

Silicate Scale Inhibitor Evaluation and Applications

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ABSTRACT

The formation of silica and silicate scales causes troublesome issues in various water-handling systems, including cooling tower, alkaline surfactant polymer flood, steam generators, geothermal wells, and sour water stripper systems, etc.

In this paper, laboratory tests were conducted under mimic field application conditions, including cooling tower, steam flood, and alkaline surfactant polymer flood. Selected chemicals were evaluated by a Kinetic Turbidity Test (KTT) method and static bottle test method. The performance of silica/silicate scale inhibitor chemistries were reviewed and discussed under the field application conditions.

This paper presents the laboratory testing data for scale inhibitor evaluation on both silica/silicate control and iron oxide and zinc hydroxide dispersancy by using the effective performance evaluation method, and provides valuable information on silicate scale inhibitor product selection under various field application conditions.

Key words: Silica/Silicate Scales, Kinetic Turbidity Test, inhibitor evaluations

INTRODUCTION

The formation of silica and silicate scales have been problematic issues in numerous operation systems, such as sour water stripper system, boiler and cooling tower, geothermal wells, steam generators, alkaline surfactant polymer (ASP) flood, and waste water disposal systems.¹⁻²¹ Silicates are primary deposit concerns in cooling tower systems with makeup water having elevated levels of silica and Ca or Mg. In a steam flood operation, produced water and spent brine off the Strong Acid Cation resins (SACs) were commingled before injection. The silica concentration in the produced water is over

300 ppm and the levels of Ca, Ba and / or Mg in the spent brine are high, which will induce silicate and other scales, including calcite and barite. Silicate scale inhibitor selections in alkaline surfactant polymer (ASP) flood are also discussed in this paper. ASP is one of enhanced oil recovery (EOR) methods designed to lower hydrocarbon interfacial tension and water-wet the formation to produce residual oil. ASP flood usually composes of uses a combination of alkali, surfactant, and polymer, which have very high pH values. When the high pH ASP flood moves through sandstone formation, quartz silica is dissolved.¹ When the alkaline ASP water meets with formation water with relatively low pH, the pH of the mixed water will decrease, which can dramatically reduce the solubility of monomeric silica. At pH below 10.5, silica begins to polymerize and form colloidal silica.²⁰ When pH is below 8.5, amorphous silica is further polymerized and subsequently forms insolubility of silica.²¹ Additionally, silicate ions complex with metal ions in the formation water may experience magnesium silicate and calcium/magnesium silicate scaling at pH greater than 8.5.²⁰ The high silica levels and high pH in ASP flood pose a great challenge for silica/silicate scale control.

This paper presents the laboratory testing data for scale inhibitor evaluation under mimic field conditions of cooling tower, steam flood, and ASP applications. The tests not only conducted on silica/silicate control, the dispersancy for both iron oxide and zinc hydroxide were also studied by using the effective performance evaluation method, and provides valuable information on silicate scale inhibitor product selection under various field application conditions.

EXPERIMENTAL PROCEDURE

Scale prediction modeling

Scaling tendencies were estimated using the scale modeling software program ScaleSoftPitzer™ version 2020 (SSP2020), an advanced software package developed by the “Brine Chemistry Consortium” at Rice University.

Scale prediction yields both the scaling potential expressed as the saturation index (SI) and the scaling tendency that is associated with the potential amount of precipitation in mg/L of a concerned scale at system conditions. The SI is a measure of the degree of super saturation of the scaling ions in an aqueous system and an indication of the driving force for the supersaturated scaling ions to form scale. SI is defined as the logarithm of the ratio between scaling ion activity product and the thermodynamic solubility product of a concerned scale. In other words,

SI < 0 the concerned scaling ions are under-saturated (no scale formation)

SI = 0 the scaling ions are at the saturation/equilibrium level

SI > 0 the scaling ions are supersaturated (tend to form scale)

The greater the SI, the stronger the driving force promoting the precipitation of scaling ions, and generally once initiated the faster the precipitation process.

The amount of equilibrium precipitation (mg/L) is the maximum amount of scale that would precipitate out of solution when the scaling ions reach the saturation/equilibrium level from the initially supersaturated state. It indicates the mass of scale that could potentially precipitate from supersaturated brine. It should be noted that the accuracy and reliability of the scale prediction results depend on several factors such as the accuracy of both the produced water chemistry data and production conditions that were used as input to the software package, as well as the correctness of the prediction model itself.

Kinetic Turbidity Tests

The Kinetic Turbidity Test is conducted with an Agilent Cary 100/300 series ultraviolet-visible (UV-Vis) spectrophotometer, which measures the absorbance of the sample solutions at a certain wavelength. Up to 12 samples are under temperature control, in a multi-sample holder with magnetic stirring in all cells. The samples can be tested simultaneously at temperatures ranging from 4°C to 95°C with

designed cuvettes that are usually made of quartz. Each cuvette has a small hole on the bottom to hold a small magnetic stir bar.

To conduct the test, a cuvette was placed in the first cell holder with 3 mL of deionized water to establish the baseline for turbidity. Anion brine is first added to the sample cuvettes. Various concentrations of inhibited anion brine are then added to each of the remaining cuvettes. Immediately before the start of the test, cation brine is then added to each of these cuvettes. The spectrophotometer reads results every 2 minutes, with a 5-second measurement time per cuvette over a 2-hour period. Testing can be longer based on the testing requests.

The kinetics application uses the absorbance versus time data to determine the rate of reaction. This function records scale formation kinetics and differentiates scale inhibitor performance by observing how fast absorbance increases. The faster the absorbance observed, the faster the scale formation. The wavelength for analysis of turbidity is 500 nm for the kinetic function.

Aerobic Bottle Tests

Aerobic bottle test was conducted with synthetic brine based on waters from the sour water stripper water analysis. Cation and anion solutions of each brine were prepared. Each anion solution was adjusted to the designed pH by purging CO₂ and N₂. After that, 50 mL anion solutions were put into a series of 4 oz. bottles, then the desired amount of scale inhibitor was dosed into bottles. After shaking thoroughly to mix anion solution and scale inhibitors, 50 mL cation solutions were added to each bottle, and these bottles were immediately inverted several times to assure thorough mixing of the components. Control and blank samples were also prepared. The control sample contained the mixture of same volume of cation solution and deionized water to simulate the case without scale formation. The blank sample contained equal mixtures of anion and cation water to represent a brine with no protection against scale formation. All bottles were capped and placed in an oven with the designed heating temperature for a period of 24 hours. Visual observations of the resulting inhibited solutions were made initially, 2 hours, and 24 hours after the addition of each scale inhibitor.

Chemicals and Materials

Fe₂O₃ is from Alfa Aesar 97% (trace metals basis), and surface area is 11.60 m²/gram, 325 mesh powder. Na₂SiO₃·5H₂O, NaCl, CaCl₂·2H₂O, etc. are from Fisher Scientific, ACS certified grade.

RESULTS

Scale tests were conducted under three mimic field application conditions in this paper: cooling water, steam flood, and ASP flood. Various chemistry products were selected for the evaluations, including the following products:

Product A: phosphonate 1+ silicate inhibitor 1

Product B: phosphonate 2+ silicate inhibitor 2

Product C: silicate inhibitor 3

Product D: phosphonate 3 + polymer 1

Product E: Silicate inhibitor 1

Product F: Silicate inhibitor 2

Product G: Silicate Inhibitor 4

Product H: Silicate Inhibitor 5

Phosphonate 1

Phosphonate 2

Phosphonate 3

Phosphonate 4

Phosphonate 5

Polymer 1

Silica/silicate scales in cooling water

A cooling tower blowdown water with high levels of silica is injected into salt water disposal (SWD) wells, and the well temperatures are 26.7°C-54.4°C (80°F-130°F). The water analysis of blowdown water listed in Table 1, and the possible silica/silicate scales were predicted, shown in Table 2. The major scales are SiO₂ and calcite, there are small amount of barite and Ca/Mg silicate. In order to prevent scale formation, effective scale treatment program is needed. Laboratory tests were conducted for selecting best fit products, and all tests were performed utilizing the synthetic brine prepared in the laboratory seen in Table 1.

Table 1
Brine composition

Ions	Unit	Brine 1	Brine 2
Na ⁺	mg/L	695	695
K ⁺	mg/L	5.70	5.70
Mg ²⁺	mg/L	4.40	4.40
Ca ²⁺	mg/L	411	411
Sr ²⁺	mg/L	5.40	5.40
Ba ²⁺	mg/L	0.30	0.30
Fe ²⁺	mg/L	0.40	0.40
Silicon	mg/L as Si	56.7	150
SO ₄ ²⁻	mg/L	1,528	1,528
Alkalinity	mg/L as HCO ₃ ⁻	166	0
Acetate	mg/L	0	100
pH, measured (STP)	pH	8.0	8.0
TDS	mg/L	3399	3399

Table 2
Scale prediction based on the above water analysis

Temp.	Pres.	pH	CaCO ₃ (Calcite)		BaSO ₄ (Barite)		SiO ₂ (crystal)		Ca/Mg Silicate	
°C	psia		SI	mg/L	SI	mg/L	SI	mg/L	SI	mg/L
26.7	14.7	8.0	0.97	28	1.49	0.49	1.20	113.61	0.47	6.83
54.4	14.7	8.0	1.10	40	1.13	0.47	0.85	103.97	1.53	1.67

Kinetic Turbidity Test Results

Kinetic turbidity tests were conducted with the selected 4 products at 54.4°C for 2 hours. To compare inhibition efficiency of different scale inhibitors, we defined the minimum effective concentration (MEC) as the minimum concentration which can completely prevent scale formation within test time duration. Inhibitor with lower MEC has higher inhibition efficiency. The testing results show that the MECs of selected products are all 2 ppm. Table 3 and Figures 1 show testing results.

Table 3
MECs of selected products by KTT

Products	KTT (mg/L)
Product A	2
Product B	2
Product C	2
Product D	2

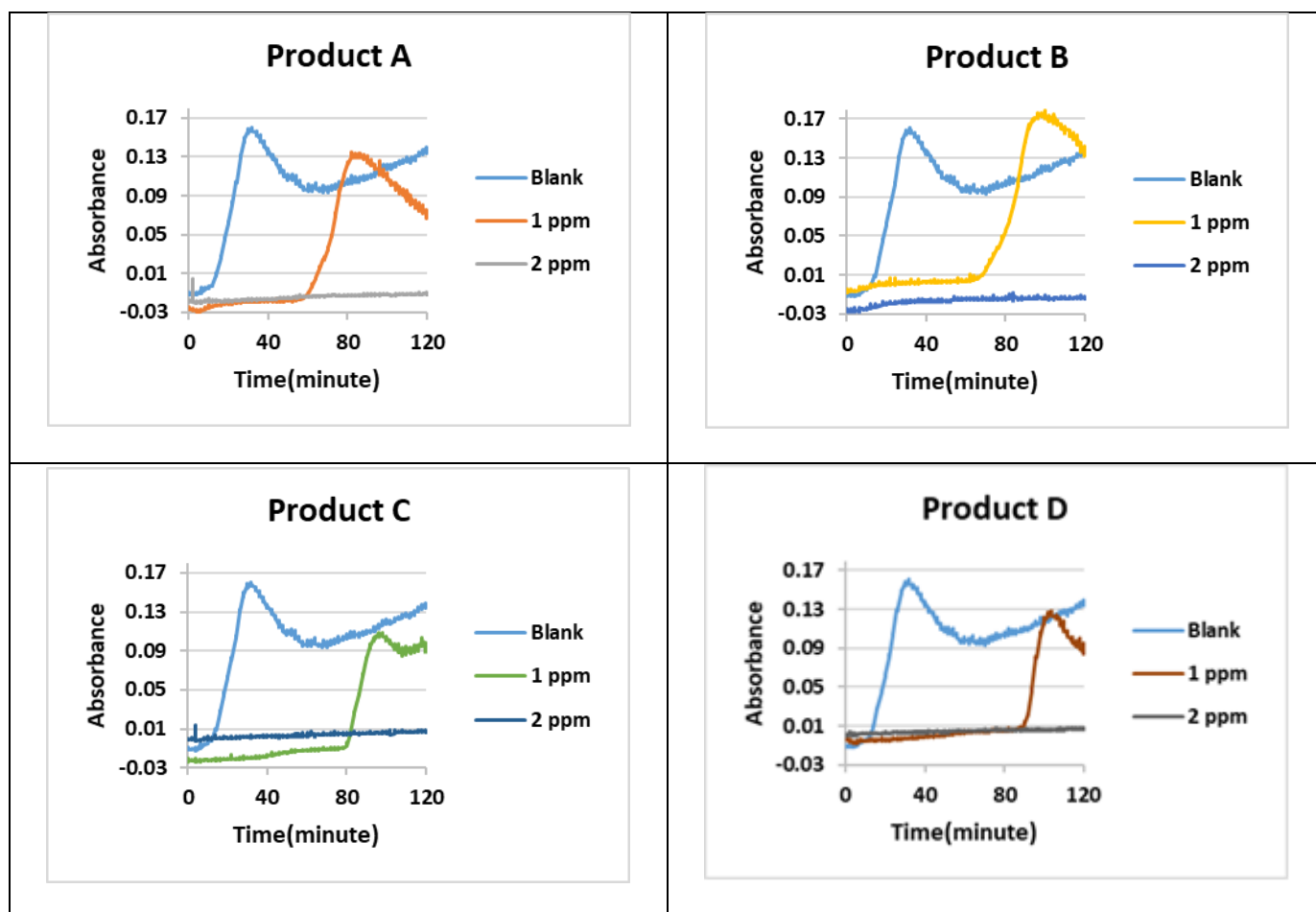


Figure 1: KTT results with Products A-D at 54.4°C.

Aerobic Bottle Test Results

Bottle tests were conducted at 54.4°C for 24 hours and 4 days to better differentiate inhibitor performance. Table 4 and Figures 2-5 show the testing results.

At 54.4°C, after 24 hours, the testing bottle of “Blank” showed a thick layer of white deposits. With 2-3 ppm selected products, there were no scale formation. In order to better differentiate scale inhibitor performance, tests were continued to run for 4 days. Product D has the best performance, and its MEC is 3 ppm. Product A has the second better performance, and its MEC is 5 ppm.

Table 4
MECs of selected products by bottle tests

Products	Bottle Test (54.4°C)-24 hours	Bottle Test (54.4°C)-4 days
Product A	2	5
Product B	2	10
Product C	3	>10
Product D	2	3

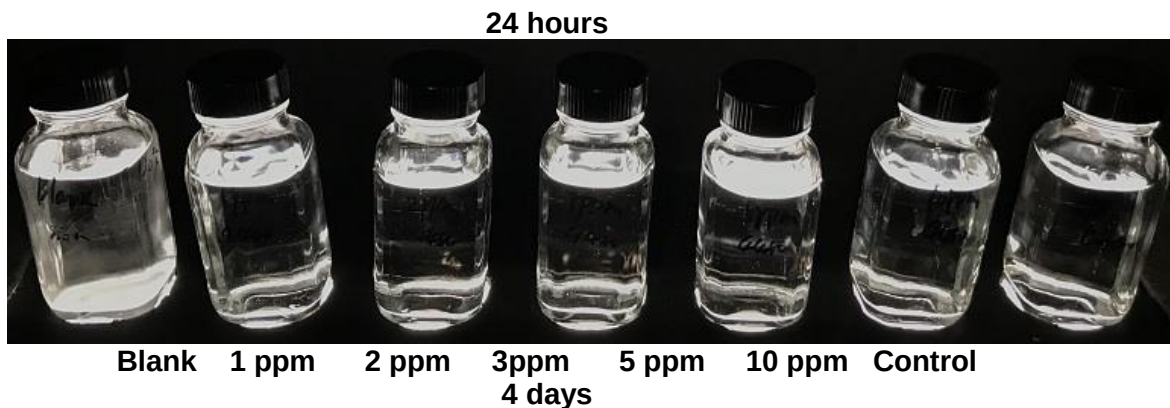


Figure 2: Bottle test results with Product A at 54.4°C.

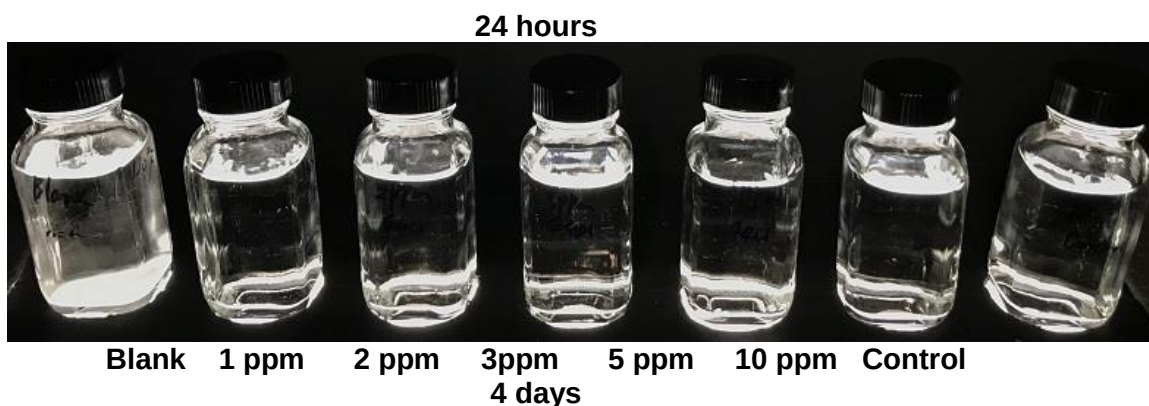


Figure 3: Bottle test results with Product B at 54.4°C.