Performance of crushed rock dust concrete exposed to sulphuric and hydrochloric acid solutions

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Abstract. This paper presents the effect of partial substitute of Ordinary Portland Cement 53 grade (OPC) by crushed rock dust (CRD) as filler material in concrete when exposed to 2% and 5% diluted hydrochloric (HCl) and sulfuric (H$_2$SO$_4$) acid solutions. OPC is partially replaced with CRD by: 0%-A40, 10%-A41, 20%-A42, 30%-A43 and 40%-A44 by weight. Visual assessment, mass loss and compressive strength are evaluated at the considered acid attack environment. The loss in compressive strength of CRD concrete has increased gradually with the increase in the CRD. It has been observed that the mass loss (%) and decrease in compressive strength of concrete cube specimens is found to be less in the case of HCl acid attack when compared with H$_2$SO$_4$ acid attack. The use of CRD in concrete as filler material showed comparable trend of decline in the compressive strength of concrete after exposed to both H$_2$SO$_4$ and HCl acid solutions.

1. Introduction
Deterioration of concrete may occur due to strong acid solutions like sulfurous, H$_2$SO$_4$, nitric, HCl and hydrofluoric acids. Bogue compounds in cement matrix when comes into contact with acids, forms soluble and easily erodible substances in concrete which leads to disintegration of concrete. H$_2$SO$_4$, HCl, phosphoric acid and muriatic acid have great impact on disintegration of concrete. If the concentration of these acids is less than 1%, the concrete will disintegrate slowly. Acetic, lactic and organic acids which are by-products of animal and vegetable fats may also cause concrete deterioration. Sulfates will also cause damage to cement matrix through re-crystallization [1-2].

Concrete produced with non-alkali reactive aggregates have more resistance to base solutions like barium, calcium, strontium hydroxide and ammonia. Among all the acids, the most corrosive nature acids are H$_2$SO$_4$, HCl, acetic, nitric and hydrofluoric acid. Some organic acids like acetic, lactic and formic acid also affect the hardened cement matrix. H$_2$SO$_4$ reacts with calcium hydroxide and forms dehydrate gypsum. H$_2$SO$_4$ also reacts with calcium aluminate hydrate gel and forms calcium sulfo-aluminate, which have a immense destructive character. HCl acid reacts with calcium hydroxide and forms soluble calcium chloride which have a dissoluble nature in water. Acid resistance of concrete will depend on the following: (i) Pore structure of cement matrix. (ii) The ability of cement matrix components to reduce the effect of acids. (iii) The products that may form in concrete due to acid corrosion.

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\begin{align*}
H_2SO_4 + Ca(OH)_2 & \rightarrow CaSO_4 \ 2H_2O \\
2HCl + Ca(OH)_2 & \rightarrow CaCl_2 \ + \ 2H_2O
\end{align*}
\]
Acid resistance test of concrete has more consideration due to corrosion of hardened cementations matrix of concrete structural element [3]. The following measures may be adopted to improve the durability of concrete: (i) By selecting the type of cement based on the site environmental conditions. (ii) By restricting the water-binder ratio. (iii) Considering sufficient quantity of cement in producing concrete. (iv) By adopting good quality of coarse and fine aggregate. (v) By applying adequate compaction required for quality and density of concrete.

2. Experimental Program

2.1. Materials and mix design

Ordinary Portland Cement (OPC) 53 grade in compliance to IS 12269:1987 [4] was used. Locally available Krishna river sand (maximum size 4.75mm) in compliance to zone III of IS 383:1970 [5] was used. Crushed stone of maximum size 20 mm in compliance to IS 383:1970 [5] was used. CRD collected from nearby stone processing units was used. CRD passing through 150µm sieve was used as partial substitute for cement (OPC). The physical properties of fine aggregate, coarse aggregate and CRD are shown in Table 1. Concrete target strength of 40 MPa designed as per IS code, IS 10262: 2009 [6] was considered as nominal concrete (A40) mix. The concrete mix proportion obtained was 1:1.39:2.91 (OPC: natural sand: coarse aggregate) with 0.38 as water to binder ratio. Table 2 details the CRD concrete mix proportions.

| S.No. | Physical Property | Result |
|-------|-------------------|--------|
| 1.    | Fine aggregate    |        |
|       | (a) Specific gravity | 2.62  |
|       | (b) Fineness modulus | 2.65  |
|       | (c) Water absorption (%) | 1.0 % |
| 2.    | Coarse aggregate  |        |
|       | (a) Specific gravity | 2.88  |
|       | (b) Fineness modulus | 6.88  |
|       | (c) Water absorption (%) | 0.50 % |
| 3.    | CRD used for partial replacement of cement | |
|       | (a) Specific gravity | 2.52  |
|       | (b) Water absorption (%) | 1.52 % |

Table 2. Concrete mix proportions

| Mix designation | CRD (%) | CRD | Cement | Fine aggregate | Coarse aggregate |
|-----------------|---------|-----|--------|----------------|------------------|
| A40             | 0       | 0   | 450    | 625.5          | 1309.5           |
| A41             | 10      | 45  | 405    | 625.5          | 1309.5           |
| A42             | 20      | 90  | 360    | 625.5          | 1309.5           |
| A43             | 30      | 135 | 315    | 625.5          | 1309.5           |
| A44             | 40      | 180 | 270    | 625.5          | 1309.5           |

CRD concrete constituents in (kg/m³)

2.2. Acid resistance test

Acid attack test was performed on 150 mm CRD concrete cubes which were cured for 28 days using water immersion method and then were immersed in 2% and 5% diluted H₂SO₄ for 28 days and then left undisturbed in natural air for a period 24 hours. A uni-axial compressive load of 0.5 MPa/Sec was applied for measuring the residual compressive strength. Similar acid resistance test was performed using 2% and 5% diluted HCl and the residual compressive strength was measured. The mass loss of CRD concrete cube specimens was estimated by measuring the mass of CRD concrete cube specimens before and after exposure to dilute acid solution [3, 7]. Fig. 1 shows the setup of CRD concrete cube specimens immersed in acidic solutions.
Various chemical tests and physical tests on the concrete resistance capacity to acid attack are developed. But there are no standard or reference procedures to conduct acid test. It is important to conduct the acid test under realistic conditions, as the concentrated acid attack will dissolve the cement matrix of concrete and no assessment of their relative quality is possible. As there are no standards for evaluating the acid resistance of concrete, visual assessment was made as shown in Table 3. Fig. 2 shows a set of concrete cubes immersed in 5% H₂SO₄ solution. Fig. 3 shows a set of CRD concrete cubes immersed in 5% HCl solution.

| Assumed Scale | Acid attack assessment |
|---------------|------------------------|
| I.            | No attack              |
| II.           | Very slight            |
| III.          | Slight                 |
| IV            | Moderate               |
| V.            | Severe                 |
| VI.           | Very severe            |
| VII.          | Partial disintegration |

**Figure 1.** Setup of cubes immersed in acidic solutions

**Figure 2.** Cubes immersed in 5% dilute H₂SO₄ solution

**Figure 3.** Cube specimens in 5% dilute HCl solution

3. Results and Discussion
Tables 4 and 5 show the 28 day cube compressive strength, residual compressive strength results and the average percentage loss in compressive strength of CRD concrete cube specimens after immersion
in 2\% and 5\% dilute H\textsubscript{2}SO\textsubscript{4} solutions, respectively. Fig. 4 shows the variation of compressive strength of A40 and CRD concrete cube specimens after immersion in 2\% and 5\% dilute H\textsubscript{2}SO\textsubscript{4} solutions for 28 days. Fig. 5 shows a set of CRD concrete cube specimens after exposure to 2\% and 5\% dilute H\textsubscript{2}SO\textsubscript{4} solutions are given in Table 6. Table 7 shows the visual assessment of CRD concrete cube specimens after immersed in 2\% and 5\% dilute H\textsubscript{2}SO\textsubscript{4} solutions.

### Table 4. Compressive strength of CRD concrete after immersion in 2\% dilute H\textsubscript{2}SO\textsubscript{4} solution

| Mix designation | CRD Content (%) | Average compressive strength (MPa) \( f_c \) \@ 28 days | Residual \( f_c \) \@ after immersion in 2\% H\textsubscript{2}SO\textsubscript{4} | Average loss (%) of \( f_c \) after immersion in 2\% H\textsubscript{2}SO\textsubscript{4} |
|------------------|-----------------|---------------------------------|---------------------------------|---------------------------------|
| A40              | 0               | 50.23                           | 42.94                           | 14.51                           |
| A41              | 10              | 52.67                           | 47.65                           | 9.53                            |
| A42              | 20              | 54.41                           | 49.65                           | 8.75                            |
| A43              | 30              | 53.22                           | 46.72                           | 12.21                           |
| A44              | 40              | 48.44                           | 40.23                           | 16.95                           |

### Table 5. Compressive strength of CRD concrete cubes.

| Mix designation | CRD Content (%) | Average compressive strength (MPa) \( f_c \) \@ 28 days | Residual \( f_c \) \@ after immersion in 5\% H\textsubscript{2}SO\textsubscript{4} | Average loss (%) of \( f_c \) after immersion in 5\% H\textsubscript{2}SO\textsubscript{4} |
|------------------|-----------------|---------------------------------|---------------------------------|---------------------------------|
| A40              | 0               | 50.23                           | 31.69                           | 36.91                           |
| A41              | 10              | 52.67                           | 35.27                           | 33.04                           |
| A42              | 20              | 54.41                           | 37.52                           | 31.04                           |
| A43              | 30              | 53.22                           | 34.31                           | 35.53                           |
| A44              | 40              | 48.44                           | 28.34                           | 41.49                           |

### Table 6. Mass loss of CRD concrete

| Mix designation | Mass loss (%) after immersion in 2\% H\textsubscript{2}SO\textsubscript{4} | Mass loss (%) after immersion in 5\% H\textsubscript{2}SO\textsubscript{4} |
|------------------|---------------------------------|---------------------------------|
| A40              | 5.8                             | 7.7                             |
| A41              | 5.7                             | 7.1                             |
| A42              | 5.9                             | 7.5                             |
| A43              | 6.4                             | 7.8                             |
| A44              | 7.3                             | 8.9                             |

### Table 7. Visual assessment of CRD concrete

| Mix designation | 2\% H\textsubscript{2}SO\textsubscript{4} | 5\% H\textsubscript{2}SO\textsubscript{4} |
|------------------|---------------------------------|---------------------------------|
| A40              | slight                          | Moderate                       |
| A41              | slight                          | Moderate                       |
| A42              | slight                          | Severe                         |
| A43              | slight                          | Severe                         |
| A44              | slight                          | Very severe                    |
The decrease in the 28 day cube compressive strength CRD concrete after immersion in diluted H₂SO₄ solutions could be accredited to the reaction of H₂SO₄ with calcium hydroxide to form dehydrate gypsum. H₂SO₄ also reacts with calcium aluminate hydrate gel and forms calcium sulfo-aluminate, which have an immense destructive character. These reactions develop peeling and substantial expansion in concrete that leads to the decline in strength, bonding and mass. Furthermore, the reduction in compressive strength of CRD concrete is increased with the increase in concentration of diluted acid solution from 2% to 5%. This could be attributed to the increase in leaching of cementitious compounds due to the reaction between the diluted acid solutions and cement paste. The severity of degradation of concrete exposed to diluted H₂SO₄ solutions depends on the quantity of cement paste that is available to react chemically. The use of CRD in concrete helps in dropping the availability of cement paste and improves the micro filling of concrete that helps in reducing the acid attack of concrete.

Tables 8 and 9 show the 28-days compressive strength, residual compressive strength and the percentage loss of compressive strength of CRD and A40 concrete after immersion in 2% and 5% dilute HCl solutions, respectively. Fig. 6 shows the variation of compressive strength of CRD concrete with CRD as partial replacement of cement after immersion in 2% and 5% dilute HCl solutions for 28 days. Fig. 7 shows a set of CRD and A40 concrete cubes after immersion in 2% dilute HCl solution. The mass loss of CRD concrete specimens after exposure to 2% and 5% dilute HCl solutions are given in Table 10. Table 11 shows the visual assessment of CRD and A40 concrete cubes after immersion in 2% and 5% dilute HCl solutions.

The decrease in the CRD and A40 concrete compressive strength after immersion in diluted HCl solution could be accredited to the reaction of HCl with Ca(OH) forming soluble calcium chloride which has a dissoluble nature in water. This calcium chloride further reacts with C₃A and forms...
ettringite and chloro-aluminate. This could be attributed to the increase in leaching of cementitious compounds due to the reaction between the diluted acid solution and cement paste.

### Table 8. Compressive strength of CRD concrete

| Mix designation | CRD Content (%) | Average compressive strength (MPa) | Average loss (%) of $f_c$ after immersion in 2% HCl |
|------------------|-----------------|------------------------------------|---------------------------------|
| A40              | 0               | 50.23                              | 47.32                           | 5.55                  |
| A41              | 10              | 52.67                              | 50.14                           | 4.80                  |
| A42              | 20              | 54.41                              | 52.52                           | 3.47                  |
| A43              | 30              | 53.22                              | 48.47                           | 8.93                  |
| A44              | 40              | 48.44                              | 45.21                           | 6.67                  |

### Table 9. Compressive strength of CRD concrete

| Mix designation | CRD Content (%) | Average compressive strength (MPa) | Average loss (%) of $f_c$ after immersion in 5% HCl |
|------------------|-----------------|------------------------------------|---------------------------------|
| A40              | 0               | 50.23                              | 42.44                           | 15.51                   |
| A41              | 10              | 52.67                              | 46.87                           | 11.01                   |
| A42              | 20              | 54.41                              | 49.32                           | 9.35                    |
| A43              | 30              | 53.22                              | 45.14                           | 15.18                   |
| A44              | 40              | 48.44                              | 41.21                           | 14.93                   |

**Figure 6.** Compressive strength of CRD concrete after immersion in 2% and 5% dilute HCl solutions.

### Table 10. Mass loss of CRD concrete

| Mix designation | Mass loss (%) after immersion in 2% HCl | Mass loss (%) after immersion in 5% HCl |
|------------------|----------------------------------------|----------------------------------------|
| A40              | 2.4                                    | 4.5                                    |
| A41              | 2.5                                    | 4.3                                    |
| A42              | 2.4                                    | 4.6                                    |
| A43              | 2.6                                    | 5.1                                    |
| A44              | 2.8                                    | 5.7                                    |
Table 1. Visual assessment of CRD concrete

| Mix designation | 2% HCl  | 5% HCl  |
|-----------------|---------|---------|
| A40             | Very slight | Slight  |
| A41             | Very slight | Slight  |
| A42             | Very slight | Slight  |
| A43             | Very slight | Slight  |
| A44             | Very slight | Slight  |

Figure 7. A set of CRD concrete cubes after immersion in 2% dilute HCl solution

4. Conclusions
The present experimental study is mainly aimed on the utilization of fines of crushed rock dust (CRD) as filler material in producing sustainable concrete. Cement is replaced with percentages (0%, 10%, 20%, 30% and 40%) of CRD by weight in producing M40 grade CRD concrete. The conclusions drawn from the experimental studies are outlined. Up to 30% CRD in concrete, the compressive strength is increased and later at 40% CRD content, the compressive strength decreased. In the case of CRD concrete cube specimens immersed in H₂SO₄ and HCl diluted solutions; the loss in compressive strength has increased gradually with the increase of CRD. It has been observed that the mass loss (%) and decrease in compressive strength of concrete cube specimens is found to be less in the case of hydrochloric acid attack when compared with sulfuric acid attack. The severity of degradation of concrete exposed to diluted H₂SO₄ and HCl solutions depends on the quantity of cement paste that is available to react chemically. The use of CRD in concrete helps in dropping the availability of cement paste and improves the micro filling of concrete that helps in dropping the acid attack of concrete.

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