Investigating set-controlling additives for Pozzolime mixtures

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Abstract. Pozzolime, PL, is a promising sustainable building material, because of its low carbon footprint on environments as compared to Portland cement. Portland cement contributes to about 7\% of the global CO\textsubscript{2} emission. The Pozzolime is produced by mixing materials cause lower CO\textsubscript{2} emission, the lime, and some industry by-products, silica fume or fly ash. Pozzolime paste exhibits longer setting time than the Portland cement mixtures. The initial setting time ranges from 20 to 21.5 hours and the final setting time ranges from 25–26.5 hours. Such characteristics limit the use of the new binder, PL. The aim of this research is to study the effect of many additives on the setting time of PL paste. The study includes the investigation of using plaster of Paris (CaSO\textsubscript{4}), natural gypsum (NG), cement kiln dust (CKD), and sodium bicarbonate (NaHCO\textsubscript{3}), as set-controllers. The results showed that the most effective set-controller was the sodium bicarbonate due to the composition of sodium hydroxide, which is considered as accelerator to the pozzolanic reaction.

Keywords
Cement kiln dust, Gypsum, Portland cement, Pozzolime, Setting time.

1. Introduction
Pozzolime was widely used for construction as the premature building material. The innovation of lime and lime-natural Pozzolan cement return to the Neolithic period (7000 BC). During Roman times, they were vastly utilized in the masonry construction of aqueducts, retaining walls, buildings, and arch bridges. The use of Pozzolime has not been continued during the history of inorganic binders because their important disadvantages including long setting time. While Pozzolime has many advantages including low cost, low permeability, high chemical resistance and very low heat evolution [1], the innovation of Portland cement in the 19th century caused a drastic reduction in the use of Pozzolime because of the higher early-age strength and faster setting time of Portland cement [1]. Nowadays, the production of Portland cements is responsible for about 6-8 \% of the global CO\textsubscript{2} emission, this fact caused the concerned specialists to seek for new binders with lower carbon footprint and lower impact on environment.

In Iraq, Kadum et al. [2] recently has developed and patented a sustainable binder called Pozzolime. This binder is a mixture of hydrated lime, fly ash and silica fume without Portland cement.
They conducted an extensive investigation for the characteristics of this binder, such as; heat of hydration, absorption, setting time, density, strength development and drying shrinkage, according to this investigation, an average initial and final setting time of 5 and 37 hours, respectively was reported. This binder exhibits its binding effect due to the pozzolanic reaction, this reaction could be defined by the chemical interaction between finely grounded siliceous or siliceous aluminous phases in Pozzolan with Ca(OH)$_2$ to produce C-S-H gel most similar to that of Portland cement with a binding property [2].

In order to have lime-Pozzolan mixtures with faster strength development and shorter setting time, different methods were suggested by many researchers, these methods include calcinations [3-6], acid treatment [7-9], prolonged grinding [10-12], curing in high temperature [13, 14] and addition of chemical activators [15-19]. Some methods did not show a significant efficiency, and some were expensive to be utilized practically [20].

The present study, the effect of many chemical activators on the setting time of Pozzolime were investigated. These activators are; plaster of Paris, natural gypsum, cement kiln dust, and sodium bicarbonate. The availability as waste materials and the cost of these activators were targeted.

2. Materials & Experimental Work

2.1. Materials

2.1.1. Lime. A commercial hydrated lime was used. Blaine fineness and chemical composition of the hydrated lime was determined by the ASTM Standards C25[21] and C204 [22], the aptness of the hydrated lime was determined by the ASTM Standard C821 [23], table 1 shows the physical and chemical properties of lime.

2.1.2. Silica fume. The physical requirement and chemical compositions of silica fume is shown in table 1, the silica fume applied in this work satisfies the physical and chemical requirement of the ASTM C1240[24].

2.1.3. Fly ash. The physical requirement and the chemical composition of fly ash utilized in this study are shown in table 1, the fly ash used in this work conforms to the chemical and physical requirement of the ASTM C 618[25].

2.1.4. Cement kiln dust. Cement manufacturing is a significant industry in the Iraq and throughout the world, this industry generated waste and by product materials, should be managed responsibly to guarantee a safe and clean environment. Cement manufacturing process generated a considerable amount of byproduct material, called cement kiln dust (CKD) [26]. Table 1 shows the chemical analysis of CKD.

2.1.5. Natural gypsum (NG). Natural gypsum was transported from Salaheddine source as a stone. It was crushed by hammer and grinding, Table 1 shows the chemical and physical analysis of the NG.

2.1.6. Sodium bicarbonate (NaHCO$_3$). Sodium bicarbonate is solid white, crystalline, commonly called as baking soda. The chemical formula of Sodium bicarbonate is NaHCO$_3$, it is a salt composed of a sodium cation (Na$^+$) and a bicarbonate anion (HCO$_3^-$), it has a slightly alkaline, salty taste, and oftentimes is found as a fine powder. Table 2 shows the chemical analysis of sodium bicarbonate.
Table 1. Chemical and physical properties of the materials.

| Property         | L*   | SF*  | FL*   | CKD* | NG  |
|------------------|------|------|-------|------|-----|
| CaO              | 87.90| 0.58 | 0.98  | 45.18| 32.9|
| SiO2             |      | 94.58| 65.65 | 11.24| 1.2 |
| Al2O3            |      | 0.1  | 17.69 | 3.24 | 0.4 |
| Oxide Content, % | Fe2O3| 0.06 | 5.98  | 1.42 | 0.1 |
|                  | MgO  | 3.25 | 0.72  | 2.1  | 0.1 |
|                  | Na2O | 0.21 | 1.35  | ---  | --- |
|                  | K2O  | 0.35 | 2.99  | ---  | 0.1 |
|                  | LOI  | 1.98 | 3.1   | 27.36| 21.5|
| Surface Area (Blaine), m²/kg | 120  | 20000| 773   | ---  | --- |
| Specific gravity |      | 0    | 2.26  | ---  | --- |

*: L= Lime; FA= Fly ash; SF= Silica fume; CKD= Cement Kiln Dust, NG= Natural gypsum

Table 2. Chemical analysis of sodium bicarbonate

| Oxide       | Content % |
|-------------|-----------|
| NaHCO₃      | 99.51     |
| Cl          | 0.37      |
| Fe          | 0.001     |
| Pb          | 0.0005    |
| SO₄         | 0.006     |
| L.O.I       | 0.2       |
| pH          | 8.33      |
| Moisture    | 0.2       |

2.2. Mix Design
Kadum et al. [2]; mixture of lime-fly ash failed to set and hardened, therefore, it decided to use a system of lime, fly ash and silica fume to resolve this problem, according to that, three reference mixes were used to produce the mixes LSF1, LSF2, LSF3, they are 30: 20, 20: 30 and 10: 40 percent fly ash to silica fume by weight, respectively, which were mixed with lime of 50 percent. Mixes LSF1, LSF2 and LSF3 with many proportions of additives plaster of Paris (CaSO₄), natural gypsum (NG), cement kiln dust (CKD), and sodium bicarbonate (NaHCO₃), were added, all ratios added are shown in figure 1.

2.3. Testing procedure
The standard consistency test was performed in accordance to the EN 196-3/1994 [27] [28] and Iraqi Standard IQS 8-1969[29] [30]. Consistency was determined by using he Vicat’s device, which measures the depth of penetration of a 10 mm diameter plunger under its own weight. To determine the initial setting time, the Vicat’s device was used. A 1 mm diameter needle was acting under its own weight on a paste of standard consistency. When the needle penetration to a point 5 mm from the bottom of the mold, was said initial setting time occurring (the time was measured from addition the mixing water to the binder).

Final setting time was determined by a needle with a metal attachment hollowed out so as to leave a circular cutting edge 5 mm in diameter and set 0.5 mm behind the tip of the needle. Final setting is
said to have occurred when the needle makes a temperament on the surface of the paste but the cutting edge fails to do so [31] [32].

3. Results and discussion

Figure 1 shows initial and final setting times of the studied Pozzolime pastes with and without activators at different dosages. The initial setting times of the Pozzolime without additives are 21.5, 20.7 and 20 hours and the final setting times are 26.4, 25.5 and 25.2 hours, for reference mixes LSF1, LSF2 and LSF3, respectively at 23°C. All Pozzolime mixes exhibit long setting time and close to other researchers [1, 2]. The chemical reaction between Pozzolan and lime in water, which leads to the formation of calcium silicates hydrates (C-S-H) is slow [33], some of the delay could be caused by the absence of ettringite [2].

![Figure 1. Initial and final setting time in hours for the Pozzolime mixtures with used activators (hr).](image-url)
All the employed additives have activated the pozzolanic reaction and more or less caused a decrease in the initial and final setting times, except for natural gypsum. Gypsum is well known for its low solubility in water. The shortage of alumina-bearing phases in Pozzolan may be another cause for this behavior.

The most effective set accelerator is sodium bicarbonate, the addition of 5% NaHCO₃ can reduce the initial and final setting time of the Pozzolime to 4.5 and 8.5 hours, respectively at 23°C. Reductions in initial and final setting times were 78 and 67%, respectively. This may be due to two reasons. The first one is probable activation of fly ash by alkali activation. Fan [34] carried out studies on the activation of fly ash using Ca(OH)₂ and Na₂SiO₃. It was found that addition of calcium hydroxide corrode the protective glassy layer on the surface of the fly ash particle and thereby, expose the reactive portion of the particle. This method of activation considerably increased the reactivity of the fly ash and reduced the setting time [34] [35]. The formation of NaOH activates fly ash and then reduce setting time:

$$\text{NaHCO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{NaOH} + \text{H}_2\text{O}$$

The other reason may be the precipitation of CaCO₃ and then reduction of the setting time. For the percentage higher than 5%, the setting time did not change significantly. The addition of 3.5% of plaster of Paris, anhydrate CaSO₄, caused the initial and final setting time of the Pozzolime to decrease to 3.5 and 16.2 hours, respectively at 23°C, in other words by 84% and 39%, respectively. The addition of CaSO₄ higher than 3.5% caused a false setting within a few minutes. The reaction of CaSO₄ with water to form gypsum could be the reason for that. CKD reduced setting time slightly, when its percentage was 15%. The reductions in initial (IN) and final (FI) setting times were 10 and 5%, respectively. This is may be due to the low reactivity of CKD.

4. Conclusions
1. All reference mixes of Pozzolime exhibit long setting time.
2. Setting time of LSF3 (silica fume 40%, fly ash 10%) less than LSF2 (silica fume 30%, fly ash 20%) and LSF1 (silica fume 20%, fly ash 30%).
3. Sodium bicarbonate is the most effective additive for the studied Pozzolime compared to plaster of Paris (CaSO₄), natural gypsum (NG) and cement kiln dust (CKD).
4. Addition of 5% NaHCO₃ to the studied Pozzolime, 50 % hydrated lime, 20 % fly ash and 30% silica fume, can considerably decrease both initial (IN) and final (FI) setting times.
5. Addition of natural gypsum (NG), increases the setting time.

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