ROCK-EVAL 7S: TECHNOLOGY AND PERFORMANCE

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Introduction

Designed and developed in the 1970s, the Rock-Eval technology have become a reference to screen the petroleum potential, type and thermal maturity of source rocks (Espitalié et al., 1977). Initially based on an open pyrolysis system with an on-line flame ionization detector (FID) for hydrocarbons detection, the device was later completed by an open oxidation system, to oxidize the rock after pyrolysis, and an on-line IR spectrometer for CO and CO₂ detection. These improvements allowed the quantification of organic carbon and mineral carbon contents in rocks (Espitalié et al., 1985). Then, thanks to suitable temperature programs, the Rock-Eval technology proved its applicability to get an insight into the occurrence and nature of accumulated hydrocarbons within reservoir sections (Lafargue et al., 1998), including unconventional reservoirs such as oil sands (Lamoureux-Var et al., 2011) and oil-rich source rocks (Romero-Sarmiento et al., 2016). More recently, this technology has been used to characterize the organic matter of recent sediments (Baudin et al., 2015) and soils (Soucémarianadin et al., 2018).

Technology and performance

Today, a new technological leap makes it possible to characterize sulfur in tandem with hydrocarbons, CO₂ and CO. As for the Rock-Eval 6 device, the new Rock-Eval 7S comprises two main furnaces, one for pyrolysis and the other for oxidation. During pyrolysis, part of the effluents passes through a combustion oven connected to the pyrolysis furnace, where the sulfur compounds are converted to SO₂. SO₂ is detected by a UV spectrometer, while the hydrocarbons and CO/CO₂ are detected respectively by the FID and IR spectrometer. After pyrolysis, the residue of pyrolysis is oxidized in the oxidation furnace. The released SO₂, CO and CO₂ are detected respectively by the UV and the IR spectrometer. The twin furnace design (pyrolysis and oxidation) is necessary to allow the formation of a permanent carbonaceous coating at the inner pyrolysis furnace surface. This coating, which is oxidized in single furnace machines, prevents further adsorption and subsequent loss of hydrocarbons interfering with hydrocarbons values (S1 and S2 peaks of the FID). This design also prevents unwanted oxidation of hydrocarbons condensed on the splitter outlet directed towards the CO/CO₂ line. The comparison of carbon and sulfur contents measured by Rock-Eval 7S and by elemental analysis showed an excellent correlation. In addition, the calibration of the device, separately in pyrolysis and in oxidation, makes it possible to quantify the sulfur content released during pyrolysis (the ‘pyrolysis sulfur content’) and the residual sulfur content. The ‘pyrolysis sulfur’ in rocks, bitumen and sulfur-rich oils is an interesting information as it is likely the source of organo-sulfur compounds and H₂S that are yielded upon geological or anthropic thermal processes.

It is also possible to quantify the organic sulfur associated with the S1 and S2 peaks of the FID. The data processing software makes then it possible to simulate, in addition to the
cracking kinetics of the organic matter, the cracking kinetics of its organo-sulfur functions. This can help deciphering the thermal cracking of sulfur-rich kerogens and source rocks.

The superposition of the SO\textsubscript{2} and hydrocarbons signals helps discriminating the organic sulfur, which is associated with the S1 and S2 peaks of the FID, and the pyritic sulfur. However, the presence of clays and/or of carbonates in rocks induces chemical reactions with sulfur compounds during the analysis, hindering the signals interpretation. In this case, an estimation of pyritic sulfur and organic sulfur contents can be obtained via a mathematical model based on parameters derived from the Rock-Eval 7S analysis (Aboussou, 2018).

Thanks to an oxidation temperature reaching 1200°C, the thermal decomposition of sulfates in rocks is feasible. Iron sulfates, magnesium sulfates and especially calcium sulfates, present in the great majority of the sedimentary rocks, can then be detected. Nevertheless, their quantification remains difficult for two reasons: calcium sulfates may not entirely decompose if at high contents; some sulfates can be neoformed during the analysis.

Conclusion

The Rock-Eval 7S allows to characterize the combined thermal reactivity of hydrocarbons and sulfur compounds, in rocks, kerogens and oils. So it is an interesting technology to investigate organic sulfur-related issues, especially those encountered in oil exploration and production, such as euxinic depositional environments, preservation of organic matter thanks to sulfur incorporation during early diagenesis, early catagenesis of sulfur-containing kerogens, sulfur-rich oils generation and \( \text{H}_2\text{S} \) emissions during production.

References


