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 interwell 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 are made at drill bit face to improve drill cuttings depth correlation. These novel tracers allow for automated detection at concentrations up to ppt level. Thus, 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 for 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 non-partitioning and partitioning interwell tracer tests and the single well tracer test [2] (Figure 1).
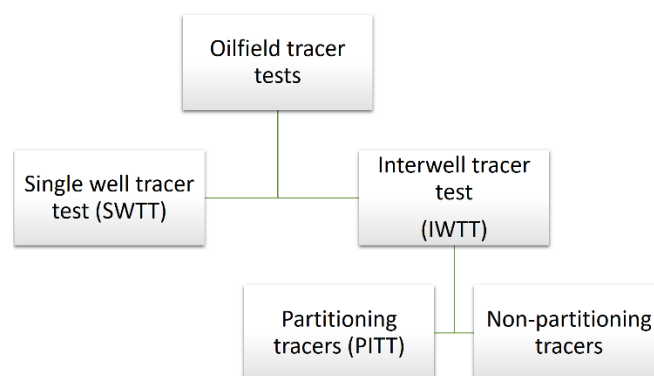

Figure 1. Types of oilfield tracer tests.
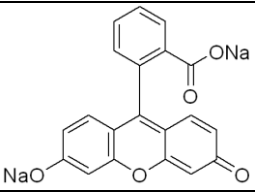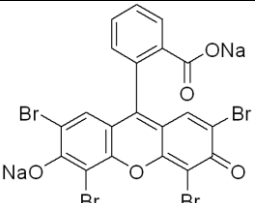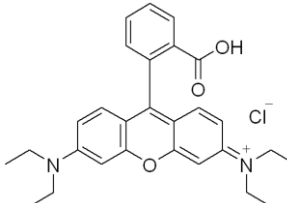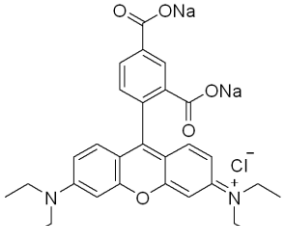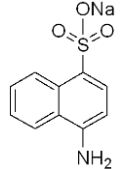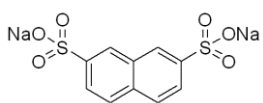
2. Fluorescent Tracers

2.1. Fluorescent dyes

Ease of sensing of fluorescent compounds is the major advantage of fluorescent dye tracers that sometimes can be performed even visually [3]. The additional interest in fluorescent tracers is paid due to the quantitative detection of fluorescent compounds is up to 10^4 times lower than for non-fluorescent chemicals. Moreover, fluorescent tracers are relatively inexpensive, readily available in commercial scale, relatively non-toxic at low concentrations, and their monitoring and quantification can be performed 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).

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

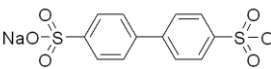| Tracer, (Emission wavelength in water, nm)	Structure	Method & Detection Limit, (µg/L)	Sorptivity
Uranine, Na-fluorescein (520 nm)[9]		-HPLC/FLD (0.03 µg/L) -HPLC/LIF– 40 fg/mL colorimetry (mg/mL level)[10] UV (fluorescein detected at 0.1–10 mg/mL)[11]	Very low
ent Eosin Y (543 nm) 525 nm[12]		0.01 Solid phase extraction spectrophotometry – 1.20 mg/L 0.02[13] digital color analysis (DCA) – 1.32 mg/L[13]	Low
Rhodamine B 540 nm 625 nm[12,13]		0.006 Solid phase extraction spectrophotometry - 0.06 mg/L[13] digital color analysis (DCA) – 0.6 mg/L [13]	Strong
Rhodamine WT 580 nm[12]		0.006 visual/UV < 100ppb]	Low-Medium
Sodium Naphthionate (420 nm) [14]		0.01 present a better detectability (pg/mL level) by fluorimetry than NSA [15]	Low
Sodium naphthalene-2,7-disulfonate (2,7-NdSA)		HPLC/FLD - 200 pg/mL [11,16]	Low

(339 nm)[16]		
4,4'-Biphenyl di-sulfonic acid so-dium salt	HPLC/FLD (10–100 pg/mL) [11] HPLC-FLD (with preconcentra-tion) < 10 μg/m3 (ppt)	Very Low

Fluorescein is stable in regular downhole conditions and have low adsorption on formation rock [8,16]. This tracer has been successfully used in a carbonate reservoirs with 82.1% recovery [17]. It should be noted, that laboratory tests showed that fluorescein could be applied in geothermal reservoirs with temperatures below 210 °C, however, this tracer quickly degrade above 260 °C and is unstable at 200 °C in the presence of oxygen [18].

Other xanthene dye tracers possess lower thermal stability. Thus, Rhodamine B is stable up to 195 °C in inert atmosphere and thermally degrade over 496 K [19]. Application of Rhodamine WT was reported to be limited only to low-temperature geothermal fields [16].

Moreover, some xanthene dyes can exhibit non-ideal behavior due to adsorption on reservoir solids and demonstrate essential retention in breakthrough times. Such performance could be accepted only for qualitative tests, that is why currently, these tracers' application is limited to fractured wells with quick reverse fluid flow (up to 5 days) [1]. Most of xanthene dyes do not possess sufficient thermal stability for application in geothermal reservoirs [16]. To overcome thermal degradation of tracers, 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, un-substituted 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 the lab and in the field geothermal applications [8,15,20–22]. These compounds possess highest thermally stability (up to 330 °C) and are resistant to adsorption to negatively charged rock in geothermal reservoirs due to tracers' strong electronegative charge. 2,7-NdSA and 2-NSA are the most stable polyaromatic sulfonic acid tested [1]. NSAs substituted with hydroxy- and amino groups were also successfully tested up to 250 °C, however, their thermal stability is lower than the one of non-substituted NSA. Biphenyl-, p-terphenyl-, and fluorenesulfonic acids demonstrated no overlap in fluorescent emission spectra with oil-based naphthalene contaminants and thus were easily detectable [15]. Among them, 4,4'-biphenyl-disulfonic acid possess thermal stability same as NSA and demonstrated very low adsorption to the rock (tested at 195 °C over 60 days), although others - terphenyl- and fluorene sulfonates were less thermally stable.

2.2. Fluorescent quantum dots

The new non-toxic tracing technology was recently developed possessing unique spectral signatures of tags, which can be detected at extremely low detection limit and are suitable for subsurface high-pressure high temperature (HP/HT) applications [23]. Carbon quantum dots are non-toxic, water-soluble, and resistant to photobleaching. Optical and fluorescence spectral properties of quantum dots are unique and visible for naked eyes under UV light at concentrations of 1 ppm. Detection of more diluted solutions can be performed with portable lab kits [24]. These tracers remain stable at the downhole conditions at temperatures up to 300 °C; it does not absorb to or damage the reservoir formation, does not have a negative impact on the environment.

Kanj [25,26] described industrial applications of carbon-based nanoparticles (A-Dots) as oil field interwell tracers. Designed for harsh HP/HT conditions, these tracers at exam-

ined to withstand temperatures over 100 °C at high salinity over 150,000 ppm in total dissolved solids and 3,200 psi pore pressure. A-Dots' detection limit is below 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 removal of rock debris from the borehole with circulation of the drilling mud. It increases uncertainties of lithology surveying and disturbs geosteering works. Unlike tracers and test methods summarized above applied for an existing wells 'survey, we proposed to develop novel testing technology with the objective to monitor drilling progress and label drill cuttings as they are made at the drill bit face. It worse to mention that first tags developed for drill cuttings labelling [27] were designed for laboratory GCMS detection. In our case, injection of fluorescent tracers for drill cuttings 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 cuttings labelling

Aiming to obtain visibly detectable fluorescent tags, we performed impregnation of few types of matrices with number of advanced fluorophores to yield up to mm-sized fluorescent assemblies. These assemblies are 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 aqueous solution of dyes (fluorescein, rhodamine B, commercial pigments) followed by drying at the vacuum oven. Poly(vinyl alcohol) was modified with fluorescein isothiocyanate (FITC) according to the published procedure [28]. Chitosan was cross-linked with glutaraldehyde in presence of commercial fluorescent pigments and subsequently lyophilized to yield dry fluorescent network.

Obtained materials were tested for stability to the conditions mimicking downhole media. Thus, samples of fluorescent loaded tags were incubated at 90 °C with aqueous brines containing formation salts NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, $NaHCO_3$ for period of 1 day up to 1 week. Degradation via hydrolysis was noted for fluorescent-modified poly(vinyl alcohol) upon exposure to electrolyte solutions over few hours. Cross-linked chitosan bearing incorporated pigment showed slight decrease in fluorescent intensity upon treatment with electrolytes over one day. Moreover, the chitosan cross-linked matrices were destroy at acidic media that limits their possible use in downhole conditions. Fluorescein and fluorescent pigments-loaded silica (Flu-SiO_2) as well as xanthene dyes-loaded superabsorbing polymer (Flu-SAP) exhibited no visible decomposition and demonstrated almost no leakage of dyes at the described conditions. Consequently, these stable matrices (Flu-SiO_2, Flu-SAP) were further tested for resistance to organic solvents (THF, ether, diesel). Among materials tested for the exposure to organic media, fluorescein- and rhodamine-loaded SAPs, fluorescein and pigments-loaded SiO_2 exhibited no visible deterioration of the fluorescent properties.

3.2. FT-IR spectroscopy characterization of tracers

SAP-based matrices loaded with xanthene dyes were further characterized by ATR-FTIR spectroscopy. Appearance of the additional absorbance signal around 1750 cm^{-1} related to stretching vibration of carbonyl group of xanthene dyes-loaded SAP compare to blank SAP matrix confirms entrapment of fluorophores inside the net of superabsorbent polymer. Quite low intensity of this absorbance signal is due to the loading of the small

quantity of the fluorophore into SAP matrix that resulted to be good enough to reach high fluorescence intensity detectable by naked eyes and camera. Increase in loading of dyes into the polymer resulted in fluorescence quenching and perceptible decay of emission up to its total loss. Thus, engineering of fluorescent loaded tags based on the polymer entrapment of emitting dyes resulted in efficient fluorescence assembly with minimal loading of emitter.

3.3. Fluorescence characterization of tracers for automated detection

Most stable of obtained fluorescence-loaded tags were characterized by spectrofluorimetry. Pre-concentration of emitting molecules within tags' matrices allows for enhanced fluorescent intensity of prepared tracers and results in possibility of their visual detection. Tags' fluorescent emission was noticeably more intense compare to background fluorescence. Some cases, interaction of polymer matrix-carriers with molecule of fluorophore resulted in bathochromic shift of fluorescence emission wavelengths as it was noted for fluorescein-loaded SAPs. Prepared fluorescent loaded tags are aimed for further downhole drill cuttings labeling tests followed by near-well head camera detection.

4. Conclusions

In this work, we innovated new concept of downhole fluorescent drill cuttings tracing engineered for on-site near-real time detection with camera and image-recognition system. Fluorescense-loaded tags are 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 cuttings depth determination would improve accuracy of drilling depth correlation and advance petrophysical characterization of formation to allow for optimal well placement.

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