

PS Acid Gas Risk Assessment at the Basin Scale*

**Xavier Guichet¹, Etienne Brosse¹, Isabelle Kowalewski¹, Pierre Bachaud¹,
Sylvie Wolf¹, and Nicolas Maurand¹**

Search and Discovery Article #51579 (2019)**

Posted July 15, 2019

*Adapted from poster presentation given at 2018 International Conference and Exhibition, Cape Town, South Africa, November 4-7, 2018

**Datapages © 2019. Serial rights given by author. For all other rights contact author directly. DOI:10.1306/51579Guichet2019

¹IFPEN, Rueil-Malmaison, France (nicolas.maurand@ifpen.fr)

Abstract

The presence of acid gases such as hydrogen sulfide (H₂S) and/or carbon dioxide (CO₂) in Exploration & Production drastically impacts the economics and human risks of a project. Being able to predict the presence of these gases in an early phase of an E&P project is thus very important to manage the risk and help the decision making. On one hand, the highest CO₂ contents (>40vol. %) are only explained by inorganic sources, either from a mantle or crust origin. A new model integrated within TemisFlowTM software has been developed to manage both fluxes of CO₂ entering the sediments in contact with the basement, and CO₂ produced by metamorphic reactions occurring in specific CO₂-prone sediments often present in the hot deep synrift facies. Once generated, the migration of CO₂ is modelled by advection both in gas phase and dissolved in the formation water. Dissolution equilibrium follows Duan et al. (2003) equation considering the effect of formation waters salinity, temperature and pressure. This allows to simulate basin-scale CO₂ distribution either in a gas phase or dissolved in the brine, through the geological times. On the other hand, high concentrations (>10vol. %) of H₂S, result from Thermochemical Sulfate Reduction (TSR) of petroleum. TSR occurs in specific high temperature H₂S-prone carbonate rich reservoirs and is very detrimental to the quality and the volume of hydrocarbon resources. To answer the H₂S risk assessment, a dedicated model has been developed. It is based on a mass balance equation according to the overall chemical reaction which has been first proposed by Uteyev (2011). The H₂S generated is related to H/C ratio of the hydrocarbon and depends strongly on sulfate minerals texture and distribution in the basin. The model allows to simulate H₂S and CO₂ quantities, as well as their distribution in a gas phase or dissolved in the basinal brine. The volume of dissolved sulfate, precipitated calcite, and the porosity evolution related to the TSR reaction is also assessed. The management of the CO₂ risk will be illustrated by cases studies inspired by (1) basin model of the Brazilian passive margins of the Central Segment of the South Atlantic Ocean basin for mantellic CO₂, (2) hot sedimentary basin of the South China Sea for metamorphic CO₂. The H₂S risk will be illustrated by a 3D basin model of Devonian carbonate reservoirs of the Nisku and Leduc formations (Alberta) that experienced TSR and may contain up to 30% of H₂S.

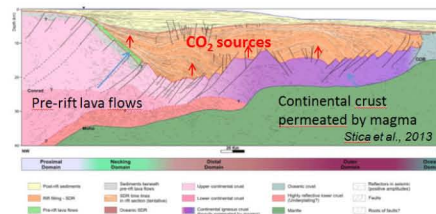
Acid gas risk assessment at the basin scale

Xavier Guichet, Etienne Brosse, Isabelle Kowalewski, Pierre Bachaud, Sylvie Wolf, and Nicolas Maurand

Mantellic CO₂

Problematic

CO₂ is one of the main volatile compounds in the lithosphere with water and methane. The origin of CO₂ can be organic or inorganic, but the high CO₂ concentrations observed in petroleum reservoirs always show an inorganic origin, i.e. of either metamorphic or mantle origin. The purpose of this paper is to (1) propose a consideration of mantellic CO₂ in basin modeling by imposing a flow condition at the base of the sedimentary pile, (2) illustrate the behavior of the CO₂ flowing by advection either in vapor form or in dissolved form in basinal brines.



Flux of CO₂

The mantellic CO₂ fluxes from the lithospheric mantle are managed via a Neumann condition at the base of the basin. This boundary condition is expressed in kg/m²/Ma and it is possible to specify a constant or spatially variable flux, constant or variable in time.

To identify the origin of CO₂, the noble gases are measured in the gas phase of the reservoir. Classically, helium isotopic ratio measurements are made to distinguish the mantle or radiogenic origin (characterizing the crust). The isotopic ratio $R = {}^3\text{He}/{}^4\text{He}$ of the mantellic helium is about 10^{-5} (or $R/R_a \sim 10^1$ with $R_a = 10^{-6}$ the ratio ${}^3\text{He}/{}^4\text{He}$ of the air), crustal helium about 10^{-8} or $R/R_a \sim 10^{-2}$ (Torgersen, 1993). A possibility for estimating mantellic CO₂ fluxes is therefore to estimate ${}^3\text{He}$ fluxes and to transfer them into CO₂ fluxes.

From R/R_a plot, the presence of mantellic He is between a flux of ${}^3\text{He}$ greater than 10^4 atoms/m²/s and a flux of 10^6 atoms/m²/s which appears as an upper bound for the ${}^3\text{He}$ flux in the sense that whatever the crustal He flux is, the mantle signature will dominate. These two values allow to define a framework for the CO₂ flux values of mantle origin by considering the ${}^3\text{He}/\text{CO}_2$ ratio of the mantle constant and of the order of 10^{-9} (Marty and Jambon, 1986).

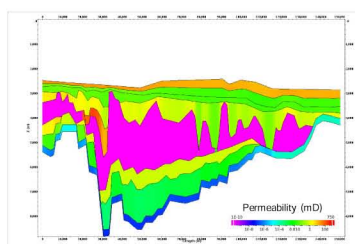
$$10^4 < F_{{}^3\text{He}} < 10^6 \text{ atoms/m}^2/\text{s}$$

$$10^{13} < F_{\text{CO}_2} < 10^{15} \text{ atoms/m}^2/\text{s}$$

Approximately: $20 < F_{\text{CO}_2} < 2000 \text{ kg/m}^2/\text{Ma}$

Dissolution of CO₂

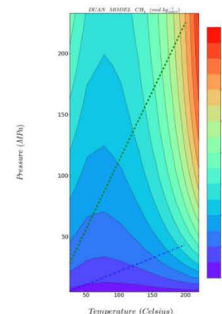
The thermodynamic parameters used for the solubilization of CO₂ in brines are extracted from Duan and Sun (2003) equation, and make it possible to calculate the solubility of CO₂ for temperatures ranging from 0° C to 250° C, pressures ranging from 0 to 200 MPa, and salinities (NaCl equivalent) ranging from 0 to 235 g/L. The masses of dissolved CO₂ can be quite high; for example at 50 MPa and 210° C the solubility of CO₂ in pure water is 120 g/L, and 40 g/L in NaCl brine of 200 g/L salinity. The dissolved CO₂ is considered to remain in the form of CO_{2(aq)} and chemically inert, which is a very strong hypothesis since CO₂ is very reactive and acts as a weak acid via equilibria with the species H₂CO₃, HCO₃⁻ and CO₃²⁻.



2D conceptual section of brazilian margin

The new calculator has been tested on a conceptual section of the Brazilian margin of the Santos Basin inspired by sections presented in congress (for example Carminatti et al., 2008)

Left Figure shows the geometry of the section in the present and the distribution of facies used. It has to notice the thick layer of salt (Ariri formation) in which windows have been installed to allow CO₂ to migrate into post-salt formations.



Modelling results

Right Figures show two series of calculations performed for constant CO₂ fluxes over time and uniformly distributed over about 2/3 of the section, these fluxes varying from 20, 200 to 2000 kg/m²/Ma. Top Figures show the results obtained for zero salinity, and bottom Figures show the results obtained for a salinity equal to 200g/L.

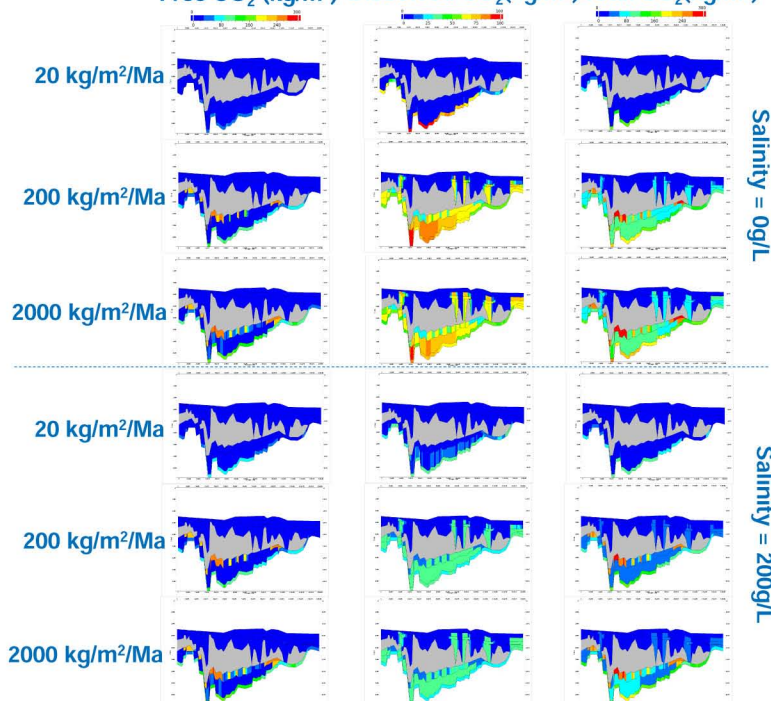
In the case of calculations performed for a CO₂ flow of 20 kg/m²/Ma constant throughout the formation of the basin, it appears that the total quantities of CO₂ present in the basin remain relatively low even with such a flow active on 115 Ma. In the case of a diffuse degassing this flow value could perhaps be used as a minimum value.

The calculator correctly responded to the increase in flow and supported the highest values. It can be observed that as soon as a continuous flow is achieved between the base and the top of the sediment, an increase in CO₂ flux become negligible for the accumulations.

The effect of formation water salinity has a direct impact on the CO₂ accumulation dissolved in water and as expected the higher the salinity, the lower the CO₂ can be dissolved.

In the case of degassing accompanying magmatic episodes, having shorter durations (a few million years), it will certainly be appropriate to use flows of the order of 100 kg/m²/Ma to generate appreciable amounts of CO₂ in the reservoirs. Studies of carbonate mineralization within matrix or faults could provide clues to better characterize the CO₂ fluxes in the history.

Free CO₂ (kg/m³) Dissolved CO₂(kg/m³) Total CO₂(kg/m³)

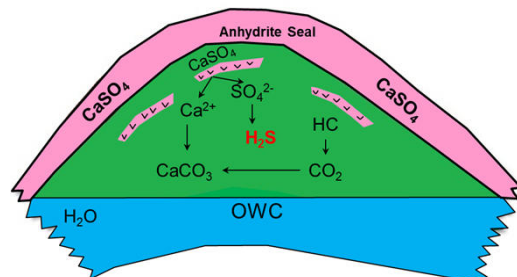


Acid gas risk assessment at the basin scale



What is Thermochemical Sulfate Reduction (TSR)?

TSR is a complex succession of free radical and redox reactions that occurs in deeply buried anhydrite-rich carbonate reservoirs during and/or after the migration of hydrocarbons under high temperatures (>110° C). The occurrence of this reaction leads to the formation of high amount of hydrogen sulfide (H₂S) by reduction of sulfates and to a decrease in the quality of the hydrocarbons by their oxidation, among others into carbon dioxide (CO₂) and organo sulfur compounds (OSC)

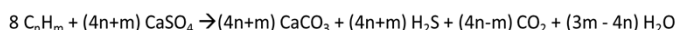


TSR risk index

To answer the H₂S risk assessment, a dedicated model has been developed within TemisFlow™ software (petroleum modeling software developed at IFPEN) with 2 types of calculations :

1- An **assessment of the reaction progress** based on a HC residence time within the TSR conditions. The principle is to correlate a Time window of TSR reaction into a TSR occurrence probability. This allows to provide a first risk index of the presence of H₂S in a reservoir.

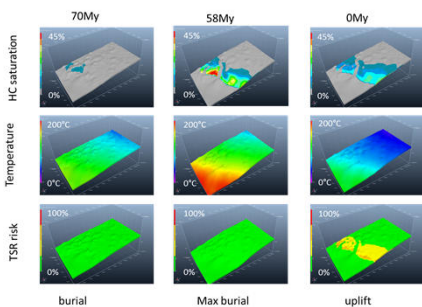
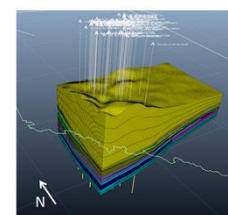
2- An **assessment of the masses of the reaction products** based on a mass balance calculation by using a stoichiometric equation of sulfates reduction into H₂S which has been first proposed by Uteyev. The result of the computation is the different masses of fluids (HC, H₂S, CO₂) and solids (Sulfate, Carbonate) generated/consumed by the reaction.



Case Study – Alberta basin

The Alberta Basin sits on a stable Precambrian platform and constitutes the foreland basin of the Rocky Mountains. During the Devonian time, the basin was subjected to the formation of extensive reefs and carbonate platforms (Nisku and Leduc formations).

The Devonian strata of the area were buried under a thick foreland basin succession due to the Laramide orogeny that ended in the early Tertiary. This burial promoted the thermal maturation of the Devonian source rock and the generation of hydrocarbons. Generated fluids migrated laterally northeastward through the carbonate complex in Leduc buildups and then in the overlying Nisku platform carbonates. Associated with the Laramide orogeny, the Alberta basin has been dominated by erosion (more than 3500 m close to the Rocky Mountains) from Paleocene onward leading to the progressive cooling of the basin.



Assessment of the reaction progress at Nisku Fm

A large dataset based on previous compilations and newly acquired data was integrated to build a 3D geological model of the basin. A specific emphasis was put on the lithostratigraphic description of Devonian strata using well and log data to build the 3D geological model. The model encompasses an area of approximately 65 400 km² and includes 32 geological intervals.

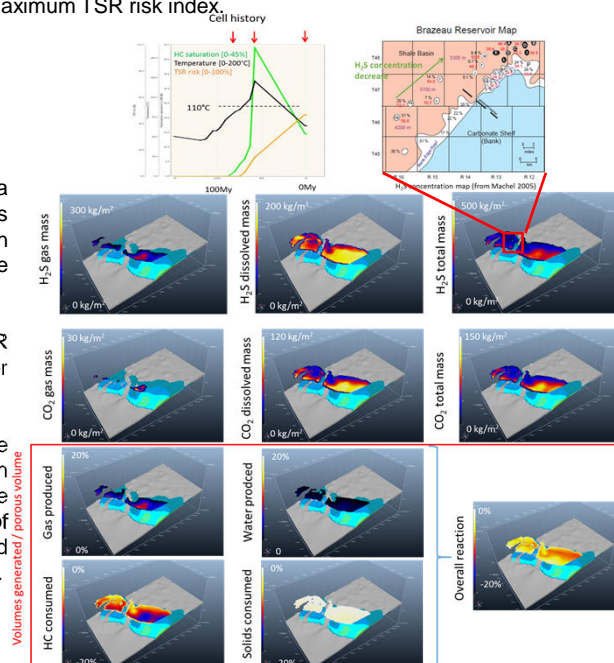
Pressure and temperature of the model were calibrated based on well data (vitrinite reflectance, temperature and pressure values at present day). The numerical results concluded to a most important TSR risk for the Nisku/Leduc intervals. The TSR risk increases with the burial occurring mainly during the Laramide orogeny. Then during the following uplift, the TSR reaction continues to occur as long as the TSR criteria are met leading to a maximum TSR risk index.

Assessment of the masses of the reaction products at Nisku Fm.

H₂S content in Leduc/Nisku formations across south central Alberta was calculated by a post-processing approach based on a mass balance equation using HC masses distribution obtained by a full Darcy migration simulation. According to the simulation assumptions, the average simulated H₂S masses are in the same order of magnitude and follow the same trends than the published values (Machel, 2005).

Computed H₂S/CO₂ amounts are controlled by the reaction progress by using the TSR occurrence probability. This allow to capture a "kinetic" effect of the reaction and better match observations.

The equation provides a complete mass balance of the reaction taking into account the mass of HC and Anhydrite consumed, the total mass of H₂S and CO₂ distributed in soluble and gaseous forms and the mass of Carbonate precipitated. A Complete volumetric balance can be calculated providing a porosity variation as a function of anhydrite and carbonate summary as well as a volume of the fluids (HC, gases and water) in the available pore space giving qualitative information on the cap rock integrity.



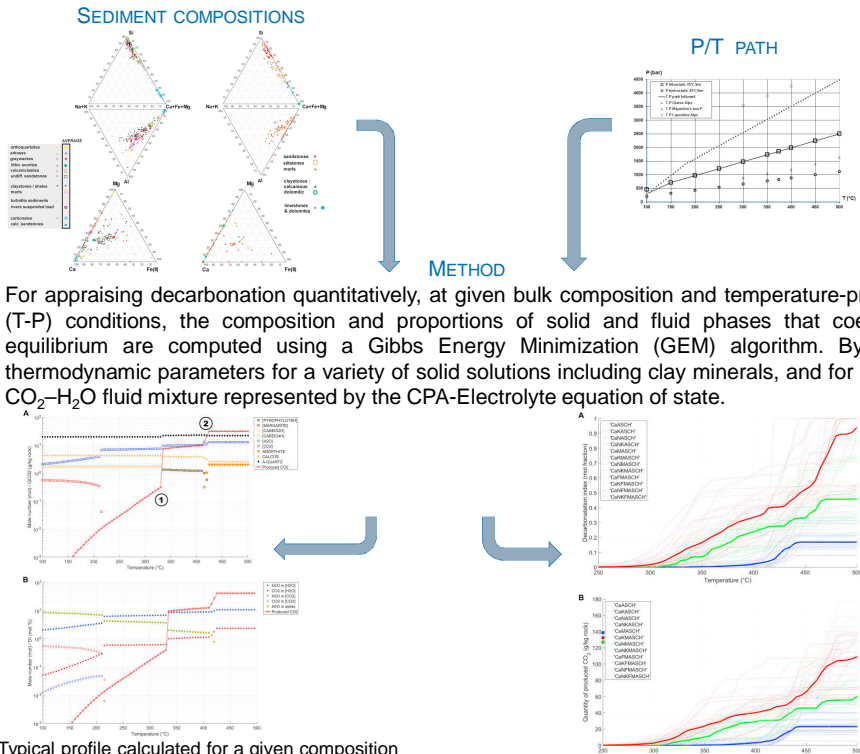
Acid gas risk assessment at the basin scale

Metamorphic CO₂

Problematic

The accumulation of CO₂ in some natural gas fields represents a risk for exploration, and calls for a way of integrating its occurrence in basin modelling. Among several possible sources we investigate mineral reactions able to take place within bottom sediments of particularly deep and hot sedimentary basins, i.e. at conditions of low-grade metamorphism (up to 500° C and 2500 bar). These reactions involve lithologies where carbonate and aluminosilicate minerals are combined to form a « mixed composition ».

Thermodynamic calculations



Typical profile calculated for a given composition along the chosen T-P path.

(a) Mole numbers of phases, and mass produced CO₂.

(b) Mole numbers of H₂O and CO₂ in the fluid phase(s) (two phases below 210° C/1.0 kbar, one supercritical phase above), and mole ratio between CO₂ present in the fluid at T/P, and CO₂ present in solid carbonates at 100° C/300 bar.

Effect of decarbonation reactions calculated for the model compositions, along the selected T-P path. It is expressed (a) as a decarbonation index ('DI'), and (b) as a massic production ('Q_{CO2}'). The median value is reported in bold type for three classes of system: 'Mg-Fe-free' (blue), 'Mg-bearing' (green) and 'Mg-Fe-bearing' (red).

Kinetic transposition

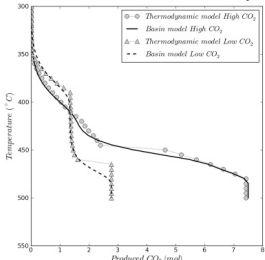
The variation of produced CO₂ with time (A) can be expressed as following:

$$\frac{\partial m_{CO_2}}{\partial t} = \frac{\partial m_{CO_2}}{\partial T} \cdot \frac{\partial T}{\partial t}$$

(A) (B) (C)

where (B) is the variation of produced CO₂ with temperature inferred from thermodynamic calculations, and (C) is the variation of the temperature with time according to the burial curve.

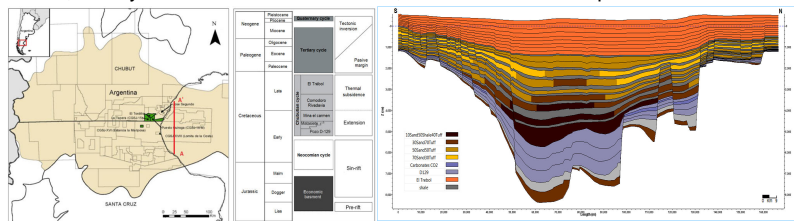
In basin modelling, sudden change of the mineral assemblage leading to an increase in the amount of CO₂ could induce numerical instabilities because of its non-continuous character along a temperature increase. To overcome this difficulty, a series of first-order kinetic steps is considered to reproduce the amount of CO₂ generated by the successive decarbonation reactions. With such a simplified procedure, even if the detail of mineral assemblages is not explicitly taken into account, the shape of the CO₂ production can be satisfactorily reproduced.



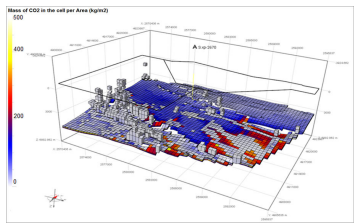
Comparison between two contrasted CO₂-prone lithologies. The 'Thermodynamic Model' shows CO₂ production calculated by the GEM thermodynamic approach. One source composition delivers less CO₂ than the other one, but the generation starts at lower temperature, i.e. sooner in the basin evolution. The 'Basin Model' represents the amount of CO₂ calculated with the basin-modelling formalism.

Basin Modelling

The San Jorge Basin is located in central Patagonia, between 44 and 47° S and 66 and 71° W. It covers a surface of approximately 170,000 km², with one third located offshore. The Somuncurá Massif bounds the basin towards the north, the Deseado Massif to the south, the continental margin of the Atlantic Ocean to the east and the Cordillera de Los Andes to the west. The basin developed during a Late Jurassic – Early Cretaceous extensional event related to the opening of the South Atlantic, and experienced Cenozoic reactivation and compression. Most of the hydrocarbon accumulations are found in the northern and southern flanks of the basin, with very few accumulations in the center, mainly due to lack of structuration, and less well developed reservoirs.



The models were generated using TemisFlow™. A first 2D model was built at basin scale to understand the basin history in terms of thermal stress and impact on source rocks maturity, timing of hydrocarbons expulsion and migration. Stratigraphic, lithological and geochemical data was integrated in this model to make it robust and reliable.



The 3D model was thus calibrated to the wells located in the area of interest, both in temperature and vitrinite reflectance. CO₂ sources were finally integrated in the model for simulation. Results allowed us to estimate the timing of CO₂ generation, expulsion, and eventually migration within the field.

Conclusion

A large range of decarbonation reactions is explored through a systematics involving 85 model compositions, and a unique T-P path typical of the targeted basins. We confirm that pure carbonate lithologies do not behave as CO₂ source in the conditions explored. In contrast, we demonstrate that mixed compositions are likely to yield CO₂ from successive mineral reactions, in which clay minerals play a prominent role. We also show that the temperature of incipient decarbonation, staggered over 325–425° C, depends on the Ca/Mg/Fe composition ratio of the bulk sediment. CO₂-prone reactions occurring from a selection of natural sediments are then presented.

* The authors would like to thank Tecpetrol for allowing the publication of this work and in particular Buchanan A.