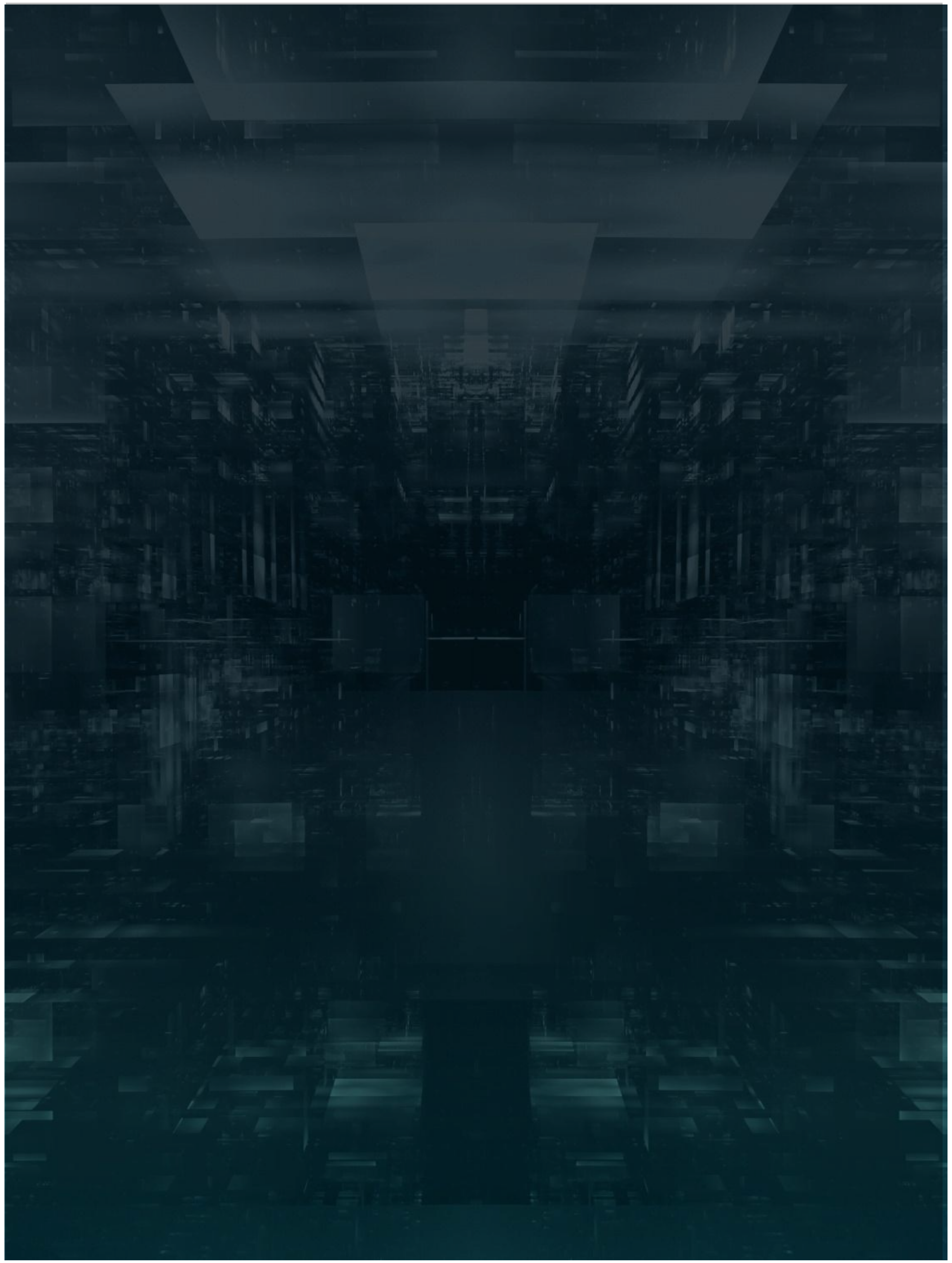
橙氢开发与CMG软件在蛇纹岩化制氢中的应用研究
Natural Hydrogen production by Serpentinization process

17th June 2025

CMG

AGENDA

1. Introduction to Hydrogen modelling in CMG
2. Concept overview of orange & gold hydrogen
3. Presenting previous work on gold hydrogen



1) Introduction to Hydrogen modelling and CMG's solutions

Hydrogen Rainbow*

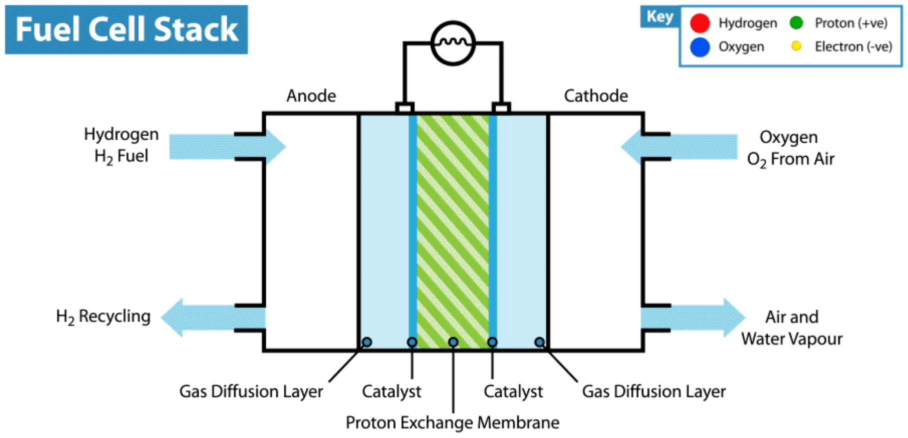
	1. White	Naturally occurring
	2. Brown/Black	Coal gasification
	3. Grey	Steam reforming of methane
	4. Blue	In case the emissions are captured and stored underground
	5. Turquoise	Methane pyrolysis
Water electrolysis	6. Pink	Nuclear energy
Water electrolysis	7. Yellow	Mix of whatever is available
Water electrolysis	8. Green	Renewables

* https://energy-cities.eu/50-shades-of-grey-and-blue-and-green-hydrogen/.

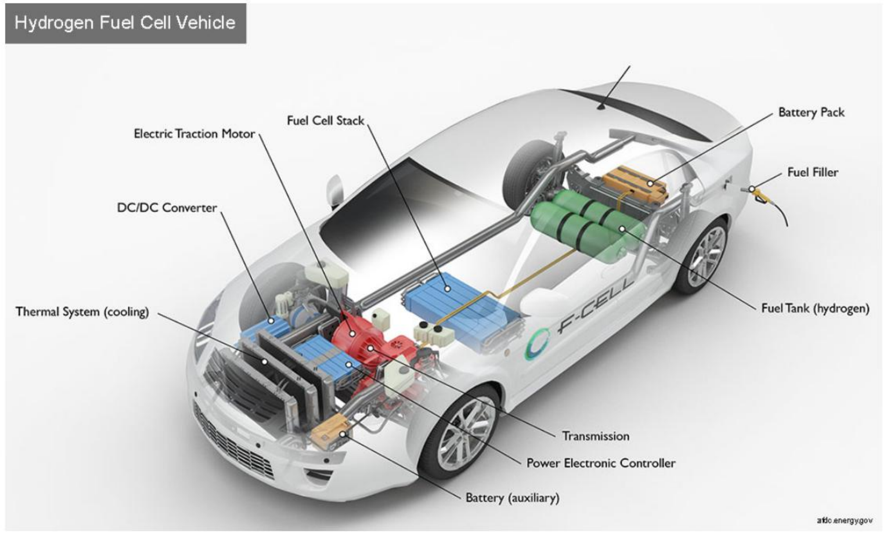
Hydrogen Applications *, **

- Energy storage
- Power-to-gas (e.g. $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$)
- Fuel cell
- Transportation

1. * Yue, M. et al. (2021)
2. ** https://www.energy.gov/eere/fuelcells/fuel-cells



The mechanism of fuel cell operation. (from ttps://www.intelligent-energy.com/technology/technology-faq/)

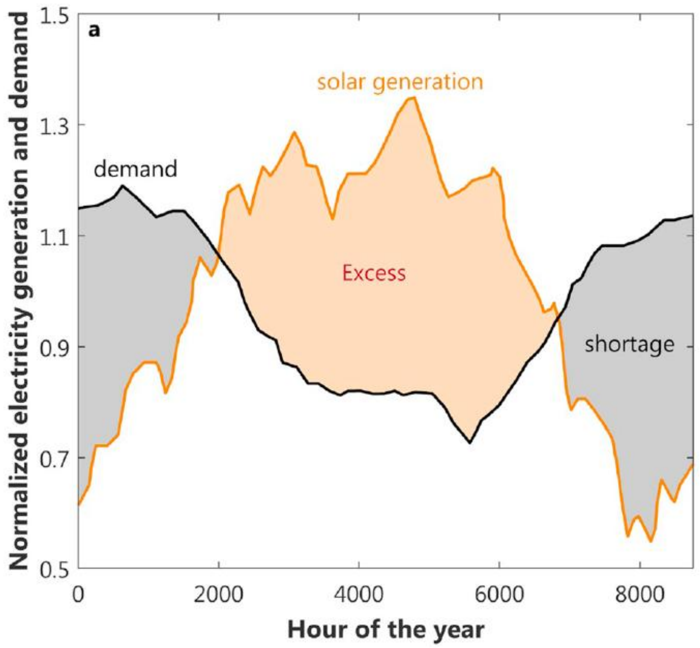


Different parts of a hydrogen fuel cell vehicle. (from https://afdc.energy.gov/vehicles/how-do-fuel-cell-electric-cars-work/)

Hydrogen Applications: Energy Storage

1. Renewable energy resources are not available year-round:

- Subject to strong fluctuations due to the local weather conditions. *
- Seasonal energy demand could be beyond their capacity.



Annual time series of weekly averages that shows the seasonal correlation of electricity demand (black line) and solar generation (orange line) for Europe. Electricity generation and demand normalized over the corresponding average value. Figure from Gabrielli, P. et al. (2020)

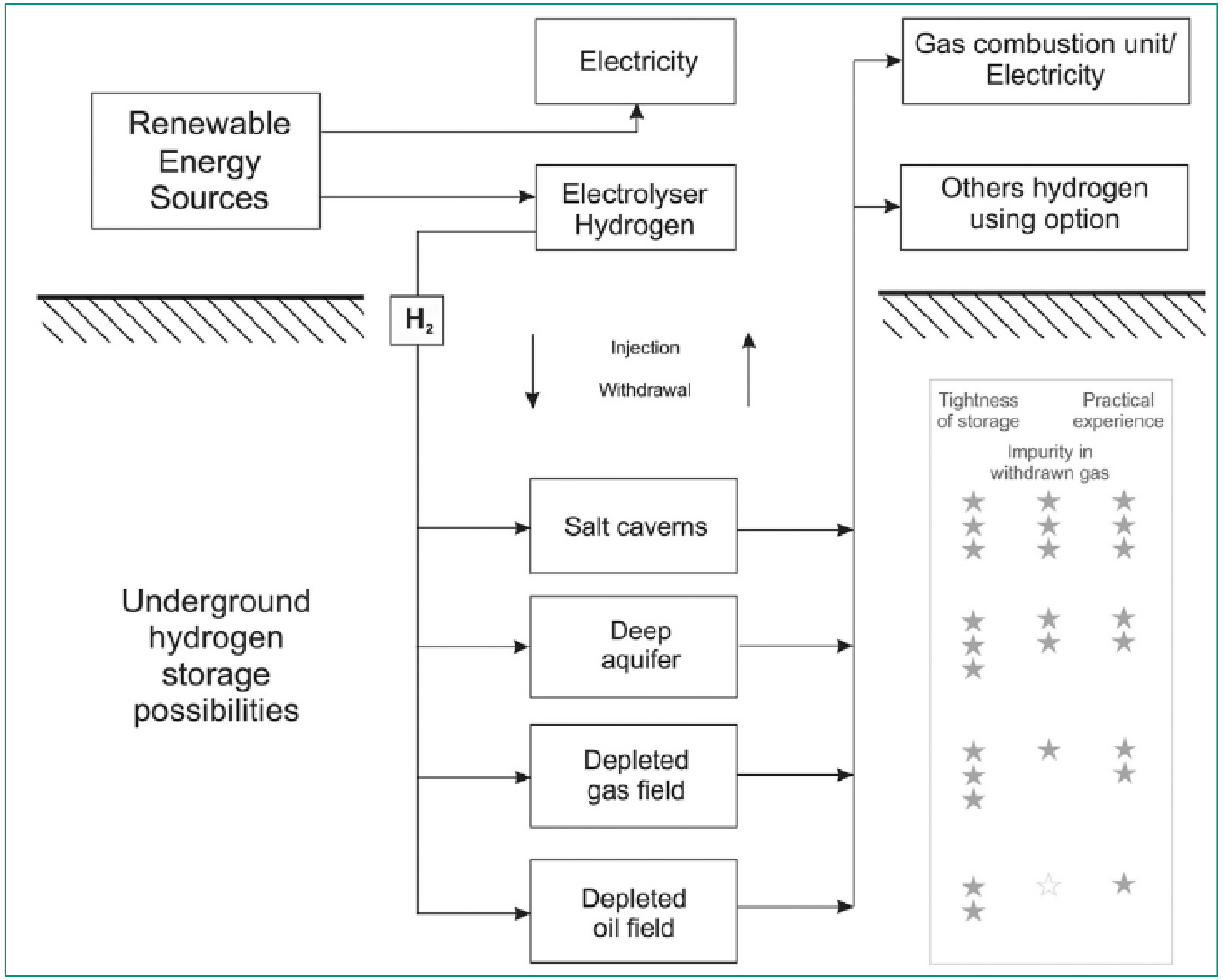
Energy from Renewables → Convert to H_2 → H_2 Storage → Convert H_2 to other energy forms → Consumption

* Pfeiffer, W.T. et al.(2017)

Underground Storage Sites

Storage cost: *

1. Depleted Hydrocarbon Deposits (US$1.23/kg)
2. Aquifers (US$1.29/kg)
3. Salt Caverns (US$ 1.61/kg)
4. Hard Rock Caverns (US$ 2.77/kg)



The concept of underground hydrogen storage in geological structures. (from Olabi, A.G. et al. (2021))

* Lord, A.S. et al. (2014)

Major Differences Between H2, CO2 and CH4*

- Hydrogen, methane, and carbon dioxide storage sites can be located in the same rock formations.
- The tightness of the underground storage site, which determines the success of the entire gas storage process, is the most important feature due to the safety of storage and its purpose.

Table 1 – Physico-chemical properties of hydrogen, methane, and carbon dioxide (based on [37]).

Properties	Hydrogen	Methane	Carbon dioxide
Molecular mass (g/mol)	2.016	16.043	44.009
Density at NTP (kg/m^3)	0.08375	0.6682	1.842
Dynamic viscosity at 20 °C (10^{-5} Pa S)	0.88	1.10	1.47
Gas constant (J/kg K)	4124.2	518.28	188.92
Specific gravity (air = 1) (–)	0.07	0.55	1.52
Critical temperature (°C)	−239.96	−82.59	31.06
Critical pressure (bar)	13.13	45.99	73.83
Critical density (kg/m^3)	31.43	162.7	468.19
Solubility in water (g/100 g)	0.00016	0.0023	0.169
Net heating value (MJ/kg)	120–141.7	50–55.5	–

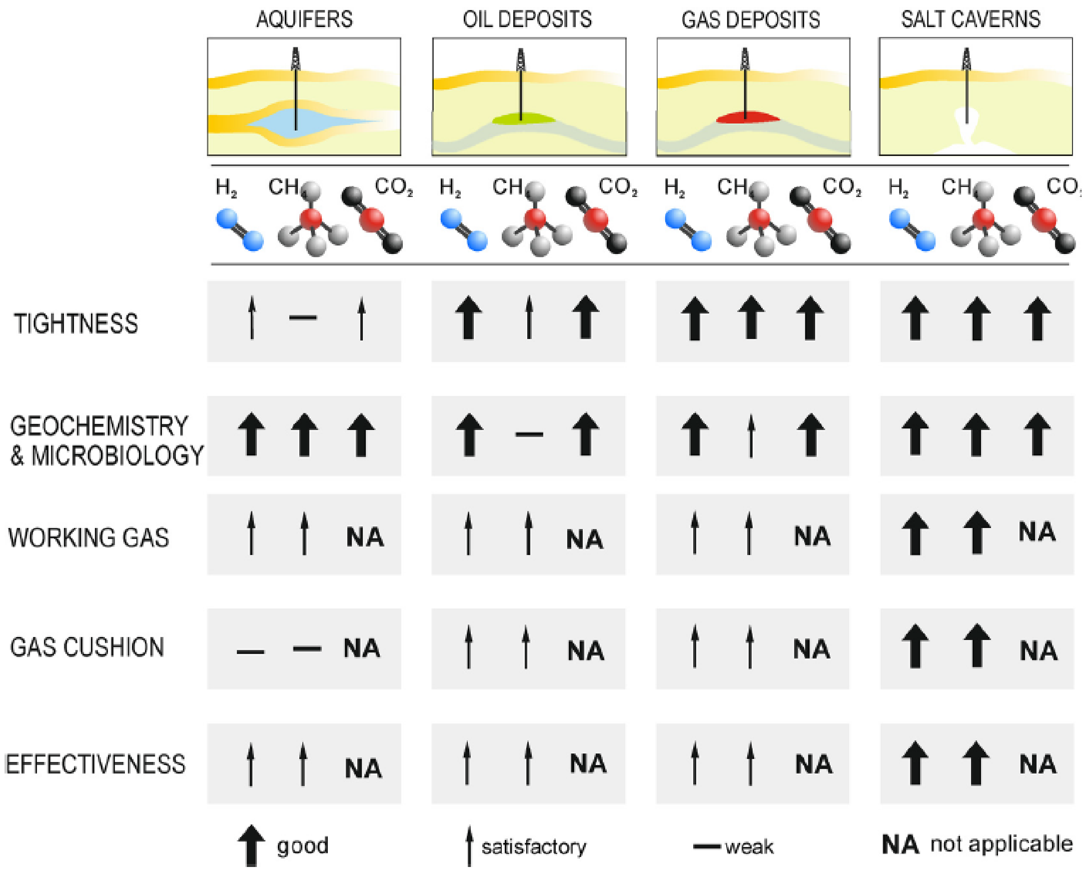
Table 2 – The impact of physico-chemical properties of hydrogen, methane, and carbon dioxide on their underground storage.

Properties	Hydrogen	Methane	Carbon dioxide
Molecular weight (g/mol)	*	**	***
Dynamic viscosity in 20 °C (10^{-5} Pa S)	*	**	***
Compressibility factor	***	**	*
Air-diffusion coefficient in excess of air at NTP (cm^2/s)	**	***	***
Critical density (kg/m^3)	***	**	*
Solubility in water (g/100 g)	***	**	*
Net heating value (MJ/kg)	***	**	n/a

*** – very favorable, ** – favorable, * – not favorable, N/A – not applicable.

* Tarkowski, R. et al. (2021)

Major Differences Between H2, CO2 and CH4



Assessment of the suitability of individual types of geological structures for underground storage of hydrogen, methane, and carbon dioxide. (from Tarkowski, R. et al. (2021))

GEM features related to H2 storage

GEM is an equation-of-state (EoS) compositional simulator which can simulate most of the important mechanisms involved in the underground hydrogen storage processes.

Relative permeability hysteresis

- Gas phase trapping

Gas solubility in aqueous phase

- Henry's law based
- K-Value based (2021 general release)

Diffusion

H_2O Vaporization

- During gas injection

Reactions

- Chemical equilibrium
- Arrhenius
- Mineral dissolution and precipitation

Geomechanics

- Change in porosity and permeability
- Cap rock integrity

Thermal Option

- Reservoir temperature could change with time

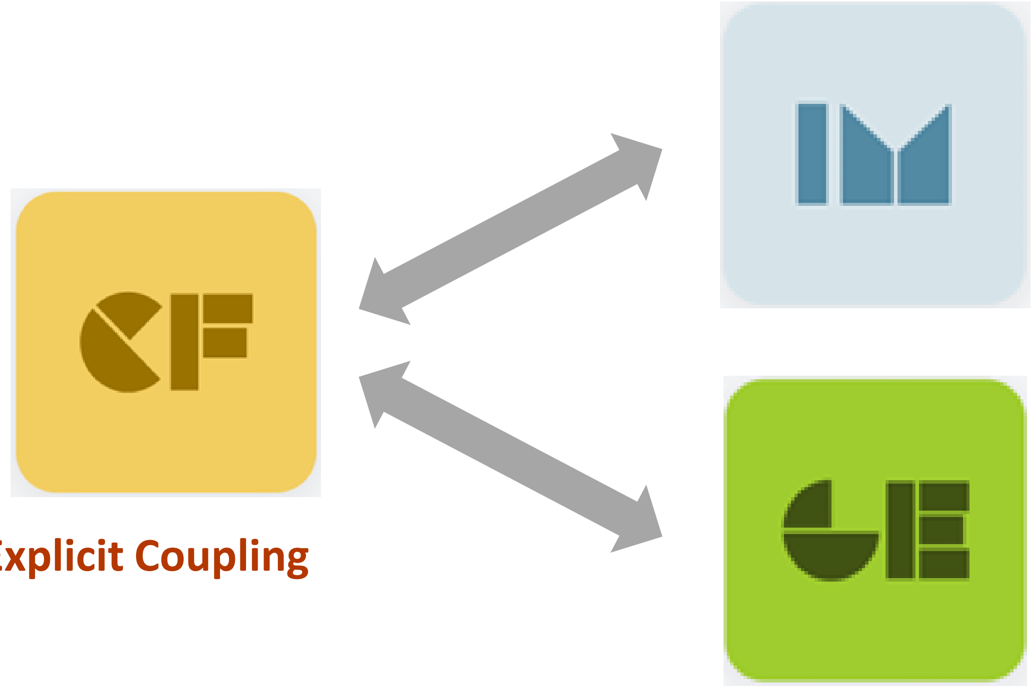
GEM and STARS Features Relevant to H_2 Storage

	GEM	STARS
Gas mixtures (density, viscosity)	X	X
Diffusion	X	X
Chemical equilibrium reactions	X	X
Mineral prec./diss. reactions	X	X
Microbial effects, souring	X (with Arrhenius style reactions)	X
Aqueous solubility	X	X
Thermal (and JT effect)	X	X
Geomechanics	X	X

- **New K-Value solubility option in GEM 2021.10**
- GEM reactions need to be done in the aqueous phase. STARS can be used to model the reactions that have a gaseous or oleic reactant/product that is not soluble in the aqueous phase.
- STARS's reactions can have an additional parameter for reaction rate dependency on the concentrations of components (useful to model Monod bacterial growth).

CoFlow for surface network modelling

Integrated production modelling with wells and facilities in CoFlow and reservoirs in IMEX or/and GEM.



Explicit Coupling

Unlimited no. of IMEX and GEM models

2) Concept overview of orange & gold hydrogen

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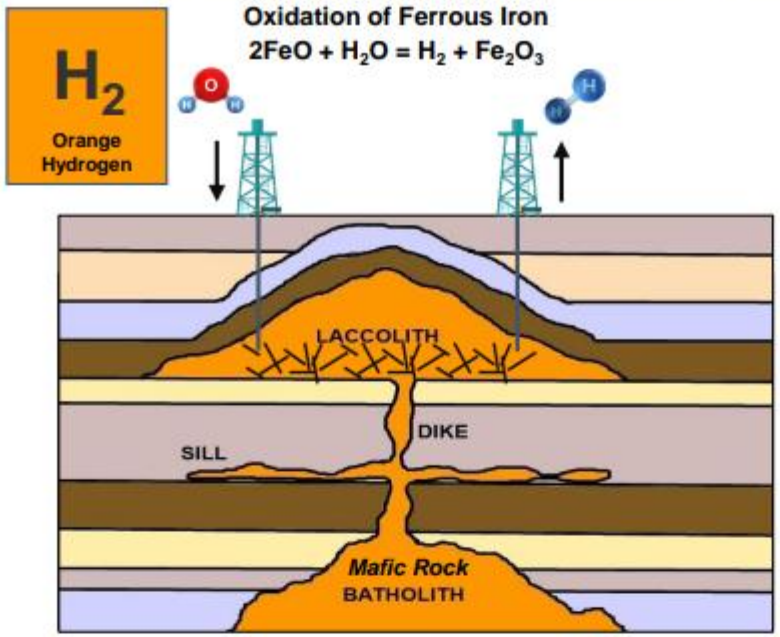
Orange Hydrogen → Induced production of natural hydrogen

Orange (Natural) Hydrogen



- **Stimulation of hydrogen generation from intrusive volcanic rocks**
- **Large and pure H_2 resources that can be produced in situ**
- **Industrial processes required – water injection, fracking**

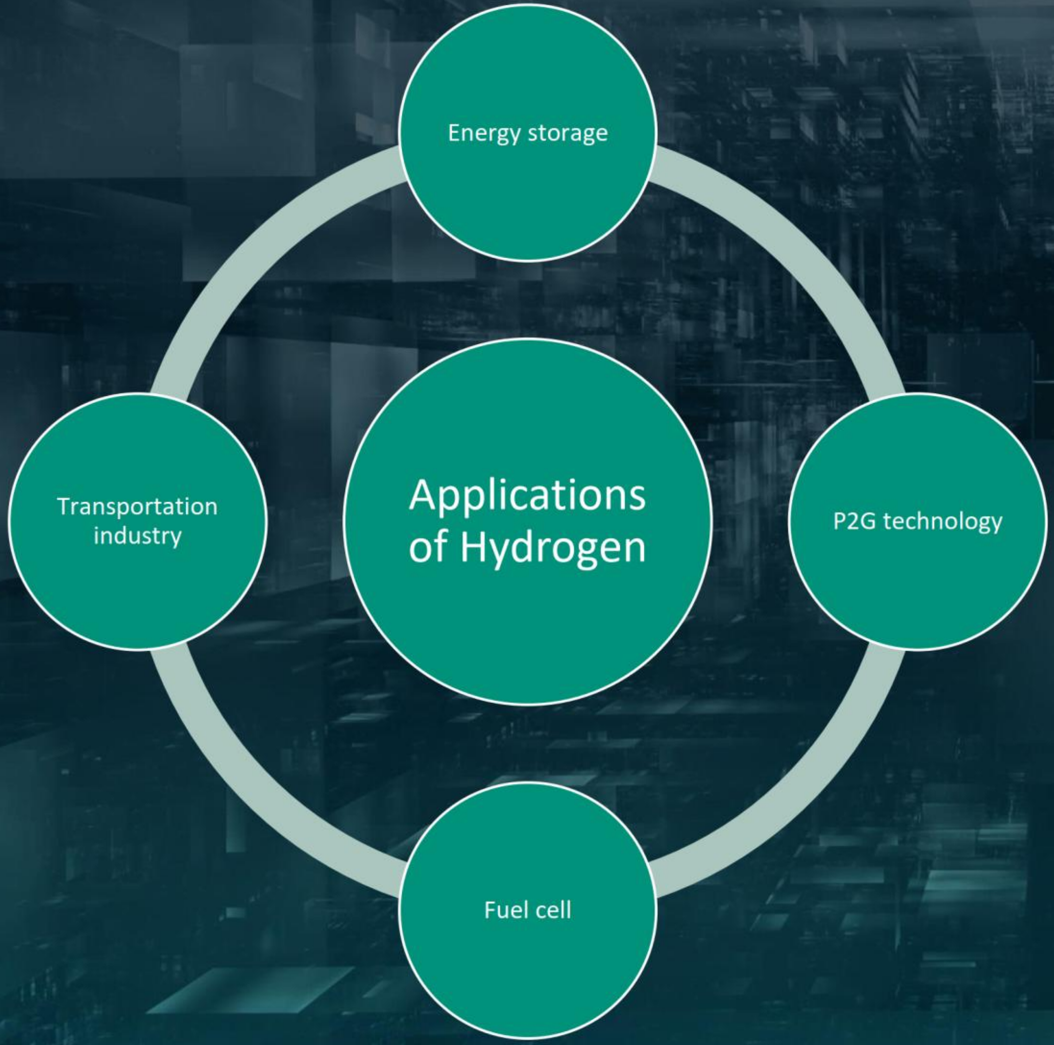
Similarities between orange and gold hydrogen

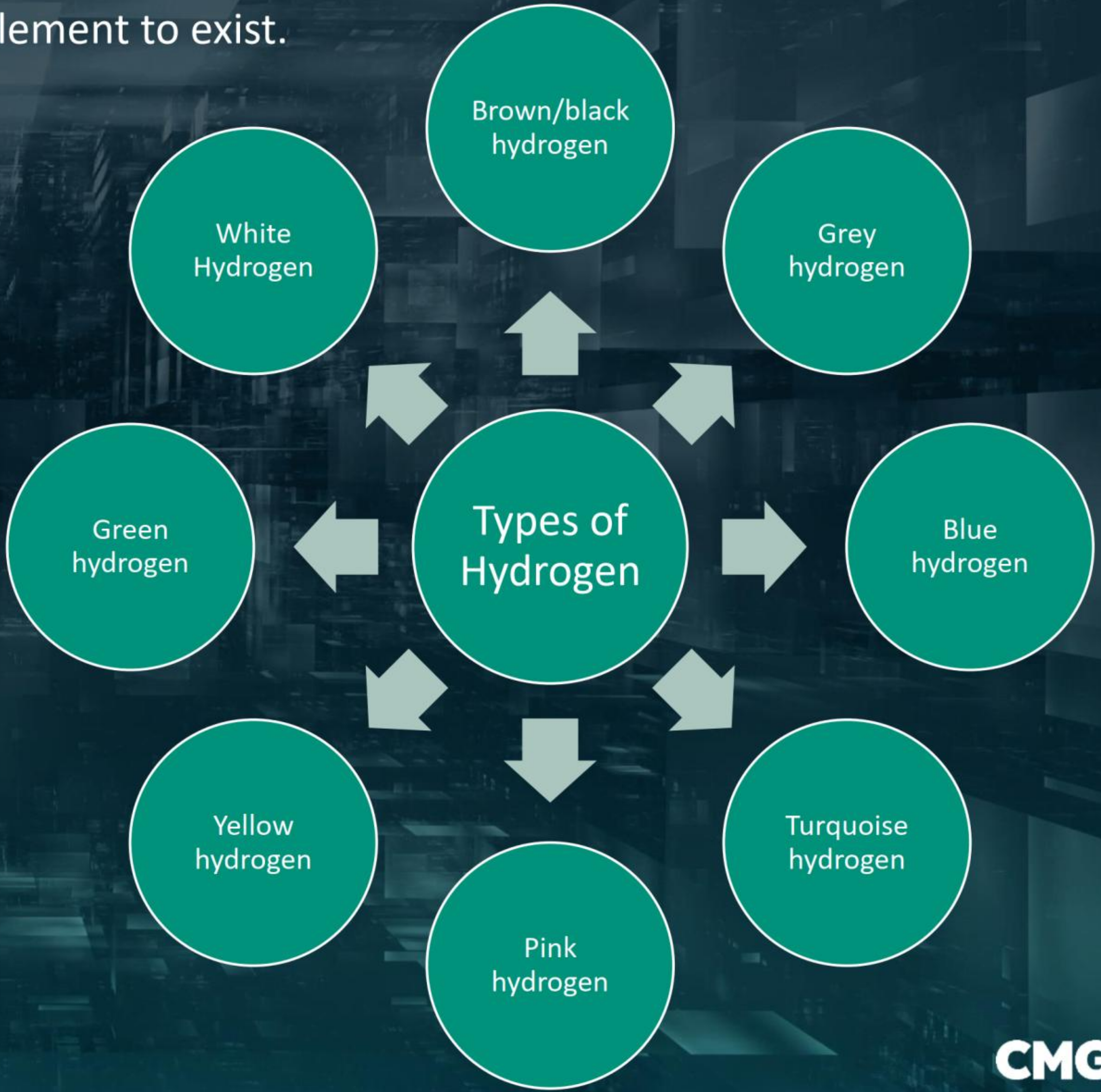
1. Generation of H_2 from oxidation reaction with minerals in mafic/ultramafic rocks.
2. Requires reaction in water phase.
3. Serpentinization reaction is the main generator of H_2.
4. Will require geochemistry reactions in GEM/STARS.
5. Main difference → Gold hydrogen occurs naturally (no induction)!

3) Presenting previous work on gold hydrogen modelling

Background of Study

- Hydrogen is the world's simplest closed-shell molecule.
- Its atomic number is 1 which makes it is the lightest chemical element to exist.





PROBLEM STATEMENT & OBJECTIVES

PROBLEM STATEMENT

1. We are only capable to manufacture the hydrogen artificially.
2. The artificial process is expensive.
3. The hydrogen energy demand keep increasing.

OBJECTIVES

1. To learn the workflow for modelling and simulation of serpentinization reaction in reservoir using GEM software.
2. To identify the factors affecting the production of hydrogen and serpentinization reaction.

SCOPE OF STUDY

1. To do a simulation study by using a thermal and advanced process simulator called GEM.
2. To model the serpentinization reaction by using the constraints and data obtained from the literature.

LITERATURE REVIEW

Theoretical Background

"

It is discovered there is accumulation production of natural hydrogen seeping through the bedrocks in the South Australia region which they called gold hydrogen Gold hydrogen is defined as the hydrogen that does not need to be manufactured artificially and it is naturally produce from Earth.

Dr. Ema Frery, Research Scientist, Commonwealth Scientific and Industrial Research Organisation (CSIRO)

"

Serpentinization reaction is a hydration and metamorphic transformation of ferromagnesian minerals, such as olivine and pyroxene, in mafic and ultramafic rock to produce serpentinite. This reaction is capable to produce H_2-rich fluids and a variety of secondary minerals like brucite and magnetite over a wide range of environmental conditions. Furthermore, serpentinization process is primarily associated with ultramafic rocks.

Holm et. al. (2015)

"

Oxidation of Fe(II) in olivine and pyroxenes leads to the reduction of water and the formation of molecular hydrogen (H2). In general reaction, ferrous iron, Fe^{2+} is oxidized by water to form ferric iron, Fe^{3+} which typically precipitate as magnetite while the water molecules, H_2O is reduce to H_2 which closely resembles to the Schikorr reaction.

Klein et al. (2013)

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PARAMETERS & IMPORTANT INFORMATION IN MODELLING SERPENTINIZATION REACTION

BASED ON PAPER FROM MUGLER ET. AL. (2016)

GENERAL REACTION OF SERPENTINIZATION & THE THERMODYNAMICS PROPERTIES OF THE ROCK

$$(MgFe)_2SiO_4 + \alpha_1 H_2O \rightarrow \alpha_2(MgFe)(OH)_2 + \alpha_3(MgFe)_{3\text{-}Fe(III)}(SiFe)_{2\text{-}Fe(III)}O_5(OH)_4 + \alpha_4 Fe_3O_4 + \alpha_5 H_2 \quad (1)$$

olivine + water → brucite + serpentine + magnetite + hydrogen

Olivine is chosen because it is main mineral in the most ultramafic rocks

Rock composition:

1. 80 wt% olivine (5.419 moles $Mg_{1.8}Fe_{0.2}SiO_4$ per kg),
2. 15 wt% orthopyroxene (1.427 moles $Mg_{0.85}Fe_{0.15}SiO_3$ per kg)
3. 5 wt% clinopyroxene (0.228 moles $CaMg_{0.9}Fe_{0.1}(SiO_3)_2$ per kg).

} Will be converted to Volume fraction

Chrysotile was used in the modelling to represent serpentine group.

Initial density of the rock = 3000 kg/m3, Pressure = 35 MPa

The thermodynamic modelling were performed using EQ3/6 version 8.0 (geochemical modelling software) with customized database – SUPCRT92

INITIAL FLUID COMPOSITION OF THE MODEL

Component	Cl^-	Na^+	Mg^{2+}	K^+	HCO_3^-	$SiO_{2(aq)}$	Al^{3+}	Ca^{2+}	Fe^{2+}	SO_4^{2-}	$O_{2(aq)}$	H_2	pH	Eh (V)
Concentration (mmolal)	545.4	464.0	37.0	9.8	2.3	0.16	2×10^{-5}	10^{-5}	1.5×10^{-6}	0	0	0	7.7	0.275

SOLID SOLUTIONS IN THE THERMODYNAMIC DATABASE

Solid solution	Components
Olivine $(Fe,Mg)_2SiO_4$	Fayalite and Forsterite
Orthopyroxene $(Fe,Mg)SiO_3$	Enstatite and Ferrosilite
Clinopyroxene $Ca(Fe,Mg)Si_2O_6$	Diopside and Hedenbergite
Serpentine $(Fe,Mg)_3Si_2O_5(OH)_4$	Chrysotile and Greenalite
Brucite $(Mg,Fe)OH_2$	Brucite and $Fe(OH)_2$
Talc $(Fe,Mg)_3Si_4O_{10}(OH)_2$	Talc and Minnesotaite
Amphibole $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$	Tremolite and Ferrotremolite

PARAMETERS OF SINGLE-PASS MODEL/U-TUBE MODEL

Notation	Definition	Values deduced from Rainbow data	Values deduced from the single-pass model
S_d	Surface of the hot-fluid discharge zone	20,000 m^2	
L_z	Domain thickness	1400 m	
W_u	Mass flux of high-temperature vent fluids	490 ± 220 kg s^{-1}	
$Q_u=W_u/S_d$	Mass flux per square meter	2.45×10^{-2} kg s^{-1} m^{-2}	
T_u	Maximum temperature of the vent fluids	360°C	
ρ_u	Density of the upflowing fluid at (P, T) = (390 bars, 360°C)	700 kg m^{-3}	
μ_u	Dynamic viscosity of the upflowing fluid	7×10^{-5} kg m^{-1} s^{-1}	
$c_p(T_u)$	Heat capacity of upflowing fluid at (P, T) = (390 bars, 360°C)	6000 J kg^{-1} K^{-1}	
h_u	Specific enthalpy of upflowing fluid	3.8×10^6 J kg^{-1}	
ρ_0	Density of the cold fluid at (P, T) = (390 bars, 2°C)	1000 kg m^{-3}	
μ_0	Dynamic viscosity of the cold fluid at (P, T) = (390 bars, 2°C)	1.6×10^{-3} kg m^{-1} s^{-1}	
$c_p(T_0)$	Heat capacity of the cold fluid at (P, T) = (390 bars, 2°C)	4000 J kg^{-1} K^{-1}	
h_0	Specific enthalpy of the cold fluid $h_0 = c_p(T_0) \times T_0$	1.1×10^6 J kg^{-1}	
T_m	Maximum temperature of the fluid due to the presence of the magma		600°C
λ	Crust's thermal conductivity		2 W m^{-1} K^{-1}
R_d	Radius of the hot-fluid discharge zone		80 m
R_r	Radius of the heating zone above the magmatic body		1320 m
L_r	Thickness of the heating zone		160 m
δ_r	Thickness of the conductive boundary layer in the heating zone		2 m
k_d	Permeability in the discharge zone		8×10^{-13} m^2
k_r	Permeability in the heating zone		10^{-13} m^2

SERPENTINIZATION RATE EQUATION

$$R = -\frac{\partial m_r}{\partial t} = K_r m_r$$

Where,

R = Serpentinization rate

K_r = rate coefficient

m_r = mass of harzburgite

The rate coefficient, K_r can be described as the equation below:

$$K_r = A\exp(-\alpha(T - T_0)^2)$$

Where,

$$\alpha = 2.5 \times 10^{-4} {}^{\circ}\mathrm{C}^{-2} \text{ and } T_0 = 270^{\circ}\mathrm{C}$$

TRANSPORT OF HYDROGEN

The transport of hydrogen is simulated by advection and diffusion which represented by equation below:

$$\phi \frac{\partial [H_2]}{\partial t} = \vec{\nabla}.\left(D\vec{\nabla}[H_2]\text{-}\vec{u}[H_2]\right) + S_{H_2},$$

Where,

D, diffusion coefficient = 10-8 m2 s-1

Φ, porosity =0.1

SH2 = production term

According to Perez et. al. (2012), it is assumed that:

1. The serpentinization reaction is the only reaction that considered.
2. The reaction zone at the site (which in this case is Rainbow site) is entirely peridotite.
3. The produced hydrogen does not react during the transport.
4. The thermos-hydraulic and transport modelling are not coupled but only solved sequentially.
5. The water consumption and heat production of the serpentinization reactions are neglected.

All these assumptions have been proved valid (Perez et. al., 2012).

RESULTS AND DISCUSSION

Rainbow site

- Located in the Mid-Atlantic ridge
- A hydrothermal vent site

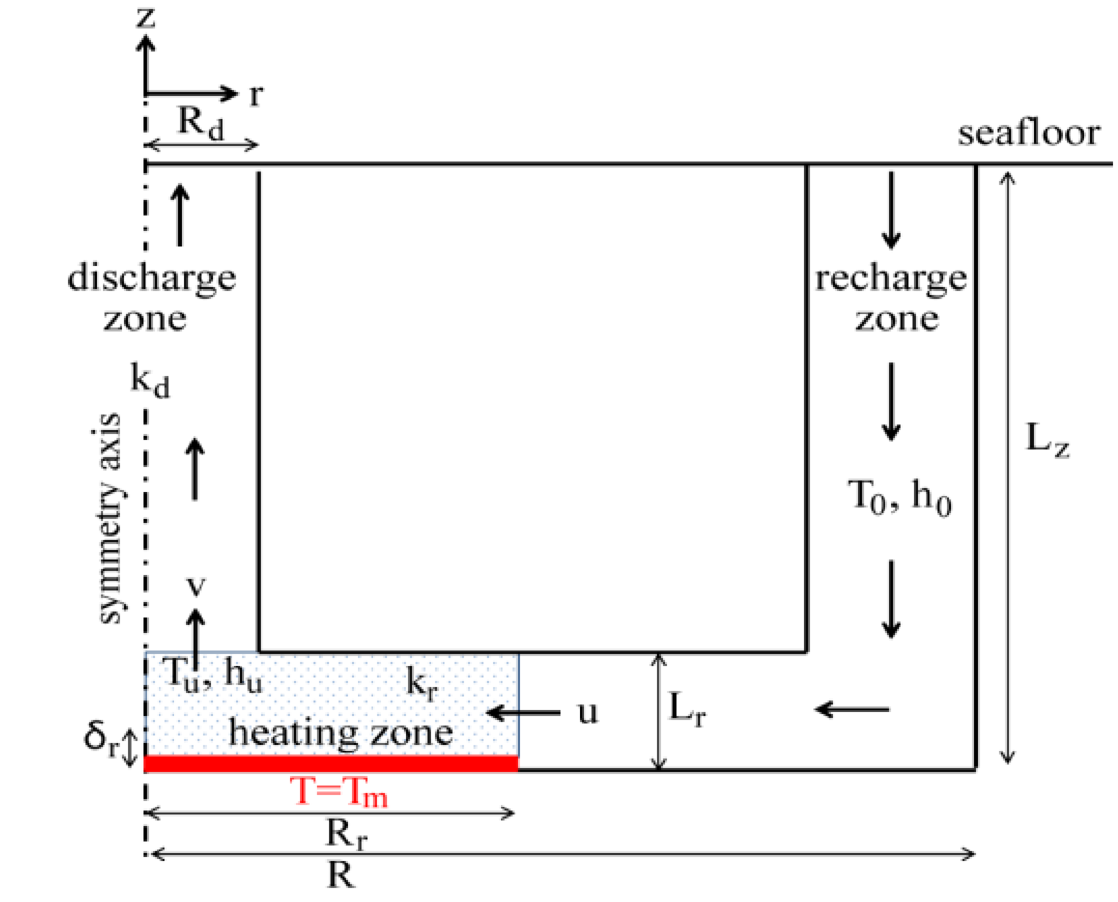
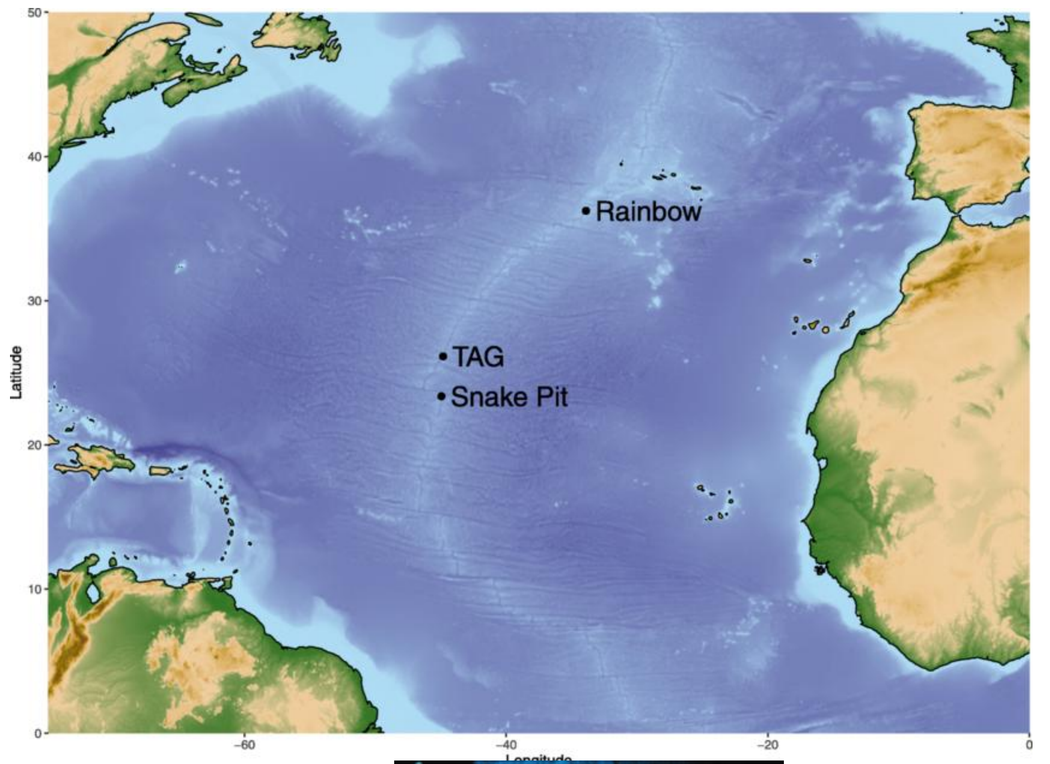
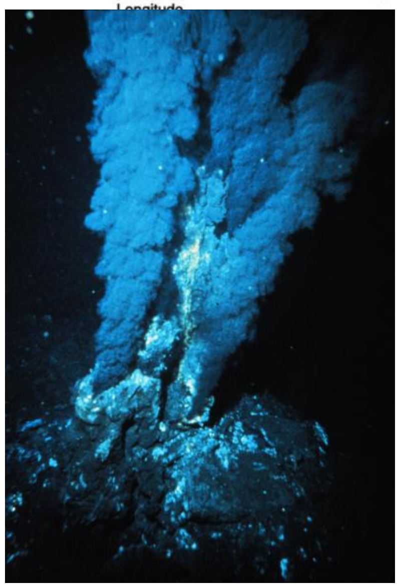


Figure 1: Configuration of the single-pass geometry used to model the Rainbow vent site.





Base model data

<u>Grid dimensions</u>

250 Ix 1 J x 140 K

10m x 80m x 10m

<u>Reservoir Properties</u>

Grid Top: 1000 m for Layer 1

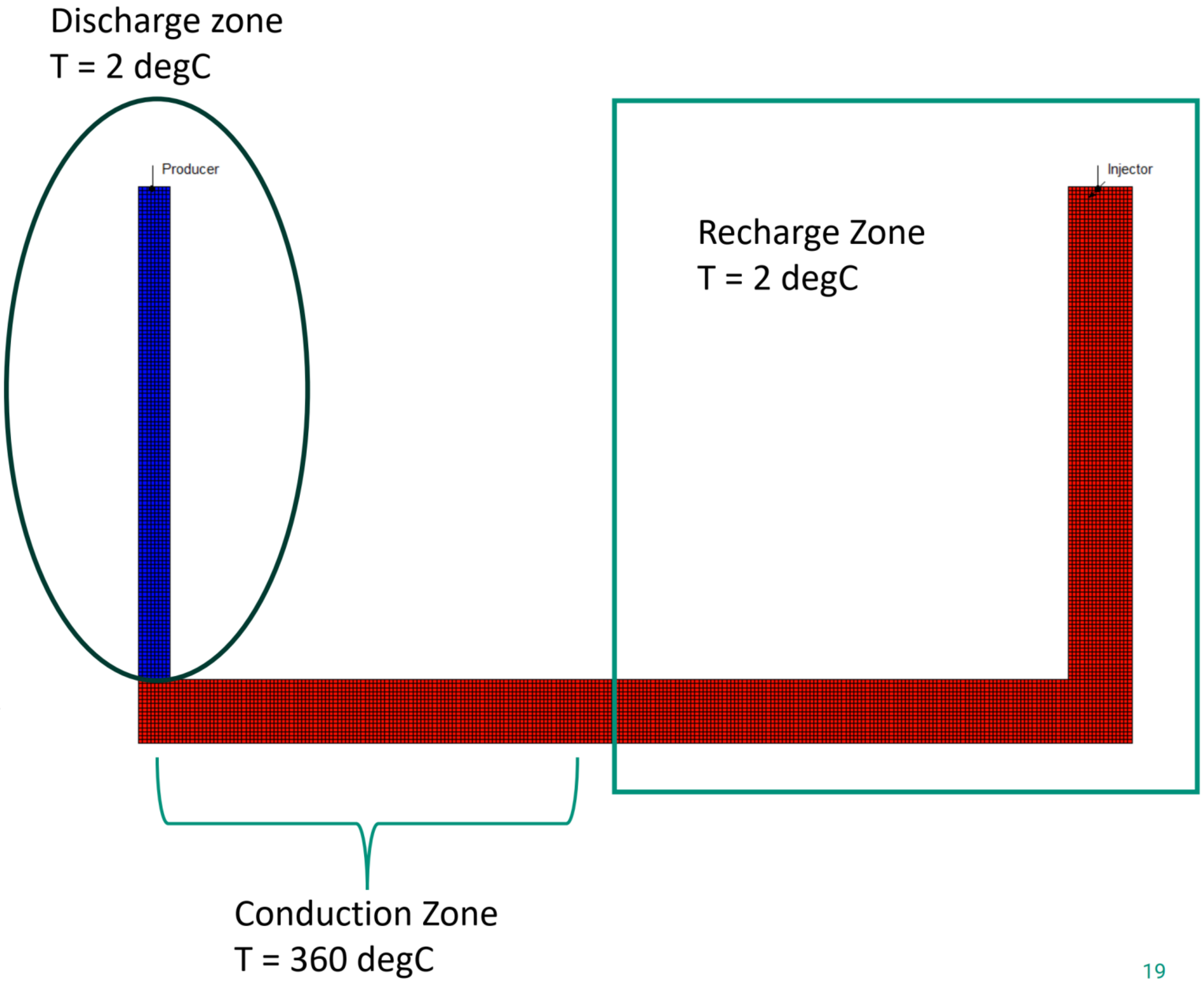
Porosity: 0.1 for whole grid

Permeability:

Recharge zone: 2000 mD for I,J & K

Conduction Zone: 2000 mD for I, J & K

Discharge Zone: 810 mD for I, J & K



Base model data

<u>Sector definition</u>

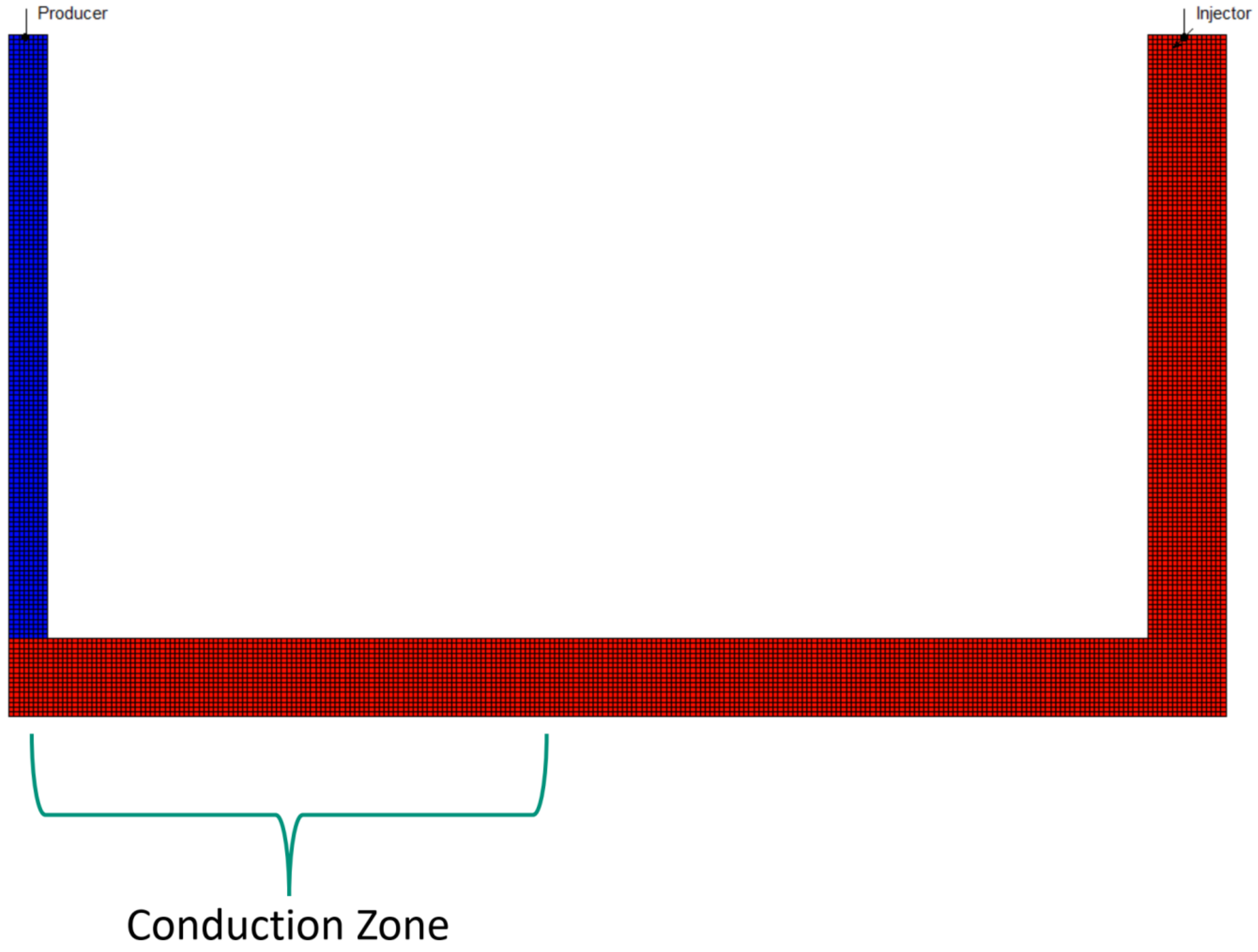
Conduction Zone

- To heat up the reservoir to provide suitable temperature for serpentinization reaction

Dimension: (1,1,125) to (132,1,139)

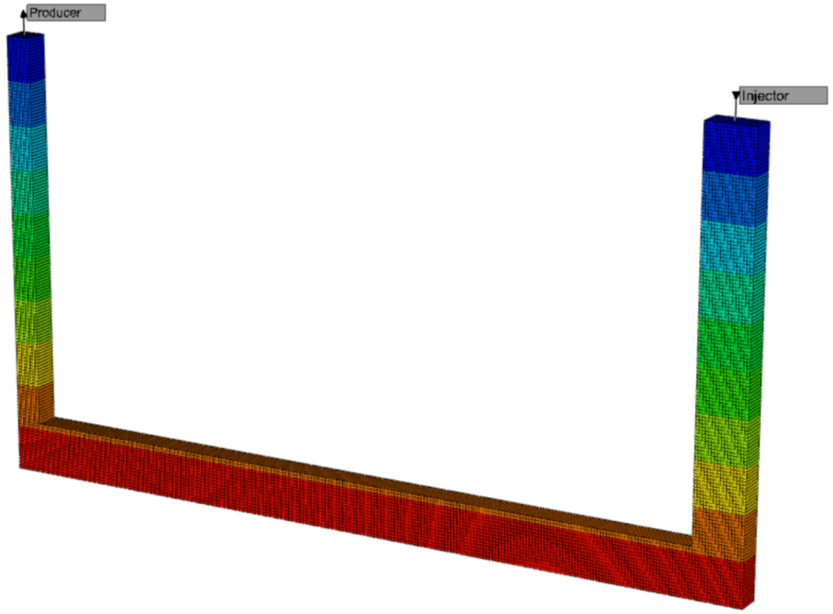
Transmissibility Multipliers for Lower Indexed-Block Faces (TRANLK) is 0 to prevent the flow at the face of the blocks.

Transmissibility Multipliers (TRANSI) is 0.



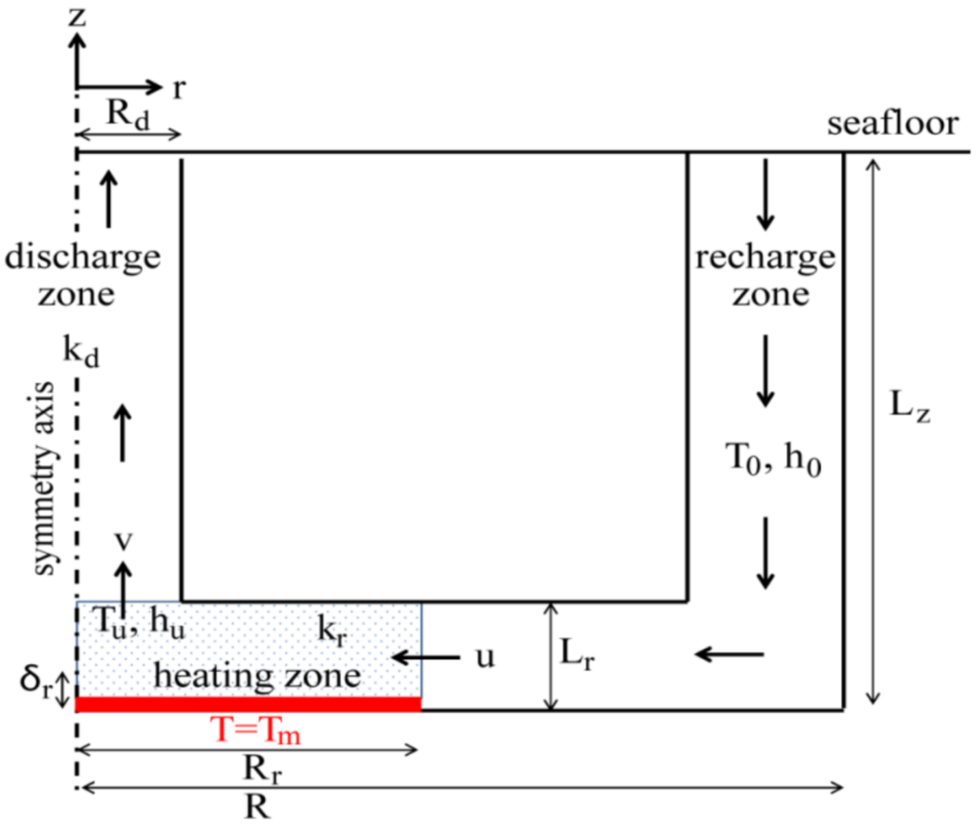
Base Model data

- Initial Field Pressure: 35 Mpa
- Reference Depth: 1005 m
- Water-Gas-Contact = 200 m
- Injection rate: 60,480 M3/DAY
- Injection period: 50 years (2000 to 2050)
- Bottom-hole Injection Temperature: 2 degC
- Density of water = 1000 kg/m3
- Viscosity of water = 1.6 cP
- Thermal conductivity of rock and fluid = 20 J/m.s.K

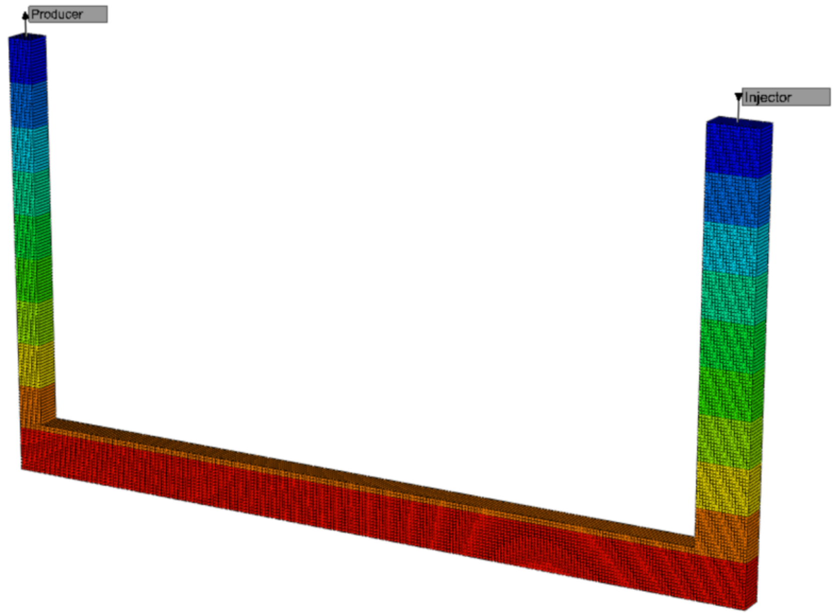


Plot Matching

From Mugler et. al. (2016)

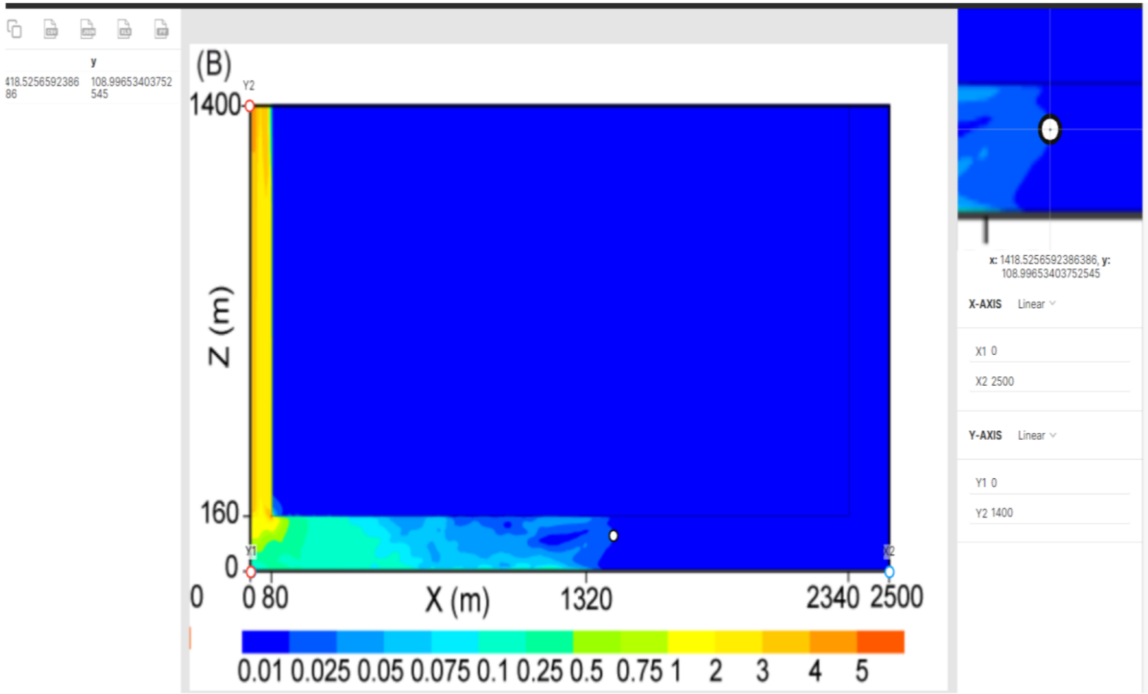


CMG Model

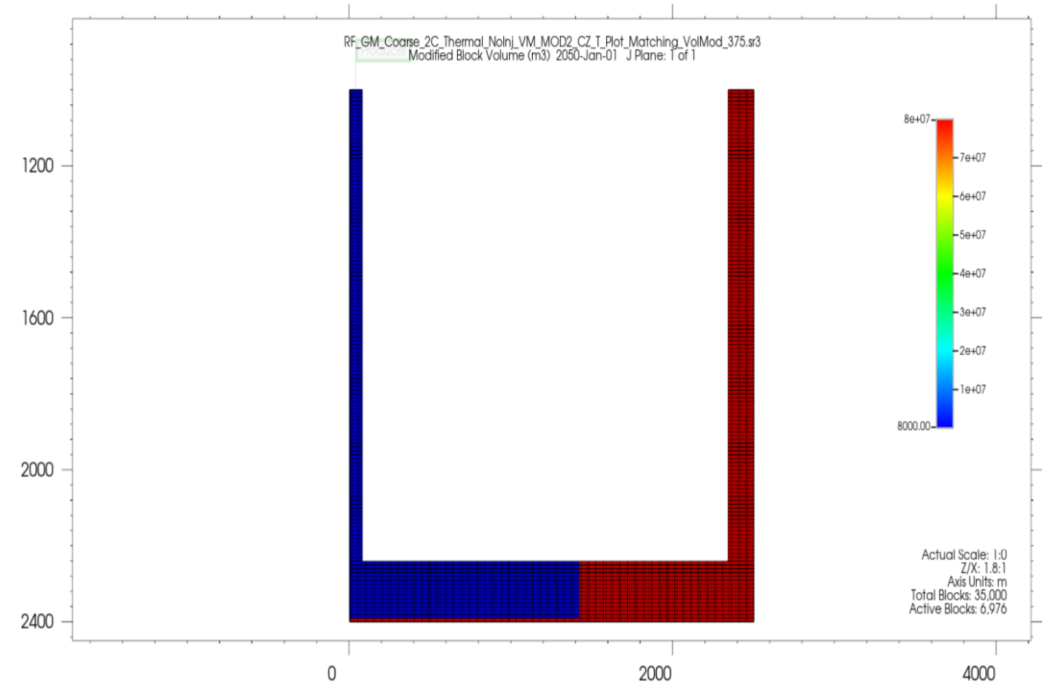


Scalar velocity Plot Matching

From Mugler et. al. (2016)



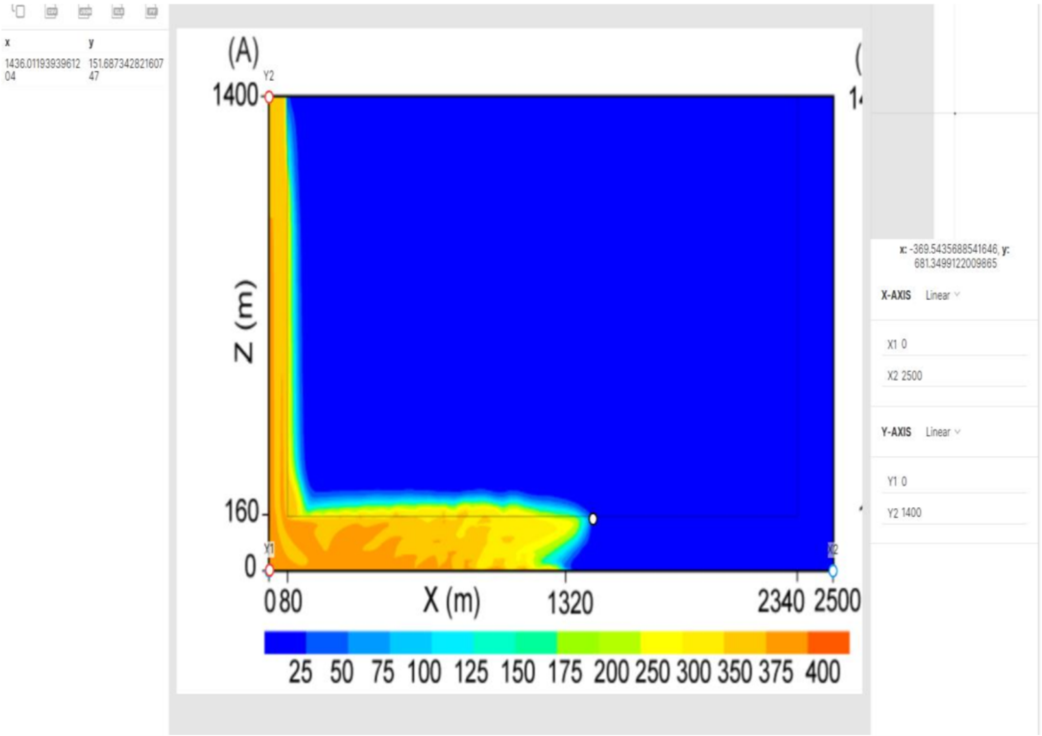
CMG Model



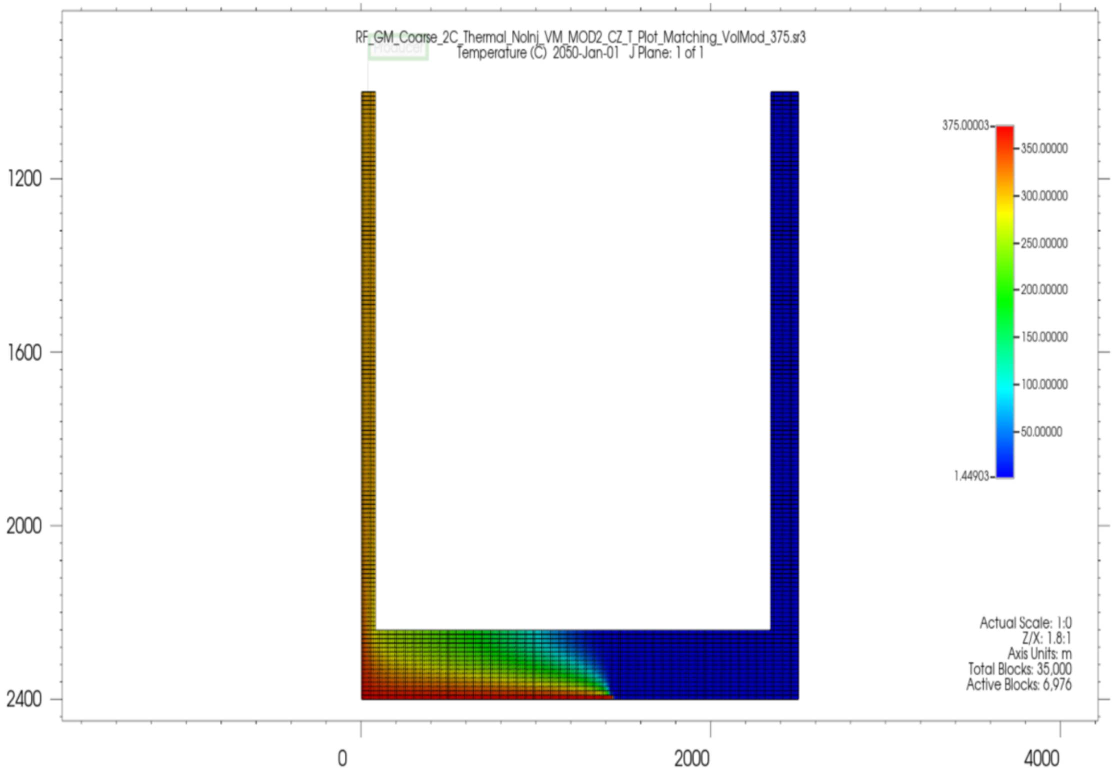
Modification made:
Extend the volume modifier to (143,1,139)

Temperature Plot Matching

From Mugler et. al. (2016)



CMG Model



Modification made:
Extend the volume modifier to (143,1,139)
Increase the thermal conductivity of rock and fluid to 200 J/m.s.K
Input the heat capacity of the rock as 2000 J/kg.K
Change the value of temperature of conduction zone to 375 degC

Geochemistry Modelling

$$(MgFe)_2SiO_4 + \alpha_1 H_2O \rightarrow \alpha_2 (MgFe)(OH)_2 + \alpha_3 (MgFe)_{3\text{-}Fe(III)}(SiFe)_{2\text{-}Fe(III)}O_5(OH)_4 + \alpha_4 Fe_3O_4 + \alpha_5 H_2$$

olivine + water → brucite + serpentine + magnetite + hydrogen (1)

Input the aqueous reaction

The hydrolysis of water and the magnesium carbonate reaction is selected.

BUILDER

Input the mineral reaction

The minerals that are selected:

Brucite

Chrysotile

Magnetite

BUILDER

Input the initial data for geochemistry

The initial composition of the aqueous phase and the volume fraction of the mineral from the paper.

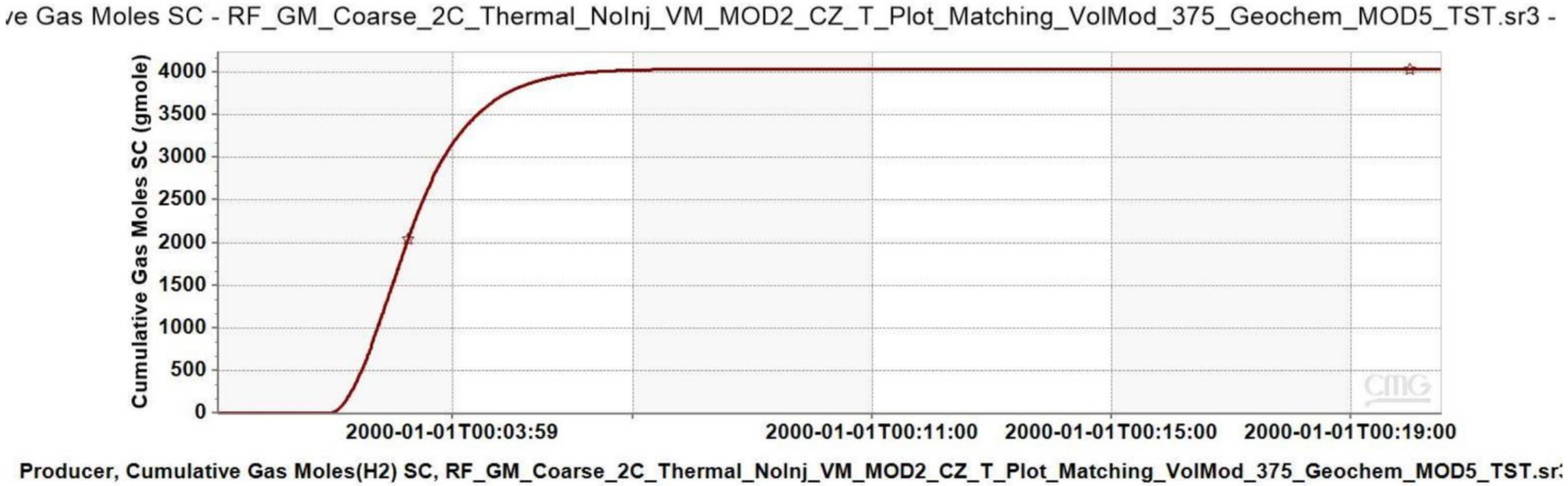
BUILDER

Input the serpentinization reaction in the dataset

Input the keywords manually in the dataset.

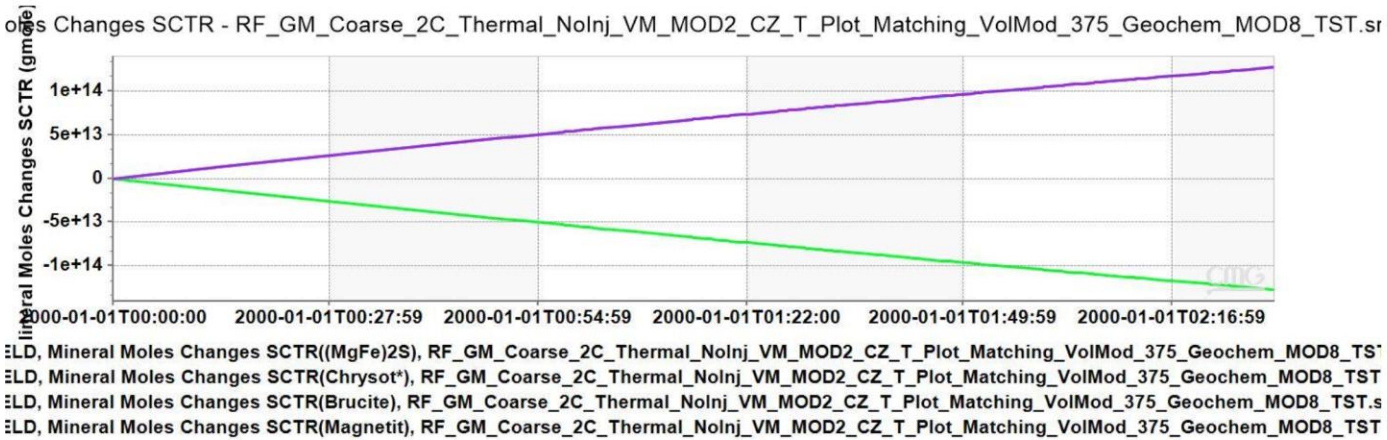
WINPROP cEDIT

Results & discussion

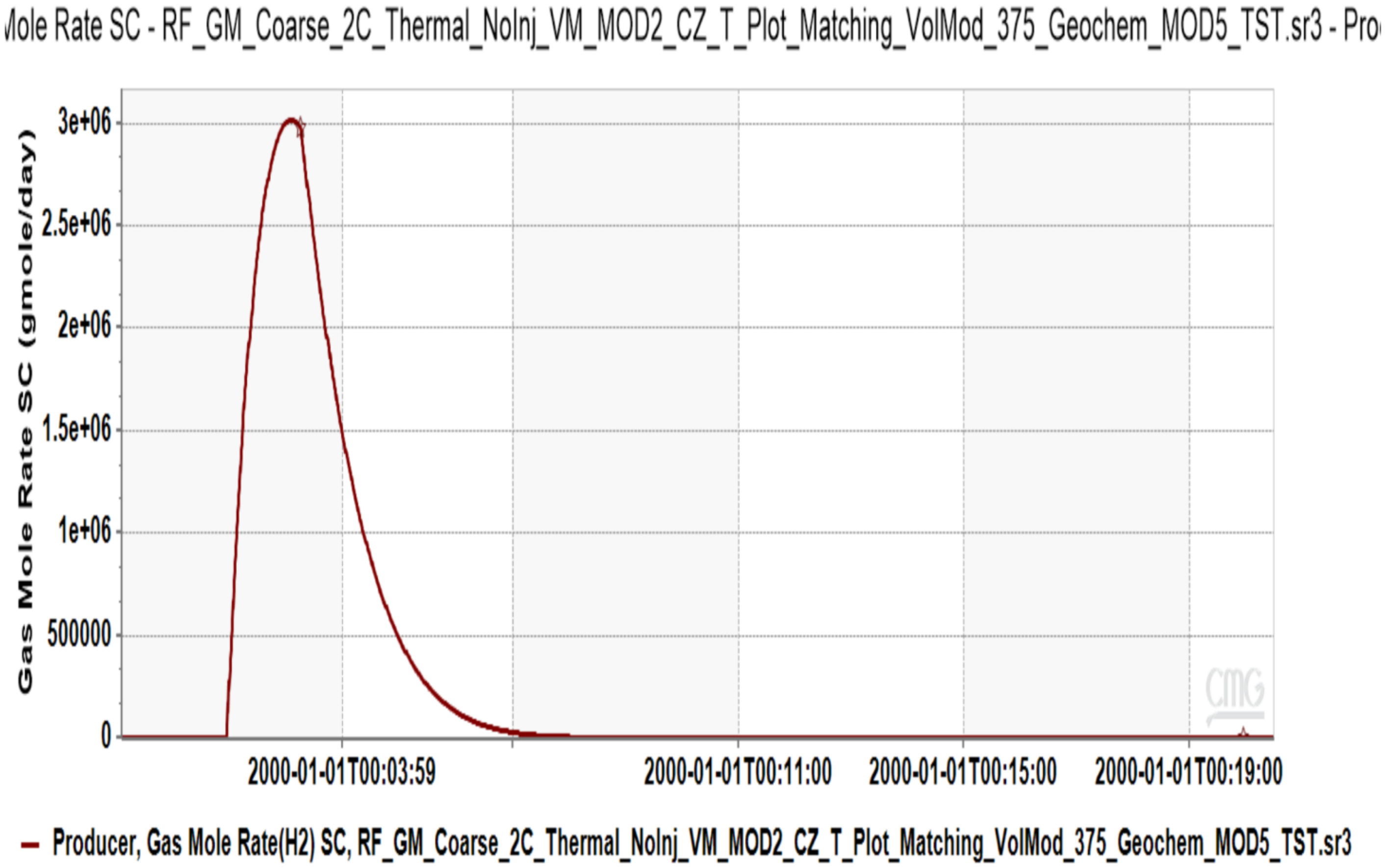


Hydrogen is produced at rapid rate on the first day but suddenly stopped due to insufficient amount of olivine.

As expected, the products: brucite, chrysotile and magnetite are precipitated while the reactant: olivine is dissolved.



Hydrogen Gas Mole Rate



Results:

- The hydrogen production rate reached its peak at 3 MMgmole/day before rapidly declining.
- The simulation stop on the first day of simulation despite the simulation date has been set to 50 years
- Typical numerical control for geochemistry is used in this simulation.
- Implicit formulation is used to grid blocks

```
DTMAX 5
DTMIN 1E-6
NORM SATUR 0.05
NORM GMOLAR 0.005
NORM AQUEOUS 0.3
MAXCHANGE PRESS 20000
MAXCHANGE SATUR 0.8
MAXCHANGE GMOLAR 0.8
MAXCHANGE MINERAL-VFR 1
```

```
CONVERGE PRESS 1.E-04
CONVERGE HC    1.E-05
CONVERGE WATER 1.E-05
CONVERGE MAXRES 1.E-04

NORTH 200
ITERMAX 200
PRECC 1e-6
```

Factors Affecting The Amount of Products (Mugler et al, 2016)

- The proportion of olivine and pyroxene in the initial peridotite
- The pressure and temperature conditions
- The ratio between initial mass of water and the initial mass of rock (w/r ratio)
- Fluid composition
- The evolution of the system composition.

Conclusion

- GEM is capable to model the serpentinization reaction in a reservoir.
- Some of data need to be altered to be suitable with the reservoir model.

Recommendation

- The project need to be revised with more suitable simulator like STARS to complete the study.
- More data are needed especially for the rock properties [redacted]