Influence of PCE-SP and calcium nitrite inhibitor on mechanical and durability parameters of concrete

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This paper presents the results on the effect of polycarboxylic ether superplasticizer (PCE-SP) and calcium nitrite based corrosion inhibitor on the mechanical and durability parameters of concrete. Effect of water to cement ratio (w/c) as well as the type of cement, namely, ordinary portland cement (OPC) and fly ash based portland pozolana cement (PPC) was also studied. The studies reveal that the compressive strengths of OPC and PPC concretes with PCE-SP are found to be similar to that of their respective control concretes (OPC and PPC concrete alone). Nevertheless, the durability parameters such as rapid chloride penetration test (RCPT) value and sorptivity were improved. Hence, the use of PCE-SP must be encouraged for making durable concrete. When calcium nitrite inhibitor (CNI) is added to the concrete, a reduction in compressive strength was noticed. Also, there was an increase in the RCPT values compared to that of control concrete. This may be due to high ionic nature of CNI, which causes more negative charges to pass through concrete. Based on the study, it can be said that CNI influences the mechanical and durability properties and hence can be used with proper care.

Keywords: Concrete, Durability, PCE Superplasticizer, Calcium nitrite inhibitor.

Introduction

Reinforced concrete (RC) is one of the best composite material for construction due to its economy, feasibility and easy mouldability. Earlier days, concrete strength was one of the most important engineering criteria for grading the quality. In the recent past, many of existing RC structures are showing signs of distress. Therefore, now a days, the paradigm has been changed from concrete strength to concrete durability. Durability of concrete plays an important role in the service life of RC structures that can be enhanced by improving its impermeability, resistance to chloride ion diffusion and abrasion resistance. This can be achieved by adding superplasticizers and mineral admixtures. Also, high performance concrete (HPC) can be produced by minimizing the water to cement ratio (w/c) with the help of superplasticizers and carefully selected mineral admixtures such as fly ash, ground granulated blast furnace slag (GGBS), metakaolin and silica fume. Now a days, most of the concrete produced in India contain one or more concrete admixtures. Chemical admixtures such as PCE superplasticizers and calcium nitrite based corrosion inhibitors are increasingly used in the concrete for improving the durability of fresh concrete and corrosion resistance. In recent years, in most high quality concrete, superplasticizers are used to achieve better fresh state properties. Many researchers reported the importance of superplasticizers (SP) and described the properties of concretes in terms of strength development, permeability, pore structure, carbonation and microstructure. Researchers like Dhir et al. and Swamy reported that superplasticizers reduce the porosity and sorptivity of concrete through water reduction and said that superplasticizers can be seen as agents of concrete durability rather than agents of concrete workability. However, it is to be noted that the dosage of SP/CNI plays an important role on strength and durability. Some physical and mechanical properties of high strength concretes made with OPC were found to be significantly reduced at higher dosages of superplasticizer. Papayianni et al., Jayasree and Gettu and others observed that the polycarboxylic ether superplasticizers (PCE-SP) provide better fluidity and durability properties than other SP products. Berke observed an increase in the chloride ion permeability due to the presence of CNI. Some researchers reported that the addition of calcium nitrite influences the hydration process of cement paste by accelerating and stabilising the formation of the crystal phase of calcium hydroxide, which leads to an increase in the micropore diameter in the hardened cement paste, and thus an
increase in chloride ion permeability compared to concrete without inhibitor. Li et al.\textsuperscript{13} observed a decrease in compressive strength of concrete with the addition of CNI and also observed that the addition of CNI changes the microstructure.

Amara et al.\textsuperscript{14} performed extensive studies on rapid chloride ion permeability (RCPT) of four different concretes with and without nitrite based inhibitor, and observed higher permeability at early ages in concretes with nitrite based inhibitor. Berke et al.\textsuperscript{15} tried various combinations of admixtures to improve the corrosion resistance of rebars in concrete. They reported that as silica fume content increases, there is a substantial decrease in chloride ion penetration (coulombs); however, there was an increase in coulombs due to the presence of calcium nitrite. They further reported that the increase in coulombs is not indicative of increased chloride ion penetration but rather due to the increased negatively charged ionic concentration in the pore water. Montes et al.\textsuperscript{16} and Ann et al.\textsuperscript{17} reported that compressive strength can increase with the presence of CNI. There is a difference in opinion among researchers about the effect of CNI on strength and durability of concrete. Hence, the objective of the present study is to investigate the effects of polycarboxylic ether superplasticizer (PCE-SP) and calcium nitrite based corrosion inhibitor on the mechanical and durability parameters of concretes made of ordinary portland cement (OPC) and fly ash based portland pozzolana cement (PPC) with different water-to-cement ratios. The results of the experimental investigation are discussed in this paper.

**Research Significance**

Chemical admixtures such as PCE superplasticizers and calcium nitrite based corrosion inhibitors are increasingly used in the concrete for specific applications such as improvement in the rheological properties and delaying the corrosion process of rebars in concrete. It is therefore, necessary to know the effects of these products on the basic strength and durability parameters of concrete, since the test data on compressive strength, chloride ion penetration, sorptivity, etc. of concretes containing PCE-SP and CNI are rather limited, which may be used as the initial indicators for the long term durability of RC structures.

**Experimental Programme**

**Materials Used**

Commercially available ordinary portland cement (OPC) and fly ash based portland pozzolana cement (PPC) of same brand, potable water, commercially available polycarboxylic ether superplasticizer (PCE-SP) and calcium nitrite inhibitor (CNI) of same brand were used. Fine aggregate of river sand and graded crushed granite with maximum size aggregate (MSA) of 20 mm and 12 mm in the ratio of 1.5:1 were used. As per the manufacturer specifications, PCE superplasticizer has a specific gravity of 1.09 and solid content is not less than 30 % by weight. The CNI contains about 30 % calcium nitrite by mass.

**Preparation of Specimens**

For the concrete mix design ACI 211\textsuperscript{18} guidelines were followed. Three water-to-cement-ratios (w/c), viz., 0.57, 0.47 and 0.37 were considered for making different concrete grades. IS 456\textsuperscript{19} guidelines on durability were followed in fixing the upper and lower limits of w/c. A slump of 25 mm - 50 mm for concretes without PCE-SP and 125 mm - 150 mm for concretes with PCE-SP was chosen keeping the water content same in both the concretes. The quantities of materials arrived per cubic meter and the dosages of PCE-SP for different w/c are presented in Table 1. The dosage of CNI adopted was 10 l/m\textsuperscript{3} (which is within the dosage range recommended by the manufacturer of 5 l/m\textsuperscript{3} to 30 l/m\textsuperscript{3}). A total of 24 mixes, which consist of 8 concretes (OPC, PPC, OPC-SP, PPC-SP, OPC-CNI, PPC-CNI, OPC-SP-CNI and PPC-SP-CNI) with three w/c (0.37, 0.47 and 0.57) were proposed. Standard specimens such as cubes of 150×150×150 mm for compressive strength, 100×200 mm cylinders for rapid chloride penetration test (RCPT) and 75×150 mm cylinders for water absorption and sorptivity were cast. After 24 hours, the specimens were removed from the mould and water cured for 28 days. Mechanical property, mainly, the compressive strength was evaluated as per IS 516\textsuperscript{20} and the other durability parameters evaluated by the following:

**Water Absorption Test**

This method was used to estimate the maximum amount of water that can be absorbed by a dry specimen and provides a measure of the total water permeable pore space. For this, 75 mm diameter and 150 mm height specimens were cast. The specimens were water cured for 28 days and then weighed. The specimens were kept in water for 24 hours and the weight was measured. This method was repeated for seven days. The water absorption was calculated by the following formula:

\[
\text{Water Absorption} = \frac{W_7 - W_0}{W_0} \times 100\\%
\]

where \(W_0\) is the initial dry weight and \(W_7\) is the weight after 7 days of water curing.

### Table 1 Quantities per cubic meter (kg/m\textsuperscript{3})

<table>
<thead>
<tr>
<th>w/c</th>
<th>Cement</th>
<th>Sand</th>
<th>CA</th>
<th>Water</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>300</td>
<td>870</td>
<td>1056</td>
<td>170</td>
<td>0.90 (0.30%)*</td>
</tr>
<tr>
<td>0.47</td>
<td>362</td>
<td>815</td>
<td>1056</td>
<td>170</td>
<td>0.91 (0.25%)*</td>
</tr>
<tr>
<td>0.37</td>
<td>460</td>
<td>732</td>
<td>1056</td>
<td>170</td>
<td>0.92 (0.20%)*</td>
</tr>
</tbody>
</table>

Note: * indicates % by weight of cement
150 mm height cylinders were kept in oven at 105±5°C for 48 hours, and the dry weights were recorded (W₁). Later specimens were allowed to cool for 24 hours at room temperature and then immersed completely in water for 24 hours. The weight of the final surface dry specimen after immersion was recorded (W₂). These tests were carried out after 28 days of water curing. The water absorption was calculated as

\[
\text{Water absorption} = \left( \frac{W₂ - W₁}{W₁} \right) \times 100 \quad \ldots (1)
\]

**Sorption (or rate of absorption of water) Test**

The performance of concrete subjected to deteriorative environments is a function of the penetrability of the pore system. In unsaturated concrete, the rate of ingress of water or other liquids is largely controlled by absorption due to capillary rise\(^21\). In the present study, 50 mm thick slices cut from cylinders of 100 mm diameter and 200 mm height were used. The slices were kept in an oven for 48 hours at 100±5°C, taken out, allowed to cool for 24 hours and weighed. Then, the slices were put on a weld mesh such that there is free access of water at the bottom surface. The water level was kept not more than 5 mm or so above the base of the specimen. Weights of the specimens were noted at 30 minutes (S₁) and 60 minutes (S₂) after test initiation by wiping off excess water with a damp tissue. The quantity of absorbed water during the time period from 30 minutes to 60 minutes was determined from the difference in weights. The sorptivity was calculated as

\[
s = \frac{\Delta S}{(A.d)t^{1/2}} \quad \ldots (2)
\]

where:
- \(s\) = sorptivity (mm/√(min.))
- \(t\) = elapsed time (min.)
- \(\Delta S\) = \(S₂ - S₁\) (g.)
- \(A\) = Surface area of specimen through which water penetrates (mm²)
- \(d\) = density of water (g/mm³)

**Rapid Chloride Penetration Test**

Rapid chloride ion penetration test (RCPT) was carried out on concrete discs as per ASTM C 1202\(^22\). Cylinders of 100 mm diameter and 200 mm height were cut into discs of 50 mm thickness. The specimens were kept in water for 24 hours for full saturation and then subjected to RCPT by impressing a 60 V current. For this, two sides of the disc are sealed in Plexiglas containers. One side of the container is filled with 3 % NaCl solution (cell connected to the negative terminal) and the other side is filled with 0.3N NaOH solution (cell connected to the positive terminal). Current was measured at every 30 minutes for a period up to 6 hours. At the end of 6 hours, the total charge passed is calculated.

**Results and Discussion**

The mechanical and durability parameters of all concretes, viz., OPC, PPC, OPC-SP, PPC-SP; OPC-CNI, PPC-CNI; OPC-CNI-SP, and PPC-CNI-SP for three w/c have been evaluated. In each case, three specimens were tested and the average values are reported. Figures 1 and 2 shows the compressive strengths (as per IS 516\(^20\)) of different concretes made of OPC and PPC with PCE-SP and/or CNI, along
with OPC concrete alone (control concrete). It can be seen that as w/c decreases, the compressive strengths increased as expected. The compressive strengths of the OPC concrete (control concrete) and the OPC-SP concrete at all w/c are close to each other. Winnefeld et al. studied the effect of molecular architecture (length of side chains, density of side chains and molecular weight of polymer) of PCE superplasticizers and observed that there was no clear trend visible about the enhancement of 28 day strengths. They also reported that longer side chain lengths, lower side chain densities tend to decrease 28 day strengths. On the other hand Sahmaran et al. studied comprehensively and reported an increase in strengths due to the presence of superplasticizers. In the present study, for the PPC-SP concrete, there is a marginal improvement in compressive strength of about 5% to 8% compared to that of PPC concrete alone. For compressive strengths of concrete with CNI (at the adopted dosage of 10 l/m³), it has been observed that there is a reduction when compared to that of the respective control concretes (refer to Figs. 1 and 2). The reduction in compressive strength of concretes with CNI is about 20% and 10%, respectively, compared to that of the respective OPC and PPC concretes. The results obtained agree with previous work, where the reduction in compressive strength has been attributed to the change in pore ratio and diameter. Test results of water absorption and sorptivity for different concretes made of OPC and PPC with PCE-SP and/or CNI along with those of the control concrete indicate that water absorption and sorptivity increases with an increase in w/c. The water absorption of OPC-SP and OPC-CNI are less compared to that of control concrete. However, the water absorption of PPC and PPC-SP are more (6% to 12%) compared to that of control concrete. Nevertheless, in both OPC and PPC concretes, it is observed that the concrete with PCE-SP performed well from the durability point of view; i.e., there is a reduction in water absorption and also in sorptivity, compared to the corresponding control concretes. This may be attributed due to better dispersion of cement particles and refinement of pore structure. Also, it has been observed that the water absorption and sorptivity values of concrete with CNI is lower by about 15% and up to 30%, respectively, for the OPC concretes; and by about 17% and up to 35%, respectively, for the PPC concretes. The concrete with CNI performed well at lower water to cement ratio (w/c = 0.37), both in terms of water absorption and sorptivity compared to that of higher w/c. Figures 3 and 4 shows the plots of RCPT values of OPC and PPC concretes with reference to control concrete. There is not much difference between the RCPT values of concrete with PCE-SP and the corresponding reference concretes, both for OPC and PPC. That means the rapid chloride permeability is not significantly affected by the presence of PCE-SP, as also observed previously by Gagne et al. Further studies are needed to comment on this. However, the RCPT values of both OPC and PPC concretes with CNI are substantially higher; i.e., 1.6 to 1.8 times that of OPC concrete and about 2.5 to 3 times that of PPC concrete (refer to Figs. 3 and 4). The higher value of RCPT for concretes with CNI can be attributed to the high ionic nature of CNI, which causes more negative charge to pass through the concrete. Similar results
have also been obtained by other researchers, such as Berke\textsuperscript{11}, Berke and Hicks\textsuperscript{26}, Ann \textit{et al}.,\textsuperscript{17} and Issa \textit{et al}.,\textsuperscript{27} Berke \textit{et al}.\textsuperscript{15} studied the effect of various combinations of admixtures and reported that there was an increase in charge passed due to the presence of calcium nitrite. They further reported that such an increase in RCPT value is not indicative of higher chloride ion penetration but rather of the increased anion concentration in the pore water. However, Ma \textit{et al}.,\textsuperscript{12} reported that the addition of calcium nitrite influences the hydration process of cement paste by accelerating and stabilising the formation of the crystal phase of calcium hydroxide, which leads to an increase in the micropore diameter in the hardened cement paste. The larger pores could lead to an increase in chloride permeability when compared to the concrete without inhibitor\textsuperscript{28}. Loulizi \textit{et al}.,\textsuperscript{29} performed RCPT studies on four different concretes with and without nitrite based inhibitor and observed higher RCPT values at early ages (≈2 times more at 33 days) in concretes with nitrite based inhibitor. From the above, it can be said that RCPT is not a good indicative of durability parameter, when CNI is present in concrete. Long term ponding test procedures such as ASTM G 109\textsuperscript{30} may be explored to assess the effect of CNI on durability of reinforced concrete.

Conclusions

Based on the experimental results obtained from this study, following conclusions can be drawn:

- In general, PCE-SP has not affected the mechanical properties, but, improved the durability parameters such as water absorption and sorptivity. The 28 day compressive strengths and RCPT values of concretes with PCE-SP are similar to that of their respective OPC and PPC concretes without PCE-SP.
- The water absorption and sorptivity values have been improved for concretes with CNI when compared with that of respective control concretes. The 28 day compressive strengths of concretes with CNI are lower; about 20% and 10% compared to that of respective OPC and PPC concretes.
- The RCPT values of concretes with CNI are higher (indicating higher penetrability); 1.6 to 1.8 and 2.5 to 3 times to that of the corresponding OPC and PPC concretes. This may be due to high ionic nature of CNI, which causes more negative charge to pass through the concrete. Long term ponding test procedures may be used to assess the effect of CNI on durability of reinforced concrete.
- Based on the investigation, it is recommended that use of PCE-SP must be encouraged to make durable concrete and CNI should be used with proper care, since, sometimes, it affects the mechanical and durability parameters negatively.

References


IS 516:1959 Indian standard Methods of tests for strength of concrete, Bureau of Indian Standards (BIS), New Delhi, 1999.


