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An assay method to determine mineral scale inhibitor efficiency in produced water

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ABSTRACT

This paper presents an easily-implemented assay method designed to detect mineral scale inhibitors, especially at low concentrations, in oil and gas produced water. The scale inhibitor concentration is determined using standard addition method, based on a semi-empirical linear relationship between scale inhibitor concentration and the logarithm of scale induction time. If a water sample contains only one scale inhibitor, this method will measure this inhibitor concentration directly. If multiple scale inhibitors are present, this method will detect their total scale inhibition efficiency. The method has successfully detected seven representative scale inhibitors at 0.3, 0.5, 1.0 mg/L in two laboratory prepared produced water samples. It has also been applied to scale inhibitor detection in real produced waters from oil field. This method features extremely low detection limit (0.05 mg/L inhibitor), applicability on a wide variety of scale inhibitors, and being easy to implement. By giving accurate determination of scale inhibitor efficiency, this method could enable better scaling control.

1. Introduction

Mineral scales often exist in oil and gas produced water, as a result of inorganic salt supersaturation (Hart and Rudie, 2006; Kan and Tomson, 2010; Kelland, 2010). The most common scales include carbonate, sulfate, and sulfide salts of divalent metal ions (Ca^{2+}, Ba^{2+}, Sr^{2+}, and Fe^{2+}) and sodium chloride (Kelland, 2010). Scale formation can reduce flow rate, water carrying capacity, and even block pipelines completely, causing a loss of millions of dollars every year (Vetter, 1972), which is still an ongoing challenge (Kan and Tomson, 2010). Delivering scale inhibitors into water systems can effectively inhibit scale formation, and they have been widely used (Kan et al., 2004; Kelland, 2010) in oil and gas produced water. The ability to accurately monitor residual scale inhibitor concentrations during these water treatment processes is essential for scale prevention. In oil and gas produced water, for example, too little scale inhibitor cannot prevent scale formation (Tomson et al., 2002), while too much scale inhibitor may precipitate with divalent ions and cause pseudo-scales (Kan et al., 1994). For instance, aminophosphonate inhibitors in supersaturation can react with calcium ions to form calcium phosphonate scale (Kan et al., 1994). Additionally, scale inhibitor overdose may cause environmental problems (Harris, 2011). Moreover, the accurate detection of residual scale inhibitor concentrations in oil and gas produced water is essential for scale inhibitor squeeze model development in oil and gas production (Graham et al., 1995). A successful squeeze model facilitates the optimization of squeeze treatment conditions and the prediction of squeeze lifetimes for future scale inhibitor applications (Graham et al., 1995; Sorbie et al., 1992).

However, it is rather difficult to determine low scale inhibitor concentrations using current detection methods, especially for polymeric scale inhibitors (Graham et al., 2010). For instance,

Abbreviations: CMI, carboxy methyl inulin; DTPMP, diethylenetriamine penta (methylene phosphonic acid); NTMP, nitrilo trimethylene phosphonic acid; PMAC, phosphorous incorporated maleic acid polymer; PPCA, phosphine polycarboxylic acid; PVS, polyvinylsulfonate polymer; SPCA, sulfonated polycarboxylic acid polymer; a, intercept; b, slope; B, blank, the solution diluted from inhibitor free water; C_f, scale inhibitor concentration in water sample; $C_f^{estimated}$, estimated scale inhibitor concentration in water sample; C_S, scale inhibitor concentration in sample (S); DF, dilution factor; EIC, equivalent inhibitor concentration; L1, L2, L3, three laboratory prepared water samples; R1, R2, R3, three real produced waters from oil field; S, sample, the solution diluted from water sample; SS1, supplemental sample 1, which is S with scale inhibitor addition of 0.1 mg/L; SS2, supplemental sample 2, which is S with scale inhibitor addition of 0.2 mg/L; t_B, the induction time of B; t_S, the induction time of S; t_{SS1}, the induction time of SS1; t_{SS2}, the induction time of SS2.

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inductively coupled plasma (ICP) is widely applied in scale inhibitor analysis by measuring phosphorus (P) concentration (Graham et al., 2010). P-containing scale inhibitors such as diethylenetriamine penta(methylene phosphonic) acid (DTPMP) can be easily and accurately detected by ICP, but many polymeric scale inhibitors do not contain P, such as sulfonated polycarboxylic acid polymer (SPCA), polyvinylsulfonate polymer (PVS), and carboxy methyl inulin (CMI). In addition, if the water sample has P-containing impurities, ICP will overestimate the inhibitor concentration (Thompson et al., 2012).

Polymeric scale inhibitors are becoming more popular because they are more stable at high temperature and often less harmful to the environment (Boak and Sorbie, 2010; Yan et al., 2012). Polymeric inhibitors are often analyzed by the hyamine method or high performance liquid chromatography (HPLC) method (Graham et al., 2010). Both methods usually require tedious pretreatment, be at a high cost per sample, suffer from interferences at low inhibitor concentrations, and do not have sufficiently low detection limits (Thompson et al., 2012). Therefore, a high demand exists for a sensitive, universal, and inexpensive method for scale inhibitor analysis.

In this paper we present a new assay method for scale inhibitor analysis. This assay method is based upon the semi-empirical linear relationship between the scale inhibitor concentration and the logarithm of barite ($BaSO_4$) scale formation induction time (He et al., 1996). This linear relationship is suggested by classical nucleation theory and confirmed by experimental observations (He et al., 1996, 1994; Mullin, 2001). Previous methods that evaluate scale inhibitor performance through barite or calcite stress tests paved the way for this assay method (Baugh et al., 2012; Collins et al., 2004). The principle of the assay method is similar to that developed for citrate measurement in biological fluids based upon calcium fluoride nucleation and crystal growth inhibition (Grases et al., 1991). In fact, this assay method detects the equivalent inhibitor concentration (EIC) of a water sample. When a water sample contains only one scale inhibitor, EIC equals to the true scale inhibitor concentration. When a water sample contains multiple scale inhibitors, EIC indicates the total scale inhibition efficiency of all scale inhibitors, which is a big advantage of this method. More information about EIC will be presented in Section 2.1. The assay method has several additional advantages that will be discussed later.

Barite was chosen as the surrogate scale in the assay method for several reasons. First, barite is one of the most common scales in the oil field (Kelland, 2010). Barite inhibitors and other inhibitors that are effective for calcite or gypsum control can generally inhibit barite as well (Kelland, 2010), which makes the assay method applicable for a wide variety of scale inhibitors. Second, barite has extremely low solubility and high stability (Blount, 1977; Shi et al., 2012). Barite precipitation can occur rapidly at high saturation index (SI). Once barite is formed, it is difficult to redissolve. Third, barite solubility is insensitive to solution pH. Unlike barite, calcite is a pH-sensitive scale. Carbonate (CO_3^{2-}) concentration changes with solution pH, which complicates the ability to calculate and control calcite SI precisely. Thus, using barite as the surrogate scale eliminates a number of problematic issues.

2. Material and methods

2.1. Principle of the assay method

A method of known additions is used to generate induction time data points and back-calculate the concentration of scale inhibitor present in the collected water sample, based upon the observed linear relationship between scale inhibitor concentration and the logarithm of the barite induction times (He et al., 1996, 1994, 1995; Mullin, 2001). The induction time is the time period from the beginning of supersaturated solution is created to the time when stable and detectable nuclei are formed (Mullin, 2001). In this study, induction times are measured through monitoring solution turbidity change by a recording turbidity meter or a laser apparatus (Yan et al., 2014). The induction time is defined as the time elapsed when the solution turbidity becomes 0.1 Nephelometric Turbidity Unit (NTU) higher than the average value of background turbidity.

Test solutions are prepared based upon the known composition of the water sample to establish an appropriate dilution and barite supersaturation. The assay method requires a dilution and addition of Ba^{2+} or SO_4^{2-} or both to the water sample during dilution to formulate a test solution that have a measurable and distinctive barite induction time to be used to determine the inhibitor concentration. In this paper, “dilution” or “dilute” refers to a specific experiment procedure of diluting the water sample to test solutions, during which required reagents will be added. The details of the dilution procedure are shown in the Section 2.2 and in Appendix A. The concentration of scale inhibitor in the water sample is denoted as C_f (mg/L) and is the property we seek to determine through this analysis.

First, estimate the scale inhibitor concentration in the water sample as $C_f^{estimated}$ (mg/L) ($C_f^{estimated}$ is a specific number). This estimate needs to be based on the operator’s past experience of scale inhibitor return from the same field. Based on $C_f^{estimated}$, the water sample is diluted to a final inhibitor concentration of 0.1 mg/L, with a dilution factor (DF), where $DF=C_f^{estimated}/0.1$. The diluted water sample is a test solution as mentioned previously and is called “Sample,” abbreviated as “S”. S contains inhibitor concentration C_S (mg/L) from innate field scale inhibitor, where $C_S=C_f/DF$. The concentration C_S can vary considerably and the method will still perform successfully. If after completing the assay analysis the ratio of the detected C_f to the estimated inhibitor concentration $C_f^{estimated}$ (ratio of $C_f/C_f^{estimated}$) is not in the range of 0.5–2.0, it means the initial estimated $C_f^{estimated}$ is probably in error, which may happen in cases of new oil fields or new scale inhibitor squeeze designs. If this happens, re-estimate the inhibitor concentration based on the first detection result and re-run the analysis to ensure a reliable inhibitor concentration.

The induction time for sample (S) will be denoted as t_S. It has been found that, for the best detection sensitivity at room temperature, log t_S should range from about 2 to 2.5 log units (i.e. t_S ranges from 100 to 300 s), and each known addition of scale inhibitor should increase the induction time by about 0.20 to 0.30 log units (roughly 200 s or more). From experience, these criteria can be met if the barite saturation index SI=2.1 at 25 °C, and if each scale inhibitor addition is made in increments that increase the total solution inhibitor concentration by 0.1 mg/L. This is illustrated in the induction times in Figs. 1 and 2 for scale inhibitor phosphine polycarboxylic acid (PPCA). Ba^{2+} and SO_4^{2-} are added during the water sample dilution to achieve SI=2.1 and a molar ratio of Ba^{2+} to SO_4^{2-} as close to 1.00 as possible, as described in Section 2.2 and Appendix A. The amount of added Ba^{2+} and SO_4^{2-} depend on the composition of the water sample; the calculation equations are in Appendix A.

Sample S with scale inhibitor addition aliquot no. 1 is called, “Supplemental Sample 1” (SS1), with total inhibitor concentration (C_{inh}) of $C_S+0.1$ mg/L and a corresponding induction time, t_{SS1}. Sample S with two scale inhibitor aliquot additions is Supplemental Sample 2 (SS2), with total inhibitor concentration (C_{inh}) of $C_S+0.2$ mg/L and a corresponding induction time, t_{SS2}. The added scale inhibitor is called reference scale inhibitor that should be the same or similar to the detected inhibitor, if known. SS1 and SS2 solution volumes are chosen so that the volume change due to