

# Integration of Thermochemical Sulfate Reduction into Petroleum Systems Modeling\*

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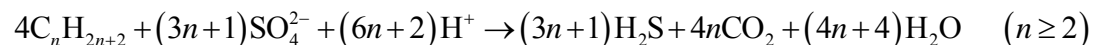
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## Abstract

Modeling of temperature, pore pressure, hydrocarbon generation, cracking, multi-component PVT analysis, and fluid flow is well established in the industry (Hantschel and Kauerauf, 2009). The focus now is on enhanced applicability of petroleum systems modeling by extending this approach. Some specific geochemical models are under development, such as modeling of biodegradation; generation and retention of bitumen components; transport and flocculation of asphaltenes; generation of biogenic gas; generation of the inert gas carbon dioxide and hydrogen sulfide. Three processes are especially important for H<sub>2</sub>S generation: thermal and bacterial cracking of sulfur-rich kerogen and oil as well as thermochemical sulfate reduction (TSR). The latter is discussed here. Understanding and predicting the occurrence of reduced sulfur in the form of H<sub>2</sub>S is of special interest due to its corrosive properties and its volatile and toxic nature.

The overall net reaction scheme of TSR can be compiled as:



Sulfate ions are assumed to dissolve from the surrounding rock matrix (e.g. from an overlying anhydrite seal) and are assumed to be the origin of most of the sulfur species. This net scheme is very basic. It does not account for the amount of partially reduced sulfur within the oil for intermediate reduction steps.

Detailed laboratory studies to reveal the nature of TSR have been performed in the past. Earlier workers (Ma et al., 2008; Zhang et al., 2007, Zhang et al., 2008; and Tang, 2009) have proposed a scheme for TSR that additionally incorporates Mg<sup>2+</sup> ions as a catalyst and Ca<sup>2+</sup> for imbibition into the reaction scheme. A kinetic scheme for quantitative modeling of TSR was finally constructed from laboratory data (Ellis et

al., 2007). This scheme accounts for the concentration of partially reduced sulfur in the HC phase and for the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  ions. Resulting  $\text{H}_2\text{S}$  yields can be extrapolated to geological timescales and calculated for arbitrary temperature histories ([Figure 1](#)).

Additional approximations and assumptions must be taken into account for applications of this scheme in petroleum systems modeling. Most important is the assumption that  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  ions are available in the HC phase and are not separated from the HCs by dissolution into pore water only. This might be justified by equilibrium dissolution reactions between all phases that equilibrate on timescales shorter than the TSR reaction kinetics. This has the important consequence that the sulfate is not consumed; it is continuously replenished from the adjacent sulfate-rich rocks. When compared with primary cracking of kerogen to oil, in which the oil-limiting quantity is the amount of kerogen, for TSR, the available oil is the limiting factor. Due to the fact that the prediction of HCs in place might be uncertain in many cases, this might be a strongly limiting factor for quantitative modeling of TSR. Another important approximation is the missing feedback of the TSR reaction to the sulfur concentration within the oil or the  $\text{Ca}^{2+}$  concentration (i.e. the resulting  $\text{CO}_2$  might dissolve into the pore water and react with  $\text{Ca}^{2+}$  and  $\text{OH}^-$  forming calcite, which reduces the  $\text{Ca}^{2+}$  concentration). However, it can be assumed in many cases that  $\text{CO}_2$  is effectively removed from the system and, in the absence of further information, it might be assumed that all rate-determining concentrations are constant. The most problematic point is the destiny of the resulting  $\text{H}_2\text{S}$ . In the case of iron-bearing rocks,  $\text{H}_2\text{S}$  might directly be destroyed. Alternatively, when iron is not present, it might dissolve into the HC phases accompanying migrating petroleum.

For effective handling of these additional complications in petroleum systems modeling, we propose a two-step approach for modeling of TSR on geological timescales within basins. In the first step we calculate an  $\text{H}_2\text{S}$  risk based on the “virtual” assumption that oil is available everywhere and throughout geological time in the basin ([Figure 2](#)). This risk has a similar meaning as a “virtual” overall transformation ratio of kerogen that could be available for oil generation everywhere. This  $\text{H}_2\text{S}$  risk allows formations to be excluded in which TSR could not have taken place. Additionally, this calculation does not need a basin model with an HC distribution in place, which is often not available. In the second step we calculate a full  $\text{H}_2\text{S}$  yield with consideration of the HC destruction and a balance of all masses. The dissolution of the  $\text{H}_2\text{S}$  component into the HC phases is calculated and taken into account in all relevant modeling steps, especially for migration. This approach to modeling  $\text{H}_2\text{S}$  will be demonstrated using a 3D case study, illustrating the impact of various input parameters on the calculated  $\text{H}_2\text{S}$  concentrations in hydrocarbon accumulations.

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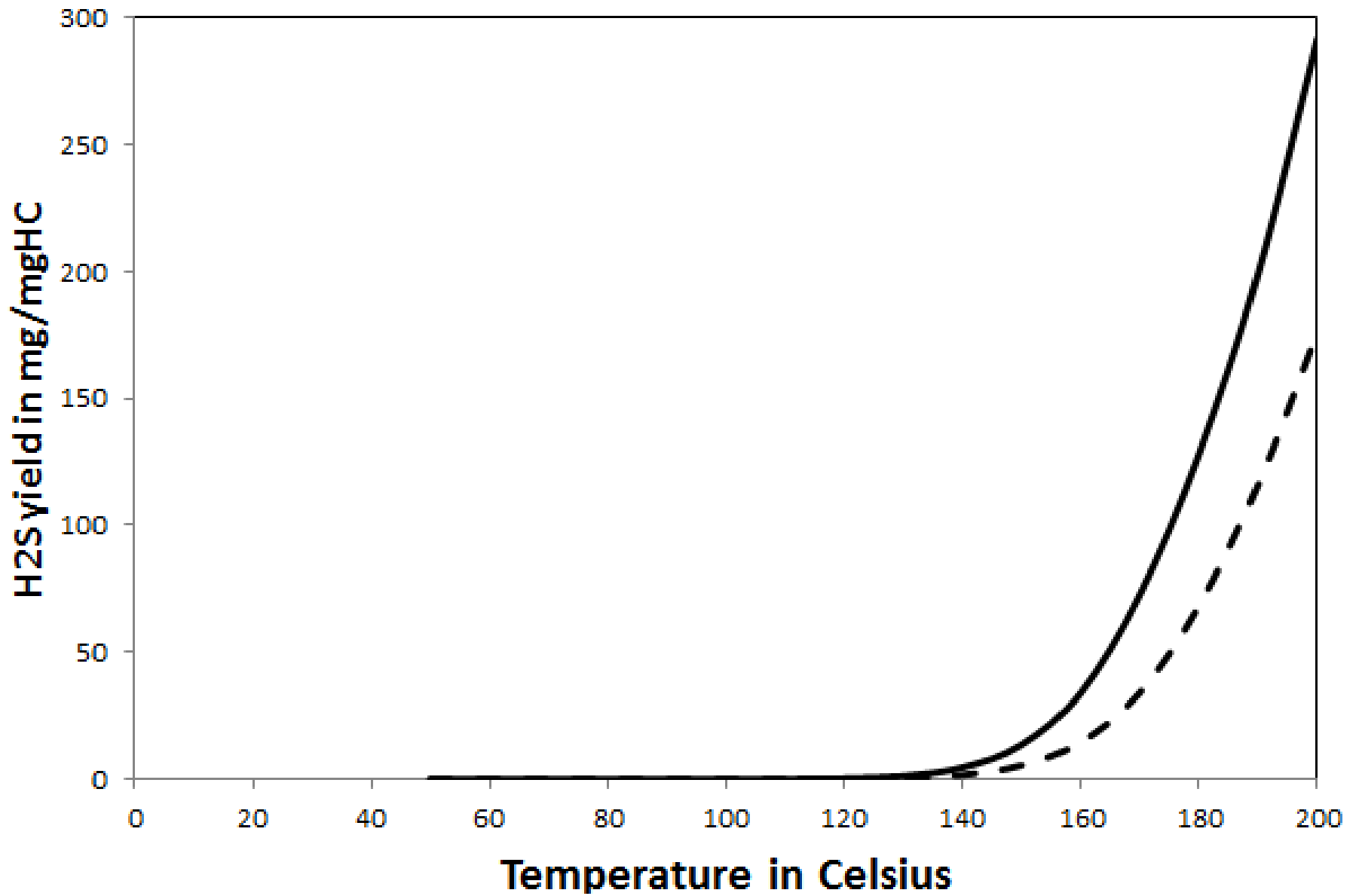


Figure 1. Two examples for H<sub>2</sub>S yield in mg/gHC for the following concentrations: sulfur 2%, SO<sub>4</sub><sup>2-</sup>: 0.05, Ca<sup>2+</sup>: 0.1, Mg<sup>2+</sup>: 0.5 solid, and 0.1 dashed (the figure is calculated with a heating rate of 2 degrees Celsius/Ma).

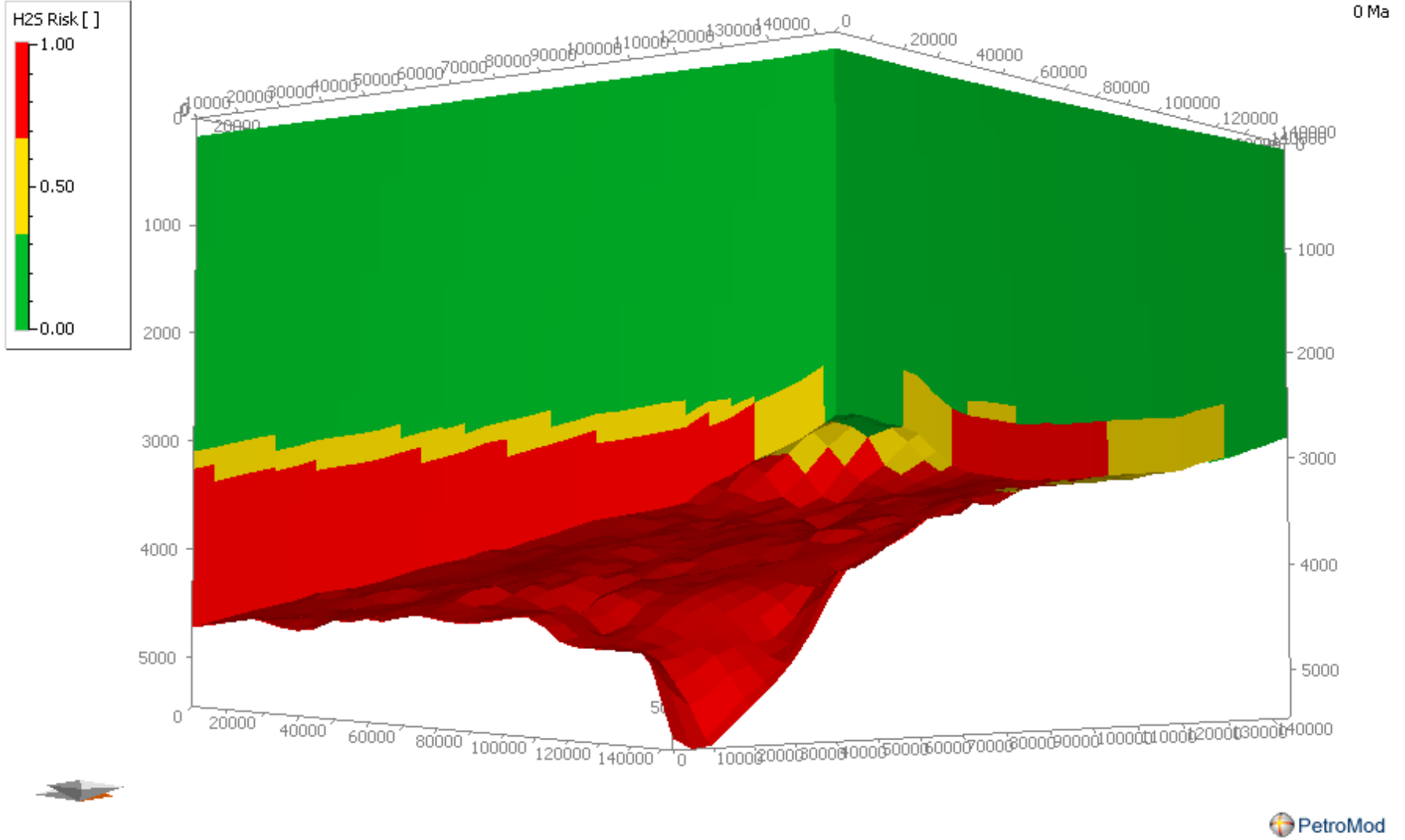


Figure 2. H<sub>2</sub>S risk in an example model, sampled into low, medium, and high risk.