Low Field NMR Evidence of Geo-Polymeric Behavior of Organic Matter in Shale and the Implications on Recovery*

Robert L. Krumm¹ and James J. Howard¹

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Abstract

The mechanism through which light oil is stored in organic matter and how it moves has implications on unconventional reservoir production scenarios. The traditional view is that this oil is found in sub-micron-sized pores observed in the organic matter of numerous shale reservoir rocks where phase behavior and flow properties are defined by established physics of confined spaces. An alternative view is that the organic matter behaves more like a plastic or polymer that can absorb certain solvents. The combination of NMR $T_1$ and $T_2$ measurements illustrate that a portion of the light oil in a hydrocarbon-bearing reservoir rock is dissolved in the solid organic matter. Differences in the relaxation mechanisms associated with $T_1$ and $T_2$ processes are the key in identifying the light oil that is captured in the organic matter. The restricted diffusion component of the $T_2$ mechanism for this captured oil generates a much faster $T_2$ relaxation component than observed in a $T_1$ measurement that lacks a diffusion mechanism. Distinct $T_1$ and $T_2$ measurements have greater resolution than the combined 2D $T_1$-$T_2$ maps that are often used in recent studies. NMR measurements on organic-rich shale and low-organic-content shale under dried and oil-saturated states illustrate the fast $T_2$ – slow $T_1$ component associated with light oil dissolved in the organic matter; this creates complex geo-polymer behavior. Thermogravimetric analysis of oil-saturated shales also shows that organic matter has geo-polymer characteristics. Comparisons made between TGA data of other polymers with sorbed solvents and organic matter with sorbed oil show similar trends. For organic-rich samples, oil evaporates at higher temperatures (200-350°C) compared with the bulk boiling point (174°C).

Reference Cited

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Robert L. Krumm¹ & James J. Howard¹
¹Premier Oilfield Group

OBJECTIVES

• Investigate if polymer theory can explain some of the observations seen with hydrocarbon interacting with organic matter.
• Compare Low Field Nuclear Magnetic Resonance (NMR) and Differential Scanning Calorimetry (DSC) of absorbent polymers and highly organic shale.

THEORETICAL BACKGROUND

SOLUBILITY PARAMETERS

• The Hildebrand Solubility Parameter can be used to explain the relationship between organic matter and hydrocarbon:
  • The Hildebrand solubility parameter comes from polymer science and is foundational based on “like dissolves like”

\[ \delta = \left( \frac{\Delta E - R \cdot T}{V_m} \right)^{1/2} \]

\( \delta \) values determined by swell tests

kerogen “sweet spot” vs. various solvents

Ulrich Ritter; Solubility of petroleum compounds in kerogen: implications for petroleum expulsion, Organic Geochemistry, Volume 34, Issue 3, 2003, Pages 319-326, ISSN 0146-6380

ORGANIC MATTER POLYMER CONCEPT

• Conceptualize organic matter as a macro-molecule that absorbs hydrocarbon in a cross-linked structure a.k.a. superabsorbent polymers

MATERIALS AND METHODS

SAMPLES

• High molecular weight sodium polyacrylate water absorbent
• Envirobond™-403 hydrocarbon absorbent
• 20% T.O.C. Green River Oil Shale

NMR

• Oxford Instruments 2MHz Geospec II
• T₁, T₂, & T₂ vs. T₁ map
• Dry, Oil Saturated, & Brine Saturated

DSC

• Ambient-300°C
• Setaram SENSYS-Evo

RESULTS

ENVIROBOND-403

Differential Scanning Calorimetry

Green River Oil Shale

POLYACRYLATE

CONCLUSIONS

• Kerogen shows polymer-like NMR tendencies
  • T₁ and T₂ shifts of bulk fluids towards faster relaxation times
  • Misidentification of fluids due to relaxation overlap
  • Non-proportional NMR signal intensity increases when saturated with fluids
• DSC showed reduced volatility of bulk fluids due to association with absorbents
• Geo-polymer kerogen model explains some observations