Abstract

Formation water sampling is important for characterizing hydrocarbon/water transition zones, understanding scaling and corrosion potential of the water, and determining compatibility between formation water and injection water. When sampling water with wireline formation testers at wells drilled with water-base muds (WBM), it is important to track mud filtrate contamination by distinguishing between formation water and mud filtrate in real time while sampling. Current techniques are mainly qualitative (e.g., resistivity sensors), use readings by stations (e.g., downhole pH measurements), or require colouring the mud (e.g., blue dye) and do not always allow a continuous quantitative monitoring.

We present a solution that allows continuous monitoring of the water sampling cleanup process as a way to better understand cleanup profiles. To achieve this goal, a fluorescent tracer was added to the mud system while drilling the zone of interest. By adding this tracer, we were able to continuously monitor the cleanup process by means of the downhole fluorescence sensor of a wireline formation tester (WFT) string. Prejob calibrations allowed us to interpret the fluorescence sensor’s reading, considering that the formation water is free of fluorescence response and that any response will indirectly indicate the presence of filtrate in the flowing fluid.

The fluorescent tracer was found appropriate to this task because it is detectable at very low concentration levels during qualification tests performed at surface conditions. Additionally, there were no detected tracer absorption issues in the reservoir affecting the process.

Field examples are presented of downhole fluid sampling operations in heterogeneous offshore carbonate systems, which are compared with laboratory results that confirm the success of this real-time monitoring solution. It also helps to improve best practices for selection of formation sampling stations and formation testers as function of the reservoir heterogeneity, wellbore drilling parameters, and formation testers’ capabilities.

Introduction

Analysis of formation water can provide crucial input to analyses during every stage in the life of a reservoir (Abdou et al. 2011). It provides information about the scaling and corrosion potential of the water, establishes the salinity of the water for petrophysical evaluation, and helps evaluate reservoir connectivity. It is a critical input to field development planning and economics.

Representative downhole water samples of the formation of interest should be free of any contamination by drilling fluids. Water-sample quality depends strongly on drilling-fluid type and on sampling technique and monitoring. Oil-base mud (OBM) usually allows acquisition of good water samples because the mud filtrate, being immiscible with water, does not contaminate the sample of formation water (Schroer et al. 2000). In contrast, water-base mud (WBM) is miscible with formation water, causing chemical reactions and mixing that can contaminate formation-water samples. For example, a WBM containing sulfates in contact with a formation water containing barium could cause precipitation of barium from the water sample. Analysis of the resulting water sample would underestimate barium content and thus underestimate scaling potential of the formation water (Raghuraman, O’Keefe et al. 2005). Good water-sampling techniques must allow for precise monitoring and control of the presence of WBM or water from the drilling fluid.

Reservoir water samples are usually collected with a wireline formation tester, comprising a probe or packer module, pumpout module, fluid analyzer and sample-collection chambers. Fluids are drawn from the reservoir into a flowline in the device, in which resistivity and optical properties are measured. Early in the sampling process, fluid content is dominated by...
drilling-mud filtrate. With continued flow, contamination by drilling fluids decreases. Traditionally, the real-time monitoring is performed using a resistivity sensor in a qualitative way and optical fluid analyzers in a quantitative way if a color tracer is used in the WBM to detect when the formation fluid is free of mud contamination. During this cleanup phase, the contaminated fluids are discharged into the borehole through the exit port. Formation fluid is collected in the sample chambers only after meeting stipulated criteria (asymptotic and constant resistivity or absence of color tracer in the sampling fluid), thus ensuring sample quality.

In the case of WBM environments, real-time contamination monitoring can be performed by measuring resistivity. This works well if there is a sufficient resistivity contrast between the WBM filtrate and formation water, but it is usually a qualitative process. Tracers are sometimes added to drilling fluids to allow calculation of the residual filtrate contamination in collected samples by subsequent laboratory analysis.

Another real-time technique developed to track WBM contamination of formation water samples is adding a water-soluble colored tracer dye to the water-base drilling fluid and employing a downhole spectrometer to monitor the cleanup from blue filtrate to colorless formation water using algorithms similar to those employed in OBM contamination monitoring (Hodder et al. 2004). By knowing the tracer dye concentration in the WBM, and monitoring the optical density (OD) on the appropriate color channels of the optical fluid analyzer in the formation tester, it is possible to determine when the level of contamination in the flowline fluid is low enough for good quality water samples to be collected.

A more recent development for monitoring water sampling in real-time is pH measurement of formation water at reservoir conditions (Raghuraman, Xian et al. 2005; Carnegie et al. 2005). The downhole pH measurement technique injects pulses of pH-sensitive dyes into the flowline of a wireline formation tester while the formation sample is flowing. These pH-sensitive dyes are different from the originally pH-insensitive tracer dye that is added directly to WBM to track contamination. The pH-sensitive dyes change color according to the pH of the fluid in the flowline. The color change is detected at the appropriate wavelengths by an optical fluid analyzer. The pH of WBM filtrates is typically much higher (7 to 10 units) than that of formation waters (5 to 6.5 units); hence, pH can be used to differentiate between the two. The variation in pH with sampling time broadly follows the trend of the resistivity sensor and can be used for contamination monitoring in OBM and WBM environments. It should be considered that water samples acquired downhole at high-pressure and high-temperature conditions usually do not retain their original pH when brought to surface. The associated temperature and pressure reductions cause acid gases, such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S), to evolve out of solution, increasing pH. Solids precipitate, also changing pH. Changes in temperature alter equilibrium constants, further modifying pH from its original downhole value. These changes are not always fully reversible when the water sample is reconditioned to downhole conditions in the laboratory, and they can introduce uncertainties when analysis of surface water and gas is used to calculate downhole pH. Hence, to obtain an accurate, robust pH value, it must be measured downhole (Raghuraman, Xian et al. 2005). In this sense, pH is a key parameter in water chemistry and plays a governing role in corrosion and scale properties; it supports real-time monitoring of water sampling in a qualitative way, as do the resistivity sensors, but pH is less affected by noise due to solids, flow rate, or temperature changes in the fluid stream.

Considering some of the limitations already mentioned in the existing water contamination monitoring techniques such as cases with small resistivity contrast between the WBM filtrate and formation waters, qualitative interpretation of the resistivity and pH sensors measurements, and limitations of the color dye tracers (cost and limited availability, scattering in the absorption channels from particulates in the flow line compromising the process, just as emulsions do in OBM), a solution was implemented that allows continuous monitoring of the water sampling cleanup process as a way to better understand cleanup profiles without altering the normal mud appearance or altering the formation characteristics. To achieve this goal, a fluorescent tracer was added to the mud system while drilling the zone of interest. By adding this tracer, we were able to continuously monitor the cleanup process by means of the downhole fluorescence sensor of a wireline formation tester (WFT) string. Prejob calibrations allowed us to interpret the fluorescence sensor’s reading, considering that the formation water is free of fluorescence response and that any response will indirectly indicate the presence of filtrate in the flowing fluid. The fluorescent dye was found appropriate to this task because it is detectable at very low concentration levels during qualification tests performed at surface conditions. Additionally, there were no detected tracer absorption issues in the reservoir affecting the process.

Reservoir water samples usually are collected openhole using a wireline formation tester and then analyzed in surface laboratories. This approach has limitations because water properties change as the sample is brought to surface. Acid gases and salts come out of solution, altering water-chemistry equilibria. Rigorous formation water analysis should consider this phenomenon and account for water properties analysis at downhole conditions.

In this paper, we first explore the factors that affect the fluorescent dye values of mixtures when two different waters are combined. Next, we study fluorescent dye sensitivity to contamination in carbonate reservoirs and WBM filtrate environments. Finally, we present the successful results from recent field tests in which these concepts have been applied.

**Theory on Downhole Fluid Analysis Measurements**

**Optical measurements.** Visible-to-near-infrared (VIS/NIR) spectroscopic measurements are widely used today as the primary method to investigate reservoir fluids under downhole conditions by a wireline formation tester. In-situ fluid analysis, which began as a means to assure quality control during fluid sampling, has evolved into a key technique for characterizing the distribution of reservoir fluid properties and for determining zonal connectivity across a reservoir.
Vis/NIR spectroscopic measurements coupled with reflection and fluorescence measurement have evolved to the degree that it is possible to measure oil/water/gas fraction; to assess oil-based mud contamination quantification; to measure gas-to-oil ratio (GOR), hydrocarbon composition (C1, C2, C3-C5, C6+), and carbon dioxide (CO2); and to provide a fluorescence measurement and a pH measurement (Schroer et al. 2000; Hodder et al. 2004; Carnegie et al. 2005; Raghu raman, O’Keefe et al. 2005; Raghu raman, Xian et al. 2005; Abdou et al. 2011).

**Fluorescence measurements.** Fluorescence data can provide insight into the dynamics of various processes after the deposition of electronic excitation energy (Turro 1978). In addition to contributing to fundamental understanding, fluorescence methods are useful in diverse applications, such as those involving crude oils (Tissot and Welte 1984). For instance, in the petroleum industry, fluorescence is routinely employed during drilling as an indicator of the presence of crude oil (DeLaune 1992). For some natural materials related to crude oils, high fluorophore concentrations produced spectral red shifts and intensity reduction of fluorescence (Durand 1980). These observations are used to help gauge the evolution of these natural materials. Recently, fluorescence lifetimes of several crude oils have been measured to evaluate molecular size and weight of asphaltene and asphaltene solubility fractions (Mullins, 2005; Badre et al. 2006).

**Fluorescence in WBM Contamination Measurements.** An alternative approach for WBM contamination measurement is to use a fluorescent dye and a downhole fluorescence detection sensor. The authors wish to stress the monitoring of this measurement at downhole conditions in real time. At the time of writing this article and to the best knowledge, all work around this topic has been done at surface conditions. Recently, fluid contamination in rock core and brine samples intended for microbiological monitoring at a CO2 storage site was performed using fluorescent dye tracers, however samples contamination analysis was performed only at the lab (Wandrey et al. 2009).

For the present case a fluorescent dye was found appropriate for the sample contamination analysis because it is detectable at very low concentration levels (to ~ 1 ppm), during qualification tests, is insensitive to pH and has a fluorescence emission peak at the correct energy for the proper downhole detection. Additionally, there were no detected tracer absorption issues in the reservoir affecting the process. Another advantage is that the fluorescent dye has a high quantum yield and is fairly valued and readily available. The downhole fluorescence detection sensor employs a geometry in which the depth of investigation is short so the measurement is less affected by scattering.

**Fig. 1** shows a simplified scheme of the downhole fluorescence detector. It has one excitation light, one reflection measurement channel, and two fluorescence detection channels. Fluorescent material as crude oil or substances containing fluorophores absorbs the excitation light energy and then emits the fluorescence light. The fluorescence light from the fluorophores can be detected with two detection channels. As only the crude oil or fluorophore substances give us a fluorescence light, and WBM / SBM filtrates emit little or no fluorescence, a fluorescence detector should be good to discriminate crude oil from SBM filtrate and formation water from WBM filtrate with fluorophores tracers. It has been already presented for the case of crude oils in the literature (Mullins 2005; Badre et al. 2006) and is reported for the first time in the case of WBM filtrate in this article.

**Laboratory Tests**

**Fig. 2(a)** shows laboratory tests of water samples with the selected fluorescent tracer illuminated by visible light and **Fig. 2(b)** shows the tests with UV light (right). With the UV illumination, fluorescence is observed (strong green color).

**Fig. 3** shows the laboratory tests with a wireline downhole fluorescence sensor performed at surface conditions using water samples from one of the studied formations, fresh and industrial water, and the typical WBM filtrate in the studied area, with the addition of the selected fluorescent tracer. The light green color emission of the fluorescence light in the WBM filtrate containing fluorophores tracers is clear.

**Fig. 4** shows the fluorescent tracer concentration versus the detected fluorescence signal using a wireline downhole fluorescence sensor which has a 470-nm excitation source in combination with a 550-nm long pass filter that allows picking up fractions of the total fluorescent emission with accuracy. A linear fit of the primary absorption peak at 550 nm with R2 values at 98% is observed. The tested fluorescent tracer has a high quantum yield that is detectable at low concentration levels (to ~ 1 ppm). However, the tests suggest that for field implementation the concentration should be between 40 and 100 ppm in the WBM filtrate.

**Field Tests**

After the laboratory tests, field jobs were performed, and the results from two field cases are presented in the following paragraphs. **Table 1** summarizes the fluid sample contamination results from the real-time analysis using fluorescence readings and the later laboratory analysis.

**Case 1**

For the selected well, the target formation was drilled with the fluorescent tracer at doses of 70 ppm in the WBM drilling fluid. Mud and filtrate samples were collected from the fluid stream going into and out of the wellbore every 50 m drilled to count with a detailed fluid database for further analysis and evaluation.

Additionally, WBM filtrate samples were prepared at different fluorescent tracer dilutions to confirm the downhole fluid
sensor response before running the tool in the wellbore. The calibration plot is presented in Fig. 5 and is the base for the real-time WBM filtrate contamination monitoring.

Fig. 6 (a, b) shows the two formation water sampling stations performed for Case 1. The locations of the wireline formation tester probe are presented together with the gamma ray (GR) and nuclear magnetic resonance (NMR) permeability indicator logs, and the real-time contamination monitoring results are shown in Fig. 6 (c, d). Fig. 7 (a, b) presents the real-time monitoring of the pumpout parameters (e.g., flow rate) with the continuous fluid resistivity and fluorescence readings from the downhole fluid analyzer sensors. Although the fluid resistivity profile is clean and reflects the cleanout process, the fluorescence readings present a better sensitivity profile and allow direct contamination quantification, as presented in Fig. 7 (c, d). Additionally, Fig. 8 (a, b) presents the downhole sensor fluorescence response together with the optical density fluid identification. As expected, the visible spectrum response for the water filtrate is not affected by the fluorescence tracer. The computed contamination results for Case 1 using the fluorescence data that are shown in Fig. 8 (c, d) agree well with the laboratory analysis as indicated in Table 1.

Besides the fluid sampling monitoring and contamination evaluation in real time, this experience helps to optimize the station selection for downhole formation fluid sampling using formation testers considering the reservoir heterogeneity, wellbore drilling parameters, and formation testers’ capabilities. In the present case, it was seen that stations at the bottom of the formation layer, mainly if thick packages were tested, were detrimental for the operation time because of the high degree of segregation of the drilling fluid filtrate inside the formation. This finding enriches the existing best practices for the studied area.

Case 2

For the selected well, the target formation was drilled with the fluorescent tracer at doses less than 10 ppm in the WBM drilling fluid.

Fig. 9 (a) shows the pumpout parameters including flow rate, pressure, temperature, resistivity, and fluorescence response for the fluid sampling station in this well section. In this case, it is observed the marked noise response of the downhole fluid resistivity sensor does not allow for clear fluid-cleanout monitoring, while the fluorescence response presents a cleaner response for the analysis. Fig. 9 (b) shows the contamination monitoring results obtained using the fluorescence response.

Fig. 10 shows that in spite of the low concentration of fluorescent tracer used in this case (less than 10 ppm), it is still possible to monitor the fluid cleanout process considering the high resolution of the available downhole fluid analyzers to monitor the fluorescence response. Fig. 10 also presents the contamination monitoring results using the fluid fluorescence response. Results agree reasonably well with the laboratory analysis as indicated in Table 1. However, for better accuracy, comparable to Case 1 (see Table 1), we suggest using fluorescent concentrations between 40 and 100 ppm in the WBM filtrate.

Conclusions

Field examples presented here clearly show the potential of fluorescence tracers as a real-time openhole logging measurement to characterize water sample contamination at downhole conditions in real time. The ability of the tracer monitoring to differentiate in real time between WBM filtrate and formation water helped to collect better formation fluid samples to optimize the reservoir characterization and the selection of formation sampling stations and formation testers as a function of the reservoir heterogeneity, wellbore drilling parameters, and formation testers’ capabilities. This is of immense value in reserves estimation as well as in planning reservoir development strategies. Furthermore, the ability to use downhole tracer data to differentiate between the formation water and filtrate or injection water will allow identification of fluid breakthrough once these reservoirs are placed on development. This can have a huge impact on optimizing completion and production strategies and for effective water management if performed early in the process and in openhole scenarios.

Field examples presented here show that to reduce the error bar in the contamination analysis based on the studied fluorescent tracer, it is better to use concentrations between 40 and 100 ppm.

In heterogeneous carbonate zones, conventional formation evaluation measurements such as openhole pressure and resistivity logs often fail to predict formation fluid types and the location of the oil/water contact because of large uncertainties associated with factors such as supercharging, capillary effects, complex and heterogeneous pore structures, wettability variations, and shoulder-bed effects. Downhole fluid analysis, which now includes the newly developed downhole fluorescence and pH measurements, offers a robust alternative for real-time formation evaluation and provides critical input for production planning and reservoir management.

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References


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**TABLE 1**—COMPARISON BETWEEN CONTAMINATION CALCULATED BY FLUORESCENCE COMPUTATION IN REAL TIME AND THE LABORATORY ANALYSIS FOR SAMPLES IN FIELD CASES

<table>
<thead>
<tr>
<th>Field Case</th>
<th>Station</th>
<th>Contamination, %</th>
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<td>Real Time Analysis</td>
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**Fig. 1**—Downhole fluorescence detector scheme.
Fig. 2—(a) Water and base oil samples illuminated by visible light and (b) UV light. With the UV illumination, fluorescence is observed in the water phase containing the fluorescent tracer (green color).

Fig. 3—Samples of water without and with fluorescent tracer under UV illumination. Fluorescence is observed (light green color).

Fig. 4—Fluorescent tracer concentration versus detected fluorescence signal showing a linear fit of primary absorption peak at 550 nm with R2 values at 98%.
Fig. 5—Fluorescent tracer concentrations versus detected fluorescence signal for Case 1 (FLDO: Fluorescence Reading).

Fig. 6—Stations 1 and 2 for Case 1. (a, b), locations of the formation tester probe and GR and NMR logs. (c,d) real-time contamination monitoring results using the fluid fluorescence response (DDM: station drawdown mobility).
Fig. 7—Stations 1 and 2 for Case 1. (a,b) Pumpout parameters including flow rate, temperature, resistivity, and fluorescence response. (c, d) Bottom, contamination monitoring results using the fluid fluorescence response.

Fig. 8—Stations 1 and 2 for Case 1. (a, b) Downhole sensor fluorescence response and optical density fluid identification. (c, d) Contamination monitoring results using the fluid fluorescence response (FLDR: Fluorescence Ratio)
Fig. 9—Station for Case 2. (a) pumpout parameters including flow rate, pressure, temperature, resistivity, and fluorescence response. (b) the contamination monitoring results using the fluid fluorescence response.

Fig. 10—Station for Case 2. Downhole sensor fluorescence response and optical density fluid identification.