

**PRELIMINARY RESULTS ON THE INFLUENCE OF STEAM INJECTION
PROCESS ON ORGANOSULFUR COMPOUNDS IN SULFATES-RICH
PETROLEUM RESERVOIRS**

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Among natural post-accumulation phenomena known to result on significant compositional changes of oils and on an increase of H₂S production (sour toxic and corrosive gas), we find biological phenomena such as Bacterial Sulfates Reduction (BSR) occurring at shallow depth (T < 100°C). Deeper thermal phenomena (T > 100°C), such as secondary cracking of oils as well as Thermal Reduction of Sulfates (TSR) in evaporitic or carbonated reservoirs, are the main processes.

TSR can also artificially be induced by the injection of hot water during Enhanced Oil Recovery (EOR) operations in shallow reservoirs containing heavy oils. Due to the high temperatures (150°C < T < 300°C) reached in the reservoirs during hot water flooding, chemical reactions involving oil, water and sulfates-rich minerals can lead to a significant increase of H₂S production and neoformation of organo-sulfur compounds (OSC), pyrobitumen in addition to CO₂ and carbonates by oxidation of the in-situ oil.

In order to better understand induced TSR mechanisms and to tentatively estimate the sulfur risk in terms of H₂S and OSC occurrence during hot water stimulated enhanced recovery operations, experimental pyrolyses were undertaken under conditions as close as possible to those prevailing in reservoirs during hot water injection. The purpose of this set of experiments was first to develop an experimental approach able to simulate induced TSR and second to determine the total sulfur balance including H₂S, soluble and insoluble OSC production rates at various temperatures. Based on the hypothesis that the three primary processes involved in natural TSR are similar to the one involved in induced TSR, i.e. (1) oxidation of organic matter (vulcanisation), (2) sulfates reduction and (3) thermal cracking, they were independently simulated in laboratory conditions and the results compared to those obtained from experiments simulating the complete TSR phenomena.

Artificial simulation using model compounds (nC₈-nC₁₄ mixture or n-hexadecanethiol), labelled or not elemental sulfur (used here as reaction initiator), deionised water and mineral (MgSO₄) were conducted at variable temperature and pressure (320°C-100

bars; 280°C-130 bars) for different residence times (for 3 to 30 days) using an inert closed system pyrolysis. The mineral/hydrocarbons/water volume ratio was initially set at 70/24/6 and then increased to 70/15/15.

Gases were quantified by gas chromatography using an external standard after separation in a vacuum line. C₆-C₁₄ fractions were quantified by gas chromatography after recovering the C₆₊ effluents with n-pentane. The C₁₄₊ fraction was recovered by extraction in dichloromethane, fractionated by liquid chromatography into saturates, aromatics and NSO compounds. Saturates and aromatics were analyzed by GC/FID and GC/MS. Finally, insoluble organic and mineral residues recovered by filtration were analyzed by Rock-Eval (carbon and sulfur), microscopy and X-Ray diffraction.

The preliminary results are as follows:

- The oxidation of organic matter, one of the elementary reaction of TSR, was reproduced under laboratory conditions as confirmed by the presence of organic sulfur in the soluble and insoluble residue, detected by GC/FID, GC/MS and RE-sulfur analysis. The sulfur-containing matter % in the residue increases as a function of pyrolysis residence time (i.e. up to 20% of sulfur incorporated within organic carbon). In presence of sulfates, higher amount of H₂S, NSO compounds and organic residue is produced compared to vulcanisation. The aromatic fractions are enriched in condensed aromatics (sulfur-containing and non-sulfur-containing aromatics) for induced TSR simulations compared to the vulcanisation one.
- The mass sulfur balance was calculated by comparison of H₂S amount which could be generated from S₀ with the experimental quantified H₂S. Subsequently, the sulfates reduction ranges from 3 to 5%. Although the presence of secondary MgCO₃ seems to be detected by RE6, its presence was not confirmed by DRX. No TSR is observed in absence of initiator (S₀ or OSC: used to generate the real initiator in reservoirs: H₂S) as well as in absence of hydrocarbons. TSR and vulcanisation seem to be kinetically controlled in our experimental conditions. However the rate of vulcanisation is very high compared to that of TSR. Therefore the alteration of hydrocarbons and formation of H₂S are kinetically controlled by the rate of sulfates reduction. The evolution of our experimental system in terms of gas-water-minerals composition using 0D fluid-rock interactions numerical model will be discussed.