

## Introduction

Hydrogen and fuel cell technologies have significant potential to enable transition to a clean, low carbon energy economy. Hydrogen is a versatile element that can be used in a variety of applications including chemical and industrial processes, oil refining and ammonia production, metallurgy, medical treatment, transportation, heating and power generation. Hydrogen has the highest gravimetric energy density of 120 MJ/kg: three times higher than gasoline, 2,5 times greater than methane, 150 times higher than a lithium battery. Hydrogen today is considered as a key enabler of the global transition to sustainable energy.

At the same time with increasing energy demand throughout the world there is a challenge to utilise fossil resources accumulated in:

- Gas and oil tight reservoirs, stranded, non-commercial and depleted fields.
- Heavy oil and bitumen deposits.
- Coal-bed methane deposits.

An innovative process of Hydrogen Generation from Hydrocarbons Sub-terrain (HGHS) is a unique solution to the problem of emission free Clean Hydrogen production and storage in hydrocarbon fields without greenhouse emissions and without relying on renewable electricity (Surguchev L. 2011, Surguchev L. and Berenblyum 2015).

Clean Hydrogen production cost by HGHS represent a fraction of the main industrial Steam Methane Reforming (SMR) central facility process cost to produce hydrogen, especially if the hydrocarbon fields cannot be commercially produced by any other known methods today (Surguchev L. et al 2017).

There are several mechanisms important for HGHS process:

- Thermal conditions in the reservoir required to achieve conversion of hydrocarbons to hydrogen in situ.
- Propagation of the thermal and conversion fronts in the reservoir.
- Placement of catalytic system components and their flow in the reservoir.
- In situ separation of hydrogen from other gases and phases.

Our recent experimental and modelling studies were addressing these mechanisms and processes to optimise and enable field application of HGHS.

## Clean Hydrogen

The HGHS process provides for producing Clean Hydrogen, with CO<sub>2</sub>/CO sequestered in situ (Figure 1). HGHS combines industry proven SMR, catalytic cracking and Thermal Enhanced Oil Recovery (TEOR) methods with new catalytic system components and agents.

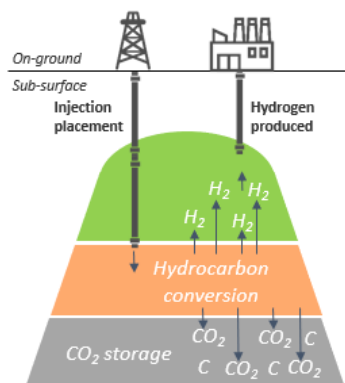


Figure 1. Schematic of the HGHS process.

Separation of lighter hydrogen from other heavier gases (CO<sub>2</sub>, CO, hydrocarbon gas) in situ can be achieved exploiting differences in their physical properties, solubility, segregation and gravity effects. Additional hydrogen purification can take place downhole in the wells or on the surface using state of the art pressure swing adsorption or membrane separation processes.

Clean hydrogen production from methane and hydrocarbons in situ involves the following main reactions:

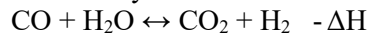
Highly endothermic Steam Methane Reforming (SMR)



Heterogeneous catalysis conversion of heavier hydrocarbons



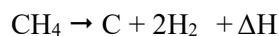
Moderately exothermic Water-Gas Shift (WGS)



Aquathermolis



At high temperatures hydrogen can be generated from methane in endothermic catalytic cracking reaction without carbon oxides formation:



Required for HGHS process thermal conditions can be achieved using different methods:

- Oxidation reactions of hydrocarbons in situ resulting from air or oxygen injection.
- Supercritical steam generation downhole in the wells.
- Microwave irradiation downhole in the well to achieve plasma temperature conditions.
- Termite exothermal chemical reactions downhole in the wells.

### *Temperature Conditions*

Experiments were performed in the sand packed quartz tube reactor (Figure 2) to study and optimise catalytic system and determine temperature requirements for effective conversion of methane to hydrogen at reservoir conditions (Ai et al. 2023). Methane conversion in SMR reaction was achieved at an equilibrium temperature ranging from 400 to 1000°C with catalyst system calcification, reduction and activation at three different temperatures. Conversion of methane to hydrogen increased from initial values of 8.6% at 800°C to 79.6% at 920°C and to 90% starting from 920°C.

In a series of bulk volume catalytic reactor laboratory experiments at temperatures ranging from 600 to 900°C and high pressures up to 500 bar, methane conversion to hydrogen reached 55-60% with SMR and catalytic cracking contributing equally to methane transformation (Surguchev L. et al 2017).

### *Hydrogen Generation and Front Propagation*

Experiments were conducted in the high-temperature, high-pressure batch reactor (Figure 2) with gas analysis unit. In the static regime the methane conversion rate achieved in these experiments with natural core material achieved almost 80% at 800°C (Afanasev et al. 2021). Specially designed combustion tube experiments (Figure 2) were performed with high temperature front propagation in the porous medium at reservoir conditions with catalytic system placement in the porous medium. Conversion rate of methane to hydrogen in this dynamic experiment achieved 35.5%.

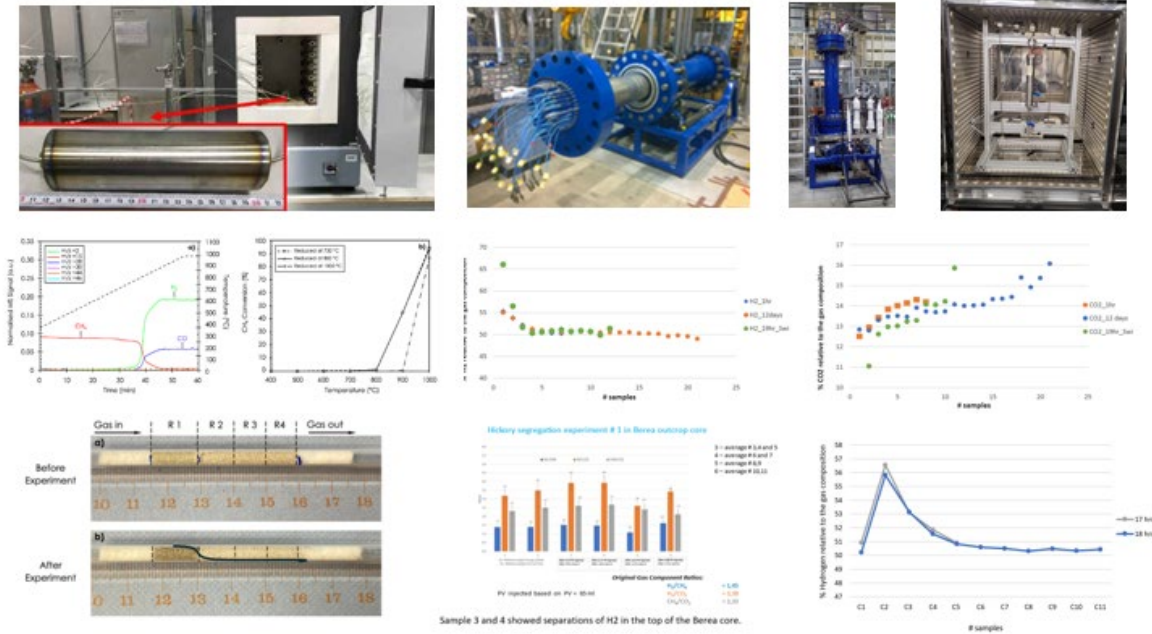


Figure 2. Experiments and laboratory studies of HGHS process.

Catalytic system can be injected in the reservoir as a precursor dissolved solution or as active catalyst compound (Ai et al. 2023). In the HGHS process the activation of catalyst with calcination and reduction is taking place in-situ. In the sand packed experiments (Figure 2) mobility of catalyst in the porous medium was studied at temperatures up to 1000°C. These experiments showed propagation of catalyst with the gas phase at reservoir conditions in SMR and autothermal reforming processes in the porous medium.

### Gases Separation

The gases separation and segregation experiments (Berenblyum et al. 2023) were conducted in the vertically mounted Berea core 26,1 cm long unit at 50 bar (Figure 2). The experiments started with saturating a dry core with a pre-mixed gas mixture (15% CO<sub>2</sub>, 50% H<sub>2</sub>, 35% CH<sub>4</sub>). After a predefined shut-in period, the gas was produced from the core, and effluent gas concentration profiles were analyzed using gas chromatography in several sets of measurements. The segregation of hydrogen in these experiments was fast occurring. Hydrogen segregation accounted for around 10-20% of original hydrogen content over vertical core. The presence of water in the rock significantly increased separation of hydrogen and other gases, primarily CO<sub>2</sub>. Segregated of the gases in the reservoir core was taking place due to their solubility and physical properties differences, and gravity effects.

### Conclusions

- The experimental studies allowed to establish detailed kinetics of the main hydrocarbon to hydrogen transformation reactions which were modelled and simulated using state of the art modelling tools. In the reactor experiments methane to hydrogen conversion rate in the porous medium achieved up to 80% at 800°C.
- Gases can be separated in the reservoir due to their solubility and physical properties differences, and gravity effects. In the reservoir core experiments the segregation of hydrogen was fast occurring, accounting for around 10-20% of original hydrogen content. The presence of water in the rock significantly increases hydrogen, CO<sub>2</sub> and other gasses separation.
- Updated and improved simulation models were set up to reduce uncertainty in HGHS process modelling.

- The HGHS processes allow to convert depleted, stranded and noncommercial fields into storage of environmentally Clean Hydrogen, that can be produced at low cost and with zero carbon footprint.
- Implementing HGHS process to produce Clean Hydrogen will remove greenhouse gas emissions from the energy production and consumption value chain.

## Acknowledgements

The author acknowledges and thanks Prof. Klaus Hellgardt and Lu Ai in Imperial College London, Morten Aara and his colleges at NORCE Research Centre for their cooperation with Hydrogen Source AS, Norwegian Research Council for financial support provided to Hickory project.

## References

1. Surguchev, L. (2011) In-situ hydrogen generation from hydrocarbons”, Offshore Heavy Oil Conference, 24-25 November 2011, London.
2. Surguchev, L. and Berenblyum, R. (2015) In-situ Hydrogen Generation from Hydrocarbons and CO<sub>2</sub> Storage in the Reservoir, Fourth EAGE CO<sub>2</sub> Geological Storage Workshop, “Demonstrating storage integrity and building confidence in CCS”, 23 - 25 April 2014, Stavanger.
3. Surguchev, L. and Berenblyum, R. (2015) Process to generate hydrogen from hydrocarbons in situ: commercial hydrogen production, carbon capture, source of thermal energy. The Third Sustainable Earth Science Conference, 13-15 October 2015, Celle, Germany.
4. Surguchev, L., Berenblyum, R., Surguchev, M. (2017) Shift to Hydrogen: 100% Recovery from Depleted and Abandoned Gas Fields, IOR 2016 – 19th European Symposium on Improved Oil Recovery, Th P001, 24-27 April 2017, Stavanger, Norway.
5. Afanasev, P., Popov, E., Cheremisin, A., Berenblyum, R., Mikitin, E., Sorokin, E., Borisenko, A., Darishchev, V., Shchekoldin, K., Slavkina, O. (2021) An Experimental Study of the Possibility of In Situ Hydrogen Generation within Gas Reservoirs, *Energies*, 14.
6. Berenblyum, R., Aarra, M., Shiran, B., Solbakken J., Djurhuus, K. (2023) Experimental Investigation of In-situ Hydrogen Segregation/Separation, IOR+ 2023 – 22<sup>nd</sup> European Symposium on Innovative & Optimised Resource Utilisation, 2-4 October 2023, The Hague.
7. Ai, L., Berenblyum, R., Hellgardt, K. (2023) Investigation of Subsurface hydrogen production mechanisms IOR+ 2023 – 22<sup>nd</sup> European Symposium on Innovative & Optimised Resource Utilisation, 2-4 October 2023, The Hague.
8. Rui, Y.; Zhu, B.; Tang, Q., Yang, C., Wang, D.; Pu, W., Tang, X. (2022) Experimental Study of the Feasibility of In-Situ Hydrogen Generation from Gas Reservoir. *Energies* 15, 8185.