Sustainable utilization of quartz sandstone mining wastes: Technical note on Chloride and corrosion resistance

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ABSTRACT
Designing concrete to attain its durability requirements is a tough challenge. Chloride ingress is one of the most severe problems affecting the durability of concrete and has been investigated extensively. There has also been a growing interest to reduce the use of conventional natural aggregates to promote sustainability in construction industry. In this study, quartz sandstones are replaced for natural coarse aggregates in concrete and tested for chloride and corrosion resistance. The study revealed that the concrete containing quartz sandstones as coarse aggregates performed well in corrosive environment. In the chloride ion penetration test, concrete with 20% quartz sandstones showed a similar pattern to that of the control concrete made solely from natural coarse aggregates.

Keywords: Chloride; Corrosion; Quartz sandstone; Sustainability

Introduction
The resistance of concrete against chloride ingress mainly depends on its porosity and the fraction of capillary pores [van Noort et al., 2106]. The main deterioration mechanism of concrete structures involved in marine environment is through chloride ingress [Ghafoori et al.,
The resistance of concrete against chloride ingress is a function of its permeability and the fraction of capillary pores therein. The lower the water/cement ratio, the greater the resistance to penetration of deleterious materials. At present, reinforced concrete structures are to be designed in such a way that they can tackle degradation related to mechanical, chemical and environmental actions [Pradelle et al., 2017].

Corrosion of steel reinforcements embedded in concrete is also considered as one of the major problems in durability deterioration of reinforced concrete structures. Corrosion not only induces expansion resulting in spalling and cracking, but also reduces the overall cross-section of reinforcement bars, thereby reducing the load-carrying capacity of a structure [Yu et al., 2017]. Due to the alkalinity of concrete pore solution, the rebar is generally in a passive state which promotes the formation of thin passive layer [Bertolini et al., 2013]. When the chloride content at the rebar level exceeds a critical value, corrosion takes place. The parameters that involve during this process are the pH of concrete, level of chloride available at the rebar/concrete interface and the electrochemical potential of steel [Glass and Buenfeld, 1997; Angst et al., 2009; Alonso and Sanchez, 2009]. Alkalinity of concrete mainly depends upon the cement type used. Improper compaction can also increase the voids at the concrete-steel interface which may acidify the pore solution thereby increasing the critical chloride threshold level [Brenna et al., 2017; Glass and Buenfeld, 2000]. Therefore, the evaluation of reinforced concrete exposed to corrosion plays an important role on maintenance and repair of reinforced concrete structures [Vedalakshmi et al., 2009; Morris et al., 2002; Reou and Ann, 2009].

In the recent trends of concrete sustainability, usage of alternative materials without sacrificing concrete durability has become a focal point of research. A huge amount of naturally occurring material sources are being consumed. So, there occurs the interest in using alternative solid
materials in concrete, e.g. quarry wastes, if possible, to reduce the landfill problem and thereby improve the overall sustainability [Kumar et al., 2016]. In this research, quartz sandstone aggregate (originating from dimension stone manufacture in Dholpur region, Rajasthan, India) was replaced for conventional natural aggregate and the obtained concrete tested for its chloride and corrosion resistance.

**Material properties and preparation of test samples**

Binding cement of 43 grade (conforming to IS 8112:1989) with a specific gravity of 3.15; normal consistency of 32%; initial and final setting time of 66 minutes and 164 minutes was used. River sand of Zone II confirming to IS 383 (1970) was used. Natural coarse aggregates of sizes 20 mm and 10 mm were used for casting of concrete cubes. Quartz sandstone aggregates in slightly different sizes of 25 mm and 10 mm were used as replacement for natural coarse aggregates. The particle size distribution, composition of aggregates, cement properties and gradation details are the same as given in Kumar et al. (2016a). The substitution of quartz sandstone was carried out in 20% steps for the whole range of 0–100% [Kumar et al., 2017]. The mix proportion of fresh concrete containing quartz aggregates is given in Table 1.

<table>
<thead>
<tr>
<th>Water-Cement Ratio</th>
<th>Cement (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Coarse aggregates 10 mm (kg/m³)</th>
<th>Coarse aggregates 20 mm (kg/m³)</th>
<th>Fine aggregates (kg/m³)</th>
<th>Minimum-Maximum Admixture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>440</td>
<td>154</td>
<td>559.35</td>
<td>683.65</td>
<td>635.47</td>
<td>0.87-0.90</td>
</tr>
<tr>
<td>0.4</td>
<td>405</td>
<td>162</td>
<td>567.45</td>
<td>693.55</td>
<td>645</td>
<td>0.86-0.89</td>
</tr>
<tr>
<td>0.45</td>
<td>342.2</td>
<td>153.9</td>
<td>589.60</td>
<td>713.29</td>
<td>662.05</td>
<td>0.86-0.89</td>
</tr>
</tbody>
</table>
Methodology

Chloride ion penetration test

The silver nitrate solution spray method is a simple and quick method to determine the chloride ion migration depth of concrete (Otsuki et al., 1992, Baroghel-Bouny et al., 2007). Cubic specimens of 100 mm size, water cured for 28 days, were allowed to permeate by 4% NaCl solution for 90 days. To maintain a constant concentration, the NaCl solution was replaced after 24 hours of immersion, then at 3rd day and then at every 7 days. The samples were tested for chloride penetration at regular intervals (at 28, 56 and 90 days). The samples were split in half and the fresh surfaces sprinkled with 0.1 N silver nitrate (AgNO₃) solution (Figure 7). The AgNO₃ reacts with the free chloride on the concrete surface and forms a white precipitate of silver chloride (AgCl). At the regions where there is an absence of free chlorides, AgNO₃ reacts with hydroxide to form a brown precipitate of silver oxide (AgO). Thus the region of colour change indicates the presence of chloride penetration (Figure 8). The white layer of silver chloride takes place when the concentration of free chloride ion is more than 0.15% by weight of cement [Güneyisi et al., 2007; Güneyisi et al., 2009].

Corrosion test

To measure the corrosion of steel reinforcements, chloride induced corrosion technique was adopted. Macro cell method (ASTM C 876-2009) was used to measure (monitor) the corrosion activities of embedded steel bars in concrete. The potential difference between anode and cathode across a standard resistor of 100 Ω was measured (Figure 1).
To prepare the specimens for corrosion test, thermo-mechanically treated (TMT) steel bars, factory manufactured by hot rolling steel wires and then passing them through water were used. Three TMT bars, as given in Figure 2 (12 mm diameter and 350 mm length) were taken and properly cleaned with a wire brush for removing the dirt and rust on the surface. Rubber shrink tube was firmly affixed on the two ends of the steel bars at a length of 75 mm. This was done to prevent that area (which is exposed outside the specimen) from getting corroded. The dimensions of concrete specimens prepared for corrosion testing (280 mm × 150 mm × 115 mm) were in accordance to ASTM G 109-2005. A total of three steel bars were used for this purpose (Figure 2). One of the steel bars was placed at the top (anode) and rest placed at the bottom (cathode) with the adequate cover prescribed by the standard code. A reservoir of 15 mm height was made at the head of the specimen for ponding.

After casting, the corrosion specimens were cured in water for 28 days by maintaining the temperature at 27 ± 2°C. The specimens were withdrawn from the curing tank and dried at room temperature for a period of 30 days. Two layers of epoxy paint were used to coat all the vertical layers of specimen. The steel bars were then wired along with a resistor of 100 Ω between the terminals (top and bottom). Along the head of specimen, 3% NaCl solution was poured and covered to minimise evaporation. The samples were then subjected to alternate wetting and drying cycles (3 days ponding, pouring out contents and 11 days drying) (Figure 3). Measurements were taken at every wetting and drying stage and were continued fortnightly. A high impedance voltmeter was used to measure the potential difference between the terminals. The macro cell current was calculated by the following equation:

$$I_j = \frac{V_j}{100}$$

Where, $V_j$ = Voltage across 100 Ω resistor.
Figure 1. Test layout from ASTM C 876
(a) Reference electrode circuitry (b) Sectional view of copper-copper sulphate electrode

Figure 2. Steel bars and concrete specimen (ASTM G 109-2005)

Figure 3. Epoxy coated specimens following ASTM G 109-2005 (drying and wetting cycles)
The total integrated current is obtained from the following equation:

$$TC_j = TC_{j-1} + [(t_j - t_{j-1}) \times \frac{(i_j + i_{j-1})}{2}]$$

Where,

$TC = \text{Total corrosion (coulombs)}$

$t_j = \text{Time in seconds at which measurement of the macro cell current is carried out}$

$i_j = \text{Macro cell current (amperes) at time } t_j.$

The accepted maximum level specified by the standard ASTM C876-2009 is 150 C.

**Results and Discussion**

The results and detailed discussions of chloride resistance test and corrosion test are as follows:

*Chloride ion penetration test*

The graphs showing the results of chloride ion penetration with respect to the percentage of quartz sandstone (Dholpur stone) are given in (Figures 4, 5 and 6).

While considering the concrete mix with water/cement ratio of 0.35, the depth of chloride ion penetration increased as the dosage of quartz sandstone (Dholpur stone) increased. The chloride penetration of the control concrete tested at various days of exposure were similar to that concrete with 20% quartz sandstone. A gradual increase in chloride penetration was noticed in the specimens beyond 20% replacement. At 90 days, chloride ion penetration was 20 mm for the concrete with 0% quartz sandstone (control concrete) and 27 mm for concrete mix with 100% quartz sandstone.
Figure 4: Chloride ion penetration of concrete mixes with w/c 0.35

Figure 5: Chloride ion penetration of concrete mixes with w/c 0.40
Figure 6. Chloride ion penetration of concrete mixes with w/c 0.45

Figure 7. Spraying of 0.1 N silver nitrate solution on freshly split concrete specimens
Figure 8. Freshly split concrete specimens showing the depth of chloride penetration after 28 days (Arrows indicate the depth of chloride penetration)

The concrete mixture with a water/cement ratio of 0.4, a similar gradual increase of penetration was observed as the quartz sandstone dosage increased. At 90 days, the control concrete recorded a penetration of 22 mm and the concrete with 100% quartz sandstone showed 30 mm penetration. The concrete specimens with 0.45 water/cement ratio showed a similar increasing trend of penetration depth. However, at 90 days, the control concrete and 20% quartz sandstone concrete showed a depth of penetration of 24 mm. A maximum depth of penetration of 32 mm was recorded for the concrete with 100% quartz sandstone at 0.45 w/c. The gradual increase in chloride penetration can be related to the privation of internal packing of quartz sandstone concrete. However, at lower water cement ratios (0.35 and 0.45), control concrete and concrete with 20% substitution showed a similar penetration depth.
Corrosion test

The macro cell corrosion for various concrete mixes were calculated at initial day (0 day), 28 days, 56 days, 90 days and 180 days for the series with water/cement ratios of 0.35, 0.40 and 0.45. The relevance of increasing the water/cement ratio is that it makes the pore system of concrete more susceptible for the migration of aqueous species such as chloride. The results are shown in Figures 9, 10 and 11.

According to ASTM C 876-2009, a least value of 10 µA has been considered to establish the indication of corrosion activity. A positive value in the macro cell current cell confirms the corrosion in progress and vice versa.

![Figure 9. Macro cell current of specimens with water/cement ratio 0.35 and various levels of quartz sandstone in coarse aggregate](image)

Figure 9. Macro cell current of specimens with water/cement ratio 0.35 and various levels of quartz sandstone in coarse aggregate
Figure 10. Macro cell current of specimens with water/cement ratio 0.40 and various levels of quartz sandstone in coarse aggregate

Figure 11. Macro cell current of specimens with water/cement ratio 0.45 and various levels of quartz sandstone in coarse aggregate
For the concrete mixes with water/cement ratio of 0.35, the early values of the control mix were -0.219 µA and the values at 180 days were -0.164 µA. Concrete mixes with 40% quartz sandstone registered a value of -0.160 µA and -0.122 µA, respectively and in the concrete mix with 100% quartz sandstone, the values were -0.159 µA and -0.116 µA, respectively. All the macro cell values were found to be gradually rising from 0 day to 180 days. From the above observations, it can be said that the control mix in all the water/cement ratios showed better resistance to corrosion. At 0.35 water/cement ratio, the substitutions 40%, 60% and 80% showed almost a similar trend with very little deviation. At 0.40 water/cement ratio, the control mix showed a macro cell current of -0.224 µA at 0 day and -0.172 µA at 180 days. At 100% replacement it was -0.142 µA and -0.104 µA, respectively. At 0.45 water/cement ratio, it was -0.187 µA at 0 day and -0.146 µA at 180 days for the control mix and -0.155 µA at 0 day and -0.109 µA at 180 days for 100% substitution.

From the observations, it was clear that the readings were showing a trend of negative to positive for all the concrete mixes i.e. increasing risk for corrosion in the course of 180 days of ponding. The observed readings were nonetheless remaining below 10 µA indicating no evident corrosion. The same conclusion can be drawn for total corrosion calculated as per ASTM G 109-2005. For all the concrete mixes, the total corrosion was less than 150 C which is the threshold value as per the standard.
Conclusions

The following conclusion may be drawn from the study,

- A similar pattern of chloride penetration depth was noticed for control concrete and concrete with 20% quartz sandstone at lower water/cement ratios (w/c < 0.40). In chloride prone areas, the substitution of quartz sandstones can be limited to 20% with proper gradation.

- From the results of corrosion test, as all the values of macro cell corrosion test were less than 10 µA, we may establish that there is no significant evidence of corrosion in the samples after 180 days of ponding. Being sedimentary type of stone, concrete having quartz sandstones tend to perform well at corrosive environments.

References


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