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The Use of Fluorescent Tracers for Inhibitor Concentration Monitoring Useful for Scale Inhibitor Squeeze Evaluation

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Abstract

A common problem, in oilfield reservoirs is mineral scale deposition. The build-up of scale inside well bores and the surrounding reservoir causes millions of dollar in damage every year. The most common remedy is to treat the formation of such minerals with scale inhibitor chemicals in a “squeeze” treatment; which is performed periodically. One of the big challenges remains the real-time and on-site control of inhibitor concentration during production. A simple and accurate method to determine the concentration of inhibitors has been developed; this method is based on the use of luminescent tracers. The multiple lifetimes as well as the differences shown in the emission and excitation spectra of the tracers appear to be suitable for the luminescence detection. The increased signal to noise ratio due to the suppression of the background resulting from the organic oil residues is used to measure the concentration of residual inhibitors in production waters. Furthermore, the use of a technique as versatile and simple as luminescence spectroscopy allows the online and/or on-site monitoring with very limited drawbacks. This paper describes the use of novel real-time scale inhibitor monitoring; this new technique will help to optimize the treatment rates of the scale inhibitor squeeze treatment.

Introduction

Limescale (calcium carbonate) that deposits on the surface of well bore will, if untreated, reduce the efficiency of the exploitation, inducing corrosion of the production chain and ultimately leading to appliance failure. Indeed, pipework scale reduces the available cross-section area, and fluids are affected by increased pipe wall friction. A larger, more power-consuming pump will be required to maintain throughput volumes, but this can only be a temporary solution to the problem. A plant that needs to be shut down for cleaning costs millions of dollar in damage every year (Moghadasi, J. *et al.* 2004-A).

The formation of a thin uniform layer of scale or wax temporarily gathers the steel corrosivity, but at long-term the stagnant conditions of deposit and electrochemical reactions will corrode the steel surfaces. The fluid leaks as well as the equipment failure have been expected with potentially dangerous consequences.

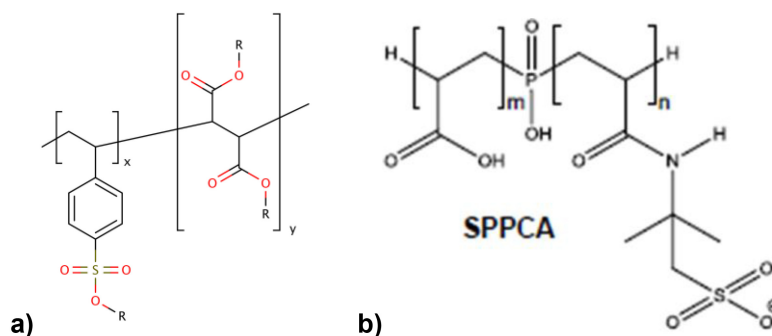


Figure 1—Representation of F11 (a) and SPPCA (b) polymer structure

Performed periodically, “squeeze” treatment is one of the most common remedies to treat the formation of such minerals. Treatment options include inhibitor chemicals, descalers, ion exchange, physical cleaning such as pipeline pigging (Collins, I.R. *et al.* 2001).

Although it is usually possible to find a chemical solution to a fouling problem, environmental and safety pressures are demanding that chemical consumption must be reduced when possible. One of the big challenges remains the real-time and on-site control of the inhibitor concentration during production in order to optimize their amount (Graham, G. *et al.* 1995; Boak, L.S. and Sorbie, K., 2010). The method for inhibitor estimation should be fast, sensitive and reproducible. Inhibitors have been showed to be excellent chelating molecules (Collins, I.R. *et al.* 2001, Jordan, M. M. *et al.* 2000); therefore it is possible to use this property in order to enhance the luminescence signal of inorganic emitters. Lanthanide ions have been found as suitable for inhibitor chelation and gives a specific emission signature depending on the (i) nature of ligand/lanthanide pair and (ii) the environment. The emission and excitation spectra as well the quantum yield and lifetime of chelated rare earth ions represent the information useful for the further scale evaluation (Liu, G. And Jacquier, B. 2005). Moreover, the emission of the lanthanide ions chelated by the inhibitor can be separated from the background fluorescence using time-resolved fluorescence; thus it is possible to estimate scale inhibitor concentration from the raw signal (Lakowicz, J. R. 2008).

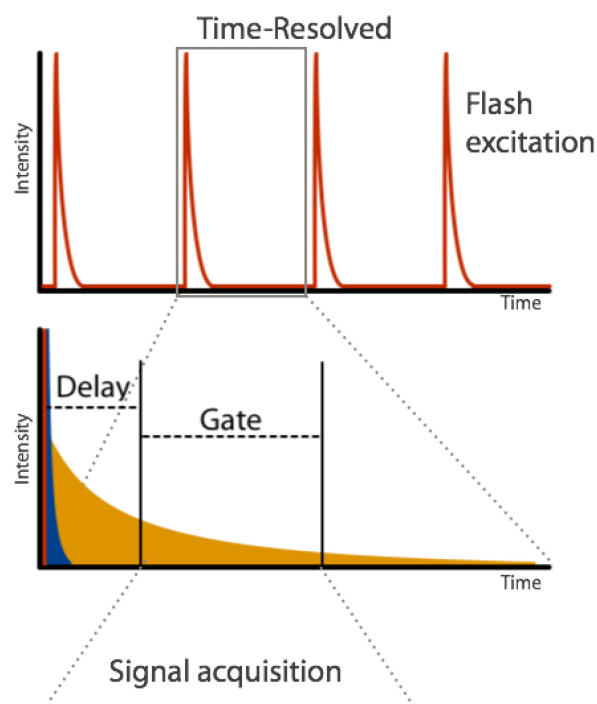


Figure 2—Time-resolved fluorescence measurement principle. At 0 s an excitation pulse irradiates the sample. Organic compounds fluorescence intensity is represented in blue; rare-earth element chelates fluorescence signal intensity is depicted in orange. Acquisition of the signal takes place during gate time.

Principle of inhibitors detection

The addition of a Tb-Light formula (chemically stabilized lanthanide ions solution) to the solution containing inhibitors allows their quantification by an easy optical procedure. The solutions of Tb-Light, distributed by Nano-H S.A.S., have been mixed with three different inhibitors: F11 (a polystyrene co-maleic acid based polymer), SPPCA (Sulfonic phosphinopolycarboxylic acid) (Figure 1), a third polymer that will be called Polymer 2 and a commercial product from Clariant named TP8106G.

Systematic optical characterizations, such as life-time, excitation and emission spectra, provide a complete picture of lanthanide - inhibitors pairs that can be further quantified in oil field.

Optical signature of lanthanide-chelating inhibitors

The main advantage of using lanthanide chelate solutions for oil-related application is their intrinsic phosphorescence emission signal that could be easily collected and separated from the noise of petroleum medium. As currently seen in bioassays, the time-resolved fluorescence technique almost suppresses the fluorescence background of the medium and enhances the intrinsic phosphorescence signal of tracers. In other words, the increase of signal-to-noise ratio drastically reduces the quantification limit below the ppb threshold (Agenet N. *et al.* 2012).

The principle of measurement is illustrated in Figure 2. The sample (a solution containing the labelled inhibitor) is illuminated by light pulses at a fixed wavelength (wavelength close to the excitation band of the lanthanide emitter), and the emission signal (the detector is placed at 90° from the incident light axis) is collected by a synchronous detection system after a delay time (Figure 3). During the time between the lamp pulse and the signal collection, all organic residues contained in crude oil emit because of their short lifetimes, whereas chelated lanthanides (the tracer) preserve their intrinsic phosphorescence signal that will be collected by the detector during the gate time. The longer lifetime of rare earth tracers represents an absolute advantage compared to organic ones in oil recovery systems because it decreases of several orders of magnitude the quantification limit.

The resulting emission spectra (Figure 4) shows the energy phosphorescence transition peaks of a terbium chelate centered at 485 nm, 545 nm and 580 nm; the only differences in intensity have been referred to the discrepancies in concentration between the various samples and to the specific complexation of inhibitors. Moreover, the shape of excitation spectra, which have been normalized at 352 nm (a specific transition peak of Tb^{3+} ions), also indicate a correlation with the specific Tb-Light – inhibitor pairs (Figure 5). The analysis of peak ratios as well their intensities in both excitation and emission spectra allows the determination of the concentration for each inhibitor species diluted in production waters.

Decay rates of lanthanide-chelating inhibitors

As described above, the fact that lanthanide chelates display ms range excited state lifetimes can help to differentiate the emission of tracers from the organic oil background signal. A simple apparatus composed by a time-resolved spectrophotometer has been set up: short light pulses centred at 230 nm irradiate the

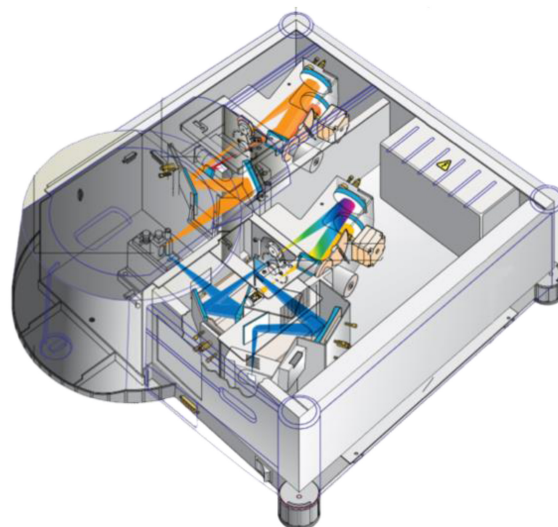


Figure 3—Schematics of the detection device. The light beam is emitted from a Xenon flash lamp and a wavelength is selected via a Czerny-Turner monochromator (blue beam); after passing through the sample chamber the resulting light is collected via another monochromator and directed to a photomultiplier (orange beam) (Courtesy of Agilent Technologies)

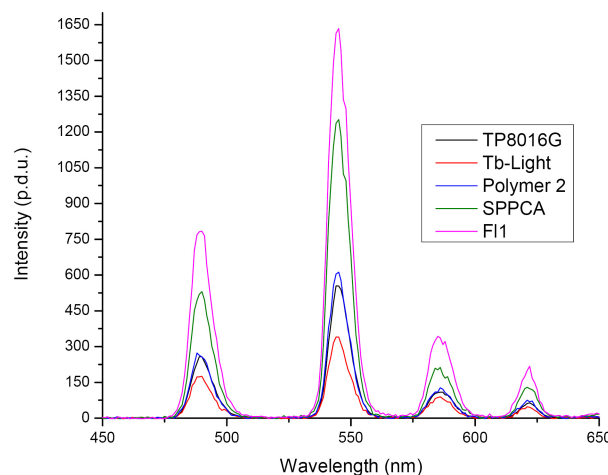


Figure 4—Emission spectra of four scale inhibitors compared to the Tb-Light reference. Emission spectra have been realized at $\lambda_{exc}=230nm$, with a delay of 0.1ms.

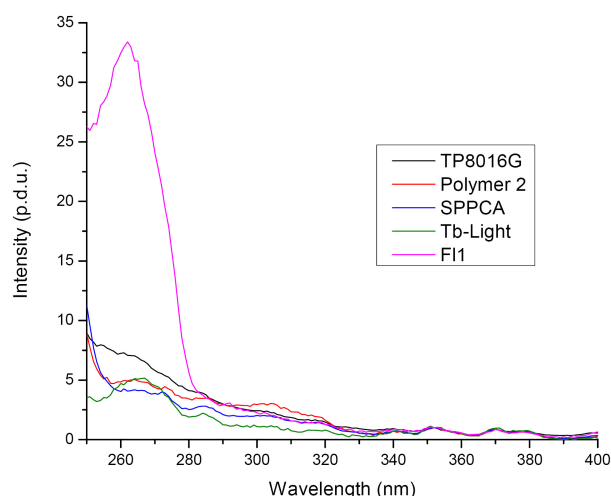


Figure 5—Excitation spectra of four scale inhibitors compared to the Tb-Light reference. Excitation spectra have been realized at $\lambda_{em}=545\text{nm}$, with a delay of 0.1ms. All spectra have been normalized at 1 at 352 nm.

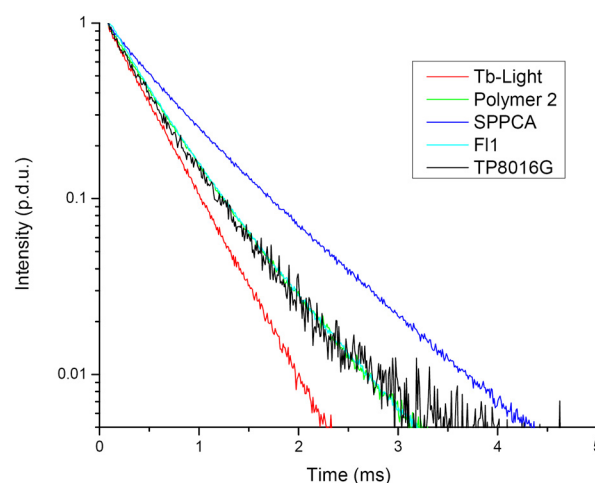


Figure 6—Luminescence decay rates of four different inhibitors and of Tb-Light as reference. All spectra have been normalized at 1. $\lambda_{exc}=230\text{nm}$ and $\lambda_{em}=545\text{nm}$.

sample and the signal at 545 nm is collected in lifetime mode. The intensity signal is traced as a function of time and the curve obtained is fitted using a multi-exponential decrease function such as:

$$I = A \cdot \exp(-t/\tau_1) + B \cdot \exp(-t/\tau_2)$$

where A and B are pre-exponential factors proportional to the concentration of each specie and τ_1 and τ_2 are unique species-dependent lifetimes. Based on the fact that terbium ions display different lifetimes as a function of environment, it is then possible to estimate the amount of the different components within the sample. Figure 6 summarizes the intensity decay curves of terbium ions for a series of inhibitor-lanthanide combination. The trend of curves has been fitted with the described equation: the Tb-Light signal can be modelled by a mono-exponential function whereas the inhibitors mixed with the Tb-Light have to be fitted with a bi-exponential curve. Indeed, the appearance of a second lifetime component is due to the fraction of terbium ions chelated by the inhibitors that gives a unique lifetime value depending on the specific chelating agent (Table 2). As expected, all inhibitors chelating terbium ions have longer lifetimes than the free terbium ions because of the suppression of phononic quenching of emitters. It is then surprisingly easy to estimate the concentration of mixture just by the calculation of A and B factors.

Inhibitors concentration determination

Experimental Setup

The use of a time-resolved spectrophotometer allows the detection of multiple scale inhibitors, even in oil-polluted waters. Before the measurement, 0.2 ml of production water coming from a French field ($\sim 50\text{g/L}$) or in a production water coming from a Qatari field ($>200\text{ g/L}$) has been doped with a fixed concentration of inhibitors (Polymer 2, SCCPA, TP8106G or FI1) ranging from 0 to 5 ppm, and placed

Table 1—Synthetic sea water composition

Salt	Concentration (g/L)
NaCl	140
KCl	0.88
MgCl ₂ ·6H ₂ O	10.66
CaCl ₂	44.25

Table 2—Lifetimes of different inhibitors chelating terbium ions

Product	τ_1	τ_2
Tb-Light	0.414	-
SPPCA	0.414	0.878
Polymer 2	0.414	0.769
FI1	0.414	0.851
TP8106G	0.414	0.971

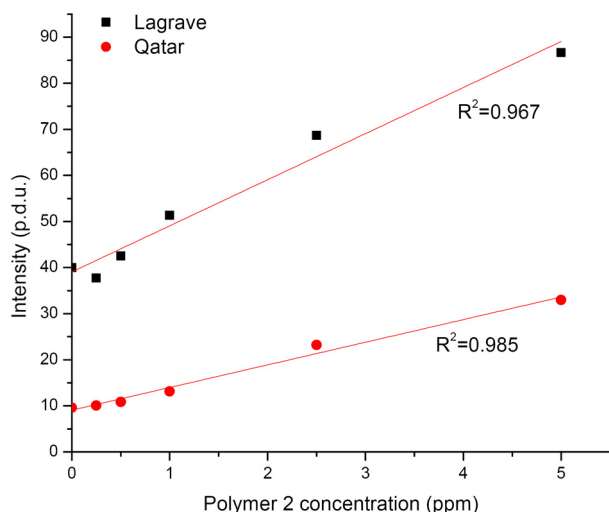


Figure 7—Intensity of the phosphorescence signal as a function of Polymer 2 concentration in two different production waters: Lagrave (black) and Qatar (red)

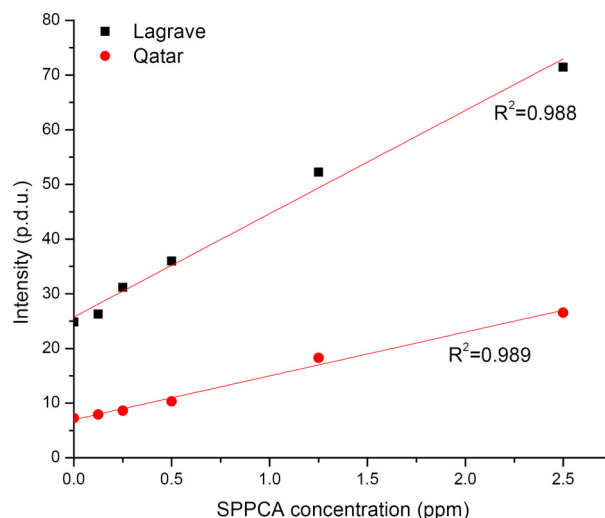


Figure 8—Intensity of the phosphorescence signal as a function of SPPCA concentration in two different production waters: Lagrave (black) and Qatar (red)

into a cuvette containing 1.8 ml of Tb-Light solution. Under magnetic stirring, the content of the cuvette is mixed and analyzed via spectrophotometry to determine the inhibitor concentration. 320 nm - pulse excitation has been realized with a Xenon Flash Lamp on Agilent Technologies Eclipse apparatus. A sequence of high energetic excitation pulses of 100 Hz frequency irradiates the sample and the signal is synchronously collected within a gate window of 3 ms between $t + 2$ ms and $t + 5$ ms after each flash. A standard Photomultiplier (PM) detector centered at 545 nm (optimized for terbium chelates) collects the emission photons (detection set-up is reported in Figure 3).

Results

Results of the detection analysis are presented in Figure 7, Figure 8 and Figure 9. For all three tested inhibitor cases, the luminescence intensity is proportional to concentration between 0 and 5 ppm; linear fittings with high ranging R^2 values (> 0.950) are found. Concentrations higher than 5 ppm display a very high absorption of the inhibitors and induce a strong inner-filter effect, which breaks the linearity of fluorescence intensity and prevents any tracer quantification. Moreover, all three experiences have been realized with two different production waters and the results confirm the validity of the experimental procedure for various production waters that come from different countries. This item opens the possibility of inhibitors quantification in multiple oil fields. In addition, it has to be noted that once the calibration curve has been realized, each sample can be analysed in a very short time (< 2 minutes). This is a major improvement over the Hyamine 1622 method currently used to dose various polymers.

Some differences have been noted between the calibration curves obtained in low salinity or high salinity waters. Those differences in fluorescence intensity are caused by a change in the environment of the fluorescent ions. However they can be easily assessed either (i) by performing a well specific

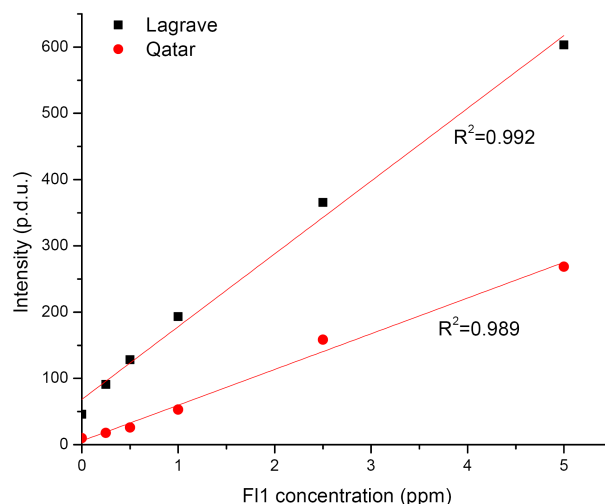


Figure 9—Intensity of the phosphorescence signal as a function of FI1 concentration in two different production waters: Lagrave (black) and Qatar (red)

calibration curve with an intrinsic reference solution (introducing a fixed amount of inhibitors) or (ii) by diluting multiple times the samples in order to lower the impurities influence on the fluorescence.

Inhibitors differentiation

As multiple scale inhibitors could be used at the same time, often mixed with other additives (corrosion inhibitors), it must be necessary to differentiate the inhibitors signal from the signal due to the mixture of other compounds. The objective of this experiment is to test the effect of different interfering chemicals on the detectability of inhibitors.

Experimental Setup

Three different sets of solutions were prepared: in one case, the inhibitors have been diluted in distilled water, in the second case in synthetic seawater (composition details in Table 1), and the last case in distilled water doped by 10 ppm of two commercial corrosion inhibitors and one commercial anti-foam additive. The sets of solutions were then prepared in order to get concentrations of SPPCA ranging from 0 to 2.5 ppm. 0.2 ml of the prepared solutions was then added to 1.8 ml of Tb-Light in a quartz cuvette and the samples analyzed via spectrophotometry to determine the inhibitor concentration.

Results

Results of the analysis are presented in Figure 10. Firstly, it appears that the solvent has an impact on the absolute value of fluorescence intensity. The linearity between luminescence intensity and concentration for all solution is nevertheless maintained but the signal is translated by an offset value. A reference sample easily helps to the estimation of such offset for every aqueous composition. Those differences can be explained by a change in the direct environment of the luminescent specie. This is due to the fact that the addition of several different species and/or ions in a lanthanide-chelate solution adds non-radiative pathways for the desexcitation of the lanthanide center, thus lowering its quantum yield and so the final luminescence intensity.

These results show nevertheless that the presence of corrosion inhibitors as well as oil is not problematic for the detection as well for the quantification of the scale inhibitors. This method remains valid if the concentrations for these interfering chemicals (corrosion inhibitors, anti-foam) stay under a reasonable limit (100 ppm).

Coreflood inhibitor detection test

To check the detectability of the inhibitors after their injection into a rock medium, a coreflood experiment has been realized in a laboratory workbench test. The experiment is divided in two parts: (i) the injection of inhibitor solution by a squeeze-like method into the rock core and (ii) the detection of inhibitors by addition of terbium tracers and their analysis by time-resolved fluorescence.

Experimental Setup

We performed the permeation experiment only with one inhibitor (SPPCA) diluted in an aqueous solution at a fixed concentration of 100 ppm. The core used is constituted by consolidated sandstone with a porous volume of approximately 50 ml. The experiment has been performed at room temperature and consists in (i) an injection of $\frac{1}{4}$ of the porous volume of the inhibitor solution at 900 ml/h followed by (ii) the injection of $\frac{1}{2}$ porous volume of synthetic sea water (Table 1). The rock core is then flooded by synthetic

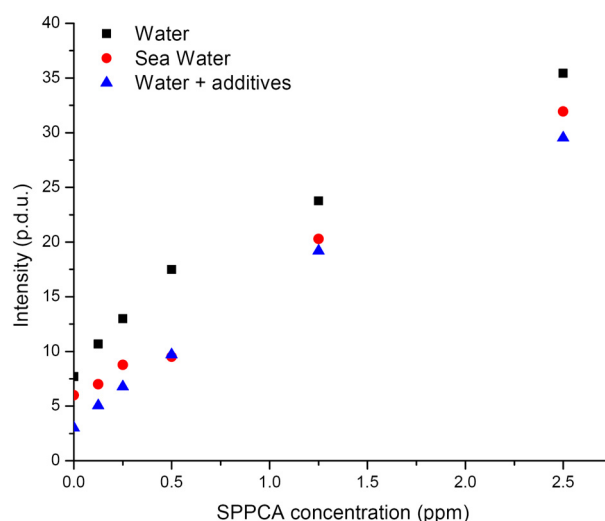


Figure 10—Intensity of the phosphorescence signal as a function of SPPCA concentration in water (black), sea water (red) and water containing three different corrosion and anti-foam inhibitors (blue).

seawater from reverse direction at 300 ml/h. 5 ml samples are regularly collected at the opposite part of injection till the accumulation of 50 porous volumes. Finally, 0.2 ml of each collected sample is then mixed with 1.8 ml of Tb-Light solution in a clean quartz cuvette and analyzed using a fluorospectrometer according to the prescribed technique.

Results

This experiment confirms the detectability of the inhibitors in rock-polluted waters and their passive interaction with the rock core. The tracer plot (Figure 11) follows the expected squeeze injections curves: after a quick increase of inhibitor signal detection till 250 ml, a drastic drop of signal followed by a steady low-concentration decrease confirm the squeeze behaviour of inhibitor. Such experience constitutes a proof of concept of fluorescence detection technique applied to coreflood assays; the fast time of signal acquisition as well the very low encumbrance of detectors allows the on-site analysis or even the online analysis with minimum adaptation.

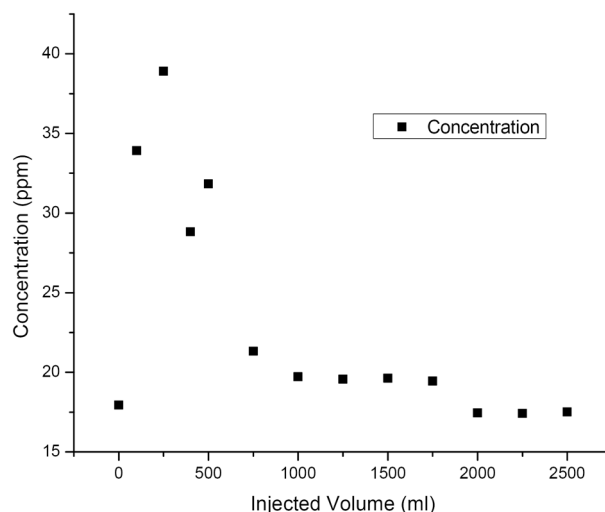


Figure 11—Perméation in a squeeze-like manner of an SPPCA solution, detection is realized with the method described in this paper

Conclusions

The residual scale inhibitor detection in oil waters has been successfully performed by time-resolved spectroscopy. Indeed, the post-addition of Tb-Light solutions to the tested sample chelates the lanthanide emitter and enhances its luminescence signal. Such signal is then collected by time-resolved spectrophotometer and leads to the quantification of the inhibitor amount per sample. The signal obtained is easily separated from the organic oil residuals background, improving the signal-to-noise ratio. We were able to quantify different inhibitors in a variety of production waters, even in presence of multiple pollutants. Moreover, a detection of inhibitor amount is also possible during simultaneous injections by studying the fluorescence decay rate signature. The final benchmark test on coreflood experiments demonstrates the high versatility of technique and the low quantification limit of inhibitors.

The easy and fast results given by the time-resolved technique opens the prospect of on-site and online quantification of inhibitors amount with some minimal adaptations depending on oil field site. Such procedure then constitutes a real breakthrough in the inhibitor concentration estimation, leading to a real-time monitoring that can improve the processes. If fouling can be controlled, there is potential to save energy, prevent equipment failure and reduce maintenance. Furthermore, a successful treatment strategy will maintain fluid flow, reduces corrosion effects and provides a safer environment. Finally, it will save money.

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