Oil Well Cement for high temperature-A review

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Abstract. Oil well cement (OWC) are widely used in oil industry both in exploration and in production of oil and gas. The purpose of OWC is to seal the annular space between metal casing and walls of a borehole. OWC has other application such as grouting and repair of offshore structure, and in cementing of other wells likes as water, waste disposal, geothermal, injection or storage. There are numerous problems such as high temperature and high pressure in the downhole condition of oil well. OWC slurry undergoes a reduction in strength (strength retrogression) with time when exposed to high temperature and high pressure. This paper reviews the OWC and its classifications, hydration process at ambient and higher temperature. Moreover, this study provides a comprehensive insight on anti-strength retrogression additives, which can potentially be use with OWC at high temperature and pressure.

1. Introduction

Oil well cementing is the process of placing a cement slurry in the annulus space between the well casing and the geological formation surrounding to the well bore [1]. The purpose of cementing is (i) to provide the zonal isolation between different geological layers, (ii) to support the casing, (iii) to protect the casing from corrosion. The exposure conditions of oil well cement (OWC) is different from the conventional construction industry. Sometimes OWC slurries are pumped to the depth of 5000 metres where the temperature and pressure can exceed of 150 °C and 100 MPa, respectively [2]. The static bottom hole temperature increases by 0.8 °C for every 30 m of the well depth in Gulf coast region [3]. The temperature can be as high as 400 °C [4] depending up on the depth and location of geothermal well. Consequently, the OWC can face additional challenges in contrast to conventional construction. Further, OWC must be able to withstand with weak and porous formation, corrosive fluid etc. at this much high temperature and high pressure (HTHP). Several additives have been explored to enhance the physical and chemical properties of OWC slurry for different purposes.

The purpose of additives are [5] (i) to alter the setting time of cement slurry under HTHP conditions of the well, (ii) to disperse cement particles, (iii) to control the fluid loss from the cement slurry, (iv) to control the shrinkage of cement after its set and hardens (v) to improve the interfacial bonding between casing and geological layer of the well, (vi) to control influx and migration of developed fluids into the cement column during setting.

Over the last decades, various types of additives are used to design the cement slurry for successful fill the space between casing and geological formation. In this paper, behaviour of cement paste at ambient and high temperature is briefly described. Moreover, an insight into the different additives explored by various researchers for oil well cementing at high temperatures and high pressures is provided.
2. Oil Well Cement (OWC)

Oil well cement is a Portland cement developed for the usage in oil and gas industry. The different types of Portland cement are widely used in the oil & gas industry to meet specific physical and chemical property set up by American Petroleum Institute (API).

2.1 Classification of OWC

Since 1924, the American Petroleum Institute (API) is establishing and maintaining standards for the worldwide oil and natural gas industry. Generally, API standards are review and revised by at least every five years. The latest API standard (10 A, 24th edition) specified the six classes (i.e., Class A, B, C, D, G and H) of oil well cement with three grades ordinary (O), moderate sulphate resistant (MSR), and high sulphate resistant (HSR) [6]. The details of available API classes of cement are present in Table 1. This latest API specification (24th edition) is identical to International Organization for Standardization (ISO), ISO 10426-1:2009. The cement of class E, class F, and class J are deleted in this latest specification. Class E and F contain the chemical retarders for controlling the thickening time under the defined conditions [7]. In reality, the identical condition as per API specification is rarely achieved and these cement is incompatible with the additional additives. Further, Class J cement is based upon a $\beta$-calcium silicate-silica composition, which is not a true Portland cement [7]. The hydration process of class J cement was very slow compare to other classes of cements.

2.2 Hydration of OWC

The four mains well know compounds present in the Portland cements are depicted in Table 2. The major constituent of Portland cement is silicate phases (C$_3$S and C$_2$S) which is more than 80 % of total materials [7]. These compounds are anhydrous. When these compounds exposed to water then they are

| Cement Class | Description |
|--------------|-------------|
| A            | This class of cement intended to use up to a depth of 1830 m from surface when special properties are not required and is available only in O grade. This cement is similar to ASTM C150, Type I cement. |
| B            | This class of cement intended to use up to a depth of 1830 m from surface when conditions require moderate or high sulphate resistance and is available in both MSR and HSR grades. This cement is similar to ASTM C150, type II. |
| C            | This class of cement intended for use up to a depth of 1830 m from surface when conditions require high, early strength and is available in O, MSR and HSR grades. This cement is similar to ASTM C150, type III. |
| D            | This class of cement is obtained by grinding clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more forms of calcium sulfate as an interground additive. There are some additives may be used during the manufacturing of class D cement [6]. This class of cement intended for use up to a depth of 1830 to 3050 m from surface when conditions require high temperature and pressures. It is available in MSR and HSR grades. |
| G            | This class of cement is obtained by grinding clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more forms of calcium sulfate as an interground additive. There are no additives other than calcium sulfate or water, or both, shall be interground or blended with the clinker during manufacture of class G well cement [6]. This class of cement intended for use up to a depth of 2440 m from surface as manufactures. It is available in MSR and HSR grades. It can be used a wide range of well depth with additional additives and retarders. |
| H            | This class of cement is obtained by grinding clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more forms of calcium sulfate as an interground additive. There are no additives other than calcium sulfate or water, or both, shall be interground or blended with the clinker during manufacture of class H well cement [6]. The composition of Class G and H cement are similar and the difference is the surface area. Class H is coarser than the class G cement. This class of cement intended for use up to a depth of 2440 m from surface. It is available in MSR and HSR grades. |
decomposed and forming hydrated compounds. The reactions of cement compounds with water and their products can be represented in the symbolic equations as [7]:

\[
2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{Ca(OH)}_2 \quad (1)
\]

\[
2\text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca(OH)}_2 \quad (2)
\]

\[
\text{C}_3\text{A} + 3\text{C}\text{S} + 26\text{H} \rightarrow 3\text{C}_3\text{A} \cdot 3\text{C}\text{S} \cdot 32\text{H} \quad (3)
\]

\[
\text{C}_3\text{A} + 3\text{C}\text{S} \cdot 32\text{H} + 2\text{C}_2\text{S} + 4\text{H} \rightarrow 3\text{C}_3\text{A} \cdot 3\text{C}\text{S} \cdot 12\text{H} \quad (4)
\]

where, the standard cement chemistry abbreviations are used, where \( \text{CaO} \) is denoted as \( \text{C} \); \( \text{Al}_2\text{O}_3 \) as \( \text{A} \); \( \text{SiO}_2 \) as \( \text{S} \), \( \text{SO}_3 \) as \( \text{S}^1 \); \( \text{Fe}_2\text{O}_3 \) as \( \text{F} \); and \( \text{H}_2\text{O} \) as \( \text{H} \).

The product \( \text{C}_3\text{S}_2\text{H}_3 \) represent calcium silicate hydrate and commonly called “C-S-H gel”. The fully hydrated cement constitutes approximately 65 % of CSH gel at ambient conditions [7]. This CSH gel contemplates as the principal binder of hardened cement, which is responsible for stability, and strength of the cement. Typically, the hydration process of Portland cement has separated into five stages as shown in Figure 1. (i) Preinduction period: This is the first stage after cement comes in contact with water and its duration is only a few minutes. This stage shows the wetting of powder and initiation of hydration, (ii) Induction period: The hydration activity has commenced in this stage and CSH gel formation initiated. The duration of this stage is a few hours at ambient temperature, (iii) Acceleration period: This stage represents the setting period of cement. During this stage, the hydration process is accelerated and formed CSH gel deposits into the available water-filled space, (iv) Deceleration period: The hydration rate of cement is decrease in this period. The duration of this stage is several hours, (v) Diffusion period: The hydration process is continuing at a slow rate and strength increases in this stage. The duration of this stage is indefinite at ambient temperature.

### Table 2. Composition of Portland Cement [7].

| Compound                      | Formula          | Abbreviated Formula |
|-------------------------------|------------------|--------------------|
| Tricalcium silicate           | \( 3\text{CaO} \cdot \text{SiO}_2 \) | \( \text{C}_3\text{S} \) |
| Dicalcium silicate            | \( 2\text{CaO} \cdot \text{SiO}_2 \) | \( \text{C}_2\text{S} \) |
| Tetracalcium aluminate        | \( 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \) | \( \text{C}_4\text{A} \) |
| Tetracalcium aluminoferite    | \( 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \) | \( \text{C}_4\text{AF} \) |

#### 2.3 Hydration at high temperature

The hydration process is effectively influenced with the increased temperature. The morphology and stability of the CSH gel are strongly dependent upon the temperature. The hydration products remain the same up to the temperature of 40 °C. As the temperature increases from 40 °C to 110 °C, certain changes may occur in the morphology of CSH gel. When the temperature increases beyond 110 °C, the metamorphosis of CSH gel will be introduced and that result in increases in permeability and decreases in the compressive strength of cement paste. This phenomenon is called as “strength retrogression”. At higher temperature, the CSH gel often convert to \( \alpha\text{-C}_2\text{SH} \) (alpha dicalcium silicate hydrate) which is highly crystalline, [7]. Consequently, the permeability of cement will increase which cause severe problem for the oil well condition.

#### 2.4 Prevention of strength retrogression

The solution for prevention of strength retrogression is reducing the lime-to-silica ratio (C/S ratio) in the CSH gel. Generally, the C/S ratio in the CSH gel is around 1.65 [2]. Many studies have shown that strength retrogression can be prevented by the addition of silica-based materials [8–9]. The conversion of \( \alpha\text{-C}_2\text{SH} \) at high temperature can be prevented by addition of 35 to 40 % silica contents (i.e., silica fume and silica flour) by weight of cement (BWOC), reducing the C/S ratio to about 1.0 [9]. In the presence of silica, tobermorite mineral (\( \text{C}_6\text{S}_8\text{H}_5 \)) is formed which preserved the high strength and low permeability at temperature of 110 °C [9–10]. As the temperature increase above 150 °C, this tobermorite mineral is transform to xonolite (\( \text{C}_6\text{S}_8\text{H}_5 \)) with up to an 11.5 % decrease in absolute volume [11]. Sometimes, tobermorite can persist up to temperature of 250 °C because of aluminium contents [11]. As the temperature further increase above 250 °C, the phase truscottite (\( \text{C}_8\text{S}_12\text{H}_3 \)) originates and is stable up to the temperature of approximately 350°C with silica quartz or 390 °C with silicic acid.
[4]. When the temperature approaches 400°C, the stability of both truscottite and xonotlite get disrupted and they would dehydrate which results in the disintegration of the set cement [7]. These nature of phase changes (Figure 2) at high temperature is dependent upon the mineralogical composition of the cement, its C/S ratio (mole of lime per mole of silica; CaO/SiO$_2$), the amount of fine particles (silica fume), and the temperature and pressure levels [12].

![Figure 1. Hydration Process of Portland Cement [7].](image)

![Figure 2. Portland cement phases with temperature versus the C/S ratio. The vertical lines shows the presence of a different phase obtained at a certain temperature condition [13].](image)

3. Additives for anti-strength retrogression

The additive used as anti-strength retrogression in OWC slurry is high silica content, which reduce the C/S ratio. The high silica content can be obtained from several sources such as silica flour, silica fume, Nano-silica, rice-husk ash, sugarcane biomass etc. An insight on various source of silica content used as anti-strength retrogression additives is presented in the following sub-sections.

3.1 Silica Flour

Silica flour simply made by grinding pure silica sand to a very fine powder. The silica flour constitutes SiO$_2$ approximately 99 % in the chemical composition [13]. It is widely used in oil well cementing industry as anti-retrogression agent. Many researchers [13–14] have studied by use of silica flour as anti-retrogression agent at high temperature. Costa et al. [13] investigated the compressive strength behaviour of class G cement slurry with addition of silica flour (0, 30, 35 & 40 % BWOC) at temperature of 38 °C and 300 °C after 7 and 28 days. Authors [13] observed that the silica flour reacted at high temperature of 300 °C, forming the xonotlite phase and improving the mechanical behaviour, especially in the slurries with 35 % and 40 % BWOC.

3.2 Silica Fume

A very fine (grey coloured) non-crystalline silica produced in electric arc furnace as a by-product of the production of elemental silicon metal or ferrosilicon alloys. Silica fume particles are extremely small, with more than 95 % of the particles being less than 1 µm (100 times finer than cement particle) with high specific surface area 20 m$^2$/g [14]. Some other names of silica fume are condensed silica fume and micro silica [15]. Silica fume particles have a high water demand and absorb excess water in cement slurry. The silica fume is very effective anti-strength retrogression additive for OWC slurry and reacts rapidly with CH to form a more compact form of CSH [14].

3.3 Nano Silica

Nowadays, Nano Silica (NS) is widely used in construction and oil well industries. NS is extremely fine silica particle with nearly about 1000 times smaller than the average cement particles [16]. The
addition of NS in cement slurry, react with calcium hydroxide (CH) and increases the amount of CSH gel, leading to a compact microstructure and improves the mechanical properties [17]. Many researchers [16–17] have investigated the NS as anti-strength retrogression additive for OWC slurry for different temperature conditions and stated that the NS has a high pozzolanic activity, which enhanced the fire resistance of cement specimens [18].

3.4 Sugarcane biomass

Many countries worldwide are producing sugarcane for many purposes. The sugarcane biomass is the residues after the sugarcane crushed and used for generally cogeneration. The composition of such residues mainly comprises of silica either amorphous or crystalline, which implies a potential application in concrete, mortars and cement slurries [19]. Anjos et al. [20] investigated the effect of the addition of sugarcane biomass waste on the compressive strength of oil well cement slurries subjected to temperature of 280 °C. Authors [20] concluded that the sugarcane biomass waste can be used as a substitute for silica flour in oil well cements subjected to high temperatures.

3.5 Ceramic Waste Powder

Ceramic waste powder (CWP) is the waste product produced during the process of polishing ceramic tiles, floor tiles and sanitary ware etc. CWP constitutes approximately 80% silicon dioxide and aluminium oxide which makes it useful for concrete technology [21]. There is limited information reported for use of ceramic waste powder for the application of OWC at high temperature. Souza et al. [8] studied the effect of ceramic waste for application in OWC slurry at high temperature and concluded that the use of ceramic waste isolated is not adequate to prevent the strength retrogression of OWC slurry at higher temperature. However, it can be use as partial replacement of silica flour in certain proportion.

3.6 Ground Granulated Blast-furnace Slag

Ground granulated blast furnace slag (GGBFS) is the slag generated from iron producing blast furnaces, which rapidly chilled in water and then pulverised into a powder. GGBFS is widely used in many cement applications where it provides enhanced durability, resistance to sulphate attack, high resistance to chloride penetration [22]. Researchers [9, 8 & 23] investigated the effect of GGBFS in OWC slurry at high temperature. Alp and Akin [23] stated that it is possible to prepare GGBFS blended OWC slurries with higher compressive strength than conventional silica blended slurries at high temperature.

3.7 Rice Husk Ash

Rice Husk Ash (RHA) is an agricultural by-product of burning rice husk in the boiler under controlled temperature. The process produces about 25% ash containing 85 to 90% amorphous silica plus about 5% alumina, which makes it highly pozzolanic [24]. Vidal et al. [25] studied the RHA as anti-strength retrogression additive for OWC slurry subjected to 300 °C temperature. Vidal et al. [25] concluded that the RHA is effective on inhibiting the cement compressive strength retrogression and it could be a sustainable alternative to commercial silica flour.

3.8 Palm Oil Clinker

Palm Oil Clinker (POC) is a waste material produced upon burning of palm oil shells and Mesocarp fibres in a boiler of palm oil mill [30]. POC generally contains 60 to 75% of silica (SiO2) content. Karim et al. [26] investigated the effect of high temperature on the compressive strength and microstructure of cement slurry containing POC and concluded that the compressive strength is significantly improved.

4. Conclusions

A comprehensive review on anti-strength retrogression additives used in oil well cement at high temperature is performed. The paper shows the hydration process of Portland cement at ambient and higher temperature. The morphology and stability of the CSH gel are strongly dependent upon the
temperature. At higher temperature, the CSH gel often convert to $\alpha$-C$_2$SH which is major cause of strength retrogression. The conversion of $\alpha$-C$_2$SH at higher temperature can be prevented by addition of 35 to 40 % silica contents by weight of cement (BWOC), reducing the C/S ratio to about 1.0. It is observed that there are many anti-strength retrogression additives available in worldwide, which enriched in high silica content. It concluded that the available waste material near to oil and gas industry, which are richest in silica content, could be use in OWC slurry for preventing strength retrogression. In the future work, authors are planning to investigate the effect of combination of these waste materials for preventing the anti-strength retrogression of OWC slurry at high temperature and high pressure.

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