

Thermochemical Sulfate Reduction (TSR): H₂S Risk Assessment at the Basin Scales*

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Abstract

High concentrations (>10vol% in reservoirs) of hydrogen sulfide (H₂S), a toxic and economically-damaging gas, result from thermochemical sulfate reduction (TSR) of petroleum. TSR occurs in high temperature carbonate reservoirs, and is very detrimental to the quality and the volume of hydrocarbon resources. Therefore, accurate TSR modeling is important to lower the risks during petroleum E&P. TSR involves complex redox reactions, that lead to petroleum oxidation and reduction of sulfates. The main products of reaction are either volatile (carbon dioxide (CO₂), H₂S) or solid (carbonate cements, pyrobitumen). The volatile products may migrate up from deeper reservoirs in both the gas and solution (either in water or in oil) phase. We developed a post-calculator approach integrated to the TemisFlow software, in order to assess maximum H₂S amounts resulting from TSR. The model is based on a mass balance approach according to the overall chemical reaction which has been first proposed by Uteyev (2011): $8 \text{ C}_n\text{H}_m + (4n+m) \text{ CaSO}_4 = (4n+m) \text{ CaCO}_3 + (4n+m) \text{ H}_2\text{S} + (4n-m) \text{ CO}_2 + (3m - 4n) \text{ H}_2\text{O}$. The stoichiometry of the reaction is clearly related to H/C ratio of the hydrocarbon. Water may either be consumed or produced by the reaction. Temperature, pressure, porosity, HC amount, and salinity are inherited from the TemisFlow calculator. A necessary additional input is the map of sulfate minerals in the basin. The model outputs are H₂S and CO₂ quantities, as well as their distribution in a gas phase or dissolved in the basinal brine. The volume of dissolved sulfate and the volume of precipitated calcite are also computed, and the porosity evolution related to the TSR reaction is assessed. An identification of areas where H₂S is expected to be present is then workable. Devonian carbonate reservoirs of the Nisku and Leduc formations (Alberta) include HC fields that experienced TSR and may contain up to 30% of H₂S. A 3D model, taking into account subsidence history and subsequent erosional profiles, of the Alberta foreland basin has been built. Results provide the timing of the Devonian petroleum system accounting for the HC charges of Devonian-Mississippian carbonate reservoirs. This study moreover investigates the impact of critical parameters (oil composition, salinity, H/C) on the production of H₂S by TSR in the Devonian Formations. Our numerical results are compared to wells data and clearly show that the H₂S production occurred mainly before the last erosion.

References Cited

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THERMOCHEMICAL SULFATE REDUCTION (TSR): H₂S RISK ASSESSMENT AT THE BASIN SCALES

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OVERVIEW

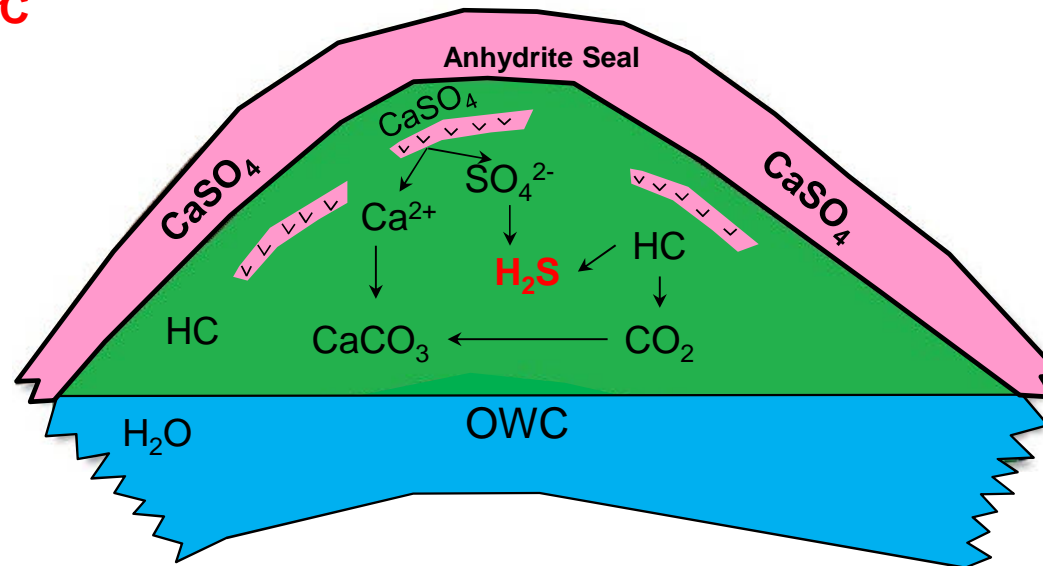
RESPONSIBLE
OIL AND GAS

- What is TSR?
- TSR risk index within TemisFlow™
 - Assessment of the reaction progress
 - Assessment of the masses of the reaction products
- Validation/discussion based on Alberta foreland basin – Nisku Devonian formation
- Conclusion and perspectives

WHAT IS THERMOCHEMICAL SULFATE REDUCTION (TSR)?

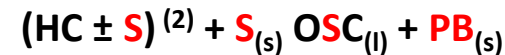
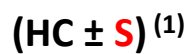
RESPONSIBLE
OIL AND GAS

Temperature > 110°C



Complex series of redox reactions

Within Carbonate (Dolomite) reservoir



Enriched in S

- Industrial context:

- TSR increases the risk in exploration

- Consequences :

- A strong decrease in the hydrocarbon potential of a reservoir due to oxidation of the oil (leading to CO₂ and carbonates).
 - A strong decrease of the quality of the produced fluids due to the formation of large amounts of H₂S (and OSC, PB)
 - A strong increase of production costs due to the highly toxicity and corrosion induced by H₂S

● 2 types of calculations

● First step of *TSR risk* - **Assessment of the reaction progress**

- based on a HC residence time within the TSR conditions
- Time window of TSR reaction = TSR occurrence probability

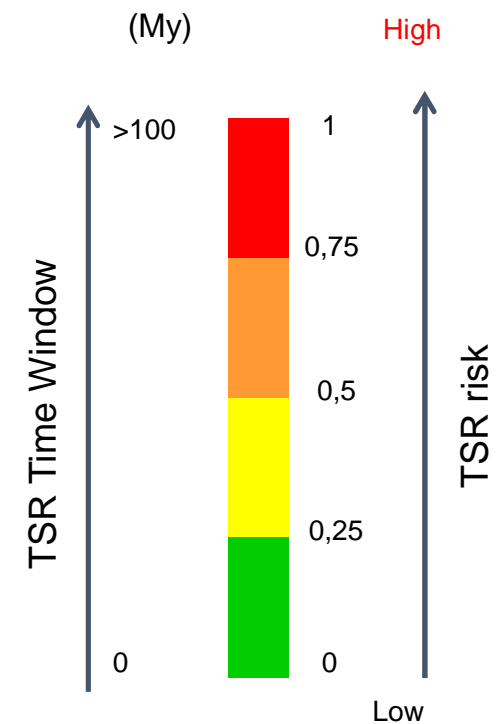
● Second step of *TSR risk* - **Assessment of the masses of the reaction products**

- based on a mass balance calculation by using a stoichiometric equation of sulfates reduction into H_2S
- Mass of fluids : HC, H_2S , CO_2
- Mass of solids : Sulfate, Carbonate

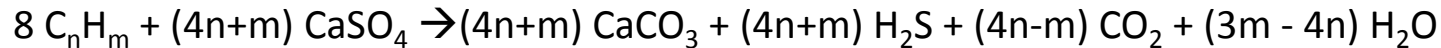
FIRST STEP: ASSESSMENT OF THE REACTION PROGRESS

RESPONSIBLE
OIL AND GAS

- **Input parameters** based on geological data (Nisku (Canada), Smackover (USA), Khuff (Abu Dhabi), ...)
 - Temperature : $T^{\circ}\text{C} > T_{\text{user}}$ (default 110°C)
 - Oil Saturation: $S_{\text{min}} (10\%) < \text{Soil} (\%) < S_{\text{max}} (90\%)$
 - Lithofacies: Sulfates source **Anhydrite %**
- **Output parameters**
 - Residence time of a cell at the TSR conditions → **TSR Time Window** in My
 - TSR Risk assessment (normalized index)
 - Equivalent of a reaction progress or TSR occurrence probability
 - Computed at present day and through geological time
 - Allow to identify the onset of the reaction and maximum occurrence probability time



SECOND STEP : ASSESSMENT OF THE MASSES OF THE REACTION PRODUCTS



Input parameters (necessary conditions)

- Parameters defined by the user
 - Maximum of HC consumption by TSR reaction (directly linked to H/C ratio)
- Parameters issued from basin modelling
 - Pressure, Temperature and salinity for thermodynamical calculation
 - Masses of HC from migration calculation
- Possibility to control the reaction progress by using the TSR occurrence probability

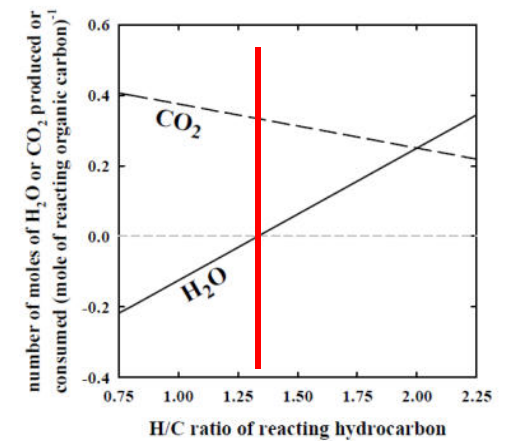
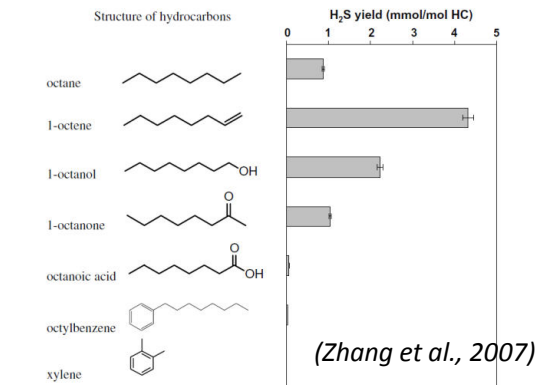
Output parameters

- Complete mass balance:
 - Mass of HC and Anhydrite consumed
 - Total Mass of H_2S and CO_2 distributed in soluble and gaseous forms
 - Mass of Carbonate precipitated
- Complete volumetric balance
 - Porosity variation as a function of anhydrite and carbonate summary
 - Volume of gases in the available porespace → qualitative information on cap rock integrity

Computation in a post-processing from migration calculation

- No migration of the products

RESPONSIBLE OIL AND GAS



(Uteyev, 2011)

CASE STUDY – ALBERTA BASIN

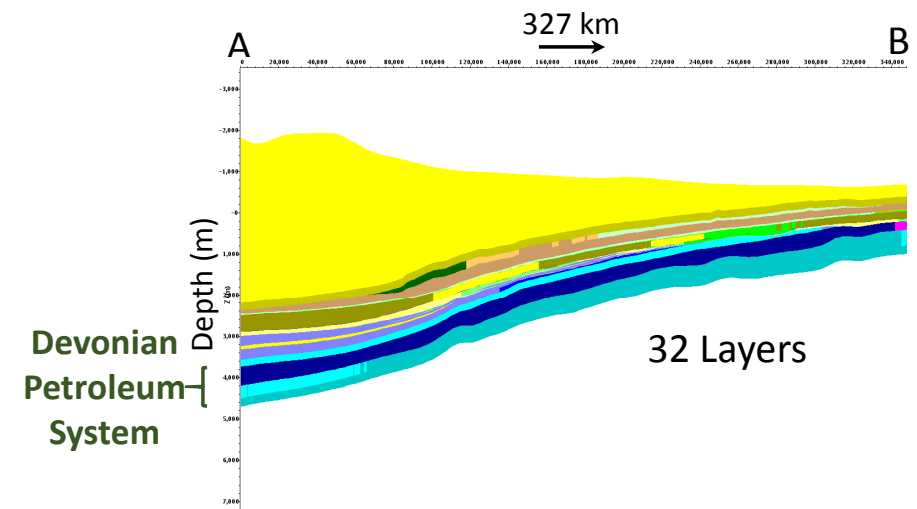
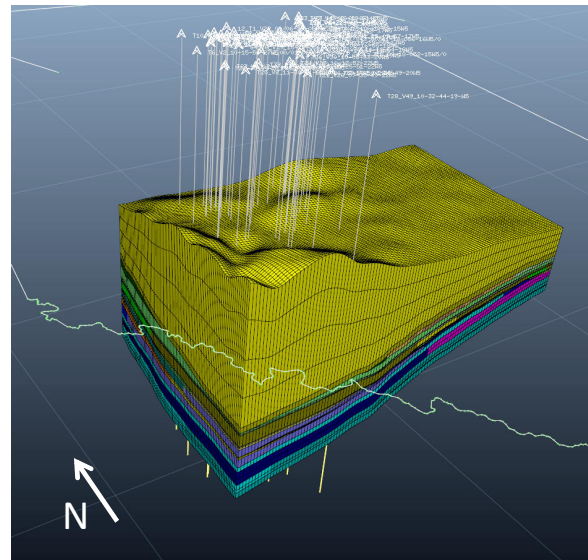
RESPONSIBLE
OIL AND GAS

3D model of Alberta foreland basin (West of Edmonton city)

Canada : Nisku/Leduc Formation, Devonien
Up to 90% H₂S, T = 125-145°C



Study Area



ASSESSMENT OF THE REACTION PROGRESS AT NISKU FM.

RESPONSIBLE
OIL AND GAS

70My

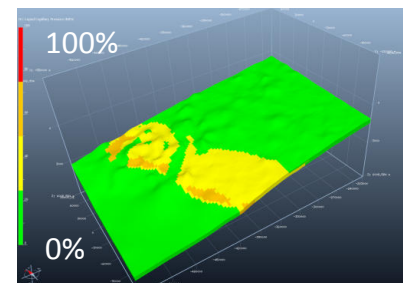
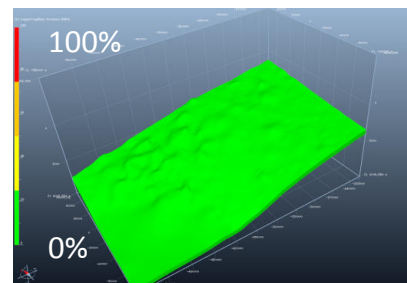
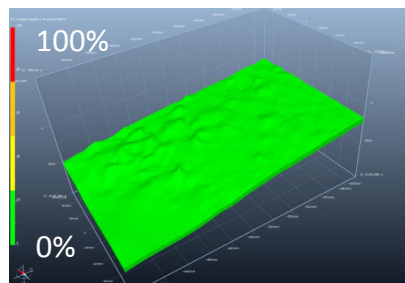
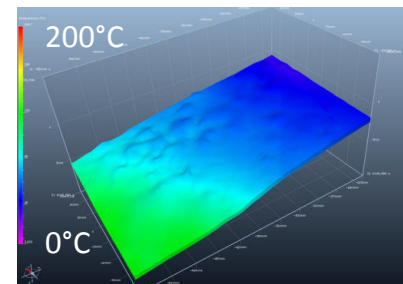
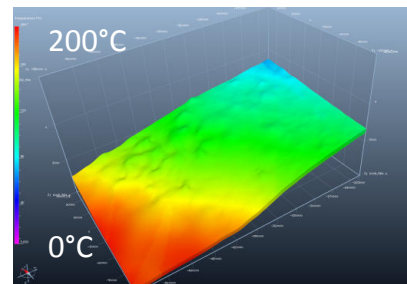
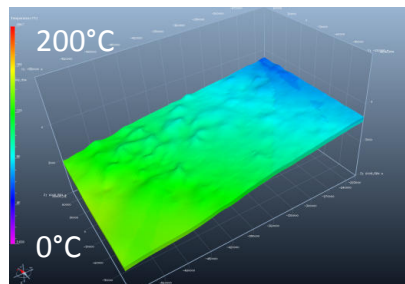
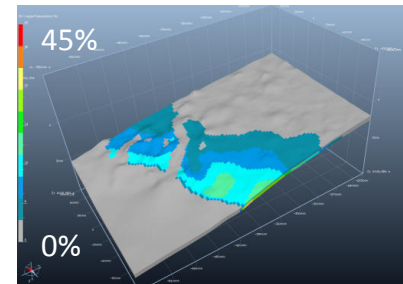
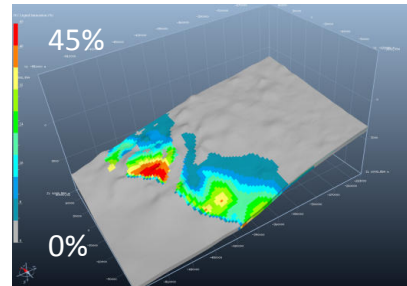
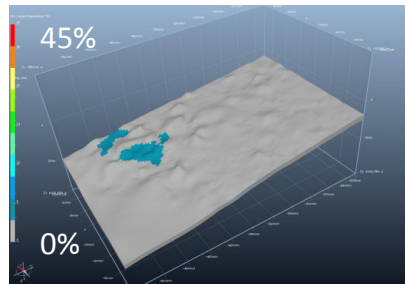
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HC saturation

Temperature

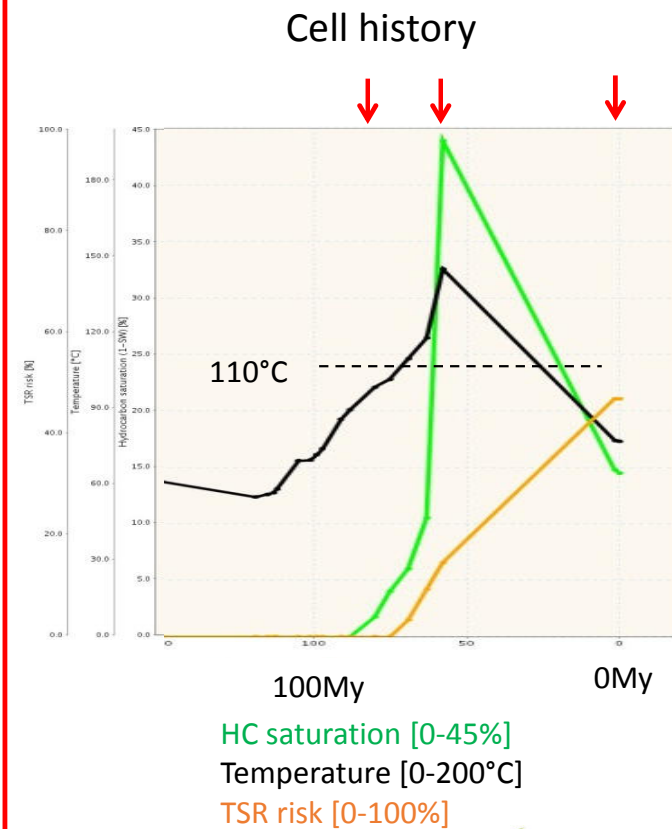
TSR risk



burial

Max burial

uplift



ASSESSMENT OF THE H₂S MASSES OF THE REACTION PRODUCTS AT NISKU FM.

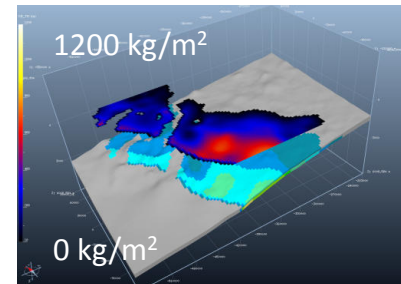
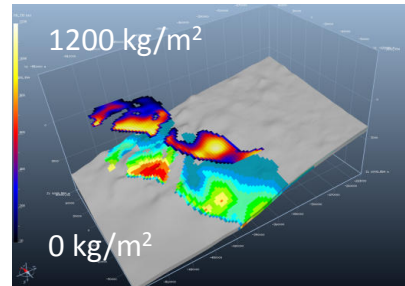
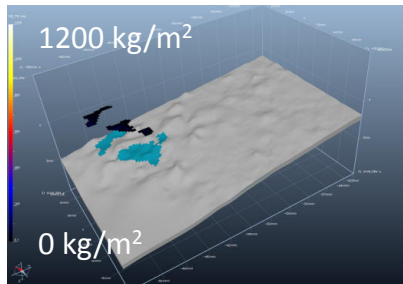
RESPONSIBLE
OIL AND GAS

70My

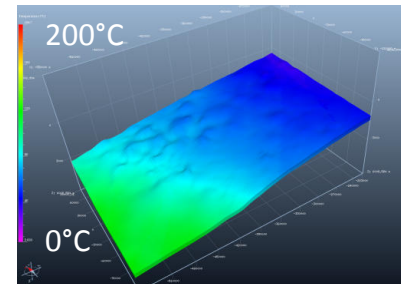
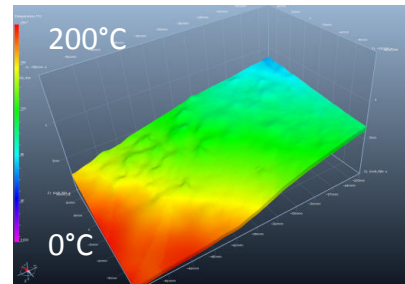
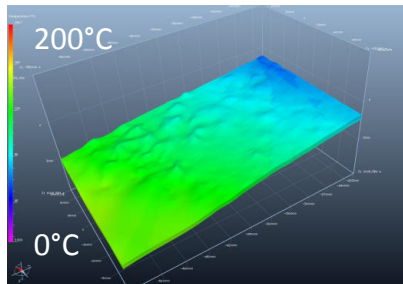
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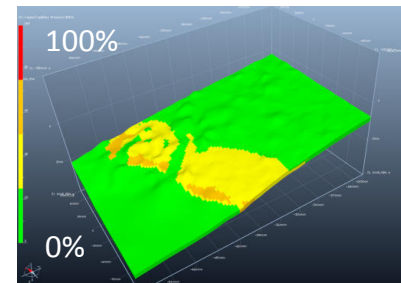
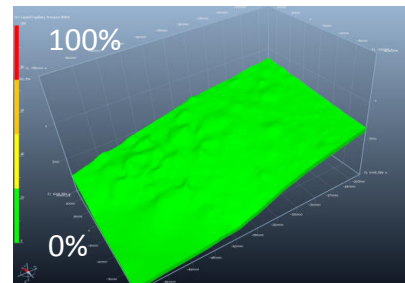
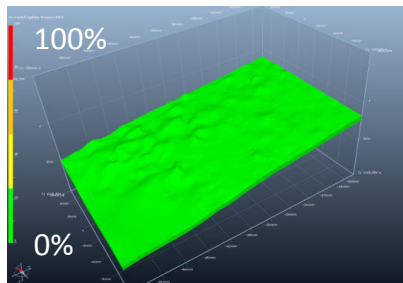
H₂S gas mass



Temperature



TSR risk



Hypothesis

- Post-pro computed by using HC saturation only (without taking into account TSR risk)

Conclusion

- H₂S gas generation does not represent a kinetic reaction

ASSESSMENT OF THE H₂S MASSES OF THE REACTION PRODUCTS AT NISKU FM.

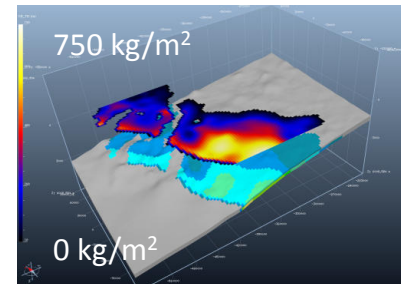
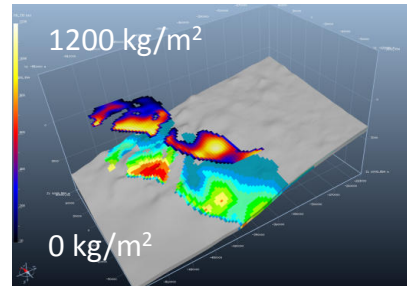
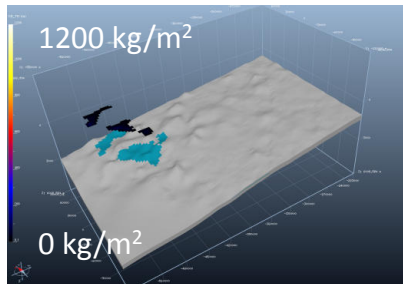
RESPONSIBLE
OIL AND GAS

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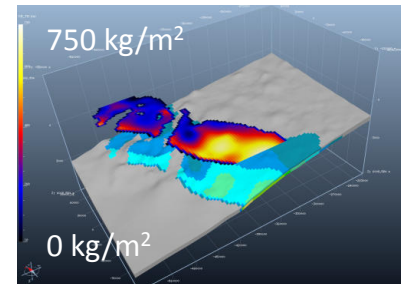
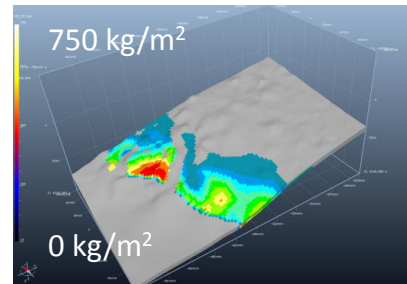
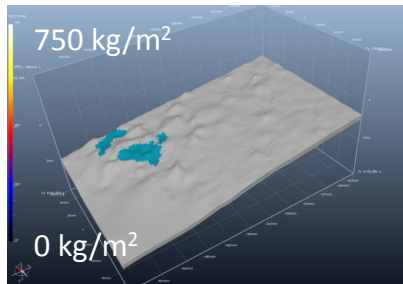
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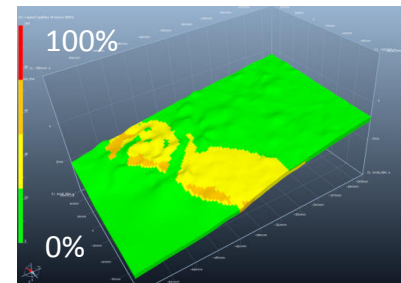
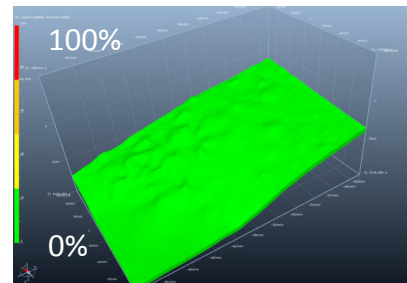
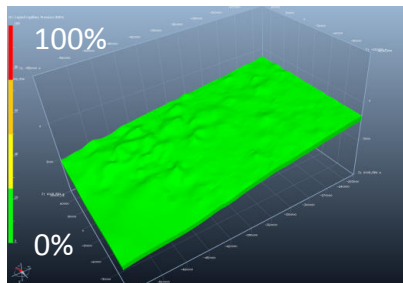
H₂S gas mass



H₂S gas mass



TSR risk

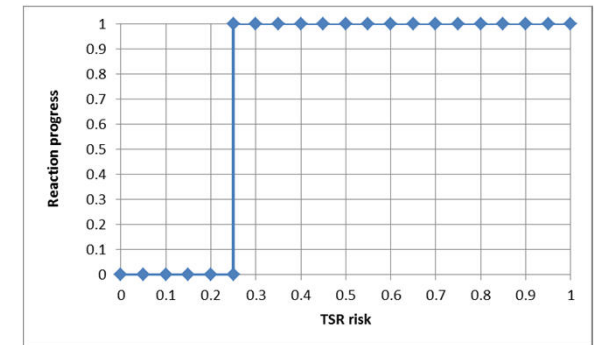


Hypothesis

- Post-pro computed by using HC saturation + starting the reaction when TSR risk is 25%

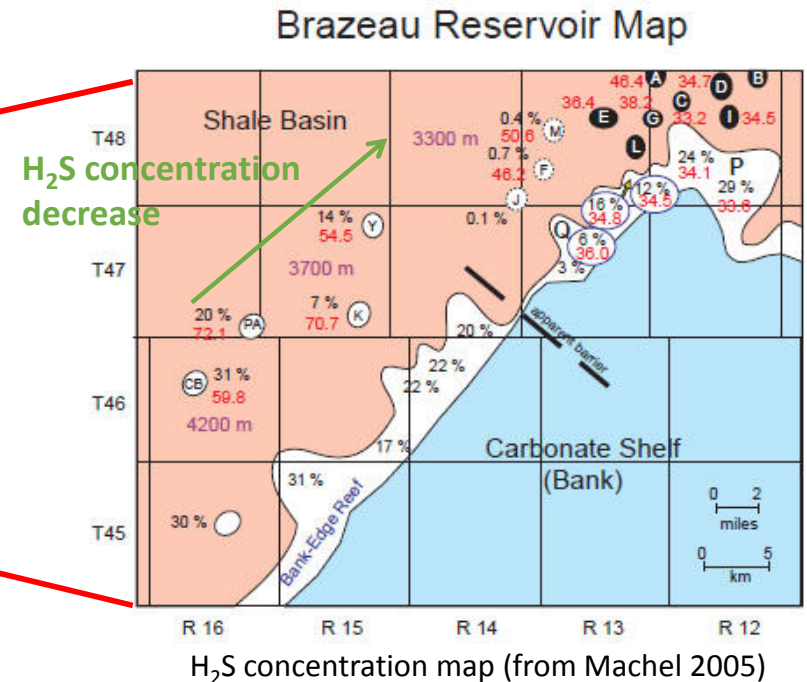
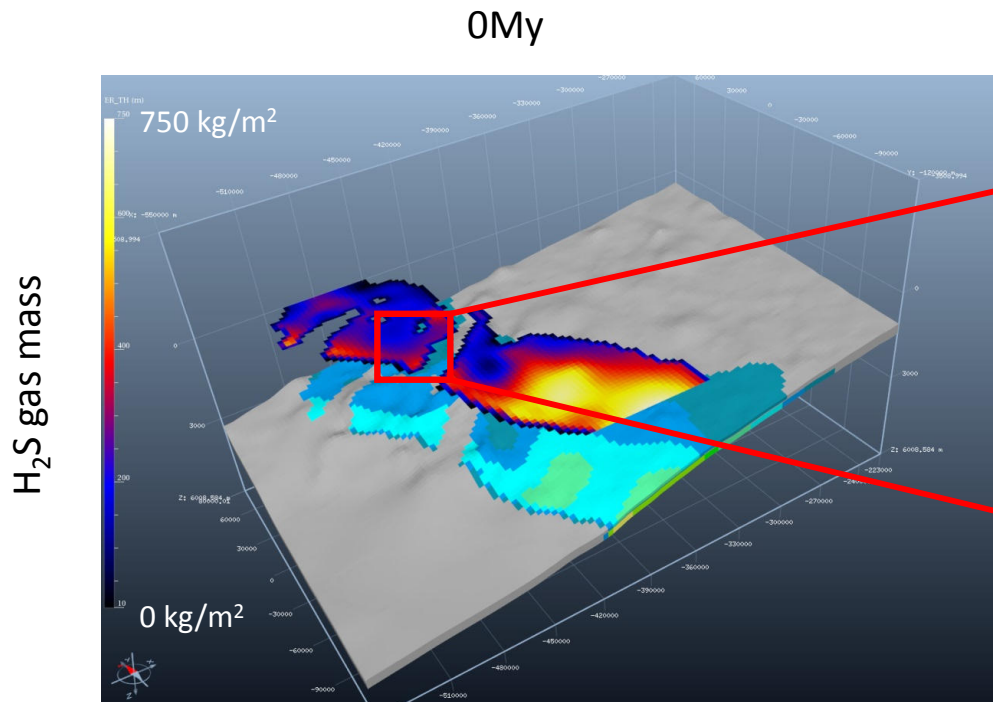
Conclusion

- H₂S gas generation better represents a kinetic reaction



ASSESSMENT OF THE H₂S MASSES OF THE REACTION PRODUCTS AT NISKU FM.

RESPONSIBLE
OIL AND GAS



- General H₂S mass trend reproduced
- No migration of generated H₂S tends to overestimate of H₂S quantities

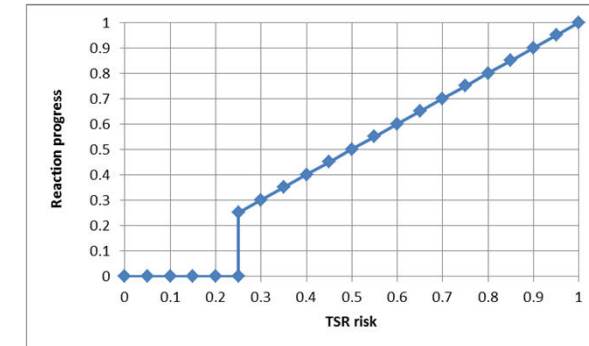
- Average H₂S Masses from Machel (2005): 300 kg/m²
 - H₂S gas = 140 kg/m²
 - H₂S dissolved = 160 kg/m²

ASSESSMENT OF THE H₂S MASSES OF THE REACTION PRODUCTS AT 0MY

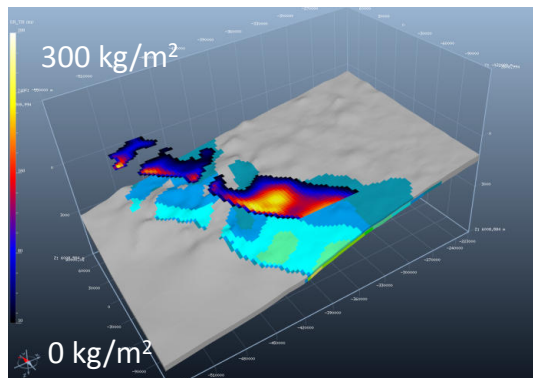
● Hypothesis

- Post-pro computed by using HC saturation + starting the reaction when TSR risk is 25% + ponderating the reaction by the TSR risk

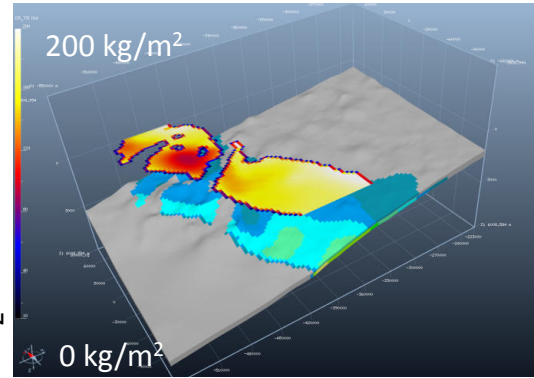
● Conclusion: H₂S masses in better agrement with measured data



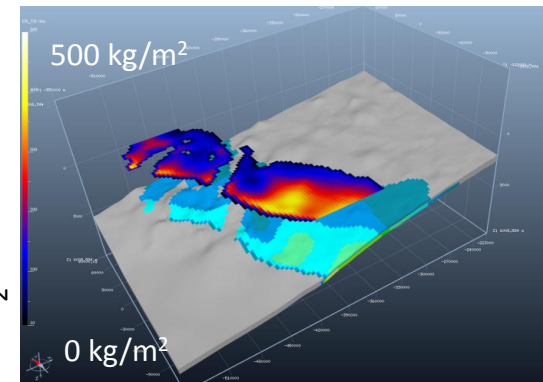
H₂S gas mass



H₂S dissolved mass

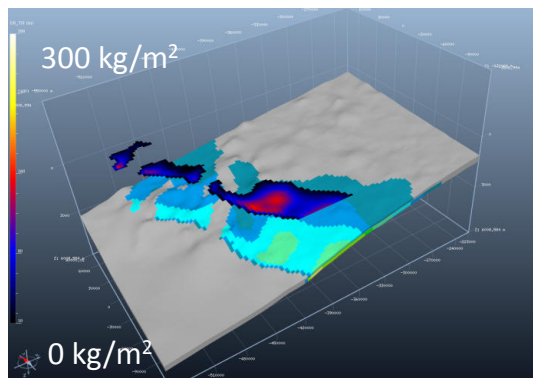


H₂S total mass

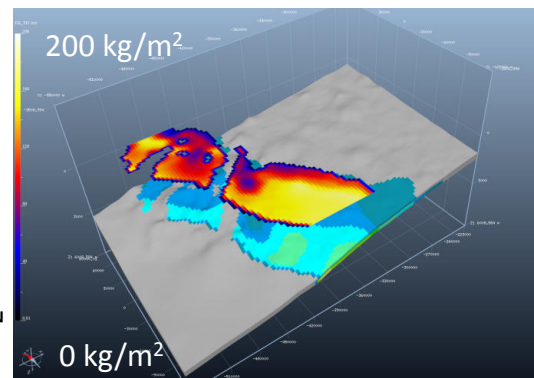


Light Oil
HC reaction
ratio: 80%

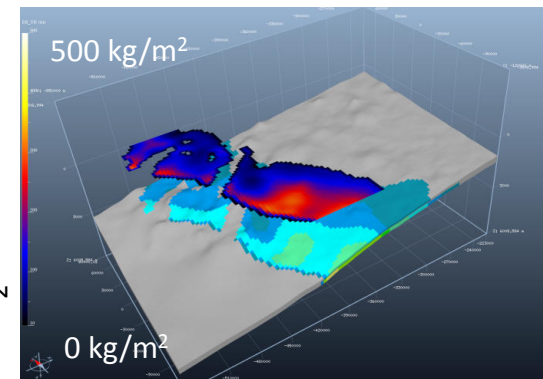
H₂S gas mass



H₂S dissolved mass

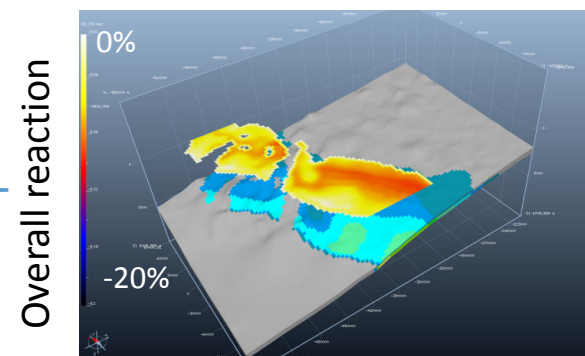
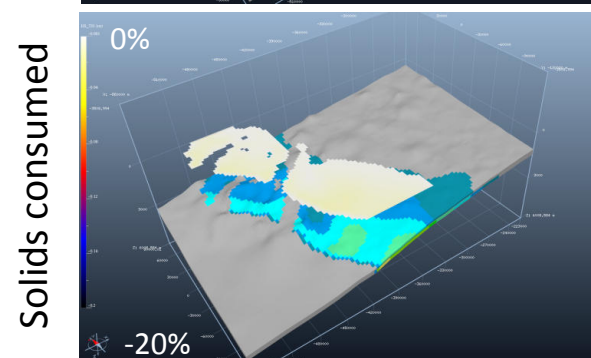
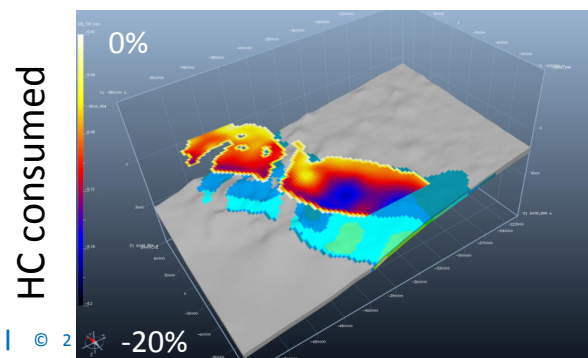
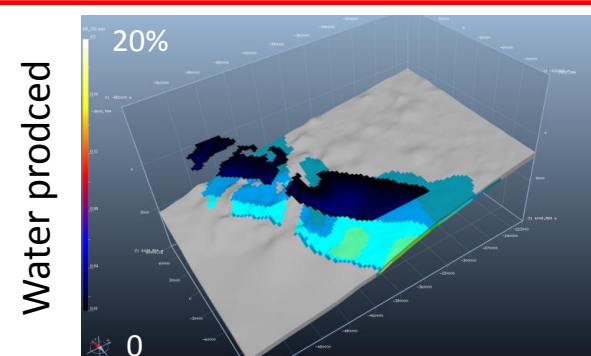
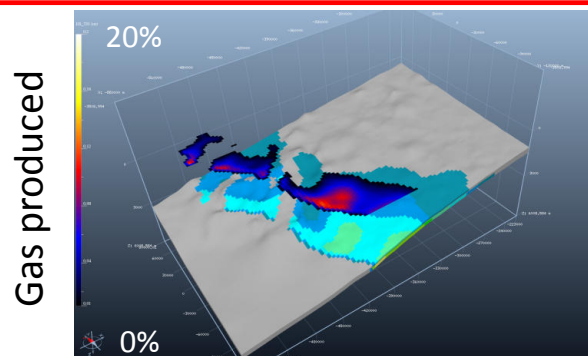
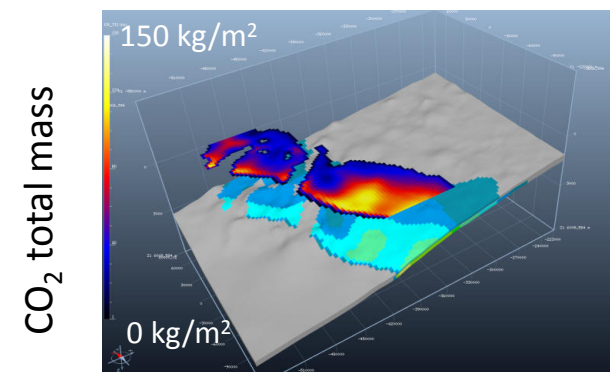
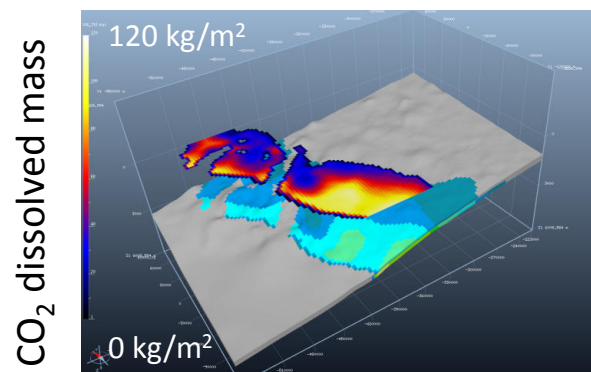
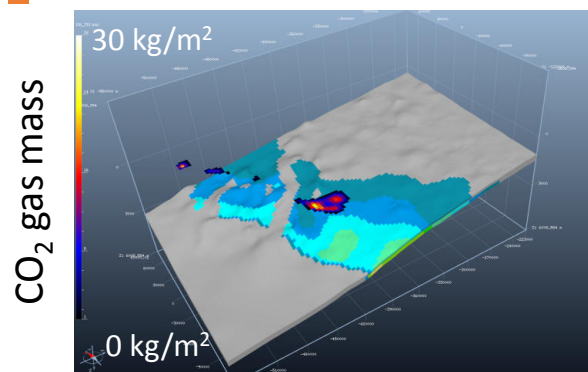
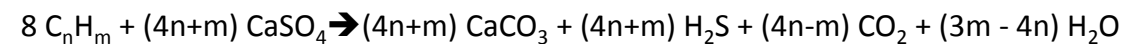


H₂S total mass



Medium Oil
HC reaction
ratio: 60%

OTHER RESULTS AT 0MY



- 2 types of calculations has been developped within TemisFlow™ to assess an H₂S risk from a TSR reaction
 - A first TSR risk on the commercial version:
 - **Assessment of the reaction progress** based on HC residence time within the TSR conditions
 - TSR Time Window (My) and TSR Risk assessment (/)
 - A second TSR risk under developpement:
 - **Assessment of the masses of the reaction products** based on a Stoechiometric equation of sulfates reduction
 - Mass/Volume of fluids (HC, H₂S, CO₂) and solids (Sulfate, Carbonate)
 - **Strengths**
 - The masses of produced H₂S and CO₂ are distributed between vapor and liquid phases
 - Compositional HC description can be used
 - Fast computation
 - **Weaknesses**
 - No migration
- Perspectives
 - migration module of TemisFlow™ in link the 3 phases flow under developpement
 - Continue the validation process with more quantitative data

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