



Proceeding Paper Fluorescent Based Tracers for Oil and Gas Downhole Applications: Between Conventional and Innovative Approaches[†]

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Abstract: Tracers are specific materials widely used in the modern oil and gas industry for reservoir characterization via single-well or inter-well tracer tests. We engineered new tracers and extended tracer test applications for on-site real-time well-drilling monitoring. Robust and cost-efficient fluorophores embedded into carrier matrices were developed to label drill cuttings as they were made at the drill bit face to improve drill-cutting depth correlation. These novel tracers allow for automated detection at concentrations up to the ppt level. Thus, the innovated tracers open the horizon to detect in real-time the drilling depth to enhance well placement and hydrocarbon recovery.

Keywords: fluorescent tracers; drill cuttings labelling; reservoir management; drilling depth correlation

1. Introduction

In the oil and gas industry, tracers are used as a monitoring and surveillance tool to obtain the information about the reservoir along with other methods, such as monitoring of production rate of reservoir fluids, 4D seismic, pressure tests, and others [1]. The tracer could be defined as an infinitesimal and identifiable part of a mass that is introduced or naturally present and can be used to keep track of this mass.

Current industrially used tracers are isotopes, dyes, chemical tracers, microelements, ions, and gases including noble gases. Tracers are commonly applied for three major types of oilfield tests–these are nonpartitioning and partitioning inter-well tracer tests and the single-well tracer test [2] (Figure 1).



Figure 1. Types of oilfield tracer tests.

2. Fluorescent Tracers

2.1. Fluorescent Dyes

Ease of sensing of fluorescent compounds is the major advantage of fluorescent dyetracers that sometimes can be performed even visually [3]. The additional interest in



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fluorescent tracers is due to the quantitative detection of fluorescent compounds being up to 10^4 times lower than for nonfluorescent chemicals. Moreover, fluorescent tracers are relatively inexpensive, readily available at the commercial scale, relatively nontoxic at low concentrations, and able to be monitored and quantified via simple, portative, and cost-efficient analytical techniques that include spectrofluorimetry, UV–Vis spectroscopy, and digital color analysis. Most well-known fluorescent molecules commonly tested in oilfield applications include fluorescein/uranine [3–6], rhodamine [1,4,7], eosin [8], and polyaromatic sulfonic acids (Table 1).

Tracer, (Emission Wavelength in Water, nm)	Structure	Method & Detection Limit, (µg/L)	Sorptivity
Uranine, Fluorescein (520 nm) [9]	NaO O O	HPLC/FLD (0.03 μg/L); HPLC/LIF (40 fg/mL) [1]; colorimetry (mg/mL level) [6]; UV (0.1–10 mg/mL) [1]	Very low
Eosin Y (545 nm) [10]	Br NaO Br Br Br Br Br	Solid phase spectrophotometry (1.20 mg/L) [11]; digital color analysis (DCA) (1.32 mg/L) [11]	Low
Rhodamine B (625 nm) [10]		Solid phase spectrophotometry (0.06 mg/L) [11]; DCA (0.6 mg/L) [11]	Strong
Rhodamine WT 555 nm [10]	O ONa O ONa O ONa O CI V O V	visual/UV < 100 ppb [12]	Low-Medium
Sodium Naphthionate (420 nm) [13]	$ \begin{array}{c} $	HPLC/FLD (pg/mL level) [14]	Low
Sodium naphthalene-2,7-disulfonate (2,7-NdSA)(339 nm) [15]	NaO, II O ^S S VIII S O	HPLC/FLD-200 pg/mL [1,15]	Low
4,4'-Biphenyl disulfonic acid sodium salt		HPLC/FLD (10–100 pg/mL) [1] HPLC/FLD (with preconcentration) < 10 µg/m ³ (ppt)	Very Low

Table 1. Fluorescent dyes in oilfield applications and their properties.

Fluorescein is stable in regular downhole conditions and has low adsorption on formation rock [8,15]. This tracer has been successfully used in carbonate reservoirs with 82.1% recovery [16]. It should be noted that laboratory tests show that fluorescein could be applied in geothermal reservoirs with temperatures below 210 °C; however, this tracer quickly degrades above 260 °C and is unstable at 200 °C in the presence of oxygen [9].

Other xanthene dye tracers possess lower thermal stability. Thus, Rhodamine B is stable up to 195 °C in inert atmosphere and thermally degrades over 496 K [17]. Application of Rhodamine WT was reported to be limited only to low-temperature geothermal fields [15].

Moreover, some xanthene dyes can exhibit nonideal behavior due to adsorption on reservoir solids and demonstrate essential retention in breakthrough times. Such performance could be accepted only for qualitative tests, which is why these tracers' application is currently limited to fractured wells with quick reverse fluid flow (up to five days) [1]. Most xanthene dyes do not possess sufficient thermal stability for application in geothermal reservoirs [15]. To overcome thermal degradation of tracers, a new class of fluorescent organic derivatives was proposed for high-temperature reservoirs that consists of polycyclic aromatic sulfonic acid salts.

Naphthalene sulfonic acid (NSA), naphthalene disulfonic acids (NdSA), and naphthalene tri-sulfonic acids (NtSA)) were suggested as novel conservative water tracers [5] for geothermal applications. Among them, unsubstituted NSAs were the most promising tracers based on their thermal stability (up to 300 °C) and good detectability. NSA, NdSA, and NtSA were successfully tested in lab and in field geothermal applications [8,14,18–20]. These compounds possess the highest thermally stability (up to 330 °C) and are resistant to adsorption to negatively charged rock in geothermal reservoirs due to the tracers' strong electronegative charge. Of those tested, 2,7-NdSA and 2-NSA were the most stable polyaromatic sulfonic acids [1]. NSAs substituted with hydroxyl and amino groups were also successfully tested up to 250 °C; however, their thermal stability was lower than the one of nonsubstituted NSA. Biphenyl-, p-terphenyl-, and fluorenesulfonic acids demonstrated no overlap in fluorescent emission spectra with oil-based naphthalene contaminants and thus were easily detectable [14]. Among them, 4,4'-biphenyl-disulfonic acid possessed thermal stability similar to NSA and demonstrated very low adsorption to rock (tested at 195 °C over 60 days); although, other terphenyl and fluorene sulfonates were less thermally stable.

2.2. Fluorescent Quantum Dots

A new nontoxic tracing technology was recently developed possessing a unique spectral signature of tags, which could be detected at extremely a low detection limit and were suitable for subsurface high-pressure high-temperature (HP/HT) applications [21]. Carbon quantum dots are nontoxic, water-soluble, and resistant to photobleaching. The optical and fluorescence spectral properties of quantum dots are unique and visible to naked eyes under UV light at concentrations of 1 ppm. The detection of more dilute solutions can be performed with portable lab kits [22]. These tracers remain stable at downhole conditions at temperatures up to 300 $^{\circ}$ C; it does not absorb to or damage the reservoir formation and does not have a negative impact on the environment.

Kanj [23,24] described industrial applications of carbon-based nanoparticles (A-Dots) as oil field inter-well tracers. Designed for harsh HP/HT conditions, these tracers were examined to withstand temperatures over 100 °C, high salinity over 150,000 ppm in total dissolved solids, and 3200 psi pore pressure. A-Dots' detection limit is below the single-digit ppm level with fluorescent emission at 460 nm.

3. Innovative Fluorescent Tracers for Near-Real-Time Drilling Depth Monitoring

Directional horizontal drilling complicates the removal of rock debris from the borehole with circulation of the drilling mud. It increases uncertainties in lithology surveying and disturbs geosteering works. Unlike tracers and the test methods summarized above that were applied for surveying existing wells, we proposed to develop novel testing technology with the objective of monitoring drilling progress and labelling drill cuttings as they are made at the drill bit face. It is important to mention that the first tags developed for drill cutting labelling [25] were designed for laboratory GC–MS detection. In our case, the injection of fluorescent tracers for drill cutting labelling as they are formed at the drill bit site combined with near-well-head charge-coupled device (CCD) camera detection and image recognition system would allow for cuttings' identification according to the depth and real-time on-site drilling depth monitoring.

3.1. Preparation and Stability Examination of Tracers for Drill Cutting Labelling

Aiming to obtain visibly detectable fluorescent tags, we performed impregnation of a few types of matrices with a number of advanced fluorophores to yield up to mm-sized fluorescent assemblies. These assemblies were made to be injected into the well with drilling mud to tag formation cuttings upon breakage of the matrix-carrier (or capsule) by a drill bit.

Various matrices were studied for the trial loading of/modification with fluorophores, including silica, ceramics, poly(vinyl alcohol), chitosan, and superabsorbent polymer (SAP) based on sodium salt of poly(methyl acrylate). Selected matrices (silica, ceramics, and polyacrylate SAP) were soaked with an aqueous solution of dyes (fluorescein, rhodamine B, and commercial pigments) followed by drying in a vacuum oven. Poly(vinyl alcohol) was modified with fluorescein isothiocyanate (FITC) according to published procedure [26]. Chitosan was cross-linked with glutaraldehyde in the presence of commercial fluorescent pigments and subsequently lyophilized to yield a dry fluorescent network.

Obtained materials were tested for stability to conditions mimicking downhole media. Thus, samples of fluorescent-loaded tags were incubated at 90 °C with aqueous brines containing formation salts NaCl, CaCl₂, MgCl₂, Na₂SO₄, and NaHCO₃ for a period between one day and one week. Degradation via hydrolysis was noted for fluorescent-modified poly(vinyl alcohol) upon exposure to electrolyte solutions over a few hours. Cross-linked chitosan, bearing incorporated pigment, showed a slight decrease in fluorescent intensity upon treatment with electrolytes over one day. Moreover, the chitosan cross-linked matrices were destroyed at acidic media, limiting their possible use in downhole conditions. Fluorescein and fluorescent-pigment-loaded silica (Flu-SiO₂) as well as xantene-dye-loaded superabsorbent polymer (Flu-SAP) exhibited no visible decomposition and demonstrated almost no leakage of dye at the described conditions. Consequently, these stable matrices (Flu-SiO₂ and Flu-SAP) were further tested for resistance to organic solvents (THF, ether, and diesel). Among the materials tested for exposure to organic media, fluorescein-and rhodamine-loaded SAPs, fluorescein and pigment-loaded SiO₂ exhibited no visible deterioration of the fluorescent properties.

3.2. FT-IR Spectroscopy Characterization of Tracers

SAP-based matrices loaded with xanthene dye were further characterized by ATR-FTIR spectroscopy. The appearance of the additional absorbance signal around 1750 cm⁻¹ related to the stretching vibration of the carbonyl group of xanthene-dye-loaded SAP compared to blank SAP matrix confirms the entrapment of fluorophores inside the net of superabsorbent polymer. The quite low intensity of this absorbance signal is due to the loading of a small quantity of fluorophore into the SAP matrix that resulted in good enough to reach high-fluorescence intensity detectable by the naked eye and camera. An increase in the loading of dye into the polymer resulted in fluorescence quenching and a perceptible decay of emission up to its total loss. Thus, the engineering of fluorescent-loaded tags based on the polymer entrapment of emitting dyes resulted in an efficient fluorescence assembly with minimal loading of emitter.

3.3. Fluorescence Characterization of Tracers for Automated Detection

The most stable of the obtained fluorescence-loaded tags were characterized by spectrofluorimetry. Pre-concentration of the emitting molecules within the tags' matrices allowed for enhanced fluorescent intensity of the prepared tracers and resulted in the possibility of their visual detection. The tags' fluorescent emission was noticeably more intense compared to the background fluorescence. In some cases, the interaction of polymer-matrix carriers with a molecule of fluorophore resulted in a bathochromic shift of fluorescence emission wavelengths, as was noted for fluorescein-loaded SAPs. Prepared fluorescent loaded tags were aimed for further downhole drill-cutting labeling tests followed by near-well-head camera detection.

4. Conclusions

In this work, we innovated a new concept of downhole fluorescent drill-cutting tracing engineered for on-site near-real-time detection with a camera and image-recognition system. Fluorescence-loaded tags were made to be injected into the well with drilling mud to tag formation cuttings according to the depth upon breakage over formation by a drill bit. Fast and simple drill-cutting depth determination would improve accuracy in drilling depth correlation and advance the petrophysical characterization of a formation to allow for optimal well placement.

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