Characterization of Silicate Scale formation : The Effect of pH on Silicate Scale Formation

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***Abstract*— One of the challenging situations or problems that engineers nowadays have been encountering in oil and gas industry is the formation of silicate scale. ASP flooding is one of the methods used to improve the oil recovery efficiency. However, this ASP flooding process could produce the silicate scale. The formation of silicate scale could be throughout overall processes, from upstream to downstream process. In ASP flooding, the water injected into the reservoir is at high pH value, injected to displace the remaining oil in the reservoir. As it propagating within the reservoir from the injection well to the production well, it will mix up with the connate water at neutral pH. This mixing of water will vary the pH of water, causing the pH condition inside the reservoir to be reduced. This reduction of pH will encourage the precipitation of silicate scaling. The lower the value of the pH, the higher the rate of the silicate scale formation. The variation of pH will produce different type of morphology. There were two methods, Fourier's Transformation Infra-Red or FTIR and also X-ray diffraction to analyze and characterize all the six samples, which were are Magnesium and Silica brine. Three samples of this brine with different condition were prepared. The first brine sample was prepared at room temperature, pH 8.5. While the second brine was at room temperature, pH 11. The third was the mixture of brine sample at room temperature, at pH 8.5 and 11-12 respectively, but taken both brine were left 22 hours before record the observation. The forth sample was magnesium silicate, the fifth sample was magnesium hydroxide and the last sample was silicon dioxide. The sample 4,5 and 6 were the pure commercial compound, used as comparison to the prepared brine. From the results obtained, it clearly showed that pH will affect the precipitation significantly. Sample with lower pH value will has higher intensity, sharp peak and also longer diffraction signals distance. Sharp peak obtained from XRD experiment indicates that there is crystal or scale present in the sample while broad peak indicates the sample is amorphous.**

Keywords*—Amorphous,Fourier transform infra-red, *pH,precipitation,scale,scaling,silica,silicate,Xray.

I. INTRODUCTION

Scale is defined as the secondary deposit of inorganic compounds that is caused by the presence of fluids in a system at least partially manmade, by which silicate scale formation is not a foreign thing in oil and gas industry [1]. Silicate scaling usually occurs and can be found mainly in three main field which are ASP flooding, geothermal brine and industrial water [2]. Figure 1 shows the example of scaling that usually deposited in pipe.

Figure 1 The scale deposition in pipe

Generally, during alkaline flooding, the injected water usually has pH 11 or higher when it sweeps the fluid within the reservoir [3]. This high pH water usually dissolves quartz in the formation, producing dissolve monomeric silica ($Si(OH)_3O\text{-}Na+$) ion, along with the water flood which remain soluble and stable in this high pH environment [4]. However, as this high pH ASP sludge propagates in the reservoir and comingles with the neutral connate water, the pH of the injected water will be reduced [3].

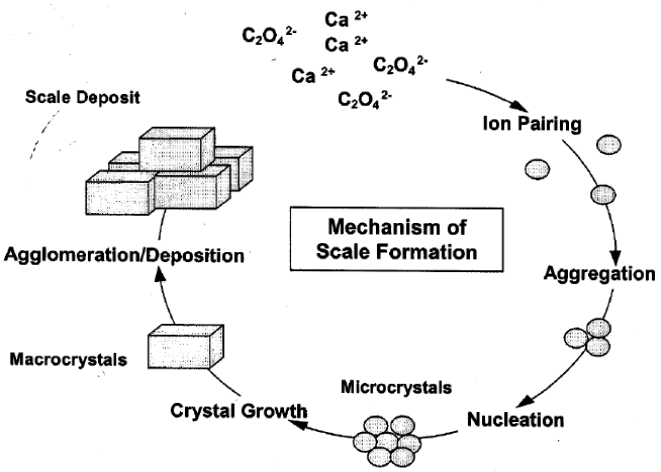

Figure 2 The scale formation process

The scaling precipitation or behavior is affected greatly by the pH, producing different results even there are swiftly changes in the pH [5]. The silicate scaling can occurs at many points in the formation or within the wellbore and this will give adverse effect to the oil production facilities [6]. This scaling can be found in the perforation tunnels, within the pipe and also clogging the equipment [7]. The purpose of this research is to study the relationship between the silicate scale formation and the pH, in effort to understand the complex mechanism of the silicate scale formation. There are many factors that can affect the rate of scaling but pH give the most significant effect to the rate of scaling [8].

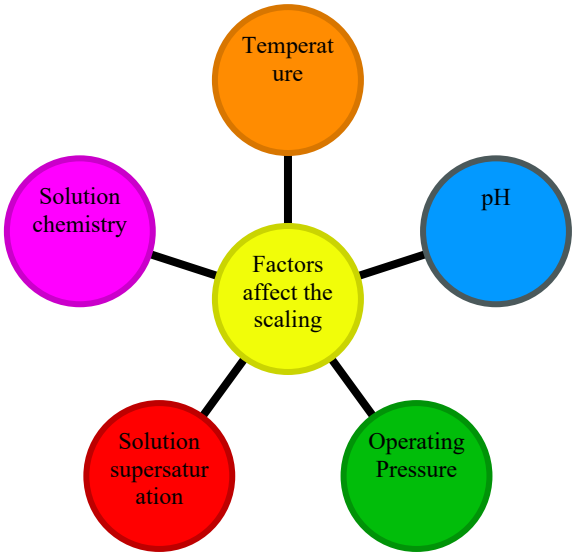

Figure 3 Factors that affect the scaling

II. METHODOLOGY

A. Materials and Method

In this study, mixed brines of magnesium brine and silicon brine were prepared to replicate the ASP leachate during ASP flooding. 1800ppm magnesium brine was prepared by dissolving 75.3 gram of magnesium chloride hexahydrate $MgCl_2.6H2O$ salt in 5 L of distilled water while 1880ppm of silicon brine was prepared by dissolving 71 grams of sodium metasilicate pentahydrate $Na_2SiO_3.5H2O$ salt in another 5 L of distilled water. In the first duplicate sample, 50ml of magnesium brine was added into 50ml of silicon brine to produce a final mixed concentration of 900 ppm Mg:940ppm Si. The pH of these brines were then adjusted to pH8.5 and left reacted at room temperature for 22 hours. The scale produced were then filtered and examine by using Fourier Transform Infra-Red (Spectrum One) (FTIR) and XRD analysis (X'Pert PRO PANalytical) using Cu-Ka radiation at a scan speed of 2.5/min.

The second duplicate brines with the same final mixed concentration were left reacted at its natural pH, approximately 10.5 and room temperature for 22 hours. While the third duplicate samples was the left reacted exactly in the same condition with the second duplicate for 22 hours before these brines were adjusted to pH8.5 and allowed to react for another 22 hours i.e. in total reaction time of 44 hours. The forth sample was magnesium silicate, the fifth sample was magnesium hydroxide and the last sample was silicon dioxide. The sample 4,5 and 6 were the pure commercial compound, used as comparison to the prepared brine. Then after the reaction of the brine, the scale produced was filtered and analyzed by using FTIR and XRD.

In the FTIR analysis, all six samples, which were three sample brines prepared above and those three pure commercial brines were crushed into fine powder and tested on the base plate of the FTIR equipment. Before testing the sample, acetone were used to clean up the base plate surface. This process was repeated before testing new sample. This was to ensure the sample did not mixed up with the previous sample, and affecting the results. The results were shown at the display monitor.

All the six samples were examined by XRD analysis (X'Pert PRO PANalytical) using Cu-Ka radiation at a scan speed of 2.5/min. All the six samples which were three sample brines prepared and the pure commercial brine were crushed and grinded to a fine powder, approximately less than ~10 µm(or 200-mesh) in size. Then the sample was put, packed and pressed into the sample holder. Then smeared uniformly onto a glass slide and put it into the instrument, push the 'Start' button and the scanning process started. After the scanning process was completed, the result was displayed on the display monitor.

III. RESULTS AND DISCUSSION

A. Fourier Transform Infra-Red (FTIR)

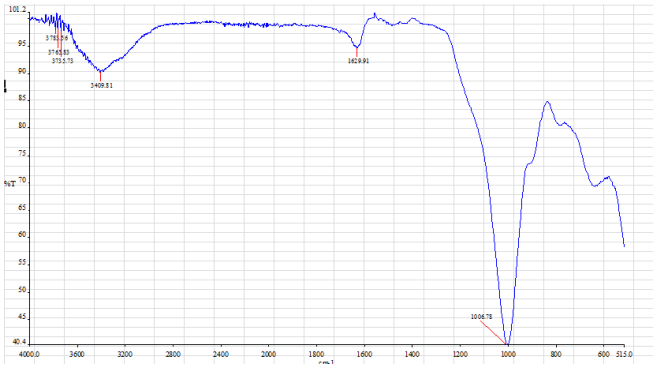

Figure 4 940 Mg:940 Si at room temperature, pH 8.5

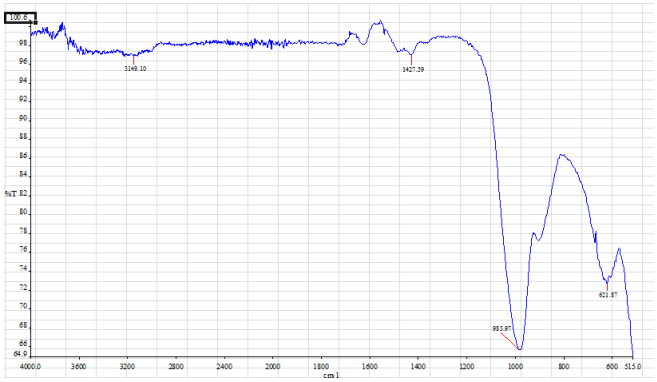

Figure 5 940 Mg:940 Si at room temperature, pH 11

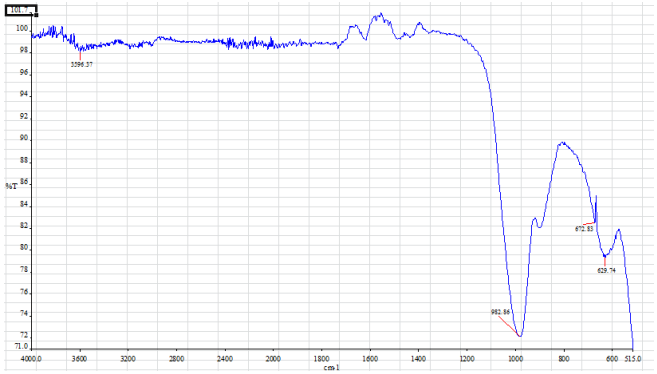

Figure 6 940 Mg:940 Si at room temperature, at pH 8.5 after 22 hours and at pH 11 after 22 hours

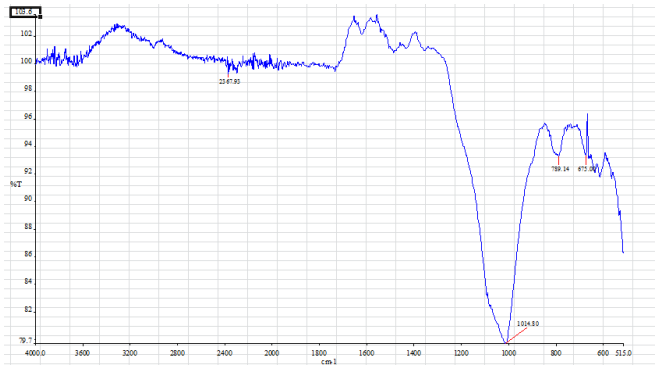

Figure 7 Magnesium silicate

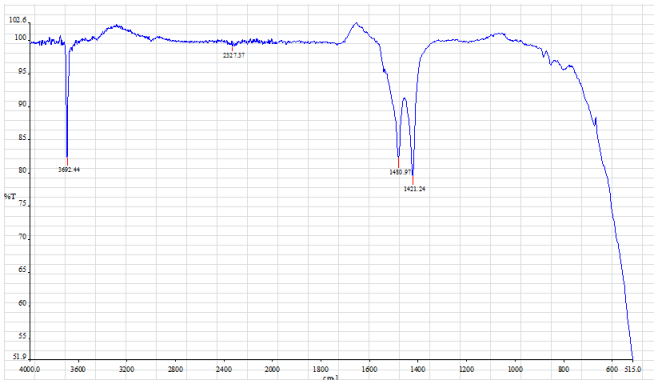

Figure 8 Magnesium hydroxide

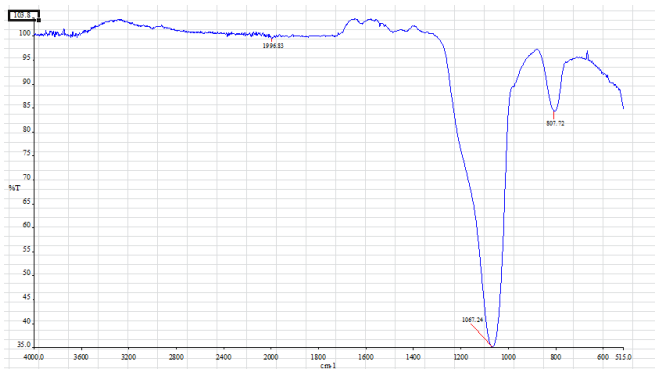

Figure 9 Silica dioxide (amorphous silica)

From all the graphs obtained, show that a broad band centered at around 3850-3150 cm^{-1}, indicates the absorption of water on the silicate surface [9]. Apart from that, it can be observed that the intense Si-O covalent bond at around 1000-1200 cm^{-1}. This indicates that the silica network was immense [9]. Next, the range from 780 to 810 cm^{-1} shows the Si-O-Si stretching. At 1000-1080 cm^{-1}, it shows the present of the Si-O stretching while at 515 cm^{-1}, represent the Si-O-Mg bending [9].

Next, the pH of the solution affect the rate of saturation and precipitation greatly. The scaling rate is directly proportional to the value of the pH. In simplest example, comparing figure 4 and figure 5, figure 4 graph has more peak compared to the graph in figure 5. Figure 5 shows less fluctuation and higher tendency of conversion to form scale.

B. X-ray diffraction (XRD)

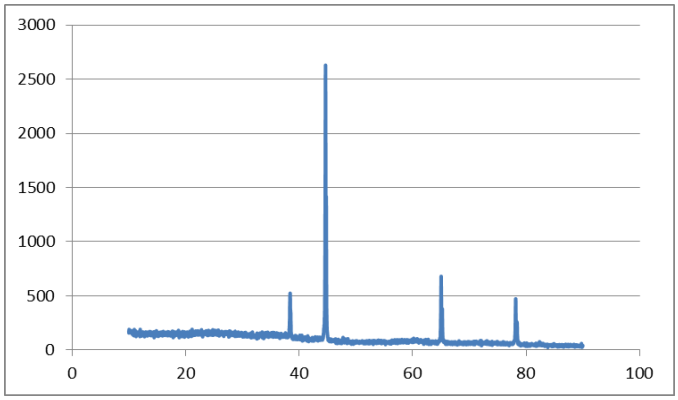

Figure 10 940 Mg:940 Si at room temperature, pH 8.5

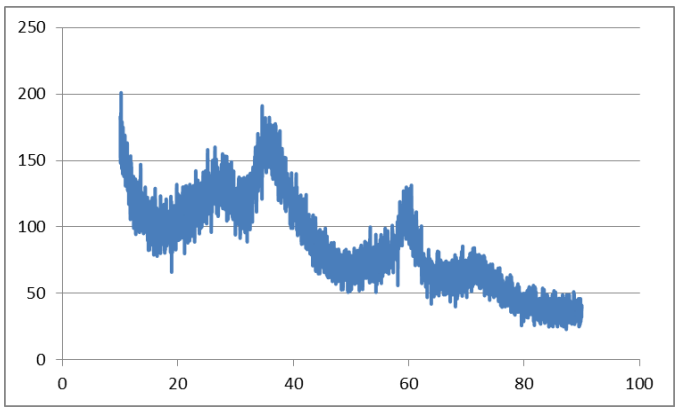

Figure 11 940 Mg:940 Si at room temperature, pH 11

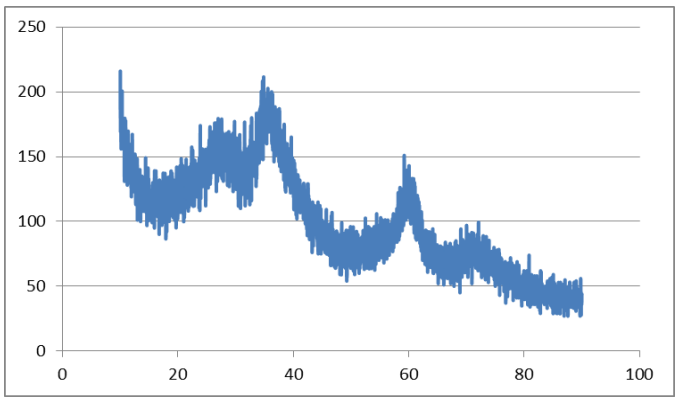

Figure 12 940 Mg:940 Si at room temperature, at pH 8.5 after 22 hours and at pH 11 after 22 hours

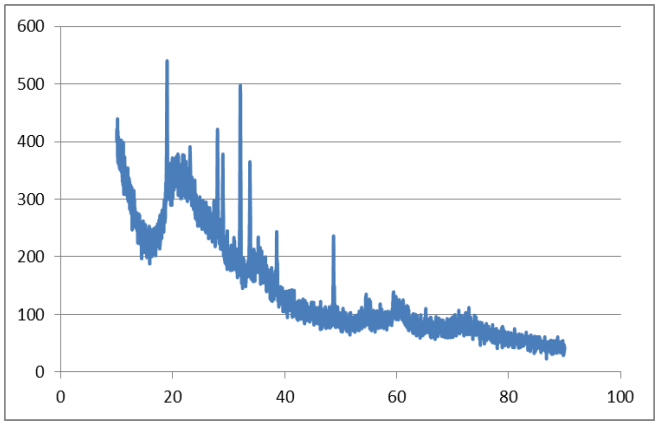

Figure 13 Magnesium silicate

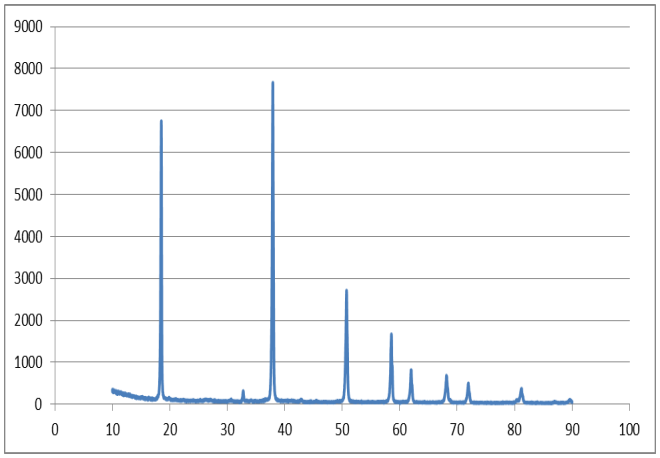

Figure 14 Magnesium hydroxide

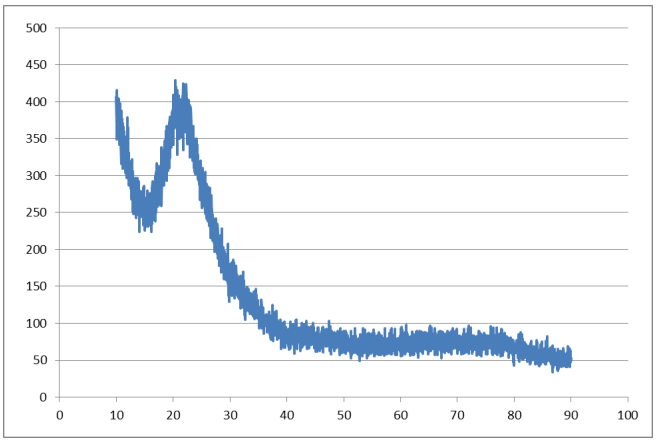

Figure 15 Silica dioxide (amorphous silica)

From graphs obtained from XRD analysis, figure 10 to figure 15, it show that there is a significant different from prepared samples with the commercial pure samples. Firstly, by comparing graph from figure 10 with graph from figure 11, it can be seen that graph from figure 11 has broader peak than graph from figure 10. Graph 10 and graph 11 had the same compound with the same concentration, but they varied in term of pH. Sample from Graph 11 has higher value of pH than sample from graph 10, means that sample from graph 11 was more 'alkalinity' than sample from graph 10.

Next, the sharp peak at graph 10 indicates that the sample has crystallinity structure, while the broad peak at graph 11 indicates that the sample is amorphous [10]. Thus, this shows that there is crystal or scale present in sample from graph 10. Apart from that, the successive peaks from sample from graph 10 was higher (intensity) compared to sample from graph 11. Thus, the hypothesis that can be made from this result is scaling formation does not favors alkaline condition [11]. From graph 10, the diffraction signals at 2Θ = 36.55°, 44.01°, 63.41° and 76.53°. While based on graph 11, the diffraction signals at 2Θ = 25.11°, 33.73°, 58.72° and 70.48°. These values clearly showed that graph 11 sample had less or the distance between signals was longer compared to graph 10.

Next, by comparing prepared samples with the pure commercial samples, graphs showed that pure commercial samples have higher and more successive peaks compared to prepared samples. This can be proved by observing figure 13 and figure 14. From figure 13, the diffraction signals at 2Θ = 18.89°, 20.10°, 27.30°, 27.70°, 30.62°, 33.53°, 37.38°, 48.62°, 53.74°, 58.36°, 59.90° and 70.50°. While based on figure 14, the diffraction signals at 2Θ = 18.12°, 31.70°, 37.81°, 50.56°, 58.36°, 61.86°, 67.96°, 71.57° and 80.32°. This showed that pure commercial samples had more successive peaks than prepared samples. More successive peaks may indicate more crystallized the structure as the crystal structure diffract the signals [12]. Apart from that, these two graphs showed that the intensities for both these graph were higher, almost as twice the intensities of prepared samples in 'alkaline' condition.

For figure 15, the graph illustrates that there was only one successive graph, and does not has many peaks as others. This is because silica dioxide or also known as amorphous silica, it does not has shape or unstructured [13]. As stated before, the broad peak indicates that the sample is not crystal, but it is amorphous.

IV CONCLUSION

The formation of silicate scale is a crucial issue that has to be highlighted and worked on in oil and gas industry. This research has achieved its main objective which is to study the effect of pH on the silicate scale formation by characterize the scale produced by various spectroscopic analysis. FTIR and XRD analysis able to analyze the chemical moieties and functional group presents in the test samples. It can be concluded that pH greatly affect the mechanism of silicate scale formation. However, a more comprehensive analysis should be done by extending the analysis using other spectroscopic techniques such as mass spectrometry, ESEM/EDAX and XRF. It can be concluded that pH affect the formation of silicate scale greatly as when the pH value decrease. Based on the results obtained, it showed that the scale produced in pH 8.5 has more successive peaks, in both FTIR experiment and also in XRD experiment. This may indicate more crystallized the structure or more scale produced as the structure diffract the signals for sample with lower pH when compared to higher pH graphs. The sharp peak obtained from XRD experiment indicates that there is crystal or scale present in the sample while the broad peak indicates that the sample is amorphous. Thus, the conclusion that can be drawn from these results is scaling favors lower pH value. Furthermore, it can be analyzed that pure commercial samples also have more successive peaks compared to prepared samples. This has shown that pure commercial samples produced more and variety type of scaling.

ACKNOWLEDGMENT

I would like to show my special gratitude to my parents, Mohd Yazid Bin Kasim and Salinda Binti Hassan for the continuous love and support to me, in terms of money and morale support throughout completing this research. I also would like to give thousands acknowledgement to my supervisor, Madam Rozana Azrina Binti Sazali for always giving support, guidance, supervision, encouragement and advices in assisting me to make this final year project a successful one. Apart from that, I also would like the laboratory technicians for always giving support, guidance and helped me in completing this research. Last but not least, my special thanks to my colleagues and friends for always boost my morale and sharing their knowledge.

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