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# Effect of Hydroxycarboxylic-Acid-Based Retarder on the Compressive Strength of Geopolymer Cement under Wellbore Conditions †

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**Abstract:** In oil well cementing, cement must flow through the casing before reaching the targeted annulus hence, a retarder must be added to provide the cement with sufficient time to reach the targeted depth before setting. At the same time, in support of the Paris Agreement, the prospect of substituting ordinary Portland cement (OPC) with geopolymer cement as the well cement material has to be further explored. Although previous studies have found that retarders can delay the strength development of the cement, the studies were conducted either at ambient conditions or using OPC hence, the findings do not apply to geopolymer cement that is exposed to wellbore conditions. In order to address the shortcomings of the studies, addition of a hydroxycarboxylic-acid-based retarder to a fly-ash-based geopolymer cement, at concentrations of up to 3% by weight of the fly ash, was performed. Slurry of the cement was aged at 100 °C and 20.7 MPa for 8, 24 and 48 h. Compressive strength tests were conducted on samples of the cement. At the 8-h aging duration, retarder concentrations of 0.5–2.0% led to strength increases of 112.7–129.4% relative to that of 0%, or the control sample, whereas that of 3.0% led to a strength decrease of 84.2%. At the 24-h aging duration, all retarder concentrations led to strength decreases of 16.4–22.5%. At the 48-h aging duration, retarder concentrations of 1.0–3.0% led to strength increases of 18.1–24.4%, whereas that of 0.5% led to a strength decrease of 16.7%.

**Keywords:** cement additive; high-pressure; high-temperature well; HPHT well; oil-well cement; thickening time

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## 1. Introduction

In oil and gas production, well cementing is performed to isolate the wellbore from the surrounding formation and support the casing as a conduit. The formation is drilled to the designed borehole size before running the casing. Cement slurry is pumped through the casing up to the annulus between the casing and formation. As the wellbore is drilled beneath the seabed, the cement is subjected to pressures of above 15,000 psi at temperatures of above 176.6 °C or 350 °F for high-pressure, high-temperature well, as defined in American Petroleum Institute (API) Technical Report (TR) 1PER15K-1 [1].

As the cement must flow through the casing before reaching the targeted annulus, a retarder must be added to provide the cement with sufficient thickening time to reach the

targeted depth before setting. The thickening time depends on the depth, pressure and temperature of the cement placement location. There are several types of retarders, namely cellulose derivatives, hydroxycarboxylic acids, inorganic compounds, lignosulfonates, organophosphonates and saccharide compounds [2].

Currently, ordinary Portland cement (OPC) is commonly adopted for well cementing. However, OPC poses environmental concerns due to the high carbon emission rates associated with its production. On 12 December 2015, the Paris Agreement was ratified by 196 parties with the aim of achieving a world that is climate neutral by 2050 by limiting global warming, which is linked to carbon emission. Substitution of OPC with waste products has been accentuated as a key measure for adhering to the agreement.

In view of the concerns with regard to the dependence on OPC and in support of the Paris Agreement, prospect of substituting OPC with geopolymer cement as the well cement material has attracted a lot of interest in research and hence has to be further explored. Studies on the strength development of geopolymer cement in the presence of retarders under wellbore conditions are needed. Although findings of previous studies have highlighted that retarders can delay the strength development of cement, the studies were conducted either at ambient conditions [3–6] or using OPC [3,7,8]. Therefore, the findings do not apply to geopolymer cement that is exposed to wellbore conditions. Although a recent study [9] adopted geopolymer cement with exposure to wellbore conditions, the study employed a lignosulfonate-based retarder hence, studies that adopt other retarder types are needed.

In order to address the shortcomings of the studies, addition of a hydroxycarboxylic-acid-based retarder to a fly-ash-based geopolymer cement, at concentrations of up to 3% by weight of the fly ash, was performed. Slurry of the cement was aged at 100 °C and 20.7 MPa for 8, 24 and 48 h. Compressive strength tests were conducted on samples of the cement.

## 2. Materials and Methods

Fly-ash-based geopolymer cement was prepared with the addition of a hydroxycarbox-ylic-acid-based retarder. The fly ash was obtained from Tanjung Bin power plant, Malaysia to be employed as the aluminosilicate source of the geopolymer cement. It is a brown powder with spherical particles as shown in Figure 1. Its chemical composition is presented in Table 1. According to American Society for Testing and Materials (ASTM) C618-19 [10], it can be categorized as a Class F fly ash. Its specific gravity is 2.75.


(**a**) (**b**)

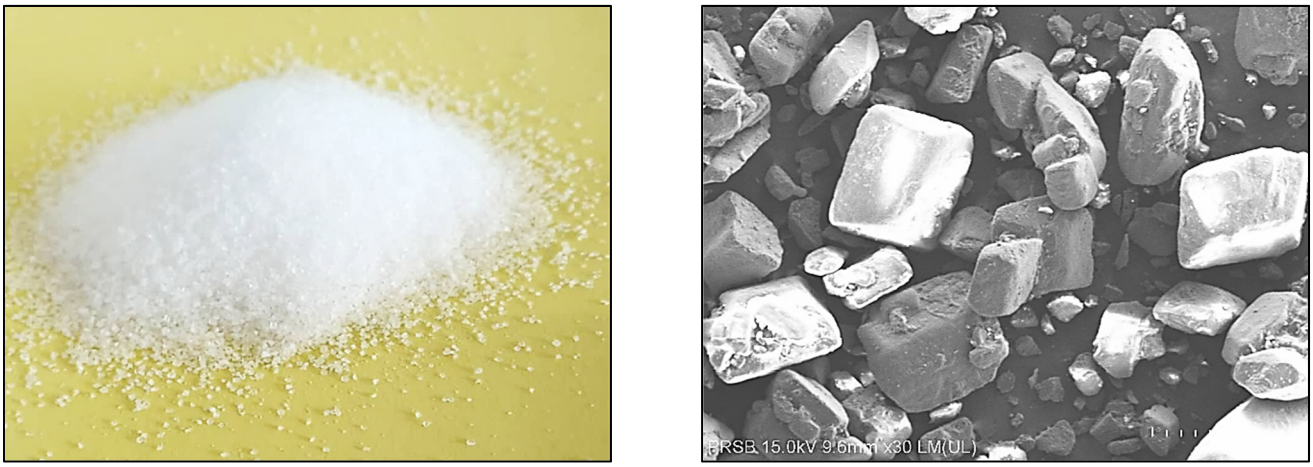
**Figure 1.** (**a**) Photo and (**b**) scanning electron microscopy (SEM) image of the fly ash employed in the present study.

**Table 1.** Chemical composition of the fly ash employed in the present study, obtained from X-ray fluorescence analysis.

| Elements/Parameter | Weight (%) |
|---|---|
| Silicon dioxide ($SO_2$) + aluminium oxide ($Al_2O_3$) + iron oxide ($Fe_2O_3$) | 71.80 |
| Calcium oxide (CaO) | 16.50 |
| Sulfur trioxide ($SO_3$) | 1.85 |
| Moisture content | 0.08 |
| Loss of ignition | 0.09 |

Sodium hydroxide (NaOH) at a concentration of 12.8 M and sodium silicate ($Na_2SiO_3$) at 50% concentration were employed as the alkaline activator of the geopolymer cement. The NaOH and $Na_2SiO_3$ were mixed at a 1:1 ratio. The ratio was determined by performing optimization tests to identify the ratio that resulted in the highest compressive strength at 8, 24 and 48 h of aging without additives.

A hydroxycarboxylic acid-based retarder that is composed of carboxyl and hydroxyl groups was added to the geopolymer cement. It is a solid white grain with granular particles as shown in Figure 2.




(**a**) (**b**)

**Figure 2.** (**a**) Photo and (**b**) SEM image of the retarder employed in the present study.

Five geopolymer cement formulations were adopted for the preparation of samples with retarder concentrations of 0.0, 0.5, 1.0, 2.0 and 3.0% by weight of fly ash (bwof), respectively. Density of the samples was fixed at 15 ppg. Weight of sample constituents for each geopolymer cement formulation are presented in Table 2.

**Table 2.** Weight of sample constituents for each geopolymer cement formulation.

| Retarder Concentration (% bwof) | Fly Ash (g) | NaOH (g) | $Na_2SiO_3$ (g) | Water (g) | Retarder (g) |
|---|---|---|---|---|---|
| 0.0 | 644.27 | 120 | 120 | 196.17 | 0 |
| 0.5 | 642.14 | 120 | 120 | 194.87 | 3.21 |
| 1.0 | 640.22 | 120 | 120 | 193.70 | 6.40 |
| 2.0 | 636.50 | 120 | 120 | 191.42 | 12.73 |
| 3.0 | 632.35 | 120 | 120 | 188.89 | 18.97 |

The fly ash and alkaline activator were mixed using a constant-speed mixer of model 686CS, manufactured by Fann Instrument, to activate geopolymerization in accordance with Clause 5 of API Recommended Practice (RP) 10B-2 [11]. The initial mixing speed was at 4000 rpm. Once the fly ash has been completely poured into the mixer, the speed was increased to 12,000 rpm and mixing was continued for 35 s. After mixing, the sample was poured into a 50 mm × 50 mm × 50 mm mold. A stirrer was used to puddle the cement slurry during pouring to prevent entrainment of air, which can affect the compressive strength of the samples.

The slurry is then conditioned in a pressurized temperature chamber at 100 °C and 20.7 MPa for 8, 24 and 48 h to undergo aging. Once the aging process is completed, the cross-sectional area of the sample was measured using a calliper ruler.

Compressive strength tests were performed on the samples in accordance with Clause 7 of API RP 10B-2 [11] using an API compressive strength tester of model 4207D, manufactured by Ametek Chandler Engineering.

## 3. Results and Discussion

Figure 3 reveals the compressive strength of the samples with respect to retarder concentration at the 8-h aging duration. Achievement of adequate early compressive strength without compromising the required thickening time is important in order to minimize costs associated with the waiting-on-cement time. Results reveal that the retarder can boost early compressive strength, which is in agreement with the results of a similar study conducted using a lignosulfonate-based retarder [9], where 0.5% bwof is the optimal concentration obtained in the present study for the hydroxycarboxylic-acid-based retarder, while that obtained in the previous study for the lignosulfonate-based retarder is 0.4% bwof [9]. Retarder concentrations of 0.5–2.0% led to strength increases of 112.7–129.4% relative to that of 0% whereas that of 3.0% led to a strength decrease of 84.2%.

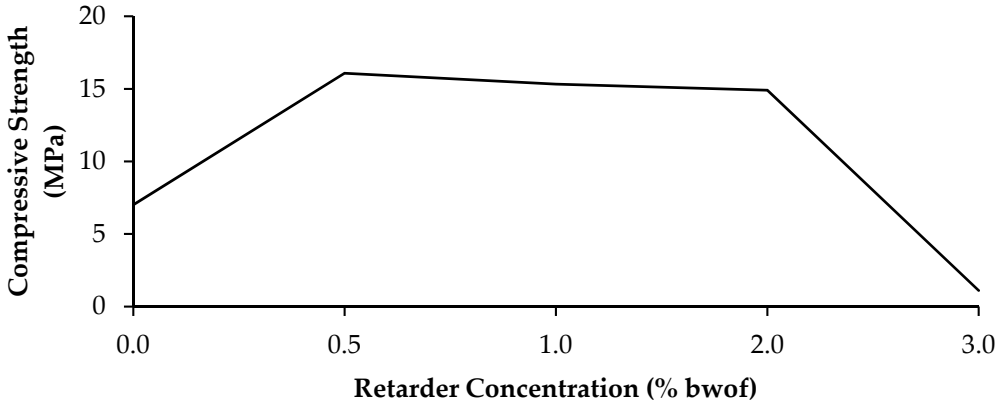



**Figure 3.** Compressive strength of the samples with respect to retarder concentration at the 8-h aging duration.

Figure 4 reveals the compressive strength of the samples with respect to retarder concentration at the 24-h aging duration. All retarder concentrations led to strength decreases of 16.4–22.5%, implying that the retarder delays the development of mid-compressive strength.

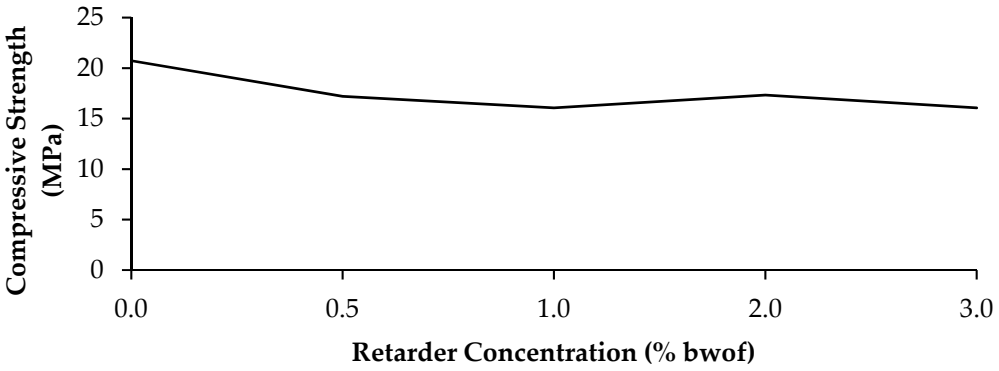



**Figure 4.** Compressive strength of the samples with respect to retarder concentration at the 24-h aging duration.

Figure 5 reveals the compressive strength of the samples with respect to retarder concentration at the 48-h aging duration. Retarder concentrations of 1.0–3.0% led to strength increases of 18.1–24.4%, whereas that of 0.5% led to a strength decrease of 16.7%, indicating that addition of the retarder increases the final compressive strength. As a hydrocarboxylic-acid-based retarder is adopted, the retarding mechanism involves a complexation retarding process, where chelating agents remove significant metal ions like calcium ions from interstitial water and alter the equilibrium of ions across the gel membrane. The lower calcium ion content in geopolymer cement than that in OPC could be the factor that delayed the effectiveness of the retarder at the aging duration of above 24 h.

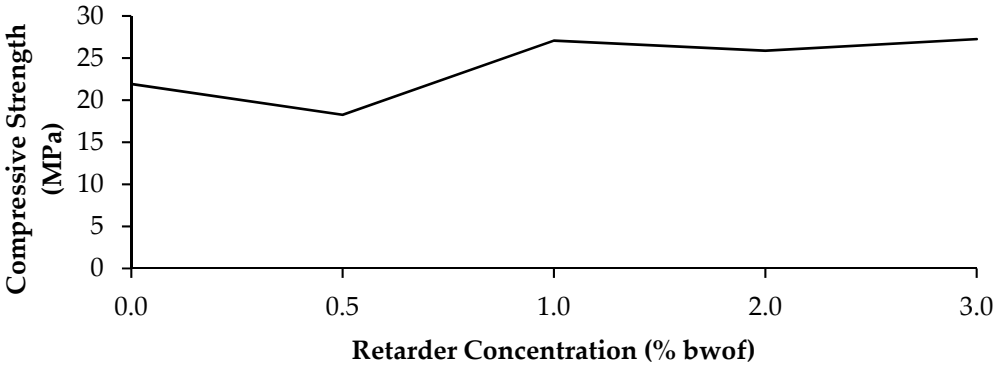



**Figure 5.** Compressive strength of the samples with respect to retarder concentration at the 48-h aging duration.

## 4. Conclusions

Effect of adding a hydroxycarboxylic-acid-based retarder on the compressive strength of fly-ash-based geopolymer cement that underwent an aging process with exposure to 100 °C and 20.7 MPa was evaluated. At the 8-h aging duration, retarder concentrations of 0.5–2.0% led to strength increases of 112.7–129.4% relative to that of 0%, whereas that of 3.0% led to a strength decrease of 84.2%. At the 24-h aging duration, all retarder concentrations led to strength decreases of 16.4–22.5%. At the 48-h aging duration, retarder concentrations of 1.0–3.0% led to strength increases of 18.1–24.4%, whereas that of 0.5% led to a strength decrease of 16.7%.

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