

Paper No.
16959



Kinetic Turbidity Test Method for Scale Inhibitor Evaluation on Multifunctional Scales

Johnathon Brooks
Baker Hughes
12645 W. Airport Blvd.
Sugar Land, TX 77478
USA

Miriam Barber
Baker Hughes
Kirkby Bank Road Knowsley Industrial Park
Liverpool Lancashire L33 7SY
United Kingdom

Haiping Lu
Baker Hughes
12645 W. Airport Blvd.
Sugar Land, TX 77478
USA

ABSTRACT

One of the critical approaches for scale control is the proper selection and use of scale inhibitors. Laboratory tests help to select the appropriate scale inhibitor with the most common testing methods, including static bottle test and dynamic scaling loop test. Recently, Kinetic Turbidity Test (KTT) has gained increased recognition as a new testing method for scale inhibitor evaluation due to short testing time, simple sample preparation, and good reproducibility. There has been a good deal of research and studies on KTT as a technique for multifunctional scales, including calcium carbonate and barium sulfate (especially low scaling brines), halite and silicates. In addition, KTT can examine dispersant effects of polymers and surfactants on scale and other solids and can work under anaerobic conditions to give mechanistic understanding in the presence of iron. This paper discusses an alternative and efficient scale inhibitor testing method and gives insight for scale treatment chemistry and dosage by comparing and contrasting the different evaluation methods for scale inhibitors.

Key words: Kinetic Turbidity Test, Scale, Testing Methods

INTRODUCTION

Scale formation during oil and gas operation is problematic. Scale deposits that build up on pipeline or heat exchanger tubes reduce flow velocities inside pipes and heat transfer. They can also cause overheating of equipment and accelerate corrosion, which may lead to equipment failure to cause expensive downtime for cleaning or repair. One of the most common and effective scale control approaches can be achieved by using chemicals.¹⁻¹⁰ Different types of scales require different types of scale inhibitor chemistry, at varying dosages. Therefore, laboratory scale inhibitor testing is a powerful approach for screening products and determining effective dosages for the treatment.

Traditional testing methods for scale testing are dynamic scaling loop (dynamic tube block) and static bottle tests. For static bottle tests, it is easy to prepare and obtain acceptable accurate results. However, visual observation during the bottle test is subjective, and using titration or ICP (Inductively coupled plasma) for obtaining scaling ion concentration, to calculate inhibition efficiency, is time-consuming. For scaling loop tests, pressure differences across a scaling coil to indicate scale formation is utilized, which introduces many uncertainty factors to the testing results, including cleaning of coils, flow rate control, brine mixing in coils, etc. The maintenance of scaling loop equipment is also time-consuming. In recent years, the KTT method has been applied for more and more scale testing.¹¹⁻¹⁵ Compared with the conventional static bottle and dynamic scaling loop tests, KTT provides information on absorbance changes with time and temperature, with up to 12 samples, in one round of testing. This provides an effective and rapid way of differentiating the performance of scale inhibitors. For unconventional type scale testing, e.g. halite and silicate, KTT can be especially helpful for obtaining good operational and reproducible data, compared with other testing methods. KTT data can also provide information on scale formation rate, in the presence of a scale inhibitor, under given testing conditions. Since dispersancy is related to turbidity, studies on the dispersancy of scale inhibitors can be performed with KTT, as this is an indicator of the capability of a chemical to disperse particles and suspend them in solutions.

In this paper, a review of the KTT method is presented for scale inhibitor performance evaluation for both common scale testing and exotic scale testing, including halite and silicates, dispersancy tests, and tests under anaerobic conditions. Thermal function of KTT on scale formation and inhibitor evaluations are also discussed. A comparison of KTT results, bottle tests and dynamic scaling loop test were also conducted. These tests indicate that KTT has good capabilities for differentiating dispersant products and selecting best performing products.

EXPERIMENTAL PROCEDURE

The Kinetic Turbidity Test is conducted with an ultraviolet-visible (UV-Vis) spectrophotometer, which measures the absorbance of the sample solutions at a certain wavelength. Up to 12 sample cells are arranged in a multi-sample holder with magnetic stirring in all cells. 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 inset cavity on the bottom to hold a small magnetic stir bar.

To conduct the tests, a cuvette was placed in the first cell holder with 3 mL of deionized water to establish a 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.

There are two basic functions of the current test:

a). Kinetic function

The kinetic function 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.

b). Thermal function

The thermal function uses absorbance versus temperature data to determine the temperature at which scale formation will be observed. This function allows changing sample temperatures at a fixed increasing/decreasing heating rate because temperature changes affect scaling tendencies. The ability to change temperatures can enable simulation of certain oil and gas production processes such as temperature decrease during brine production downhole or surface temperature increase when brine

passes the heater treater. Utilizing the thermal function can help simulate the field conditions and provide more realistic information on scale inhibition.

DISCUSSIONS

Kinetic Turbidity tests have been used for the following studies:

- Scale formation kinetics for calcium carbonate (calcite), calcium sulfate, strontium sulfate, etc, and their inhibitor evaluations;
- Scale formation kinetics for exotic scales, halite, silicates, etc.
- Scale inhibitor/dispersant dispersancy evaluations;
- Scale inhibitor/dispersant dispersancy evaluations under anaerobic conditions;

Before going into kinetic turbidity test methods, the concept of turbidity is introduced.

Turbidity

Turbidity is used to indicate a measure of the relative clarity of water. It is caused by the interaction between light and suspended particles in water, which impede the transmittance of light through a water sample and convey a qualitative characteristic to water. Turbidity is not a direct measurement of suspended particles in water but, instead, a measure of the scattering effect of suspended particles on light. Turbidity is defined as an “expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.” by the American Public Health Association (APHA).¹⁶

A directed beam of light remains relatively undisturbed when transmitted through absolutely pure water, but even the molecules in a pure fluid will scatter light to a certain degree. Therefore, no solution will have a zero turbidity value. In samples containing suspended solids, the manner in which the sample interferes with light transmittance is related to the size, shape and composition of the particles in the solution and to the wavelength (color) of the incident light. The color of suspended solids and sample fluid are significant in scattered-light detection. A colored substance absorbs light energy in certain bands of the visible spectrum, changing the character of both transmitted light and scattered light and preventing a certain portion of the scattered light from reaching the detection system.

During scale testing, when scale crystals start to form from small nuclei, light scattering intensifies as particle concentration increases. When scale particles increase, scattered light strikes more and more particles, multiple scattering occurs and absorption of light increases. When particulate concentration exceeds a certain point, detectable levels of both scattered and transmitted light drop rapidly, marking the upper limit of measurable turbidity. Decreasing the path length of light through the sample reduces the number of particles between the light source and the light detector and extends the upper limit of turbidity measurement.

Scale Formation Kinetics for Common Scales and Their Inhibitor Evaluations

Scale testing for calcium carbonate, calcium sulfate, strontium sulfate, etc, with the kinetic function are the most common tests with KTT. The kinetics application uses 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 an increase in the absorbance is observed, the faster the scale formation. Good reproducibility under testing condition ranges (room temperature to 95°C, ambient pressure) can be achieved. During the testing, the time from when the cation and anion waters start to mix to the time scale formation begins to become evident is defined as induction time or scaling time. This can be used to indicate how fast scale formation is observed.

Figure 1 shows an example of KTT results for both calcium carbonate and barium sulfate scale inhibitor performance evaluations. Blank is the test without the addition of any scale inhibitors. The absorbance of Blank increased right after the test started, which indicates scales form right after the mixing of cation and anion waters. With 30 ppm of Scale Inhibitor A, absorbance did not have an abrupt increase until after 30 minutes, which shows that 30 ppm of Scale Inhibitor A can postpone scale formation for 30 minutes. With an increase of scale inhibitor dosages from 35 ppm to 55 ppm, scaling time was postponed longer, and there was no absorbance increase at 55 ppm within 120 minute-testing time. The testing results show how fast scales form under testing conditions with and without various dosages of scale inhibitors. The minimum effective concentration (MEC) of scale inhibitors within the testing time is considered the minimum dosages for scale treatment, which is recommended for field applications as a starting treatment dosages. For this case, the MEC is 55 ppm.

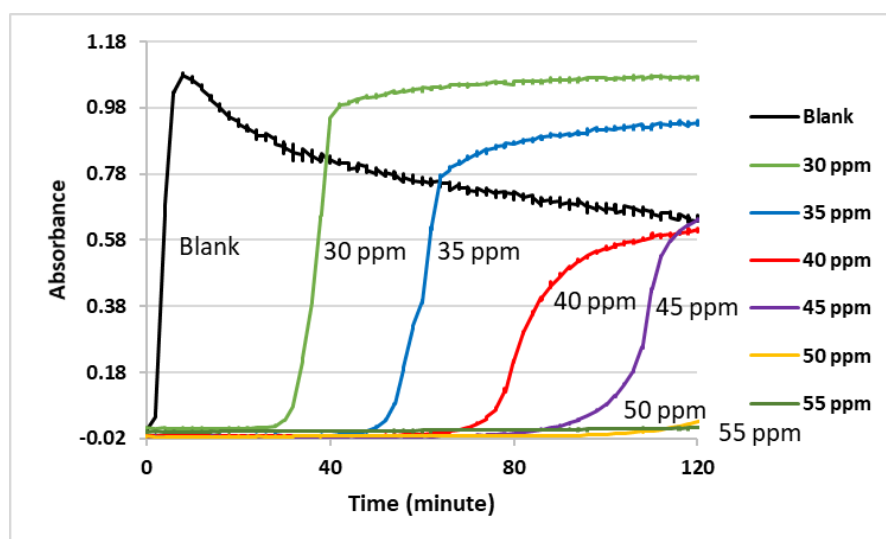


**Figure 1: Kinetic turbidity test results with kinetic function for Scale Inhibitor A at 25°C
KTT for Halite Testing**

For exotic type scale testing, e.g. halite and silicate, KTT can be especially helpful for obtaining good operational and reproducible data, compared with other testing methods. For halite testing, there is not an industry-recognized test method for laboratory testing of halite because of the difficulty in controlling the amount of halite precipitation and reproducibility during the tests. There are several available testing approaches for the laboratory testing of halite scale, including:

1. Produce supersaturated solutions by cooling of solutions saturated at higher temperatures;²²⁻²³
2. Mix with more soluble chloride salt to force precipitate out the NaCl, including CaCl_2 , MgCl_2 , LiCl , etc.;²⁴
3. Mix methanol with halite-saturated brine to precipitate out NaCl.²⁵

KTT has been used for halite testing recently.^{12, 15, 17} Compared with bottle tests and dynamic scaling loop test, KTT method is sufficient for halite testing since the large precipitated amount of halite will not exceed the limit of the turbidity measurements, and may provide more reliable and reproducible results than other testing methods. A good example for KTT on halite tests was illustrated in the Lu's 2015 paper. In this paper, KTT was conducted with various halite saturation brines to find out at what level of saturation index (SI), the tests can be properly designed for inhibitor evaluations.

Figure 2 shows the KTT results for halite testing with SI ranges of 0.00-0.14 at 25°C. The higher the SI, the faster the absorbance increase observed, which indicates faster scale nucleation and crystal growth. When SI=0.14, absorbance increases to the highest value, ~1.5, and halite formation occurred right after the mixing of two brines. The absorbance signals fluctuate due to the reflection of the large halite particles suspended in the brines by the stirring bars. The high absorbance indicates large amount of scale formation and crystal growth, and/or increasing particles suspended in the brine. When

SI decreases, induction time increases and longer time is needed for observable absorbance. At SI=0.06, induction time increases to ~3 minute, and at SI=0.04, induction time increases to ~5 minutes. When SI=0.02, induction time increases to ~60 minutes.

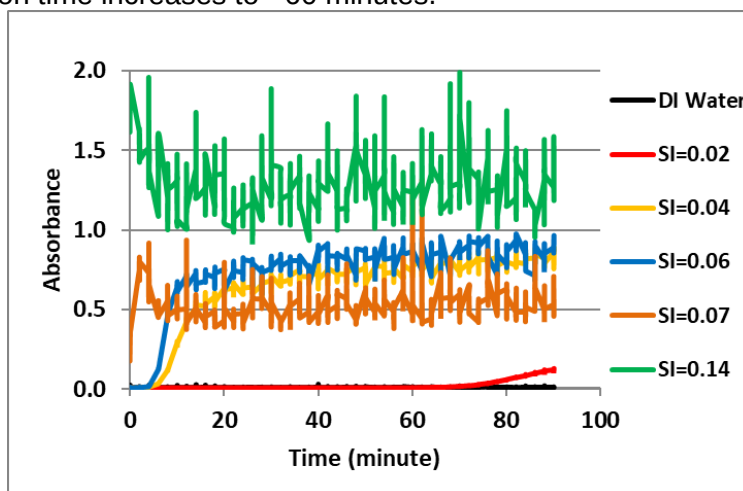


Figure 2: Kinetic turbidity test results for halite SI between 0.00-0.014

Based on the results from Figure 2, the brine of SI=0.06 was selected for the scale inhibitor performance test. With SI=0.06, 100-4,000 ppm Scale Inhibitor B was used in the testing (Figure 3). The induction time of Blank, 100 ppm, 500 ppm, and 1,000 ppm were all ~3 minutes. When the dosage increases to 2,000 ppm, the induction time was ~13 minutes, and absorbance increases slower than using the lower dosages until the end of testing. The absorbance increases slowly with starting dosages of 1,000 ppm, indicating that the effects of scale inhibitors are at the borderline range to prevent scale nucleation from increasing turbidity in the brines with the increasing test time. If the dosages of scale inhibitor are greater than the borderline dosages, scale formation will be inhibited. However, if the dosages of scale inhibitor are lower than the borderline dosages, the scale formation cannot be prevented. When the dosages were increased to 4,000 ppm, there was almost no absorbance change or scale formation observed.

This example shows KTT can produce consistent and reproducible testing results for halite scale inhibitor evaluation in spite of the large amount of halite scale formation in the system, which are very difficult to achieve by bottle tests and dynamic scaling loop tests.

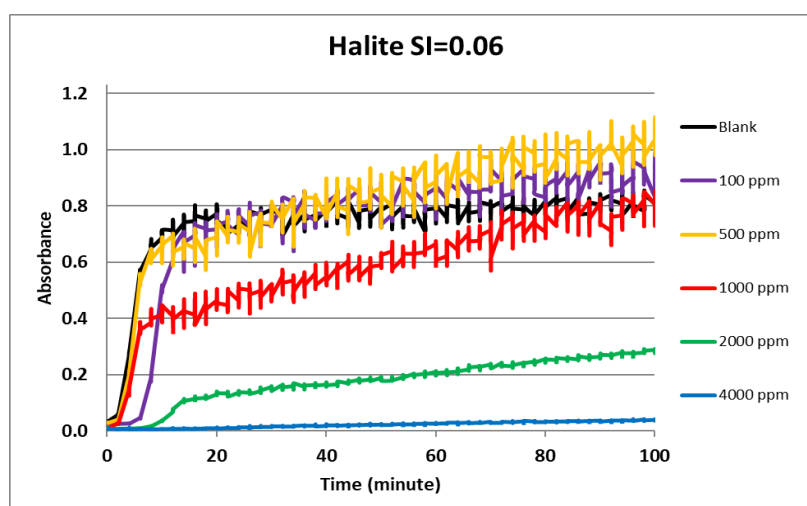


Figure 3: Kinetic turbidity test results for halite SI=0.06 with 100-4,000 ppm Product A