

Laboratory study of compatibility and interaction of scale inhibitor with oilfield chemicals for ASP flooding chain

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The application of alkaline-surfactant-polymer (ASP) flooding has successfully enhanced oil recovery up to 20% in Daqing oilfields. Most notably, there is a significant obstacle on the scaling deposition along the produced fluid gathering and transportation chain. Firstly exemplified by the scaling of an ASP flooding zone in Daqing oilfield, newly designed and synthesized scaling inhibitors were investigated on the compatibility with the ASP chemicals and treatment agents. By a series of lab studies, the compatibility and interaction of scaling inhibitor with the chemical agents, including surfactant, polymer, defoamer, demulsifier and anti-deposition agent, are clearly exhibited. But the demulsifier changes in slight range. Based the data, the performance and mechanism of the interaction on the chemicals using in the produced fluid treatment are proposed and discussed. In addition, the strategy of chemicals usage, including the injection mode and amount, is suitably specified and adapted for the ASP flooding chain.

Keywords: Compatibility; Enhanced oil recovery; Oilfield chemical; Scale Inhibitor.

INTRODUCTION

Many ASP flooding technologies have successfully and successively been studied and applied to Daqing oilfield [1-2]. Four pilot tests were conducted in order to further enhance oil recovery and collect technical and practical experiences for extending the ASP pilot. It has been revealed that the ASP floods can successfully enhance oil recovery up to 20% in Daqing oilfields [3-4]. With the succession of the ASP flooding, significant obstacles were found during the production of the ASP pilots. Most notably, there is the scaling of produced fluid treatment chain [5]. It is the presence of the scaling deposition that gives rise to numerous problems. The formations of mineral scale deposits upon tubing, casing, perforations, and even the formation face itself, can constrict fluid flow of the treatment chain and thereby curtail the production rate of oil wells.

Oilfield chemicals were injected to an oil chain at different positions from the production to transportation. All the varied sectors in oil production generally were seeking chemicals dependently to assist in special operations, for drilling wells, for producing oil or transporting oil through pipeline. The oil chemicals were used for many purposes such as the defoaming, demulsifying, anti-depositing and scale inhibiting by an addition of varying amounts. The point has generally been accepted that it is not possible for

efficient and cost-effective production of oil without the use of suitable chemicals. So as to a good solution of the scaling deposition, the chemicals were used for in the ASP flooding chain. In the present ASP case, three types of chemicals exist in the produced fluids operation chain composed of the residual flooding chemicals, such as alkaline, surfactant and polymer. Over the last several years, the chemical treatment usages, such as defoamer, demulsifier, scale inhibitor and anti-deposition agent, have increased in the variety and amount, which is apparent in the ASP flooding. The flooding is characterized with produced fluid containing the concentrated silicon ions originated from concentrated alkaline and high viscosity caused from viscous polymer [6]. Generally, the highly concentrated alkaline is pumped in the well in the process of ASP flooding. The strong alkaline causticizes some materials in the oil reservoir. The scaling material is formed in all the touching sectors. This scale is deposited in/on the well or transportation system, resulting in a critical stop of the operation. Additionally, the properties of the produced fluid could be affected by the flooding agents on the same system. This introduces two primary concerns: the difficulty in silicon scale deposition, and the difficulty in demulsification for oil/water separation [6-9].

A present trend can be indicated that the increase in chemicals is due to the fact that oilfields are entering a high scaling operation and increasing requirements for oil treatment and water treatment. The efficient ASP flooding production generally relies on the adaptability and adoption of specific

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chemicals to prevent scale deposition, corrosion, and foaming. Consequently, many works has been done for the application of treatment chemicals for the oil region and ASP flooding chain. In Daqing oilfield, many treatment chemicals have been investigated and developed for the efficient and cost-effective treatment of ASP produced fluid in ASP flooding [7-9]. As a case, the development of the scale inhibitor used in ASP flooding has gone through the single dose to the compounded mixture and from water-suitable agents to especially Si-adapted chemicals [6-9].

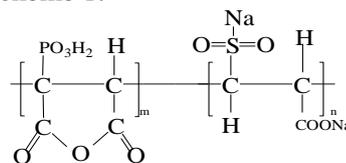
While the performance test is an important step in selecting appropriate chemicals in field applications, the compatibility of the chemicals with the other chemical materials used in the same operation system is critical to performing chemical treatment program. Extensive chemical formulation, laboratory test, and field verification are required to ensure that operation chemicals will compatible with chemicals system adopted to oil/water separation, oil processing and water treatment. In ASP flooding applications, particularly for the developing agents whose performances are not readily accessible without aid of the historical experiences, the compatibility of chemical system with any scale inhibitor is a key part of the effective flow process. Until now, the systematical study on the chemical compatibility has not reported for the ASP flooding chain of Daqing oilfield. This paper focused on compatibility of a developing scale inhibitor, typically applied to the ASP flooding pilot test in Daqing oilfield, with chemical system materials such as the residual chemicals, defoamer, demulsifier and anti-deposition agent. A comprehensive study of scale inhibitor -chemicals interaction and mechanism was implemented and discussed. These compatibility data can enhance the selection process for existing production, optimize material selection, design in the development stage for new chemicals, and facilitate formulation of new products.

EXPERIMENTAL SECTION

Formula and structure of ASP treatment chemicals

Recently, main types of scale inhibitors, such as phosphonate, polyphosphonate, aminopoly-carboxylate and surfactant agent, have been used for an efficient operation in the water flooding and polymer flooding. The current tendency is to research and develop the phosphonate-based polymer with varied functional groups. For meeting the unique requirements presented by the ASP flooding and the environment, a new type of scale

inhibitor has been designed and developed in this study. The formula and structure is schematically shown in scheme 1.



Scheme 1. Formula and structure of the scale inhibitor

The scale inhibitor, consisting of phosphonate, sulfonate and carboxylate groups on the long carbon bone, is a polymer. The soluble Ca, Mg and Ba ions in the ASP fluid can be stoichiometrically chelated by functional groups on the chain to prevent soluble silicon ion from the codeposition.

The defoamer, demulsifier and anti -deposition agent have effectively been adapted and adopted to this flooding treatment system. The compositions are simply illustrated as follows:

Defoamer-Fluorine-grafted polysiloxane (oil soluble);

Demulsifier-Phenolic resin-EO-PO polymer (oil soluble);

Anti-deposition agent-Long carbon chain grafted by phosphonate, sulfonate and carboxylate group;

Polymer-Polyacrylamide, M.W. 2500x104;

Surfactant-Long-chain alkylbenzene sulfonate.

All the chemicals were provided by the oilfield. The chemicals were used in the lab as received without further modification and purification.

Produced water and preparation in experiments

The specific produced fluids employed in the experiment was sampled from a pilot zone of the ASP flooding in Daqing oilfield. Based on the compositions of the produced fluid, the produced water was simulated with the original ion concentrations of 50 ppm Ca^{2+} (Mg^{2+}), 133 ppm CO_3^{2-} , 3184 ppm HCO_3^- and appropriate silicon ion.

Measurement of performance of the scaling inhibitor

The performance of the scaling inhibitor was indicated by an efficiency of the scale inhibiting. According on a standard of the PetroChina Company, the efficiency is evaluated by shown as:

$$E = (C_2 - C_1) / (C_0 - C_1) \times 100\%$$

Where, C_0 is Ca^{2+} concentration of the initial solution, mg/L or ppm; C_1 is Ca^{2+} concentration of the equilibrated solution without adding the scale inhibitor, mg/L or ppm; C_2 is Ca^{2+} concentration of the equilibrated solution with adding the scale inhibitor, mg/L or ppm.

RESULTS AND DISCUSSION

Analysis of produced fluid in ASP flooding system

In the manifold system of the ASP produced fluid, first newly developed scale inhibitor as shown in scheme 1 was injected to individual well, which was transported to a gathering center through mixed flow lines. Then defoamer and demulsifier were added to the system for easy separation of oil and water. The oil stream was inputted to oil processing sector and the water stream was treated by injection of anti-deposition agent. The scale inhibitor entirely got through the gathering and transportation system on the chain. In consequence, the scale inhibitor encountered in the ASP chemicals, defoamer, demulsifier and anti-deposition agent existing in the system. The scale inhibitor will interact with three agents. This is the starting point and final objective for this study.

Effect of polymer on performance of the scale inhibitor

By setting temperature at 50°C, putting 20 ppm scaling inhibitor into the simulated produced water solutions with 50, 100, 200, 300, 400 and 500 ppm polymer, the results of the PAM-effect on the efficiency are shown in Fig.1.

As shown in Fig.1, the efficiency of scaling inhibitor was decreased as the PAM concentration was increased. It means that the PAM polymer can affect the inhibition process. Due to the amount of residual polymer in the solution, the viscosity is increased and the solution flow gets worse. The scaling inhibitor could not be well distributed in the solution for catching the scaling cations. So, the cations can readily be combined with the anions to form the scale sediment.

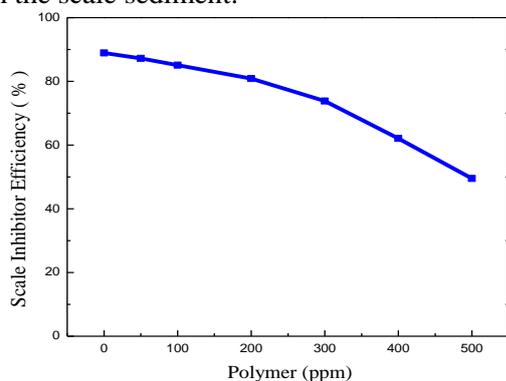


Fig. 1. Effect of polymer on performance of the scale inhibitor

Effect of surfactant on performance of the scale inhibitor

For testing the effect of surfactant on the scaling

inhibitor, 20 ppm of the scale inhibitor was added into the simulated produced water solutions with 50, 100, 150, 200 ppm of surfactant in 50°C. The results are shown as in Fig.2.

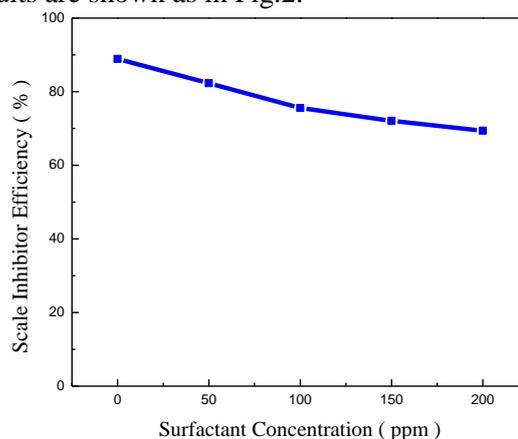


Fig. 2. Effect of surfactant on performance of the scale inhibitor

As indicated in Fig.2, the addition of the surfactant leads to a decrease of the efficiency. Even with the low concentration, the surfactant got worse than the no-adding solution. It is considered to be caused by the surfactant absorption closely with the scaling inhibitor. If the surfactant molecular is absorbed on the long chain of scaling inhibitor molecular, the steric hindrance will get increasing, and the big steric hindrance will get Ca^{2+} difficultly combined with scale inhibitor. As the result, the scale inhibitor efficiency is decreased.

Effect of demulsifier on performance of the scale inhibitor

As shown in Fig.3, 20 ppm of scaling inhibitor was adding into the simulated produced water solutions with 0, 5, 10, 20, 30 and 50 ppm of demulsifier for keeping for 24 hrs in 50°C.

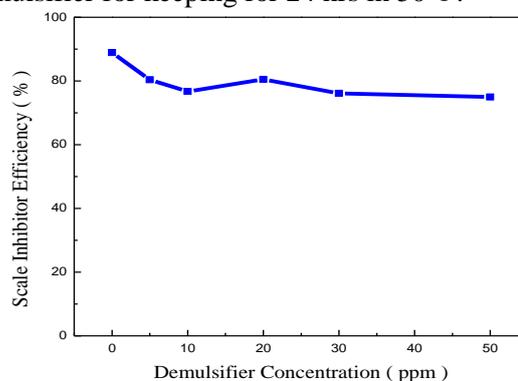


Fig. 3. Effect of demulsifier on performance of the scale inhibitor

As shown in Fig.3, the percentage of the inhibition was slightly decreased. Specifically speaking, the demulsifier makes inhibition

percentage decrease on the small range. This means the appropriate compatibility is presented by two agents by the wide concentrations in this condition.

Effect of defoamer on performance of the scale inhibitor

Firstly by putting 20 ppm of the scale inhibitor into the simulated produced water solutions with 0, 15, 25, 35, 45 and 100 ppm of defoamer in 50°C, then the test for the effect of defoamer on the efficiency was performed. The results are shown as Fig.4.

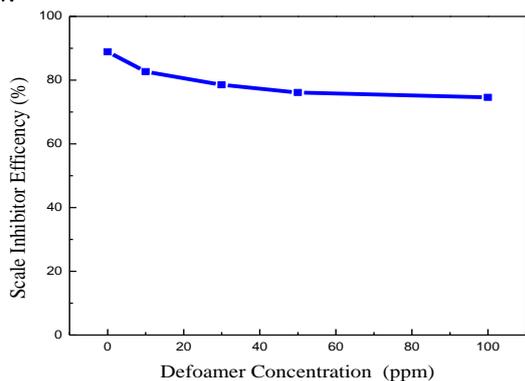


Fig. 4. Effect of defoamer on performance of the scale inhibitor

As demonstrated in Fig.4, the efficiency of the scaling inhibition was decreased with increasing the defoamer concentration. It implies that the addition of defoamer agent will have an impact on the inhibition percentage. If firstly adding the scaling inhibitor (without defoamer), the agent will be complexed efficiently with the Ca^{2+} ions. But the inhibition efficiency was slowly decreased when the defoamer concentration is increasingly added.

The results show the incompatibility of the scale inhibitor with the defoamer, resulting in decreasing the anti-scaling performance in existence of two agents under the condition.

Effect of anti-deposition agent on performance of the scale inhibitor

For testing the influence of anti-deposition agent on the scaling inhibitor, 20 ppm of the scale inhibitor was added into the simulated produced water solutions with 0, 10, 20, 30, 60, 90 ppm of anti-deposition agent in 50°C.

As shown in Fig.5, the results display that the addition of the anti-deposition made the efficiency slightly increasing. Even in very low concentration, the anti-deposition made better than the original solution. The profile of the anti-deposition-scale inhibitor curve exhibits the good compatibility of the scale inhibitor with the anti-deposition agent for leading to lifting scaling performance in existence of two agents under the condition.

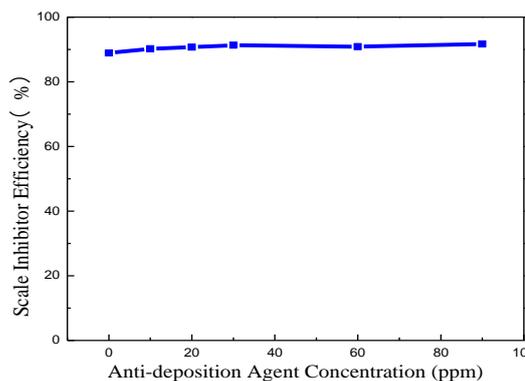


Fig. 5. Effect of anti-deposition agent on performance of the scale inhibitor

Comprehensive mechanism of compatibility and interaction between scale inhibitor and chemicals

Oilfield scaling. Generally, oilfield scales are formed by inorganic crystalline deposits that originates from the precipitation of solids in the reservoir and production system. The scale deposition results from changes in the ionic composition, pH, pressure and temperature of the reservoir and production. Common scaling compounds are calcium carbonate, barium sulphate and their complexes. The most common remediation is against the formation with chemical scale inhibitor in a “squeeze” treatment when the formation of sulphate or carbonate scale becomes a problem in produced fluids [9].

ASP flooding scaling mechanism. The formation of scaling in ASP flooding chain is very complicated. The scaling characteristics of the system consisting of Ca-Mg-Ba-Si in ASP flooding were presented by our previous paper [10]. It is different from water and polymer flooding by high Si and surfactant concentration. The dissolution of reservoir minerals by the strong alkaline enables the soluble Ca-Mg-Ba-Si materials into the reservoir fluid, which causes a serious scaling while occurring in changes of pressure, temperature, unstable thermodynamics and chemical incompatibility [11]. The scales in ASP flooding chain are mainly composed of carbonate and silicate. The $CaCO_3/MgCO_3$ particles serve as a grain for the precipitation while the silicon gel acts on a binder for coalescence of small particles. Silicon ion promotes the deposition of $Ca(Mg)CO_3$ particles. In this course, the inhibition of $CaCO_3/MgCO_3$ formation plays an important role in the control of the scaling.

The scaling formation ASP flooding is built by three steps: (1) soluble Ca-Mg-Ba ions plus Si ions from reservoir water and minerals in high solubility; (2) with lowering the solubility in change of temperature and pressure, molecule bond and

arrangement to form minicrystals, and begin to granulating; (3) lots of crystals to congregate, deposit and cause the scaling promoted by silicon ions.

ASP flooding scaling inhibiting mechanism. Phosphonate, sulfonate and carboxylate groups were one of the most common types of nonpolymeric or multipolymeric scale inhibitors, which have been used in the operation of the water and polymer flooding. In our case, phosphonate, sulfonate and carboxylate group were embedded in the scale inhibitor chain for ASP flooding. The groups are known to serve as the strong adsorbing scale inhibitor onto carbonates. The scale inhibitor is capable to chelate Ca-Mg-Ba ions to keep them soluble and to prevent carbonate from the deposition. Meanwhile, the silicon gel is prohibited from the codeposition.

Scale inhibitor-chemicals interaction and mechanism. The chemical compositions, as shown in section 2.1, reveal that the used chemicals are not able to undergo a chemical reaction between chemicals. It should be expected that interactive chemical reactions can not occur in the condition. Therefore, other types of interactions will be proposed as follows.

Scale inhibitor-demulsifier interaction. The demulsifier, existing in the chain, can be ionized while dissolved in the produced water. The scale inhibitor molecules are absorbed on the ionized demulsifiers. In this case, the scale inhibitor chains are entangled and lose the capability of chelating scaling ions. A liquid crystal phase will be formed to reduce the reverse action while adding high amounts of the demulsifier. In consequence, the inhibition percentage is slightly decreased, and then keeps flat in the curve.

Scale inhibitor-defoamer interaction. Hydrogen ions can be released while the defoamers are dissolved in the oil-water emulsion. The molecule chains of the defoamer are negatively charged, resulting in absorbing the scale inhibitor molecules and suspended solids. In this case, the scale inhibitor loses the positive function and the solid aggregation accelerates the scaling. In consequence, the inhibition percentage is sharply decreased, and gets worse with increasing the defoamer concentration.

Scale inhibitor-anti-deposition agent interaction. As shown in scheme 1, the anti-deposition agent consists of grafted phosphonate, sulfonate and carboxylate groups. The groups are known to be the strongly effective scale inhibitor like the scale inhibitor. So, the anti-deposition agent displays a positive compatibility with enhancement of the

scale inhibition.

For the detailed solution, our ongoing studies are being directed toward probing and proving this interaction and mechanism.

CONCLUSION

The study reports the compatibility and mechanism of the scale inhibitor combined with chemicals along the ASP flooding chain. The summary is listed as follows.

(1) The test of scale inhibitor exhibits that the scaling efficiency is decreased as the surfactant and polymer concentration are increased. That means the ASP chemicals will affect the inhibition percentage.

(2) The anti-deposition agent appears in positive compatibility while the negative effect of the demulsifier and defoamer on the scale inhibitor. But the action of the demulsifier changes in slight range.

(3) The interactive mechanism is attributed in the ionization of the demulsifiers, hydrogen ionization of the defoamers and effective functionalization of the anti-deposition agent.

(4) For the strategy of chemical usage, the adding sequence and dosage can be suitably specified and adopted for the ASP flooding chain by using the lab data.

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