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**Quantitative Prediction of H<sub>2</sub>S Using Advanced Chemistry of Basin Modeling**

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Thermal Sulfate Reduction (TSR) reactions play an important role in both exploration and production. For exploration, currently oil-cracking models for down-dip oil prediction do not include TSR reactions. This limits significantly our ability to predict oil cracking and H<sub>2</sub>S risk analysis. From a production perspective, drilling a sour well without existing facilities for H<sub>2</sub>S removal significantly reduces the rate of return on investment since the well must be kept shut in until a sulfur removal unit can be installed. A technique for predicting the H<sub>2</sub>S content of produced gas would therefore enable wells to be drilled with optimum materials and techniques.

Preliminary work using closed system hydrous and non-hydrous pyrolysis in sealed gold tubes has been performed with various model compounds; high and low sulfur oil, and different types of sulfate species. We will present our latest results on (1) timing of TSR reaction (basin modeling approach), (2) role of elemental sulfur and its reaction with oil, (3) mechanistic study and rate controlling factors for TSR process, (4) role of dolomite and other minerals, (5) role of H<sub>2</sub>S and labile sulfur, and (6) diagnostic method to determine whether crude oil has gone through a TSR process.

Experimental and theoretical evidence suggests that magnesium plays a significant role in controlling the rate of TSR in petroleum reservoirs. A novel reaction mechanism for TSR is proposed that involves the formation of contact ion-pairs between Mg and SO<sub>4</sub>. Ab initio quantum chemical calculations show that the formation of [MgSO<sub>4</sub>] contact ion pairs changes the symmetry of the sulfate ion [SO<sub>4</sub><sup>2-</sup>] from T<sub>d</sub> to C<sub>2v</sub> and consequently increases the S-O bond length making sulfate easier to be reduced. It is proposed that TSR may proceed as a two-stage reaction initially involving the slow reduction of MgSO<sub>4</sub> to H<sub>2</sub>S followed by a more rapid sulfate reduction reaction catalyzed by H<sub>2</sub>S. The recognition of the two-stage reaction for overall TSR process may help to explain why previous estimates of TSR activation energies were so divergent.

Thermochemical sulfate reduction (TSR) of model compounds and whole crude oils was investigated to determine the influence of hydrocarbon type on the reaction. The model compound experiments show that the type of hydrocarbon involved can significantly affect the extent of TSR reaction, and the difference in hydrocarbon reactivity involved in sulfate reduction

mainly depends on the type of functional group present. For the model compounds studied, the relative reactivity during TSR is 1-octene > 1-octanol > 1-octanone > n-octane > octanoic acid > octylbenzene > xylene. Crude oil composition can dramatically affect the onset temperature of TSR. Although the model compound experiments clearly demonstrate the variable reactivity of different hydrocarbon types during TSR reactions, the observed trends for sulfate reduction during the whole oil experiments indicate that the labile sulfur content in oil may be more significant in controlling TSR reaction rates than the hydrocarbon chemistry.

The effect of thermochemical sulfate reduction (TSR) on gas generation, residual saturated hydrocarbon compositional alteration, and solid pyrobitumen formation were investigated. The TSR reaction dramatically lowers the stability of hydrocarbons leading to increases in gas dryness and GOR. While their concentrations decrease, the relative distributions of n-alkanes do not change appreciably from the original composition, and consequently, are non-diagnostic for TSR. However, distinct molecular changes related to TSR are observed Pr/nC17 and Ph/nC18 ratios decrease at a faster rate under TSR compared to thermal chemical alteration (TCA) alone. TSR promotes aromatization and the incorporation of sulfur and oxygen into hydrocarbons leading to a decrease in the saturate to aromatic ratio in the residual oil and in the generation of sulfur and oxygen rich pyrobitumen. These findings could provide a diagnostic geochemical signature of the extent of TSR and prove useful in identifying TSR in settings where TSR has occurred.

The kinetics of reactions between elemental sulfur and petroleum hydrocarbons show that the average value for the activation energy required to reduce elemental sulfur to hydrogen sulfide by hydrocarbons was calculated to be  $193 \text{ kJ mol}^{-1}$  ( $46 \text{ kcal mol}^{-1}$ ). The results demonstrate that under typical geologic conditions the rate of reduction of elemental sulfur to hydrogen sulfide by petroleum hydrocarbons is quite rapid. The maximum time for substantial amounts of elemental sulfur to persist in contact with petroleum hydrocarbons is estimated to be no more than a few million years in cool reservoirs, and in hotter reservoirs the half-life of elemental sulfur may be as short as hundreds of years. Consequently, the presence of elemental sulfur in petroleum reservoirs is expected to lower the thermal stability of oil and raise the maximum depth at which oil occurs within a basin (thermal deadline). These results suggest that any elemental sulfur observed in petroleum reservoirs today is unlikely to have been derived from the source rock that generated the oil, but rather was probably formed more recently through the reduction of sulfate by hydrogen sulfide.

Thermochemical sulfate reduction (TSR) in initial  $\text{H}_2\text{S}$  presence was investigated and a new mechanism of how initial  $\text{H}_2\text{S}$  presence is able to catalyze the sulfate reduction was proposed. The experiments show that the in-situ pH of water solution can significantly affect the extent of TSR reaction. The rate of TSR is proportional to the initial partial pressure of  $\text{H}_2\text{S}$  under the same temperature and pH condition, suggesting that the presence of  $\text{H}_2\text{S}$  can greatly lower the activation energy of hydrocarbons reacting with sulfate. Our preliminary experimental observation of  $\text{H}_2\text{S}$  reacting with hydrocarbons shows that an appreciable amount of thiols and sulfides (named as labile sulfur species) forms, and the presence of labile sulfur species in oils can significantly lower the onset temperature of TSR. Thus, we proposed that the formation of reactive labile sulfur species produced from  $\text{H}_2\text{S}$  reaction with hydrocarbons are most likely the reactive intermediates for  $\text{H}_2\text{S}$  initiation for TSR.

A new kinetic model to predict hydrogen sulfide formation was developed based on our experimental simulation, molecular modeling and thermodynamic modeling of formation water chemistry. A new technique is now available that specifically assess H<sub>2</sub>S risk prediction and TSR effect to petroleum thermal stability and petroleum quality. By combining hydrocarbon types (mainly labile sulfur contents in oils), the formation water chemistry including Mg, Ca and SO<sub>4</sub> concentration and reservoir thermal history with a PC-based model of hydrocarbon oxidation kinetics, we are able to predict: H<sub>2</sub>S risk degree, H<sub>2</sub>S yield, onset temperature of TSR, gas quality (e.g., sourness), and oil quality (organic sulfur incorporation).