

Determining the fluorescent components in drilling fluid by using NMR method

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Abstract Fluorescent additives can reduce drilling operation risks, especially during high angle deviated well drilling and when managing stuck pipe problems. However, they can affect oil discovery and there is a need to reduce the level of fluorescents or change the drilling fluids to prevent loss of drilling velocity and efficiency. In this paper, based on the analysis of drilling fluids by NMR with high sensitivity, solid and liquid additives have been analyzed under conditions with different fluorescent levels and temperatures. The results show that all of the solid additives have no NMR signal, and therefore cannot affect oil discovery during drilling. For the liquid additives with different oil products, the characterizations can be quantified and evaluated through a T_2 cumulated spectrum, oil peak (T_{2g}), and oil content of the drilling fluids. NMR can improve the application of fluorescent additives and help us to enhance oil exploration benefits and improve drilling operations and efficiency.

Keywords Fluorescent additives · Drilling velocity and efficiency · NMR analysis · Well logging · Drilling fluids

1 Introduction

Low-field NMR logging plays an important role in formation evaluation, including pore structure, porosity, permeability, and fluid types in reservoirs. Recently, NMR logging has been applied in unconventional reservoirs, including shale gas and tight sandstone (Coates et al. 1999; Prammer et al. 1994; Murphy 1995; Lizhi 1998). The NMR experiment technique has the advantages of being a rapid and nondestructive analysis. Also, NMR can return many reservoir parameters (Coates et al. 1999). Recently, low-field NMR logging and experiment analysis have been used extensively in formation evaluation. However, in petroleum engineering, the NMR technique is used less. Considering the safe drilling operations, during drilling the deep well, ultra deep well, extended reach well, or horizontal well; or managing the drilling problems such as stuck pipe or tool and string failure, the drilling fluids should be added into many additives including solid types (sulphonated bitumen, brown coal, etc.) and liquid types (diesel oil, crude oil, etc.) with high fluorescence intensity. If oil layers cannot be identified and evaluated immediately by mud logging, the fluorescent levels of the drilling fluid can reach the 4th level (5 mg/l). When the fluorescent level of the drilling exceeds the 4th level standard, the drilling fluids should be changed or circulated to improve drilling velocity and efficiency. For example, in Well BT6 of the Bamai oilfield in the Xinjiang area, it took more than 17 days to drill for the fourth time. Discrimination between the fluorescent additives and the crude oil in formation is necessary for efficient oil exploration, exploitation, and drilling operations.

Aiming at these problems, long-term research has been carried out by the mud-logging experts leading to the development of many methods including gas chromatograph

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and quantitative fluorescence techniques (Xixian et al. 2000; Fuhua et al. 2001a, b; Xiexian et al. 2003; Xingli et al. 2007). Although these methods can resolve some problems, they can only qualitatively describe the fluorescence characterizations based on the variable curves or the differences among chromatographs, and they cannot identify the different sources of mixed oils. In the “National Eleventh Five Year” plan in China, the exploration and development strategy focused on unconventional resources such as shale gas, tight sand, etc. In extracting these resources, horizontal wells are generally drilled with oil-based fluids, which demand new technology to distinguish the fluorescent sources from fluid additives or formation oil show. Through the use of performance parameters, analysis parameters, and detection limits of the spectrometer, NMR analysis with high fluid sensitivity has been used to differentiate the fluorescent characteristics of the solid and liquid additives including: (1) different fluorescent levels in the crude oil; (2) variable temperatures; and (3) added relaxation reagent or not. Through trial and error, a new technique has been established to quantitatively identify fluorescent additives and crude oil in the formation.

2 Experiment

2.1 Experiment spectrometer

Two spectrometers used for the normal and variable temperature experiment were produced by the NiuMai electronic technology company in Shanghai, China. The parameters of the spectrometers are shown in Table 1.

2.2 The samples

Solid additives were taken from wells in the Xinjiang area, including sulphonated bitumen, sulphonated lignite, temperature-resistant and salt-resistant filtration-reducing agents, CXB-1, CMP-3, non-fluorescent lubricant, SMP-1,

SMP-2, ammonium salt, CMC-HV, CMC-LV, and kalium polyacrylate.

The crude oil samples were derived from some exploitation wells in the Jiyang depression in China. The densities of the five samples were 0.77, 0.83, 0.8974, 0.9455, and 0.9712 g/cm³ respectively. The water-based drilling fluids were taken from 1491.71 m depth of Well S14-7 in the Jiangsu oilfield with a density of 1.13 g/cm³. This well did not reach the target zone, with no fluorescent additives or formation oil.

3 Analysis results and applications of the solid additives

Fourteen types of solid additives were dissolved in water, drilling fluids, and relaxation agents and then analyzed by NMR. In addition, some additives were dissolved in drilling fluid and then analyzed with variable temperatures. The results indicate that the additives have no NMR signal.

Two possible reasons for the results are: (1) the fluorescent additives are mostly composed of the high molecular functional group such as benzene rings, carboxyl groups, and hydroxyl groups, etc. These additives containing aromatic rings have fluorescent characteristics, but the hydrogen atoms in the compounds occur as high molecules (Fuhua and Huisheng 2000). Therefore, due to the shielding effect, the chemical shift of the hydrogen atoms is so high that they have no signal with the low-frequency NMR method used. (2) The velocity or the density is inversely proportional to relaxation (Ranhong et al. 2007). The solid additives are dissolved in the drilling fluids with high velocity and exceed the detection limit of the NMR spectrometer, leaving the NMR signal very weak.

3.1 Results and analysis under the normal temperature condition

Drilling fluids with different proportions of solid additives were analyzed by the MR-DF type of NMR spectrometer. The results show that there is no new peak in the T₂ spectrum. After adding the 2000 ppm relaxation reagent, the T₂ spectrum shows only one peak (Fig. 1), which indicates that these additives have no NMR signal.

After adding some additives, including the temperature resistant and salt tolerant filtrate reducer, SMP-1, SMP-2, ammonium salt, carboxy methyl cellulose CMC-HV, CMC-LV, high molecular, and kalium polyacrylate, the T₂ spectrum on the right side shows a small peak. When adding relaxation reagent, the peak disappears (Fig. 2). The peak is generated by hydration and the relaxation reagent can shield the water signal. The amplitude of the hydrated peak is proportional to the content of the fluorescent

Table 1 The parameters of two spectrometers used in experiment

Spectrometer type	MR-DF NMR	MicroMR NMR
Resonance frequency	22.621 MHz	22.307 MHz
Magnetic strength	0.53T	0.52T
The probe coil diameter	15 mm	10 mm
Inter-echo spacing(TE)	0.2 ms	0.18 ms
Wait time(TW)	500 ms	1000 ms
The control temperature	31.99–32.00 °C	32–150 °C
Pulse sequence	CPMG	CPMG

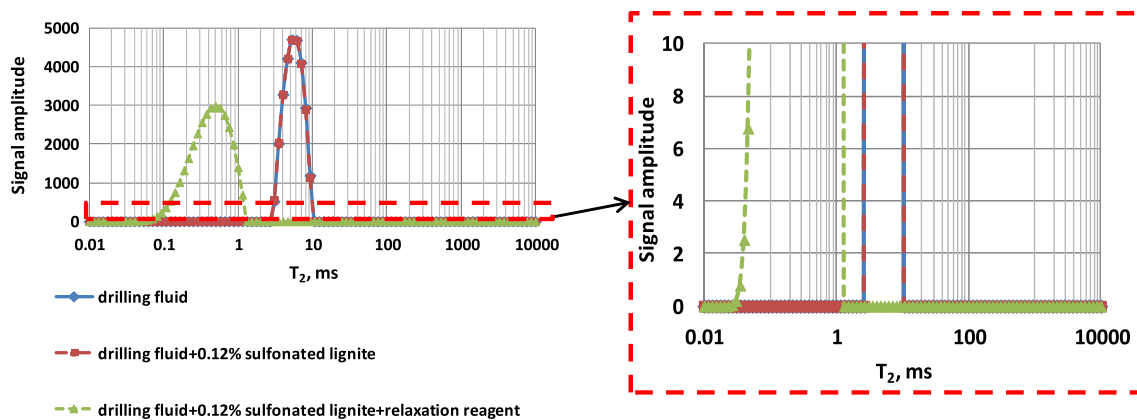


Fig. 1 The NMR response characteristics of the sulphonated lignite

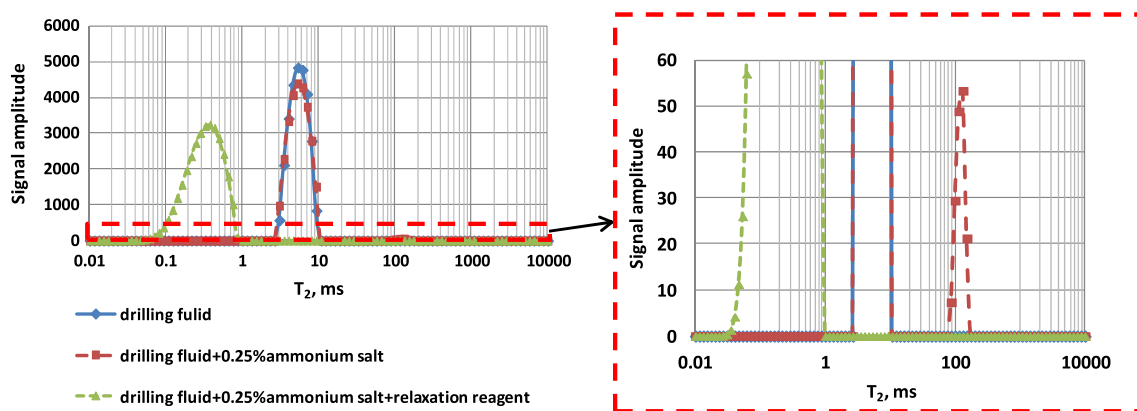


Fig. 2 The NMR response characteristics of the ammonium salt

additives. These additives can reduce the water loss of the drilling fluid, because they contain abundant hydrophilic radicals (carboxyl and oxy groups) and integrate closely with the clay grains in any position. The water molecule is polarized and changed into a hydrated layer (Fengyin et al. 1991; Chuanguang et al. 1996).

3.2 Results and analysis of the high temperature experiment

The sulfonated bitumen was analyzed under the temperature of 90 and 150 °C by the MicroMR spectrometer. Because the sample holder of the variable temperature detector was not composed of tetrafluoride, it was necessary to use glass tubes instead, which produced some signal and affected the results. When sulfonated bitumen was added to the drilling fluid, the T_2 spectrum showed a small peak on the left side of the drilling fluid peak, indicating clay-bound water under the high temperature condition. When the drilling fluid is added by the sulfonated bitumen and relaxation reagent, the T_2 spectrum shows that the sulfonated bitumen has no signal (Fig. 3).

3.3 Application examples

During the Well S14-7 operations, drilling fluids were added two ton weight of sulphonated bitumen at a depth of 1490 m. Fluid analyzed by NMR showed one T_2 spectrum peak with an area of 26,453.97. With the addition of the relaxation reagent, the T_2 spectrum also displayed one peak. Furthermore, the drilling fluids were continuously supplemented by $MnCl_2$ at 2-m intervals while drilling. At a depth of 2036 m, one new peak appeared with an area of 107.61. The content of crude oil calculated was 0.41 % (Fig. 4). When the well was completed, this interval was interpreted as an oil layer.

4 Experiment results and application of the liquid fluorescent additives

Liquid fluorescent additives consist of oil products, such as white oil, diesel oil, and crude oil. Generally, when the density of the drilling fluid is less than 0.9 g/cm³, the

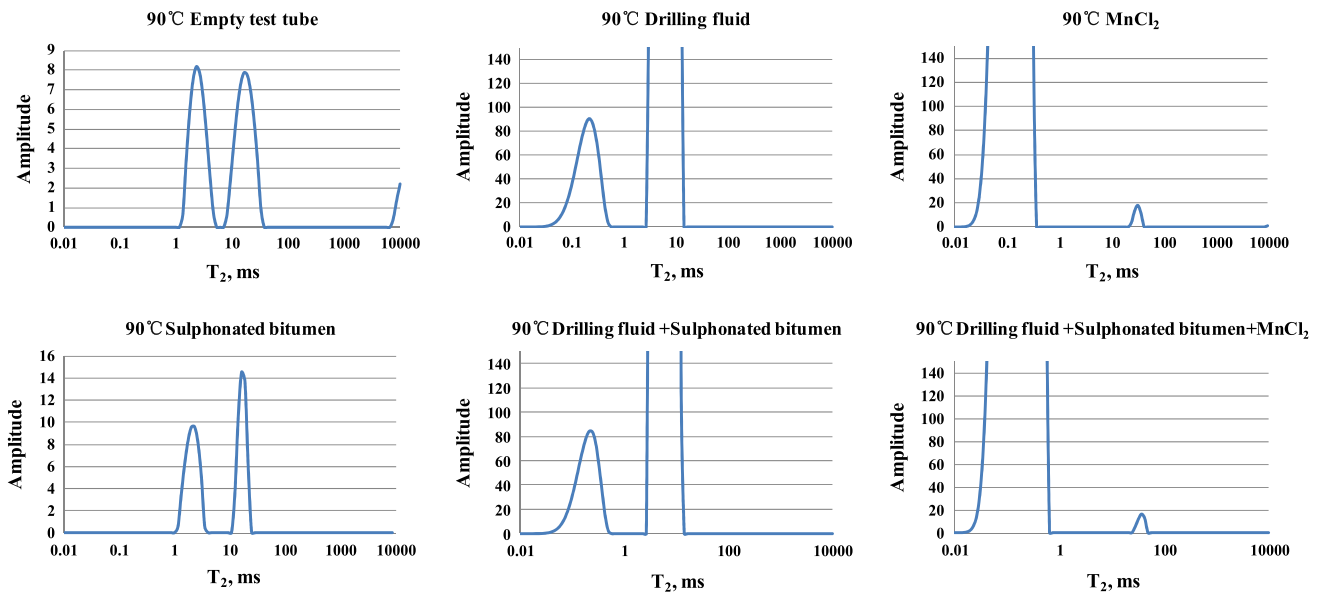
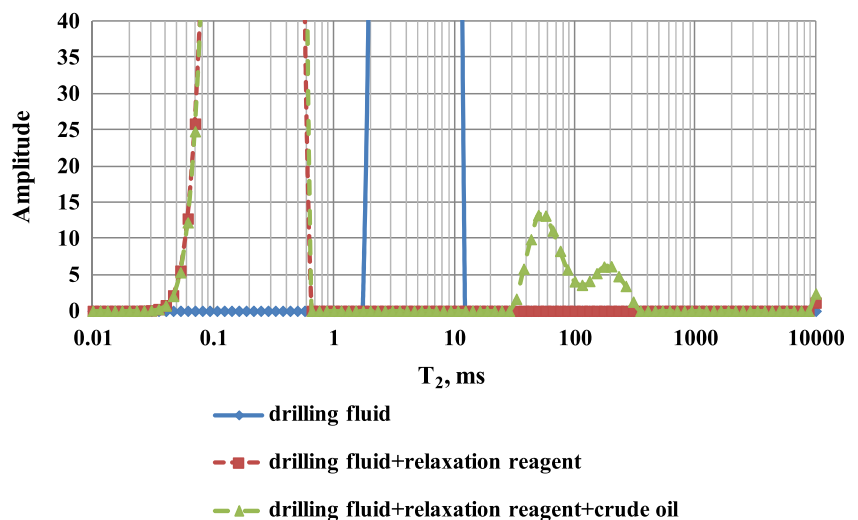


Fig. 3 The T_2 spectrum distribution of sulphonated bitumen under the condition of the 90 °C temperature

Fig. 4 The T_2 distribution of the drilling fluid in Well S14-7



oil peak and drilling fluid peak can be separated (Xiaoqiong et al. 2011). However, when the density is more than 0.9 g/cm³, the oil peak and drilling fluid peak may overlap. In this case, the drilling fluids should be analyzed by the 2D-NMR method a relaxation reagent employed to discriminate the oil and drilling fluids signals.

4.1 The computed method of the oil content

The content of the oil in the drilling fluid usually can be computed by the peak area ratio and calibration methods.

4.1.1 Peak area ratio method

When the oil and water signals are separated by the 1D NMR or 2D NMR technique, the oil content can be expressed by the ratio of the oil signal area and the total signal area. While the oil and drilling fluid signals should be separated by adding relaxation reagent, the oil content can be expressed by the ratio of the oil signal area supplemented by MnCl₂ to the total area without addition of MnCl₂. Oil quality can be determined because the oil has a different response signal based on hydrogen content. Oil content should then be corrected based on oil quality. The advantage of this method is that there is no need to establish a linear equation based on multiple samples; one

sample can calibrate the spectrometer. However, the oil content calculated is a relative ratio and this method is not suitable for on-line analysis.

4.1.2 Calibration method

Having calibrated by the different oil content of the samples, the correlation of the amplitude or area of the oil and oil content can be calculated. Based on the results, the oil content of the samples can be computed by the oil signal area or amplitude and also should be calibrated for oil quality (Fig. 5). This method computes the absolute oil content and is suitable for on-line analysis, but it requires a series of standard samples with different oil quality.

The source of the florescent matter can be quantitatively identified based on the oil peak (T_{2g}), the oil content, and

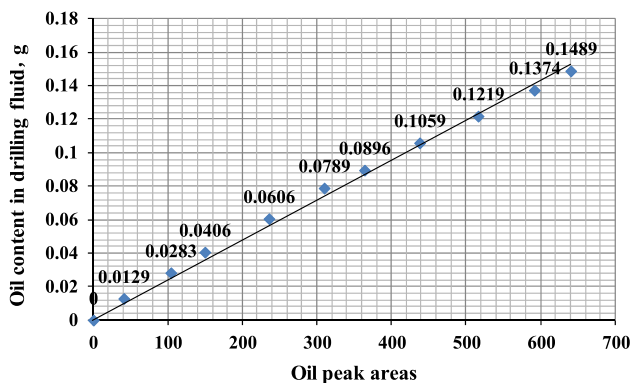


Fig. 5 The correlation chart between the oil peak areas and the drilling fluid

the T_2 cumulative spectrum after the standard overlying spectrum. Because the amount of the samples is different in each analysis, to be able to compare results this method should be calibrated. The procedure is as follows: before the analysis of the samples, the sample is massed by electronic balance as W_{di} (di is depth). The quantity of the sample is 10 g, and the amplitude of T_2 can be calibrated by $10/W_{di}$. In this way a T_2 cumulative spectrum can be obtained for each sample.

5 Application examples

During the drilling process for Well W349-26, at a depth of 2695 m, the drilling fluids were added by the 8 ton weight of white oil. From the NMR results of the drilling fluids at 2697 m depth, one new peak showed on the right side of the drilling fluid and the oil content was 4.21 %. After continuous analysis, at 2850 m the oil content of the drilling fluids changed and the density of the oil became heavier. The T_{2g} spectrum was reduced from 64 to 46 and the oil content reduced to 2.97 %. These observations indicated a new oil layer. At 3307 m, the oil quality changed again. The T_{2g} spectrum decreased from 46 to 42 and the oil content was 1.85 %. From the T_2 differential and cumulative spectrums, the oil quality varied in the depth so that the florescent source could be identified and evaluated quantitatively.

In virtue of the standard process of the T_2 and cumulative spectrums, three groups stand out for the drilling fluids: the first one was at depths of 2697 and 2700 m; the second one was at a depth of 2850 m; the third one was at depths of 3307, 3312, 3347, and 3365 m (Fig. 6).

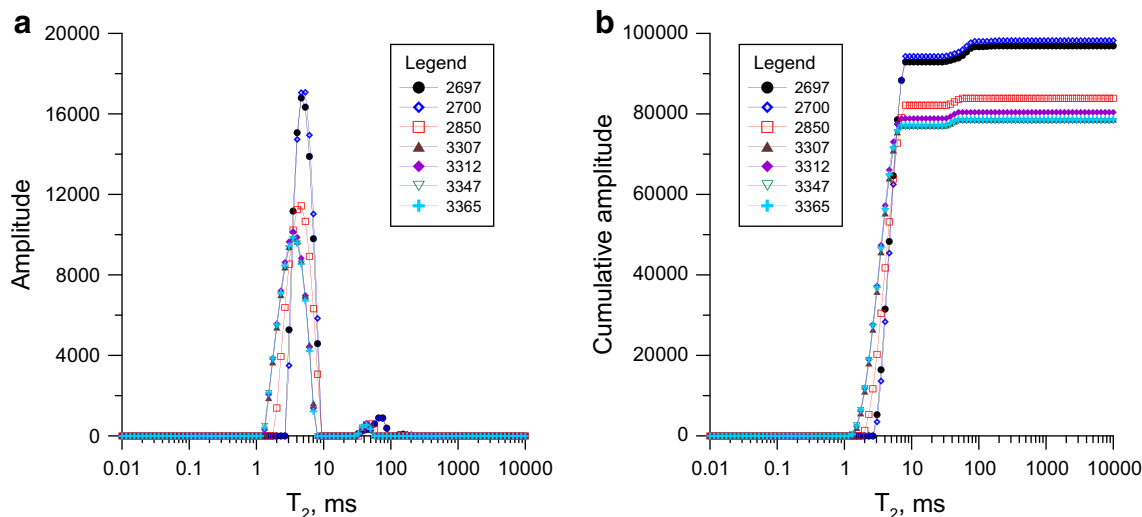


Fig. 6 The T_2 distribution of drilling fluids in Well W39-29 (a T_2 differential spectrum; b T_2 cumulative spectrum)

6 Conclusions

In drilling fluids, additives improve drilling efficiency and can be divided into two types: solid and liquid additives. Solid additives include sulfonated bitumen, SMP-1, SMP-2, ammonium salt, carboxy methyl cellulose CMC-HV, carboxy methyl cellulose CMC-LV, etc. Liquid additives include diesel oil, white oil, or formation crude oil. Through two types of NMR additive analysis, the NMR signal of the drilling fluid can be determined. Both types of additives can be easily distinguished by NMR analysis. NMR technology can also effectively distinguish the NMR signal response between solid fluorescent additives and the crude oil in the formation and definitively resolve the problem that the additives have on the discovery of oil layers.

According to the standard T_2 cumulative spectrum and T_{2g} of the oil peak, liquid additives can be identified accurately and quantitatively evaluated by the oil content even if mixed with similar source oil. This method overcomes the weakness both of the gas chromatography and the quantitative fluorescence technique.

Using the NMR drilling technique absolutely settles the problem of the identification and evaluation of fluorescent matter in the drilling fluid. In short, this technique enhances oil exploration and improves drilling operations and efficiency.

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