Evaluation of CO$_2$ sequestration efficiency by Pozzolime concrete

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Abstract: Reducing CO$_2$ emissions from cement industry is vital. Portland cements manufacturing is responsible for 5 – 8 % of global greenhouse gases. Therefore, using alternative binders in concrete is necessary to reduce the environmental impact of cement. This work goals to investigate the efficiency of Pozzolime concrete in CO$_2$ sequestration from the environment and then to convert it into calcium carbonate inside the concrete. The Pozzolime concrete was tested at the ages of 14, 28 and 56 days with two moist-curing ages; 14 and 28 days. The studied mixes were exposed to 15 and 25 % of CO$_2$ concentration for a period of 24 hours. The efficiency was evaluated through compressive strength, carbonation depth, CO$_2$-uptake and weight change. The results showed that higher concentration of CO$_2$ for exposure of 24 hours caused a significantly higher carbonation depth. The maximum CO$_2$ uptake was recorded at the age of 14 days for Pozzolime concrete, when exposed to 25% concentration of CO$_2$.

Key word
Carbonation depth, CO$_2$ up-take, Pozzolime, Sequestration

1. Introduction
The Greeks knew the Lime and it was commonly used by the Romans. The Romans as well knew how to create a hydraulic binder, i.e. Lime- natural Pozzolanic cement by addition of materials, such as brick powder, volcanic ash or, pottery and tiles to lime [1]. In greenhouse gases (GHG) classification, the CO$_2$ is the most important gas, which has a major influence on the climate change and international warming. Cement industry only produces approximately 5 - 8 % of the global total CO$_2$ emission [2]. Lime could be considered as an ecological binder due the needs of lower creation energy, lower CO$_2$ emission during production and CO$_2$ preoccupation by carbonation on setting [3]. For Portland cement, hydration causes the gain of strength and makes concrete to attain a reliable value on the 28 days. However, the Pozzolan reaction with lime is relatively slow, therefore, this mixture needs more than 28 days to develop such reliable strength [4]. Carbon oxide CO$_2$ reacts with calcium oxide Ca(OH)$_2$ inside the concrete to form calcium carbonate as shown in the following equation-1:

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad \text{...(Eq. 1)}$$

This reaction speeds up to achieve strength. In the industries of bricks, blocks, and cement boards, it is a known procedure to cure these products by injecting CO$_2$ gas through a sealed chamber at a favorite temperature from 25 – 65 °C, and specified pressure, 0.83 MPa. This process needs moisture and porous structure to achieve its best results [5].
In Iraq, Kadum et al. [6] recently has 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. They conducted an extensive investigation of the characteristics of this binder, such as; heat of hydration, setting time, density, absorption, strength development and drying shrinkage. This study aims to investigate the efficiency of Pozzolime concrete in CO$_2$ sequestration from the environment and then to convert it into calcium carbonate inside the concrete.

2. Experimental program

2.1 Materials

2.1.1 Hydrated lime. Hydrated lime is primarily composed of calcium dioxide Ca(OH)$_2$. The hydrated lime used, was obtained from the Karbala plant for cement and lime, and conforming to the Iraqi specification NO. 807 /2004 [7]. The chemical analysis and physical tests are shown in Table 1.

| Chemical analysis | Components | Test results | Limits |
|-------------------|------------|--------------|--------|
|                   | CaO + MgO  | 72.73        | Minimum 65% |
|                   | SiO$_2$    | 2.29         |         |
|                   | Al$_2$O$_3$| 1.07         |         |
|                   | Fe$_2$O$_3$| 0.22         |         |
|                   | 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%    |
|                   | Available CaO% activity | 70.01 |         |

2.1.2 Cement. Type V (Sulfate-resisting Portland cement) was used in this research to activate the Pozzolanic reaction and reduce the setting time of Pozzolime concrete. The physical and chemical properties conforming to ASTM C 150-15 [8] and IQS Iraqi Specifications Standard 5-1984[9] as shown in Table (2) below.

2.1.3 Silica fume. Mega-Add MS (D) type Densified Micro- silica fume was used by the CONMIX construction chemical company. At 7 days the pozzolanic activity index was 132.4 %. The chemical and specific surface of the used silica fume is shown in Table (2) and are conforming to the ASTM C1240 [2].

2.1.4 Aggregate. In this research used local crushed river gravel as coarse aggregate with a maximum size (5-14) mm. Sulfate content of 0.071%, and with fine aggregate from Al-Ukhaider, Karbala and conforming to zone (2) IQS NO. 45 /1984[11].

2.1.5 High-range water reducer. A third generation of superplasticiser "high range water reducing" admixture that used in research manufactured by BASF Company beneath the marketable label Glenium 51 to reach a desired workability. The admixture meets the requirements of Type A and type F in ASTM C 494[3].

Table 1. Chemical analysis and physical tests of hydrated lime

| Table 2. Chemical and physical tests of cement | Components | Test results | Limits |
|---------------------------------------------|------------|--------------|--------|
|                             | CO$_2$%     | 2.26         | 5% Max. |
|                             | Residue on 90µm | 2.1         | 10 % Max. |
|                             | Slaking time | 22           | 5-30 in  |
Table 2. Chemical analysis of Silica fume and Sulfate-resisting Portland cement

| NO. | Components                      | Sulfate-resisting Portland cement | Silica fume |
|-----|---------------------------------|-----------------------------------|-------------|
| 1   | Cao                             | 58.75                             | 1.21        |
|     | SiO₂                            | 20.38                             | 91.1        |
|     | Al₂O₃                           | 3.52                              | 0.02        |
|     | Fe₂O₃                           | 4.68                              | 0.01        |
|     | MgO                             | 3.21                              | 0.01        |
|     | SO₃                             | 1.88                              | 0.22        |
|     | Na₂O                            | 0.27                              | 0.21        |
|     | K₂O                             | 0.50                              | 0.15        |
|     | Loss on ignition                | 3.8                               | 2.98        |
|     | Insoluble residue               | 1.2                               | -           |
|     | Lime saturation factor          | 0.93                              | -           |
| 2   | Surface area (Blaine) m²/Kg     | 280                               | 20000       |

2.2 Mixes and curing systems

Based on the work of Kadum et al. [6], and trail mix. The mix proportions were selected for two Pozzolime mixes, P1 and P2, as shown in Table 3. The mixes were water-cured for two periods: 14 and 28 days. Then, the group that was cured for 14 days was tested for carbonation at the ages of 14, 28 and 56 days. Meanwhile, the group that was cured for 28 days was tested for carbonation at the ages of 28 and 56 days.

Table 3. Mix proportions and properties

| Mix | Hydrate lime kg/m³ | Cement kg/m³ | Silica fume kg/m³ | Fine Agg. kg/m³ | Coarse Agg. kg/m³ | WB ratio by wt. | HRWR by wt. of cement, % | Compressive Strength, MPa | Density, kg/m³ |
|-----|--------------------|--------------|-------------------|-----------------|-------------------|-----------------|--------------------------|--------------------------|----------------|
|     | 7d                 | 28d          | fresh             | 28d dry         |
| P1  | 220                | -            | 220               | 550             | 950               | 0.45            | 2.9                      | 110                      | 17.5           |
|     |                    |              |                   |                 |                   |                 |                          |                          | 2240           |
| P2  | 300                | 25           | 100               | 545             | 950               | 0.5             | 2.5                      | 120                      | 16.6           |
|     |                    |              |                   |                 |                   |                 |                          |                          | 2210           |

2.3 CO₂ exposure chamber

The system in Figure 1 a schematic illustration of the CO₂ "sealed chamber". It is provided with CO₂ with different concentrations, under 140 KPa pressure from the container with a gas. The Pozzolime concrete samplings were tested at the ages of 14, 28 and 56 days, they placed in the chamber, then the CO₂ gas was provided to the sealed chamber under concentrations of 15 and 25 %. The clement chamber consumes a Relative Humidity (RH) range up to 50 % and with temperature about 40°C. The samples put inside the chamber for 24 hours. At all time of testing the temperature and moisture remained under observation by thermocouples.
2.4 Testing program

2.4.1. Compressive strength. The compressive strength test was done according to the BS EN 12390 [13]. The cubes have the clearance dimensions of "100*100*100" mm. They take an average of three values of cubes through the test. Tests were carried out at ages of 14, 28 and 56 days.

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

2.4.3. Weight change. When put the samples inside the CO2 sealed chamber, weight of specimens will change due to chemical reaction (because of exposure to CO2 concentrations at 15 and 25 % for 24 hours). The percentage of changes was taken by mathematical methods (the change in weight of the original weight) [16].

2.4.4. CO2 uptake. The weight gain was measured to calculate CO2 uptake for concrete specimens during the exposure period as showed in equation-2 [17]. Carbonation calculated by formula below and from water loss collected by spongy paper which, added to the final mass. Through in view of the system as a sealed system, it was imposing to include the vaporized water that was primarily inside the samples prior to carbonation.

\[
\text{CO}_2 \text{ uptake (\%)} = \frac{(\text{Final mass} + \text{Mass of water loss - initial mass})}{(\text{Mass of Binder})} \quad \text{…..(Eq. 2)}
\]

3. Results and discussion

3.1 Compressive strength

As illustrated in Table 4, the compressive strength of Pozzolime concrete was significantly affected by CO2 concentration, exposure time, and wet curing period. Results showed that exposing to CO2 for 24 hours causes a higher increase in strength.
Table 4. The compressive strength development of Pozzolime concrete with different CO₂ exposures

| Testing age with curing program | Compressive strength, MPa |
|---------------------------------|---------------------------|
|                                 | Mix P1 with CO₂ concentration, %, in chamber: | Mix P2 with CO₂ concentration, %, in chamber: |
|                                 | 0 | 15 | 25 | 0 | 15 | 25 |
| 14 day wet                      | 17.5 | 18.1 | 19.9 | 16.6 | 17.1 | 18.3 |
| 28 day wet                      | 25.5 | 26.1 | 27.3 | 23.4 | 23.9 | 24.1 |
| 28 day-14d wet                  | 21.8 | 22.3 | 23.0 | 22.5 | 23.1 | 23.9 |
| 56 day-14d wet                  | 24.4 | 26.2 | 27.9 | 23.1 | 23.9 | 24.7 |
| 56 day-28d wet                  | 28.6 | 29.1 | 30.3 | 23.9 | 24.4 | 25.9 |

For mix P1, the increase in compressive strength at the age of 14 days of water curing was 3.4 and 13.7 % for 15 and 25 % of CO₂ gas concentration, respectively. The effect of water curing is obvious at the age of 28 days. For curing at 14 days only and testing at 28 days the increase was 2.3 and 5.5 % for 15 and 25 % of CO₂ gas concentration respectively. Meanwhile, for 28 days curing the increase in strength is very clear and it was 2.3 and 7.0 % for 15 and 25% of concentration respectively. At the age of 56 days the increase at 14 days curing only was 7.4 and 14.3 % for 15 and 25 % of CO₂ concentration, respectively. Same trends were diagnosed for mix P2. This gain in compressive strength for two mixes P1 and P2, is due to the formation of calcium carbonate, which densified the microstructure. The increase in compressive strength also starts from the exothermic nature of carbonation reaction that will increase the heat and cause quick solidification [18]. Results also indicated that the curing time with exposing concrete to CO₂ % at an earlier age, provides higher gain in compressive strength [16]. This due to the development of more hydration products that block the pores and reduce the next entrance of CO₂ to the matrix [19]. The strength increasing slightly for mixing P1 than the P2 at an early age, while at age 28 days approximately the same, but at later age 56 days the mix P2 increasing than mix P1.

3.2 Carbonation penetration depth

The results of carbonation depth are shown in Table 5. These measures were done by using digital caliper. The results displayed that the greatest recorded depth was 9.12 mm at the age of 56 days with 14 days of wet-curing only and with 25 % of CO₂ concentration for mix P1. However, for mix P2 the maximum penetration depth was 20.1 mm at age of 56 days for 14 days of wet-curing and 25 % of CO₂ concentration. On the other hand, the minimum values were 2.1 and 4.21 mm at the age of 28 days with 14 days of wet-curing for zero CO₂ concentration for mixes P1 and P2 respectively. This could be due to the consequent reaction of lime with the CO₂.

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

| Testing age with curing program | Average carbonation depth, mm |
|---------------------------------|-------------------------------|
|                                 | Mix P1 with CO₂ concentration, %, in chamber: | Mix P2 with CO₂ concentration, %, in chamber: |
|                                 | 0 | 15 | 25 | 0 | 15 | 25 |
| 14 day wet                      | 0 | 4.31 | 5.21 | 0 | 6.31 | 7.21 |
| 28 day wet                      | 0 | 3.45 | 4.62 | 0 | 6.85 | 8.62 |
| 28 day-14d wet                  | 2.10 | 5.38 | 8.12 | 4.21 | 10.55 | 12.15 |
| 56 day-14d wet                  | 2.85 | 6.78 | 9.12 | 6.67 | 16.18 | 20.10 |
| 56 day-28d wet                  | 5.43 | 5.81 | 6.45 | 5.15 | 9.84 | 11.31 |

Generally, the reduction in depth from the age of 14 to 28 days could be due to the continuous hydration that filled the pores and reduced the entrance of more CO₂ to the matrix [19, 20].

3.3 Weight change
Table 6 declares that the specimens of Pozzolime concrete have increased in weight with different CO₂ exposures when compared to the reference mixes [16]. The maximum increase in weight was at early age for 14 days wet curing and 25 % CO₂ concentration. The recorded values were 2.83 and 3.11 % for mixes P1 and P2, respectively. This could be attributed to the carbonation of lime which densifies the microstructure of concrete [21]. There was a detection of water loss in lime under pressure. It is well known that the carbonation of lime would produce water. Therefore, calculation of water loss should take into account both original mixing water and water released from lime carbonation [22].

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

| Testing age with curing program | Weight change, % |
|--------------------------------|------------------|
|                                | Mix P1 with CO₂ concentration, %, in chamber: | Mix P2 with CO₂ concentration, %, in chamber: |
|                                | 15 | 25 | 15 | 25 |
| 14 day wet                      | 2.37 | 2.83 | 2.71 | 3.11 |
| 28 day wet                      | 2.32 | 2.53 | 2.68 | 2.87 |
| 28 day-14d wet                  | 1.97 | 2.33 | 2.38 | 2.56 |
| 56 day-14d wet                  | 1.73 | 1.83 | 1.87 | 2.01 |
| 56 day-28d wet                  | 1.45 | 1.56 | 1.61 | 1.80 |

3.4 CO₂ uptake

Table 7 lists the CO₂ uptake that was determined via the increase in weight from CO₂ exposure with initial mass and with the drying binder of Pozzolime concrete as explained previously, the mass of carbonated Pozzolime finally is including the water loss, and the weight of original dry binder [16]. The maximum CO₂ uptake value was 4.278 % at the age of 14 days of wet-curing and 25 % concentration for mix P2. Meanwhile, the corresponding value for mix P1 was 3.578 %, i.e. About 20 % reduction in uptake. This trend was observed for all calculated values and that could be due to the less available lime in mix P1. Another concluding remark was that the reduction in uptake with the increase in wet-curing period and testing age and that could be explained by the blocking of pores through early carbonation and reduction of permeability due to continuous hydration [19].

Table 7. The CO₂ uptake percentage of Pozzolime concrete with different exposures

| Testing age with curing program | Average of CO₂ uptake % |
|--------------------------------|--------------------------|
|                                | Mix P1 with CO₂ concentration, %, in chamber: | Mix P2 with CO₂ concentration, %, in chamber: |
|                                | 15 | 25 | 15 | 25 |
| 14 day wet                      | 2.556 | 3.578 | 2.951 | 4.278 |
| 28 day wet                      | 2.813 | 2.973 | 3.043 | 3.501 |
| 28 day-14d wet                  | 2.588 | 2.760 | 2.989 | 3.264 |
| 56 day-14d wet                  | 2.385 | 2.504 | 2.751 | 2.861 |
| 56 day-28d wet                  | 2.233 | 2.478 | 2.578 | 2.890 |

4. Conclusions

The following conclusions can be drawn from the current study:

1. Results showed that exposing specimens to CO₂ gas for 24 hours causes an increase in compressive strength due to carbonation process.
2- Exposing concrete to CO₂ at earlier ages, yields higher increase in compressive strength due to more pours and calcium oxide Ca(OH)₂ able to react with CO₂ gas.
3- The maximum measured carbonation depth values were 9.12 and 20.1 mm for Pozzolime mixes P1 and P2, respectively, at the age of 56 days with 14 days of wet-curing and 25 % of CO₂ concentration due to P1 more finest materials and densify than P2.
4- The increase in CO₂ concentration at the early age of exposure will increase the weight of concrete for all tested Pozzolime mixtures.
5- The maximum CO₂ uptake by Pozzolime concrete happens when it is exposed to higher CO₂ concentration and for longer duration of exposure at an early age.
6- The increase of lime in the mix will increase the CO₂ uptake at early age more than the later age.

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