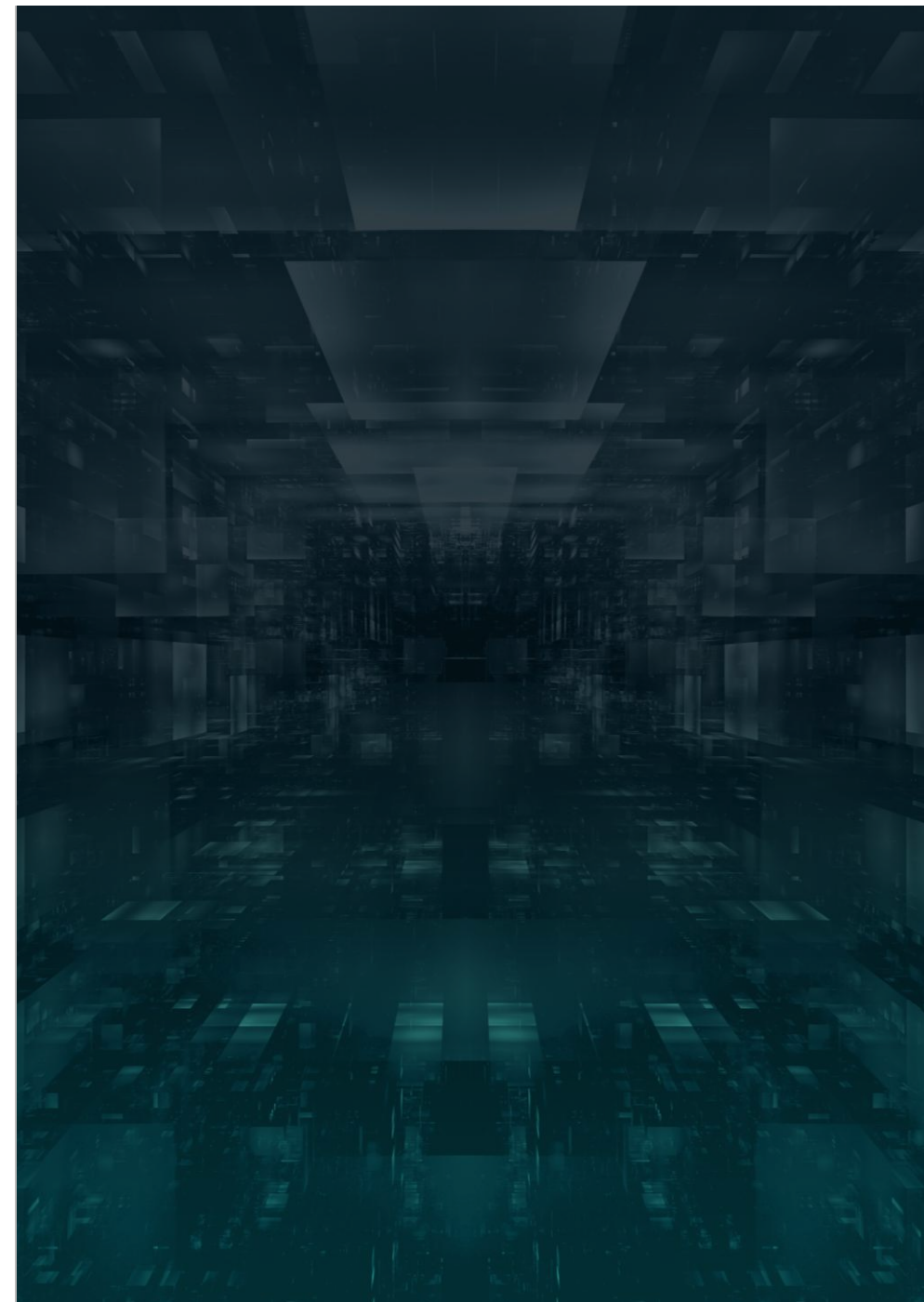


日本天然气田制碘生产过程模拟 Coupled Geochemistry Simulation for Iodine Production

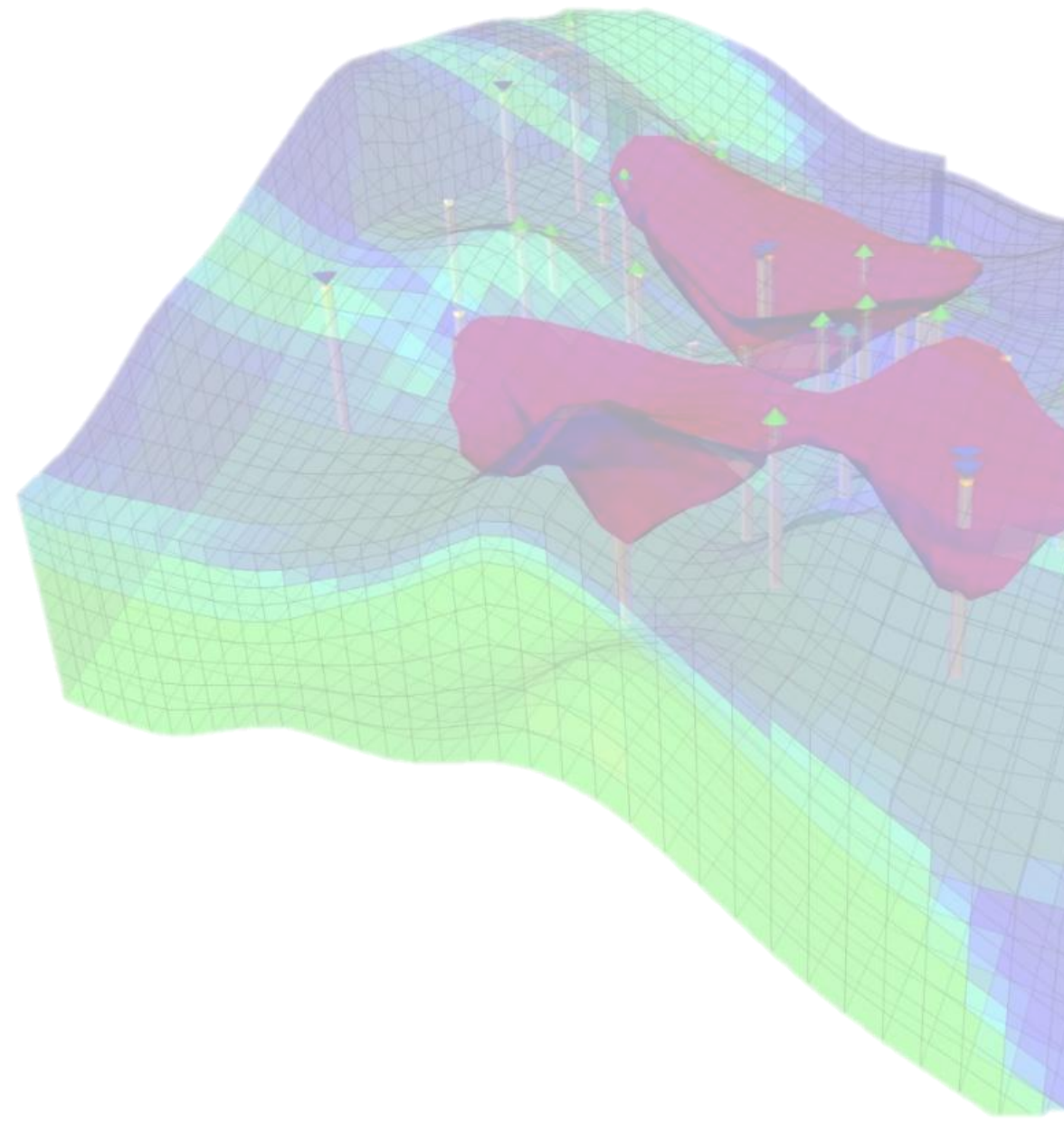
June 2025

AGENDA

- 01 Introduction
- 02 Simulator - GEM
- 03 Gas Solubility
- 04 Geochemistry
- 05 Case Study
- 06 Conclusions



Introduction



Why iodine modeling is important?



GEM™



世界に誇る資源

千葉県は世界第2位のヨウ素産出地

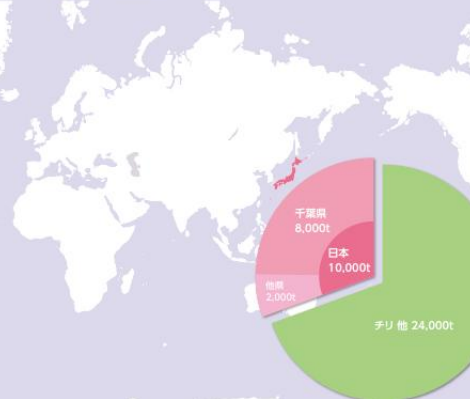
ヨウ素は地球上で海水、海藻、かん水、鉱物（礫石）などに含まれていますが、経済的に採取できる地域は極めて限られています。

千葉県は、1900 年前後より海藻からヨウ素を生産する中心地でした。1934 年、大多喜町でかん水からのヨウ素の生産が開始され、九十九里地域に広がり現在に至っています。

世界のヨウ素生産量は年間約 34,000t で、そのほとんどを日本とチリが占め、日本は全体の約 30% を生産しています。このうち、千葉県は日本の約 80%、世界の約 4 分の 1 である約 8,000t を生産しています。千葉県における可採埋蔵量が約 400 万 t と推定されることから、現在の生産量で換算すると約 500 年分に相当します。

千葉県で生産されるヨウ素は飲米をはじめとして世界各地に輸出されており、今後も安定した供給を期待されています。

●世界のヨウ素年間生産量

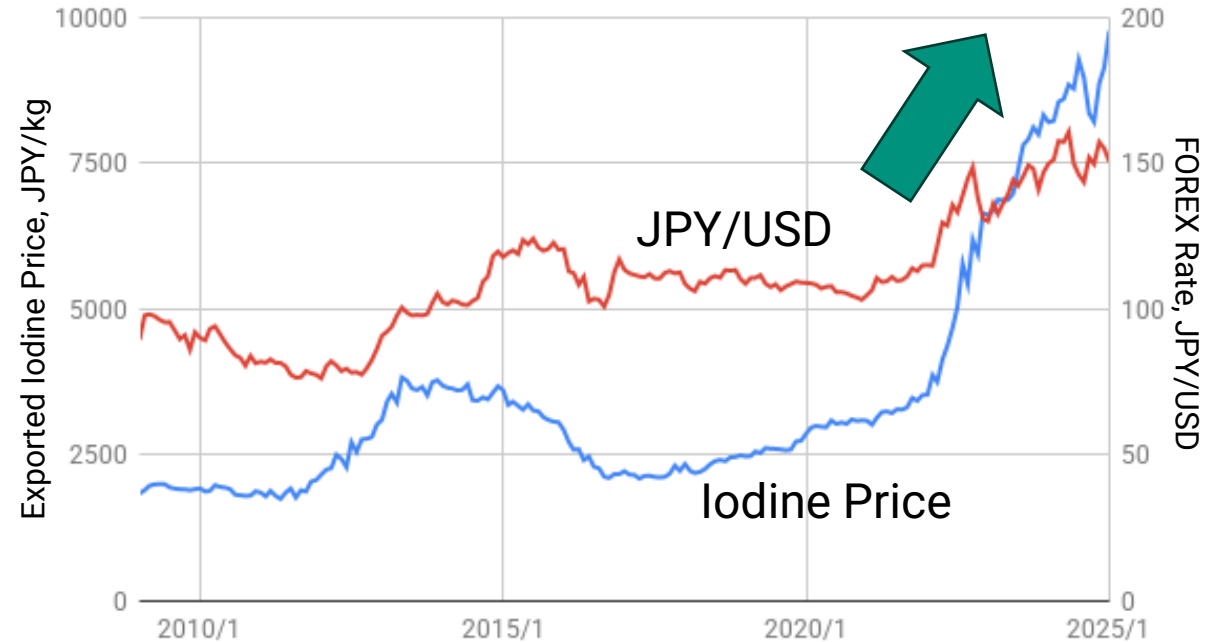


ヨウ素(結晶)



各種ヨウ素製品

Long-Term Trend of Iodine Price

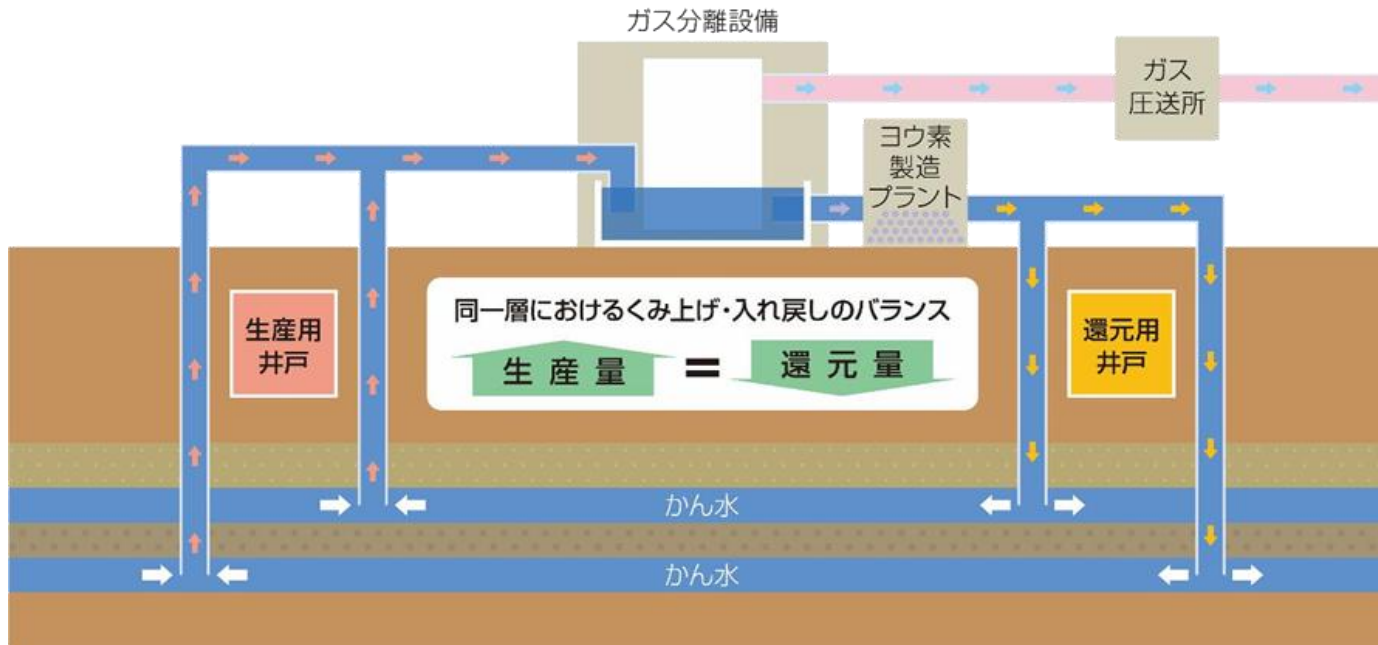


Courtesy Ryusuke Matsuyama

Source: [千葉県の天然ガスとヨウ素, 天然ガス鉱業会, 2022](#)

Iodine production operation in Japan

Schematic of the production system in Niigata^{*1}



- Natural gas and iodine are produced **with water**
- Natural gas is separated at the surface and pumped into the sales pipeline
- **Produced water is re-injected** to the original reservoirs (100% water recycling)

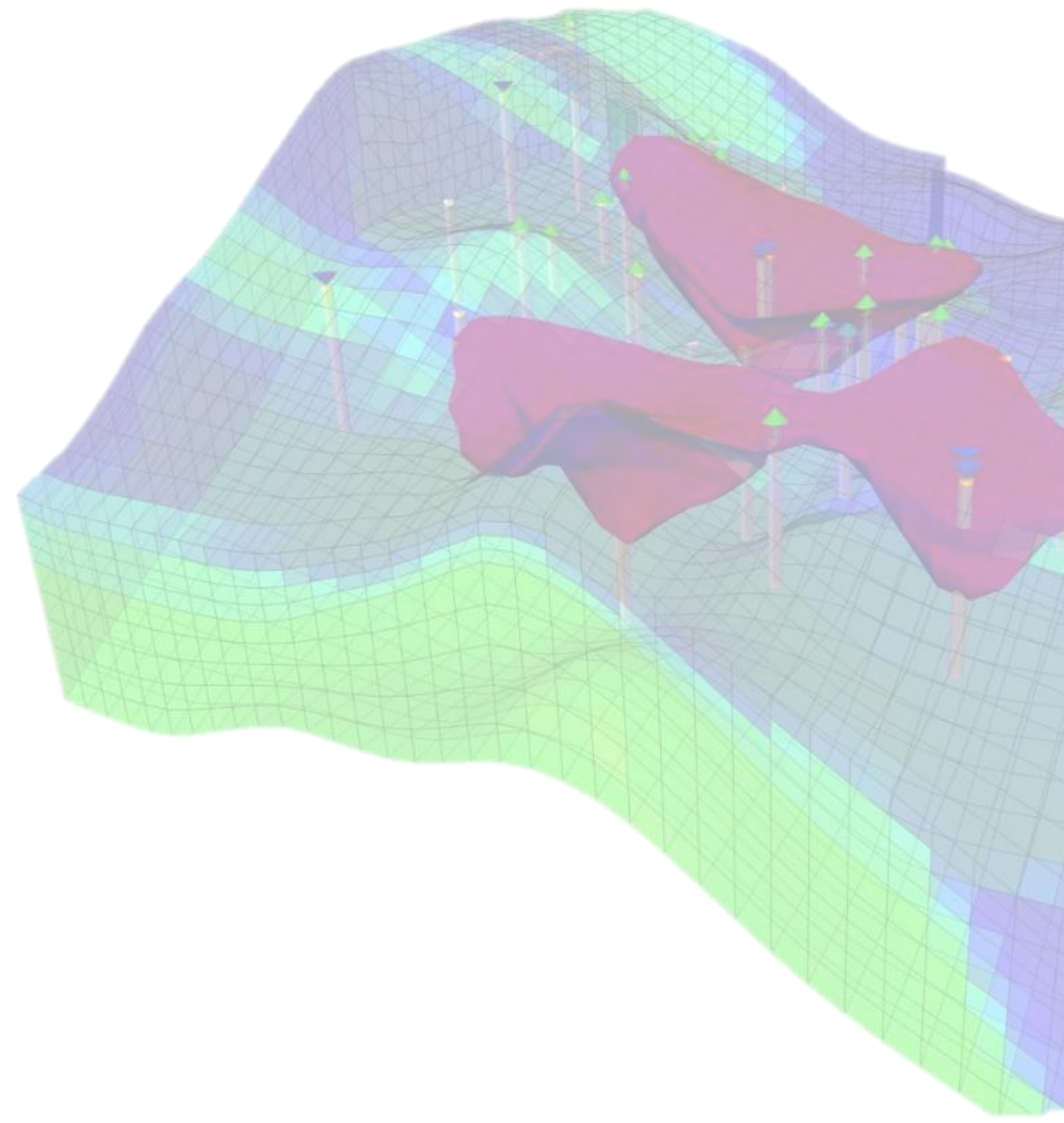
Produced fluid characteristics

Gas components ^{*2}	CH ₄	96.2 vol%
	CO ₂	3.5 vol%
	N ₂	0.3 vol%
Aqueous components ^{*3}	I ⁻	130 ppm
	NH ₄ ⁺	270 ppm
	Li ⁺	0.82 ppm
	Na ⁺	10,900 ppm
	Cl ⁻	18,100 ppm
	K ⁺	270 ppm
	Ca ²⁺	165 ppm
	Mg ³⁺	350 ppm

Source:

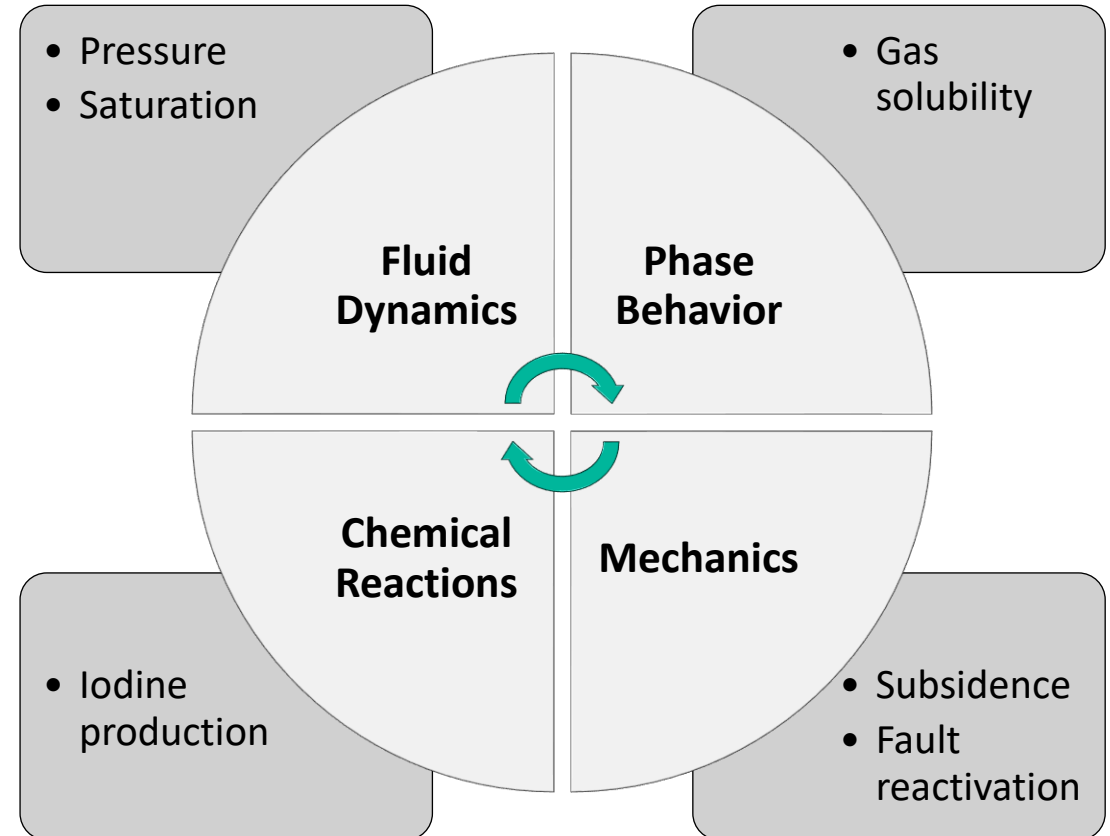
*1 <https://www.gas-youso.com/> *2 <https://www.tohoeearthtech.co.jp/business/naturalgas/> 3* <https://fiu-iodine.org/studies/>

Simulator - GEM

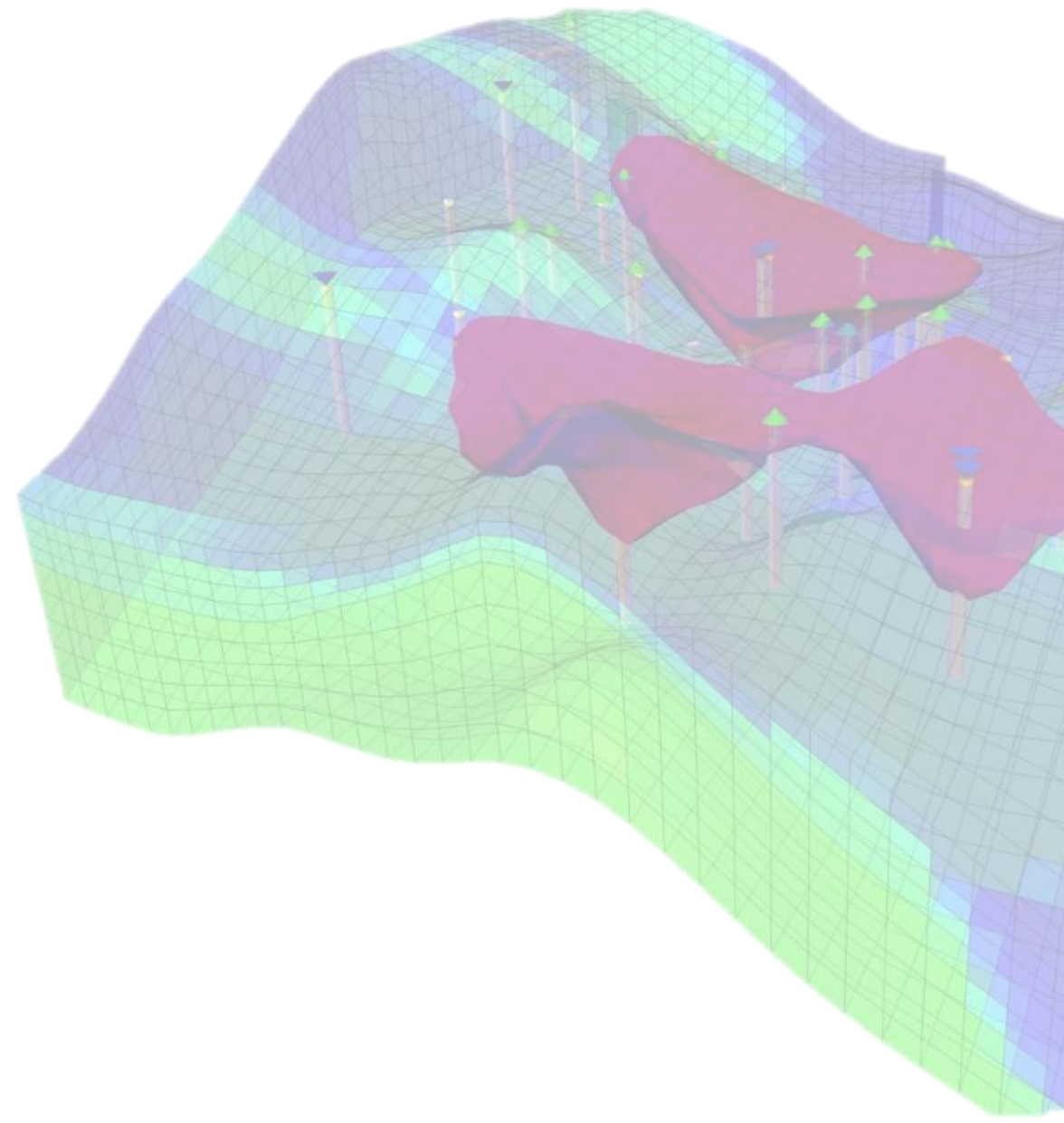


GEM: Underground Fluid & Energy Flow Modeling Tool

- Convective and dispersive flow
- Gas solubility in aqueous phase
 - Peng Robinson / Soave-Redlich-Kwong EOS
 - Predictions of brine density and viscosity based on pressure, temperature, and salinity
- Geochemistry
 - Aqueous equilibrium reactions
 - Mineral dissolution and precipitation reactions
- Geomechanics
 - Cap rock integrity
 - Subsidence/surface heave
 - Thermal fracturing
 - Faults reactivation



Gas Solubility



Gas Solubility in the Aqueous Phase (Henry's Law)

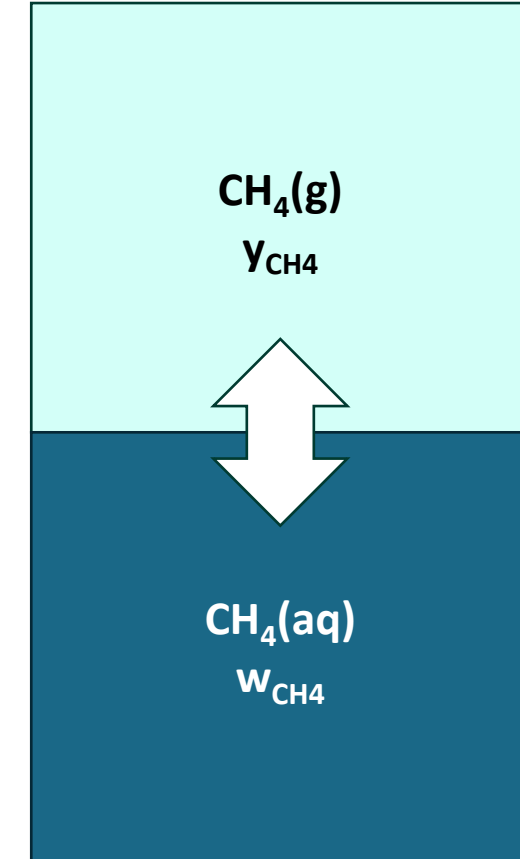
Gas dissolution into the aqueous phase is reversible at equilibrium



$\text{CH}_4(\text{g})$	Methane in the gas phase
$\text{CH}_4(\text{aq})$	Methane in the aqueous phase

Gas solubility in the aqueous phase depends on:

- Pressure
- Temperature
- Salinity





GEM Keywords for Gas Solubility in the Aqueous Phase

*SOLUBILITY HENRY	Gas solubility based on Henry's law
*HENRY-CORR-C1	Henry's constant for CH ₄
*SALINITY-CALC *ON	Salinity correction for Henry's constant
*AQUEOUS-DENSITY *ROWE-CHOU	Brine density calculation
*AQUEOUS-VISCOSITY *KESTIN	Brine viscosity calculation

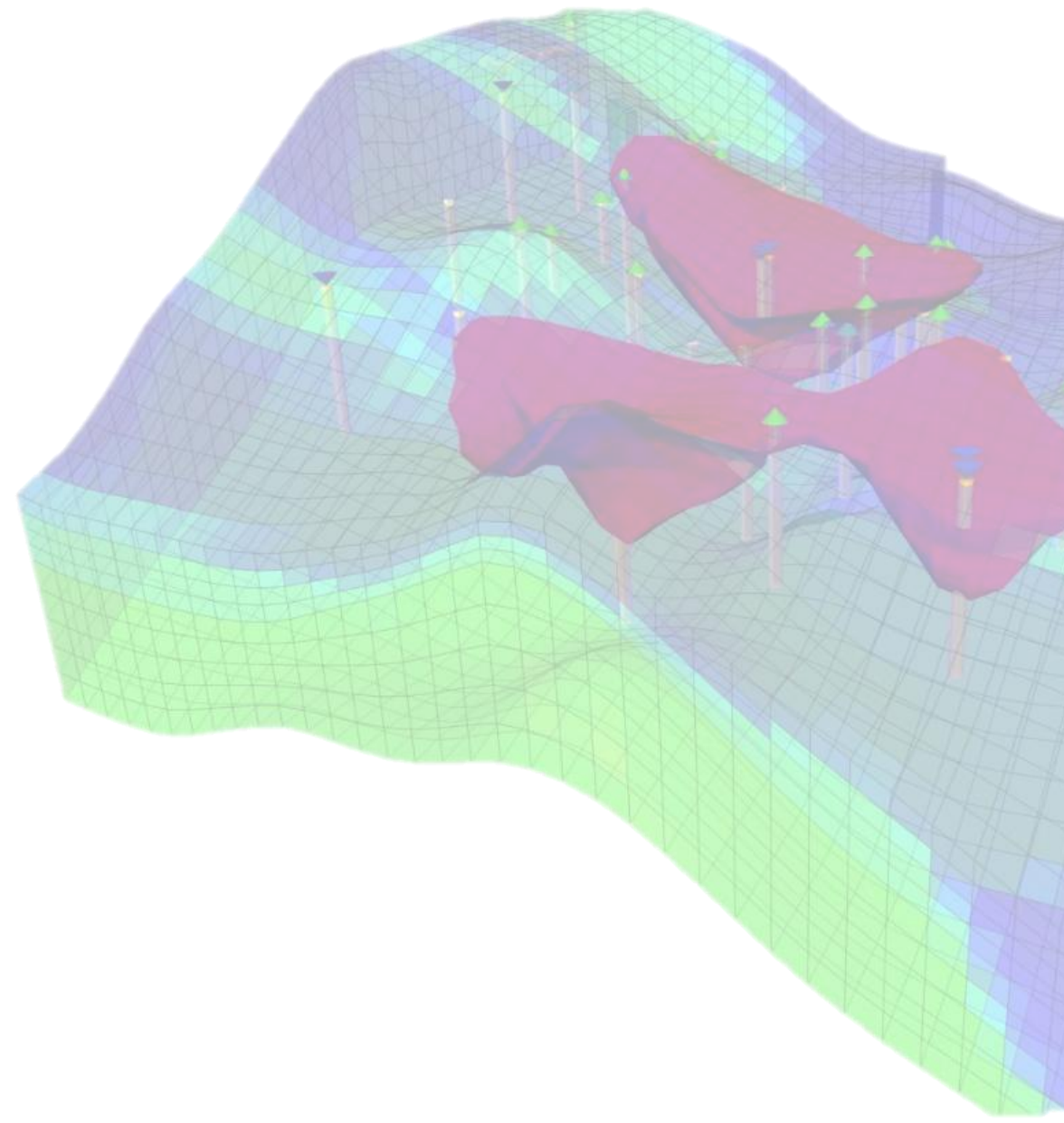
Example

DENWS 1020
CW 4.5E-7
SOLUBILITY HENRY
HENRY-CORR-C1
AQFILL OFF
AQUEOUS-DENSITY ROWE-CHOU
AQUEOUS-VISCOSITY KESTIN

*HENRY-CORR-C1

This keyword activates the use of Harvey's correlation for CH₄ Henry's constant. Use of this option makes the Henry's constant a function of pressure, temperature and salinity. This correlation is applicable up to 150° C and 700 bar.

Geochemistry



Geochemical Databases in CMG



GEM™

GEM-GHG aqueous and mineral species reaction selection

Reaction Type Selection

☒ Aqueous Species Reactions

☐ Mineral Species Reactions

Chemical Equilibrium Equation Derivatives

☐ Analytical ☒ Numerical

Mineral Precipitation/Dissolution Rate Equation Derivatives

☐ Analytical ☒ Numerical

Additional Component Selection

☐ Include Na+ and Cl- ions

Geo-chemistry Database: Thermo.dat

Find Reaction Containing: Next Previous ☒ Geo-Chemistry Format II

Database Available Reactions

1: (NpO2)2(OH)2++ + 2.0 H+ = 2.0 H2O + 2.0 NpO2++

2: (NpO2)3(OH)5+ + 5.0 H+ = 5.0 H2O + 3.0 NpO2++

3: (PuO2)2(OH)2++ + 2.0 H+ = 2.0 PuO2++ + 2.0 H2O

4: (PuO2)3(OH)5+ + 5.0 H+ = 3.0 PuO2++ + 5.0 H2O

5: (UO2)2(CO3)(OH)3- + 4.0 H+ = 2.0 UO2++ + 3.0 H2O + HCO3-

6: (UO2)2(OH)2++ + 2.0 H+ = 2.0 UO2++ + 2.0 H2O

7: (UO2)3(OH)4++ + 4.0 H+ = 3.0 UO2++ + 4.0 H2O

8: (UO2)3(OH)5+ + 5.0 H+ = 3.0 UO2++ + 5.0 H2O

9: (UO2)3(OH)7+ + 7.0 H+ = 3.0 UO2++ + 7.0 H2O

10: (UO2)4(OH)7+ + 7.0 H+ = 4.0 UO2++ + 7.0 H2O

11: (VO)2(OH)2++ + 2.0 H+ = 2.0 VO++ + 2.0 H2O

12: (VO)2(OH)5- + 5.0 H+ = 2.0 VO++ + 5.0 H2O

13: AgCl = Ag+ + Cl-

14: AgCl2- = Ag+ + 2.0 Cl-

15: AgCl3-- = Ag+ + 3.0 Cl-

16: AgCl4--- = Ag+ + 4.0 Cl-

17: AgF = Ag+ + F-

18: AgSO4- = Ag+ + SO4--

19: Al(O-phth)+ = Al+++ + (O-phth)--

20: Al(O-phth)2- = Al+++ + 2.0 (O-phth)--

21: Al(OH)2+ + 2.0 H+ = Al+++ + 2.0 H2O

22: Al(OH)3 + 3.0 H+ = Al+++ + 3.0 H2O

23: Al(OH)4- + 4.0 H+ = Al+++ + 4.0 H2O

24: Al(SO4)2- = Al+++ + 2.0 SO4--

Selected Reactions (Custom reaction in RED)

82: CO2(aq) + H2O = H+ + HCO3-

83: CO3-- + H+ = HCO3-

355: OH- + H+ = H2O

OK Cancel

phreeqc.dat

Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N., 1980, PHREEQE—A computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 80–96, 195 p. (Revised and reprinted August, 1990.)

minteq.v4.dat

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J., 1990, MINTEQA2/PRODEFA2--A geochemical assessment model for environmental systems--version 3.0 user's manual: Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, 106 p. (<https://www.epa.gov/sites/production/files/documents/SUPPLE1.PDF>)

thermo.dat

Wolery TJ, Jove-Colon CF, Jareck, RL. Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems. ANL-WIS-GS-000003 Rev 01. Sandia National Laboratories: Las Vegas, Nevada, ACC: DOC.20070619.0007; 2007. (<https://www.nrc.gov/docs/ML0907/ML090770163.pdf>)

Reactions



Reaction Type	Reactions	What is needed	GEM Keywords
Aqueous Chemical Equilibrium Reaction	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	Initial Molality (H^+ and OH^-)	*MOLALITY-AQUEOUS
		Equilibrium Constant	*LOG-CHEM-EQUIL-COEFS
Mineral Dissolution & Precipitation	$\text{NaI} = \text{Na}^+ + \text{I}^-$	Initial Molality (Na^+ and I^-)	*MOLALITY-AQUEOUS
		Equilibrium Constant	*LOG-CHEM-EQUIL-COEFS
		Initial Volume Fraction (NaI)	*VOLUMEFRACTION-MINERAL
		Reactive Surface Area	*REACTIVE-SURFACE-AREA
		Activation Energy	*ACTIVATION-ENERGY
		Reaction Rate Constant	*LOG-TST-RATE-CONSTANT

Source: [日本が資源大国？それはヨウ素, 化学と教育, 64巻5号, 2016](#)

Chemical Equilibrium Constant and Activity

- Governing equation is the equality between activity products and K_{eq} (Chemical Equilibrium Constant)



$$K_{eq}(T) = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{a_{\text{CO}_2(\text{aq})} \cdot a_{\text{H}_2\text{O}}}$$

'a' is the activity which is also a measure of concentration

$a_{\text{H}_2\text{O}}$	≈ 1
a_i	$= \gamma_i \cdot m_i$
γ_i	= activity coefficient of species i
m_i	= molality of species i (moles i / kg H_2O)

Activity coefficients models in GEM:

- Ideal solution: $\gamma_i = 1$ (default)
- Debye-Hückel model
- B-dot model
- Pitzer

GEM vs PHREEQC for K_{eq} calculation

- GEM and PHREEQC adopt different formulae to calculate K_{eq}

GEM

$$\log_{10} K_{eq}(T) = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$$

T is in °C (Celsius)

PHREEQC

$$\log_{10} K_{eq}(T) = a_0 + a_1T + a_2T^{-1} + a_3 \log_{10} T + a_4T^{-2}$$

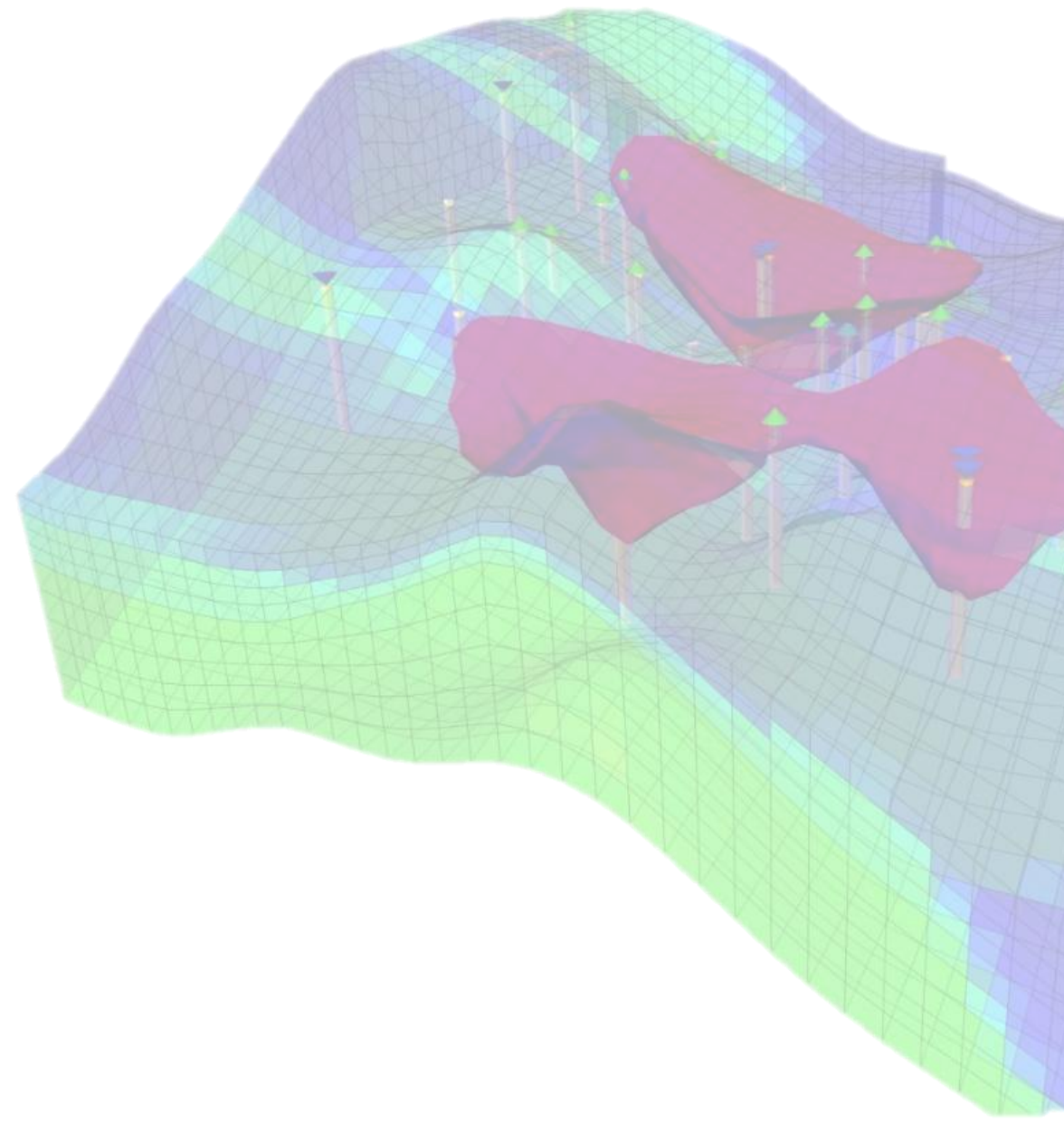
T is in K (Kelvin)

```
1.000I- + 1.000Na+ = NaI
-llnl_gamma 3.4
log_k -1.553
delta_h 6.654 #kJ/mol #97sve/sho
-analytic 6.9652453E+2 1.1039538E-1 -3.8647875E+4 -2.5339072E+2 2.2785916E+6
#References = LogK/DGf: 97sve/sho; DHf/DHr: Internal calculation; S°: 97sve/sho; Cp: 97sve/sho; V°: 97sve/sho;
```

GEM 2025.10 can directly read PHREEQC format

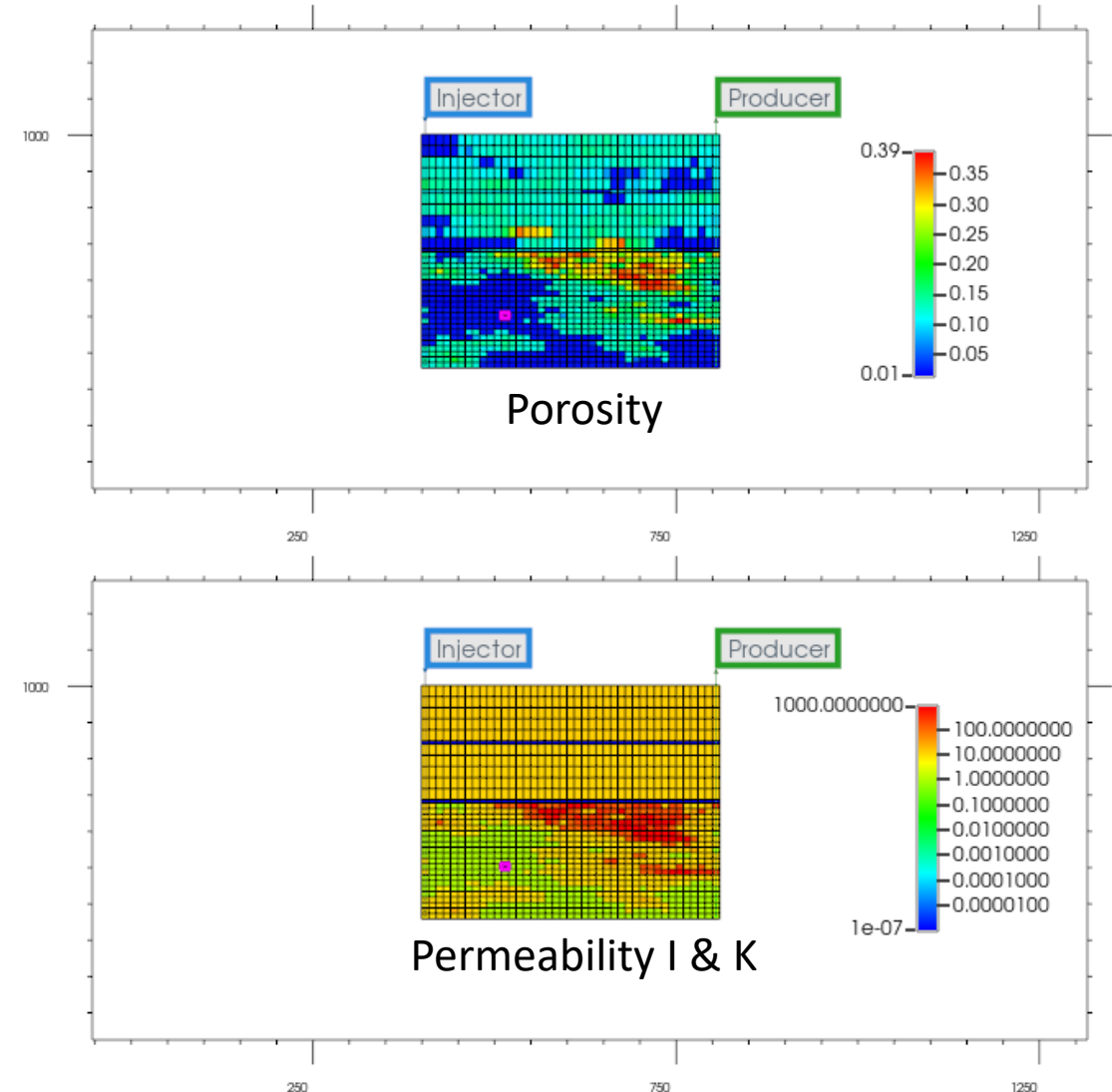
Source: [THERMODDEM](#)

Case Study



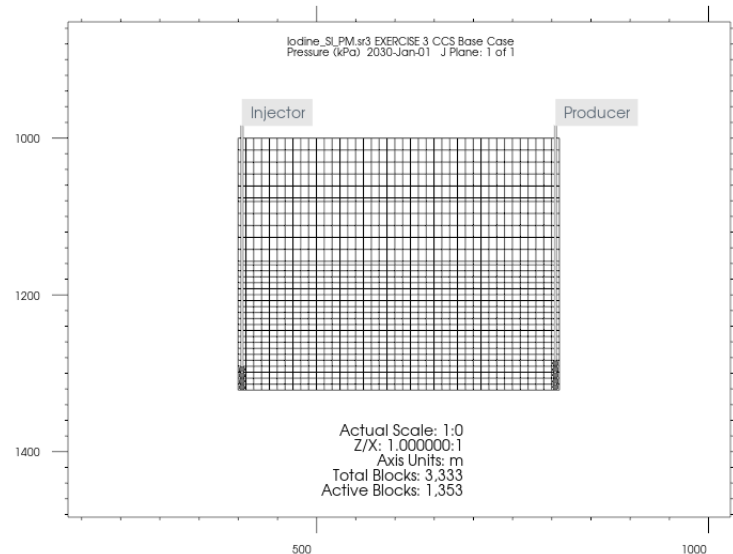
Reservoir and Fluid Description

- 2D Cross-Sectional Model
- Dimension: 400 m x 100 m x 199 m
- Reservoir Top: 1,000 m
- Reservoir Thickness: 159.6 m
- Well Spacing: 400 m
- Kv/Kh: 0.1
- Initial Ion and Mineral Conditions
 - Na⁺: 10,766 ppm (0.468 mol/kg)
 - I⁻: 100 ppm (0.000788 mol/kg)
 - NaI: 8.15E-08 bulk volume fraction
- Initial Pressure: 1,000 kPa at 1,000 m
- Initial Water Saturation: 99.9999%
- Initial Gas Composition
 - CH₄: 96.5%
 - CO₂: 3.5%



Well Description

- Injector
 - Water Injection Rate: 100 m³/day
 - Bottom Hole Pressure: 16,000 kPa
- Producer
 - Water Production Rate 100 m³/day
 - Bottom Hope Pressure: 8,000 kPa
- Voidage Replacement Ratio
 - Water Recycling: 100% (**GCONI** + **RECYCLE WATER**)



GEM Dataset

```
GROUP 'I' ATTACHTO 'FIELD'
GROUP 'P' ATTACHTO 'FIELD'
```

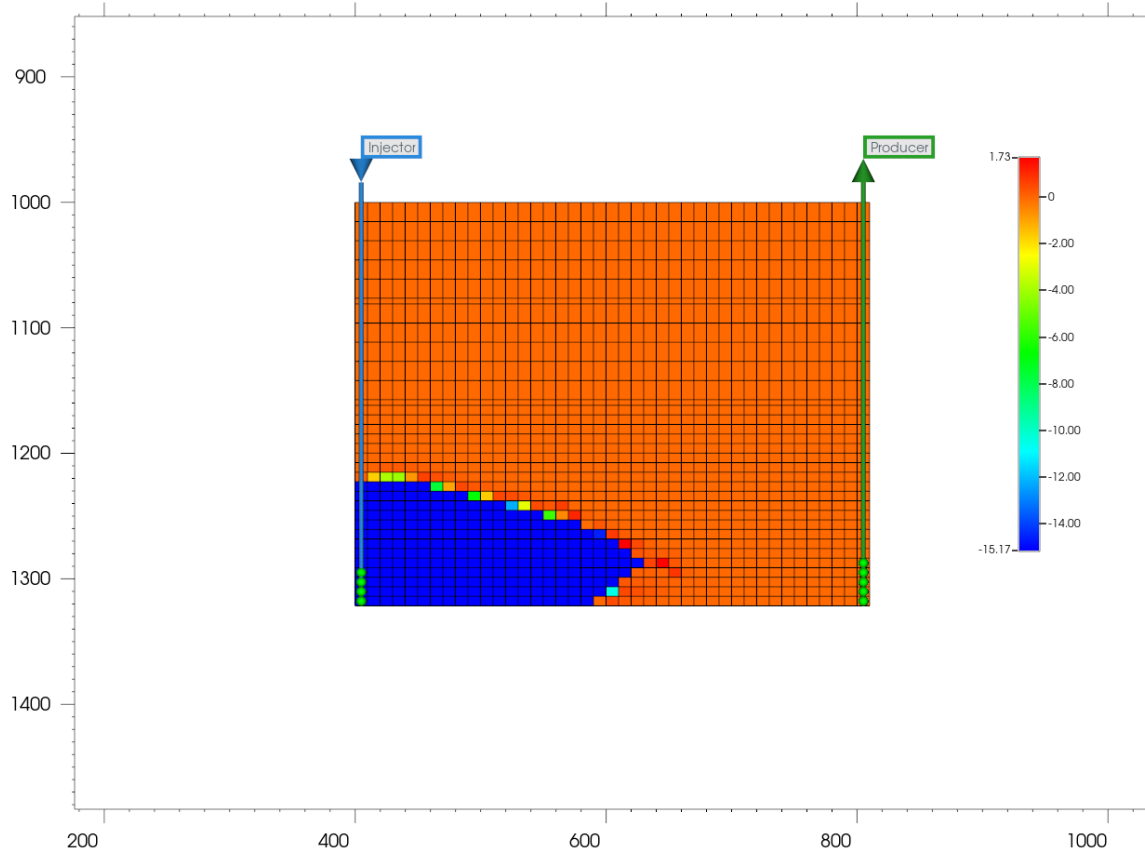
```
WELL 'Injector'
INJECTOR 'Injector'
INCOMP WATER
OPERATE MAX STW 100.0 CONT REPEAT
OPERATE MAX BHP 14000.0 CONT REPEAT
**          rad geofac wfrac skin
GEOMETRY K 0.3048 0.37 1.0 0.0
PERF      GEO 'Injector'
** UBA          ff          Status Connection
   31 1 30      1.0 OPEN    FLOW-FROM 'SURFACE' REFLAYER
   31 1 31      1.0 OPEN    FLOW-FROM 1
   31 1 32      1.0 OPEN    FLOW-FROM 2
   31 1 33      1.0 OPEN    FLOW-FROM 3
```

```
WELL 'Producer'
PRODUCER 'Producer'
OPERATE MAX STW 100.0 CONT REPEAT
OPERATE MIN BHP 8000.0 CONT REPEAT
**          rad geofac wfrac skin
GEOMETRY K 0.3048 0.37 1.0 0.0
PERF      GEO 'Producer'
** UBA          ff          Status Connection
   71 1 29      1.0 OPEN    FLOW-TO 'SURFACE' REFLAYER
   71 1 30      1.0 OPEN    FLOW-TO 1
   71 1 31      1.0 OPEN    FLOW-TO 2
   71 1 32      1.0 OPEN    FLOW-TO 3
   71 1 33      1.0 OPEN    FLOW-TO 4
```

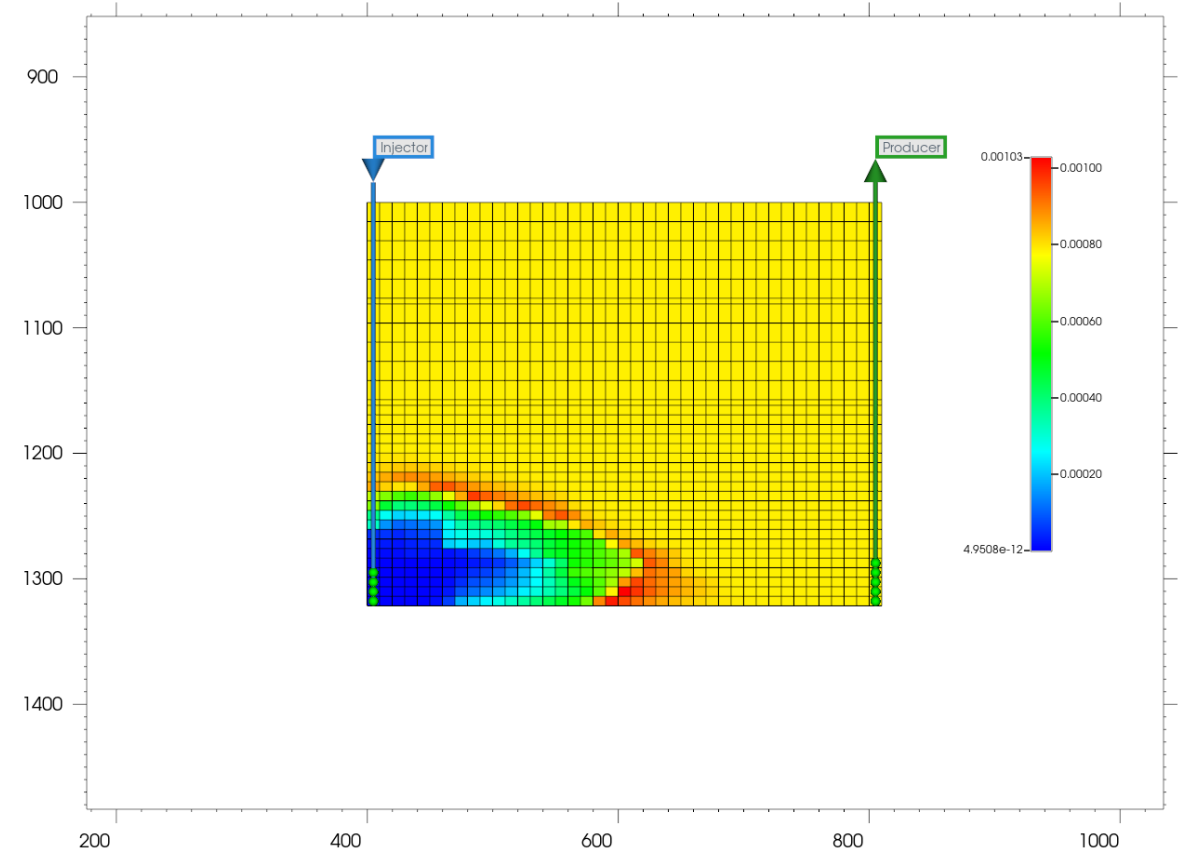
```
WELL 'Producer' ATTACHTO 'P'
WELL 'Injector' ATTACHTO 'I'
GCONI 'FIELD'
RECYCLE WATER 1.0
```

5-Year Production Simulation Results (1)

Dashboard: IK 2D View



Mole Change in NaI Mineral (gmol)

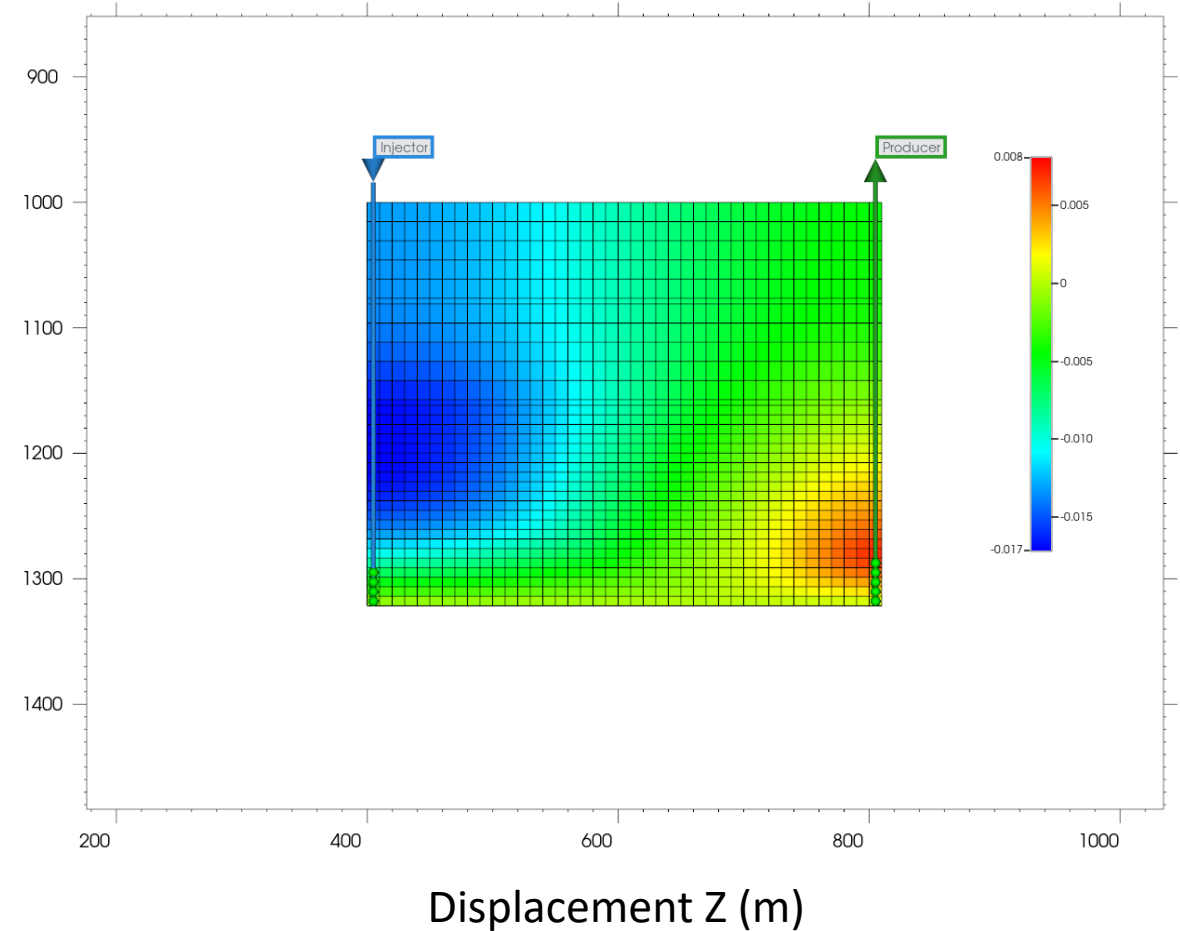
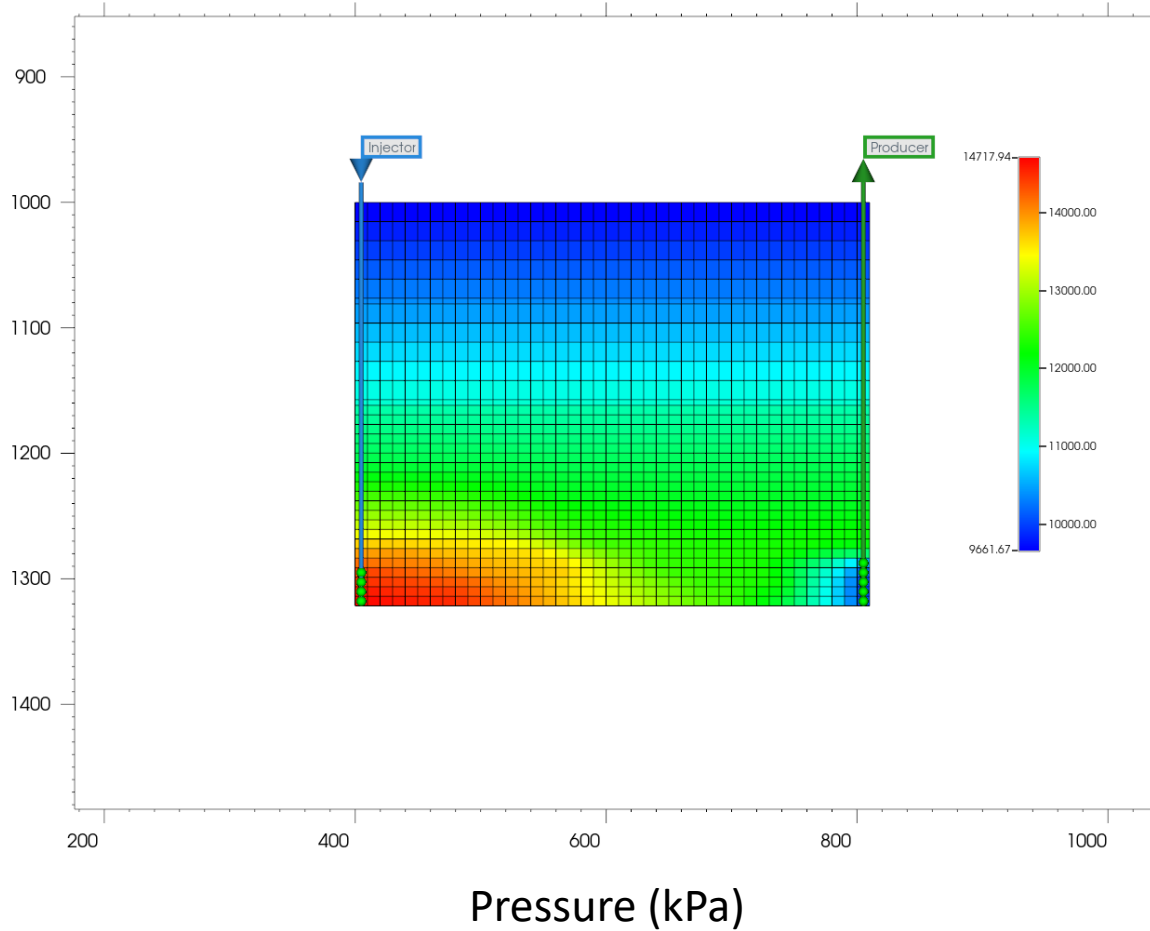


Molality of I^- (mol/kg)

5-Year Production Simulation Results (2)



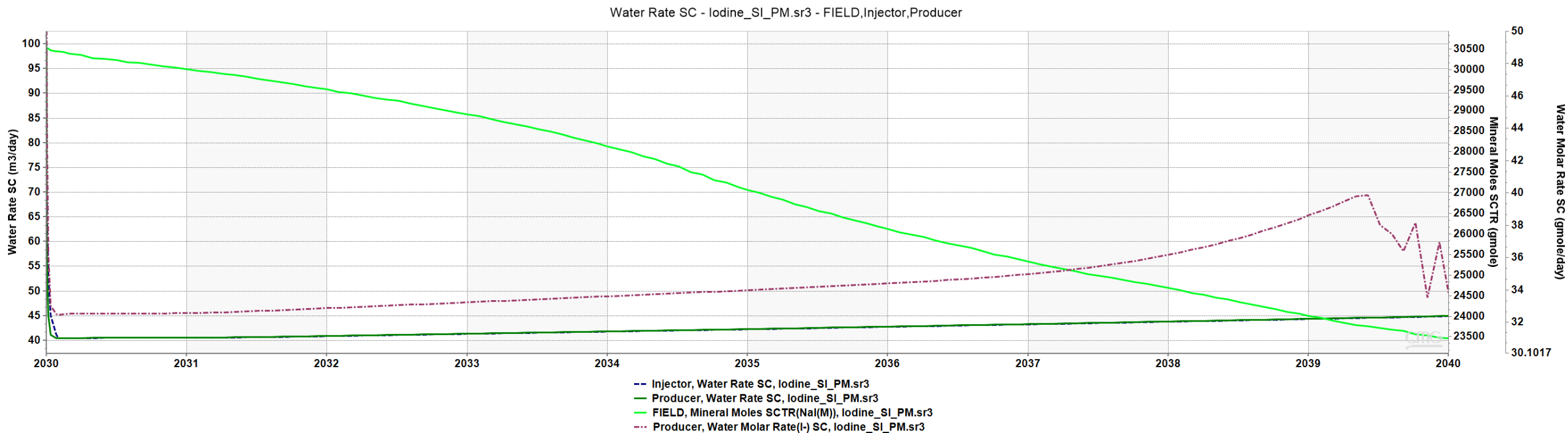
Dashboard: IK 2D View_1



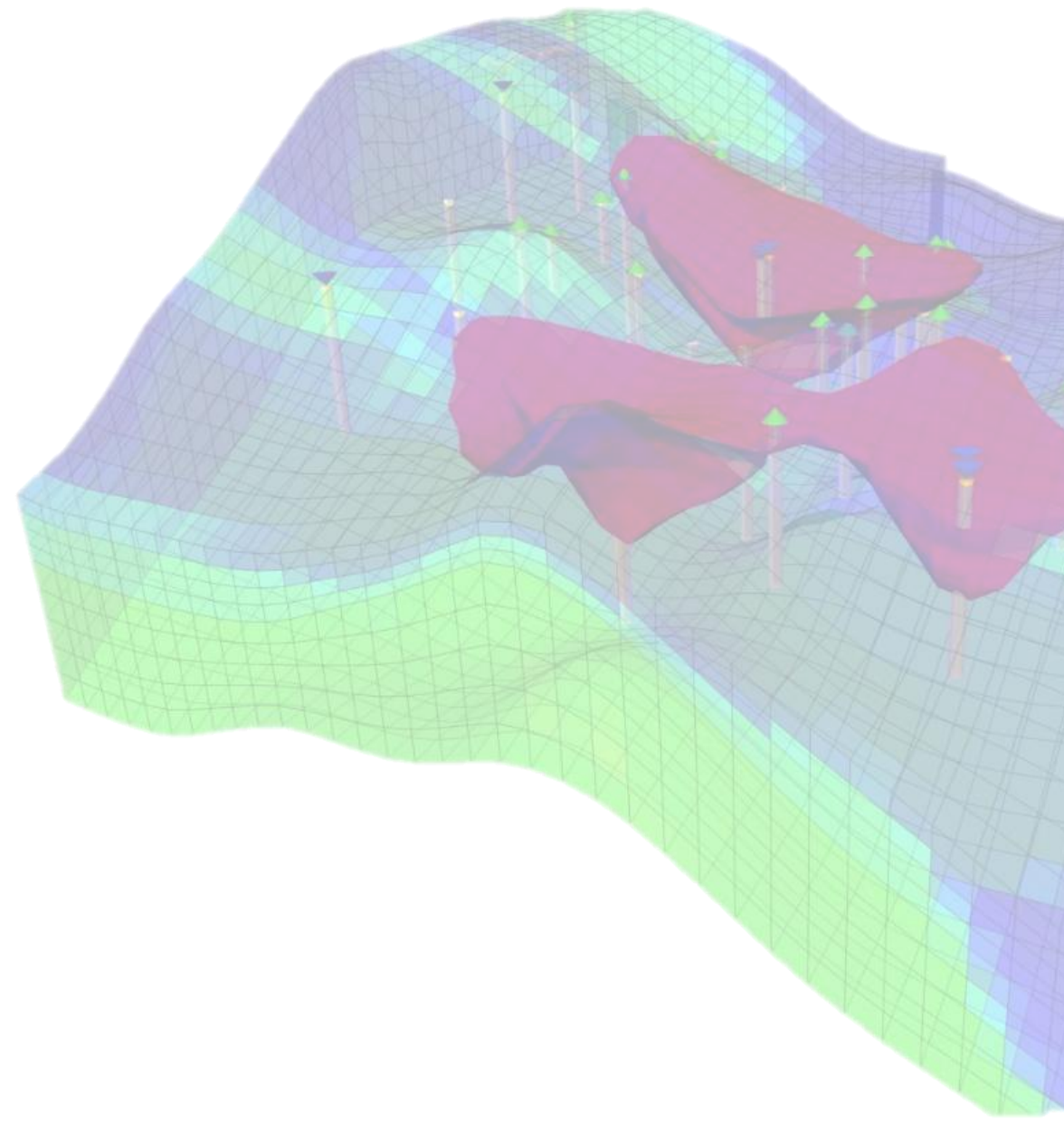
10-Year Production Profile



EM™

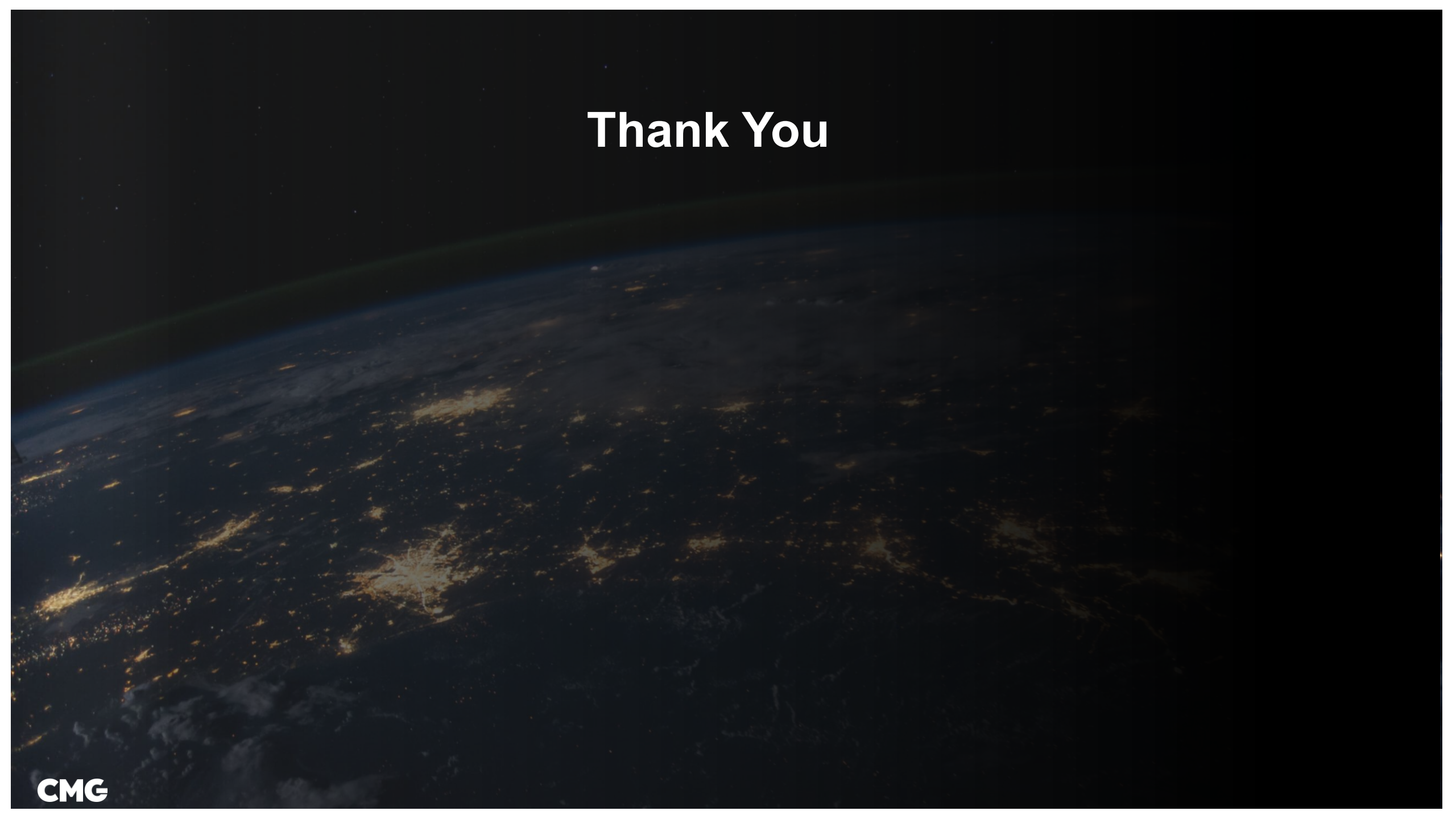


Conclusions



Conclusions

- GEM has been used to simulate domestic gas field operations
- Henry's law-based method is the most straightforward approach to calculate gas (methane and CO₂) solubility in the aqueous phase
- Adding the iodide ion (I⁻) and sodium iodide (NaI) coupled with the sodium ion (Na⁺) into the geochemistry calculation enables the iodine production estimation and risk analysis
- The impacts of water production and injection can be characterized by the geochemical & geomechanics coupling

A wide-angle view of Earth from space, showing the curvature of the planet and city lights at night. The Earth's surface is dark, with numerous bright yellow and orange lights from cities and towns scattered across the landmasses. The atmosphere is visible as a thin blue layer along the horizon. The background is the deep black of space.

Thank You