

Investigation of Scale Inhibitor Interference on Sulfate Measurement and Method to Remove the Interference

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ABSTRACT

The sulfate level in the effluent of sulfate removal unit (SRU) is usually continuously monitored for quality assessment. SulfaVer 4 method of Hach Company is a commonly used technique for sulfate measurement, and it is based on turbidity measurement caused by barite formation. The residual scale inhibitors in the effluent of SRU were observed to interfere sulfate measurement by inhibiting barite formation. Twelve different types of scale inhibitors were investigated on their impact on sulfate measurement. It was found that phosphonate, phosphate ester, and certain poly-carboxylate scale inhibitors do not interfere sulfate measurement, but sulfonate co-polymer and phosphino-polycarboxylate scale inhibitors showed strong interferences, i.e., the measured sulfate levels were lower than the actual concentrations. Several pre-treatments for the test sample were attempted to remove the interference. One pre-treatment method, called “Fe²⁺ thermal aging”, was found to completely removed scale inhibitor interference on sulfate measurements without causing any side effect. The method has been verified with both synthetic brine and field brine. This pre-treatment method can also help improving the accuracy of residual scale inhibitor analysis.

Keywords: scale inhibitor, sulfate, Hach, SulfaVer 4, iron

INTRODUCTION

Seawater injection is commonly utilized for offshore wells to maintain or increase oil production; however, treatment for seawater before injection is always necessary to reduce or remove bacteria, dissolved oxygen, sulfate, and other impurities¹. Seawater typically has >2000 mg/L sulfate. Without proper sulfate removal, such high levels of sulfate can cause not only barium sulfate, strontium sulfate, and calcium sulfate scales, but also reservoir souring and H₂S corrosion in the presence of sulfate reducing bacteria (SRB)². Therefore, sulfate removal from seawater is critical before seawater injection into reservoir. Sulfate removal unit (SRU) is essentially composed of a series of ultrafiltration (UF) membranes and/or

nanofiltration (NF) membranes². The sulfate level in the effluent of SRU requires continuous monitoring for quality assessment.

SulfaVer 4 method of Hach Company is one of the most common ways for sulfate measurement, as it is fast and easy to conduct in the field. The principle of SulfaVer 4 method is to provide the pillow which contains barium to react with the sulfate in the test sample to form barium sulfate (i.e. barite). With a stabilizing agent, the formed barite can suspend in the solution and hence solution turbidity increases. The higher the sulfate level, the more barite formed and the higher turbidity³. Nevertheless, if the test sample contains scale inhibitors which can inhibit barite formation, the detected sulfate level will be lower than the real concentration. Scale inhibitors were often added in SRU to prevent scale formation (e.g., calcium sulfate)⁴, and the residual scale inhibitor still exists in the effluent. SulfaVer 4 method was also used in other areas, for example wastewater treatment, to monitor sulfate^{3,5}. Residual scale inhibitors could also exist in those water samples.

Considering the potential interference of scale inhibitors on sulfate measurement, this research investigated the impact of 12 different types of scale inhibitors at different doses on sulfate measurement, and attempted several approaches to remove the interference. Finally, one effective approach was found to be able to remove scale inhibitor interference effectively without causing any further interference on sulfate measurement. This scale inhibitor removal method also has other applications which will be discussed in this paper.

EXPERIMENTAL PROCEDURE

Test brines

Both synthetic and field brines were used in this research. Table 1 displays the synthetic brine composition. Sulfate level varied from 10 mg/L to 70 mg/L.

Table 1
Synthetic Test Brine Composition

Ion (mg/L)	Test brine
Na ⁺	40,621
K ⁺	496
Mg ²⁺	1,881
Ca ²⁺	5,889
Sr ²⁺	192
Cl ⁻	79132
SO ₄ ²⁻	10 to 70
pH (no unit)	6.0

Scale inhibitors

Twelve different types of scale inhibitors were tested in this research. Table 2 shows the chemistries of the twelve scale inhibitors. The scale inhibitors were added into test samples before sulfate measurement or pre-treatment.

Table 2
Test Scale Inhibitors

Scale inhibitor	Chemistry
A	Phosphonate 1
B	Phosphonate 2
C	Phosphonate 3
D	Phosphonate 4
E	Phosphonate 5
F	Phosphate ester
G	Acrylic copolymer
H	Poly-acrylate
I	Poly-maleate
J	Phosphino-polycarboxylate
K	Sulfonate copolymer
L	Acrylic sulfonated copolymer

SulfaVer 4 Method

Sulfate was measured by SulfaVer 4 method of Hach Company. A Hach spectrophotometer is needed. The method details are available online³. In summary,

1. Take two clean sample cells, and fill each cell with 10 mL test sample.
2. Add one SulfaVer 4 sulfate reagent powder pillow to one sample cell, and shake the cell thoroughly. Leave the other cell as “blank” without adding powder pillow. Allow 5 minutes reaction time.
3. Put the “blank” cell into Hach spectrophotometer and press “ZERO”.
4. Put the cell with powder added into Hach spectrophotometer and press “READ”. The sulfate level will be detected. The sulfate detection range of this method is 0 – 70 mg/L. If the sulfate level is higher than 70 mg/L, dilute the test sample before analysis.

Interference removal methods

Three methods were attempted to remove the interference of scale inhibitor on sulfate measurement.

- 1) Fe^{2+} thermal aging method. The procedure is as follows:
 1. Prepare a FeCl_2 stock solution with 5,000 mg/L Fe^{2+} . Keep the stock solution in refrigerator at 4 °C (39 °F) before use.
 2. Add 12 mL test sample brine into a clean bottle, and then add adequate amount of FeCl_2 stock solution into test sample to make the final Fe^{2+} concentration of 50 mg/L. Cap the bottle firmly.
 3. Place the above bottle into oven at 60 °C for 15 hours. Afterwards, take the bottle out and let it cool down at room temperature.
 4. Filter the sample in the above bottle with 0.45 μm hydrophilic filters and take the filtrate for sulfate measurement.
- 2) Fresh Fe^{3+} method. The procedure is as follows.
 1. Prepare a FeCl_3 stock solution with 10,000 mg/L Fe^{3+} :
 2. Add 12 mL test sample brine into a clean bottle, and then add adequate amount of FeCl_3 stock solution into test sample to make the final Fe^{3+} concentration of 50 mg/L or 200 mg/L.
- 3) Fe_2O_3 solid method. Fe_2O_3 solid has the purity of 99%. The procedure is as follows:
 1. Add 12 mL test sample brine into a clean bottle, and then add 0.02 g Fe_2O_3 solid into test sample. Cap the bottle firmly, and shake the bottle thoroughly.
 2. Place the bottle in the oven at 60°C for 4 hours and 24 hours. After the designed aging time length, take the bottle out and let it cool down at room temperature.