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Applicationon of Quantitative Fluorescence Analysis in Oilfield Development

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Abstract: Fluorescence analysis technology has played a very important role in petroleum geology, especially in the early stage of exploration, oil migration of graduate students, and discovery of light oil in logging.

Keywords: Logging,extinction,Fluorescenceanalysis,Spectrogram,Flooded

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I. THEORETICAL BASIS

Since crude oils contain aromatic hydrocarbons that have fluorescent characteristics, the electromagnetic radiation absorbed by it will disturb the electronic structure inside the aromatic ring and make it in an excited state, that is, it will cause emission of radiant energy during the decay of ultraviolet radiation.We call that fluorescence.In addition to light gasoline and paraffin, petroleum and most of it's products, whether they are themselves or dissolved in organic solvents, can emit light under ultraviolet irradiation and become fluorescent.The luminescence of oil depends on its chemical structure.Polycyclic aromatic hydrocarbons and non-hydrocarbons in petroleum cause luminescence while saturated hydrocarbons do not emit light at all.The fluorescence of light oils is light blue, the petroleum with more gums is green and yellow, and the petroleum or asphaltenes with more asphaltenes are brown fluorescent.Therefore, the luminescent color varies with the nature of the petroleum or asphalt material and is not affected by the nature of the solvent, while the luminescence intensity is related to the concentration of petroleum or asphalt.

Since the luminescence phenomenon of petroleum is very sensitive, as long as the solvent contains one hundred thousandth of oil or asphalt material, it can emit light.Therefore, in oil and gas exploration, fluorometric analysis is often used to identify whether oil samples contain oil, and the composition and content can be determined.The use of fluorescence microscopy to study petroleum geology issues mainly includes the following aspects: the formation of oil reservoirs, reservoirs, and migration of petroleum.,especially since it has evolved from a crude qualitative analysis to a quantitative analysis.In the process of energy conversion, the energy level of the emitted light is lower than that of the absorbed excitation light. The molecules that can emit fluorescence have a certain excitation and emission spectrum, and can be quantitatively analyzed according to the spectrum.

II. CONVENTIONAL FLUORESCENCE ANALYSIS

The cuttings fluorescent logging technology is a conventional logging method for the discovery of oil and gas layers in drilling.For a long time, domestic cuttings fluorescent logging has been using the method introduced from the Soviet Union in the 1950s. It is cutting debris that is soaked with chloroform or carbon tetrachloride, extracting oil components, and irradiating with ultraviolet light to visually observe the color and luminous intensity of cuttings.The contrast method is used to determine the fluorescence level of the rock debris.The use of conventional cuttings fluorescent logging has the following weaknesses:a. Fluorescent quenching effect of carbon tetrachloride on crude oil, especially for coal oil, condensate oil, and some light oils, may result in the loss of oil and gas layers, especially light oil and gas layers during the logging process;b.The method used for on-site logging is to visually observe the rock debris under the UV light to find oil and gas layers. This method may miss a lot of light oil, because the visible light range is 400-800nm, but the light oil;c.During the drilling process, due to the needs of the project, additives such as modified asphalt and lubricants are often mixed in the drilling fluid. Due to the introduction of such fluorescent additives, fluorescence logging becomes difficult and fluorescent interference occurs.It is not even possible to distinguish the oil layers.

The wavelength of the best excitation light of the petroleum inclusions in cores and cuttings at the logging site is 250-330 nm. The fluorescence emission wavelength in this excitation wavelength range is 260-600 nm, and the main peak appears in the range of 300-400 nm.The lighter the wavelength of the emitted light, the visible wavelength of the naked eye is 390-700 nm, so most of the fluorescence emitted by the petroleum inclusions is invisible light to the naked eye.The function of the conventional fluorescence logging tool is to place the chloroform soaking solution of the drilling sample while drilling in the fluorescent box, and observe the fluorescence level through the naked eye under the irradiation of the fixed wavelength lamp to judge the oil and gas display.Due to the subjective nature, limitations and arbitrariness of macroscopic observation of fluorescence, it is easily interfered by the additives of drilling fluids, so conventional logging tools often lose their proper effects, especially when the drill bit encounters a light oil reservoir. Conventional fluorescence logging instruments hardly detect the fluorescence of light oil layers.

III. QUANTITATIVE FLUORESCENCE ANALYSIS

Quantitative fluorescence logging is a method of quantitatively detecting the fluorescence level and fluorescence intensity of oil contained in a rock sample during the oil drilling process. The logging method is based on the oil content and the oil quality to determine the condition of oil in the formation.Quantitative fluorescence logging can have the following effects:Quantitative fluorescence logging is beneficial to the discovery of light oil layers;Helps to determine the formation's oily water condition, can help explain the oil and water layers; quantitative fluorescence logging spectroscopy can be used for oil source tracking and comparison;Can detect various oils from condensate to heavy oil;Can intuitively reflect the oil characteristics of crude oil;Can effectively discriminate the fluorescence interference of natural crude oil and drilling fluid additives;Can be used in drilling site environment.

The new generation of oil fluorescence quantitative analyzer has the following advantages:a.Hexane extraction can increase the sensitivity of crude oil fluorescence analysis by 10-35 times;b.It is not easy for light oil to leak, correcting the old concept that coal oil, condensate oil, and some light oils did not fluoresce, pointing out that the fluorescent wavelengths of coal oil, condensate oil and some light oils are not directly visible to human eyes.Observe the 400-800nm range, which can completely reveal the light oil's intensity that cannot be observed by the naked eye;c.Solved the problem of fluorescent interference of modified asphalt in drilling fluid additives;d.Make quantitative fluorescence logging successful.

The two-dimensional fluorescence has a wavelength scanning characteristic, and light oil and heavy oil can be more accurately distinguished according to the shape of the wavelength-scanned fluorescence spectrum.According to the calibration work curve of crude oil samples from adjacent wells at the same level, the oil content of the rock sample can be quantitatively measured, and the problem that the conventional fluorescence can only distinguish the fluorescence level with the naked eye and can not be accurately quantified can be solved.The effect of fluorescence due to additive contamination can be effectively eliminated.

The process of performing two-dimensional quantitative fluorescence analysis is as follows:

Before the test, the oil sample from the same well with the same source as the oil source should be collected as the standard sample. The instrument should be calibrated to detect the fluid additive to determine the background value.Take 1.0 g of rock sample and put it in a test tube that has been filled with 5 ml of n-hexane reagent for 15 minutes. If the sample is soaked in color, dilute properly.Put the prepared rock sample solution into a quartz cell, scan the fluorescence spectrum of the sample, or determine the fluorescence analysis value of the sample.In the quantitative fluorescence logging spectrum, the main peak wavelength ofλ(nm), the main peak fluorescence intensity INT, and the oil index R are determined as the characteristic values of the fluorescence spectrum.The main peak wavelengthλmain: the wavelength corresponding to the highest peak of the fluorescence spectrum; the main peak fluorescence intensity INT main:The fluorescence intensity value corresponding to the highest peak of the fluorescence spectrum;Oil Index R:The ratio of the fluorescence intensity at a wavelength of 350nm to 380nm to the fluorescence intensity at a wavelength of 310nm to 330nm.

Now, three-dimensional fluorescence analysis has also made a preliminary exploration.The three-dimensional fluorescence phenomenon may have an important connection with hydrocarbon accumulation theory and the generation and evolution of crude oil. With the help of fluorescence analysis technology, it may be helpful to explore the theory of hydrocarbon migration and migration [2].

IV. COMPARISON OF OIL SOURCES

The crude oil group consists of four parts: saturated hydrocarbons, aromatic hydrocarbons, asphaltenes, and nonhydrocarbons.Using the characteristics of the aromatic components in the crude oil group component that can fluoresce under ultraviolet light, the properties of the crude oil can be judged based on the difference in the wavelength of the main fluorescence peak and the oil index R, and the fluorescence analysis data of the sample can be statistically analyzed,then we get the criteria.In the sample from the same oil source, the oil extraction materials are generally similar. By comparing the fluorescence spectrum of rock-like bitumen extracts of hydrocarbon source rocks and rock-like asphalt extracts containing oil samples, it can be inferred that their oil sources are related,the more similar the shape of the spectrum, the more likely it is that they belong to the same oil source.

V. FLUORESCENT IMAGE TECHNOLOGY ASSESSING WATER FLOODING

The research of the fluorescence image technology to determine the flooding status of the oil layer is an exploratory and groundbreaking task research. It's purpose is to find a new way to improve the interpretation accuracy of the oil layer flooding.The use of fluorescence microscopy to study the developed flooding of reservoirs is currently the only "visible" analysis technique that can directly observe the distribution and state of oil and water in rock pores.Fluorescence image analysis technology combines fluorescence microscopy with image semi-quantitative analysis techniques to study the microscopic characteristics of the distribution of oil and water in rock after oil layers are subjected to different degrees of flooding,It not only can clearly reflect the different composition and content of hydrocarbons and the occurrence mode of petroleum hydrocarbons in rocks, but also can directly reveal the relationship between the distribution of petroleum hydrocarbons in cores and rock structure, structure, and secondary fracture-cavity,Quantitatively quantify the oil, water content, face ratio, oil content, and moisture content in the rock pores to determine the washed and flooded conditions of the developed reservoir.

The basis of judging the flooding status of oil layer using fluorescence image technology:Fluorescent image technology can be used to determine the status of oil flooding, and comprehensive judgments can be made from various aspects such as fluorescent color, fluorescence intensity, luminous pore area, and image characteristics of the oil layer at different levels of water washing.Since water flooding first drives out crude oil components with lower density and lower viscosity, as the degree of crude oil production increases, the content of non-hydrocarbon and asphaltenes in the remaining crude oil in the rock gradually increases, so the oil layer after being washed changes in fluorescence characteristics and light emitting area.Although the oil in different regions may have different fluorescent colors due to compositional differences, the law of red shift and intensity of fluorescent wavelengths does not change as the oil becomes heavier.,this gives us a theoretical basis for using fluorescent images to observe and study the extent of oil wash.

1. the important signs of flooded oil layer

(1) .Fluorescence image characteristics of Water

Free water in the pores of oil reservoirs is an important sign of oil flooding.Water as a special component is undoubtedly a very important research object in the research of fluorescence image technology for judging flooding.Water does not have luminescence properties, but because aromatic compounds and their derivatives have weak hydrophilicity, water containing traces of aromatic compounds should show a special fluorescent color, thus confirming the presence and distribution of water in the washed oil layer.The water in the pores appears blue-green and green fluorescence.From this, it is possible to clearly observe the various optical properties of the pores and the distributional boundaries with other components.During the displacement test of the lithography model to study the mechanism of formation of microscopic water flooding and remaining oil, we can observe the special product formed by water flooding in larger pores—dynamic oil droplets. There are also a large number of studies on the formation of oil beads and the research of trapping mechanism at home and abroad,In the study of fluorescence images of flooded oil reservoirs, we often observe that these "fine"oil droplets in the water channels usually exhibit light characteristics of light oil components,the fluorescence is mostly bright white, yellow or green yellow.This phenomenon provides evidence for our judgment of the water-containing pores.In the fluorescent image of a strongly flooded reservoir, the pores are mostly occupied by water,the tiny oil droplets "suspended" in the pore free water. under the reflected light, these small oil droplets also showed the misty light property of the oily asphalt, while they were black in the single polarized light.

(2) Influence of Washing on Fluorescence Characteristics of Oil Layer

Due to the development of water injection in oil fields, the physical and chemical changes in crude oil will occur inevitably.This change may be intuitively reflected by differences in fluorescence characteristics such as fluorescence color, luminous intensity, luminous area, and distribution of oil layers, and these differences become the basis for discriminating flooding of oil layers.

A. The effect of washing intensity on the fluorescent color of oil layer

As mentioned before, the color of the fluorescence mainly depends on the composition and molecular structure of the luminescent material.For strongly flooded reservoirs, because the crude oil composition in the reservoir tends to heavier as the degree of washing deepens, the pores are basically occupied by water.The fluorescent color shows grey-green fluorescence of water containing traces of light aromatic compounds, and the fluorescent color of the crude oil adsorbed on the edge of the rock is hard to separate from the rocks.

In the water wash image, most of the fluorescence was bright yellow, showing the dissolution and enrichment effect of water on the light components of the crude oil, and the part still retained the brown color of the unwashed crude oil.In the weak oil wash image of the oil layer, the crude oil in the pores shows a strong brownish-yellow brown color, indicating that the oil content is relatively high, and the crude oil is not substantially washed.In fluorescent images of unwashed oily oil layers, the fluorescence color appears tan.Since the molecules of the luminophores only excite the electrons in their ground state and emit energy by releasing the corresponding photons, they can emit fluorescence.Conversely, if these excited ground-state electrons do not all release energy back to the ground state by emitting light quanta, but instead radiate energy to dissipate part of the energy through the interior of the material molecule, the fluorescence intensity will inevitably weaken, and the luminescent color will also darken.This phenomenon often occurs in environments where the concentration of luminescent substances is sufficiently high, known as fluorescent "self-etching" (or "extinction") phenomena.

The oil layer has never been washed to strong washing, and it's fluorescence color has undergone a transition from a strong ancestral yellow-yellow-white-tan color.The color density of the former is an extinction phenomenon, and the dark brown color of the latter shows that only the heavy components adsorbed by the argillaceous matter are strongly retained in the heavily watered oil layer, and the intermediate process indicates the relative enrichment effect of water on the aromatics and light components.Therefore, observing the change of fluorescence color can help qualitatively discriminate the extent of oil flooding.

B.Effect of different degree of washing on luminous intensity

Because the fluorescence intensity is only proportional to the concentration of the luminescent material in a certain range, the luminescence intensity is weakened due to the self-eclipsing phenomenon in the environment where the concentration of the luminescent material is sufficiently high. Therefore, the oil asphalt content in various washing stages of the oil layer is reduced.For oil layers and weak water-flooded layers, due to the extinction phenomenon, the fluorescence intensity is weak and non-uniform, and the coexistence of local water and oil has strong luminosity.For medium water washing, the oil content in the pores is still high. Due to the emulsifying and dispersing effect of water washing, the concentration of luminescent substances is moderate, the extinction phenomenon is weakened, the luminous intensity is relatively high, and the entire visual field is bright.In strong wash images, most of the pores are filled with water, the oil content is very low, and the residual asphaltene crude oil has very weak emission intensity.It should be pointed out that for strong oil washing layers, although there is a corresponding difference in luminescence intensity due to the difference in the nature of the pores and the degree of water washing, the luminescence intensity is generally reduced as the degree of washing gradually increases, and the luminescence intensity decreases with the gradual reduction of crude oil.

C. Effect of Washing Degree on Luminous Emission Area and Distribution of Oil and Water in Pore

As the degree of water washing increases, the ratio of oil to water in the pores of oil layers gradually decreases, resulting in a decrease in the light emitting area of the oil in the pores and a corresponding change in the distribution of the oil in the pores.For the fluorescence of the weak water wash layer, the total light emitting area of the oil is large, and the pore-filled body is oil, and the water is only partially looming in the pores;For the medium wash, the fluorescent color is bright yellow, the light emitting area is reduced compared to the weak wash, the main pores have been occupied by water;For strong washing, the pores are filled with water and the luminous area of the oil is significantly reduced.In the case of ultra-strong water washing with a test oil content of 99.8%, most of the pores are occupied by water, and some heavy crude oil components remain on the small pores and on the edge of the rock, and the light components that are slightly soluble in water gradually decrease,the fluorescent color in the pores gradually darkens, the fluorescence intensity also decreases, showing a very weak halo.

2. Characteristics of fluorescence images of different flooding conditions in oil layer

Fluorescent image features are a combination of fluorescent color, luminous intensity, luminous area, oil-water distribution characteristics and ratio.The fluorescence color, luminous intensity, and oil-water distribution characteristics are the qualitative indicators for evaluating the degree of oil washing and flooding, while the oil and water effective luminous area (face ratio) and oil-water distribution ratio are semi-quantitative indicators for measuring the flooding status of the oil layer.According to China's grading standard for water-flooded layers, it is divided into three types: non-flooded-weak flooding, medium flooding, and strong flooding, and corresponding transition types.

(1)Not Flooded And Weak Flooded

Non-flooded rock samples show good glow and all pores contain oil,interparticle pores are extremely bright, with relatively little water.However, due to the phenomenon of fluorescence self-eclips, the heavy component of the crude oil masked the fluorescence of the aromatic component, resulting in the oil layer of the unflooded oil is usually a relatively strong orange, yellow brown to brown, light intensity.Partial oil layer visible partial light accumulation.For weak flooding and non-flooded water, the fluorescent color is relatively lighter and the intensity is slightly higher. The green fluorescence and oil droplets of water can be seen in a few large pores.We define the section with a percentage of oil-bearing area greater than 60% and a percentage of water-bearing area less than 40% as a weak flood layer.

(2)Medium Flooded

Rock samples in moderately flooded oil-bearing wells show uneven luminescence, and pores (especially larger interconnected pores) or fissures are often filled with water;Interparticle pores, such as impregnation and luminescence, are still good, and the fluorescent colors of oil and water are relatively bright, and the overall luminous intensity is high, with bright white, green and white, and yellow and white as the main colors.Due to the water flooding subdivision standard, the comprehensive water content of the test oil is set to 40%~80% as a medium flood, and the range is wider. There are also obvious differences in the fluorescence images of flooded water in the same level, which can be further subdivided into weak flood, medium flood, medium Strong flood.In the medium-weak flooding image, a small amount of water can be observed in the pores. The fluorescent color of the oil asphalt surrounding the water is bright yellow, and the gum pitch located far from the water is preserved well.In the medium flooded image feature, the water-bearing area increases significantly, and the connected or larger pores are already basically occupied by water.In the medium-strong and near-strong flooded fluorescence images, the fluorescence area is reduced and the luminescence intensity is weakened. The water in the pores is diffusely distributed or exhibits the characteristics of water and oil emulsification.According to the image characteristics of the water-infusing layer, we set 40%-60% of the oil-bearing area and 40%-60% of the water-containing area as the middle water-flooded layer.

(3) Strong flooding

When the oil layer enters the strong flooding stage, the water content in the pores of the rock sample is nearly saturated, and the light components in the oil layer are lost as the degree of water washing increases,most of the residual asphaltene components that are not easily desorbed by water are adsorbed by the argillaceous cement, and the fluorescence color at the edge of the pore gradually changes to the dark color of the heavy component.Since the concentration of the aromatic light components that can be preferentially eluted by water gradually decreases, the luminous intensity of the water in the pores also decreases, the color gradually darkens, and the luminous intensity of the interparticle pores is impaired.In the end, only traces of low-molecular hydrocarbons are adsorbed on the edge of some pores, showing a very faint halo, and no trace of crude oil is visible at most of the pore edges.We define the strong water-flooded zone with an oil-bearing area of less than 40% and a water-containing area percentage of more than 60%.Strong water-flooded layers have partial similarities in image characteristics and moderate flooding when combined water content is less than 90%.

Application summary

The new method of using the fluorescence image analysis technology to judge the water flooding status of reservoirs is based on a large amount of experimental research work and has been established through continuous exploration and repeated comparisons.The various flooding patterns in this article are verified by test oil.from these we can draw the following basic understandings:

A. The oil layer fluorescence film directly records various characteristic information of different water washing levels of the oil layer. The fluorescence image technology can capture this information from the fluorescence microscopy scale.These physical and chemical changes in the crude oil in the oil layer are directly reflected in the differences in the fluorescence microscopic characteristics, and these differences become the basis for discriminating the degree of oil washing with fluorescence image technology.

B. Different flooding degrees of oil layers have different fluorescence image characteristics.These characteristics include the fluorescence color of the reservoir, luminous intensity, oil-water luminous area, oil-water distribution characteristics, ratio qualitative and semi-quantitative indicators, and they are related to the oil reservoir flooding conditions.

C. High quality flakes are the basic guarantee for correctly identifying the free water and its distribution in the oil layer;Undistorted grinding of fluorescent flakes is the basis for accurate acquisition of fluorescent image data;High-resolution, true-color fluorescent images are the conditions for correctly identifying the flooded condition of the oil layer.

D. Due to the limited work we have done, the criteria for determining flooding levels may need to be revised due to different areas,The depth of research needs to be further strengthened. in-depth research needs to be done in terms of the relative permeability of oil and water and the impact of crude oil properties on flooding.The preliminary research results only confirmed the feasibility and high credibility of the technology. With it's "visible" technological advantages, it will surely play a role in the development of the oil field.

In summary, the fluorescence image technology uses intuitive, graphical analysis and interpretation to discriminate oil-bearing conditions, and has a high scientific and technological content. It is a new weapon to overcome the problem of low accuracy in the interpretation of reservoir flooding,it is also the only analytical technique that can directly observe and judge the water flooding status of the reservoir.If the technology is integrated with the comprehensive evaluation method of organic geochemistry, the theoretical and research methods of reservoir geochemistry will be used to comprehensively study the flooding degree of the reservoir from the two perspectives of "seeing" and "touching",it will be a new approach to the scientific evaluation of the evaluation of flooding.

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