

Slagment Cement Improve the Cement Resistance Toward Acids Attack During Acidizing Treatment

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Abstract: Acidizing treatment in past experience shows several zonal isolation problems after the treatment. This study presents the effect of the acid treatment toward class G cement and slagment cement as the improvement method to improve the cement resistance toward the acid. Lab experiments were conducted by immerge the respective cement cubes into 12% HCl/3% HF solution for 40 min before several analysis were conducted. Based on the result, the mass loss and compressive strength loss of the cement cubes decrease as the curing temperature and pressure increase due to more evenly distributed cement chemical composition crystal in high curing condition as shown in Scanning Electron Microscopy (SEM) analysis. From X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis, only the first layer of the cement cubes shows chemical component change due to the reaction between the acid. This study found that, replacing class G cement to slagment cement can reduce the mass loss and compressive strength loss up to 72% and 82%, respectively.

Key words: Acidizing treatment, class G cement, hydrochloric acid, hydrofluoric acid, slagment cement

INTRODUCTION

Well stimulation is a method applies in production well in an effort to enlarge old channels or to create new path in the producing formation well (Schechter, 1992). There are many techniques used in well stimulation now days such as explosive fracturing, hydraulic fracturing, acidizing and steam injection (Allen and Robert, 1993). The oil companies today is trying to find the comparatively low cost treatment in well stimulation and acidizing is one of the best choice to be implement. Acidizing treatment can be divide into fracturing acidizing and matrix acidizing which are base on its application (Williams *et al.*, 1979). Base on the earlier record, acidizing treatment were performed as earlier as in 1896 and can be apply either in carbonate or sandstone reservoir (Phil and Lullo, 2003).

Past experience shows, although acidizing treatment give a good impact to the oil and gas production, the acids used in the treatment give some effect to oilwell cement such as zonal isolation problem. It was note that, Prudhoe Bay field performance data showed 75% of the squeezed well broke down when acidized compare only 30% of the squeezed wells that have not been acidized (Brady *et al.*, 1989).

Silva *et al.* (1996) studies the effect of acid on the zonal isolation in static and dynamic condition by considers the factors that influence the reaction. The result

shows that the factors that influence the acid attack are surface defect, cement slurry composition and acid solution composition. While Motta *et al.* (1996) find that by replacing HCl with acetic acid the cement solubility can be reduce especially in high temperature condition.

Al-Taq *et al.* (2009) studies the effect of acid type and concentration on oil well cement and recommends a new technique that can reduce acid attack. Result showed that 10 wt% acetic + 1.5 wt% HF acids are suitable to be used as a full strength mud acid in acid stimulation with less cement attack. The authors also recommend using latex as the additive in reducing the cement solubility toward the acid.

This study present the finding of the study on the effect of different temperature and pressure condition on cement solubility and compressive strength loss, chemical composition change of cement and lastly slagment cement as a new approach to improve acid attack toward oil well cement.

MATERIALS AND METHODS

Class G oilwell cement: In this study portland class G cement be selected as the base line cement for comparison with slagment cement. The selection be made base on the common Malaysia oilfield well depth which is up to 8000 ft. Class G oilwell cement is made from raw materials such as clay and limestone (Smith, 1989). It was note that

Table 1: Curing condition

Sample	Temperature (°F)	Pressure (psi)
1	90	3000
2	150	3000
3	200	3000
4	175	3000
5	175	4000
6	175	5000

(Hewlett, 1998; Taylor, 1997) when cement are mixed with water they form two primary hydration products that are Calcium-Silicates-Hydrate (C-S-H) and calcium hydroxide (Ca(OH)₂). C-S-H comprise approximately 70 wt% while Ca(OH)₂ around 15-20 wt% of the hydrated cement. The average of CaO/SiO₂ ratio of the C-S-H is about 1.7 (Taylor, 1997).

Slagment cement: Slagment is a combination between Ordinary Portland Cement (OPC), Blast Furnace Slag (BFS) and silica with the percentage distribution of 65, 35 and 12.5%, respectively. Blast furnace slag is a non-metallic product which consists essentially of silicates and aluminosilicates of calcium (Hewlett, 1998). BFS are normally used in construction industry as one of the cement additive for application that requires sulphate or sea water resistance, low permeability, low expansion and high durability (Ghosh, 2002). Meanwhile, silica is an additive used in oil well cement to maintain low permeability and high compressive strength under high temperature conditions (Smith, 1989).

General experiment procedure: There are five main stages in the experiment procedures which are preparation of the cement cubes, preliminary analysis on the cement cubes, preparation of the acid solution, expose of the cubes to the acid and analysis of the cement dissolved by the acid. All of the experiment procedures are conducted at Universiti Teknologi PETRONAS laboratory in January 2011 and it take about eight month to complete all of the experiment procedures.

To prepare cement cubes, cement slurry were prepared first by mixing the right amount of cement and water requires using constant speed mixer by following the step in API recommended practice 10B-2 (API, 2005). The ready cement slurry were poured into the 2 in cubic molds before the cement slurry were cured for 8 h in the HTHP curing chamber under the desired temperature and pressure as stated in Table 1. After the curing process, the samples will be examined and only the best cubes will be taken before the initial mass were recorded. For each curing condition, six samples needed for the experimental purpose.

For preliminary analysis stage, there are four main analysis were conducted which are compressive strength, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). For XRD, XRF and SEM analysis, the cement cubes were cut into

two slices with 3 mm in thickness. The purposes of this earlier analysis are to examine the initial condition of the cement cubes.

In this study, the main acid that was used is 12% HCl/3% HF acid solution. The acid solution was prepared by dissolving 143.6 g of ammonium bifluoride (NH₄F₂) into 3 L of 15% HCl acid concentration. Reaction between HCl with NH₄F₂ will produce HF and this method usually used in the industry.

A beaker of 3 L of the acid solution is placed in thermostatically controlled water bath. The second beaker with the same volume of water is needed and will be place alongside the first beaker as a temperature controller because HF reacts with the glass of the thermometer. After the beaker is place in the water bath, the acids solution is heated until it reaches 65°C. As soon as the acid reaches this temperature, the cement cube immediately place in the beaker of acid. The cubes will be left in the beaker for exposing purpose for about 40 min.

Forty minutes after exposed test, the cube were removed from the solution and allowed to dry at room temperature for about 1 h. Then, the cubes were weight and the final mass was recorded. The solubility of cement by the acid is expressed in terms of mass loss, according to Eq. (1):

$$Mass\ Loss(\%)_{(1)} = \left[\frac{Initial\ Mass - Final\ Mass}{Initial\ Mass} \right] \times 100 \quad (1)$$

Then, the cement cubes will be analysis once again with the same method as in the preliminary analysis stage. Comparison between the initial and final condition of the cement cubes were investigated. From there, the mass loss, compressive strength loss and chemical component change were determined.

Finally, after investigate the result of class G cement, the worst curing condition that was used to produce class G cement cube were selected as the curing condition for slagment cement. The selection is made because it is easier to observed any changed to the cement cubes before and after the acid attack. The experiment procedure were apply are the same as class G cement but only one curing condition used this time.

RESULTS AND DISCUSSION

Solubility and compressive strength loss of class G cement: Figure 1 shows the SEM-BSE image of sample 1 and sample 6 before and after the acid attack. In a polished cement surface the anhydrous grains appear brighter than the hydration products, which have a lower atomic number (Hewlett, 1998; Taylor, 1997). So, the unhydrated cement grain appeared bright, Ca(OH)₂ appeared slightly darker, other hydrated product still darker (C-S-H) and the pores appear as the most black. Base on the observation, the depth of penetration of

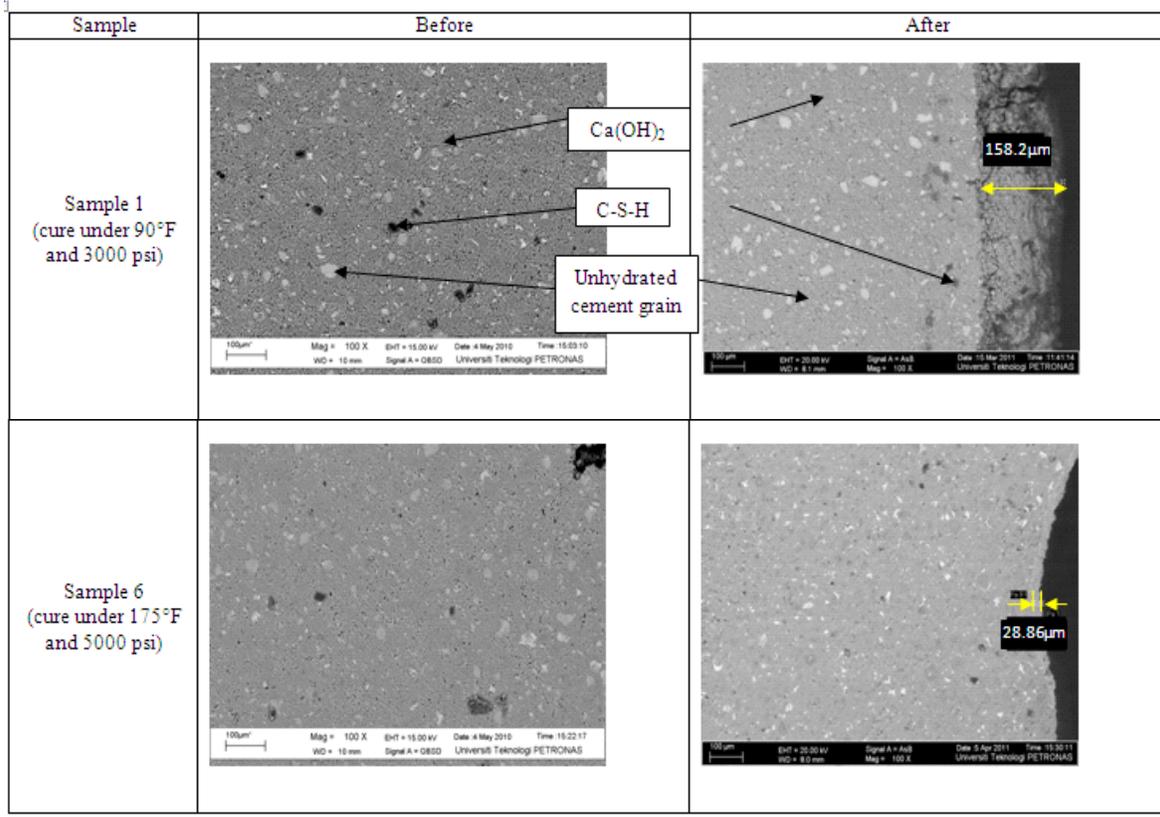


Fig. 1: BEM-SEM image of class G cement cured under different temperature and pressure condition

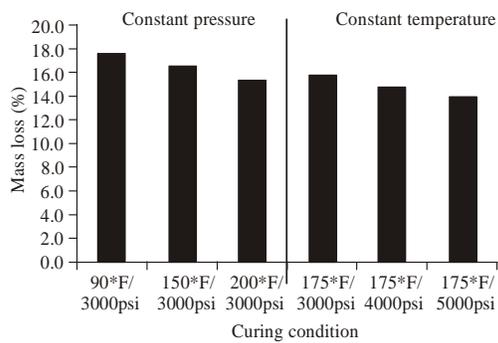


Fig. 2: Mass loss with different curing condition

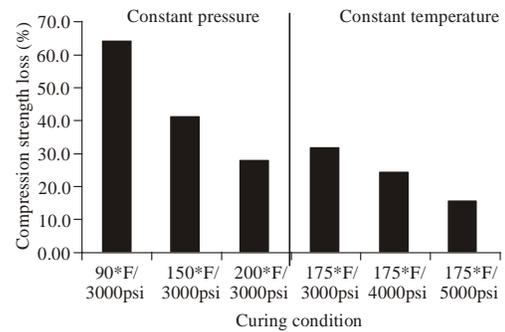


Fig. 3: Compression strength loss with different curing condition

sample 1 is the highest which is 158.2 µm while sample 6 had the smallest depth of penetration with 25.86 µm in length. This is because as the temperature and pressure increase, the degree of hydration increases (Hewlett, 1998). Increasing of degree of hydration will result in smaller and more evenly distribution of Ca (OH)₂ crystals. This provide a more uniform and effective barrier to acid attack.

From Fig. 2 and 3, it was observed that, the mass loss and compressive strength loss decrease as the curing

condition increase because the cement chemical components are more distributed and uniform at high curing condition. This will result in decreasing of cement permeability. Permeability is the key factor that controls the rate of acid attack toward the cement. When the permeability is low, the acid attack toward cement is limited to the surface or otherwise the acid attack spreads into the interior. So, it will reduce the change of the acid solution to attack the cement more depth and less compressive strength loss were record.

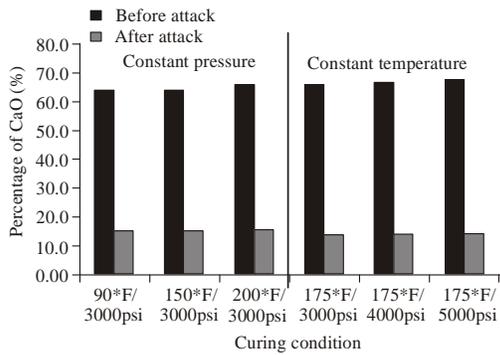


Fig. 4: Percentage of CaO

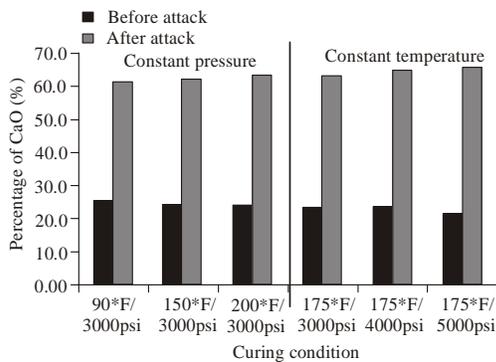


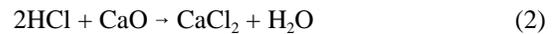
Fig. 5: Percentage of SiO₂

Chemical composition change: The initial condition result from XRD analysis shown portlandite, calcite and C₃S grain appear on the first and second layer of the cement. After the cement was exposed to 12% HCl/3% HF solution, there are a few new chemical components appear on the first layer of the cement while there are no changes on the second layer. The components are amorphous silica, Calcium Chlorine (CaCl₂) and Fluorite (CaF₂). CaCl₂ is expected appear from the reaction between CaO and HCl while CaF₂ is expected from the reaction between HF and calcium of the cement. CaF₂

appear as a white protecting layer on the surface of the cement cubes. The same case was observed on all cubes irrespective of the curing conditions of the cement and acid concentration.

Base on XRF analysis, the main composition of cement cubes is CaO and SiO₂ with the average percentage of 67-63% and 21-24%, respectively. The percentages of CaO and SiO₂ before and after attack is represent in Fig. 4 and 5.

After the acid attack, the percentage of CaO decreases while the percentage of SiO₂ increase as represent in the bar chart. The attacked cement cubes show significant decreasing in percentage of CaO where the range percentage reduce from 67-63 to 12-15% while range percentage of SiO₂ increase from 21-24 to 60-64%, respectively. Form the literature hydrochloric acid will react with CaO while hydrofluoric acid with SiO (Kalfayan, 2000). Reaction between HCl and CaO will produce calcium chloride and water while the reaction between HF and SiO₂ will produce silicon tetrafluoride and water. Silicon tetrafluoride (SiF₄) is a soluble gas and is capable of undergoing further reaction when held in solution by pressure. The reaction equation is shown below:



Increasing of SiO₂ is cause by high rate of reaction between HCl and CaO but the reaction between HF and SiO₂ is low because HF is a weak acid and the ability of the molecules to separate is low. In term of curing condition as the temperature and pressure increase, less among of CaO and SiO₂ were react with the acid solution because the permeability of the cement reduce.

Slagment cement as a new approach to improve cement resistance: In this study, slagment cement was used to replace class G cement as a new approach to

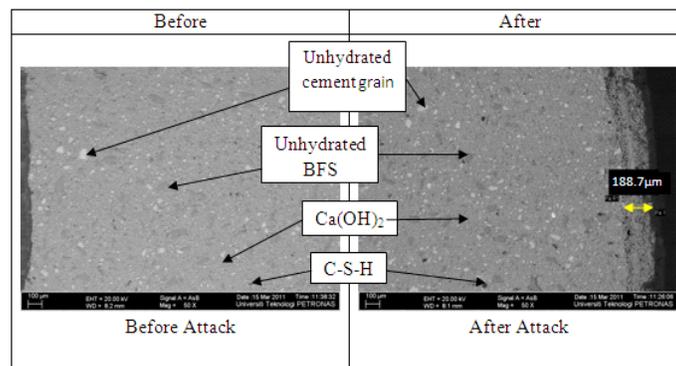


Fig. 6: SEM-BSE image of slagment cement before and after acid attack

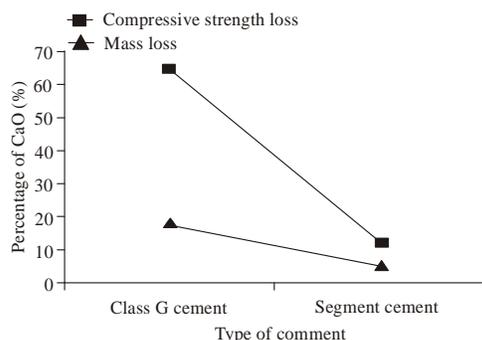


Fig. 7: Mass loss and compressive strength loss with different cement type

improve the cement resistance toward the acid attack. Figure 6 shows the SEM-BSE image of the slag cement before and after attacked by 12% HCl/3% HF. The unhydrated cement grains appear to be bright with well defined and sharp boundaries. The unhydrated BFS appear slightly darker than the unhydrated cement grain. The Ca (OH)₂ component is much darker than BFS grain, but appears as a region with diffused outlines. The remaining darker area is of C-S-H phase.

The depth of penetration of slag cement is 188.7 μm and it is longer than the depth of penetration of class G cement with the same curing condition. This is because the development of early strength of slag cement is lower compared to the class G cement and thus the permeability is much higher in the slag cement in the early stage hydration development since it was cured for only 8 h.

Replacing class G cement with slag cement shows a success in improving cement resistance. Figure 7 displays the mass loss and compressive strength loss of the slag cement after being attacked by 12% HCl/3% HF. From the observation the percentage of mass loss is reduced from 17.6% for class G cement to 4.9% for the slag cement. Compressive strength loss also shows some improvement where the previous loss is 64.15% but reduce to 11.69% after using slag cement.

Blast furnace slag is self-cementing, which means it does not require calcium hydroxide to form cementation products such as C-S-H but it cannot be used by itself because the amount of cementation products formed and the rate of formation are insufficient for engagement in oilwell cementing application (Hewlett, 1998; Taylor, 1997).

Silica fume is of very small particles and it can enter the space between the particles of the cement easily. The ability to enter pores spaces between the cement will make the cement more denser and the cement will have low permeability and porosity. It will result in less acid solution that can penetrate into the cement and less chemical reaction occur.

XRD and XRF result indicated that C-S-H produced during the hydration of a slag is lower in calcium and higher in aluminum and magnesium than the C-H-S formed during the hydration of class G cement. Since the calcium is lower in the slag, the reaction between the acid especially to the calcium compound is less.

CONCLUSION

The worst class G cement sample attacked by 12% HCl/3% HF is sample 1 and the best sample that has high cement resistance is sample 6. Decreasing of the depth of penetration, mass loss, compressive strength loss and chemical component changes from sample 1 to 6 is because of the degree of cement hydration increase. Result, more even distribution of Ca (OH)₂ which provides uniform and effective barrier to acid attack.

The cement cured at 175°F and 5000 psi gives the smallest compressive strength loss and smallest change in the percentage of CaO and SiO₂ component because at high curing condition the permeability is more low which can avoid acid to penetrate into the cement cubes and react with the chemical component of the cement.

Slag cement can improve the cement resistance toward acid because the content of calcium inside the cement is less as compare to class G cement. That means less acid reaction between the chemical components of slag cement with the acid. This slag cement have potential to be commercial in well cementing application for acidizing treatment well.

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