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Utilization of Mineral Sequestration for CO₂ Capturing in Car **Parks and Tunnels**

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Submitted: 21/09 /2019 Accepted: 16/12/2019 Published: 25/05/2020 KEYWORDS ABSTRACT Decreasing the emissions of CO_2 that come from vehicle exhaust, Carbonation depth, CO₂ up-take, Pozzolime, especially in car parking and tunnels, is so vital. CO₂ emissions cause pervious concrete. corrosion to a reinforcement of concrete. Thus, there is a need to provide a layer that protects the reinforcement from the reach of this harmful gas. This work goals to investigate the efficiency of using board units from Pozzolime concrete and pervious concrete to sequestrate CO_2 from the environment and then to convert it into calcium carbonate inside the concrete. The units have dimensions of (200×400×40±5). All specimens were cured in a water tank after about 48 hours after casting. Then paint the sample from all surfaces (three layers) excluding the top surface. The pervious concrete and Pozzolime specimens, at age of 28 days, were put in the chamber, then the gas was supplied to the chamber with concentrations of 15%, 25%, and 50 %, for 24 hours. The efficiency was evaluated through carbonation depth, CO₂-uptake, and weight change. The results showed that the maximum CO_2 uptake was recorded at the age of 28 days for Pozzolime concrete when exposed to 50% of CO_2 concentration.

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1. Introduction

The increased gas emissions to the environment, from industrial activities and vehicle exhaust, and their effects on global warming encouraged many researchers to find new technologies to reduce their concentrations, especially in closed areas. This condition might be increased in car parking or in the tunnels [1]. The tunnels are built with reinforced concrete and one of the problems that affect those tunnels is the corrosion of steel reinforcement due to the carbonation, which affects their safety [2].

The carbonation process derives as a result of the chemical reaction of acidic gas (generally CO_2) from the atmosphere with alkalis of concrete. Alkalinity is coming mainly from calcium hydroxide $Ca(OH)_2$ in hardened concrete. Carbon dioxide CO_2 can penetrate concrete through its pore structure, to react chemically with $Ca(OH)_2$ to form calcium carbonate. The carbonation begins from the top surface, then gradually transfers into the structure of concrete, making a carbonate layer as shown in figure 1 [2]. Lime could be considered as an ecological binder due to the needs of lower creation energy, lower CO_2 emission during production, and CO_2 preoccupation by carbonation on setting [3]. The pozzolanic reaction with lime is relatively slow, therefore, this mixture needs more than 28 days to develop such reliable strength [3].



Figure 1: Illustration carbonation process and pH variation in concrete with time [4].

Kadum et al. [5] recently have developed a sustainable binder patented and called Pozzolime. This binder is a mixture of hydrated lime with silica fume, fly ash and included no Portland cement. Another method to capture CO_2 from the environment is by using pervious concrete [6]. This type of concrete contains little or no fine aggregate to create significant voids content. Therefore, this will create a highly permeable structure, normally, between 15 to 35 % voids are reached in the hardened concrete [6, 7]. This study aims to investigate the efficiency of producing a board from this type of concrete for CO_2 capturing from the environment and then to convert it into calcium carbonate inside the concrete to reduce their impact on the environment and corrosion of reinforced concrete.

2. Experimental program

I. Materials

a. Cement

Portland cement Type V was utilized in this study to reduce the setting time of Pozzolime concrete. The chemical properties and physical requirements are met ASTM C 150-15 [7] and IQS 5-1984 [8] as displayed in Table 1.

b. Silica fume

The Mega-Add MS type (D) was used. It is a densified micro silica fume. At the age of 7 days the activity index of pozzolanic was 132.4 %. The chemical properties and specific surface of silica fume are displayed in Table 1 which indicates that it follows the ASTM C-1240 [9].

Components %	Portland cement	Silica fume
CaO	58.75	1.21
SiO ₂	20.38	91.1
Al ₂ O ₃	3.52	0.02
MgO	3.21	0.01
SO ₃	1.88	0.22
Na ₂ O	0.27	0.21
K ₂ O	0.50	0.15
L.O.I.	3.8	2.98
<u>I.R.</u>	1.2	
L.S.F	0.93	
Surface area (Blaine), m ² /kg	280	200
C3S	54.55	
C2S	18.8	
СЗА	1.42	
C4AF	14.23	
Initial setting, min.	228	
Final setting, hrs.	6:13	
Compressive strength, MPa		
3 days	23.5	
7 days	27.8	

Table 1: the chemical and physical properties of cement and silica fume

c. Hydrated lime

It was obtained from the Karbala manufacture for cement and lime. It meets the requirements of the Iraqi specification IQS NO. 807 /2004 [10]. Table 2 shows its physical and chemical properties.

d. Aggregate

Crushed coarse aggregate with (14) mm maximum size and 0.071% sulfate content, has been used. The fine aggregate grading follows zone (2) with fineness modulus of 2.68. Its sulphate content is 0.14%. It is in compliance with IQS NO. 45 /1984 [11]

	Components %	Test results	Limits IQS.
	CaO + MgO	72.73	Minimum65%
	SiO ₂	2.29	
	Al ₂ O ₃	1.07	
	Fe ₂ O ₃	0.22	
Chemical	MgO	0.44	5% Max.
	Fe ₂ O ₃ + Al ₂ O ₃ + SiO ₂	3.58	5% Max.
	SO ₃	0.2	
	Loss on ignition	22.7	
	Ca(OH) ₂	92.52	85% Min.
	CaO% activity	70.01	
physical	Residue on 90µm	2.1	10 % Max.
	Slaking time	22	5-30 Min.

 Table 2: The physical and chemical analysis tests for hydrated lime.

e. High-range water reducer

Glenium 51, a third generation of "high range water reducing" admixture was used in the study. It is manufactured by BASF Company. The admixture meets the requirements of Type A and type F in ASTM C 494 [12].

II. Mixes and curing systems

According to the previous research [5], and trail mix. It was selected two mixes for Pozzolime concrete (P1 and P2) and one mix for Pervious concrete, as illustrated in Table 3.

Table 5. Why proportions and properties										
Mixes				Materials	6				Properties	
-	Hydrate	Cement	Silica	Fine	Coarse	W/B	HRWR by	Slump	Compressive	Density
	lime	kg/m ³	fume	Agg	Agg.	ratio	wt. of	mm	Strength MPa	kg/m ³
	kg/m ³	-	kg/m ³	.kg/m ³	kg/m ³	by wt.	cement, %		-	-
P1	220	-	220	630	950	0.45	2.9	110	25.5	1987
P2	300	25	100	605	950	0.5	2.5	120	23.4	1945
Pervious	-	375	-	-	1800	0.34	0.5	80	28	1920

Table 3: Mix proportions and pro	perties
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The dimensions of the units are (200 \times 400 \times 40±5 mm) for both pervious concrete and Pozzolime concrete.

All specimens were cured until the age of 28 days in the water tank after about 48 hours from casting. After the 28 days of curing the units removed from the water and then using paint (polymer base) the sample from all surfaces (three layers) excluding the top surface as in figure 2. The painting the surface to ensure that the exposed surface only from the top, later. Then, it was tested in the carbonation chamber at the age of 28 days.



Figure 2: painting specimens before exposure to CO₂ gas

III. CO₂ chamber

Figure 3 represents a schematic graphic of the CO_2 "sealed chamber system". It is fed with CO_2 gas with different concentrations (15, 25, 50%), under the pressure of 140 kPa. The Pozzolime concrete

and pervious concrete specimens were tested at the age of 28 days of curing. They put in the chamber for 24 hours, and then the CO_2 was fed into the sealed chamber. The chamber has a relative humidity (RH) of 50- 60% and a temperature of 38-40°C.



Figure 3: Schematic illustration of the CO₂ sealed chamber

IV. Testing program

a. Flexural strength

A $(200 \times 400 \times 40\pm 5)$ mm of unit boards of pervious and Pozzolime concrete was used for flexural strength. Flexural strength was determined by using a machine of hydraulic compression of (2000) kN capacity. The test was conforming to the ASTM C 78-06 [13]. Tests were carried out at the age of 28 days of curing for all mixes.

b. Carbonation depth

The carbonation depth was tested by phenolphthalein indicator according to the BS EN 14630:2006 [14]. Phenolphthalein is a liquid used to indicate the variation in alkalinity. The variation in treating concrete color from purple to white grey means that the pH drops beneath 8.5 in a water solution. The depth of carbonation represents the distance from the top surface to the purple front and measurements were done by visual check by digital calibrate [15].

c. Weight change

The percentage of weight, due to exposure to CO_2 , was measured mathematically (the change in weight relative to the original weight), following the procedure of previous research [17].

$d. CO_2 uptake$

 CO_2 uptake was estimated by the weight gain of concrete specimens during the exposure period, according to equation-1 [16].

CO2 uptake (%) = (Final mass + Mass of water loss - initial mass) / (Mass of Binder)(Eq. 1)

3. Results and Discussion

I. Flexural strength

Table 4 and figure 4 indicate that the flexural strength, of all mixes and under all exposure conditions, satisfy the requirements of Iraqi specification IQ.S. 1042/1984 [17] for tiles, which means that they are suitable to be used as boards. Results also indicate that the flexural strength of pervious concrete is higher than that of pozzolime concrete at 28 days age. This is maybe due to the slow rate of strength development of pozzolime concrete. Table 4 and figure 4 indicate also that the flexural strength of all types of concrete mixes increases with an increase of CO₂ concentration which they exposed to. This can be attributed to the filling-up of pores by the carbonation products CaCO₃ [18].

CO concentration %	Flexural strength (MPa) at age 28 days			
CO_2 concentration 76	Pervious concrete	<i>Pozzolime mix(P1)</i>	Pozzolime mix(P2)	
15%	5.25	4.56	4.73	
25%	5.61	4.75	4.86	
50%	5.83	4.92	5.15	

Table 4: Flexural strength of all mixes



Figure 4: Flexural strength at age 28 days for all mixes

II. Carbonation penetration depth

Table 5 and Figure 6 indicate the depth of carbonation in pozzolime concrete, which exposed to different concentrations of CO_2 . It was conducted by digital caliper after spray the fracture surface with the Phenolphthalein indicator, as shown in Figure 5. The results show that the higher depth was 12.65 mm associated with the 50% of CO_2 concentration and (24hrs.) exposure period of 28 days age for the Pozzolime mix P2. The lowest value was 2.11 mm for 15% of CO_2 concentration and (24hrs.) at 28 days age for pervious concrete.

	Average of the carbonation penetration depth (mm) at age 28 days					
<i>CO</i> ₂ %	Pervious concrete	Pozzolime mix one (P1)	Pozzolime mix two (P2)			
15%	2.11	4.47	6.74			
25%	3.32	7.95	8.63			
50%	5.05	9.17	12.65			

Table 5. The Carbonation depth in Pozzolime concrete with different CO₂ exposures



Figure 5: Spray the fracture surface with Phenolphthalein indicator

The Pozzolime mix one P1 has great value (9.17mm) with 50 % of CO_2 concentration and (24hrs.) of the exposure period at 28 days age. The reduction may be due to the filling of voids and pores with the products of the hydration of cement, that reduce the ingress of CO_2 and its reaction with Ca(OH)₂ [19,20]. However, the internal pore structure for a mixture of a high percentage of silica fume was denser than that of a mixture with lower content of silica [19]



Figure 6: Average of carbonation depth for all mixes.

III. Weight change

Table 6 and Figure 7 show that the increase in CO_2 concentration increases the weight of the concrete specimen in comparison with the original weight. The final product of the reaction is calcium carbonate CaCO₃ which has a higher density than Ca(OH)₂, and a new creating calcium carbonates can cause a modification from 0.1 to 1 µm, as a result of new CaCO₃ crystal growing [18, 22].

CO %	Weight change % at age 28 days				
CO ₂ %	Pervious concrete	Pozzolime mix one (P1)	Pozzolime mix two (P2)		
15%	1.99	3.11	3.49		
25%	2.75	3.35	4.15		
50%	3.15	4.01	4.66		

Table 6: The Weight change percentage of Pozzolime concrete with different CO₂ exposures

The maximum increase in the percentage of weight is 4.66% at age 28 days of curing and 50% of CO_2 concentration for Pozzolime mix two P2. While the maximum value reached to 4.01% for Pozzolime mixing P1 and for pervious concrete was 3.15%. This is because the formed calcium carbonate CaCO₃ has a higher density than Ca(OH)₂ [20]. A significant amount of water loss was detected in lime under pressure. This is because the carbonation of Ca(OH)₂ produces water. The calculation of water loss would take account of both original mixing water and water released from the carbonation of Ca(OH)₂ with CO₂ [16]. Also from the results, the weight gain due to the carbonation process to Pozzolime concrete mix two P2 is higher than that for mix one P1 and pervious concrete due to higher Ca(OH)₂ that can be reacted with CO₂.



Figure 7: The percentage of weight change at age 28 days for all mixes

V. CO₂ uptake

Table 7 and Figure 8 indicate the CO_2 uptake of pozzolime concrete exposed to different exposures. Results indicate that the CO_2 uptake was very low. This may be due to the loss of more than 25% of the mixed water caused by vaporization by the exothermic reaction and heat rise during the carbonation process [21].

Table 7: T	he CO ₂ uptake	percentage of Pozzolime	concrete with	different exposures
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$CO_{0}/$	CO_2 uptake % at age 28 days				
$CO_2 \%$	Pervious concrete	Pozzolime mix one 1 (P1)	Pozzolime mix two 2 (P2)		
15%	6.72	8.15	9.21		
25%	8.56	9.41	11.87		
50%	10.56	11.79	12.60		

The most water loss was detected in lime under pressure. Because the carbonation of $Ca(OH)_2$ produces water, the calculation of water loss would take account of both original mixing water and water released from the carbonation of $Ca(OH)_2$ with CO_2 [16]. The highest significant value was 11.79% and 12.6% of CO_2 uptake at age 28 days for Pozzolime concrete mix one P1 and Pozzolime concrete mix two P2 respectively. Also, the higher value of pervious concrete was 10.56%. It occurs because of evaporation due to exothermic reaction and by the rising the heat of mixture due to higher exposure of $CO_2\%$.



Figure 8: CO₂ uptake of all mixes at age 28 days

4. Conclusions

The following conclusions were extracted from the current study:

1- The flexural strength, of all mixes and under all exposure conditions, satisfy the requirements of Iraqi specification IQ.S. 1042/1984 for tiles, which means that they are suitable to be used as boards. These boards can be used as a lining layer to protect reinforced concrete from the effect of carbon gas emissions.

2-Pozzolime is more effective in sequestration of CO₂ than pervious concrete.

3- Mix P2 of pozzolime is more effective in sequestration of CO_2 than that of mixed P1 of pozzolime because of less fine materials.

4- The higher carbonation depth and CO_2 uptake were 12.65 mm and 12.6%, respectively associated with the 50% of CO_2 concentration and (24hrs.) of exposure in samples of pozzolime- mix 2.

5- The increase of lime in the mix increase the CO_2 uptake.

6- The maximum calculated CO_2 uptake by Pozzolime concrete happens when it's exposed to higher CO_2 concentration.

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