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Abstract

Polymer flooding is being pilot tested for the first time in the Schrader Bluff viscous oil reservoir at the Milne Point field on Alaska North Slope. One of the major concerns of the operator is the impact of polymer on the oil production system after polymer breakthrough, especially the polymer induced fouling issues in the heat exchanger. This study investigates the propensity of polymer fouling on the heater tubes as a function of different variables, with the ultimate goal of determining safe and efficient operating conditions. A unique experimental setup was indigenously designed and developed to simulate the fouling process on the heating tube. The influence of heating tube skin temperature, tube material, and polymer concentration on fouling tendency was investigated. Each test was run five times with the same tube, and in each run, the freshly prepared synthetic brine and polymer solution were heated from 77 °F to 122 °F to mimic field operating conditions. The heating time and fouling amount were recorded for each run. Cloud point measurement has also been conducted to find the critical temperature at which the polymer in solution becomes unstable and precipitates out. The morphology and composition of the deposit samples were analyzed by environmental scanning electron microscopy and X-ray diffraction, respectively. It has been found that the presence of polymer in produced fluids would aggravate the fouling issues on both carbon steel and stainless steel surfaces at all tested skin temperatures. Only higher skin temperatures of 250 °F and 350 °F could cause polymer induced fouling issues on the copper tube surface, and the fouling tendency increased with polymer concentration. At the lower skin temperatures of 165 °F, no polymer-induced fouling was identified on the copper tube. The cloud point was determined to be between 220 °F and 230 °F. A critical temperature that is related to the cloud point of the polymer solution was believed to exist, below which polymer induced fouling would not occur and only mineral scale deposited, but above which the polymer would aggravate the fouling issue. The heating efficiency of the tube would be reduced gradually as more fouling material accumulates on its surface. If polymer precipitated and deposited on the surface, it would bond to the mineral crystals to form a robust three-dimensional network structure, resulting in a rigid polymer induced fouling. The study results have provided practical guidance to the field operator for the ongoing polymer flooding pilot test on ANS

Introduction

The Alaska North Slope (ANS) contains about 12 billion barrels of viscous oil (20-2,000 cP) which is mainly located in the "West Sak-Schrader Bluff" formations (Pospisil, 2011). The development pace of this vast resource has been very slow due to high development costs and low oil recovery using conventional waterflood. Even after three decades of development efforts by multiple operators, the total viscous oil production rate from all ANS fields just reached 56,000 barrels per day by May 2017 (Cheng et al. 2018). Although thermal EOR methods have been recognized as the most effective techniques to recover heavy oil, they are impractical on ANS because of the high cost of generating steam in the Arctic and the potential of thawing the permafrost which would lead to severe environmental impacts. Recently, polymer flooding has attracted attention and become a promising EOR technique in viscous and heavy oil reservoirs due to the extensive application of horizontal wells and the advancement of polymer flooding technology. Currently, the US Department of Energy (DOE) and Hilcorp Alaska are cosponsoring an advanced polymer flooding technology pilot test in the Schrader Bluff viscous oil reservoir with an in-situ oil viscosity of 330 cP (Dandekar et al., 2019).

The EOR performance of polymer flooding in heavy oil reservoirs has been proven by extensive laboratory studies including experiments, simulation and field applications all over the world, while the current field pilot test (Dandekar et al., 2019) results are encouraging. However, the potential issues of produced fluids treatment resulting from polymer breakthrough are still the main concerns for the operators. Once polymer breaks through, it may cause severe emulsification issues reducing oil and water separation efficiency and aggravate the scaling and fouling issues in production facilities, especially on the heater tubes in the heat exchanger. Therefore, this study focuses on investigating the potential of polymer induced fouling on the heater tubes in the heat exchanger used on ANS.

Mineral fouling caused by salts such as calcium carbonate, calcium sulfate, and barium sulfate, is one of the most commonly encountered issues in any oil production system, which can cause significant production problems and substantial economic costs (Crabtree et al. 1999). The mineral fouling issue is generally more severe under high-temperature conditions in the heat exchangers, which has been extensively investigated by researchers. For example, Wylde et al. (2010) reported severe $CaCO_3$ scale issues on fire tubes and higher scaling potential for Calcite at elevated skin temperature. Also, they evaluated the typical scale inhibitors' performance at elevated temperatures using Dynamic Scale Loop (DSL), and they found no tested scale inhibitors were stable to prevent scale formation at the temperature of fire tubes. Kazi et al. (2015) investigated the effect of solution concentration, velocity, and material type on fouling issues in heat exchangers, and they found that with increasing temperature and concentration, the amount of deposited mass increased significantly due to higher nucleation rates. They also found that materials with higher thermal conductivity, such as aluminum, had a higher scale formation in comparison to materials with lower thermal conductivity, such as stainless steel. Then Teng et al. (2017) investigated the calcium carbonate deposition on a double-pipe heat exchanger with different heat exchanging surfaces, and they also studied the influence of various parameters on calcite deposition. They found that a higher concentration of Calcite and higher temperatures led to faster deposition whereas high velocity of fluids reduced the deposition rates due to increased shear stress. Recently, with the wide application of chemical EOR techniques, more severe fouling issues have been noticed in the production system, which is attracting much attention to academics and industry.

In the production systems of chemical EOR projects, besides the typical mineral scaling, fouling issues may directly result from applied chemicals, such as alkali, polymer, and surfactant. Even the used chemicals may react with the minerals aggravating the mineral fouling issues. Previously, the study of Moradi and Doe (1987) had demonstrated that hydrolyzed polyacrylamides (HPAM) could precipitate when hard brines were present, especially under high-temperature conditions (above the cloud point), since the calcium ions could bind with the polymer due to reacting or crosslinking with the acrylic group of HPAM. Recently, studies have been conducted to investigate the fouling issues in production systems of chemical EOR projects. Cao et al. (2007) reported their novel techniques to solve the severe scaling

issues associated with the downhole pumps in producers of an ASP flooding project in Daqing Oilfield, China. Wylde et al. (2011 and 2013) and Zheng et al. (2011) reported and summarized the chemicals, especially the polymer-induced issues in oil and water separation and processing systems in chemical EOR projects, and they all recognized that the problems were particularly challenging in heat exchangers which were commonly used to promote oil and water separation by heating the produced fluids. That is because the extremely high skin temperature of the heating tube can decompose the produced HPAM, which would coat the heating tube, further elevating skin temperatures and causing a more challenging scaling regime so that the mineral scale propensity would be further enhanced. Wylde et al. (2011) and Wang et al. (2017) investigated the influence of polymer on mineral scale formation and the performance of commonly used scale inhibitors using the DSL method and static bottle test method. Their study results confirmed that, in the presence of polymer, the overall fouling propensity could be significantly enhanced, and the effectiveness of the typical scale inhibitors could be significantly deteriorated, especially under higher skin temperature conditions. Besides, Wang et al. (2017) analyzed the scale deposits obtained from the bottle test using an ESEM and XRD techniques. They found that the morphology and polymorph of the scale were significantly changed due to the strong interactions between the polymer and mineral deposits, which may make the polymer-induced fouling more challenging to be prevented and removed using conventional techniques. Mittal et al. (2018) also investigated the influence of polymer on fouling in production systems using the DSL method. They found that the polymer cloud point is the critical temperature above which the polymer can enhance the scaling propensity, but lower than the cloud point, the polymer even can inhibit mineral scale. These studies imply that a new and unique technique may be needed to treat the EOR polymer-induced fouling issues. Although DSL is the most commonly used method to study the fouling problems, it cannot evaluate the fouling tendency quantitatively by calculating the fouling rate and does not allow us to observe the fouling process and severity visually. Also, the inside diameter of the tubing is so small that fouling/deposit samples generally cannot be obtained from the DSL test for morphology and composition analysis. Scale precipitates can be obtained from static bottle tests which can only be conducted at low temperatures (< 212 ºF/100 ℃) for ESEM and XRD analysis, though these scale precipitates may not accurately represent the fouling material on the heating tube surface generated at high temperatures (> 212 ºF/100 ℃).

In this study, a new experimental device has been specially designed and built in-house, which can simulate the extremely high skin temperatures of the heating tube, to investigate the EOR polymer-induced fouling issues in the heat exchanger. The fouling tests have been first conducted to identify the primary influence factors for the fouling tendency on the heating tube surface. The influence of various factors, including skin temperatures of the heating tube (165 ºF/74 ℃, 250 ºF/121 ℃, and 350 ºF/177 ℃), polymer concentrations (0 ppm, 80 ppm, 160 ppm, 400 ppm, 600 ppm, and 800 ppm), and heating materials (copper, stainless steel and carbon steel) on the overall fouling rate, has been studied. The influence of fouling on heating efficiency of the heating tube was also studied by analyzing heating time change. Also, cloud point measurement has been carried out to determine the cloud point of the prepared polymer solutions through temperature scanning (165 ºF/74 ℃ - 250 ºF/121 ℃). Besides, the fouling materials directly deposited on the high-temperature copper heating tube has been collected for ESEM and XRD analysis. Eventually, all the results have been carefully analyzed and discussed.

Experiment Method

Materials
The detailed water analysis of the formation brine of the pilot reservoir is listed in **Table 1.** The pH of the formation brine was reported to be 6.9, and the hardness of the formation brine was reported to be 1706 ppm. The synthetic brine is prepared by using deionized water, reagent grade sodium chloride (24923.6 ppm), sodium bicarbonate (206.3 ppm), and calcium chloride (1710.0 ppm), where the sodium represents the monovalent cations and the calcium represents the divalent cations in the formation brine, respectively.

Also, the synthetic brine maintains similar total dissolved solids (TDS) and hardness as the formation brine of the pilot test reservoir, which should show a similar fouling/scaling tendency as the formation brine.

The polymer used is Flopaam 3630s, which is a linear copolymer comprised of acrylamide and acrylic acid, hydrolyzed to 30%, and with a tight molecular weight range of 18-20 Million Dalton, and it is provided by SNF FLOPAAM[TM] Inc. The tested heating tubes are made from copper, carbon steel, stainless steel, respectively, and all have ¼ inch OD, as shown in **Figure 1**. The special high-temperature resistant Pyrex glass bottles with strong sealing and a digital control dry oven with glass window have been employed to conduct the cloud point measurement.

Experimental setup and equipment

A new experimental device has been specially designed and built in-house to simulate the heating process of the heat exchanger at Milne Point, which can operate under extremely high skin temperature conditions (up to 428 °F/220 °C). **Figures 2** and **3** show the schematic and the picture of the actually built experimental setup.

Table 1 – Composition of formation brine

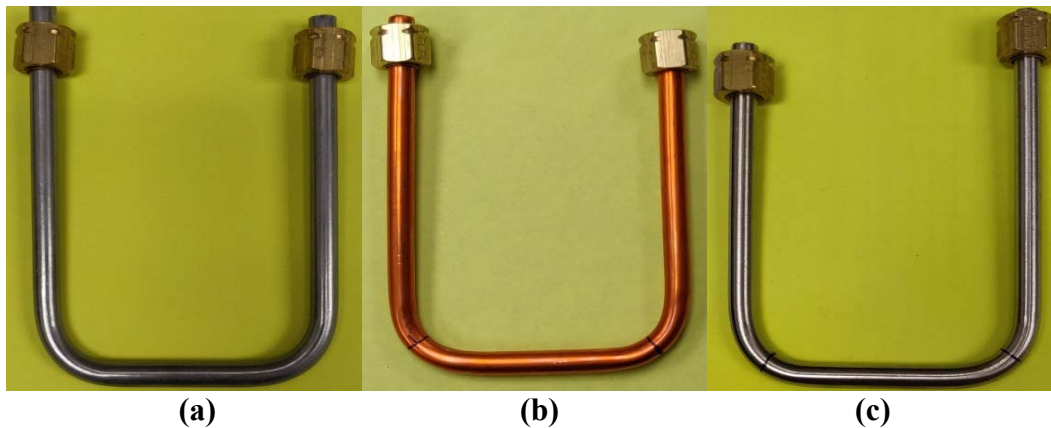| Ions	Concentration (ppm)
Sodium (Na^+)	10086.5
Potassium (K^+)	80.2
Magnesium (Mg^+)	281.6
Calcium (Ca^{2+})	200.7
Strontium (Sr^{2+})	17.4
Barium (Ba^{2+})	33.7
Iron (Fe^{2+})	0.5
Chloride (Cl^-)	15973.1
Silica (SiO_2)	16.7
Bicarbonate (HCO_3^-)	150
TDS	26840.4

(a)   (b)   (c)

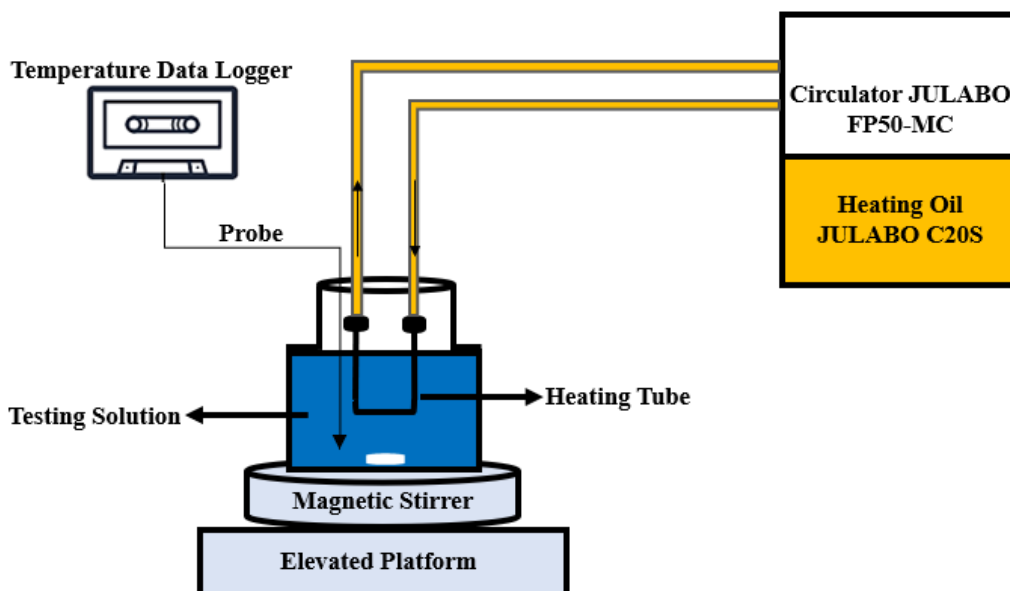Figure 1. Heating tubes (a) Carbon steel (b) Copper (c) Stainless steel

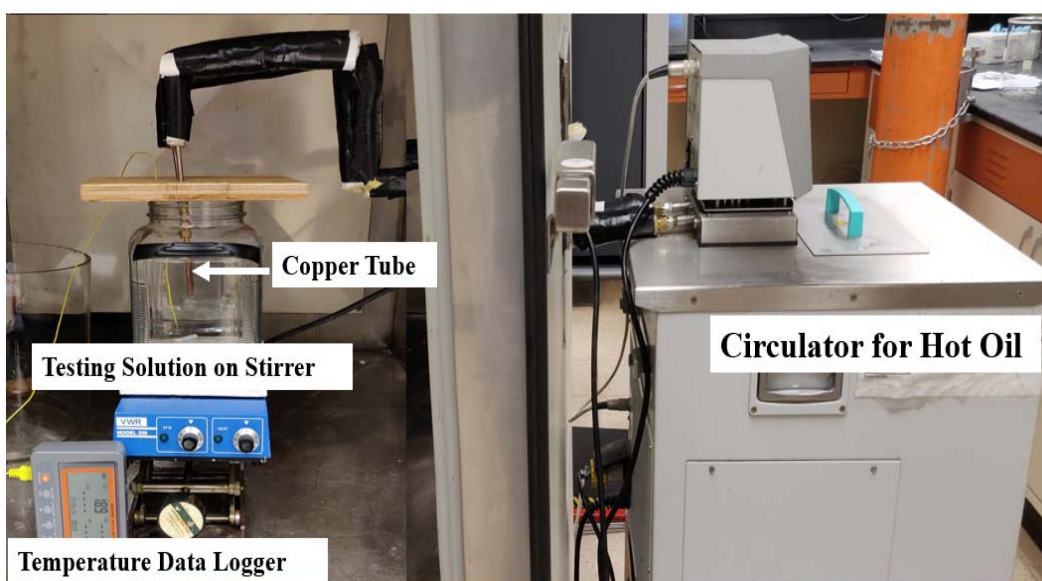Figure 2. Schematic of fouling test setup

Figure 3. Actual experimental setup for fouling test

The Julabo FP50-MC heating circulator, which is filled with thermal bath fluid (C20S), with a heating range of 32 °F/0 °C to 428 °F/220 °C, is used to heat the tubes to desired skin temperatures. The U-shaped heating tube is used to heat the prepared solution in the glass container directly. The magnetic stirrer is used to continuously stir the solution during the heating process to keep uniform heating. A temperature probe associated with a data logger is used to monitor and record the solution temperature change. An analytical balance with 0.01 mg accuracy is used to measure the mass of the heating tube before and after each test to calculate the amount of fouling. Additionally, ESEM and XRD facilities are employed to analyze the morphology and composition of the fouling deposits accumulated on the U-shape heating tube surface, respectively.

Experimental scenarios

In order to investigate the influence of various factors, including heating tube surface temperature, tube material, and polymer concentration, on fouling tendency, extensive fouling tests have been designed and conducted, as listed in **Table 2**.

Experimental procedure

The designed fouling deposit test procedure is briefly described as follows:

1. Prepare the test solution: The synthetic brine is prepared by adding sodium chloride (24923.6 ppm), sodium bicarbonate (206.3 ppm), calcium chloride (1710.0 ppm) into deionized water, and continuing to stir the solution until all the salts are dissolved. A polymer mother solution of 2,000 ppm is prepared by continuously mixing the polymer and synthetic brine for at least 48 hours until the polymer is completely dissolved and no lumps are remaining. The pH value of the prepared polymer mother solutions was measured to be 7.35. Subsequently, the polymer mother solution is diluted by adding the synthetic brine to prepare the test solution associated with the desired to-be-tested polymer concentration. Three liters of the prepared test solution is poured into the glass jar for the test. The glass jar is then placed into a dry heating oven to preheat the test solution to an initial temperature of 77°F/25 °C.

2. Preheat the metal heating tube: The metal tube is bent to the designed dimension of the U-shape. The U-shaped metal tube with the compression nuts is weighted as W_1. The U-shape metal tube is connected to the heating circulator, and the heating circulator started to preheat the metal tube to the designed to-be-tested skin temperatures, which are 165 °F, 250 °F, and 350 °F, respectively, in this study. The temperature probe measures the tube skin temperature at different positions until the stable desired skin temperature is achieved.

3. Heat the test solution for fouling test: Once the stable desired skin temperature is achieved, the metal tube is immersed in the test solution to heat it. At each tested skin temperature (165 °F, 250 °F, and 350 °F, respectively), the solution is always heated from 77°F to 122°F/50 °C, which are the corresponding inlet and outlet temperatures of the fluids in the heat exchanger on the pilot site. During the test, the heating circulator is kept running to heat the test solution continuously, while magnetically stirring the solution to achieve uniform heating. The temperature of the test solution is monitored by the temperature probe and logged using a data logger every 15 seconds until the test solution reaches the temperature of 122°F.

4. Determine the fouling amount: Once the test solution is heated to 122°F, the heating circulator is stopped and the test solution is removed immediately, while the U-shape metal tube is allowed to cool down to room temperature. Then, the U-shape metal tube is disconnected from the heating circulator, and the inside of the tube is cleaned thoroughly using a solvent to remove the residual heating oil. The outside of the tube is cleaned carefully using water while avoiding the loss of any deposit. After cleaning, the metal tube is dried completely, and its dry weight is measured to be W_2. Thus, the fouling amount during the test can be calculated as (W_2-W_1).

For each fouling test, the steps 1 to 4 are repeated 5 times, i.e., 5 runs, using the same U-shape metal tube but with a fresh batch of a testing solution in every run. After five runs, the fouling materials accumulated on the surface of the U-shape metal tube are scraped off and collected for morphology and composition analysis using ESEM and XRD, respectively.

The cloud point measurement procedure is briefly described as follows:
1) The oven is preheated to the test temperature;
2) The prepared polymer solutions with different concentrations (0ppm, 160ppm, 400ppm, and 800ppm) are transferred to the special Pyrex glass bottles, and then the glass bottles are kept inside the oven at the test temperature for 24 hours;
3) After 24 hours, the glass bottles are taken out from the oven, and carefully observe whether there is any precipitate, cloudiness or phase separation in the solution, and take a photo of the glass bottles;
4) The oven is preheated to the next designed test temperature, and repeat steps 2) and 3) until all the pre-determined temperature points are tested.

Table 2 – Experimental scenarios

Material	Skin temperature (°F/°C)	Polymer concentration (PPM)
Copper	165/74	0
		80
		160
		400
		600
		800
	250/121	0
		80
		160
		400
		600
		800
	350/177	0
		80
		160
		400
		600
		800
Stainless steel	165/74	0
		800
Carbon steel	165/74	0
		800

Results and Discussion

Effect of skin temperature on fouling tendency

The influence of heating tube skin temperature on the deposit rate at various polymer concentrations is shown in **Figure 4**, where the deposit rate is defined by the following equation,

$$Deposit\ rate = \frac{Cumulative\ deposit\ amount\ in\ 5\ runs\ (mg)}{Total\ heating\ time\ in\ 5\ runs\ (min)} \tag{1}$$

The calculated deposit rate is a quantitive parameter to represent the fouling severity on the heating tube surface. The fouling tendency is commonly used to describe fouling severity qualitatively. Thus, the higher the fouling tendency, the higher the deposit rate, representing more fouling severity on the heating tube surface in this study.
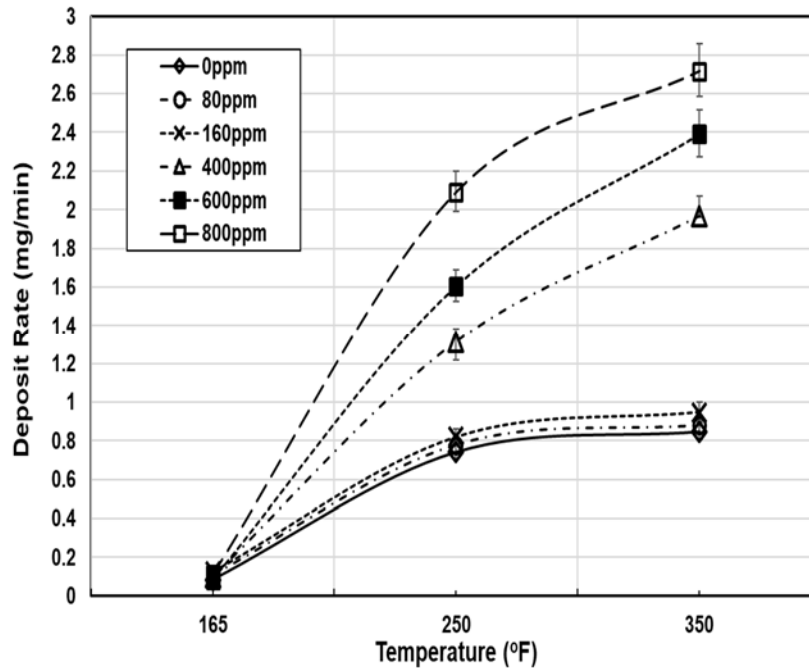
Figure 4. Deposit rate on copper tube vs. the tested skin temperatures at various polymer concentrations

As can be seen from **Figure 4**, at the same polymer concentration, the deposit rate generally increases with the skin temperature but is much more pronounced between 165°F and 250°F (i.e., the curve slope between 165°F and 250°F) than between 250°F and 350°F. This phenomenon confirms that skin temperature is one of the critical factors affecting the fouling tendency on the heating tube surface, which is consistent with previous studies (Shupe 1981, Ramsden and McKay 1986, Moradi and Doe 1987, Seright and Skjevrak 2015, Xiong et al., 2018). That is because the temperature can significantly affect the degree of hydrolysis of polyacrylamide in the solution (Muller et al., 1980; Moradi-Araghi and Doe 1987; Oliveira et al., 2019). In general, if the degree of hydrolysis of polyacrylamide is lower than the desired value (generally 30%), the HPAM can stably exist in the solution and will not precipitate (Xiong et al., 2018). At higher temperatures, such as 250°F and 350°F used in this study, the degree of hydrolysis can be significantly higher than 30%. The excessive hydrolysis of polyacrylamide will make the HPAM unstable in the solution and precipitate due to complexing with divalent ions, especially calcium ion, in the brine. Once the precipitated polymer deposits on the heating tube surface, the coated heating tube will be overheated, which further enhances mineral scale propensity. Thus, more severe fouling issues are caused, which eventually damages the heating tube due to overheating. Higher temperatures, such as 250°F and 350°F in this study, also can increase the rate of chain scission of the polymer backbone and decompose polymer via intramolecular imidization of amide groups, which can make the HPAM unstable in the solution and tend to precipitate. This could further aggravate the fouling issues. A detailed explanation of polymer degradation mechanisms can be found in the literature (Xiong et al., 2018).

Effect of polymer concentration on fouling tendency
The influence of polymer concentration on the deposit rate at different skin temperatures has been described in **Figure 5**. As can be seen, at a lower skin temperature of 165°F, the deposit rates at different polymer concentrations are almost the same with and without polymer; however, at higher skin temperatures of 250°F and 350°F, the deposit rates increase steadily with the increase of polymer concentration.
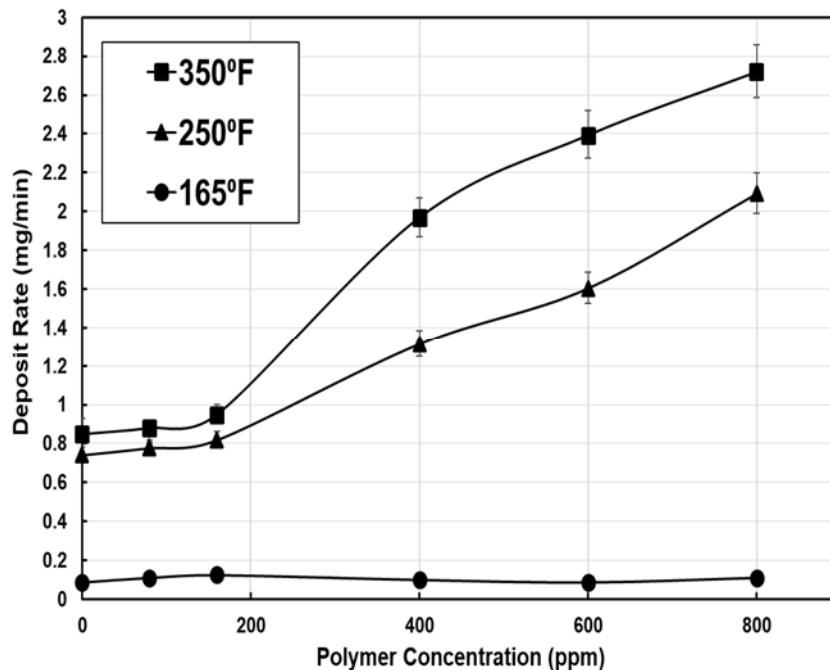
Figure 5. Effect of polymer concentration on deposit rate on copper tube

Note that the scale deposited on the tube surface at 0 ppm concentration of polymer should be pure mineral scale. The test results showed that, at 165°F, the deposit rates are nearly the same as that of pure mineral scale regardless of the polymer concentration. This finding implies that, at 165°F, it does not matter what the polymer concentration is, only mineral scaling might occur on the heating tube surface. It is believed that is because the lower skin temperature of 165°F in this study would not cause excessive hydrolysis or decompose the HAPM directly, the HPAM could stably exist in the solution and will not precipitate, and the fouling issues will not be aggravated. Therefore, the skin temperature of 165°F, which is the current operating temperature of the heat exchanger on the pilot site at Milne Point, should be safe to treat the produced fluids associated with various polymer concentrations. However, at higher tested skin temperatures of 250°F and 350°F, the deposit rates increased with polymer concentrations and were all significantly higher than the deposit rate of pure mineral scale. This finding indicates that the higher tested temperatures of 250°F and 350°F already made the HPAM unstable in the solution and precipitated due to excessive hydrolysis or direct decomposition, aggravating the fouling issues. Thus, 250°F and 350°F are not safe operating temperatures for the heat exchanger. According to our analysis and interpretation of the experimental results, there may exist a critical temperature between 165°F and 250°F, where the polymer fouling effect begins to manifest. Below the critical temperature, the HPAM will not precipitate and only mineral scaling occurs on the tube surface, so the existence of polymer in the produced fluids will not aggravate the fouling issues. However, above the critical temperature, the HPAM will precipitate and aggravate the fouling issues. Besides, we believe this critical temperature may be related to the cloud point of the polymer used. Additional experimental tests are being conducted to confirm this finding.

Figures 6 to 8 visually depict the accumulated fouling after 5 runs on the tube surface associated with respective skin temperatures of 165°F, 250°F, and 350°F at different polymer concentrations.
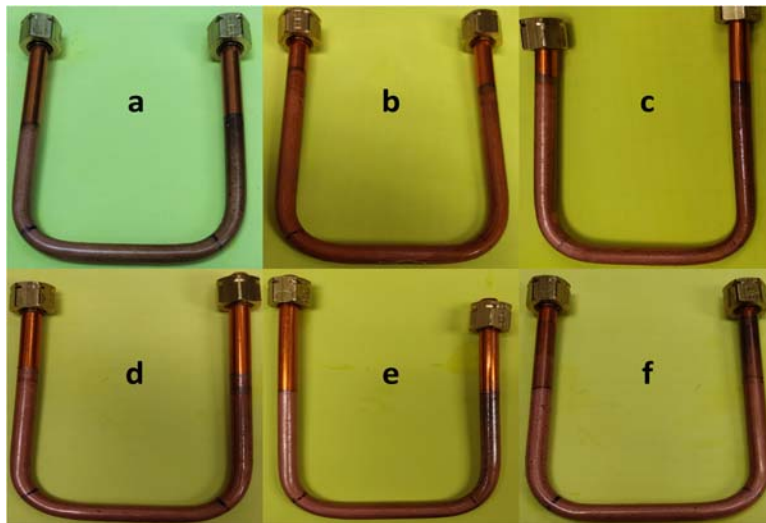
**Figure 6. Accumulated fouling on copper tube surface at165℉ at polymer concentration of:
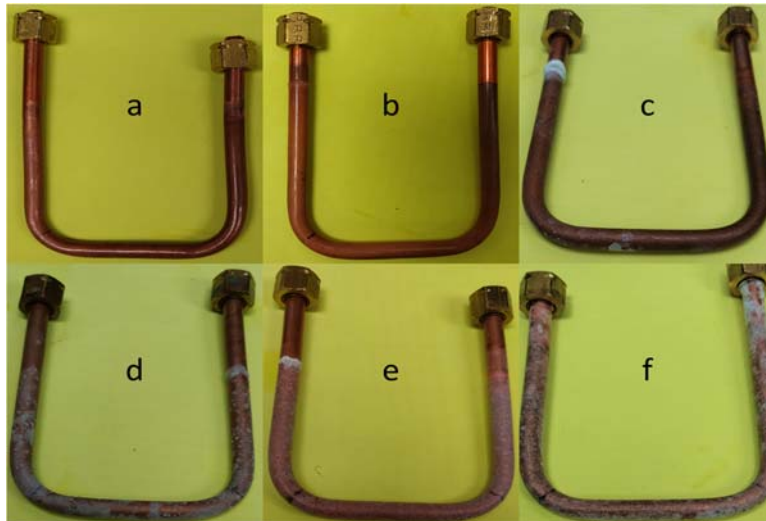(a) 0ppm, (b) 80ppm, (c) 160ppm, (d) 400ppm, (e) 600ppm, (f) 800ppm**

**Figure 7. Accumulated fouling on copper tube surface at 250℉ at polymer concentration of:
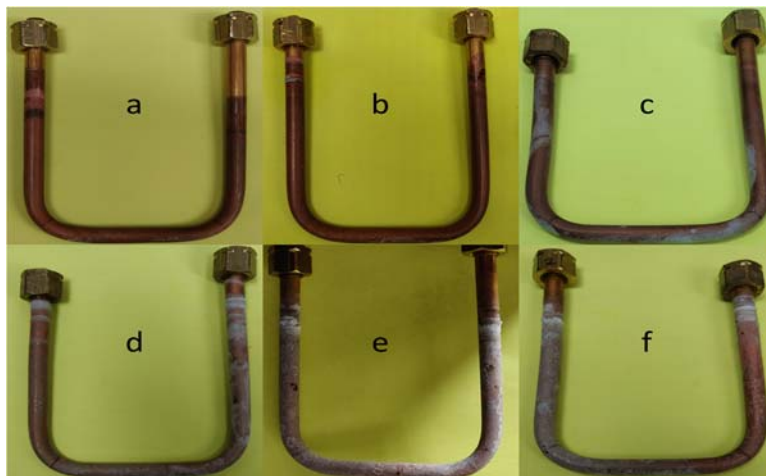(a) 0ppm, (b) 80ppm, (c) 160ppm, (d) 400ppm, (e) 600ppm, (f) 800ppm**

**Figure 8. Accumulated fouling on copper tube surface at 350℉ at polymer concentration of:
(a) 0ppm, (b) 80ppm, (c) 160ppm, (d) 400ppm, (e) 600ppm, (f) 800ppm**

As can be seen obviously from **Figure 6**, compared with **Figure 6** (a) which shows the pure mineral scale, no aggravated fouling issues were identified from **Figure** 6(b) to 6(f) due to the existence of different concentrations of polymer at 165°F. However, from the comparison of **Figure** 7(a) and **Figure** 8(a) with **Figure 7**(b) to **7**(f) and **Figure 8**(b) to **8**(f), respectively, it is clear that adding polymer into the solution would significantly aggravate the fouling issues at higher temperatures of 250°F and 350°F, and the higher the polymer concentration, the more severe the fouling. Therefore, **Figures 6** to **8** qualitatively confirm our quantitative findings drawn from **Figure 5**. Additionally, when we scraped the fouling materials from the tube surface for ESEM and XRD analysis, we found the pure mineral scale was brittle (refer **Figures 14** and **15**) and easily scraped off, but the aggravated fouling material with polymer was tougher and much more difficult to scrape off. This finding indicates that if the heat exchanger were not operated properly, once polymer-induced fouling occurred on the tube surface, it would be much more difficult to remove using the common mechanical methods.

Effect of fouling on heating efficiency
Figure 9 shows the time needed to heat testing solutions with different polymer concentrations from 77°F to 122°F at the skin temperatures of 165°F, 250°F, and 350°F, respectively. Here, we focus on analyzing the trend of each individual curve, i.e., the heating time change with the run number at each polymer concentration, but we did not intend to compare different curves with different polymer concentrations. As shown in **Figure 9** (a), there is no common trend for each curve, and each curve is associated with some fluctuation at a lower test skin temperature of 165°F. However, **Figures 9** (b) and (c) show a generally increasing trend with the run number for each individual curve at higher tested skin temperatures of 250°F and 350°F, respectively. The small fluctuations associated with the heating time trend of each curve in **Figure 9** (a) may result from the weak adhesiveness of mineral scale on the tube surface. As mentioned previously, only the mineral scale would be produced and deposited on the tube surface at the lower skin temperature of 165°F, which was easily scraped off. Thus, the mineral scale may alternatively deposit on the tube surface and then be washed off, which may cause an alternate change in the heating efficiency of the tube. Accordingly, the heating time in different runs has fluctuated. However, at 250°F and 350°F, polymer-induced fouling would be deposited on the tube surface, and they generally could not be washed off. Thus, the accumulation of polymer-induced fouling would continuously reduce the heating efficiency of the heating tube, which explains the consistent increase in heating time of each curve in **Figures 9** (b) and **9** (c).

(a)   (b)
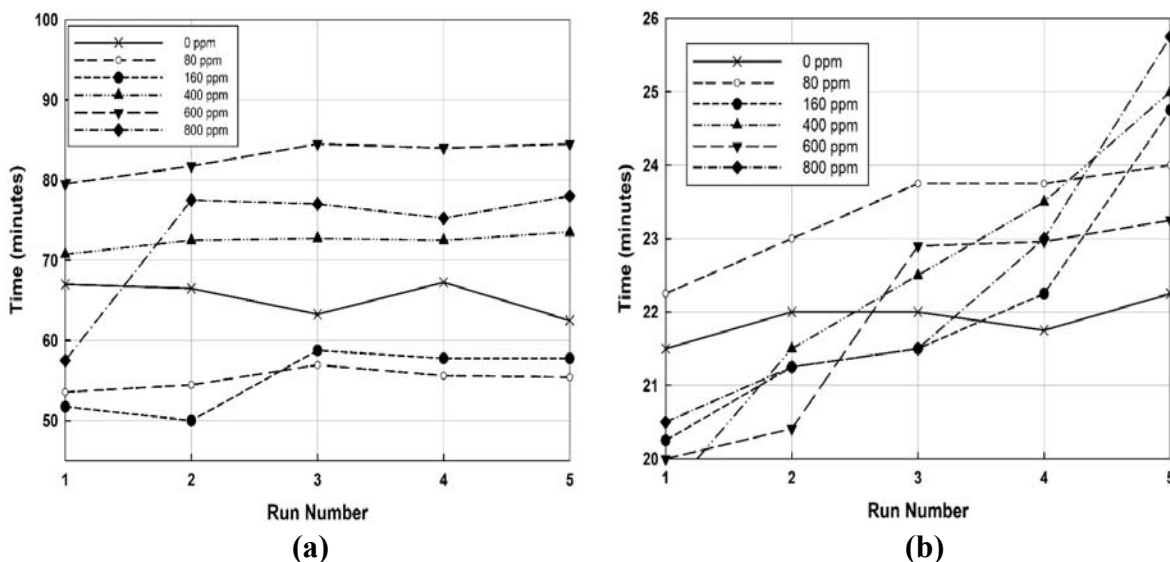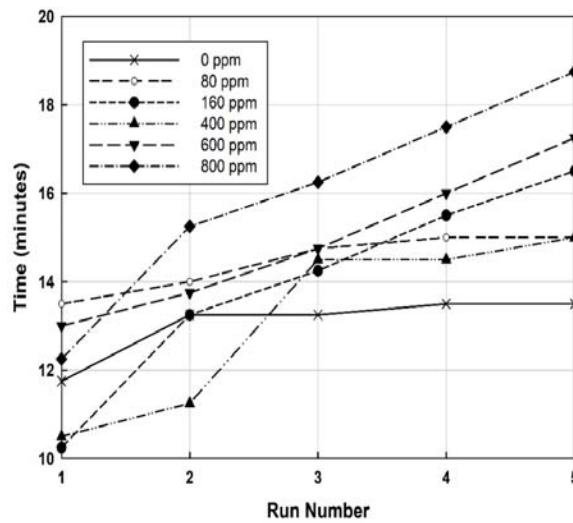
(c)
Figure 9. Effect of fouling on heating time of each test at (a) 165°F, (b) 250°F, and (c) 350°F

Effect of heating tube material on fouling tendency
The influence of heating tube material including copper, carbon steel, and stainless steel on fouling tendency also has been investigated. For each heating tube material, the fouling tendency was evaluated without the polymer (0 ppm) and at 800 ppm polymer concentration. Note that all the tests were conducted at the skin temperature of 165°F since the carbon steel and stainless steel tubes could not be heated to the stable higher skin temperatures of 250°F and 350°F (see Table 2). **Figures 10** shows the accumulated fouling or deposit after 5 runs on the tube surface, and **Figure 11** illustrates the calculated deposit rates for each tube material at 0 ppm and 800 ppm polymer concentrations, respectively. Our interpretation of previous tests (**Figures 4 – 8**) has confirmed that the existence of polymer in the solution would not aggravate the fouling issues on the copper tube surface at a lower skin temperature of 165°F.
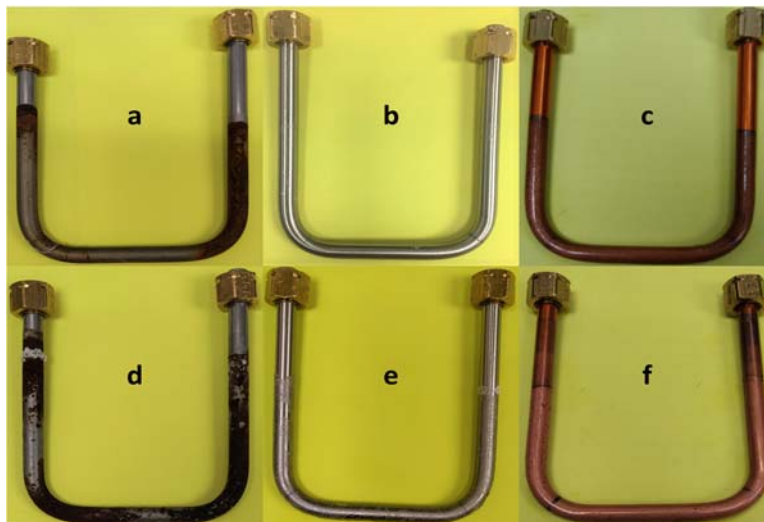

Figure 10. Accumulated fouling on tube surface at 165°F: (a) Carbon steel, 0ppm (b) Stainless steel, 0ppm (c) Copper, 0ppm (d) Carbon steel, 800ppm (e) Stainless steel, 800ppm (f) Copper, 800ppm
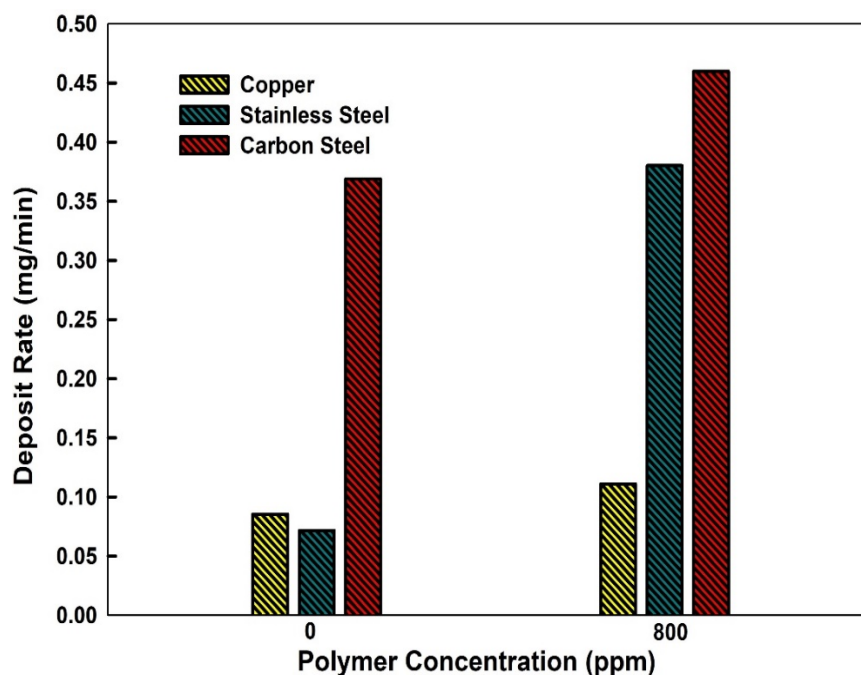
Figure 11. Deposit rates of different heating tube material

As can be seen from **Figure 10**, compared with stainless steel and copper, there was much more rust which may be iron oxide deposits on the surface of the carbon steel tube, which can explain why the deposit rates on the carbon steel tube surface were higher than those on the stainless steel and copper surface at either polymer concentrations as shown in **Figure 11**. In addition, compared to **Figure 10**(a), with 800 ppm polymer in the test solution, we could observe more rust and some additional white deposits which were believed to be polymer-induced fouling on the surface, as shown in **Figure 10**(d). This observation indicates that the redox reactions on the carbon steel surface may be intensified with the existence of polymer in the solution. Since previous tests have confirmed that lower skin temperature of 165°F cannot directly cause polymer fouling issues on the surface, the observed polymer fouling material in **Figure 10**(d) may result from the redox reactions and their products. This finding tells us that the existence of polymer in the solution would aggravate the fouling issues on the carbon steel surface even at a lower skin temperature of 165°F, which can be further confirmed by the fact that the deposit rate on carbon steel surface at 800 ppm polymer concentration was higher than that without polymer (i.e., 0 ppm) in the solution, as shown in **Figure 11**.

As can be seen from **Figure 10**(b), the stainless steel surface was still clean after all tests if there was no polymer in the solution. However, the stainless steel surface would be coated with a white fouling layer which was also believed to be polymer-induced fouling if 800 ppm polymer existed in the solution. That is why the calculated deposit rate on the stainless steel surface at 800 ppm polymer concentration was significantly higher than that at 0 ppm polymer concentration, as shown in **Figure 11**. Thus, we can confirm that the existence of polymer in the solution can aggravate the fouling issues on the stainless steel surface even at lower skin temperature of 165°F. Besides, as can be seen from **Figure 11**, at 800 ppm of polymer concentration, the calculated deposit rate on copper tube surface was much lower than those on both carbon steel and stainless steel surfaces. Without the polymer, the deposit rates on the copper tube and stainless tube surface were much lower than that on the carbon steel surface. These calculated higher deposit rates at either polymer concentrations all result from the aggravated polymer-induced fouling issues, which has been explained. However, without the polymer, the calculated deposit rate on the copper tube surface was a little bit higher than that on the stainless steel surface. As mentioned previously, only the mineral scale deposited on the surfaces without polymer in the solution. Under the same test conditions, we found that the heating time needed for stainless steel tube was much longer than that for the copper

tube due to the lower heat conductivity of the stainless steel tube. Thus, according to Equation (1), the calculated deposit rate on the copper tube surface was higher than that on the stainless steel surface. All of these findings indicate that copper tube would be the best choice for heat exchanger from the technical viewpoint to treat the produced fluids, especially when polymer exists in the produced fluids.

Cloud point measurement
As shown in **Figure 12**, the temperature at which the cloudy appearance of the solution was first observed at 230 ºF/110 ℃. Therefore, it is believed that the cloud point of the prepared polymer solutions should be between 220 ºF/104 ℃ and 230 ºF/110 ℃.

(a)

(b)

(c)
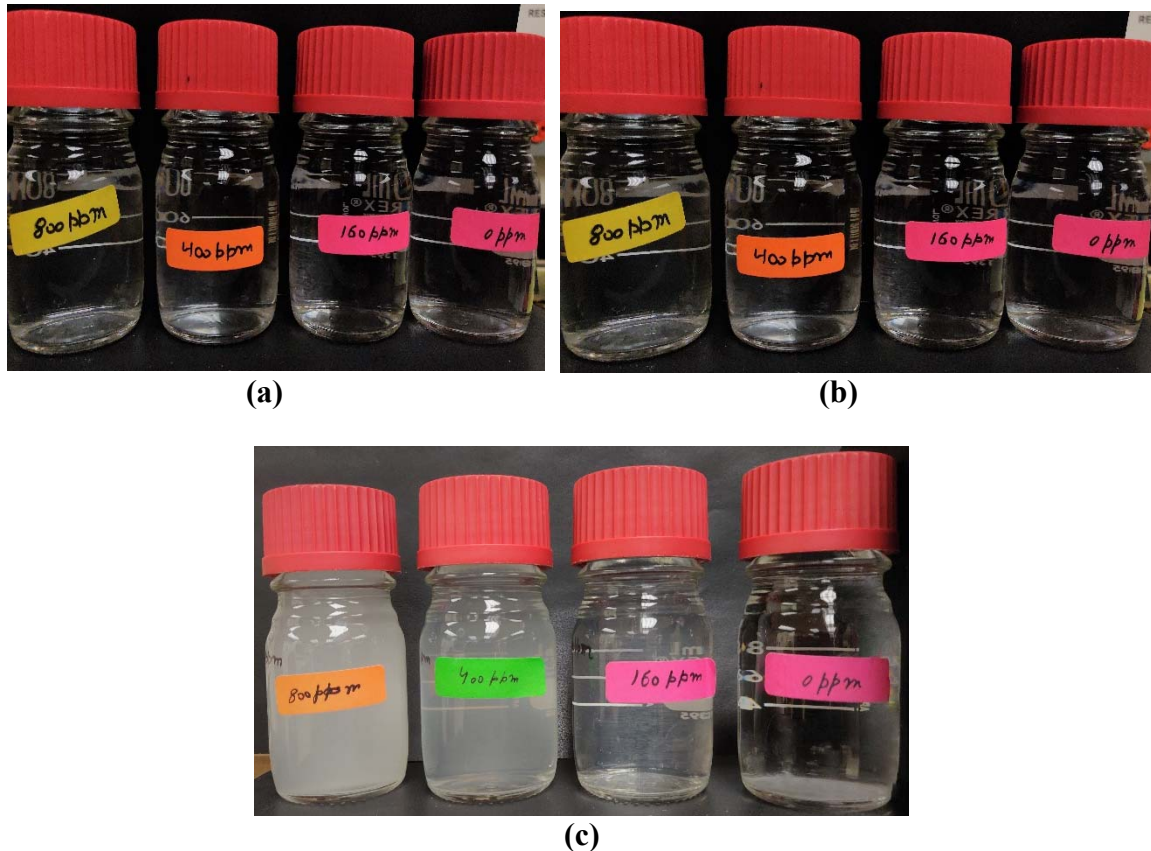
Figure 12. (a) Freshly prepared polymer solutions before a test, (b) Polymer solutions after heating at 220 ºF/104 ℃ for 24 hours, and (c) Polymer solutions after heating at 230 ºF/110 ℃ for 24 hours.

According to our observation, when the test temperature points are lower than the cloud point, the polymer solutions were all clear without precipitate no matter how long they were heated at that temperature, which implies that the prepared polymer solutions are very stable and would not precipitate out below the cloud point. However, once above the cloud point, the polymer would precipitate out very quickly, causing the cloudiness of the solution. In our test, we observed the cloudy appearance of the polymer solutions in 30 minutes after we started the test at 230ºF/110℃. We also observed that the amount of precipitate increased with the elevating of the temperature. These tests further confirmed that temperature has a significant effect on the hydrolysis rate of polymer, which is consistent with the findings of Ryles (1988). At elevated temperatures, the pendent amide grouds tend to hydrolyze more, therefore increasing the total carboxylate content in the solution. As hydrolysis increases, the excess hydrolyzed polyacrylamides, if in the presence of divalent metal ions, such as Ca^{2+}, would interact strongly with them to form precipitates. These findings and mechanisms are consistent with our fouling experiment results. At 165ºF/74℃ which is below the cloud point, the polymer hydrolysis rate is relatively low, so the

polymer could stably exist in the solution and would not precipitate out. That is why the fouling tendency would not be aggravated at this skin temperature. However, at 250ºF/121℃ and 350ºF/177℃ which are above the could point, the polymer hydrolysis rate is significantly enhanced, and excess hydrolyzed polyacrylamides interact with the Ca^{2+} in the solution to precipitate out, aggravating the fouling tendency. Therefore, the cloud point of the polymer solution is a critical temperature, below which the polymer would not enhance the fouling tendency regardless of the polymer concentration, but above which, the existence of polymer in the solution would aggravate the fouling issues.

Effect of polymer on morphology and composition of the deposit
The impacts of polymer on the morphology and composition of the fouling deposit on the heating tube surface can also be reflected in the ESEM and XRD analyses. In this study, only the fouling deposit on the copper tube surface generated at the skin temperature of 350ºF, as shown in **Figure 8**, was characterized by ESEM. The ESEM pictures of fouling deposits at respective polymer concentrations of 0 ppm, 160 ppm, 400 ppm, and 800 ppm are shown in **Figure 13**.
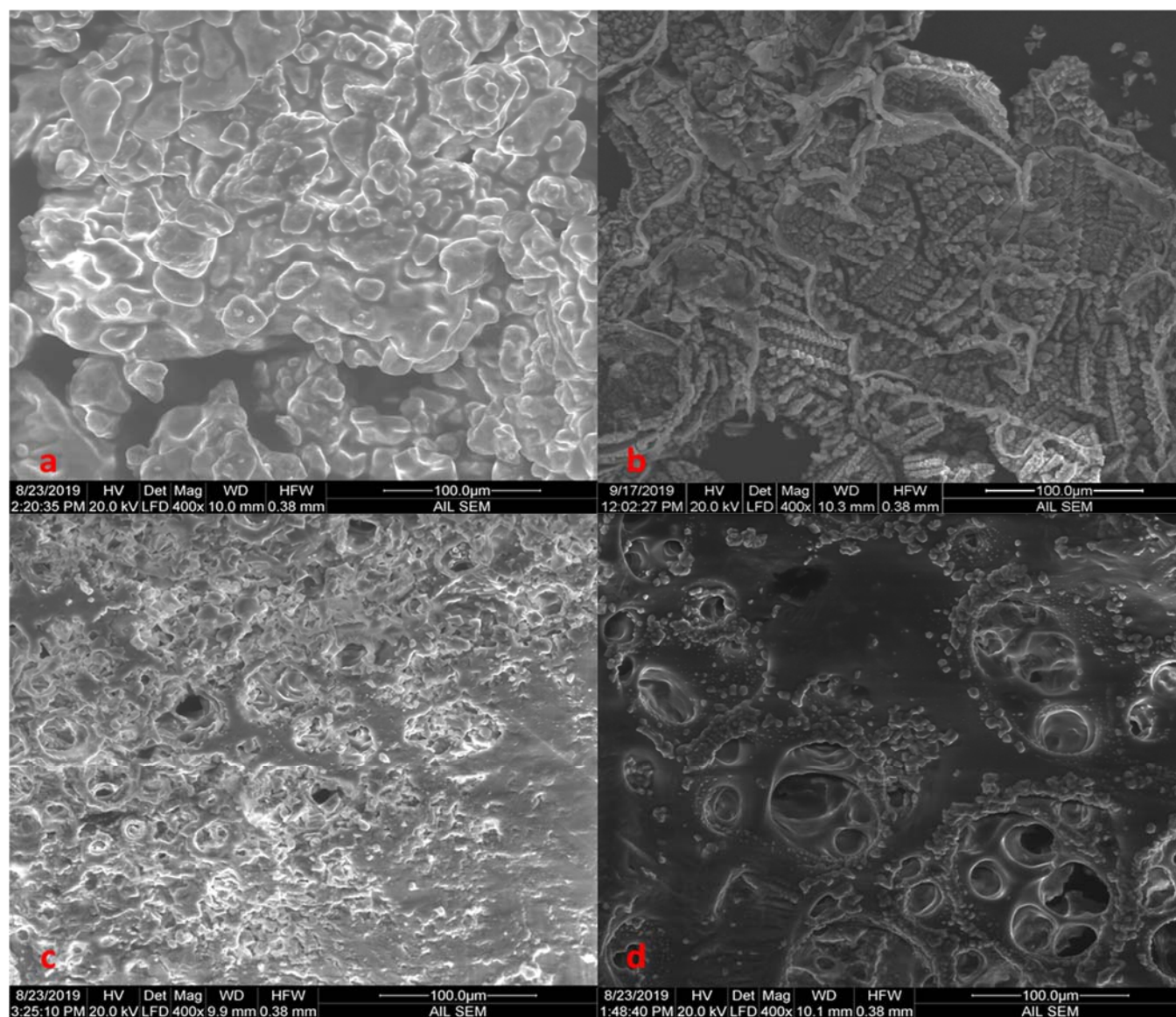

Figure 13. ESEM pictures of fouling generated at the polymer concentrations of (a) 0 ppm (b) 160 ppm (c) 400 ppm (d) 800 ppm on the copper tube at a skin temperature of 350ºF

Figure 13(a) shows the morphology of the pure mineral scale since the polymer concentration was 0 ppm (i.e., there was no polymer in the solution). As can be seen, the mineral crystals are irregular and naturally compact together, so the bonding between the mineral crystals is weak and the mineral crystals generally have less adhesion on the tube surface, which can explain why the pure mineral scale is brittle and easily scraped off as mentioned previously. Compared to **Figure 13**(a), **Figures 13** (b), (c), and (d) illustrate that morphology of the polymer-induced fouling is different from that of pure mineral scale. As can be seen, once the polymer precipitated and deposited on the tube surface, it would be bonded to the mineral scale crystals forming a three-dimensional network structure, becoming denser with the increase of polymer concentration. In general, this kind of network structure of polymer-induced fouling is stronger than the simple compaction of the pure mineral scale, and it also has more adhesion to the tube surface. That is why, as mentioned previously, the polymer-induced fouling was tougher and more challenging to be scraped off.

Among the deposit samples characterized in **Figure 13**, two of them were analyzed by XRD to compare their composition difference. The results of XRD analysis have been depicted in **Figure 14**, where the blue color represents the XRD pattern of deposit generated using 800 ppm polymer solution while the red color represents the XRD pattern of deposit generated using 0 ppm polymer solution (i.e., without polymer in the solution). The compound codes below the pattern represent sodium chloride - Halite (01-070-2509) and calcium carbonate - Calcite (00-066-0867). It is necessary to point out that XRD analysis is only able to identify mineral salts of sodium and calcium in the deposit, but polymer fouling cannot be identified as diffraction peaks in the XRD pattern, since X-Rays cannot detect elements below sodium and polymer is only composed of carbon, hydrogen, oxygen, and nitrogen. Furthermore, the compositional analysis for the two deposit samples was also conducted by HighScore Plus software based on the obtained XRD patterns.
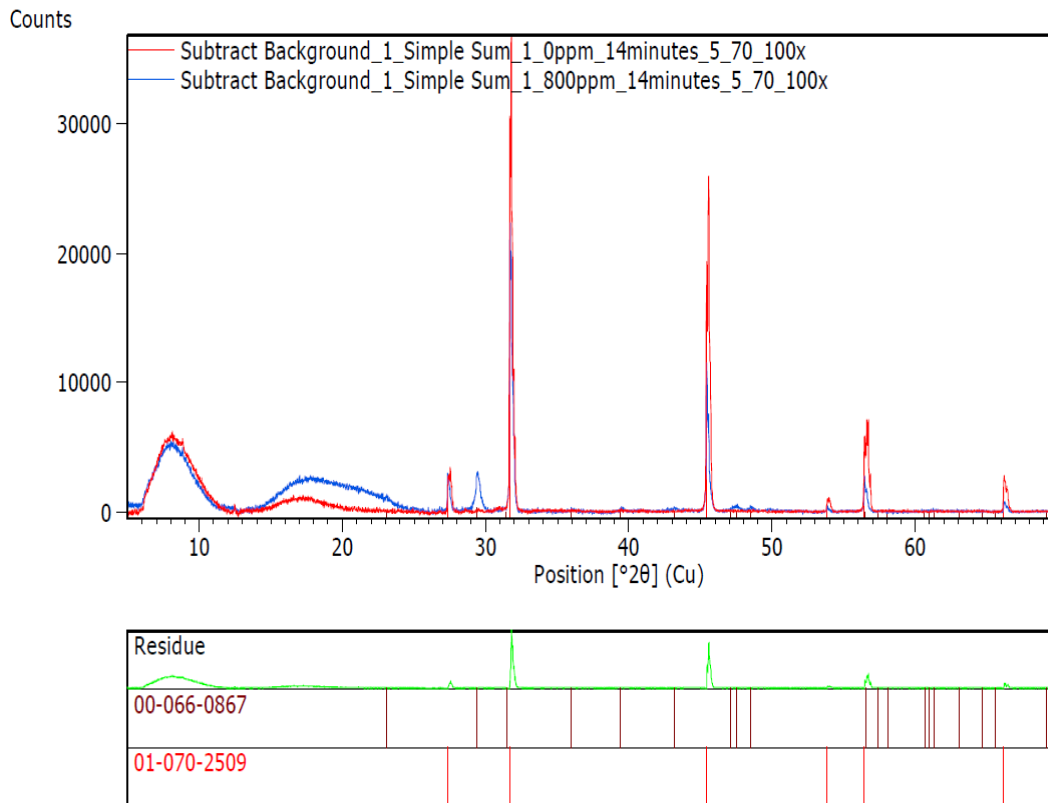

Figure 14. XRD scan of deposit on the copper tube at a skin temperature of 350℉ at the polymer concentrations of 0 ppm and 800 ppm. Note the compound codes of Halite (01-070-2509) and Calcite (00-066-0867)

As can be seen from **Figure 14**, the most significant difference in the two patterns occurs at the angle of approximately $2\theta = 29$ which represents calcite ($CaCO_3$) peak. The peak at $2\theta = 29$ was obtained in the blue pattern (with polymer) but it was absent in the red pattern (without polymer). This difference indicates that, compared to the solution without polymer, the presence of polymer in the solution may cause one more type of calcite mineral scale. Besides, noticeable background noise can be observed in the two patterns between the angles of $2\theta = 15$ and $2\theta = 24$, which may represent some byproducts resulting from the interaction between polymer and mineral salts. Since X-Rays cannot detect C, H, O, and N, these byproducts cannot be detected as a peak in the pattern. According to compositional quantification results for mineral scale in both deposit samples, it has been found that 98% of the mineral scale is Halite and the remaining 2% is Calcite in the deposited sample generated from the solution without polymer. However, the presence of polymer in the solution decreased the Halite composition in the mineral scale to 80% and increased the calcite composition to 20%. Therefore, this finding further confirms the previous conclusion that the presence of polymer in the produced fluids can enhance the mineral scale propensity.

Conclusions

The tests performed in this study to investigate the fouling tendency on the heating tube surface, especially when polymer exists in the produced fluids, yield the following general conclusions:

1. At a lower skin temperature of 165°F, the existence of polymer in the fluids would not aggravate the fouling tendency on the copper tube surface, but it would enhance the fouling tendency on the carbon steel and stainless steel surfaces. However, at higher skin temperatures of 250°F and 350°F, the fouling tendency on the copper tube surface would be enhanced by polymer, and it generally increased with the polymer concentration.
2. Thus, only from the technical viewpoint, the copper tube would be the best choice in this study for the heat exchanger used on the pilot site.

In addition, the following conclusions are drawn based on the fouling tests conducted only using the copper tubes:

3. The cloud point of the prepared polymer solutions was determined to be between 220°F/104°C and 230°F/110°C. There exists a critical temperature that is believed to be related to the cloud point of the polymer solution, below which the polymer would not enhance the fouling tendency regardless of the polymer concentration but above which the existence of polymer in the solution would aggravate the fouling issues.
4. With fouling material accumulating on the tube surface, the heating efficiency of the tube would be reduced, which is the main reason causing overheating of the heating tube and its eventual failure.
5. Compared to the pure mineral scale, the polymer-induced fouling possesses a stronger three-dimensional network structure, making the fouling material harder and more difficult to be removed from the tube surface.
6. The presence of polymer in the fluids can alter the characteristics of the mineral scale.

In summary, the current operating skin temperature of 165°F at the pilot site should be a safe operation condition, which, however, may not be able to treat produced fluids of polymer flooding effectively. To promote the water-oil separation efficiency for the ongoing polymer flooding pilot test, the skin temperature of the heat exchanger could be increased up to 220 °F, which would not make the HPAM unstable and precipitate. Although the HPAM would not break down and precipitate out under 220 °F, the currently used carbon steel heating tube may still be subjected to aggravated polymer-induced fouling issues since redox reactions on the carbon steel tube surface may cause HPAM to precipitate.

Acknowledgment

Nomenclature

ANS - Alaska North Slope
DSL - Dynamic Scale Loop
EOR - Enhanced Oil Recovery
ESEM - Environmental Scanning Electron Microscopy
HPAM - Hydrolyzed Polyacrylamide
OD – Outer Diameter
TDS - Total Dissolved Solids
XRD – X-ray Diffraction

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