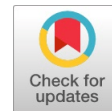


Chemical Modifications of Recycled Concrete Aggregate

Sankalp Kaushik, Pravindra Singh Bhan



Abstract: The necessity for environmental sustainability has prompted the utilization of recycled concrete aggregates (RCA) sourced from structural demolition sites for the production of recycled aggregate concrete (RAC). The primary element impacting the quality of recycled concrete aggregate (RCA) is the mortar paste that adheres to the natural aggregate (NA). The cement mortar adhered to recycled concrete aggregate exhibits higher porosity and water absorption levels, along with reduced strength compared to mortar made with natural aggregate. These characteristics negatively impact both the mechanical properties and durability of fresh and hardened concrete incorporating recycled concrete aggregate. As a result, it is crucial to enhance the interface by improving the surface of the aggregate or by removing the mortar adhered to the NA. Methods for achieving this include surface modification of the aggregate or removing adhered paste from the natural aggregate (NA). This research involves treatment with acidic solutions, particularly hydrochloric acid (HCl) and sulphuric acid (H₂SO₄), for removing mortar layers from RCA. It analyses the impact of these solutions on the mechanical properties of aggregates and the durability of concrete incorporating RCA.

Keywords: Recycled Aggregate, Recycled Aggregate Concrete, Residual Mortar, Sulphuric acid, Hydrochloric acid.

Abbreviations:

CDW	Construction and demolition waste
NA	Natural aggregates
RAC	Recycled aggregate concrete
RCA	Recycled concrete aggregate
IS	Indian Standards
IRC	Indian Road Congress

I. INTRODUCTION

Construction and demolition waste (CDW) refers to the debris generated during the construction, renovation, and dismantling of buildings, bridges, and other structures. In developing countries, approximately 95% of the produced CDW is disposed of in landfills or through illegal dumping in unoccupied areas, along riverbanks, and on roadways. CDW contributes significantly to worldwide waste generation, making it a primary environmental concern. For instance, China generated over 2.4 billion tons of CDW overall.

Altogether, the European Union (EU) produced 850 million tons of CDW. The United States is one of the top producers of CDW worldwide, generating more than 600 million tons. India contributes 530 million tons to CDW generation annually.

Many researchers have explored the use of recycled aggregates (RA) in concrete as an eco-friendly alternative to natural aggregates (NA). This approach aims to efficiently utilise CDW, mitigate the over-exploitation of natural aggregates, and maximise ecological, environmental, and economic benefits in construction. Recently, recycled concrete aggregates (RCA), obtained through processes such as crushing and washing waste concrete, have gained attention for their comparable physical and mechanical properties to those of natural aggregates. Their use not only reduces natural resource consumption but also cuts processing costs, aligning with sustainability goals. The high potential for CDW recycling and reuse has sparked significant market interest in incorporating RA into construction materials and projects. However, the physical and mechanical properties of RA are inferior to those of NA due to the loose pore structures within the old mortar. In comparison to natural aggregate, recycled aggregate (RA) exhibits increased porosity, water absorption, and crushing value, with the crushing process generating microcracks that limit the application and development of RA. To enhance the performance of RA, it becomes imperative to strengthen it. This strengthening process primarily involves physical enhancement technology and chemical enhancement technology, aimed at removing or improving the weak cement mortars on the aggregate surface to enhance its physical properties. Chemical enhancement technology is widely preferred due to its simplicity, minimal equipment requirements, non-destructive impact on grading, and effective strengthening results.

Currently, prevalent techniques in chemical enhancement encompass acid strengthening, polymer emulsion strengthening, pozzolanic cement mortar strengthening, sodium silicate strengthening, and carbonization strengthening. The application of acid solutions facilitates the removal of cement mortar from the aggregate surface, thereby augmenting the aggregate's performance. This research paper exclusively focuses on chemical treatment methodologies.

A. Chemistry of Acid Treatment in RCA

The process entails the dissolution of cementitious materials and the subsequent removal of adhered mortar from the surface of the Recycled Concrete Aggregate (RCA) particles. Acid treatments are used to enhance the properties of RCA, thereby increasing its applicability in concrete-related applications.

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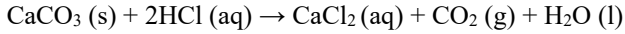
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During acid treatment, the acid interacts with the calcium silicate hydrates (C-S-H) and calcium hydroxide (Ca(OH)₂) phases found in the cement paste adhered to the aggregate particle surfaces.

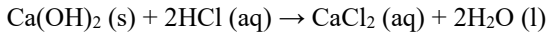
B. Reaction with HCL:

In the case of hydrochloric acid (HCl), the primary reaction involves the dissolution of calcium carbonate (CaCO₃) and calcium hydroxide (Ca(OH)₂) as per the following chemical equations:

Dissolution of calcium carbonate:



Dissolution of calcium hydroxide:

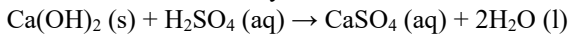


These reactions result in the release of carbon dioxide gas (CO₂) and water (H₂O), along with the formation of calcium chloride (CaCl₂), which is soluble in water and can be washed away from the RCA particles.

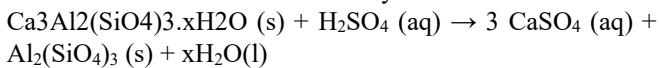
C. Reaction with H₂SO₄:

When sulphuric acid (H₂SO₄) reacts with the cementitious materials in the mortar adhered to the RCA particles, it leads to the dissolution of calcium hydroxide and calcium aluminate hydrates. The reactions involving sulfuric acid are as follows:

Dissolution of calcium hydroxide:



Dissolution of calcium aluminate hydrates:



II. LITERATURE REVIEW

Tang et al., 2019, [1] utilized a 0.5 M solution of sulfuric acid (H₂SO₄) to treat recycled concrete aggregate (RCA) by pre-soaking it for 24 hours while intermittently shaking it within the acidic solution. Subsequently, to eliminate any residue from the acidic solution, the treated RCA underwent washing and immersion in water for an additional 24 hours. The post-treatment outcomes revealed a 10% decrease in water absorption compared to the untreated RCA.

Kim et al., 2018, [2] Investigated the impact of acid treatment on recycled concrete aggregate (RCA) by subjecting it to hydrochloric acid (HCl) and sodium sulfate (Na₂SO₄) in an acidic solution. The ratio of aggregate to acid was maintained at 1:4.5, corresponding to a concentration of 1.2 M, with immersion for 48 hours. Additionally, the solution was replenished after 12 hours of pre-soaking. The findings indicated a reduction of 38.6% for HCl-treated RCA and 34.9% for Na₂SO₄-treated RCA.

Wang et al., 2017, [3] Conducted an experiment where the recycled concrete aggregate (RCA) was pre-soaked in acetic acid (CH₃COOH) solutions at ambient temperature, with varying acid concentrations (1%, 3%, 5%), and immersion durations (1, 3, and 5 days). The study revealed a reduction in water absorption ranging from 9% to 19% across all RCA samples. Notably, the RCA treated with 1% acetic acid exhibited the lowest water absorption performance. The authors attributed the increased water absorption in RCA treated with higher concentrations of acetic acid to the formation of more pores in the treated samples. This pore formation is believed to result from the dissolution of

hydration products and potentially some non-acidic materials present in the acetic acid solution.

Saravankumar et al., 2016, [4] Investigated the enhancement of water absorption in recycled concrete aggregate (RCA) by treating it with hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and nitric acid (HNO₃) at a concentration of 0.1 M. After pre-soaking the RCA for 24 hours, the study revealed improvements in water absorption of 10%, 11%, and 13% for HCl, HNO₃, and H₂SO₄ treatments, respectively.

H.K.A. Al-Bayati, P.K. Das, S.L. Tighe, H. Baaj, 2016, [5] Immersed recycled concrete aggregate (RCA) in acid solutions, specifically hydrochloric acid (HCl) with a purity of 37% and acetic acid (C₂H₄O₂) with a purity of 99.7%, both at a concentration of 0.1 M, for 24 hours at ambient temperature. The findings indicated that treatment with HCl was more effective than treatment with acetic acid.

Pandurangan et al., 2016, [6] Conducted experiments involving concrete mixes incorporating recycled concrete aggregate (RCA) to evaluate the pull-out force between steel and concrete. The mixing ratio by weight adhered to the ACI method, 1:2.18:2.82 (cement:sand: gravel), with a cement content of 380 kg/m³ and a water-to-cement (w/c) ratio of 0.45 for concrete class M35. The replacement ratio of RCA was 91.5%. The findings revealed that the compressive strength improved upon treating the recycled aggregates, reaching over 95% of the strength achieved by concrete containing only natural aggregates (NA).

Al-Bayati et al., 2016, [5] Examined the impact of acidic solutions, including hydrochloric acid (HCl) and acetic acid (C₂H₄O₂), on recycled concrete aggregate (RCA). The treatment involved immersing the RCA in solutions with a concentration of 0.1 M for 24 hours. The results demonstrated a reduction in water absorption of 4.22% for HCl and 4.33% for C₂H₄O₂-treated RCA. Purushothaman et al., 2014, [7] conducted experiments on recycled concrete aggregate (RCA), treating it with hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) at a concentration of 0.1 M. The RCA, which was divided into five particle sizes (20.0, 16.0, 12.5, 10.0, and 4.75 mm), was pre-soaked for 24 hours. The results revealed a reduction in water absorption of 41% and 58% for HCl and H₂SO₄ treatments, respectively, compared to untreated RCA.

Ismail and Ramli, 2013, [8] investigated the immersion of recycled concrete aggregate (RCA) in low concentrations of hydrochloric acid (HCl), specifically at 0.1 M, 0.5 M, and 0.8 M, along with varying pre-soaking durations of 1, 3, and 7 days, aiming to enhance the characteristics of RCA. The findings indicated a reduction in water absorption ranging from 1% to 28%. Notably, more significant reductions were evident at concentrations of 0.5 M and 0.8 M, particularly with smaller RCA particle sizes. Moreover, the study concluded that the duration of pre-soaking in the acidic solution did not significantly influence the reduction in water absorption of RCA.

V.W.Y. Tam, C.M. Tam, K.N. Le, 2007, [9] Conducted an extensive investigation into the removal of residual mortar on recycled concrete aggregate, employing three acids: hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and phosphoric acid (H₃PO₄). The recycled concrete aggregate was pre-soaked in a 0.1 M acid solution for 24 hours at 20°C, followed by rinsing with water to eliminate traces of sulphate (SO₄⁻), chloride (Cl⁻), and phosphate (PO₄) from the aggregate. The levels of SO₄⁻ and Cl⁻ remained within specified limits. Furthermore, the mechanical properties of recycled concrete produced from the treated aggregate exhibited significant improvement.

III. OBJECTIVES

This review paper aims to comprehensively analyze the physical properties of RCA, focusing on its structural, mechanical, and durability characteristics. Additionally, it seeks to evaluate chemical treatments employed to enhance these properties, thereby elucidating their effectiveness in improving the overall quality of RCA. Furthermore, the paper intends to investigate the strength properties of concrete mixtures incorporating modified RCA, to provide insights into the feasibility and sustainability of utilizing modified RCA in concrete construction applications.

IV. METHODOLOGY

A. Materials

- In our project, we have utilised Ordinary Portland Cement (OPC) of grade 53, which adheres to the specifications outlined in IS 12269:1987 and has a specific gravity of 3.14.
- River sand conforming to IS: 383 zone-2 specifications has been employed, exhibiting specific gravity and water absorption values of 2.52 and 1.21%, respectively.
- The coarse aggregate utilized in this project possesses a specific gravity of 2.85 and a water absorption rate of 0.60%.
- The RCA used in this study has a specific gravity of 1.98 and a water absorption rate of 3.29%. Sourced from a demolished building in Kamla Nagar, Agra, the RCA underwent careful collection, where concrete lumps were manually broken down into smaller fragments and sieved to achieve a particle size between 10 and 20 mm.

B. Mix Proportion

By IS code 10262-2019, a concrete mix tailored for M30 grade was formulated, featuring a water-cement ratio of 0.48. The proportions of constituent elements for the blend are delineated in Table 1.

Table 1: Mix Proportion

Concrete Grade	M30
W/C Ratio	0.48
Cement (kg/m ³)	411
Sand (kg/m ³)	627
Coarse Aggregate (kg/m ³)	1177
Water (kg/m ³)	197

C. Process of Obtaining RCA

Demolished building concrete was taken from a site



They were crushed into smaller pieces with the help of a hammer.



The moisture is removed and dried well in an oven.



Aggregates were separated into different sizes through the sieve analysis.



Pretreatment methods for improving the properties of RCA



Tests on modified recycled aggregates

D. Pretreatment Method and Technique for Improving the Properties of RCA

The modification approach involving acid treatment for recycled concrete aggregates sourced from waste concrete relies on the chemical interaction between acidic solutions and the recycled aggregates. Hydrochloric acid, sulfuric acid, acetic acid, phosphoric acid, and similar acidic solutions are commonly employed for acid washing. These acidic solutions undergo a chemical reaction with substances adhering to the surface of recycled aggregates, such as cementitious materials and pollutants. This reaction results in their dissolution or detachment, effectively eliminating surface adherents. Here, we have utilized hydrochloric and sulfuric acid for the dissolution of the mortar layer adhered to the aggregate.



Figure 1 Chemical Reaction Between RCA and Acids



Figure 2 Impurities Left: Illustrating the Removal of Adhered Mortar From RCA



Figure 3 Chemically Treated RCA after 48 hours: H2SO4 (Left Pan), HCl (Right Pan)

The acid treatment modification method proves to be effective in removing cementitious materials and pollutants, enhancing particle shape, and increasing the number of active sites and chemical reactivity on the surface of recycled aggregates. It also improves their bonding capability and interaction with the cementitious matrix.

E. Experimental Procedure

a. Aggregate Crushing Value

The aggregate crushing value provides a measure of resistance to crushing under a gradually applied compressive load. Selecting aggregates with a low aggregate crushing value is crucial for producing high-quality pavement. According to Indian Standards (IS) and Indian Road Congress (IRC) specifications, the aggregate crushing value for coarse aggregates used in cement concrete pavement surfaces should not exceed 30%. Likewise, for concrete applications other than wearing surfaces, the aggregate crushing value should not exceed 45%.

b. Aggregate Impact Value

Toughness refers to a material's capacity to withstand impact. As vehicles traverse roads, aggregates endure impacts, leading to fragmentation. Hence, aggregates require ample toughness to endure impact-induced disintegration, a trait evaluated through the impact value test. This examination assesses the resilience or shock resistance of coarse aggregates, which is critical for evaluating their suitability in road construction under dynamic loading conditions. Aggregates used in road surfaces and bases must endure repeated impact stresses without significant deterioration. The impact value test enables engineers and construction experts to ascertain the ability of coarse aggregates to withstand fracturing under impact loads, ensuring the longevity and robustness of road pavements.

c. Specific Gravity

Specific Gravity, defined as the ratio of an aggregate's weight to that of an equivalent volume of water, plays a crucial role in assessing material strength and quality. Typically, aggregates characterised by low specific gravity demonstrate weaker properties in comparison to those exhibiting higher specific gravity values. This metric assumes pivotal importance in evaluating the quality and density of coarse aggregate, thereby facilitating the formulation and assessment of concrete mixes tailored for various construction endeavours.

d. Water Absorption

The water absorption test for coarse aggregates is performed to assess their capacity to absorb water, which is crucial for evaluating their suitability in concrete and construction applications. This examination provides valuable insights into the porosity and permeability of the aggregates, both of which can significantly impact the characteristics and efficacy of concrete blends. Aggregates exhibiting excessive water absorption might result in drawbacks such as diminished strength, heightened permeability, and potential durability issues in concrete structures.

V. RESULTS AND DISCUSSION

Table 2: Physical Properties of Aggregate

Sr no.	Particulars	Values			
		Natural Aggregate	Recycled Concrete Aggregate	HCL treated RCA	H2SO4-treated RCA
1	Specific Gravity	2.85	1.98	2.45	2.45
2	Water Absorption	0.60	3.29	2.87	2.25
3	Impact values	11.04	17.88	15.45	15.11
4	Crushing values	18.10	34.28	30.60	28.65

- **Specific gravity:** The chemical treatment with sulphuric acid and hydrochloric acid has resulted in a higher specific gravity for the RCA compared to the untreated RCA, indicating increased strength of the aggregates. This outcome from the chemical treatment is satisfactory.
- **Water Absorption:** RCA sourced from demolished concrete consists of crushed stone aggregate with residual old mortar adhering to it, resulting in a water absorption rate of approximately 3.29%, which is notably higher than that of natural aggregates. However, post-treatment, there is a significant decrease in water absorption, bringing it to a range that aligns closely with natural aggregates. The most essential improvements in water absorption are observed after treatment with sulfuric acid (H2SO4).
- **Crushing and Impact Values:** Recycled aggregate exhibits relatively lower strength when subjected to various mechanical forces compared to natural aggregate. According to IS 2386 part (IV), the permissible limits for crushing and impact values on concrete wearing surfaces are 30% and for surfaces other than wearing surfaces, it's 45%. Remarkably, the crushing and impact values of recycled aggregate fall within the specified limits set by the Bureau of Indian Standards (BIS). Consequently, based on the crushing and impact test results, it is feasible to utilize recycled aggregate for applications other than wearing surfaces. Moreover, treating recycled concrete aggregate (RCA) with H2SO4 yields more favourable outcomes in comparison to treatment with HCl, indicating potential improvements in its properties for various applications.

Table 3: 28-day Compressive Strength

Replacement of NA	0%	10%	20%	30%
Untreated RCA	39.5	36.64	33.98	30.44
HCL treated RCA	-	37.72	34.39	32.68
H2SO4-treated RCA	-	37.99	34.78	33.20

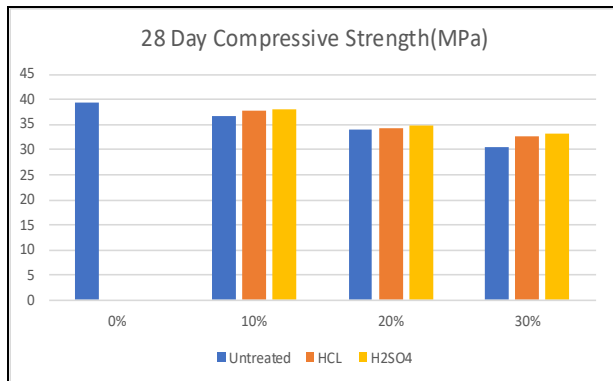


Figure 4: 28-day Compressive Strength

- Compressive strength: As expected, it appears that the compressive strength of concrete incorporating recycled concrete aggregate (RCA) tends to decrease as the percentage of replacement of natural aggregate (NA) with untreated RCA increases. However, when the RCA is treated with either HCl or H₂SO₄, there seems to be an improvement in the compressive strength compared to untreated RCA. Specifically, for both HCl-treated and H₂SO₄-treated RCA, the compressive strength increases compared to untreated RCA.
- This suggests that the chemical treatment of RCA has a positive effect on its performance in concrete mixtures, potentially mitigating some of the negative impacts associated with using untreated RCA. In conclusion, while the replacement of NA with untreated RCA results in a decrease in compressive strength, the use of treated RCA, particularly with HCl or H₂SO₄, shows potential for enhancing the compressive strength of concrete mixtures.

VI. CONCLUSION

- Incorporating recycled aggregate up to 30% does not compromise the structural functional requirements, as indicated by the test results.
- Numerous tests performed on recycled aggregates, along with a comparison to natural aggregates, align with the standards outlined in IS 2386, affirming their satisfactory performance after treatment.
- The use of recycled aggregate is viable for applications other than wearing surfaces, as indicated by crushing and impact test results. Notably, treatment with H₂SO₄ leads to the most significant improvements in water absorption, crushing, and impact values. Additionally, both H₂SO₄ and HCl treatments result in significantly improved compressive strength at 7 and 28 days compared to untreated RCA, suggesting their effectiveness in enhancing concrete properties.

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Ethical Approval and Consent to Participate	No, the article does not require ethical approval or consent to participate, as it presents evidence that is not subject to interpretation.
Availability of Data and Materials	Not relevant.
Authors Contributions	All authors have equal participation in this article.

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