



# Carbonation Effects and Its Mitigation Measures in Concrete/Cement Mortar Mass Made of Cent Percentage Recycled Coarse and Fine Aggregates

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## ABSTRACT

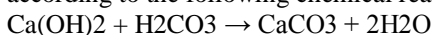
The recycled demolished concrete aggregate obtained from processing unit contains the maximum amount of calcium hydroxide (lime) and these lime in reaction with atmospheric carbon dioxide and forming a calcium carbonate and reducing the PH of the aggregates and making the aggregates mass carbonated. These carbonated aggregates when used in concrete/cement mortar results in intense carbonated mass with PH of the mass less than 9 and thereby damaging the mass and rendering it unfit for its intended use. The research deals with the process and technique dealing with improving the surface and internal structure of the recycled aggregate mass obtained from processing plants and making it fit for its usage in production of concrete /cement mortar mass and analyzing the process of the carbonation in the concrete/cement mass prepared with conventional and treated and untreated demolished concrete coarse and fine aggregates. The results obtained have shown a surface modification and surface treatment methods founds to be an effective solution countering the carbonation of the aggregates and the treatment helps in retaining the hydroxide ion concentration (OH<sup>-</sup>) and its usage in the concrete/cement mortar mass helps in retaining the alkalinity at par with conventional concrete and makes mass more dense and self resilient.

**Key Words:** Recycled Aggregates, Surface Modification, Surface Treatment, Carbonation, Strength

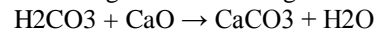
## 1. INTRODUCTION

### 1.1 General

Weathering carbonation, or atmospheric carbonation, occurs in concrete when calcium compounds react with carbon dioxide (CO<sub>2</sub>) from the atmosphere and water (H<sub>2</sub>O) in the concrete pores. First, the CO<sub>2</sub> reacts with the water in the pores to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>). The carbonic acid then reacts with the calcium compounds contained within the hydration products that are present in mature concrete, mainly calcium hydroxide. Calcium carbonate (CaCO<sub>3</sub>) forms according to the following chemical reaction:



Once the Ca(OH)<sub>2</sub> has carbonated and is depleted from the cement paste, the calcium-silicate-hydrate gel (C-S-H) can be decalcified thereby allowing the liberated CaO to carbonate according to the following chemical reaction:



The depletion of calcium hydroxide will cause the concrete pore solution pH to drop below 13. The pH can reach as low as 8 for fully carbonated concrete. Concrete with ferrous reinforcement requires a high pH to ensure the stability of the protective passive layer on the surface of the reinforcement. A drop in the pH level can cause the passive layer to deteriorate, thereby making the reinforcement susceptible to harmful corrosion. This is a particular issue if the reinforcement is exposed to aggressive agents such as chloride ions. The corrosion products occupy a greater volume than the original ferrous reinforcement and, in a hardened, mature microstructure, can create internal stresses that cause cracking of the concrete cover. For clarification of how this pH reduction actually happens, it's important to understand that pH, a term deriving from the German words for "power of hydrogen," is a measure of the hydrogen ion concentration in a water solution. The pH scale ranges from 0, representing very acidic substances such as car battery acid, to 14, representing very alkaline substances like sodium hydroxide, also known as lye. Pure water is considered neutral at a pH of 7.

Calcium hydroxide contains two hydrogen ions and is a main source of strength in a concrete matrix. Calcium carbonate contains zero hydrogen ions. After some of the calcium hydroxide is consumed during the carbonation process and is partially replaced by calcium carbonate, hydrogen ions still exist in the matrix but at a lower concentration. The weaker hydrogen ion concentration reduces the concrete's pH. Exposure conditions, primarily the relative humidity, can have a significant effect on the depth of carbonation and the amount of CO<sub>2</sub> absorbed over time. In general, carbonation only occurs when the relative humidity is between 40 and 90%. If the relative humidity is too low then there is insufficient water in the pores for CO<sub>2</sub> to dissolve to form the carbonic acid needed to react with the calcium compounds. If the humidity is too high then the CO<sub>2</sub> pore network is full of water and ingress of the carbon dioxide is inhibited. When the relative humidity is in a moderate range the conditions are ideal to

promote a greater carbonation depth and thus a higher CO<sub>2</sub> absorption. The recycled demolished concrete aggregates which are obtained from processing plant contains the cement hydrated paste adhered to the individual grains of the aggregates and these adhered paste contains the byproduct of the cement hydration process i.e to the maximum extent the lime, these lime upon exposure to the atmospheric air and to the rains has made the atmospheric carbon dioxide to ingress into the grain of the recycled aggregates mass and the increased CO<sub>2</sub> reacts with calcium hydroxide (Ca(OH)<sub>2</sub>) and forms a calcium carbonate and thereby making the aggregates susceptible to carbonation. And also as gathered from the literature review the usage of the carbonated aggregates in concrete/mortar mass will result in carbonated mass which will be unfit for its usage in any type of work. The effective way of reducing the carbonation of the aggregates, is immediate drawl of the processed aggregates from processing plant and removing the reusing the excess lime in initiation of rehydration process by way of surface treatment methods and also imparting the surface modification by way of removing the surface defects or localized cracks on the processed aggregates and on these processed aggregates the various surface treatment methods will be employed in mitigating the carbonation.

### 1.2 Objectives of The Work

- To identify cause of carbonation in recycled demolished concrete coarse and fine aggregates.
- To employ a surface modification and surface treatment methods on the recycled aggregate mass in mitigating the carbonation effects.
- To study the impact of hydroxide (OH<sup>-</sup>) ion concentration and its effects on carbonation and the contribution of surface modification and surface treated methods in enhancing the hydroxide ion concentration.

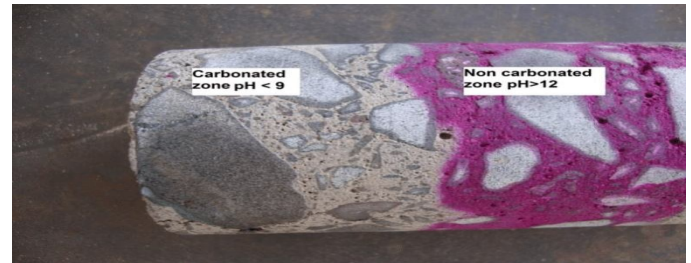
### 2. EFFECTS OF CARBONATION

As defined in the introduction, carbonation of concrete is a process by which Carbon di-Oxide from the air penetrates into the concrete and reacts with calcium hydroxide to form calcium carbonates. Conversion of Ca(OH)<sub>2</sub> into CaCO<sub>3</sub> by action of CO<sub>2</sub> by itself is not reactive. In the presence of moisture, CO<sub>2</sub> changes into dilute carbonic acid which attacks the reinforcement and also reduces alkalinity of concrete. In this test Phenolphthalein solution is used as indicator. Application Carbonation of concrete is one of the main reasons for corrosion of reinforcement. Oxygen and moisture are the other components required for corrosion of embedded steel. In this test, the depth of carbonation is determined. The rate of carbonation depends on the grade of concrete, permeability of concrete, whether the concrete is protected or not, depth of cover, time, etc.

### 3. EVALUATION OF CARBONATION

The test done as per the specifications defined in ISO 1920-12:2015(en) testing of concrete-Part12: Determination of the carbonation resistance of concrete. Procedure for carbonation test: This test is most commonly carried out by spraying the

indicator on freshly exposed surfaces of concrete broken from the structure. Carbonation depth is accessed by using a solution of phenolphthalein indicator that appears pink in contact with alkaline concrete with pH value in excess of 9 when the concrete is not carbonized. Colourless at lower levels of pH value when concrete is carbonated and the protective layer gets destroyed and the steel is exposed to corrosion.



Source:- <http://www.ircen.gov.in/LAB/res/html/Test-34.html>

**Figure 1:** Specimen for Carbonation Test on Concrete

The measure of the pH value also helps in understanding the nature of the carbonation i.e., A pH reduction in steel-reinforced concrete is more troublesome than in non-steel-reinforced concrete. The highly alkaline environment of concrete, which usually has a pH in excess of 12, creates a protective, passivating oxide layer around steel, protecting the reinforcement from corrosion. Carbonation is capable of reducing a concrete's pH to a value less than 9, which significantly weakens, or could even eliminate, the steel's protective layer. It's important to note that the pH scale is logarithmic of hydroxide ion concentration, the more the hydroxide concentration it is more alkaline and since it is a logarithmic which meaning that each step on the scale changes the pH by a factor of 10. This means a five point drop on the pH scale, as experienced by a concrete sample with an initial pH of 13 that drops to 8 after bi-carbonation, is a 100,000-fold reduction in the concrete's pH. The measure of Hydroxide ion concentration helps in assessing the source and mitigation measure to be initiated to control the parameters.

Calculation of OH<sup>-</sup> Concentration.

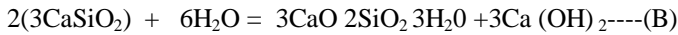
$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= -(\log_{10}^{(\text{OH}^-)}) \\ (\text{OH}^-) &= (10^{-\text{pOH}}) \\ (\text{OH}^-) &= (10^{-(14-\text{pH})}) \quad \text{--- (A)} \end{aligned}$$

Measurement of pH is done as per the test procedure defined in ASTM C 25, "Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime" as per that Mix 10 g (0.35 oz) of sample with 200 mL (6.8 fl oz) of deionised water. Stir for 30 minutes, and let the solution stand for 30 minutes. Measure pH with a pH probe and meter. Report pH value to four significant figures; The same technique employed on the aggregate and concrete/cement mass by using their powder for preparation of the solution as defined in ASTM C 25. Measurement of the Electrical conductivity of the solution made for measurement of pH can be used to access the carbonation of the material as the generation of carbon dioxide in the material will cause the increase in the conductivity and any increase in the conductivity of the material with the standard reference level will help in studying the impact of the carbonation and also the molecules capacity of releasing the carbon dioxide ions.

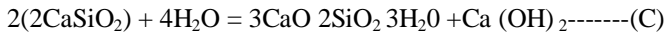
**4. EXPERIMENTAL WORK**

The recycled demolished concrete aggregate samples as obtained from the processing plant were tested for carbonation and as observed from the below pics ,it was found that the recycled demolished concrete aggregates so obtained from the processing plant are carbonated and the main cause of the carbonation is the formation of excess lime in the recycled demolished concrete aggregate surface, When cement is added to the conventional aggregates along with water the following is the resultant chemical reaction and these after concrete formation when demolished will contain excess lime ,the detail reaction process and byproduct formed is as explained,

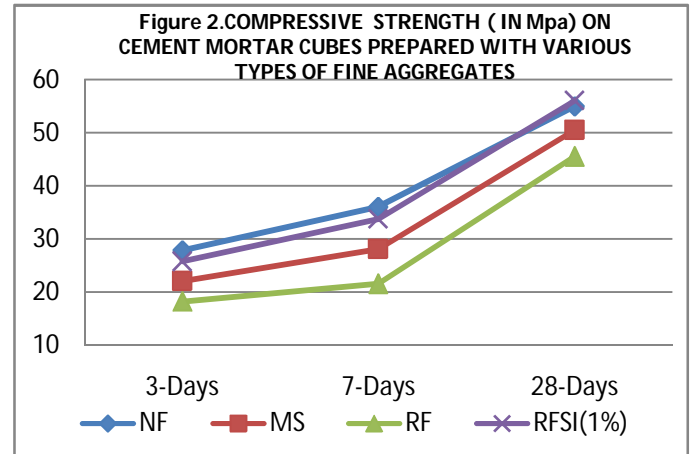
**1. Tricalcium Silicate**



**2. Dicalcium Silicate**



These excess lime which is the byproduct remain on the surface of the recycled demolished concrete aggregates and which upon reaction with atmospheric moisture and carbon dioxide converts the lime into calcium carbonate and thereby making the aggregate mass carbonated. The best way of preventing the carbonation is by ways of using the excess lime produced is by generation of rehydration process and also with an intention of the cent percentage utilization of recycled demolished coarse and fine aggregates in concrete/cement mortar preparation. The tests were done in the laboratory, on recycled demolished concrete coarse and fine aggregate with various surface modification and surface treatments techniques viz., surface modification by ball mill method to remove the surface defects and minor cracks etc from the aggregate surface and on these modified aggregates various treatment techniques such as Densification, Hydrophobization, Polymerization and a combination of Densification and Polymerization and on treated aggregates physical properties have been evaluated and on the improved properties the best combination has been selected and on these combinations, the concrete /cement mortar cubes specimens were casted and tested for its compressive. Based on the test results it was found that a densification process of surface treatment method is effective in improving the properties of the aggregates and the concrete/cement mortar mass prepared with these aggregates i.e., a final combination of 2.5% of lithium silicate treatment on a recycled demolished concrete coarse aggregate and 1% colloidal silica dioxide treatment on demolished concrete fine aggregate found to be the best treatment for its usage in concrete and 1% colloidal silica treatment on recycled fine aggregate in its usage in preparation of cement mortar. The test values of compressive strength on cement mortar are depicted in figure 1. Table 01 depicts the Mix design adopted on concrete samples.

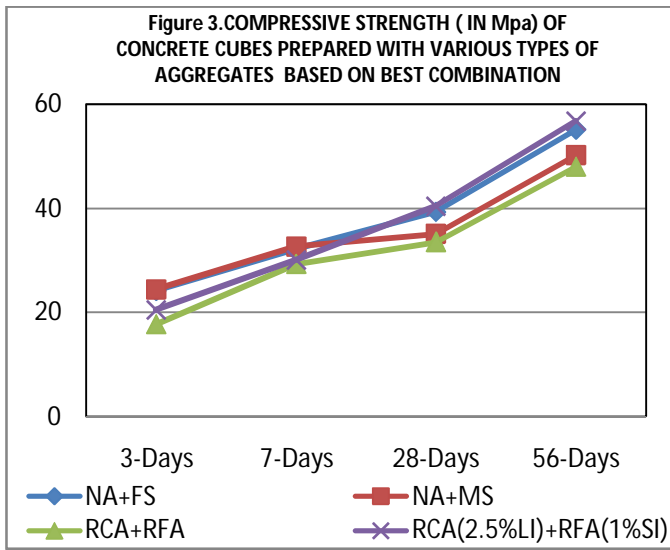


**Table 1:** M30 Grade Concrete Mix Design Using Different Types of Coarse and Fine Aggregates

Final Proportion of materials at the site	NCA+N FA	NCA+M-Sand	RCA+R FA	RCA(2.5%LD)+RFA(1%SD)
Water(ltr)	161.278	176.65	210.14	223.98
Cement(Kg)	350.22	350.22	350.22	437.77
Chemical Admixture(ltr)	2.98	2.98	2.98	0
Fine Aggregate(kg)	698.865	688.57	536.7	613.94
Coarse Aggregate(kg)	1190.72	1190.72	1152.94	1179.57

**4.1 Mechanical Properties on Hardened Concrete**

With the usage of a final combination of 2.5% of lithium silicate treatment on recycled demolished concrete coarse aggregate and 1% colloidal silica dioxide treatment on demolished concrete fine aggregate, to test its mechanical properties on concretes a set of cubes were casted and tested for compressive strength. And the same were compared with that of concrete cubes casted with Natural Coarse and fine aggregates and also compared with set of cubes and cylinders prepared untreated recycled demolished coarse and fine concrete aggregate .The results on the same are graphically presented at Figures 3.All the mechanical properties on hardened concrete prepared with treated recycled demolished concrete coarse and fine aggregates have shown improved performance as compared with that of concrete made of untreated recycled demolished concrete aggregates,



### 4.2 Carbonation of Concrete

As defined in the introduction carbonation of concrete is associated with the corrosion of steel reinforcement and with shrinkage. Carbonation is the result of the dissolution of CO<sub>2</sub> in the concrete pore fluid and this reacts with calcium from calcium hydroxide and calcium silicate hydrate to form calcite (CaCO<sub>3</sub>). Aragonite may form in hot conditions. Within a few hours, or a day or two at most, the surface of fresh concrete will have reacted with CO<sub>2</sub> from the air. This action will be sever in metropolitan cities. Gradually, the process penetrates deeper into the concrete at a rate proportional to the square root of time. After a year or so it may typically have reached a depth of perhaps more than 1 mm for dense concrete of low permeability made with a low water/cement ratio, or up to 5 mm or more for more porous mass. The affected depth from the concrete surface can be readily shown by the use of phenolphthalein indicator solution. The phenolphthalein indicator solution is applied to a fresh fracture surface of concrete. If the indicator turns purple, the pH value is above 8.6. Where the solution remains colourless, the pH value of the concrete is below 8.6, suggesting carbonation. A fully-carbonated paste has a pH of about 8.4. In our study we have used the same on 28 days cured sample that were kept exposed to outside atmosphere for 180-days and on these crushed cubes and the core samples the Phenolphthalein indicator was applied to study the depth of carbonation. And from images enclosed it can be seen that that in concrete mass prepared with conventional aggregates and with treated aggregates the inside mass has been tuned into purple and whereas in concrete mass prepared with recycled aggregates has shown in patches area purple colour formation. Which shows that at 180-days of exposure the concrete mass prepared with treated coarse and fine aggregate is less susceptible to carbonation and its behaviour is at par with that of concrete mass prepared with conventional aggregates Whereas in concrete mass prepared with untreated aggregates has shown sever affect to carbonation. Similar we can see the above affect on treated and untreated coarse and fine recycled concrete aggregates, the treated aggregates has shown purple colour formation, which indicates that in treated aggregates the rehydration process was initiated and acidic

behaviour was converted into alkaline nature. These was mainly due to lithium silicate, where the lithium which being top in periodic table and in alkaline group is light in weight and highly reactive compared to counter parts in periodic table and it is easily soluble in water, these lithium silicate upon treatment on aggregates imparts a alkaline nature to the aggregates and to the concrete mass, the lithium silicate also react with calcium hydroxide covering the substrate, forming complex tri-calcium silicate compounds that keep moisture out. These compounds block the micro pores in concrete, practically eliminating moisture absorption into the concrete substrate. The above reaction of the lithium silicate in treated and in untreated aggregates and in concrete mass can be measured exactly with measurement of the pH of the respective mass and the same was done as per the procedure defined in ASTM, The sample of each mass which is under study has been extracted and diluted with deionised water and tested for its pH using the Portable digital pH meter, the pH value obtained and the calculated Hydroxide ion concentration using equation A, has been depicted in the below figure. On the same solution for different sample under test study, the test for electrical conductivity was conducted using the portable electrical conductivity measuring instrument. The images of the testing process and its obtained values are depicted in Table.2



Figure 4. Measurement of the pH and EC of the Solutions

Table 2. pH value and Hydroxide Ion Concentration of Different samples under study

Sl No	Description of the Material	pH Value	Hydroxide Ion Concentration (OH-) (moles/liter)	Electric al Conductivity (µS/cm)
1	Untreated Recycled Demolished Concrete Coarse Aggregate	8.5	0.00000316	4090
2	Untreated Recycled Demolished Concrete Fine Aggregate	8	0.00000100	4300
3	Treated Recycled Demolished Concrete Coarse Aggregate	11	0.00100000	3650

4	Treated Demolished Concrete Fine Aggregate	Recycled Concrete	10.5	0.00031622	3800
5	Concrete Prepared with Aggregates	Prepared with Convention	12	0.01000000	3950
6	Concrete Prepared with Recycled Aggregates	Prepared with Untreated	9	0.00001000	4200
7	Concrete Prepared with Treated Recycled Aggregates	Prepared with Recycled	12.3	0.01995262	3400
8	Cement Prepared with Convention Aggregates	Mortar with Fine	12.5	0.03162277	3780
9	Cement Prepared with M-Sand	Mortar Prepared with	12	0.01000000	3890
10	Cement Prepared with Untreated Recycled Aggregates	Mortar with Fine	9.5	0.00003162	4240
11	Cement Prepared with Recycled Aggregates	Mortar with Fine	12.7	0.05011872	3640



a. Untreated Recycled Coarse Aggregate



b. Treated Recycled Coarse Aggregate



c. Untreated Recycled Fine Aggregate

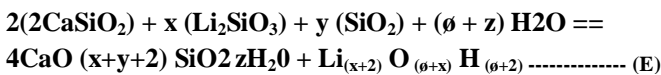
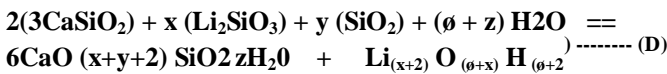


d. Treated Recycled Fine Aggregate

Figure 6: Carbonation effect on Concrete Mass Prepared with Different Types of Aggregates



The above defined tests are done on the core samples extracted from concrete core samples at 56-days and tested for carbonation and the depth of discoloration is more in concrete made of treated recycled aggregates and it is least carbonated. The hydroxide concentration in the concrete and cement mortar mass can be explained in detail with below mentioned chemical reactions,



By comparing the equations B, C, D, E it can be observed that Hydroxide Ion has been transferred from calcium to lithium and availability of the freely available hydroxide ion is nil in the concrete mass prepared with treated recycled demolished concrete coarse and fine aggregates, whereas the availability of these hydroxide ion is abundant in untreated recycled demolished concrete aggregates. From electrical conductivity also it can be inferred that the electrical conductivity of the concrete/mortar mass prepared with treated recycled aggregates is less as compared with that of the concrete/cement mass prepared with the conventional aggregates and with that of the untreated recycled aggregates. This clearly indicates that presence of CO<sub>2</sub> and its release leads to an increase of the electrical conductivity of the material. This increase in the electrical conductivity is due to the dissolution of calcite with release of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> in the presence of moisture.

Figure 5. Carbonation affect on Untreated and Treated Coarse and Fine Recycled Concrete Aggregates

**a. Conventional Concrete Mix**



**b. Concrete made of Untreated Recycled Coarse and Fine Aggregates**



**c. Concrete made of Treated Recycled Coarse and Fine Aggregates**



**Figure 7:** Effect of Carbonation on Concrete Core Sample

**5. EDITORIAL POLICY**

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**6. CONCLUSIONS**

1. The surface modification and surface treatment method proves an effective technique in improving the performance of

the recycled demolished concrete coarse and fine aggregates against carbonation.

2. The concrete and the cement mortar mass prepared with surface modified and surface treated recycled aggregates proves to mitigate carbonation and improves the pore structure and thereby acting as a barrier for percolation of CO<sub>2</sub> and Cl.

3. The surface treatment method adopted using the lithium silicates and silica hydroxide controls the movement of hydroxide ions (OH<sup>-</sup>) and makes them bonded with lithium. Thus on overall restricting the movement of free hydroxide ions, thereby is preventing the carbonation action. Further, the free movement of Ca<sup>+</sup> is restricted as it reacts with silica dioxide and form calcium silicate. Thus preventing and providing overall control on carbonation.

4. Electrical conductivity of the material proves to be an effective tool in accessing the movement of CO<sub>2</sub> and its effects on carbonation, and in present study it indicates the extent of carbonation.

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