





# Fluorescent Tracers for Drill Cuttings Labelling-Compatibility with Oil-Based Drilling Mud, Long-Term Stability, and Possibility of the Recovery <sup>+</sup>

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**Abstract**: Tracer testing is a well-established technique the oil and gas industry. By introducing tracers into drilling fluids, the depth of origin of drill cuttings can be identified. However, the compatibility of fluorescent tracers with oil-based drilling mud, their long-term stability, and the feasibility of tracer recovery are crucial factors to consider. In this study, we evaluated the possibility of tracer recovery and reuse after four months of exposure to OBM. The hot rolling test mimicking mud and cuttings circulation at the well conditions demonstrated stability of tracers over the weeks. It was noted that tracers could still be detected visually. Thus, we have developed novel, highly stable fluorescent tags suitable for downhole drill cuttings labeling application.

Keywords: fluorescent tracers; drill cuttings labelling; hot rolling test

# 1. Introduction

Tracers play an important role in reservoir characterization in the modern oil and gas industry, complementing other techniques such as production rate analysis and 4D seismic imaging [1–3]. These specialized compounds are used to identify fluid pathways, evaluate reservoir connectivity, and optimize production strategies. The addition of tracers to drilling fluids can provide valuable information for reservoir characterization and optimization of well placement. Several studies have investigated use of fluorescent tracers in reservoir monitoring [4,5]. While traditional tracer applications have provided valuable insights into reservoir behavior, recent advances in tracer technology have expanded the range of tasks that tracers can perform.

One such application is the use of fluorescent tracers to determine the depth of formation of drill cuttings. There is a challenge associated with drilling operations that relates to the identification of the origin of the drill cuttings, which can provide valuable information about the geology and reservoir productivity.

Previously, we reported the synthesis and laboratory characterization of novel composite fluorescent tags [6]. In this study, we investigated distinct properties required for such materials in downhole applications. Specifically, we examined the extended stability of tracers under conditions mimicking the well site and evaluated the effect of these tracers' additives on the rheological characteristics of drilling mud. Fluorescent tracers are particularly useful for drill cuttings tagging applications because they can be easily detected and tracked at the wellhead via camera and image recognition system.

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**Copyright:** © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). In summary, the use of tracers in the oil and gas industry has evolved significantly over the years, with new technologies enabling more complex tasks to be performed. The use of composite fluorescent tracers represents a promising approach for identifying the depth of formation of drill cuttings, providing valuable insights into reservoir lithology, and facilitating optimal production strategies.

## 2. Materials and Methods

## 2.1. Materials

We purchased Fluorescein; rhodamine B; and HPLC-grade petroleum ether from Sigma Aldrich (St. Louis, MO, USA). We purchased commercial super-absorbent polymer (SAP) based on sodium polyacrylate (Prod.# C001B1) from Orbeegun (Moscow, Russia). Oil-based drilling mud was obtained on our laboratory with a density of 1.25 g/cm<sup>3</sup>. We used all materials and solvents without further purification. We prepared all aqueous solutions with deionized water (18.2 M $\Omega$ \*cm), Sartorius, Arium<sup>®</sup> (Göttingen, Germany).

#### 2.2. Procedure for Preparation of Dye-Loaded Tracers by Super-Absorbent Polymer

We obtained laboratory batches of the tracers by scaling up and modification of the procedure we had previously used in our work [6]. Fluorescent dye (fluorescein or rhodamine B) (400 mg) was completely dissolved in 1000 mL of water under vigorous stirring for 1 h at room temperature. SAP (200 g) was then added to the resulting solution and left to soak fluorophores under rotary agitation for half an hour at room temperature. During this time, complete absorption of the dye solution into the SAP matrix occurs. The resulting wet tracers were dried over 12 h at 70 °C under vacuum of 10 mbar, resulting in two batches of SAP loaded with fluorescein (or rhodamine B), with a fluorophore to matrix ratio of 2 mg to 1 g.

## 2.3. Method of Tracers Testing by Hot Rolling

Evaluation of the tracer's stability in the presence of drilling mud is conducted in accordance with ISO 10416:2008, «Petroleum and natural gas industries — Drilling fluids — Laboratory testing», Chapter 23, «Shale-particle disintegration test by hot rolling». The mud sample and tracers are placed in a mud-aging cell and sealed; cell is then put into a roller oven. The test was conducted in two different ways: with and without drill cuttings. The cells are constantly rolled at a temperature of 80 °C for 16 h. After cooling the cell, the mixture is poured into sieves to determine weight losses and visually inspect the cell content.

#### 2.4. Method of Assessment of Fluorescent Intensity and Recovery Possibility

The fluorescence characteristics of tracers were evaluated visually at the daylight and under ultraviolet (UV) light. The tracers were separated from the drilling fluid and drill cuttings via sieves after the hot roll test. Certain tracers were also subjected to petroleum ether washing followed by filtration.

#### 3. Discussion

The present study employed an improved method to produce fluorescent tracers, which was successfully scaled up to hundreds gram level. The scaling process resulted in few notable outcomes. Firstly, it led to a reduction of 87.5 vol.% in solvent consumption. The reduction of solvent volume facilitated a reduction in the overall time cycle for tracer production by more than twice. Secondly, the implementation of rotary agitation improved the uniform distribution of the fluorophore in the polymer matrix, further refining the tracer production process. The obtained tracers are shown in Figure 1.

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**Figure 1.** Fluorescent tracers under UV light. tracers based on superabsorbent polymer loaded with Rhodamine B (1); tracers based on superabsorbent polymer loaded with fluorescein (2).

Furthermore, in this work, we investigated properties required for use of materials in downhole applications. Specifically, we conducted hot rolling tests for fluorescent tags that simulates mud circulation in the well in the presence of drill cuttings and without it. This way we studied the compatibility of SAP-based fluorescent tracers with oil-based drilling fluid. Moreover, this test can be used to assess long-term stability and the possibility of recovery of the tags.

## 3.1. Shale-Particle Disintegration Test by Hot Rolling

A hot rolling test is performed with the mud sample and shale particles that are mildly aggregated by rolling (or tumbling) for given period at elevated temperature. Typically, the mud sample and shale particles are sealed in a mud-aging cell and placed in roller oven that tumbles cells continually for 16 h or overnight.

Hot rolling experiments were designed to investigate the behavior of tracers under consecutive stages that closely mimic real well conditions. Tests were conducted in two specific ways: one using drill cuttings and the other without. This approach allowed to simulate step wisely the conditions encountered in oil drilling operations and evaluate the stability of tracers at each stage.

Firstly, we examined tracers' behavior under high-temperature conditions with oilbased drilling mud only. This experiment is mimicking stage of the tracers' transport towards the drill bit site with the drilling mud flow. Next, we introduced drill cuttings into the aging cell to assess the combined effects of drilling mud and formation cuttings on tracers' stability at high-temperature conditions. This consequent stage mimics tracers' and drill cuttings' flow back towards annulus with circulation of drilling mud. According to this methodology, we aimed to obtain accurate data on the behavior of tracers in actual drilling environments, which could ultimately assist the development of effective tracers' tracked drilling practices.

Examined tracers exhibited mechanical and chemical stability to the conditions of hot rolling tests, including tumbling in pure OBM and in OBM with additives of drill cuttings.

Weight losses of fluorescent tracers and drill cuttings sieved after hot rolling tests are summarized in Table 1. Images in Table 1 represent the visual performance of tracers after a hot rolling aging test at 80 °C for 16 h. Tracers exhibited mechanical and chemical stability to the examined test conditions for up to a week of exposure.

		-	
	_	Type of Tracers	
		5 wt.% SAP	5 wt.% SAP
		-Rhodamine B	-Fluorescein
	The mass of the recovered tracers on the sieve, %_	98.7	96.3
Sample without drill cuttings	Image of a sieve with recovered tracers		
Sample with drill cuttings	The mass of the recovered tracers on the sieve, %	99.5	97.2
	Image of a sieve with recovered tracers		

Table 1. The results of tests for disintegration of particles of drill cuttings with tracers in OBM.

3.2. Assessment of Fluorescence Intensity of Tracers for an Automated Detection System and Evaluation of Recovery of Fluorescent Tracers

The novelty of proposed in our work reservoir lithology monitoring is in engineering of fast and efficient method of multicolored tagging of drill cuttings according to the depth and further automated detection and accurate depth assignment via camera and image recognition system in the near-real-time mode. The use of fluorescent tags eliminates the need for labor-intensive drill cuttings sampling, transportation, and laboratory analysis, that results in a more efficient workflow for geo-navigation while drilling. To estimate the possibility of detection of tracers' fluorescence via UV-camera, photographs of tracers after hot rolling test were recorded at the day light and under UV (Figure 2).



**Figure 2.** Images of tracers after hot rolling test recorded at the daylight and under UV: 1-tags after hot rolling test without drill cuttings; 2-tags after hot rolling test with drill cuttings; 3-tags washed with petroleum ether after hot rolling test without drill cuttings; 4-tags washed with petroleum ether after hot rolling test with drill cuttings.

Tracers obtained based on sodium polyacrylate matrix possess polar oleophobic surface, which is crucial for lack of wettability of tags in oil-based mud. This characteristic ensure that the surface of tracers remain clean and free from contamination, even after prolonged exposure to OBM. Experiments demonstrated that obtained tracers were well detectable after multiple hot rolling test cycles, indicating potential for their recovery and reuse. These findings proved that fluorescent tags developed in this study are compatible with oil-based drilling mud and remain detectable after at least five times treatment with mud emulsion.

We conducted supplementary tests to assess the feasibility of fluorescent tracers' recovery and reuse upon long-term exposure to OBM. During these studies, we successfully retrieved batch of Rhodamine B-stained tracers from the oil-based drilling mud after aging for 4 months. Recovered tracers retained their shape and size, as well as visual detectability (refer to Figure 3)-without significant alterations in fluorescence intensity.



**Figure 3.** Image of SAP-rhodamine B-based tracers recovered after 4 months exposure to OBM under UV light.

## 4. Conclusions

In this study, we developed an up-scale method to produce hundreds of grams of fluorescent tracers with improved time-efficiency and fewer solvents consumption. Furthermore, we evaluated the compatibility of fluorescent tracers with oil-based drilling mud, their long-term stability, and the feasibility of tracers' recovery after long-term exposure to drilling mud. We demonstrated that tracers could withstand exposure to OBM up to 4 months without significant changes in fluorescence intensity. Our findings suggest that the fluorescent tracers developed in this study are highly stable under conditions mimicking downhole media upon transport to drill bit site with drilling mudflow and upon backward circulation with formation cuttings. Current results provide valuable insights into the use of fluorescent tracers for labeling drill cuttings in the oil and gas industry. Future studies will be focused on the development of tags' detection technology.

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