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Raman Spectra of hydrocarbon in returned drilling fluid using co-focal laser Raman microscopy

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Abstract. Hydrocarbon detection while drilling (HDWD) is important for obtain proper drilling performance. In this report, Raman spectra for hydrocarbon in returned water based drilling fluid have been acquired using He-Ne laser (633nm) excitation. The relative intensities of several Raman bands are found to depend on the concentration of hydrocarbon in returned drilling fluid. Spectra are interpreted as indicating that Raman spectra could be used as potential method for HDWD.

Introduction

Hydrocarbon detection while drilling is important for obtain proper drilling performance. To achieve this goal, the fluid properties need to be measured in time with sufficient accuracy. Therefore, the industry has implemented a set of standards describing the parameters to be measured and the methods of measurement. While drilling, drilling fluid flows down the drill pipe, through nozzles in the bit, then back up the annulus between the pipe and the well bore wall, carrying the cuttings produced by bit's actions on the rock and formation fluids, form a drilling fluid circulating system (Fig.1)[1]. Because the circulating system of drilling fluid need a longer circulating time as the drilling depth increasing, the traditional surface measurement device can not provide real-time down-hole information. Measurement While Drilling (MWD) tools are generally capable of taking directional surveys in real time. The measured data are stored in MWD tools and some of the results can be transmitted digitally to surface using mud-pulse telemetry. Certain MWD systems have the capability of receiving encoded control commands which are sent by turning on and off mud pumps and/or changing the rotation speed of the drill pipe. These messages allow the drill bit to be steered in a desired direction. Most MWD tools contain an internal gamma ray sensor. MWD tools can also provide information about the conditions at the drill bit. This may include: rate of penetration, rotational speed of the drill string , smoothness of that rotation, type and severity of any vibration downhole, downhole temperature , torque and weight on bit, measured near the drill bit ,mud flow volume. While in shit paper, we report the Raman spectra for hydrocarbon in returned water based drilling fluid, which could be used as potential method for hydrocarbon detection while drilling. Raman spectroscopy has been applied extensively as structure and diction probe and is one of the important methods to deeply study. Raman spectroscopy is based on the effect of radiation being scattered with a change of frequency. It was in 1928 that Indian scientist Raman and Krishnan[2] discovered the scattering effect that is named after Raman and that earned him a Nobel Prize in 1930. Raman spectroscopy is nowadays steadily gaining on importance for online analysis of chemical reactions and increasingly for many other real-world applications. Raman spectroscopy yields detailed information about molecular vibrations, and Raman spectroscopy is useful not only in identifying molecules but also shedding light on molecular structures[3-4]. But so far, the method has not yet applied to the hydrocarbon in returned drilling fluid.

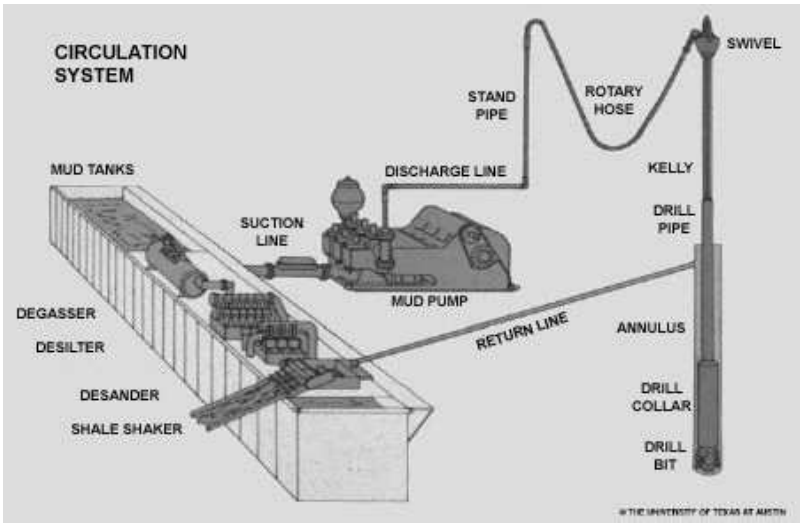

Fig. 1. Schematic of the circulating system: The drill bit, drill collar, annulus, drill pipe, kelly and swivel are depicted in the upper right. Drilling mud flows through the mud return line (center) upon its return to the surface from the hole to the shale shaker (upper left), then to the adjacent desander, desilter and degasser back to the mud tank (upper left). Mud passes through the suction line, and the mud pump (center) circulates the mud through the discharge line (above), the stand pipe (upper right) through the rotary hose (right) and the swivel (lower right), back to the kelly and into the drill pipe.

In this paper, we aim to test validity of Raman hydrocarbon detection in returned drilling fluid without further preprocessing. In section 2, we introduced the experimental instruments and Experiment procedure. Then in section3 we give out the Raman spectra of hydrocarbon in returned drilling fluid. In section 4, we discussed Future advancements for HDWD. This approach is illustrated by the assignment of several bands in Raman spectra of returned drilling fluid.

Organization of the Text

Experimental

1.1 Instruments

The Raman spetra was detected by using a Lab RAMARAMIS Raman spectrometer (Lab RAM HORIBA Jobin Yvon, Edison, NJ) with a He-Ne laser (λ = 633 nm, a laser power of 17 mW) as an excitation source (Santis, Baldi,2004; Park) . The instrument conditions were: 200 μm co focal hole, 150 μm wide entrance slit, 1200 g/mm grating, and 50× objective Olympus lens. Data processing was performed using LabSPEC 5 (HORIBA Jobin Yvon). The samples were mounted in a computer-controlled, high-precision x–y-z stage. To determine the DC, spectra of the uncured resins and beam samples were acquired over a range of 500–3600 cm−1.

1.2 Returned drilling fluid

Returned Water based drilling fluid was obtained from Shengli Oilfield well Yong 216. The medium containing in per 1000mL returned drilling fluid sample: H2O 650g, solid compositions(including rock fragment 150g, BaSO4 70g, NaCl 40g,bloating clay 25g, Carboxymethylcellulose sodium 20g, Ferrochrome Lignosulfonate 10g, other formation mineral 10g) 325g.

1.3 Returned drilling fluid

Original returned drilling fluid samples are available and used without further purification. The returned drilling fluid was injected into quartz glass capillary tube(Diameter :0.9-1.1 mm, thickness 0.10-0.15mm, West China Medical Instrument Factory) with pipette， then both ends of the quartz glass capillary tube were sintered with an alcohol lamp, to prepared the returned drilling fluid sample A. With double-distilled, deionized water, ethanol (AR) was diluted to 50% concentration, to obtain hydrocarbon solution B. Take 400ml hydrocarbon solution B and 500 ml returned drilling fluid, add

water to 1000 ml, to obtain 20% of hydrocarbon returned drilling fluid solution C. Take 100ml hydrocarbon solution B and 500ml returned drilling fluid, add water to 1000 ml, to obtain 5% of hydrocarbon returned drilling fluid solution D. Finally, we injected solution B,C,D into with pipette, then sealed both ends of the quartz glass capillary tubes by sintering.

1.4 Experiment procedure

The spectral region and spectral pre-processing used in the this paper were chosen by the following procedure：(i) using no spectral pre-processing, we get the Raman spectra of returned drilling fluid sample A, 50% concentration ethanol solution sample B, ethanol and returned drilling fluid mixture solution samples C and D. (ii)The quartz glass capillary tubes containing the solution samples were placed under the lens of Raman spectra device. Through the screen window, we adjusted the x–y-z stage to make the laser beam focus at the solution inside quartz glass capillary tubes . For each sample, we detected the Raman spectra three times at three different positions on each samples. (iii) Once we get the three Raman spectra for each sample, we choose and calculated the average spectra of the three spectra for each sample as the Raman spectra for each sample. (iv)The Raman spectra of quartz glass capillary tube were subtracted from each samples' Raman spectra.

Result and discussion

Raman shift is known as the fingerprint region and contains the majority of the Raman bands used uniquely identify a particular material. Because CCO stretching modes' Raman spectra band is 877cm-1-1089cm-1 , OH stretching modes' Raman spectra band is 3100-3500 cm-1, CH2 and CH3 spectra band is between 1089-3100 cm-1. In this paper, the Raman signal was collected in the spectral interval of 500cm-1 until 3600cm-1.

The Raman spectra of the returned drilling fluid sample A is depicted in Fig.2(a). The Raman spectra of returned drilling shows an increasing strong fluorescence background without strong Raman peak for wave numbers<3000 cm-1. This background increase is probably due to the large amount of organic in rock fragment. Since sample C and D all contain returned drilling fluid, which exhibit strong fluorescence, we used baseline correction tool in Origin 8.0 to subtracted the effect of background fluorescence and enhance the Raman spectra signal of functional group in ethanol.

Fig.2(b) is the Raman spectra of 50% concentration ethanol solution sample B，and five spectra bands could be distinguished from each other：(i) Spectra band 2800-3050cm-1 is the CH stretching modes;(ii) Spectra band 3100-3500 cm-1is the OH stretch and OH bend modes,(iii) Spectra band 877cm-1，1044cm-1,1089cm-1 are the (CCO) stretching modes,(iv) Spectra band 1279cm-1 is the CH2 wagging vibrations, (v) Spectra band 1461cm-1 is the CH3 wagging vibrations.

Fig.2(c) is the Raman spectra of 20% of hydrocarbon returned drilling fluid solution sample C. As the Raman spectra of sample A, sample C also shows an increasing strong fluorescence background for wave numbers<3000 cm-1. Since the launch of photomultiplier noise will increase with the square root of the incident light, very strong fluorescence background in the returned drilling fluid sample will lead to increased fluctuation noise, and Signal-to-noise ratio (SNR) of spectra will decreased significantly. Compare with the Raman spectra of ethanol solution sample B, sample C could identify three spectra band of sample B: spectra band (i)(iii)(v), the spectra band(ii) of OH stretch and OH bend modes and spectra band(iv) of CH2 wagging vibrations are all Submerged in the background fluorescence.

Fig.2 (d) is the Raman spectra of 5% of hydrocarbon returned drilling fluid solution sample D. Sample D and sample C have similar background fluorescence, but with little ethanol composition, SNR of sample's Raman spectra is smaller than sample C. Compare with the Raman spectra of ethanol solution sample B, sample D could identify two spectra band of sample B: spectra band (i)(iii), the spectra band(ii) of OH stretch and OH bend modes, spectra band(iv) of CH2 wagging vibrations and spectra band (v) of CH3 wagging vibrations are all Submerged in the background fluorescence. As shown in fig.1, Spectra band 2800-3050cm-1 of CH stretching modes are all strong in sample B, C and D, can be used as the characteristic peaks of hydrocarbons detection[5-6].

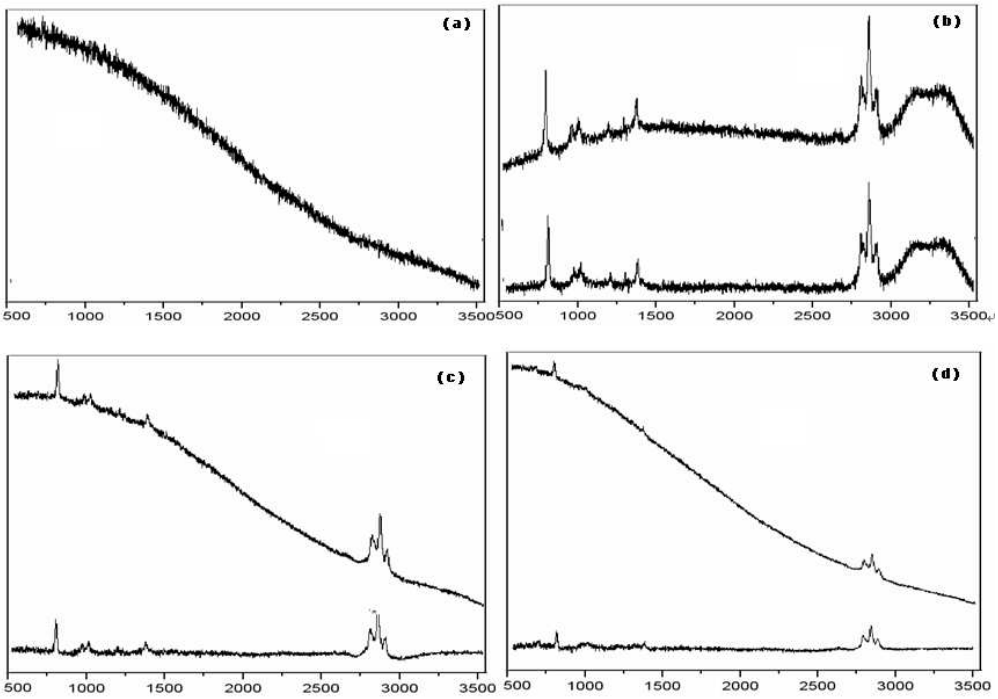

Fig.2 Raman spectra of mixed solution of ethanol and returned drilling fluid

Future advancements

3.1 Instrumentation improvements

Fluorescence can overwhelm Raman signals in some cases. Methods to deal with fluorescence include time resolved Raman spectroscopy and the use of longer wavelength excitation lasers [7]. The Raman effect occurs on timescales of picoseconds. Fluorescence, which can be orders of magnitude more intense than the Raman signal occurs on timescales of nanoseconds. Thus picosecond time gating of the laser and the spectrometer can be used to discriminate the Raman signal from the fluorescence [8]. Industrial applications often use a 785 nm laser, which does not induce as much fluorescence as a 633 nm laser. However, the intensity of the Raman scattered signal decreases with increasing wavelength. Therefore reduction of fluorescence must be weighed against the resulting reduction in signal. In some cases fluorescence will decrease over time with continued exposure to the excitation beam. Thus simply waiting for about five minutes can result in spectra with less fluorescence and identifiable peaks. Additionally, decreasing the laser power can reduce fluorescence to the point that longer exposure times can be used to detect mineral peaks. Both of these effects were observed during laboratory analyses.

3.2 In-situ Raman spectra hydrocarbon detection while drilling

As ambient drilling fluid and mud cake around the well bore wall will produce a contribution to the acquired spectrum. Therefore advanced data processing techniques will be required to remove the ambient seawater component, particularly if the data will be used to obtain Raman spectra of fluid in formation directly.Laboratory work is needed to better characterize the Raman spectrum of drilling fluid at the pressures, temperatures, and fluid compositions found at target formation. Due to the heterogeneous nature of targets such as rocks and bacterial mats, a better method of visually locating the laser spot is required. A through-the-lens visualization system would be ideal, however to implement this requires the addition of a movable mirror (introducing a possible failure point) or a beam splitter (which would reduce optical throughput). Additionally, although Raman spectroscopy does not require sample preparation, in some cases it may be necessary to split rock samples in situ to allow analysis of the sample interior.

Conclusions

Raman spectroscopy was used to study the hydrocarbon diction in drilling fluid. Some structure assignments were discussed in the observed spectra. These spectra can be distinguished from each other. Comparison of the Raman spectra of returned drilling fluid with different ethanol concentration, the intensity of Raman spectrum changes significantly. These spectra provide the basic information necessary the track the change of hydrocarbon concentration in drilling fluid. Example of Raman spectra of drilling fluid shows that the spectra band 2800-3050cm-1 of CH stretching modes can be used to HDWD.

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