

Ultrafine GGBS and calcium nitrate as concrete admixtures for improved mechanical properties and corrosion resistance

M. Pradeep Kumar^a, K.M. Mini^a, Murali Rangarajan^{b,c,*}

^a Department of Civil Engineering, Amrita School of Engineering - Coimbatore, Amrita Vishwa Vidyapeetham, India

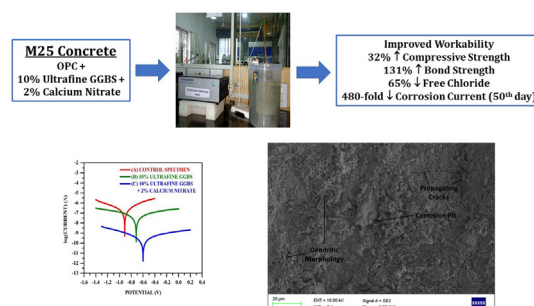
^b Center of Excellence in Advanced Materials and Green Technologies, Amrita School of Engineering - Coimbatore, Amrita Vishwa Vidyapeetham, India

^c Department of Chemical Engineering and Materials Science, Amrita School of Engineering - Coimbatore, Amrita Vishwa Vidyapeetham, India

HIGHLIGHTS

- Effects of ultrafine GGBS and Ca(NO₃)₂ on rebar corrosion of M25 concrete.
- Ultrafine GGBS and Ca(NO₃)₂ increase compressive strength, reduce free chloride.
- Ultrafine GGBS slows oxygen reduction, Ca(NO₃)₂ promotes Fe(OH)₃ passivation.
- Five orders of magnitude reduction in corrosion current on Day 50.
- Pitting and intergranular corrosion from SEM images.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports the modification of ordinary Portland cement with ultrafine ground granulated blast furnace slag (GGBS) as a mineral admixture and calcium nitrate as a chemical admixture and examines how mechanical and corrosion properties are improved by this modification. Ultrafine GGBS with average particle size of 4–6 μm was introduced as a replacement mineral admixture (10%) to ordinary Portland cement while calcium nitrate was introduced as a chemical admixture at 2% amount of cementitious material, in the preparation of concrete. X-ray diffraction studies on powdered concrete showed that the amount of silica in the concrete increases with the introduction of GGBS. Calcium hydroxide was converted to calcium silicates. Ultrafine GGBS reduced the workability and water absorption and increased the compressive strength of the concrete (18%) and the bond strength of the steel rebar (45%). Adding calcium nitrate further reduced water absorption of the concrete but improved workability, compressive strength (32%) and bond strength (131%). The pH of the concrete powdered solution became more alkaline with the replacement of ultrafine GGBS and addition of calcium nitrate. Free chloride content dropped by 39% and 65%, respectively, with the introduction of GGBS and nitrate. Corrosion behaviour of the concrete specimens were studied using measurement of open circuit potentials, linear polarization resistance and Tafel polarization in an accelerated corrosion medium of 3.5% NaCl and 1 M sulphuric acid. Corrosion potential and current of the control specimens decreased with time for 40 days after which an increase was observed. Ultrafine GGBS shifted the corrosion potential in the cathodic direction, indicating retardation of the cathodic reaction (ex. oxygen reduction). Calcium nitrate, on the other hand, shifted the corrosion potential anodically by promoting the formation of a passive film of iron(III) hydroxide on the steel surface. Corrosion currents in GGBS and nitrate-modified concrete decreased by 200-fold compared to the control specimen on the first day, and by 480-fold on the 50th day (150-times smaller than the

* Corresponding author at: Center of Excellence in Advanced Materials and Green Technologies, Amrita School of Engineering - Coimbatore, Amrita Vishwa Vidyapeetham, India.

E-mail address: r_murali@cb.amrita.edu (M. Rangarajan).

specimen modified with GGBS alone). Finally, scanning electron microscopy images of the corroded rebar at the end of 50th day indicate that pitting and intergranular corrosion occurs, with its extent reduced significantly by the introduction of admixtures. These results demonstrate that ultrafine GGBS and calcium nitrate as admixtures enhance the mechanical properties of concrete and reduce the corrosion of rebar.

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1. Introduction

Corrosion of steel rebar in concrete is a major problem that adversely affects the durability and service life of a concrete structure. Expansion of steel bars due to rusting exerts tensile stress on concrete. Since concrete cannot withstand tension, cracks occur leading to brittle failures. This problem is exacerbated particularly in marine and underground structures. In fact, steel has a typical protective passive layer, which is preserved as an oxide or a hydroxide layer when it is in contact with the concrete, owing to the high alkalinity of concrete. However, chloride penetration promotes local corrosion such as pitting and intergranular corrosion mechanisms. Carbonation, on the other hand, causes a uniform depassivation in the carbonated areas of the concrete. These eventually result in deboning, loss of strength leading to structural failure.

Many approaches have been undertaken for corrosion protection in concrete, particularly in marine environment. These include surface treatment of steel by modifying coatings, cathodic protection by maintaining a sacrificial anode at a more negative potential than the rebar, electrochemical removal of chloride, and the use of corrosion inhibitors or inhibiting admixtures [1–3]. The first three approaches require significantly higher fixed and operational costs. On the other hand, a judicious choice of partially modifying the ordinary Portland cement (OPC) or the concrete preparation process by addition of new materials can not only reduce the corrosion rate of the structure but also improve the mechanical properties of the concrete. This approach is cost-effective and simple to use. Along these lines, many attempts have been documented in the literature. Efforts in this area have examined the use of either mineral admixtures, including in micro-to-nanometre scales, or corrosion inhibitors.

Influence of mineral-based additives to Portland cement on the corrosion of the steel reinforcement was studied by Andrade et al. [4]. It was found that slag cement is more resistant against chloride but less resistant towards carbonation compared to the ordinary Portland cement. Introducing fly ash in the concrete and its effects on the corrosion of rebar was examined in NaCl solution by Montemor et al. [5] using electrochemical impedance spectroscopy (EIS). They observed decrease in the rate of corrosion and delayed corrosion initiation due to increase in resistivity of concrete with replacement of fly ash. Accelerated corrosion studies such as those conducted by Gerengi et al. [6] used 1 M HCl as the medium and the effects of minerals such as diatomite and zeolite on the corrosion behaviour of steel rebars were examined. Over a span of 6 months, the mix containing zeolite offered higher resistance to corrosion compared to diatomite.

Sharmila and Dhinakaran [7,8] investigated the effect of ready-made and ground granulated blast-furnace slag (GGBS) on the durability the mechanical properties of high-strength concrete. It was observed that ground slag provided better compacted microstructure density and filled micro-voids and thereby performed better than readymade slag. Teng et al. [9] examined the use of ultrafine GGBS and studied the mechanical properties, chloride migration coefficient and electrical resistivity of the hardened concrete. The use of finer-size materials increased the surface area

of particles in the concrete, improving the apparent rates of hydration and pozzolanic reactions. Haruehansapong et al. [10] examined the effects of nanometer-size silica on the compressive strengths of cement mortars. The effects of both size and the amount of addition were studied. It was found that smaller the size of the nano-silica, more the agglomeration. Therefore, for a size less than 40 nm, there was no improvement in the compressive strength of the concrete. The nano-silica particles promoted pozzolonic reactions, reduced pore sizes and resulted in compact microstructures.

Recently, studies such as Dave et al. [11] have attempted the introduction of small quantities of multiple additives such as fly ash, metakaolin, ground granulated blast furnace slag and silica fume, i.e., as a quaternary mixture, to examine the mechanical properties including workability, compressive, tensile and flexural strengths, and rapid chloride penetration and sulphate attack of the different proportions of the mixture. However, these studies [4–11] have not examined the corrosion behaviour of steel rebars in these modified concretes.

Söylev and Richardson [12] reviewed the use of corrosion inhibitors for steel in concrete, specifically aminoalcohols, nitrites and monofluorophosphates. Inhibitors typically resist corrosion by anodic, cathodic or mixed mechanisms. *Anodic inhibitors* which shift the corrosion potential of steel in the anodic direction by delaying iron dissolution, ex. calcium and sodium chromate, sodium nitrite and sodium benzoate. *Cathodic inhibitors* resist the cathodic reaction of corrosion, viz., oxygen reduction, often by preventing oxygen transport along steel surface, shift the corrosion potential further cathodically and cause a decreased rate of corrosion. Sodium hydroxide, sodium carbonate, silicates, phosphates and polyphosphates are typical examples. *Mixed inhibitors* work both at anodic and cathodic regions on the steel surface, resisting both reactions, often without a significant shift in the corrosion potential. These are typically organic compounds with amine, alcohol and other polar groups. Besides exploring the mechanism of inhibitor action in chloride-contaminated and carbonated concrete, they also reviewed studies the permeability of inhibitors into concrete, and properties such as air content and density, workability, hydration and setting time, bond strength, tensile strength, compressive strength, modulus of elasticity and durability.

Saraswathy et al. [13] considered the addition of various corrosion inhibitors such as potassium chromate, stannous chloride, sodium nitrite and sodium benzoate. They found that admixtures containing hydroxide, citrate and stannate increased compressive strength and slowed down the corrosion of steel, thereby enhancing the durability of reinforced concrete. Saricimen et al. [14] explained the effectiveness of two proprietary concrete inhibitors, one an alkanolamine inhibitor used as an admixture and the other a water-based inorganic inhibitor, in retarding rebar corrosion. A + 4 V anodic potential was impressed on the rebar to promote accelerated corrosion and time-to-cracking of the specimens was measured. The water-based corrosion inhibitor prolonged the time to crack. It was found that this inhibitor formed a passivating film on the steel and retarded chloride-initiated local corrosion. An EIS-based analysis of the effects of calcium nitrite on the corrosion of pre-passivated steel rebar in chloride-contaminated simulated

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