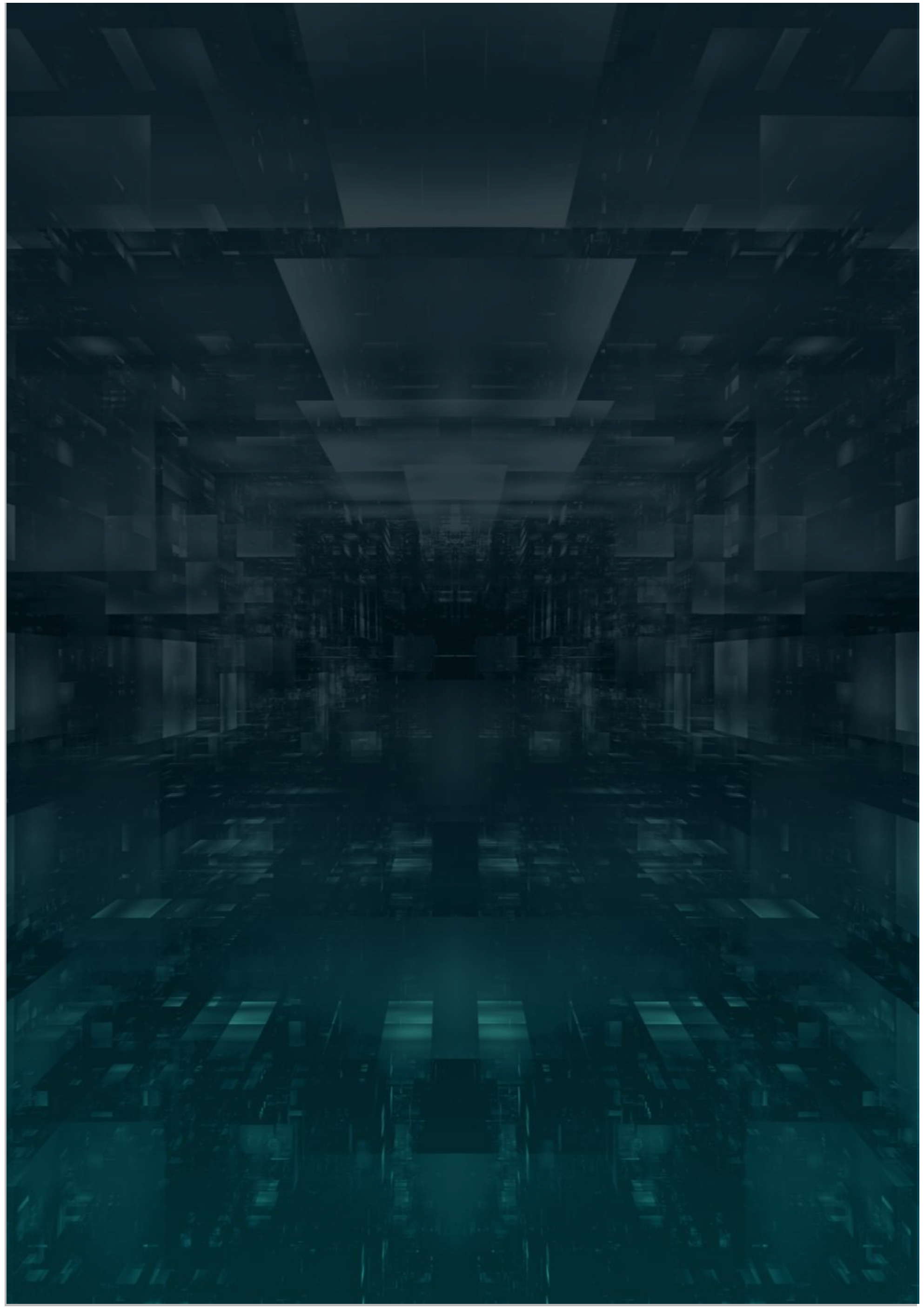
日本天然气田制碘生产过程模拟
Coupled Geochemistry Simulation for Iodine Production

June 2025

CMG

AGENDA



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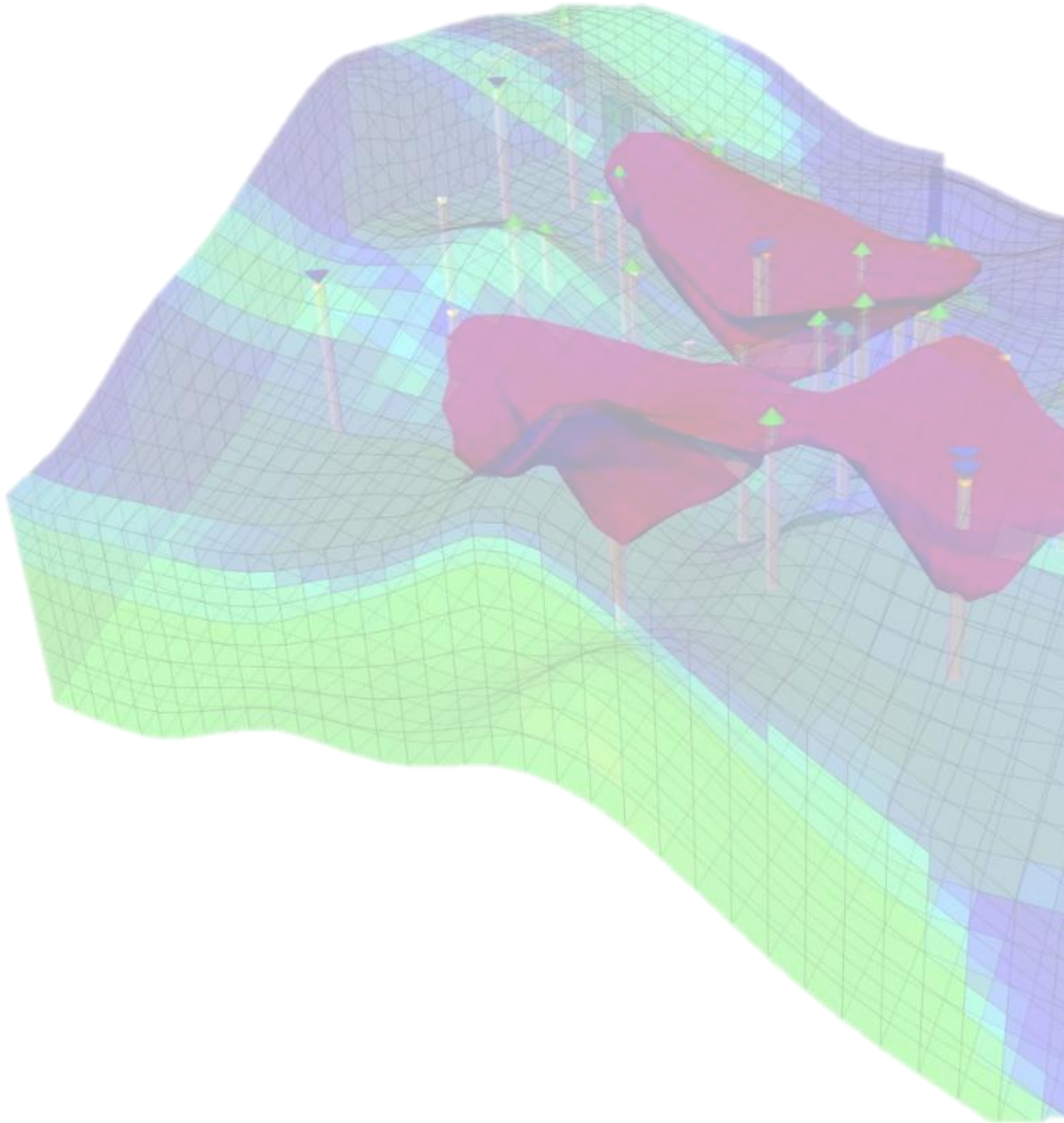
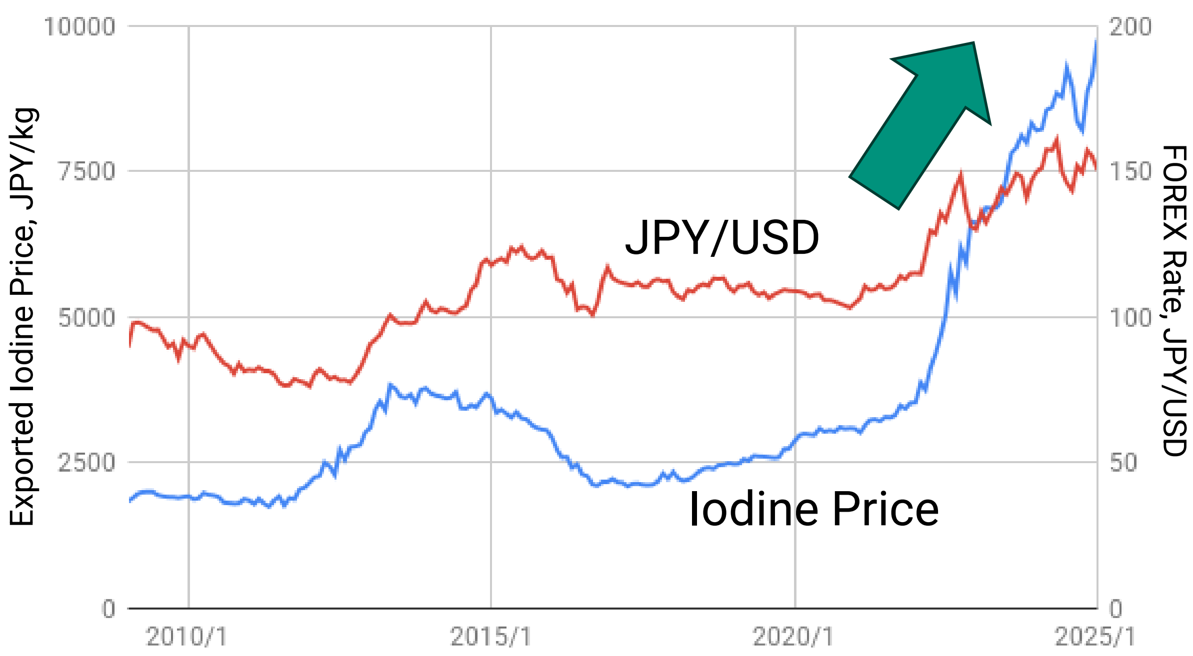


Introduction

Why iodine modeling is important?

Long-Term Trend of Iodine Price

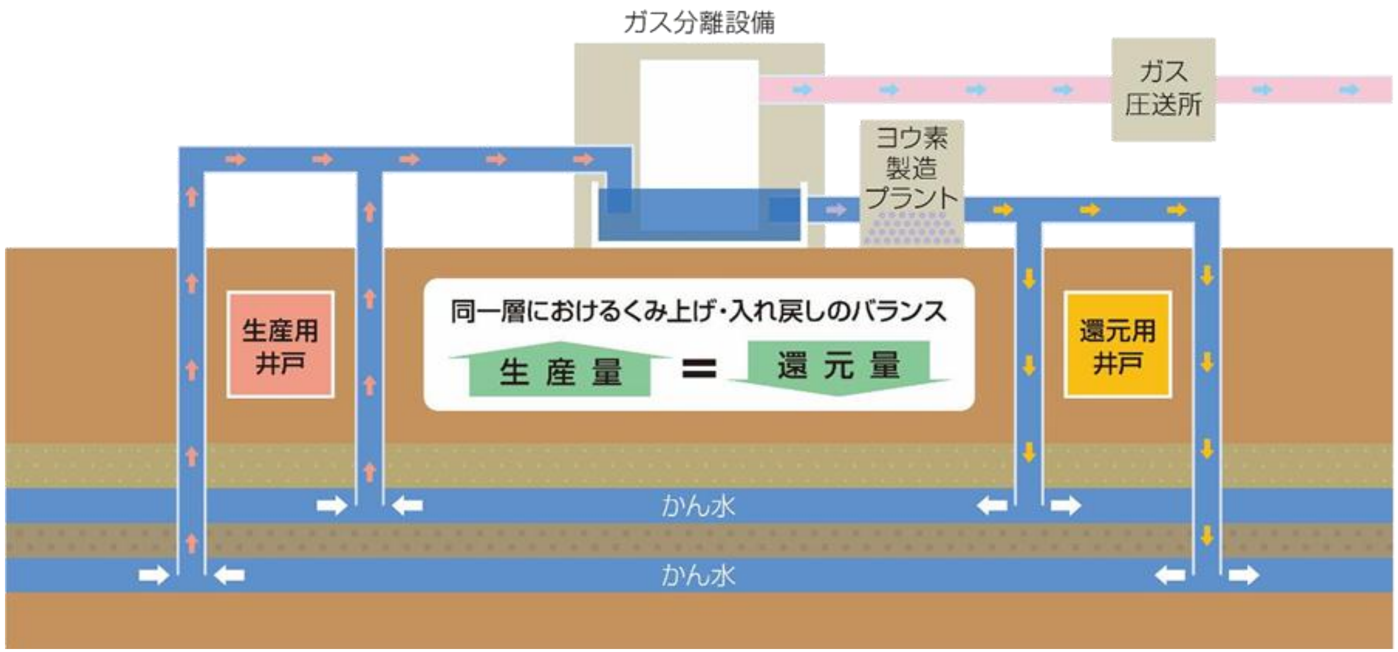


Courtesy Ryusuke Matsuyama

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]



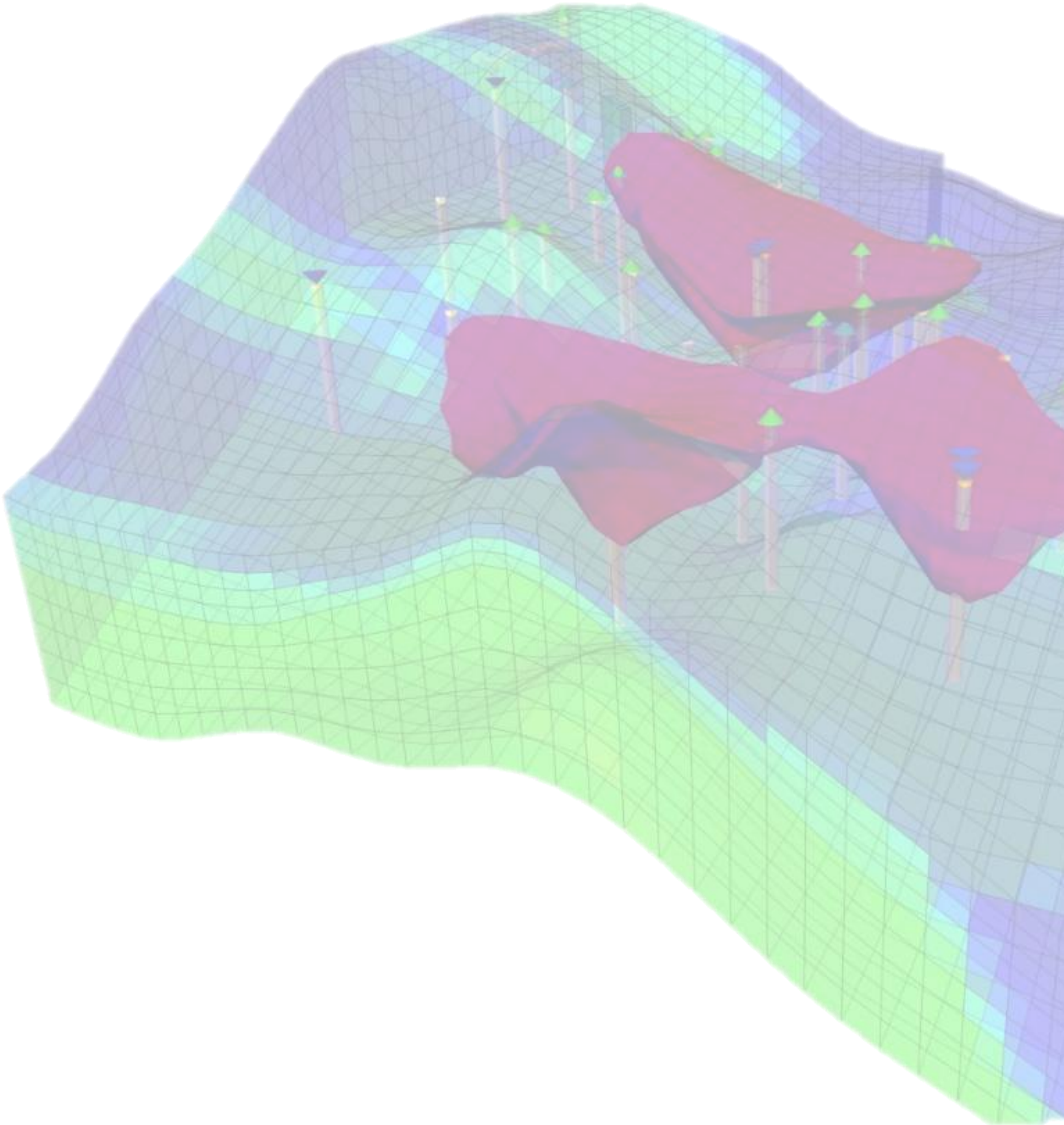
- Natural gas and iodine are produced **with water**
- Natural gas is separated at the surface and pumped into the sales pipeline
- **Produced water is re-injected** to the original reservoirs (100% water recycling)

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

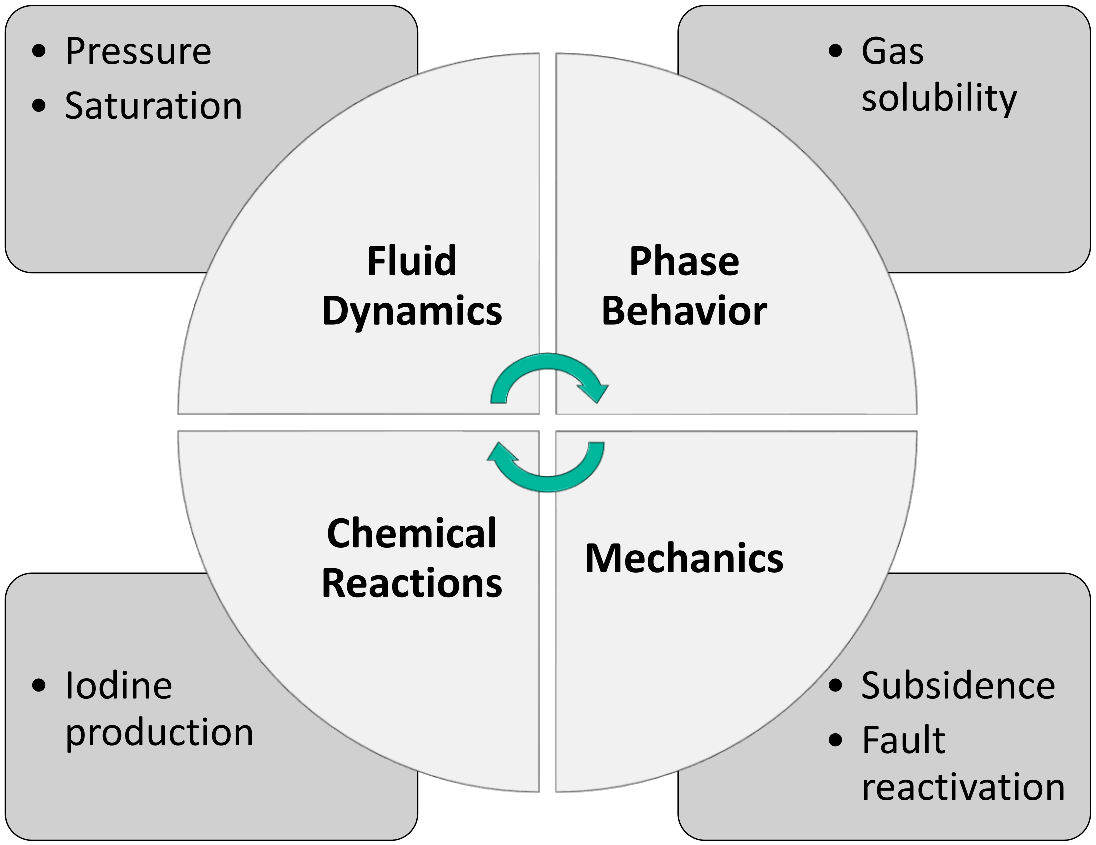
Source:
*1 https://www.gas-youso.com/ *2 https://www.tohoearthtech.co.jp/business/naturalgas/ 3* https://fiu-iodine.org/studies/

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



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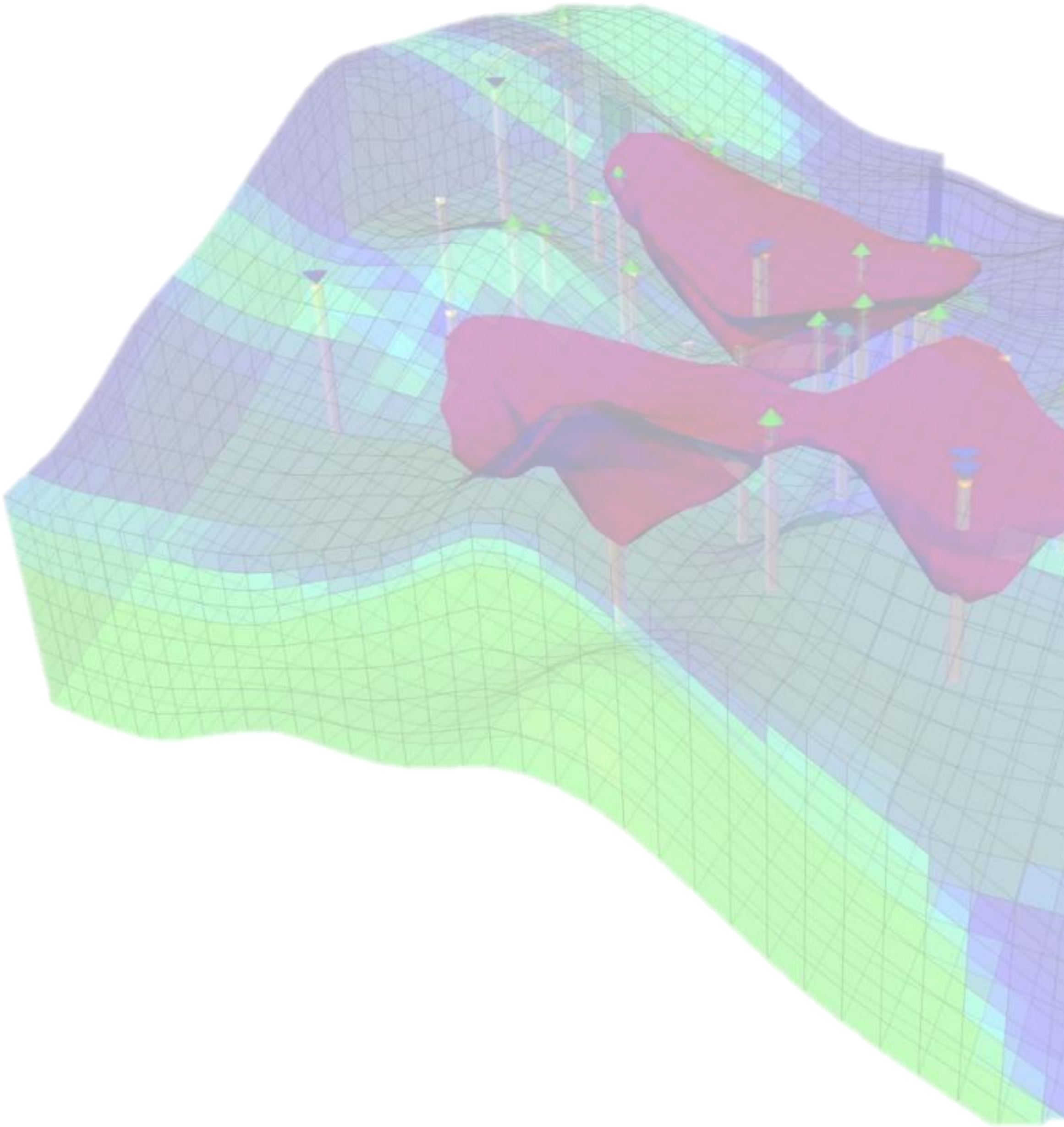
Gas Solubility



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

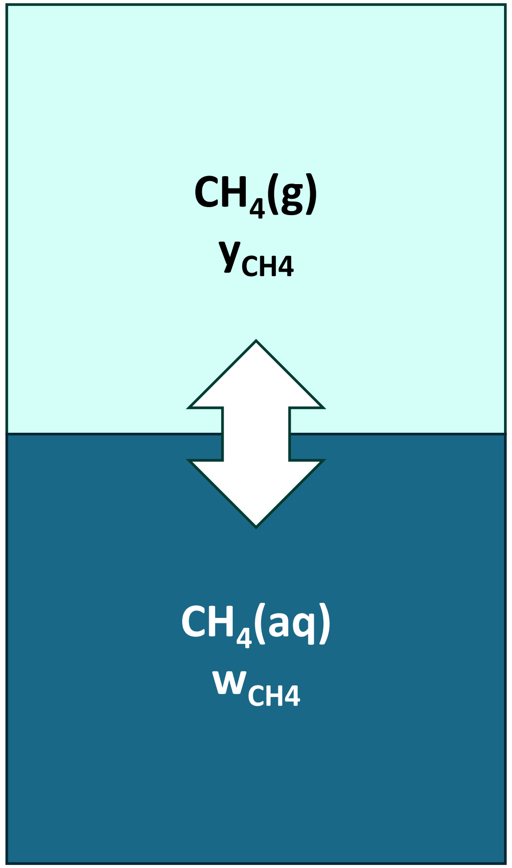
Gas dissolution into the aqueous phase is reversible at equilibrium

$$CH_4(g) \leftrightarrow CH_4(aq)$$

$CH_4(g)$	Methane in the gas phase
$CH_4(aq)$	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

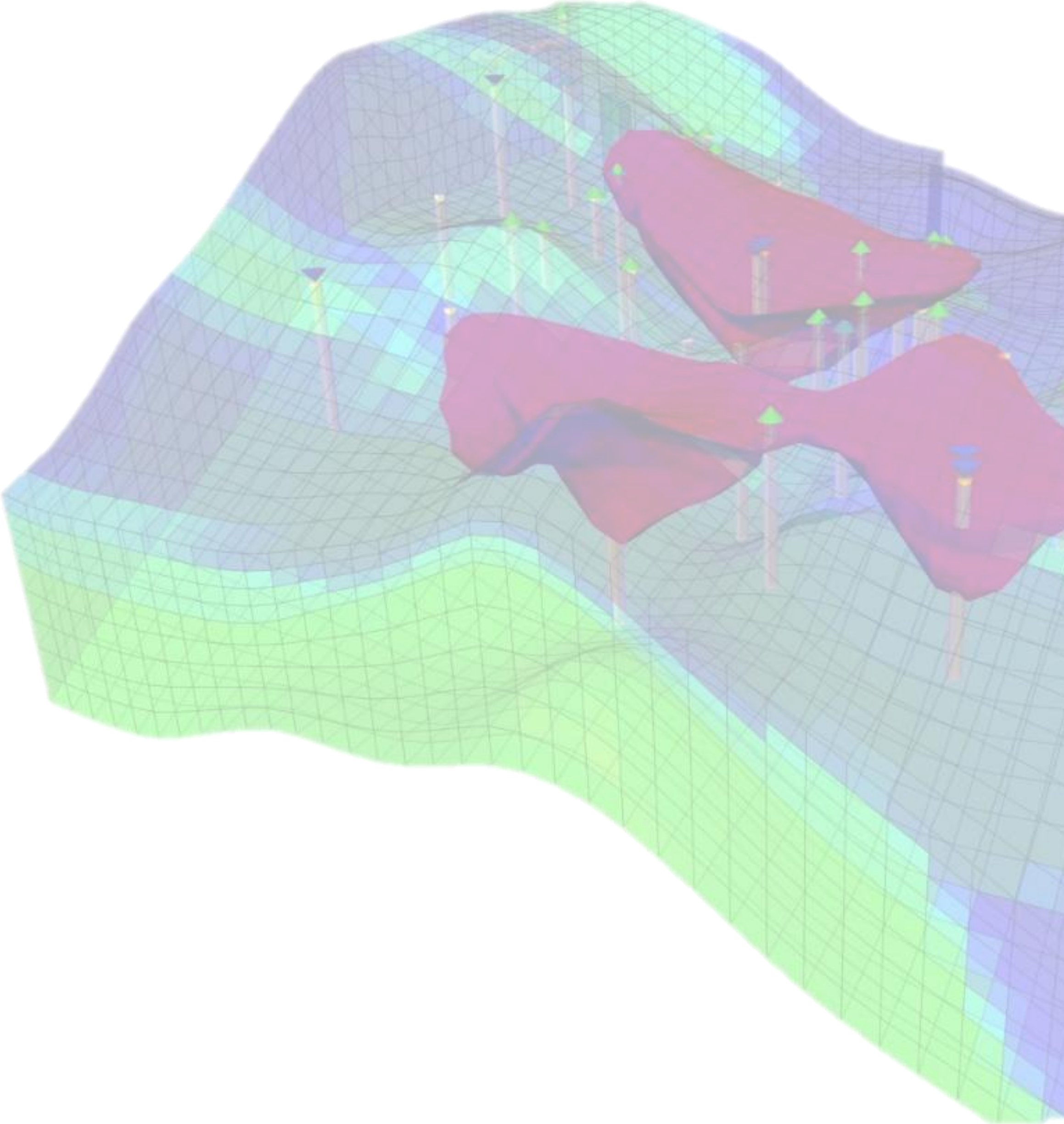
Example

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

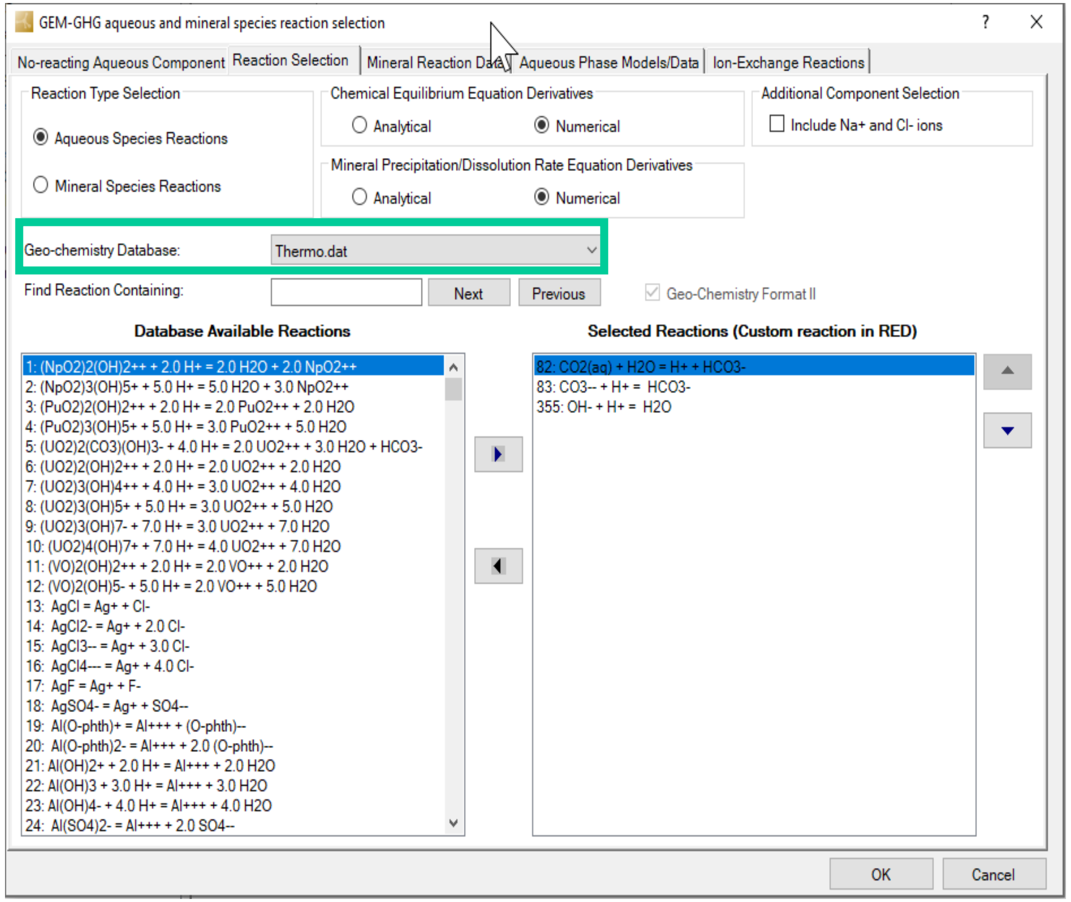
*HENRY-CORR-C1

This keyword activates the use of Harvey's correlation for CH_4 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



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	$H_2O = H^+ + OH^-$	Initial Molality (H^+ and OH^-)	*MOLALITY-AQUEOUS
		Equilibrium Constant	*LOG-CHEM-EQUIL-COEFS
Mineral Dissolution & Precipitation	$NaI = Na^+ + I^-$	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

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

$$CO_2(aq) + H_2O = H^+ + HCO_3^-$$

$$K_{eq}(T) = \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{CO_2(aq)} \cdot a_{H_2O}}$$

'a' is the <u>activity</u> which is also a measure of concentration

a_{H_2O}	$\approx$	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)

<u>Activity coefficients models</u> 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}

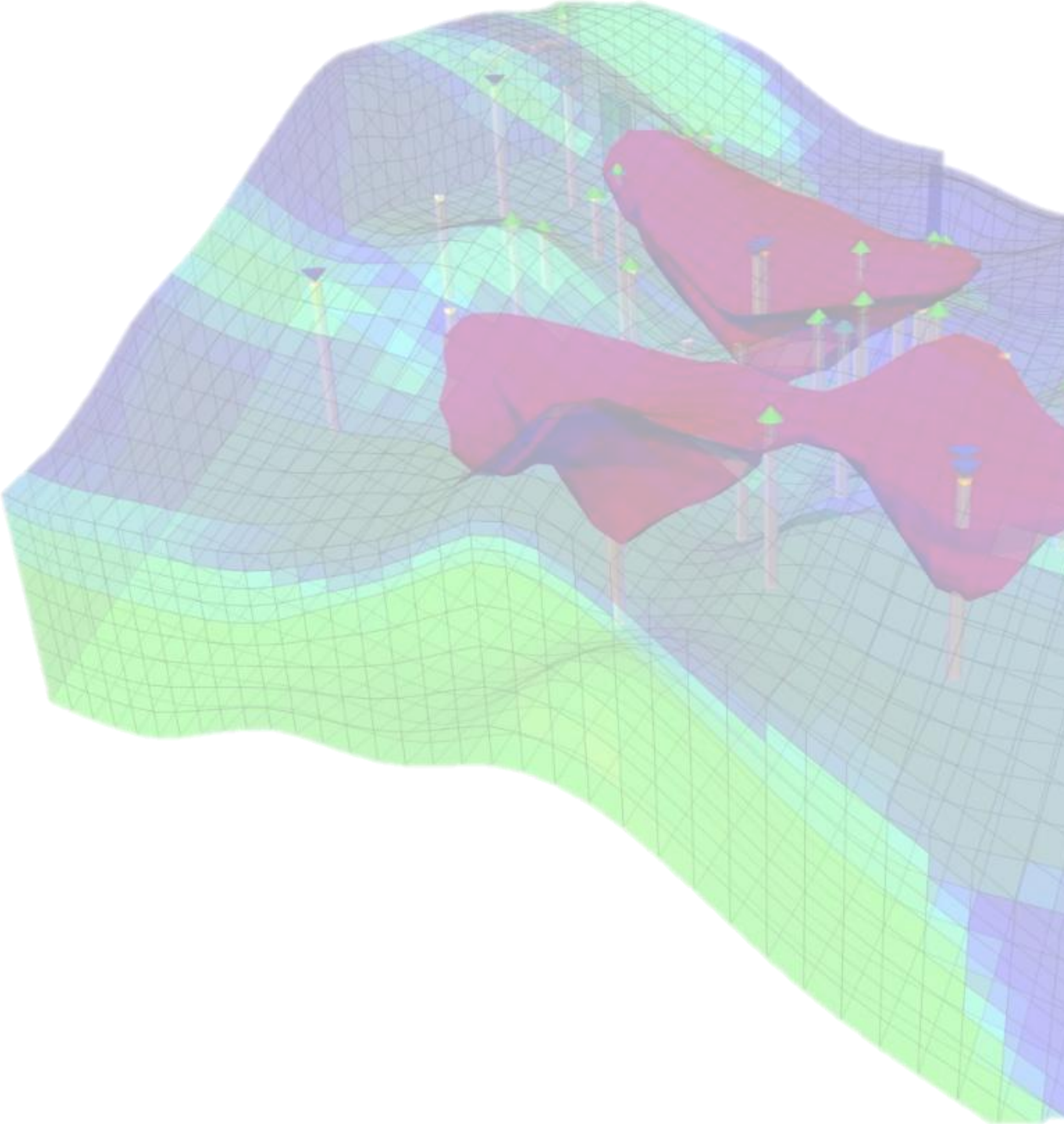
GEM	$\log_{10} K_{eq}(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4$	**T is in °C (Celsius)**
PHREEQC	$\log_{10} K_{eq}(T) = a_0 + a_1 T + a_2 T^{-1} + a_3 \log_{10} T + a_4 T^{-2}$	**T is in K (Kelvin)**

```
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

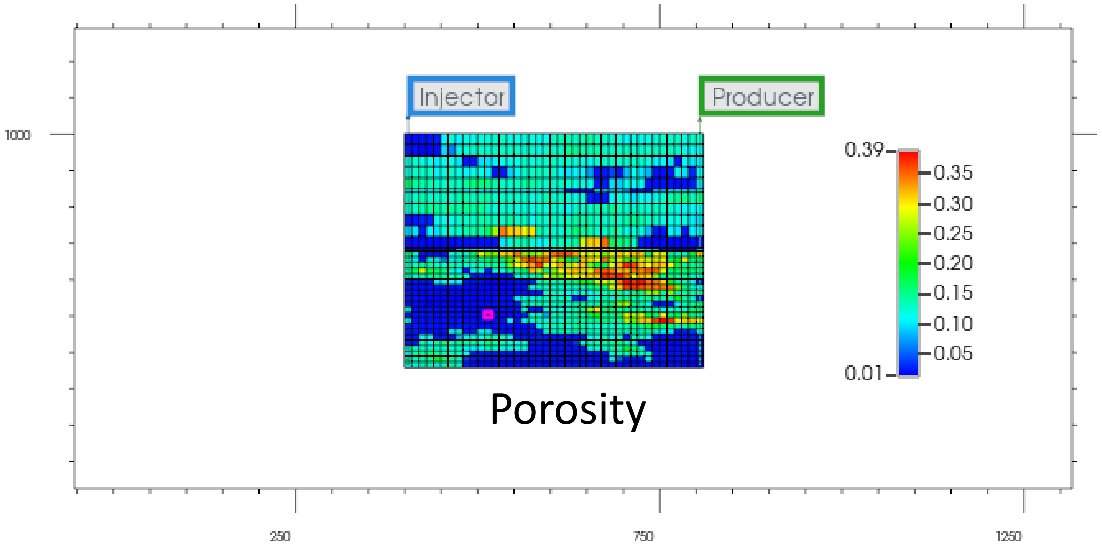
Source: THERMODDEM

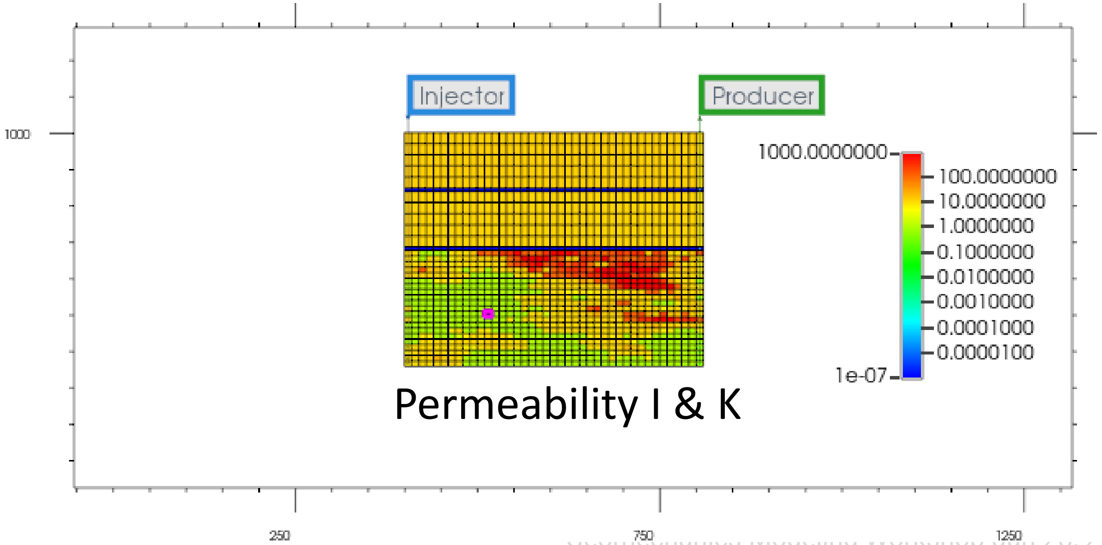
Case Study



Reservoir and Fluid Description

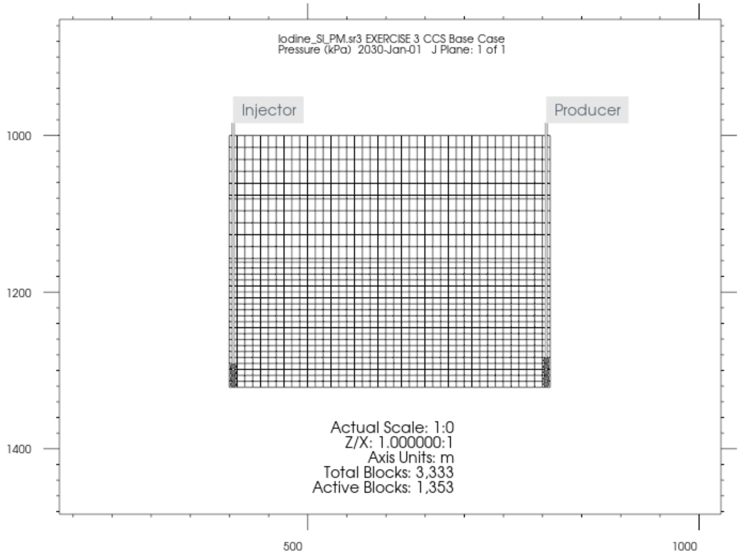
- 2D Cross-Sectional Model
- Dimension: 400 m x 100 m x 199 m
- Reservoir Top: 1,000 m
- Reservoir Thickness: 159.6 m
- Well Spacing: 400 m
- Kv/Kh: 0.1
- Initial Ion and Mineral Conditions
  - Na^+: 10,766 ppm (0.468 mol/kg)
  - I^-: 100 ppm (0.000788 mol/kg)
  - NaI: 8.15E-08 bulk volume fraction
- Initial Pressure: 1,000 kPa at 1,000 m
- Initial Water Saturation: 99.9999%
- Initial Gas Composition
  - CH_4: 96.5%
  - CO_2: 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
```

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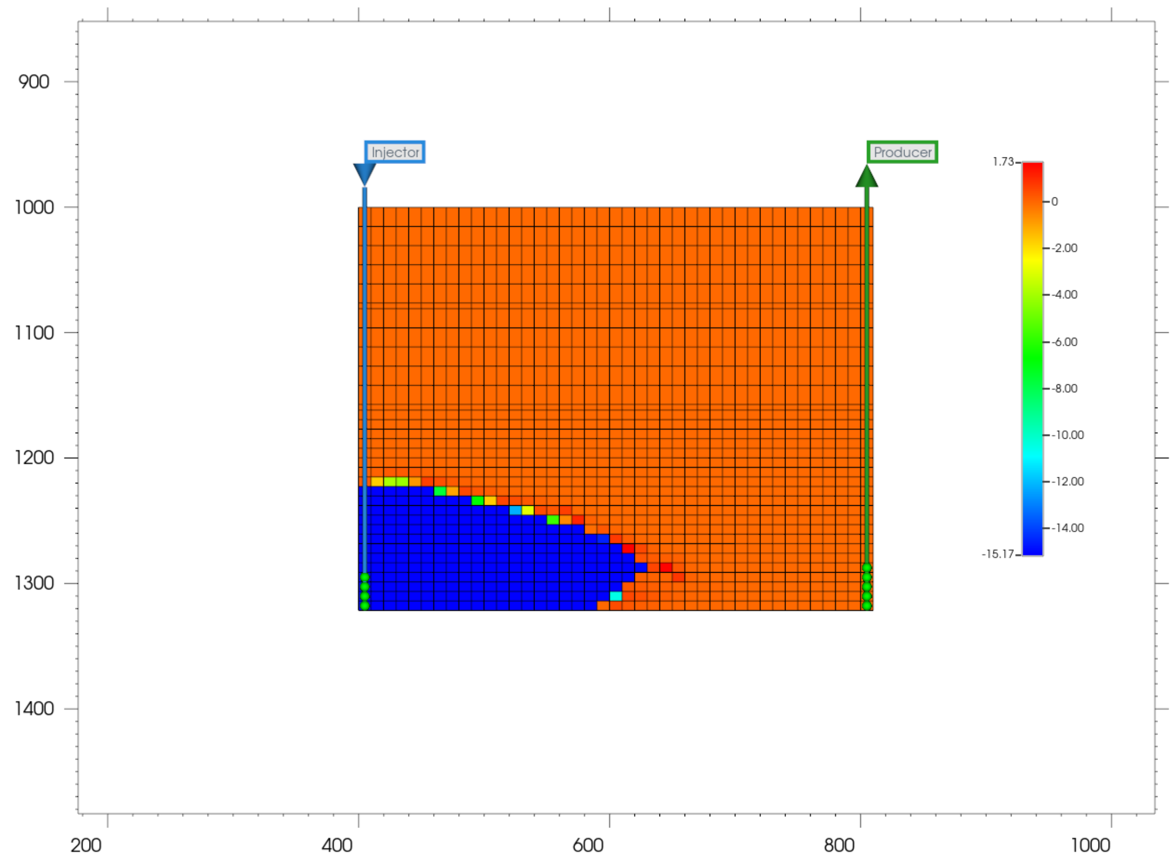
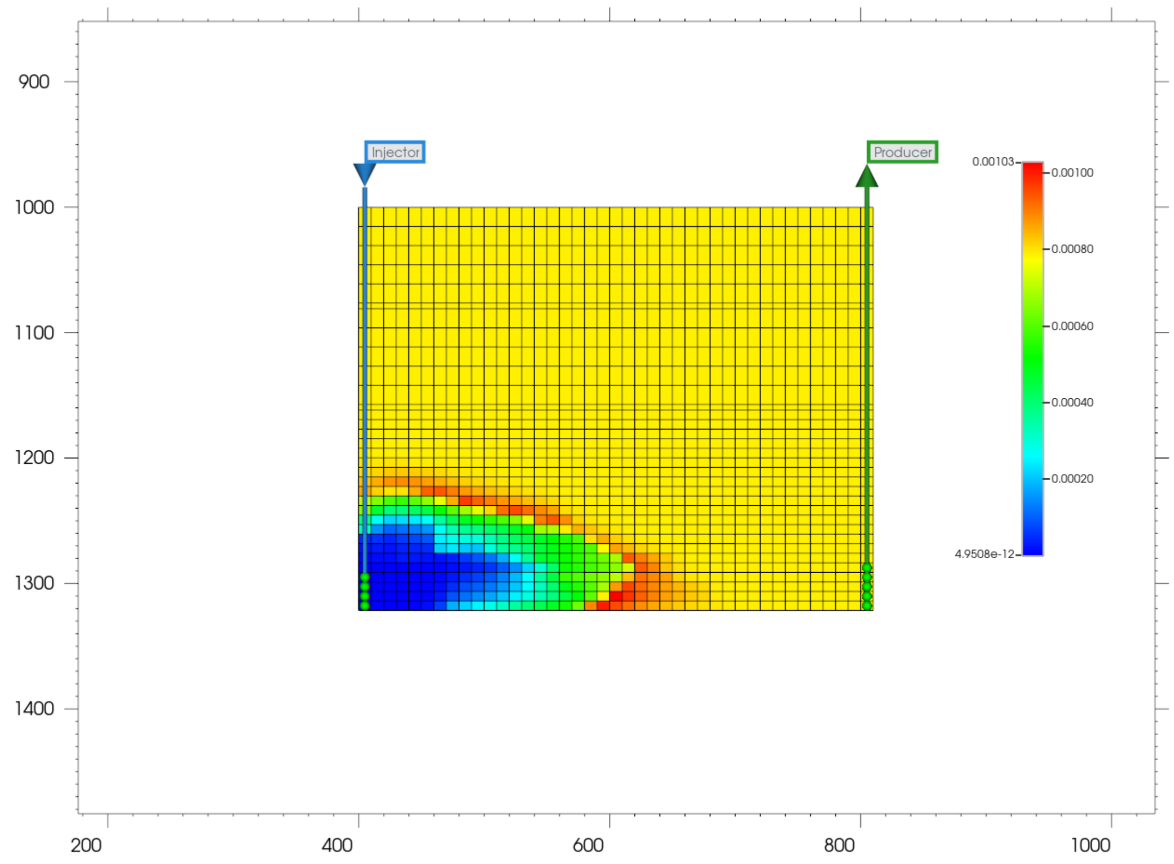
5-Year Production Simulation Results (1)

Dashboard: IK 2D View



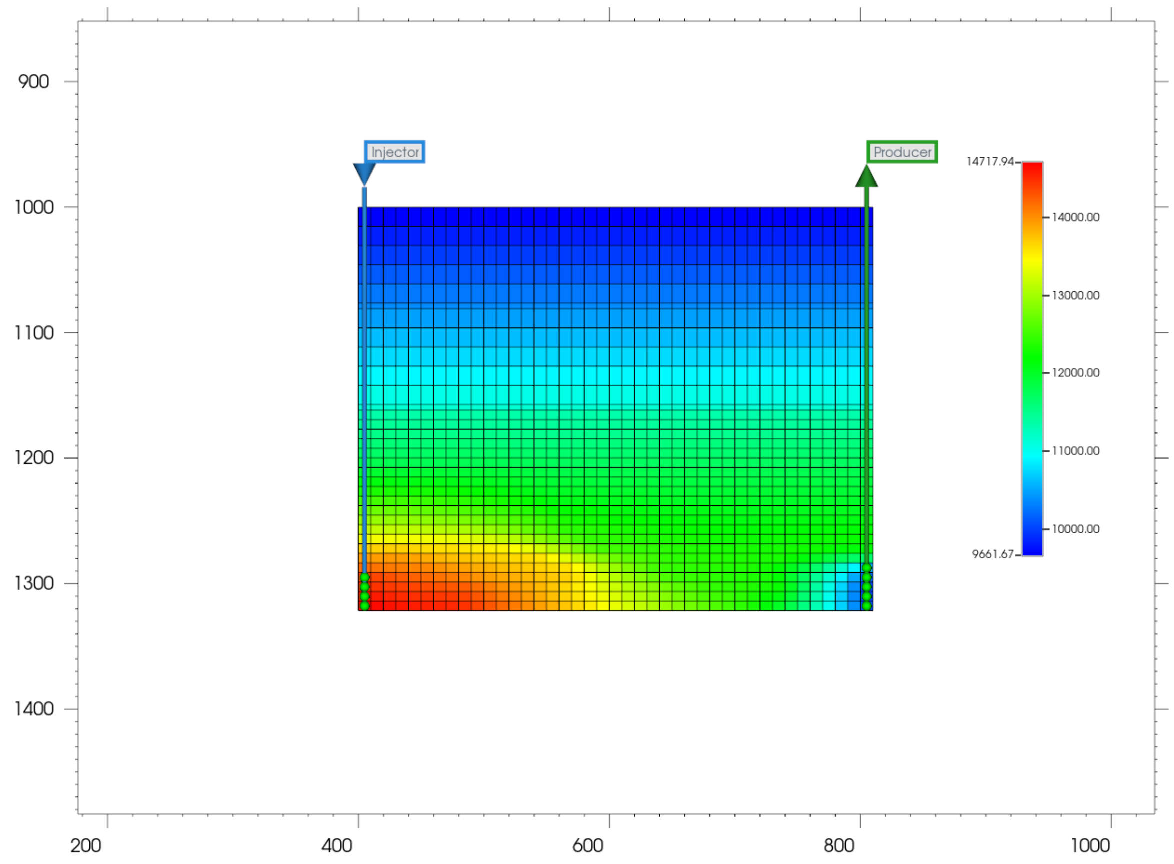
Mole Change in NaI Mineral (gmol)



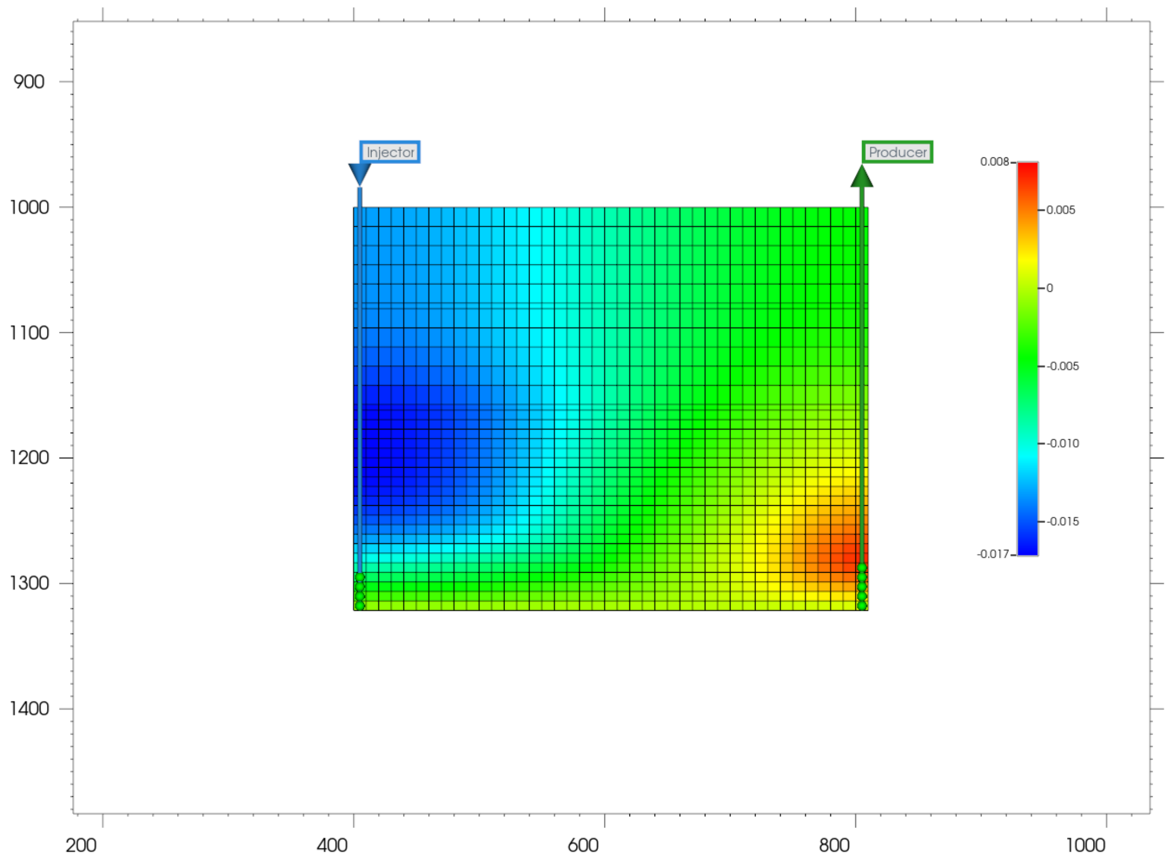
Molality of I^- (mol/kg)

5-Year Production Simulation Results (2)

Dashboard: IK 2D View_1

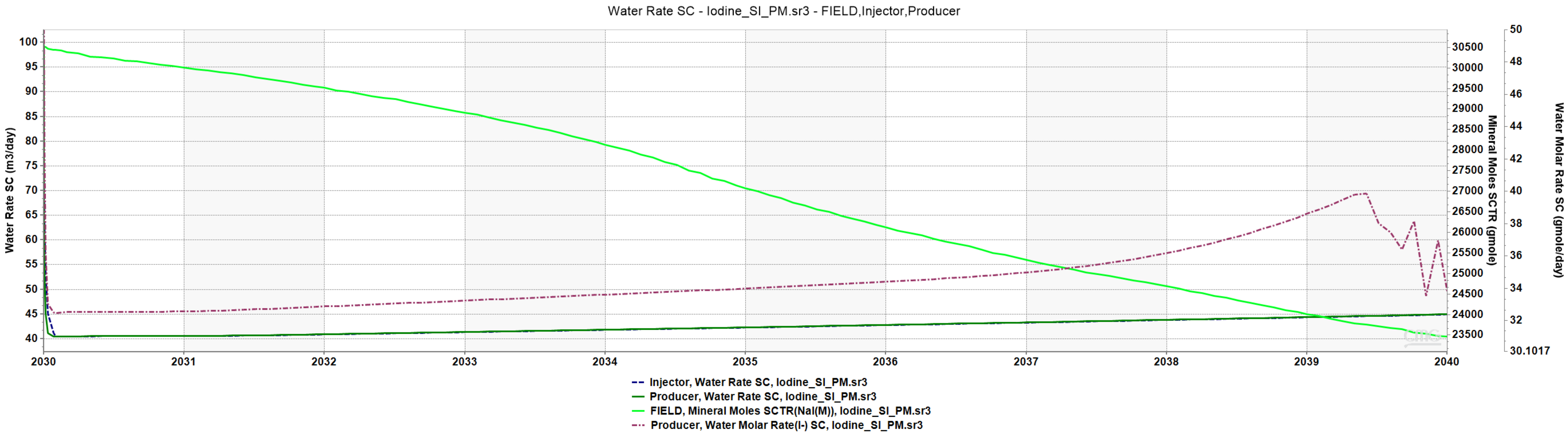


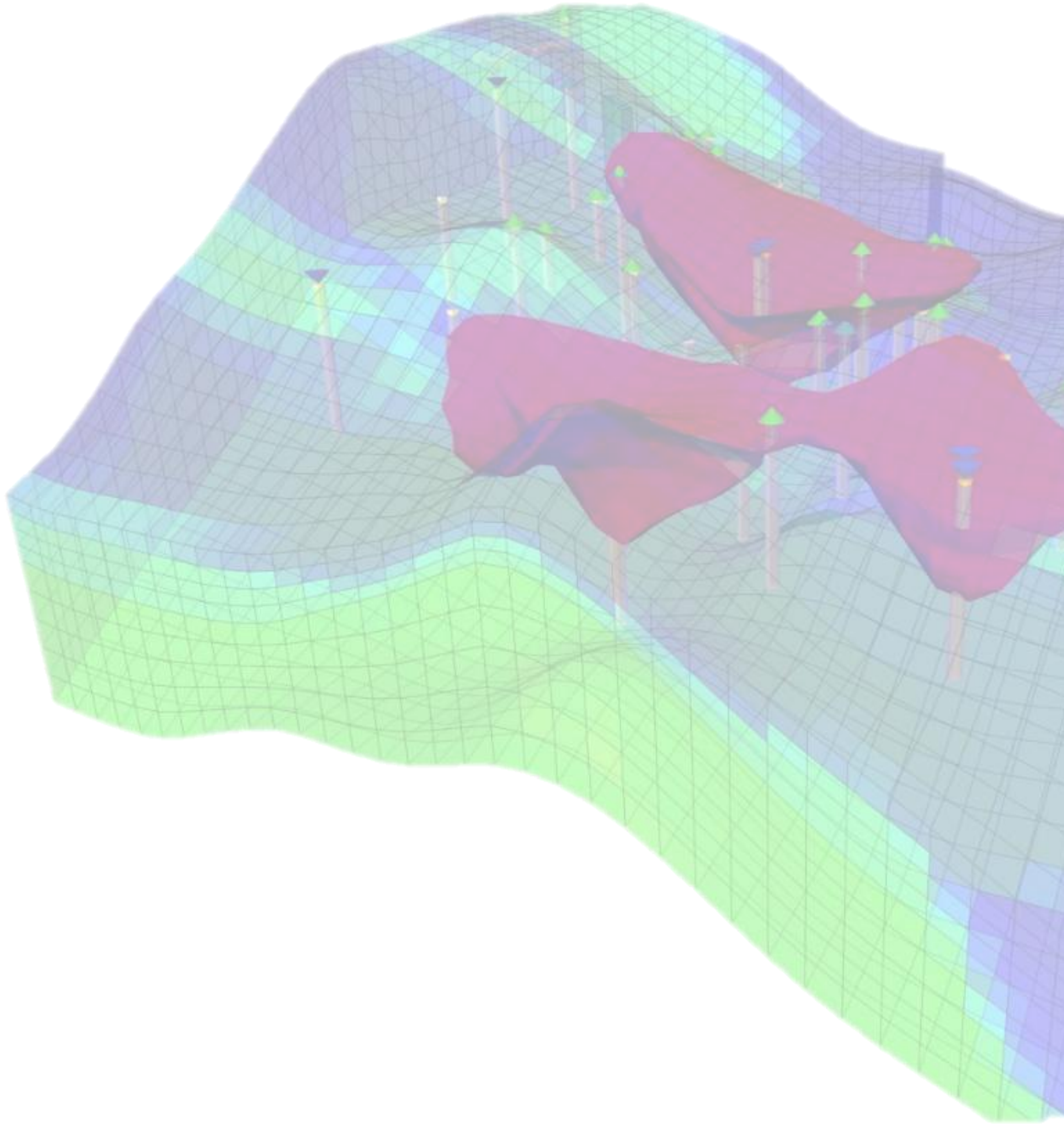
Pressure (kPa)



Displacement Z (m)

10-Year Production Profile





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 CO_2) 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

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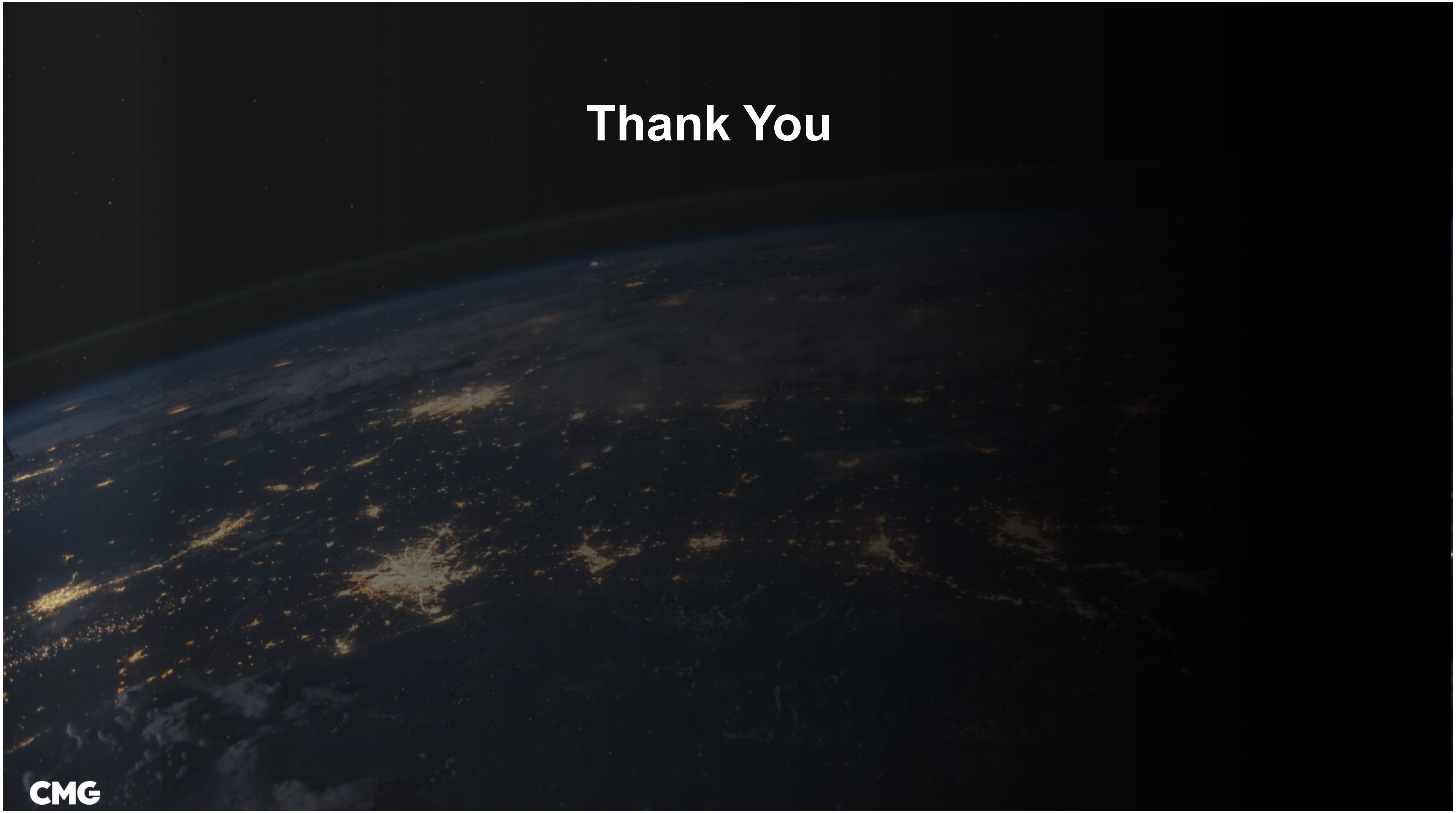
Thank You