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Impact of NO_2 co-injection on geological carbon sequestration

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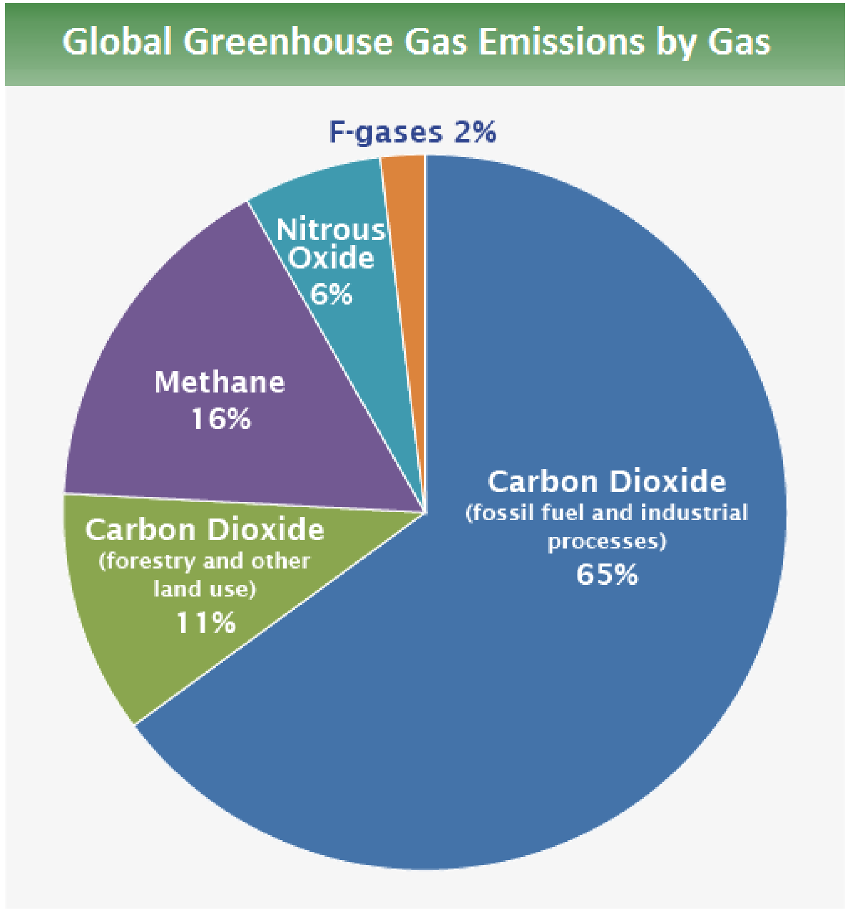
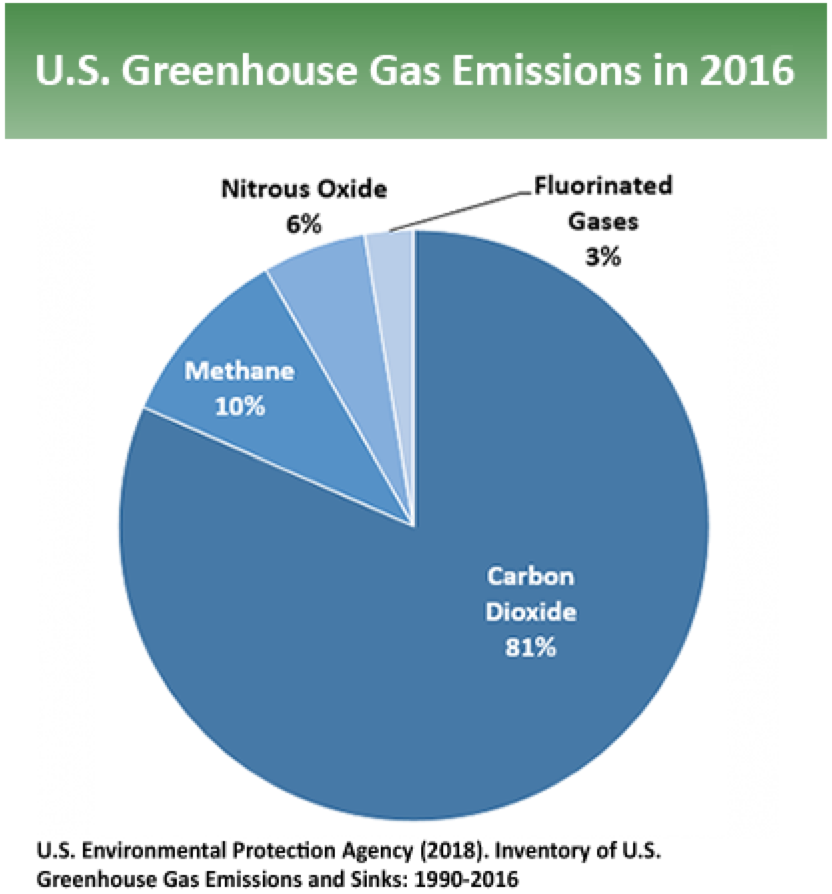
Outline

- Introduction
  - Overview of geological CO_2 storage
- Objectives
- Method/case study
- Results
- Conclusions

Motivation



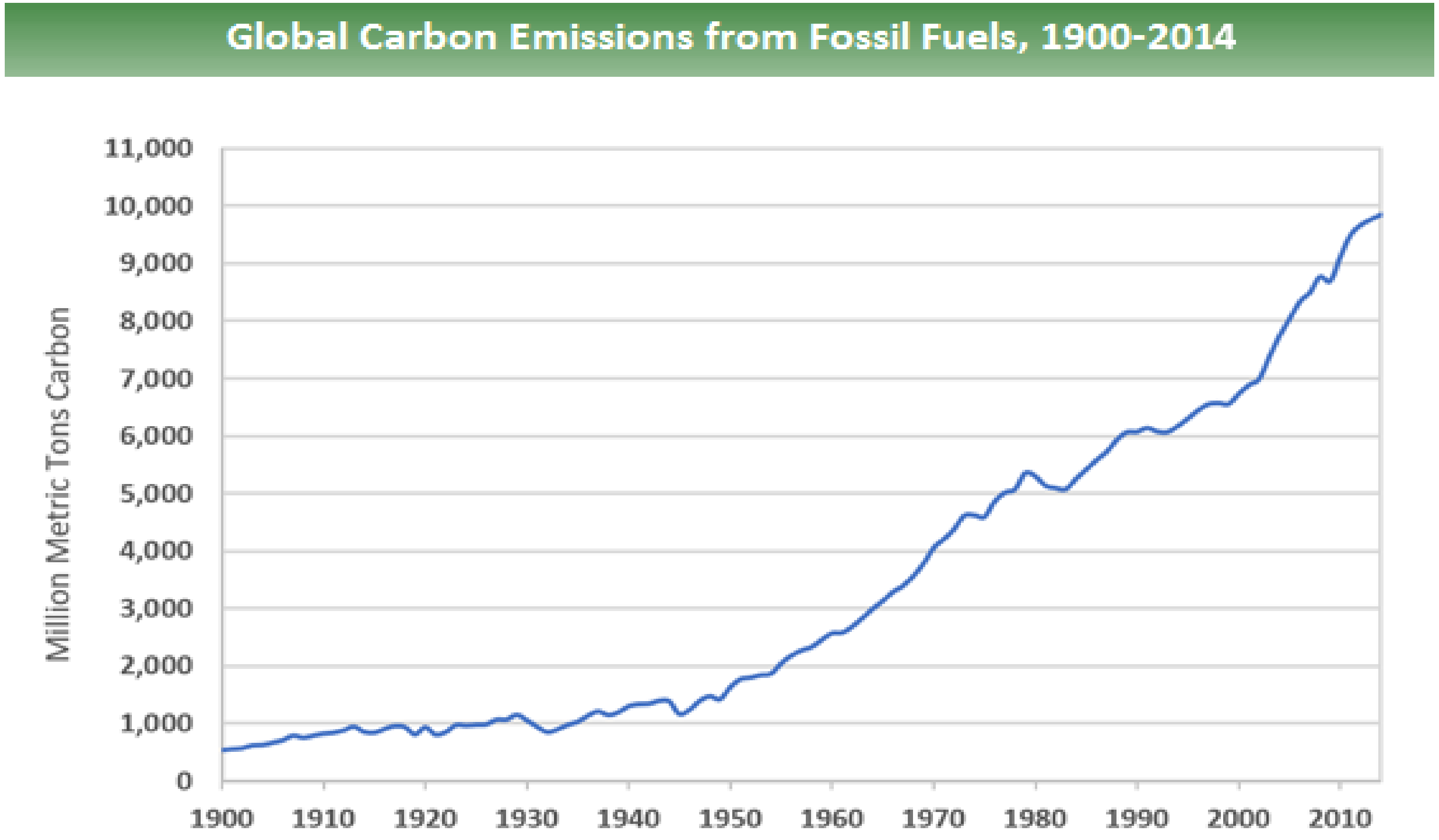
Source: IPCC 2014 (based on emissions from 2010)



Total U. S. Emissions in 2016 = 6,511 Million Metric Tons of CO_2 equivalent

Figure 1: Global and U.S. Greenhouse gas emission

Motivation



Source: Boden et al., 2017

Figure 2: Trends in global emissions

Overview of Geological CO_2 Storage

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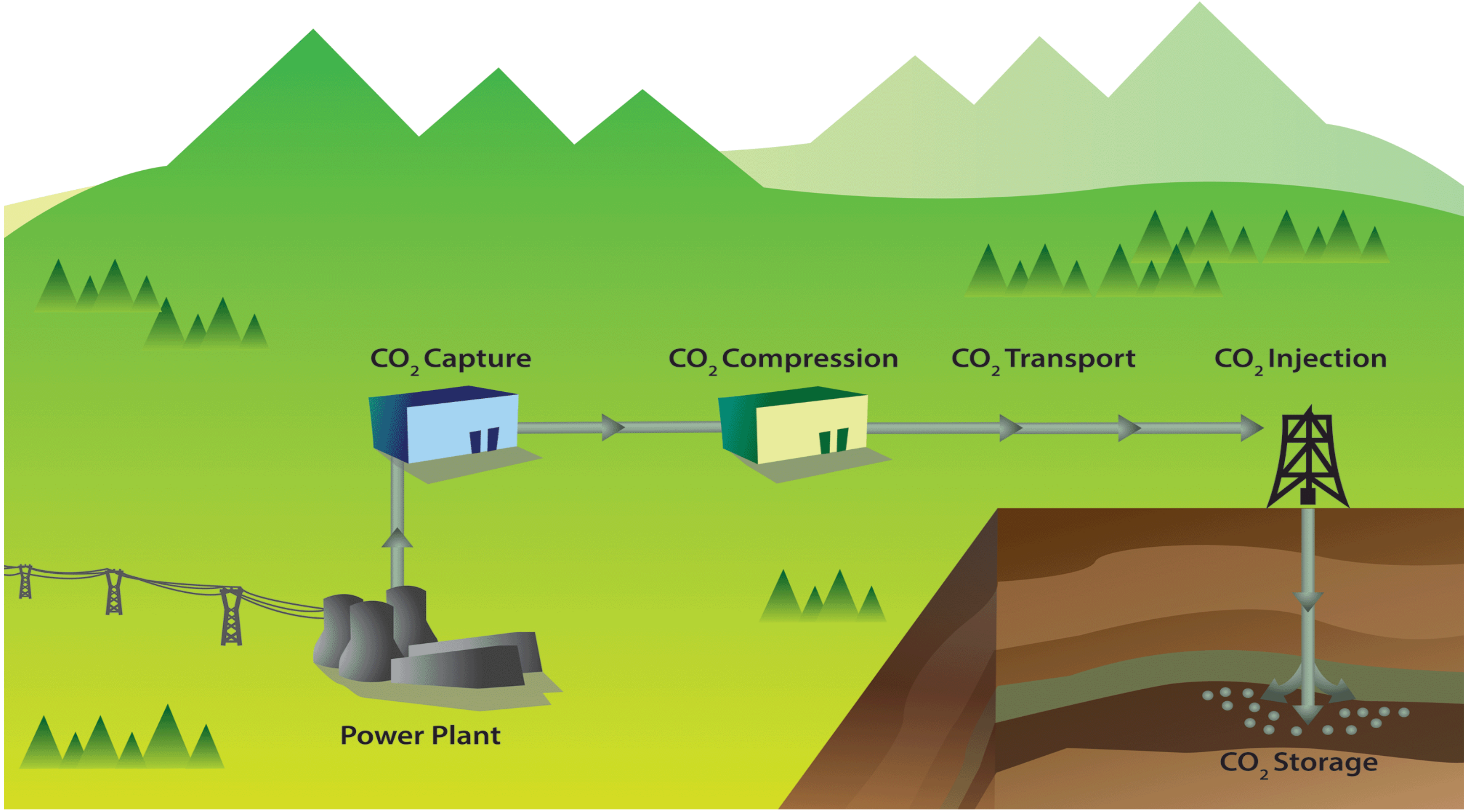

Figure 3: The concept of geological carbon sequestration (figure adopted from Smit *et al., 2014)*

Geologic Storage Capacity

Table 1: Storage capacity for several geological storage options. The storage capacity includes storage options that are not economical.

Reservoir type	Lower estimate of storage capacity ($GtCO_2$)	Upper estimate of storage capacity ($GtCO_2$)
Oil and gas fields	675	900
Unmineable coal seams (ECBM)	3-15	200
Deep saline formations	**1,000**	**Uncertain, but possibly 10^4**

Sources: IPCC, 2005

CO_2 Storage Projects in Saline Formations

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Table 2: Saline formations where CO_2 storage has been done or is currently in progress

Project Name	Country	Injection start (year)	Approximate average daily injection rate(tCO_2 d^{-1})	Total (planned) Storage (tCO_2)
Sleipner	Norway	1996	3,000	20,000,000
Frio	U.S.A	2004	177	1,600
Snohvit	Norway	2008	2,000	40,000,000
Gorgon	Australia	2018	10,000	120,000,000

Sources: IPCC, 2005; https://sequestration.mit.edu/tools/projects/

CO_2 Trapping in Geologic Formations

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- Structural trapping : CO_2 trapped in the pore spaces as moveable immiscible fluid phase
- Residual trapping: CO_2 trapped in small pores and can't be mobilized
- Solubility trapping: Solubility of CO_2 in water
- Mineral trapping: Reaction of CO_2 with minerals and precipitation of carbonates

Chemistry of CO_2-NO_2 in brine

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In this study, we will focus on CO_2-NO_2 co-injection in a limestone-dolomitic formation.

- Chemistry of CO_2-brine interaction

$$CO_2\ (g) \leftrightarrow CO_2\ (aq)$$
$$CO_2\ (aq) + H_2O \leftrightarrow H_2CO_3\ (aq)$$
$$H_2CO_3\ (aq) \leftrightarrow H^+\ (aq) + HCO_3^-\ (aq)$$
$$HCO_3^-\ (aq) \leftrightarrow H^+\ (aq) + CO_3^{2-}\ (aq)$$

- Chemistry of NO_2-brine interaction

$$2NO_2\ (g) + H_2O\ (l) \leftrightarrow NO_2^-(aq) + NO_3^-\ (aq) + 2H^+(aq)$$

Knowledge gap

- Flue gas steam captured from the point sources often contains small amount (0.15 to 2%) of impurities such as NO_x and $SO_{x.}$
- Purifying the injected CO_2 stream will be costly.
- These impurities may change the geochemistry when co-injected with CO_2?
- Changes in geochemistry may lead to changes in mineralogy and porosity of the formation?

Objectives

The objectives of the study are to quantitatively estimate the effect of CO_2-NO_2 co-injection on

1. changes in pH of the brine-rock-CO_2 system
2. changes in mineralogy or porosity of the formation
3. changes in solubility of CO_2 in brine or solubility trapping

Method

- TOUGHREACT 3.3/ECO2N developed by Lawrence Berkeley national Laboratory, Berkeley, USA has been used to simulate CO_2-brine-rock system.

- The mineralogy of the hydrologic layers considered for the simulations is based on Dollar Bay Formation (Roberts-Ashby and Ashby, 2016), located within the South Florida basin.

Running the Test Case

Mineralogy and porosity for the simulations are based on well log data of the Dollar Bay Formation (Roberts-Ashby and Ashby, 2016), located within the South Florida basin.

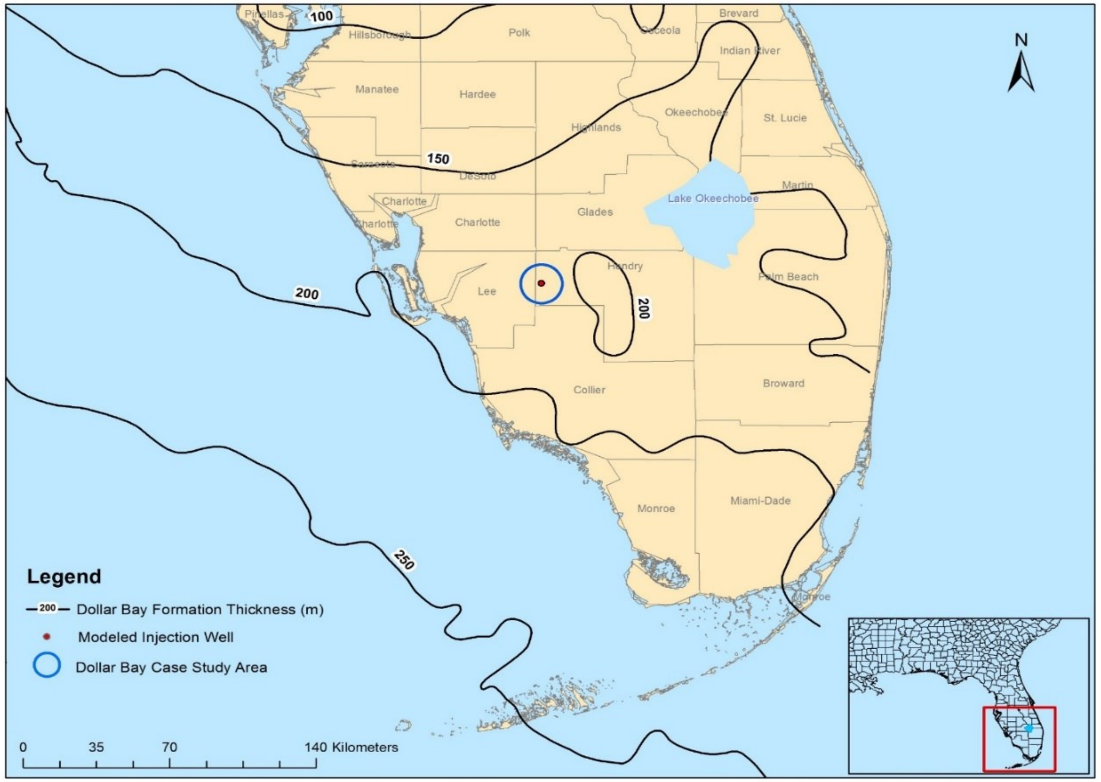

Figure 4 : Dollar Bay Formation

Case Study : Dollar Bay Formation

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Table 3: Physical and chemical properties of the layers

Layer	Layer Thickness (m)	Calcite (volume fraction of mineral phases)	Dolomite (volume fraction of mineral phases)	Anhydrite (volume fraction of mineral phases)	Porosity	Vertical Permeability (m^2)	Horizontal Permeability (m^2)
1	3.66	0.01	0.93	0.06	0.15	3.95e-14	3.95e-13
2	7.92	0.94	0.00	0.06	0.06	4.93e-15	4.93e-14
3	16.16	0.94	0.00	0.06	0.04	2.47e-15	2.47e-14
4	1.22	0.94	0.00	0.06	0.02	1.97e-16	1.97e-15
5	1.82	0.94	0.00	0.06	0.04	2.47e-15	2.47e-14
6	3.36	0.01	0.93	0.06	0.15	3.95e-14	3.95e-13
7	5.48	0.01	0.93	0.06	0.19	3.95e-14	3.95e-13
8	1.22	0.94	0.00	0.06	0.07	4.93e-15	4.93e-14
9	12.2	0.94	0.00	0.06	0.04	2.47e-15	2.47e-14
10	8.52	0.94	0.00	0.06	0.02	1.97e-16	1.97e-15
11	7.94	0.01	0.93	0.06	0.07	6.91e-15	6.91e-14

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Model Simulation Parameters

Table 4: Reservoir parameters

Parameter/condition	Value
Temperatures	75 °C
Initial pressure (top layer)	386 bar
Brine salinity (mass fraction NaCl)	6 %
Injection rate	32 kg/s
Injection period	50 years
Total thickness of the layers	69.5 m
Radial distance	10,000 m
Initial pH	7.0
NO_2	0, 0.15, 1, and 2%

Conceptual model of CO_2 Injection

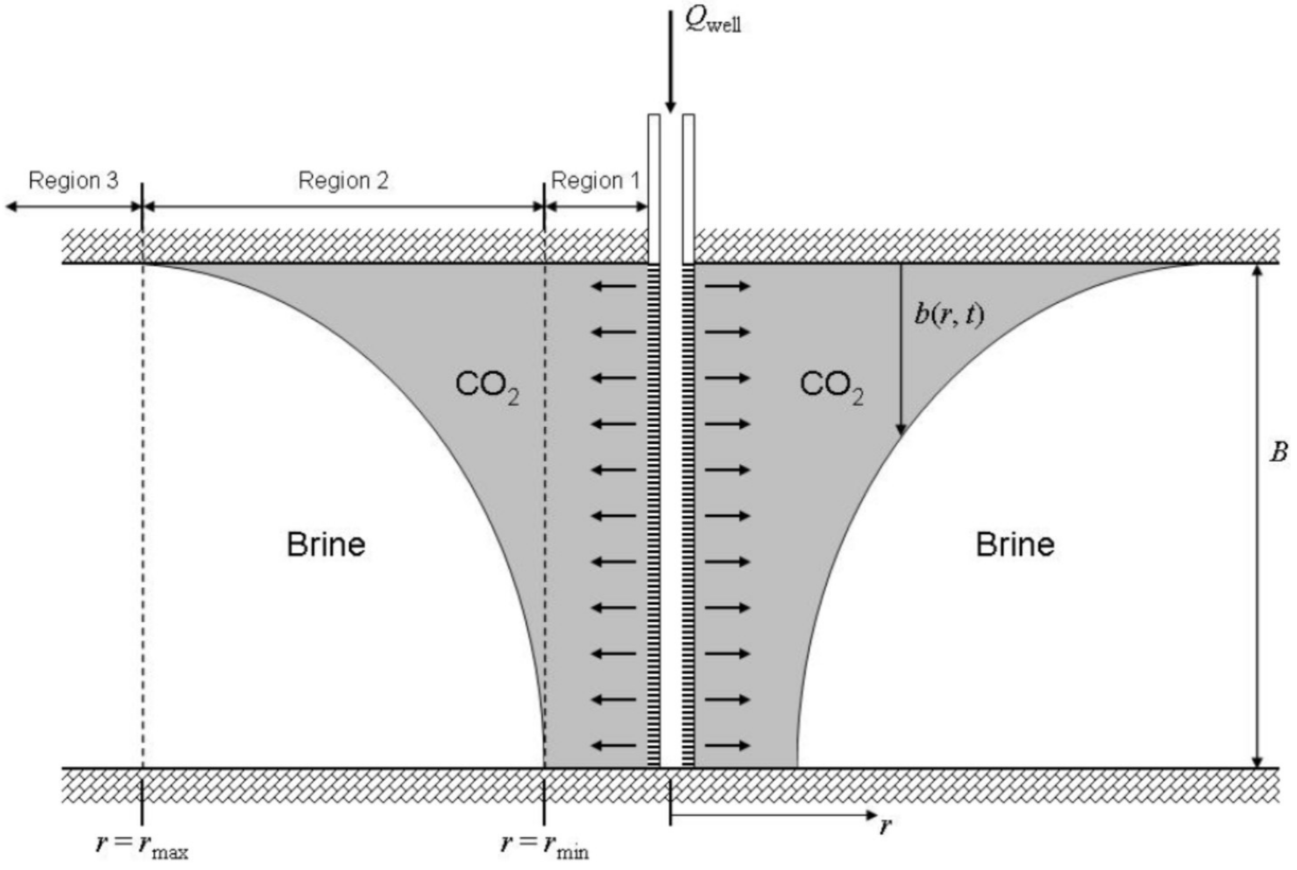

Figure 5: Conceptual model (adapted from Nordbotten et al., 2005).

Results

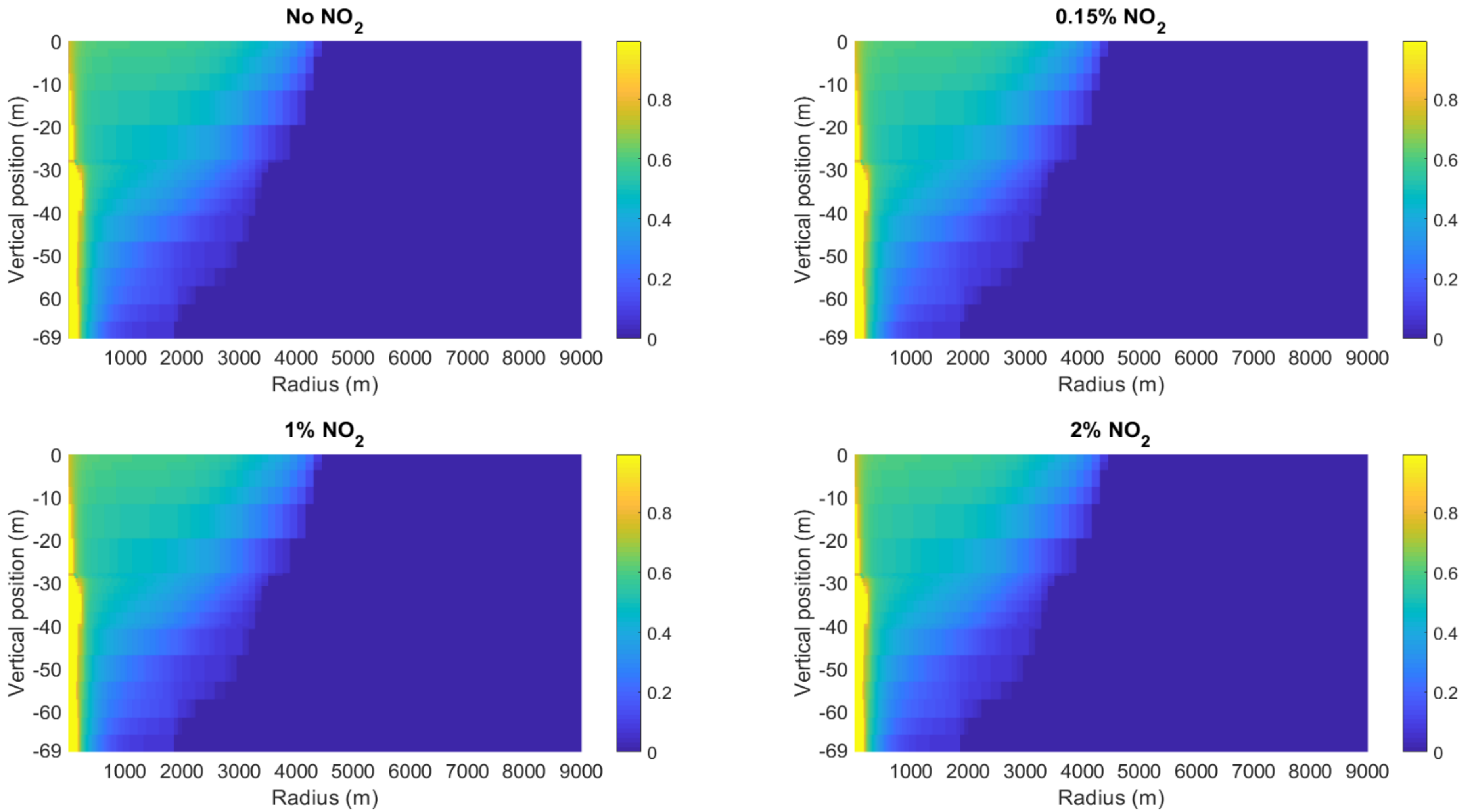

Figure 6: Gas saturation after 100 years

Results

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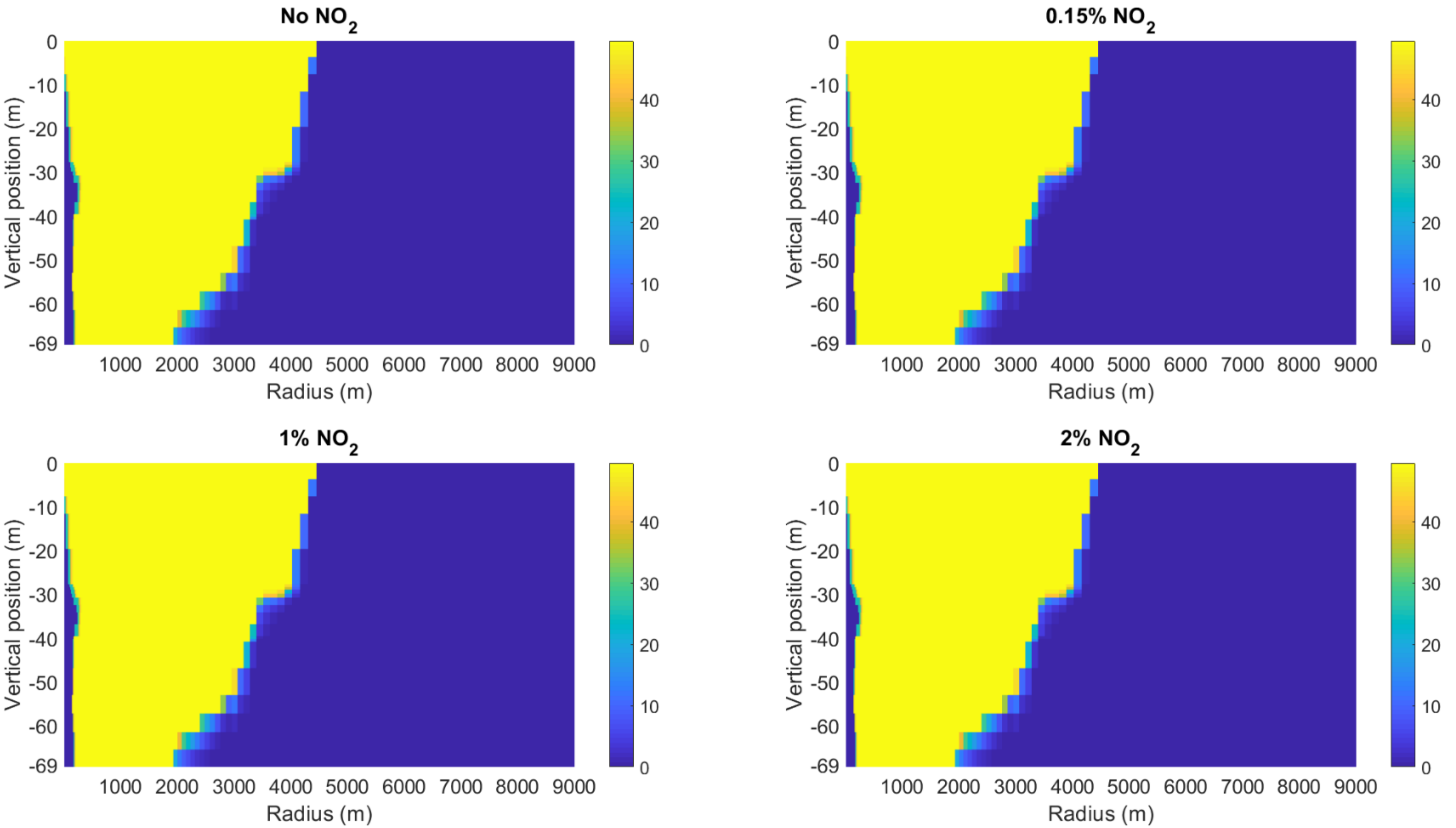

Figure 7: Dissolved CO_2 concentration after 100 years

Results

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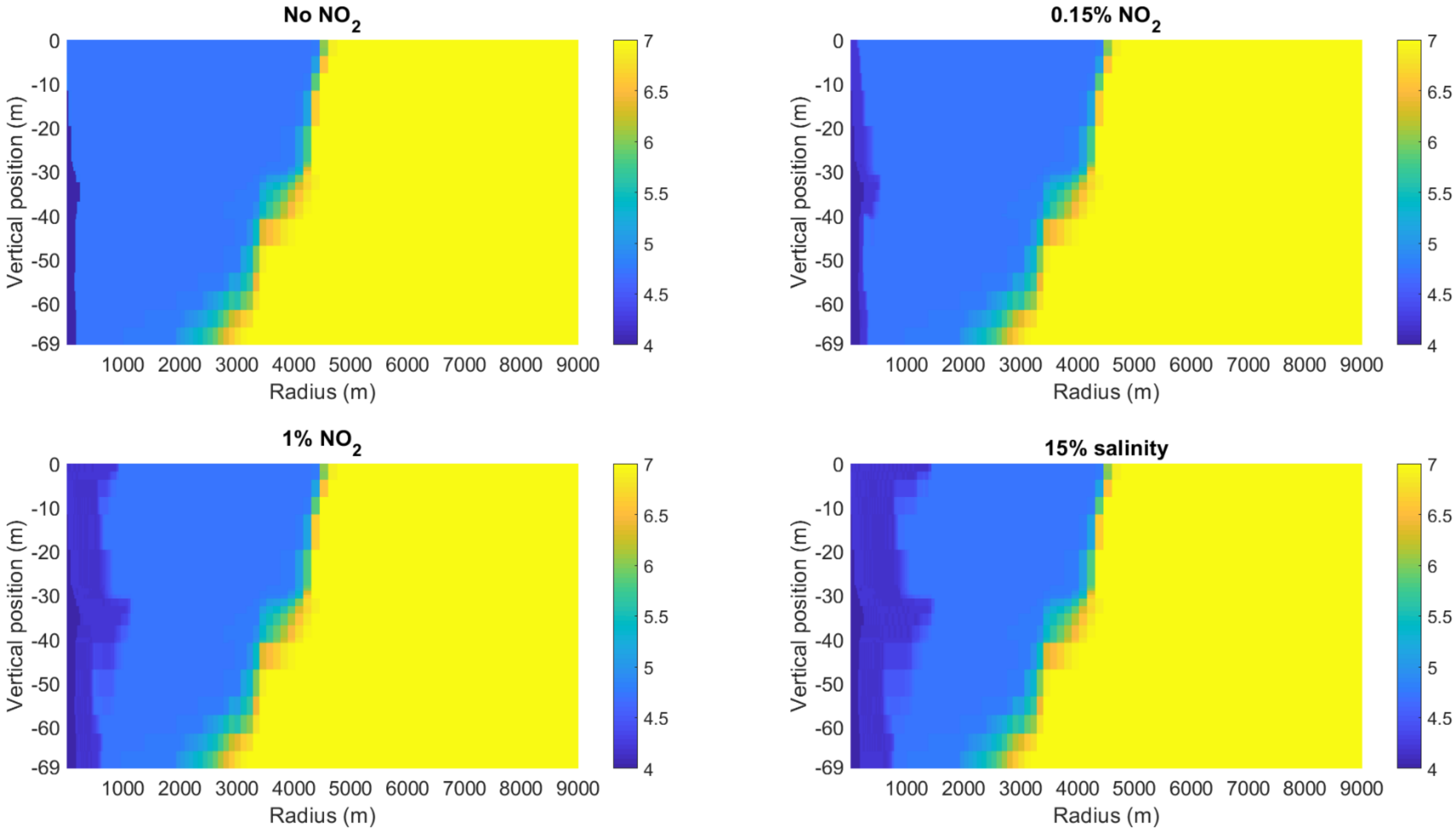

Figure 8: pH of the formation after 100 years

Results

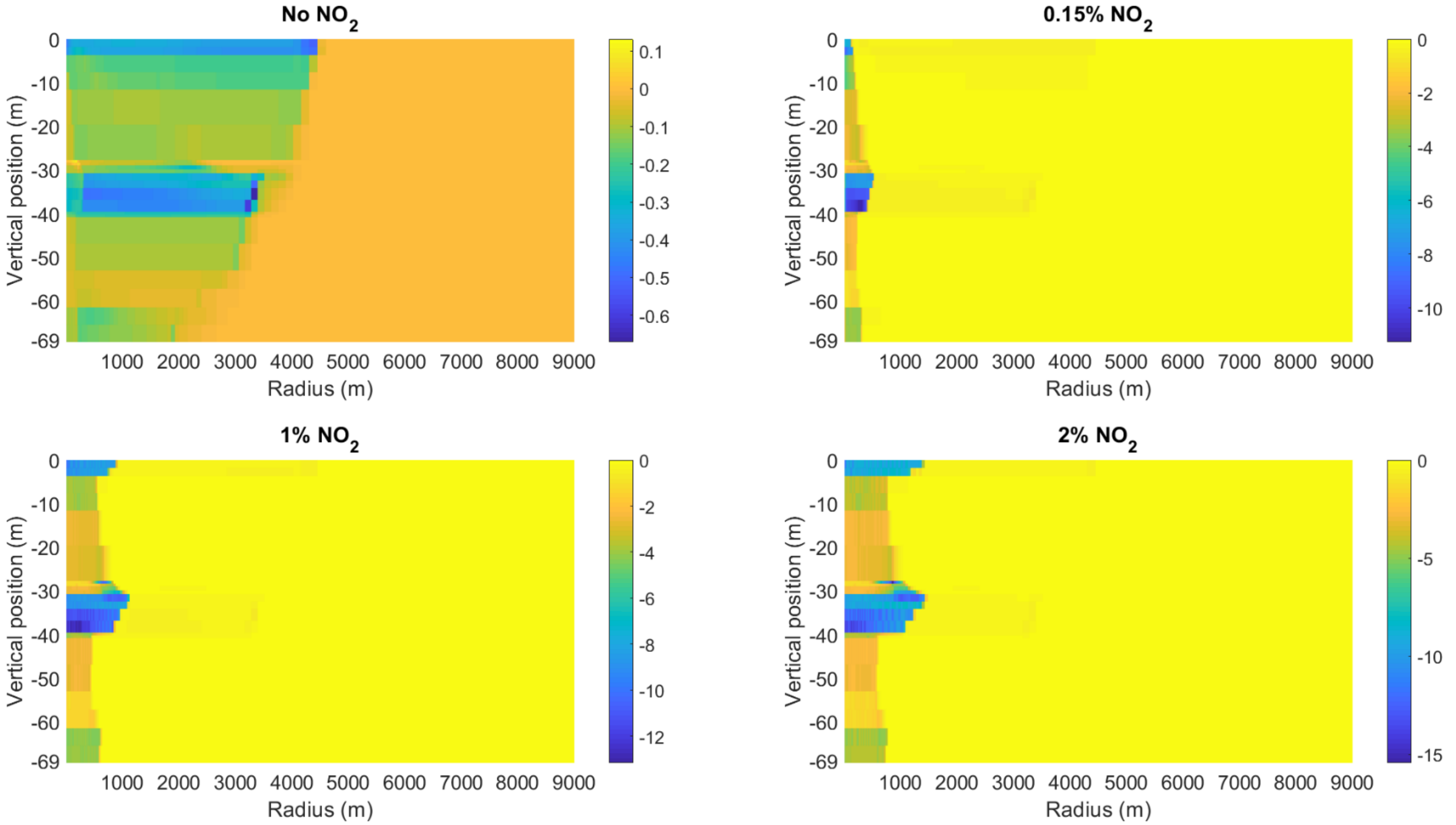

Figure 9: Changes in Calcite after 100 years

Results

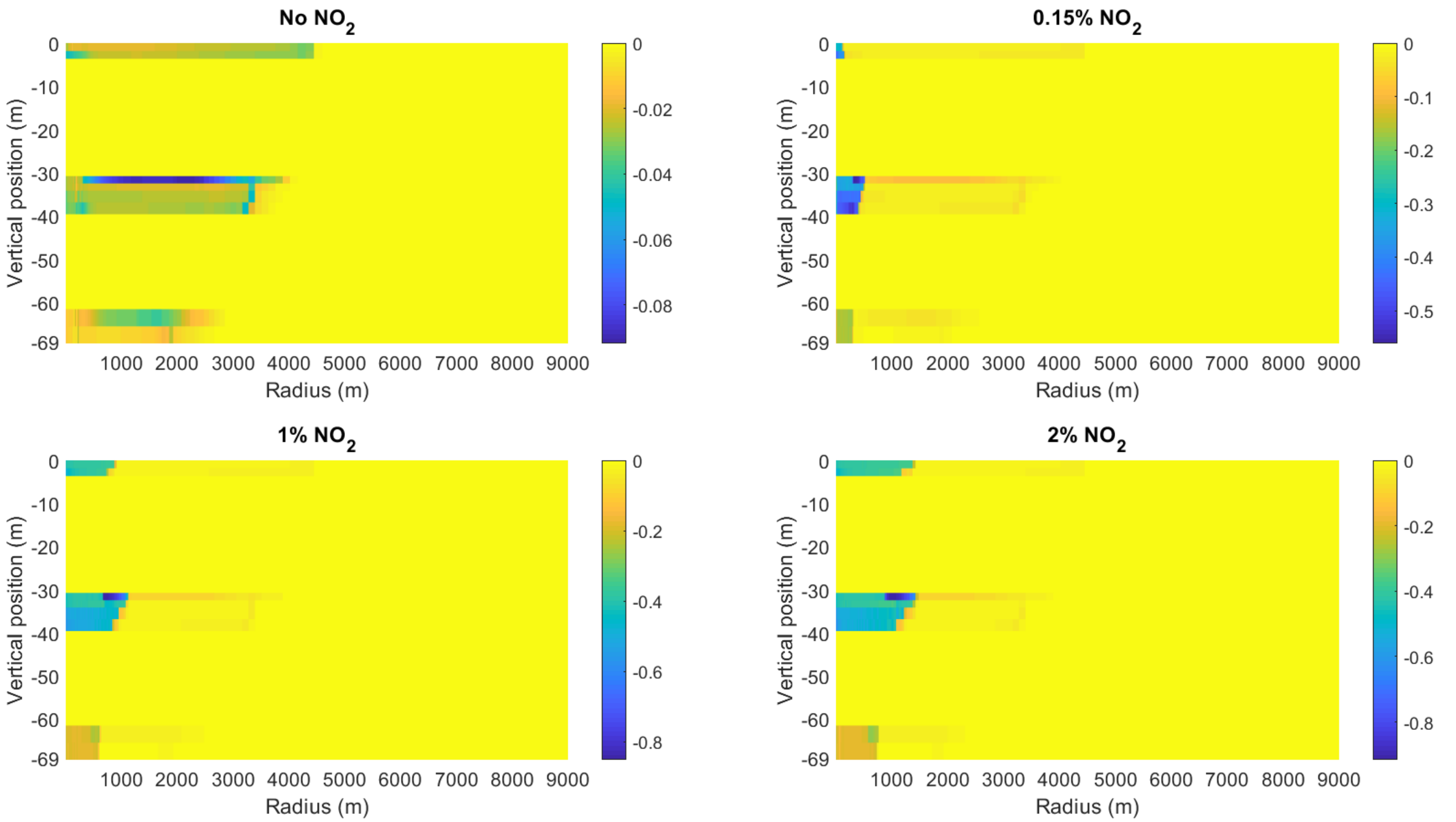

Figure 10: Changes in Dolomite after 100 years

Results

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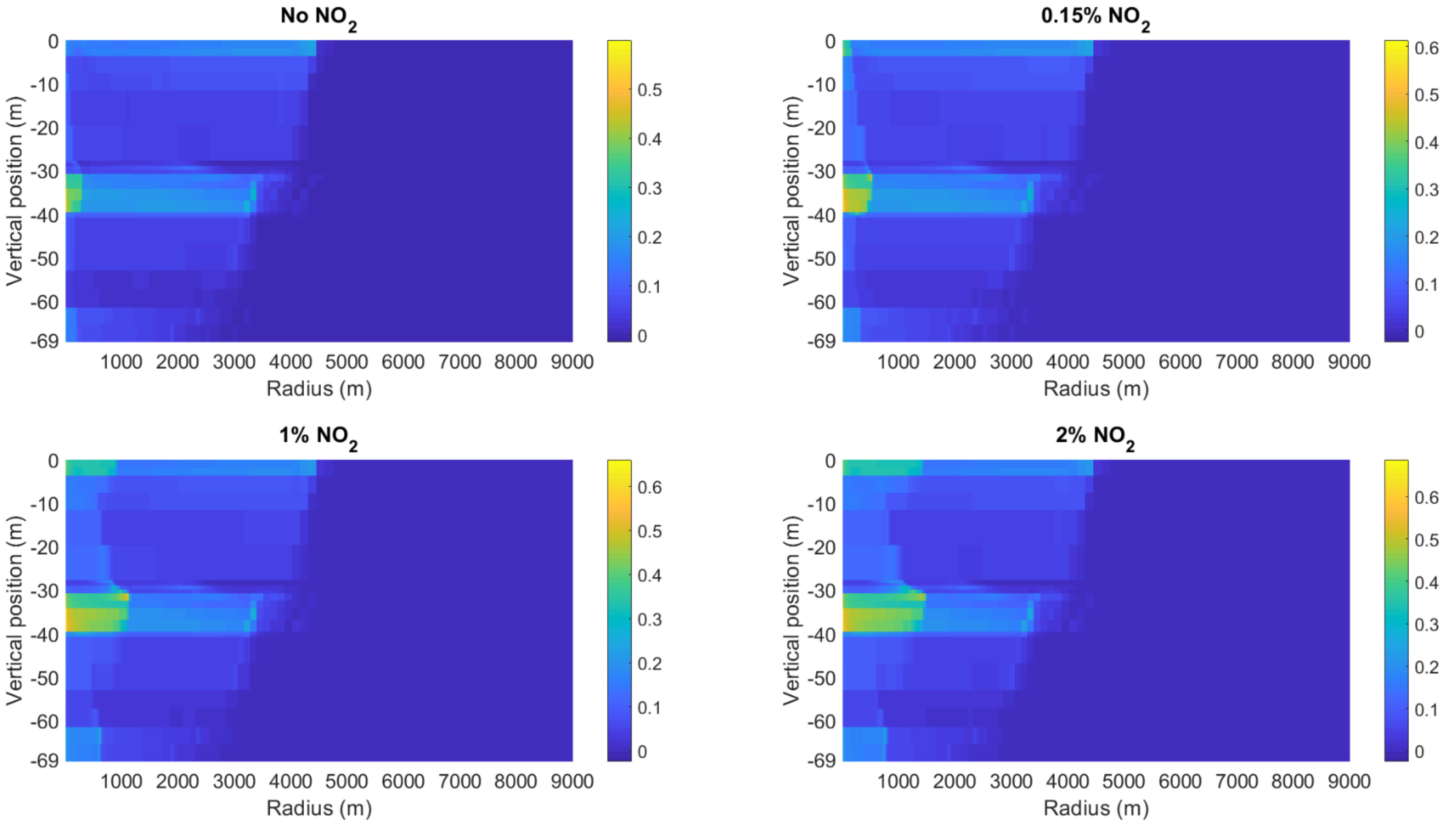

Figure 11: Changes in Anhydrite after 100 years

Results

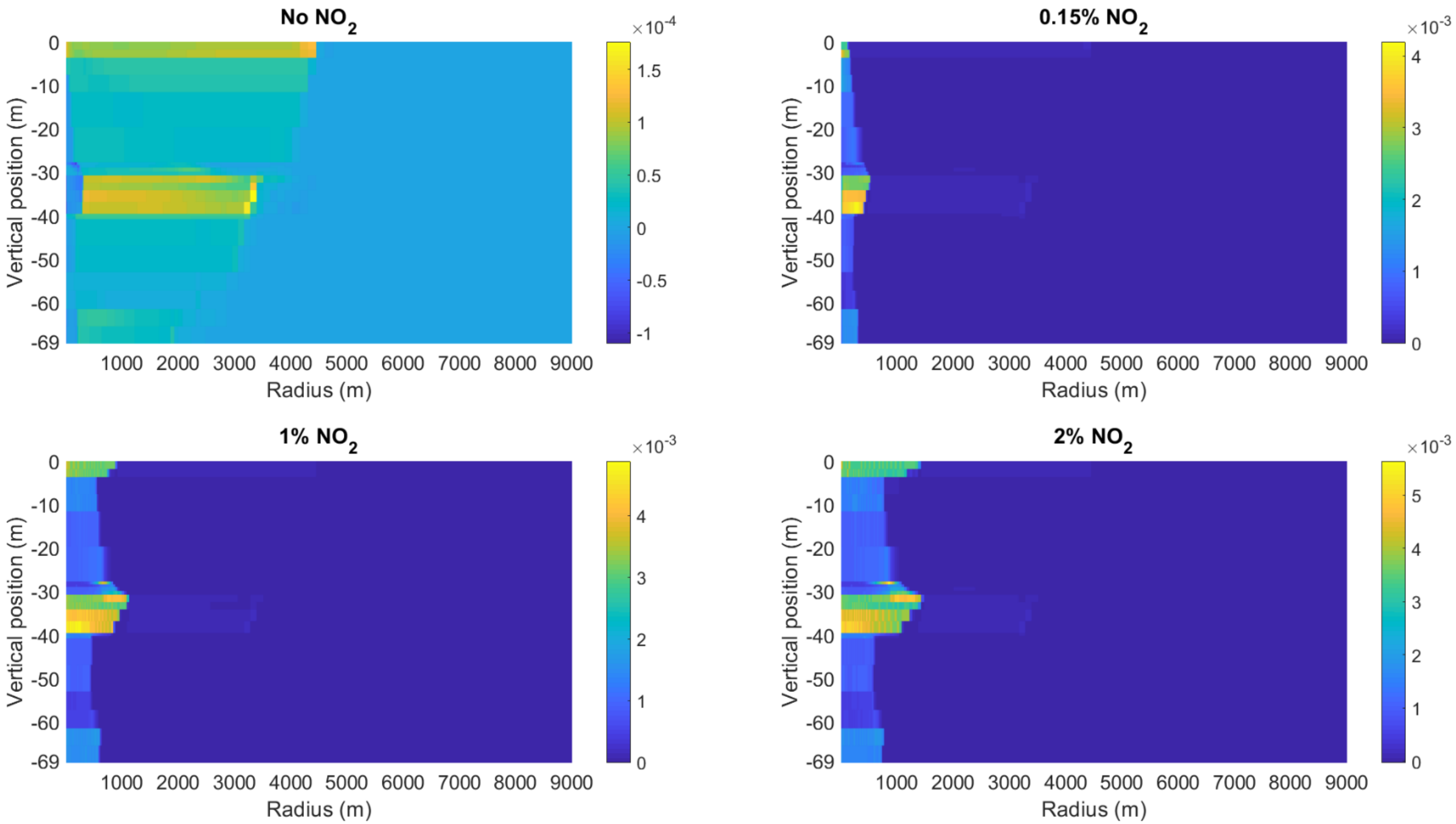

Figure 12: Changes in Porosity after 100 years

Conclusions

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- CO_2-NO_2 co-injection drives higher acidification of native brine, pH dropping to 4.1 with NO_2 co-injection, compared to 4.8 in case of pure CO_2 injection.
- Due to higher degree of acidification in the outreach of NO_2 plume, there is higher dissolution (nearly 10 times) of carbonate minerals like Calcite and Dolomite.
- Similarly, the magnitude of anhydrite precipitation was higher in NO_2 outreach zone (much lesser magnitude as compared to the dissolution).
- Due to changes in mineralogy, net change in porosity is nearly 10 times higher in NO_2 outreach zones.
- Solubility trapping of CO_2 doesn't vary much. For pure CO_2, it is 6.33 Mt as compared to 6.39 Mt in case of pure CO_2.

Acknowledgement

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