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Efficiency of Scaling Inhibitors in Geothermal Fluids at High Temperature and High Pressure

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ABSTRACT

This paper is aimed at reviewing the results obtained by the assessment of the performance of scaling inhibitors and their efficiency in geothermal wells at high temperature and high pressure (HPHT) conditions. As a fluid is pumped out of a geothermal reservoir it suffers a drastic change in the temperature and pressure. Since the reservoir fluid or water constitutes of a number of dissolved minerals, these minerals suffer a shift in the equilibrium and hence precipitation takes place. This commonly known phenomenon of 'scaling' affects the reservoir properties and hence the efficiency of the geothermal wells by hindering the flow of fluid through pipelines, valves, etc. A special class of compounds known as scaling inhibitors is used widely to reduce the scaling during the process of extraction of geothermal fluids. But the problem does not solve here as the scaling inhibitors that are used at such high temperature and pressure conditions along with high salinity in the reservoirs are not actually tested for use at such vigorous conditions which results in the decrease in their efficiency. Hence to test these scaling inhibitors a qualitative and quantitative approach was made. The methods used for the same were: (a) jar or bottle test which is carried out in a reactor at static conditions, and, (b) the dynamic tube blocking test (TBT). Inhibitors used were phosphonates, polyacrylates, polyaspartates and a carboxymethylated polysaccharide. Scales were $CaCO_3$, $CaSO_4$ and $BaSO_4$. It was found that the efficiency of the scaling inhibitors decreased at HPHT conditions in the static batch test. The flow rate and capillary geometry also affected the scaling inhibition in TBT.

1. INTRODUCTION

Corrosion and scaling is one of the most common and annoying problems faced by the engineers working in the geothermal fields. The water in the reservoir exists in equilibrium with a high composition of dissolved minerals. As the water is extracted from the reservoir the equilibrium shifts, and, as a result precipitation of various minerals takes place (Zotzmann et al., 2018). This precipitation often leads to the formation of scales on the walls of the equipment like pumps, valves, pipes, etc. In certain cases, these minerals, precipitated as scales, react with the metal equipment and thus start to corrode them and they may also reduce the injectivity of the reservoir (Saadat et al., 2010; Zotzmann et al., 2018; Regenspurg et al., 2010; Wanner et al., 2017). Obstructing the precipitation of these minerals is very important so that the machines work properly and last longer. The precipitation of $CaCO_3$ in water has a few important consequences in ocean chemistry studies, geo-science researches, CO_2 emission problems and biology. It is the chief component of scales precipitated from natural water. The useless expenses associated with scaling were approximately 1.5 billion Euros per annum in France (Rosset et al., 1992). Similarly, the expenses were about 3 billion USD in Japan, 0.8 billion USD in Great Britain and 9 billion USD in the USA (MacAdam and Parsons, 2004). Hence, it is crucial to prevent the scaling process to reduce the unnecessary losses. The degree of efficiency of any scaling inhibitor is influenced by several physicochemical parameters like temperature, pH, pressure, degree of super-saturation of sulfates, carbonates etc. as well as the degree of super-saturation of the inhibitor, etc. This paper takes in corrosion and scaling, the assessment of some scaling inhibitors based on their scale inhibition property as well as their impact on the environment.

2. CORROSION AND SCALING AS AN INTERRELATED PHENOMENA

The fouling due to precipitation and that due to corrosion is the same as scaling phenomena. The precipitation or crystallization fouling occurs generally due to the environmental conditions whereas the corrosion fouling occurs as a result of the interaction of the metal with the environment. There can be different ways of interaction between the two based on their reactivity with each other to produce different compounds which are seen as scales on the metal equipment. Corrosion waits for the material to die or be inactive.

Usually, the parent material decreases in mass. However, scaling is more of depositing of material on the parent material.

The process of scaling is generally linked with the deposition of mineral on the surface of the equipment. Nevertheless, the studies in surface scaling are much less in numbers than that in bulk precipitation. But in the past few years there has been increased stress on studies in the surface phenomenon by the researchers (Graham et al., 2001; Labille et al., 2002; Morizot et al., 2000; Morizot, 1999).

3. SCALING INHIBITORS

Scaling inhibitors are special compounds that are used to delay, reduce or stop the processes of scaling in the geothermal wells. The scaling inhibitors are generally developed for the applications in oil and gas fields and other water heating, waste disposal, and cooling systems (Graham et al., 2003; Sullivan et al., 1996; Choi et al., 2002).

But, while using in geothermal systems the effectiveness of these chemicals reduces considerably due to the high pressure, high temperature and high salinity in the reservoir (Zotzmann et al., 2018). The performance of these inhibitors is affected by the pH, temperature and pressure conditions, presence of other chemicals, and the concentrations of calcium and magnesium ion levels in the brine mixtures.

3.1 Types of Scaling Inhibitors

Scaling inhibitors are usually divided into three categories:

3.1.1 Inorganic Phosphates

These are low-priced, easy to prepare and readily soluble compounds containing phosphorous. These innocuous chemicals work effectively at low treatment conditions especially in $CaCO_3$ scaling. However, at moderate temperatures, they easily hydrolyze to form organophosphates that have very low inhibition capacity.

3.1.2 Organophosphorous Compounds

These include organic phosphate esters and other phosphonates. Phosphate esters are quite good in $CaCO_3$, $CaSO_4$ and $BaSO_4$ inhibition whereas phosphonates can be used with a wide variety of characteristics. They are also used on calcium and barium scales along with strontium scales. Within the range 150°F-160°F (65-71°C), phosphate esters can act as very effective inhibitors for calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$) scales. Nevertheless, these commonly used inhibitors can be fatal to aquatic organisms and are known to cause eutrophication problems (Hasson et al., 2011; Lattemann and Höpner, 2008).

3.1.3 Organic Polymers

They have excellent thermal and hydrolytic abilities and are effective in acidic environment, particularly for $BaSO_4$ inhibition. They are durable at 400°F (204°C) and even higher temperatures and are normally efficient at very low concentrations in restricting $CaCO_3$ and $BaSO_4$ scales in waters having fewer amounts of scale-forming ions.

As far as the toxic nature of scaling inhibitors is concerned, some inhibitors meeting the environmental requirements have been tested in accordance with the inhibition efficiency (Zotzmann et al., 2018; Reddy and Hoch, 2001; Choi et al., 2002).

3.2 Mechanism of Scale Inhibition

Scaling starts with the formation of sub-particles or ion clusters. This is known as nucleation. The size of this cluster is usually ≥10 ions as smaller ion clusters are not stable thermodynamically. These clusters keep on growing on crystal surface and become attached to it. Once the crystals become large enough, they fall out from suspension in the fluid and deposit as scales (Tomson et al., 2003).

The inhibitors are generally designed to obstruct the nucleation, crystal growth or both. During early nucleation period, they stick to the scaling ions, thus, disrupting the ion-cluster at the premature stage of equilibrium before it reaches the critical size for nucleation. Hence, the inhibition phenomenon involves physical mechanisms instead of chemical reactions (Tang et al., 2008; Hasson et al., 2011).

There are different test methods designed for evaluating the efficiency of the scaling inhibitors and understand how well the inhibitor is acting upon the site of scaling, and thus, help in quantifying the inhibition capacity by calculating the Minimum Inhibitor Concentration (MIC).

4. MINIMUM INHIBITOR CONCENTRATION

The threshold level of inhibitor used for given required amount of inhibition is referred to as the Minimum Inhibitor Concentration (MIC) or Minimum Effective Dose (MED). For the concentrations much above MIC both bulk as well as surface scaling is prevented. On the other hand, concentrations marginally below MIC tend to augment the scale growth for a wide limit of temperatures. In fact, for given brine solution, reducing to almost 50% of MIC may lead to enhanced scaling on the metal surface (Graham et al., 2005). In general, for a given test procedure, lower value of MIC indicates better a performance of scaling inhibitor and vice-versa.

5. EVALUATION OF THE EFFICIENCY OF SCALING INHIBITORS

Generally, there are two types of test used at the laboratory scale for testing the effectiveness of scaling inhibitors.

5.1 Static Jar or Bottle Test

This test is easy, cheap and can give the details about the characteristics of scale and the action of inhibitor on it when used along with other techniques. In this test the extent of scaling can be measured by changing different measureable parameters (Zotzmann et al., 2018). The static jar test is usually performed at normal temperature or sometimes, at raised temperatures at atmospheric conditions. On the other hand, for geothermal applications, the reservoir state is characterized by HPHT conditions. Therefore, the inhibitory effect must be evaluated under these conditions (Zotzmann et al., 2018; Sorbie and Laing, 2004) and hence the reactor apparatus and sensors should be designed to work under these conditions.

Talking about the evaluation of the effectiveness of several polycarboxylate calcite inhibitors, their MIC at HPHT was judged against the MIC at ambient conditions. Almost every inhibitor showed compatibility with high salinity.

It has been found that measurement of electrical conductivity is not a suitable parameter for observing the scaling process in geothermal fluids. Rather, decrease in the pH was a better indicator of calcite scaling. A huge difference has been observed in the inhibition capacity of the scaling inhibitors used at HPHT conditions with that at normal laboratory conditions. It was clearly observed that a greater amount of inhibitor was required for achieving the same effect of inhibition at HPHT conditions as compared to the normal conditions, thus, justifying the necessity of determining the MIC values of the inhibitor to be used in the well at the HPHT conditions (Zotzmann et al., 2018).

5.2 Dynamic Tube Blocking Test (TBT)

In contrast to static jar test, TBT is performed under dynamic pumping situation of fluid in which the HPHT conditions can be varied as per the requirement (Bazin et al., 2005). Since TBT does not have any standard methodology for testing the efficiency of scaling inhibitors (Graham et al., 2002; Bazin et al., 2005) it gives rise to different ranking of inhibitors for different methods applied. It has been found that capillary geometry and flow rates are crucial in determining the efficiency of the inhibitors (Bazin et al., 2005).

As it is known that the inhibitor efficiency is very sensitive to pH variations, it was found that crystal growth inhibitors, like phosphonates, are more sensitive to pH variations as compared to nucleation inhibitors like polymers (Bazin et al., 2005). On the other hand, opposite observation has been made on changing the flow rates. Higher flow rates in TBT favor nucleation inhibitors, showing maximum efficiency when the flow rate is maximum. However, a negative correlation has been observed in case of phosphonates as the effectiveness decreased with an increase in the flow rate (Bazin et al., 2005). Considering the geometry of the capillary tube, high flow rates lead to greater temperature variations and high shear stress which may affect the scale growth leading to error in the evaluation of scaling inhibitor efficiency (Bazin et al., 2005). So it can be easily said that the efficiency of the inhibitors is also affected by variations in the pH and flow rate of the fluid which cannot be ignored in the case of geothermal systems.

6. ENVIRONMENTAL IMPACTS OF ANTI-SCALANTS

Like most conventional polymers, anti-scalants or scaling inhibitors are built so that they can sustain for a greater amount of time and persevere for several years even after disposal. The phosphorous based inhibitors are of major concern as they can assist in eutrophication in sea water (Lattemann and Höpner, 2008). One of the most versatile and bio-degradable polymers is poly-aspartic acid having a number of potential applications (Thombre and Sarwade, 2005).

7. "GREEN" SCALING INHIBITORS

The most commonly used scaling inhibitors are polymeric in nature and are generally made to sustain for several years even after they are disposed. Of major worries are inhibitors based on phosphorous compounds as they lead to eutrophication problems (Hasson et al., 2011; Lattemann and Höpner, 2008). These chemicals when discharged in the water can have different effects on the aquatic life (Hasson et al., 2011; Lattemann and Höpner, 2008). There are various factors that can explain about the extent up to which these effects are observable such as quantities of mineral discharged, toxicity, exposure of aquatic life to the chemicals, type of organism and so on (Hasson et al., 2011).

Due to these reasons the need for "green" scaling inhibitors has increased in the past few years. New anti-scalants are being designed that are biodegradable and have a lesser impact on the environment without compromising with the inhibition efficiency at minimal cost (Hasson et al., 2011). One of such newly developed biodegradable polymers is a mixture of citric acid, hydroxyethylidene diphosphonic acid (HEDP), acrylate copolymer, and isothiazolone, at a formula ratio of 2:4:4:1 (Hasson et al., 2011; Choi et al., 2002). Presently, based on laboratory studies, polyaspartic acid is said to be the most versatile biodegradable polymer having a range of potential applications. Nevertheless, the field studies are limited.

8. CHALLENGES FACED WHILE USING THE SCALING INHIBITORS

Polymeric chain inhibitors are the most common choices for scaling inhibition as they are thermally stable as well as compatible with the environment. But it must be noted that the temperatures experienced by the inhibitors in geothermal wells are much higher and thus the inhibitors need a greater attention before being used in such an extreme condition. Change in behavior of the mineral and change in the interaction between the mineral and the inhibitor are obvious at such conditions which cannot be ignored. Varying flow rates in the geothermal systems can affect the working of the scaling inhibitors in the geothermal fluids and, hence, is a matter of concern.

9. CONCLUSION

The phenomenon of scaling is not new for the geothermal systems and so is the use of scaling inhibitors. These chemical compounds not only restrict the unwanted precipitation of minerals present in the geothermal fluids but also reduce the undesirable expenses on the equipment caused due to scaling. But, though they seem to be advantageous at normal atmospheric conditions it is necessary to evaluate such inhibitors as per the standards at par with a particular geothermal system. Varying temperature and pressure conditions tend to change the Minimum Inhibitor Concentration from that found at normal conditions which in some cases may even enhance the scaling process and exacerbate the problem. The geothermal fluid can have varying mineral compositions and flow rates which again acts as a crucial factor that can affect the performance of the inhibitor.

10. FUTURE SCOPE OF SCALING INHIBITORS

Apart from the conventional applications of the scaling inhibitors in geothermal wells, some of them have found their use in the water heating and cooling systems. Looking at the major concerns related to the use of such chemicals, environmental effects are really important. Development of more environment friendly anti-scalants can be a much prospective domain of study. Although there have been some studies conducted on such inhibitors, but, talking about the geothermal systems, on field tests are required. Moreover, more and more studies on the performance of such inhibitors at HPHT conditions are required to understand the behavior of these chemicals at such harsh conditions and ultimately to develop the desired inhibitors with a broader scope of use for different applications.

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