

Effect of aqueous chemistry on the thermal stability of hydrocarbons in petroleum reservoirs

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The thermal stability of hydrocarbons under geologic conditions is of significant interest for petroleum geochemists due to its effect on the gas to oil ratio (GOR) and the maximum depth of oil occurrence within sedimentary basins. While most previous research in this area has focused on the kinetics of organic thermal reactions, the effects of inorganic species contained in formation waters and reservoir minerals are increasingly being recognized as a significant contributor to this process. The oxidation of hydrocarbons via the reduction of sulfate (TSR) is one example of an organic-inorganic reaction that plays a critical role in controlling the thermal stability of hydrocarbons in some reservoirs. Gibbs free energy calculations suggest that these reactions are energetically favorable at typical reservoir temperatures, yet non-catalyzed TSR reactions involving anhydrite have never been simulated in the laboratory at temperatures below 800°C. This suggests that the rate of TSR must be controlled by some unidentified kinetic factors.

We have conducted a series of hydrous pyrolysis laboratory experiments in order to investigate the role of formation water chemistry on the thermal stability of petroleum hydrocarbons. Our results show that the chemical composition of aqueous solutions in contact with hydrocarbons significantly affects the rates and pathways of hydrocarbon cracking and oxidation. More specifically, the ionic strength and major ion concentrations (e.g., SO_4^- , Ca^+ , Mg^{2+} , etc.) can influence the onset temperature of oil cracking to form natural gas, and the amount and composition of gas generated (e.g., CO_2 , H_2S , CH_4 , etc.). The predominant mechanism appears to be the reduction of reactive sulfate ion-pair species coupled with hydrocarbon oxidation.

Oil-anhydrite TSR reactions in the Permian Khuff Fm, Saudi Arabia

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Thermochemical sulfate reduction (TSR) occurs when anhydrite reacts with petroleum resulting in calcite, H_2S and other reduced sulfur compounds. Analysis of data from 10 wells from the sour Permian Khuff Fm from Ghawar and neighboring fields in Saudi Arabia using geochemistry, stable isotopes, fluid inclusions and petrography has confirmed that H_2S is due to TSR. Anhydrite has been replaced by calcite and sulfur. However, of all the various types of anhydrite, only nodules composed of microcrystalline anhydrite have undergone TSR. Replacive calcite is poorly developed in many cases with much anhydrite remaining even in reacted nodules. Some wells have no finely crystalline anhydrite, and thus have no H_2S . Fluid inclusion analysis revealed that: (1) the initial charge was oil, later displaced or diluted by gas, (2) TSR occurred in the presence of oil between 113°C and 135°C. TSR thus occurs at a lower temperature with oil than with dry petroleum gas (Worden et al. 1995). Based on petrography and fluid inclusion analysis, TSR is only at an early stage in Ghawar. This may be due to one of: lower temperatures than in other sour gas provinces, recent cooling, the recent emplacement of less reactive petroleum (i.e. gas) or the isolating effect of TSR calcite that grows on the finely crystalline anhydrite nodules. The petroleum seems to have been altered by TSR since there is a correlation between the overall H_2S percentage and both the sulfur content and the sulfur isotope ratio of the liquid petroleum. As H_2S , due to TSR between anhydrite and petroleum, accumulated there was back-reaction of H_2S with remaining liquid phase petroleum and the generation of a suit of dibenzothiophenes. With advancing TSR and increasing H_2S concentration, the oil progressively changed from typical petroleum $\delta^{34}\text{S}$ values ($\geq 0\text{‰}$) to the sulfur isotope ratio of Permian anhydrite (+9‰). TSR in liquid petroleum accumulations thus not only results in the replacement of anhydrite by calcite and petroleum fluids by H_2S , it also results in the generation of new sulfur bearing organic compounds.

Reference

Worden R.H., Smalley P.C. and Oxtoby N.H. (1995), *Ass. Am. Petrol. Geol. Bull.* **79**, 854-863.