

# EXPERIMENTAL STUDY ON THE EFFECTS OF RESERVOIR MINERALS ON THE OCCURRENCE OF THERMOCHEMICAL SULPHATE REDUCTION IN NAUTRE

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## Introduction

Thermochemical sulfate reduction (TSR), a prominent organic-inorganic interaction between sulfate and hydrocarbons, refers to the reduction of sulfate to sulfide coupled with the oxidation of hydrocarbons to carbon dioxide in petroleum reservoirs within a sedimentary basin (Orr, 1974). Up to now, most TSR-associated hydrocarbon reservoirs have been discovered in carbonate rather than silicate reservoirs in nature. This is mainly supposed to be caused by the enrichment of substantial metal irons in silicate reservoirs, which can react immediately with hydrogen sulfide to form the metal solids and hence interrupt this reaction. In contrast, carbonate reservoirs are assumed to be more clean with containing less metal irons, hydrogen sulfide generated in TSR can be preserved and then act as a catalyst to make it happen continuously (Machel, 2001).

Compared to that in deeply buried hot carbonate reservoirs with the temperature of  $\geq 100$ – $120$  °C, TSR discovered in silicate reservoirs has been documented to be inhabited in a much cooler thermal regime with the temperature of  $70$ – $100$  °C. Except for that in the Upper Permian Ravnefjeld black shale Formation, Wegener Halvø, East Greenland (Pedersen et al., 2003), TSR in the other silicate reservoirs was believed to take place in deeper hot formations rather than in situ (Zhang et al, 2005; Mankiewicz et al., 2009) due to the impossibility of inducing TSR extensively in silicate reservoirs under such low thermal regimes in accordance with the traditional wisdoms in carbonate reservoirs. However, geofluids containing dissolved sulfates can migrate from the deeply buried formations into shallow silicate reservoirs along the faults, and/or porous carrier beds, providing a good opportunity for the occurrence of TSR within silicate reservoirs. The remaining question is the temperature. Low temperature thresholds for petroleum generation and thermal cracking can be expected due to catalytic functions of clays (Goldstein, 1983; Tannenbaum et al., 1985; Kissin, 1987). This leads us to speculate whether or not reservoir minerals, in particular clays, can play a similar role in TSR. If this does occur, it can provide an alternative explanation for the occurrence of TSR in a relatively low temperature regime within silicate reservoirs.

In order to make a better understanding of the effects of reservoir minerals in TSR, we conducted a series of pyrolysis experiments to simulate the process of TSR in the laboratory with the absence and presence of inorganic minerals occurred in petroleum reservoirs, including montmorillonite, illite, quartz, calcite and dolomite. The pyrolysis temperature was set to  $360$  °C under a constant confining pressure of  $50$  MPa heating for  $12$ ,  $48$  and  $312$  h, respectively. This study should add additional values on the occurrence of TSR within sedimentary basins in nature.

## Results

Gaseous compounds, C<sub>7-9</sub> light hydrocarbons, C<sub>9+</sub> normal alkanes and organic sulfur compounds were quantitatively analyzed in the pyrolyzed residues. The results show that C<sub>9+</sub> *n*-alkanes decrease with experimental duration time increasing or TSR ongoing accompanied with the increases in hydrogen sulphide, toluene, C<sub>2</sub>-benzenes, benzothiophenes and dibenzothiophenes. Compared to the experiments with no mineral additives, experiments with the presence of silicates are comparatively depleted in C<sub>9+</sub> *n*-alkanes and enriched in hydrogen sulfide, light monoaromatics and organosulfur compounds; experiments with the presence of carbonates demonstrate the opposite, indicating that silicates accelerate and carbonates reduce the reaction rates of TSR. Catalytic effects of clays are in the favour of generating molecules, which are prone to be oxidized in TSR. This is supported by the lower ratios of isoalkanes to *n*-alkanes such as *i*-C<sub>4</sub>/*n*-C<sub>4</sub>, *i*-C<sub>5</sub>/*n*-C<sub>5</sub> and methylhexanes/*n*-C<sub>7</sub> in experiments containing clay minerals. Carbonates are assumed to reduce the concentrations of H<sup>+</sup> and thus HSO<sub>4</sub><sup>+</sup> by dissolution at the beginning stage of TSR as indicated by significant generation of carbon dioxide at 12 h. According to the results of this study, it is possible for TSR to occur in a specific cooler silicate reservoir when compared to TSR in a hot carbonate reservoir. This leads to the difficulties in identifying TSR in silicate reservoirs, if no enough hydrogen sulphide left.

## Conclusions

Reservoir minerals can play an important impact on the occurrence of TSR. Silicates accelerate and carbonates reduce the reaction rate of TSR. Accordingly, TSR can take place in silicate reservoirs within a relatively lower thermal regime. The role of reservoir minerals in TSR provides an alternative explanation for deciphering the plausible mechanisms for the occurrence of TSR under geologic circumstances. Kinetic models with the purpose of predicting the onset temperature of TSR and burial depth of sour gas reservoirs should hence be taken into consideration of the effects of reservoir minerals.

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