixed with 50 ml distilled water in a glass container. The solution was heated to boiling (100°C), then stirred magnetically for 90 seconds before sealing to avoid air entrapment.

Titration Procedure:

A 20 ml aliquot of the prepared solution was tested for pH using a digital pH meter. Potentiometric titration was then performed using $AgNO_3$ solution added in 0.1 ml increments. Base and platinum electrodes connected to a dual-channel potentiometer were immersed, and readings were recorded after each addition. This procedure was repeated for all prepared solutions.

4. RESULTS AND DISCUSSION

Among all cementitious materials, OPC, RHA, and Metakaolin maintained the highest alkalinity, while Silica Fume, Fly Ash, and Shale Powder showed slightly lower but stable pH values, all remaining within the safe alkaline range.

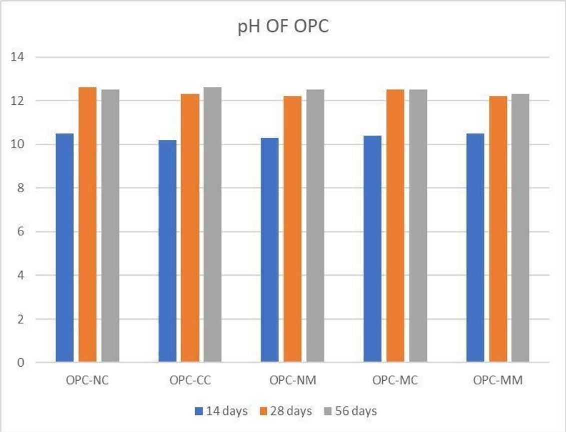

Figure 1: pH values of OPC

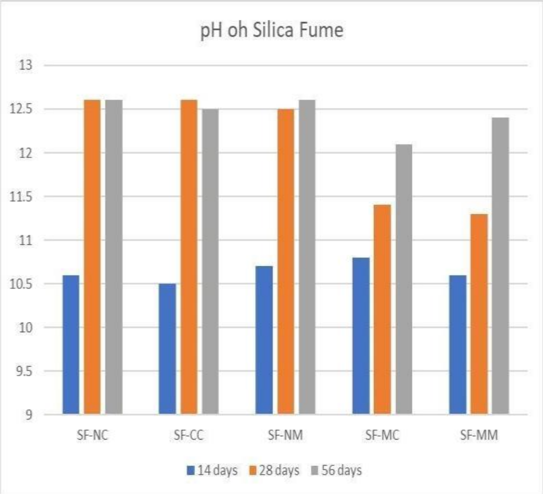

Figure 2: ph values of silica fume

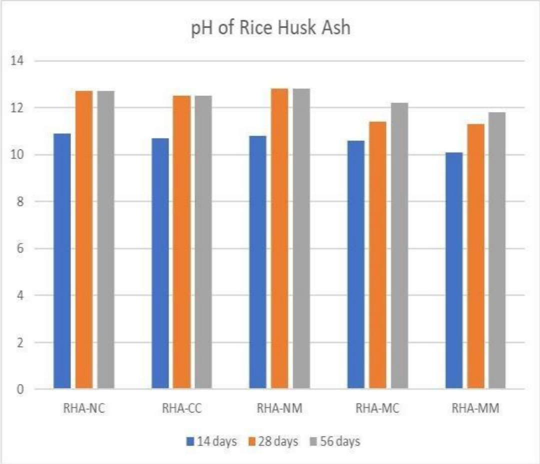

Figure 3: ph values of Rice Husk Ash

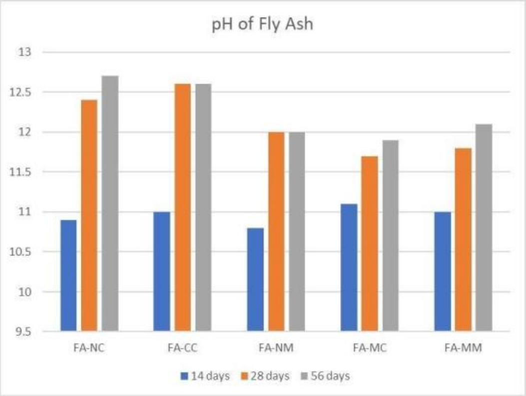

Figure 4: ph values of Fly Ash

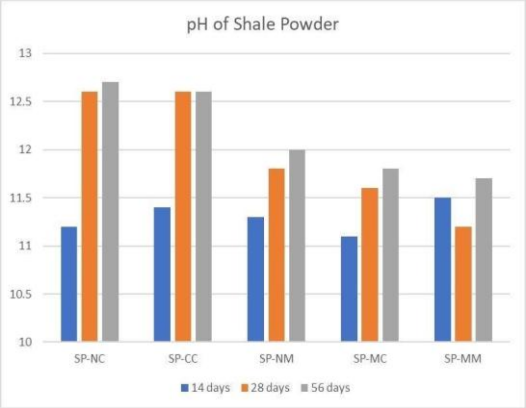

Figure 5: ph values of Shale Powder

Comparison of pH with different cementitious materials

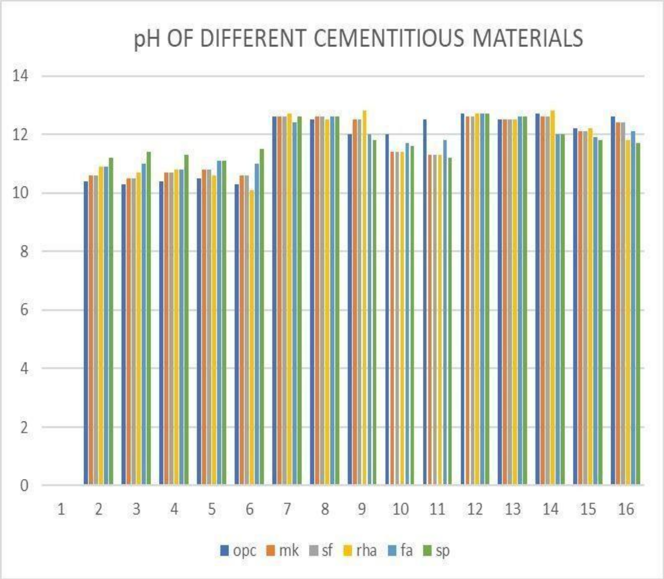

Fig:4.6 Ph values of different cementious materials

5. CONCLUSION

Chloride binding was studied in cement pastes with 10% Fly Ash, Metakaolin, Silica Fume, Shale Powder, and Rice Husk Ash at 23°C.$CaCl_2$ solution showed the highest chloride binding, followed by $MgCl_2$ and NaCl ($CaCl_2 > MgCl_2 > NaCl$).

Metakaolin exhibited the greatest chloride binding capacity among the supplementary cementitious materials.

In $CaCl_2$-exposed pastes, chloride binding occurs through:

- Formation of Friedel's salt
- Formation of calcium oxychloride
- Adsorption of chloride ions by C–S–H gel

Friedel's salt binding increases with chloride concentration and levels off beyond 2.0 M.

Calcium oxychloride formation is more pronounced at lower temperatures and begins at lower chloride concentrations in the $Ca(OH)_2$–$CaCl_2$–H_2O system

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