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A Study on CO₂ Adsorption of Zeolite Plasters and its Effects on Durability Properties of RCC Members, Concrete Tiles and Floorings

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ABSTRACT

Nowadays the CO₂ concentration in the atmosphere is drastically getting increased leading to serious effect like global warming. To hold this in control Zeolite molecular sieves can be used as plasters on the surface of concrete members and tiles. These surface plasters can adsorb CO₂ on their surfaces to form monodentate carbonate species. Sealing them with sealers like PVC coatings can lock CO₂ and these tiles can be commercialized as a product. Sand can be fully replaced in the mortar and these Zeolite plasters are applied over the Concrete cubes to adsorb large quantity of CO₂ at their surfaces. Here the Zeolite 4A is plastered over the surface of concrete and its CO₂ adsorbing capacity per sq.m area was studied. The Strength properties of Zeolite Plastered Concrete (ZPC) and Conventional Concrete (CC) were compared. Further its effects on durability properties of concrete like Carbonation depth, Fire Resistance at three different temperatures of 250°C, 500°C, 750°C and variations in their strength properties due to this over the ages were studied. The ZPC show better results in CO₂ adsorption and fire test than that of CC.

Key words: CO₂ Adsorption, Zeolite Plasters, Concrete Durability

INTRODUCTION

Concrete is an economical, versatile and highly successful construction material used to build structures. Cement is the main ingredient for concrete. But the cement manufacturing plants release about 0.85 ton of CO₂ for every 1 ton of cement manufactured [7]. Thus they increase the amount of CO₂ in the atmosphere there by increasing the rate of Global warming. The concrete structures like chimneys in thermal power plants, cement manufacturing plants and the structures lying nearby highly traffic areas are subjected to severe environmental conditions throughout its service life. So the structures need to satisfy two main things such as strength and durability. There are many methods available for capturing CO₂ [2] Here Zeolite 4A (artificially manufactured Zeolite) was used to adsorb CO2. Zeolites fall under two categories namely Natural Zeolites [3] and Artificial Zeolites manufactured from various materials like flyash [1][5]. Research has been done previously by using Zeolite as natural pozzolanic material [6]. Eskandari et al [11] have used Zeolite as a micro particle in concrete and its durability were investigated by Electrical Resistivity (ER) and Rapid Chloride Penetration Test (RCPT) at the ages 28 and 90 days. Their results show Zeolite has an increased resistance to chloride penetration and increased electrical resistivity. Here ZPC in the form of tiles are suggested to be used in the Cement manufacturing plants, so that these plasters can adsorb the CO₂ at their source. A small chamber has been built before the Chimney exhaust portion. These ZPC tiles were placed there and the effluent was allowed to pass through, after the attainment of maximum adsorption limit these tiles must be sealed using PVC coatings. These PVC coated ZPC tiles can be commercialized later. The main objectives of this work is to determine the CO₂ adsorbing capacity of Zeolite by titration method [8], compressive Strength, Fire Resistance and Water absorption capacity of ZPC cubes.

MATERIALS

Cement

Cement used in this investigation was 53 Grade Ordinary Portland cement confirming to IS: 12269[9]. The specific gravity of cement was 3.15 and having initial and final setting time of 45 min and 560 min respectively.

Fine Aggregate

The fine aggregate was conforming to Zone-II according to IS: 383[10]. The fine aggregate used was obtained from a nearby river source. The specific gravity was 2.67, while the bulk density of sand was 1.43 gram/c.c.

Coarse Aggregate

Crushed granite was used as coarse aggregate. The coarse aggregate was obtained from a local crushing unit having 20mm nominal size, well graded aggregate according to IS: 383[10]. The specific gravity was 2.83, while the bulk density was 1.52 gram/c.c.

Zeolite 4A

Zeolite 4A is a molecular sieve available in market in pellet and cylindrical forms. Here pellet form size of 2 to 3mm was used. They have a Si/Al ratio of about 2 (lesser the ratio more would be the rate of adsorption). Fig.1 shows the physical appearance of Zeolite 4A and Table 1 shows its Chemical Composition. They are used to adsorb CO₂ [4].



Fig.1 Zeolite 4A

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Chemical Component	% of Chemical Component
Silicon dioxide (SiO ₂)	54.50
Aluminium oxide (Al ₂ O ₃)	27.15
Ferric oxide (Fe ₂ O ₃)	01.44
Calcium oxide (CaO)	01.68
Magnesium oxide (MgO)	01.20
Sodium oxide (Na ₂ O)	02.04
Sulfur trioxide (SO ₂)	00.50
Potassium oxide (K ₂ O)	01.42
Loss on ignition	10.32

Table - 1 Zeolite 4A Chemical Composition

CASTING, CURING AND TESTING

The concrete mix of M25 grade was prepared in a laboratory mixer with the capacity of 120kg. For each group, total of 9 samples of cube specimens with the dimension of 150 mm were prepared. The specimens were kept in laboratory conditions for 24 h until demoulding and kept for curing. These concrete after curing were plastered with Zeolite plasters at a ratio of 1:3 (1 part of cement: 3 parts of Zeolite pellets) as shown in Fig. 1. Then they were placed in Carbonation chamber shown in Fig. 2 to study the rate of adsorption of CO₂. Tiles of 0.75inch and 1inch were cast as shown in Fig. 3, 4 respectively. Further to study their durability properties, different tests such as Carbonation Test, Fire Test, Water absorption and Compressive Strength over ages were conducted.



Fig.2 ZPC cubes



Fig.4 0.75inch ZPC Tiles



Fig.3 Carbonation Chamber



Fig.5 1 inch ZPC Tiles

CO₂ ADSORPTION

The cube specimens after plastering with Zeolite were placed in CO_2 atmosphere. The initial amount of CO_2 from the fire source is noted and the final reading after passing through cubes is noted. The difference in level is the amount of CO_2 adsorbed and it was calculated by Titration method.

Titration method for Calculating Amount of CO₂

The exhaust CO_2 gas is passed into a balloon containing excess of NaOH (Sodium Hydroxide) solution where it is absorbed and converted to equivalent amount of Sodium Carbonate. Containment of CO_2 in such a closed environment provide necessary contact time with NaOH for complete absorption. The resulting mixture containing excess of Sodium Hydroxide and Sodium Carbonate is treated with standard HCl. Titration to the first colourless phenolphthalein endpoint neutralizes the excess NaOH and converts all of Sodium Carbonate to Sodium bicarbonate. Continuation of titration to second methy orange endpoint converts all Sodium bicarbonate to water and CO_2 . The difference in millilitres between the first and second endpoints is used to calculate the CO_2 present in the exhaust.

The amount of CO_2 = (Volume of Titrant in L × Molarity of standard acid x Molecular Weight of CO_2)

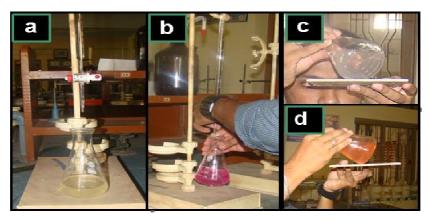


Fig.6 a) CO₂ absorbed Sodium carbonate solution b) Titration in progress c) First end point d) Second end point

DURABILITY TESTS CONDUCTED

Compressive Strength

The cube specimens were tested on compression testing machine of capacity 200 Tonnes. The bearing surface of the machine was wiped off clean and any loose sand or other material removed from the surface of the specimen the load applied was increased continuously at a constant rate until the resistance of the specimen to the increasing load breaks down and no longer can be sustained. The maximum load applied on the specimen was recorded. The compressive strength results for specimens without and with Zeolite plastering at 28days, 56days and 90days were tabulated and compared

Carbonation Test

The carbonation test was performed on 18 cubes of standard size 150x150x150mm in which 9 cubes with Zeolite plastered over its surface and 9 without. They were placed in CO_2 environment for 28 days after that they were split into two parts. A pH indicator solution, i.e. phenolphthalein, was sprayed on the obtained cross sections in order to determine carbonation depth. The reported carbonation depth is the mean value of 24 measured depths per disk. Table 6 gives an overview of the results of the accelerated carbonation tests.

Fire Test

Fire test was performed as per ASTM E 119-15 (Standard Test Methods for Fire Tests of Building Constructions and Materials). The standard cubes were placed in electric furnace at 250°C for 2hours and then tested for its compressive strength. The change in compressive strength is noted down. This procedure is repeated for 500°C and 750°C.

Water Absorption

Water absorption test was done as per ASTM C140-11a. The test specimens was immersed in water at a temperature of 60 to 80°F (15.6 to 26.7°C) for 24 to 28 h such that the top surfaces of the specimens are no less than 6 in. (152 mm) below the surface of the water. Specimens were separated from each other and from the bottom of the immersion tank by at least 1/8 in. (3.1 mm). The cube was removed from the water and allowed to drain for 60 to 65 s by placing them on a 3/8-in. (9.5-mm) or coarser wire mesh, visible surface water was removed with a damp cloth;

weighed and recorded as W_s (saturated weight). Specimens were dried in a ventilated oven at 212 to 239°F (100 to

weighed and recorded as W_s (saturated weight). Specimens were dried in a ventilated oven at 212 to 239 F (100 to 115 °C) for not less than 24 h and dried specimens weight was noted as W_d (oven-dry weight).

The percentage of absorption = $\frac{W_s - W_d}{W_d} \times 100\%$

Where W_s = saturated weight of specimen (kg), and W_d = oven-dry weight of specimen (kg).

RESULTS AND DISCUSSION

CO₂ Adsorption

The amount of CO_2 adsorbed was calculated using Titration method [9] each day and it was found that the rate of adsorption decreases and becomes nil on 40^{th} day. The Fig. 1 and Table-1 shows the details of Amount of CO_2 adsorbed per day. From calculation the CO_2 adsorbing capacity of Zeolite was found to be 83.67 g/m².



CO2 Amount

CO3 Amount

CO4 Amount

CO5 Am

Fig.7 Cubes exposed to CO₂ atmosphere

Fig.8 Rate of adsorption by ZPC Cubes

Table 2 - Rate of adsorption of CO₂ by ZPC Cubes

Day	Initial CO ₂ reading (g)	Final CO ₂ reading (g)	Amount of CO ₂ Adsorbed (g)	Day	Initial CO ₂ reading (g)	Final CO ₂ reading (g)	Amount of CO ₂ Adsorbed (g)
1	5.89	0.14	5.75	21	5.89	2.29	3.60
2	5.89	0.26	5.63	22	5.89	2.41	3.48
3	5.89	0.37	5.52	23	5.89	2.59	3.30
4	5.89	0.44	5.45	24	5.89	2.59	3.20
5	5.89	0.53	5.36	25	5.89	2.80	3.09
6	5.89	0.65	5.24	26	5.89	2.96	2.93
7	5.89	0.72	5.17	27	5.89	3.12	2.77
8	5.89	0.89	5.00	28	5.89	3.36	2.53
9	5.89	0.94	4.95	29	5.89	3.58	2.31
10	5.89	1.01	4.88	30	5.89	3.70	2.19
11	5.89	1.09	4.80	31	5.89	3.90	1.99
12	5.89	1.15	4.74	32	5.89	4.15	1.74
13	5.89	1.26	4.63	33	5.89	4.30	1.59
14	5.89	1.36	4.53	34	5.89	4.52	1.37
15	5.89	1.47	4.42	35	5.89	4.76	1.13
16	5.89	1.59	4.30	36	5.89	4.98	0.91
17	5.89	1.68	4.21	37	5.89	5.26	0.63
18	5.89	1.80	4.09	38	5.89	5.49	0.40
19	5.89	2.09	3.80	39	5.89	5.68	0.21
20	5.89	2.18	3.71	40	5.89	5.89	0.00

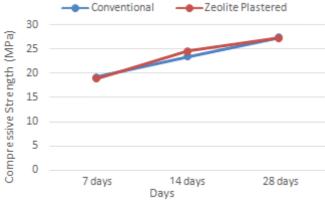
Table - 3 Compressive Strength of Cubes at Different Ages

Days	Compressive Strength (MPa)		
	CC	ZPC	
7	19.194	18.920	
14	23.450	24.560	
28	28.420	28.221	
56	29.120	29.026	
90	29.562	29.428	

Totally 135.55 g of CO_2 was adsorbed by 1.62 m² area of Zeolite Plaster in 40 days. Thus the CO_2 adsorbing capacity is found to be 83.67 g/m². From the experimental results approximately 10,159 m² area of ZPC surfaces exposed to CO_2 atmosphere for 40 days to adsorb 0.85 ton of CO_2 .

Compressive Strength

Fig. 2 and Table-1 shows the details of Compressive Strength of conventional concrete with and without Zeolite plasters. There is no much deviation in compressive strength. Hence, it can be concluded that with addition of Zeolite plasters there is no change in compressive strength at all ages.



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Fig.9 Compressive Strength of Cubes at different ages

Fig.10 Cube tested for its compressive strength in UTM

Table – 4 Comparison of Carbonation Depth for CC and ZPC at 3 different ages of CO₂ exposure

Days	Carbonation Depth (mm)		
	CC	ZPC	
28	1	0	
56	3	1	
90	6	2	



Fig.11 Carbonation depth of CC at 28 days CO₂ exposure – 1mm



Fig.12 Carbonation depth of ZPC at 28 days CO₂ exposure – 0mm







Fig.13 Carbonation depth of CC at 56 days CO₂ exposure – 3mm Fig.14 Carbonation depth of ZPC at 56 days CO₂ exposure – 1mm

Carbonation Depth

Table – 5 Reduction in Compressive Strength of Cubes exposed to 3 different temperatures at different ages

Temperature ('C)	Days	Compressive Strength (MPa)	
		CC	ZPC
	28	28.420	28.221
Room Temperature	56	29.120	29.026
	90	29.562	29.428
250	28	24.23	24.56
	56	24.85	24.96
	90	24.96	25.23
500	28	22.02	23.24
	56	23.12	24.18
	90	24.28	24.89
750	28	21.56	22.05
	56	21.96	22.65
	90	22.34	23.45

Fig.15 Carbonation depth of CC and ZPC at different ages of CO₂ exposure

Days

Carbonation Depth

Fig. 3 and Table-1 shows the details of Carbonation Depth at various ages of conventional concrete with and without Zeolite plasters. The Carbonation Depth is much less for Zeolite plastered concrete and over ages there is much deviation in Carbonation Depth. The Zeolite on the surface of concrete adsorbs the CO₂ thus by reducing the penetration. Thus, if it is used in RCC members there is possibility of reduction in corrosion rate. Hence, it can be concluded that the Zeolite plasters reduce Carbonation Depth and thereby protecting the reinforcement in concrete.

Fire Test

Fig. 3 and Table-1 shows the details of the reduction in compressive strength when exposed to temperatures of 250°C, 500°C and 750°C respectively in an Electric Furnace. At early temperatures the loss in compressive strength of Zeolite plastered concrete is less while comparing with the conventional one but when they are exposed to elevated temperatures like 500°C they show very much less reduction in compressive strength. This is because when Zeolite plastered concrete is exposed to elevated temperatures they tend to desorb the captured CO₂. Thus they act as a fire protection shield on the surface of the concrete and will be helpful in case of fire accidents.

Water Absorption

Fig.19, 20 and Table-5 shows the details of the Water Absorption capacity of Zeolite plastered tiles of 0.75inch thickness. The rate of Water Absorption is slightly increased on addition of Zeolite but it is within the permissible limit of 12%.



Fig.16 Cube tested for its Compressive Strength after Fire exposure

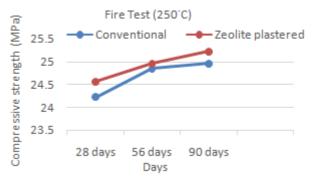


Fig.17 Reduction in Compressive Strength for CC & ZPC @ 250 C

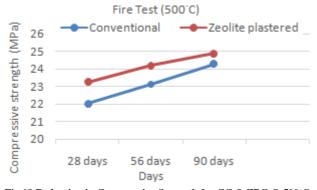


Fig.18 Reduction in Compressive Strength for CC & ZPC @ 500 $^{\cdot}\mathrm{C}$

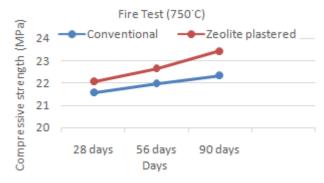


Fig.19 Reduction in Compressive Strength for CC & ZPC @ 750°C



Fig.20 ZPC Tile in Saturated Condition



Fig.21 ZPC Tile in Dry Condition

Table – 6 Comparison between the Percentages of Water Absorption of CC and ZPC Tiles of 0.75inch Thickness
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	Saturated Weight (g)	Dry Weight (g)	% of Water absorption	Average % of Water Absorption
	806	789	2.15	
CC Tiles	825	809	1.98	2.13%
	814	796	2.26	
	845	810	4.14	
ZPC Tiles	905	870	3.86	3.87%
	887	855	3.61	

CONCLUSION

Based on the experimental investigations, the following conclusions have been drawn:

- The Compressive strength of ZPC is more or less same when compared with that of CC.
- The Carbonation Depth reduces at the rate of 67% in ZPC when compared to CC thereby reducing the possibility
 of reduction in corrosion rate.
- The rate of reduction in compressive strength at 250°C reduces to 12.2% in ZPC when compared to CC. At higher temperatures above 500°C the variation in percentage reduction in ZPC increases to 21.8% due to desorption of adsorbed CO₂ acting as a fire retarding layer.
- The water Absorption capacity of Zeolite plastered Tiles were within limits and hence it can be used as a commercial product after sealing the Zeolite surface with PVC coatings.

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