In-situ Injection of Hydrogen Gas in the Opalinus Clay

A. Vinsot, M. Lundy, Andra, CMHM, F-55290 Bure, France
T. Fierz, B. Yeatman, Y. Lettry, Solexperts AG, CH-8617 Monchaltorf, Switzerland

Introduction

Steel components are generally used in the design of deep geological repositories for high-level radioactive waste. After closure of the underground disposal galleries, anoxic corrosion of steel is expected to produce hydrogen gas. Studies are performed to evaluate what will happen to this hydrogen in an underground repository. Among these studies is the "Hydrogen Transfer" (HT) experiment, which was implemented in 2009 in the Mont Terri Rock Laboratory to study *in-situ* the diffusion of hydrogen in Opalinus Clay. A second objective of this experiment was to evaluate whether hydrogen could be consumed by chemical reactions with the rock.

The experimental concept of the HT experiment is based on gas circulation within a borehole (Vinsot *et al.* 2008a, 2008b). During the initial phase in 2009 the natural rock gas and pore-water production and composition at the test location were determined. The first hydrogen injection followed in June 2011.

Pure hydrogen was added into the main gas flow circuit loop of the experiment using a Teledyne Isco 500D syringe pump. The Solexperts dosage, control and monitoring software (DCAM) was used to control the pump injection rate, to perform automatic pump refills, to monitor test parameters, and to display real-time values and graphics. The data was automatically transferred to the Andra's data acquisition system (SAGD) and to the Solexperts data visualization website (WebDAVIS) so the progress of the experiment could be monitored by appropriate personnel using an internet browser.

The design of this *in-situ* test was described in detail in Vinsot *et al.* (accepted) together with the experimental results regarding the evolution of hydrogen concentration in the circulating gas. The present paper focuses on the hydrogen injection setup and on the monitoring results regarding the injected volume of hydrogen.

Experimental Design

The Mont Terri Rock Laboratory is located in a tunnel in the Jura Mountains, in northwestern Switzerland at a depth of around 300 m below ground level (http://www.mont-terri.ch). It is a "methodological laboratory" (cf. Delay *et al.* accepted) in the Opalinus Clay. Opalinus Clay is a Jurassic age, well consolidated claystone with a hydraulic conductivity below $3 \cdot 10^{-12}$ $m \cdot s^{-1}$ (Thury and Bossart, 1999).

The experiment's hardware consisted of equipment installed into a borehole and two surface modules, shown in Figure1:

- Borehole equipment installed into the ascending borehole BHT01
- A water-sampling module
- A gas circulation and dosage control/monitoring module

Borehole Equipment

The borehole equipment consisted of a multi-packer system built by Solexperts that isolated both 5 m-long and 50 cm-long intervals in the borehole. Gas circulation and pore-water collection were performed in the 5 m long interval. Pore-pressure measurement was performed in the 50 cm long interval.

Water Sampling Module

The water sampling module was used for water composition monitoring. The module made it possible to collect the borehole water by gravity at a controlled flow rate. The module included a pressure controller, a digital balance, and samplers. All components in contact with the sample fluid were made of PEEK (polyetheretherketone).

Gas Circulation and Dosage Control/Monitoring Module

The gas circulation module included a circulation pump, a gas-flow controller, ten stainless steel cylinders which could be disconnected to perform gas sample analyses, a solid H2scan's HY-OPTIMA™ H_2-detector probe, a Teledyne Isco 500 D syringe pump (dosage system), and control/monitoring software. The maximum gas volume in the gas circulation module was about 0.9 L. The gas circulation lines were made of stainless-steel. A probe was connected to a Raman spectrometer for in-line partial pressure measurements of the molecular gases (H_2, N_2, CO_2 and CH_4) present in sufficient quantities (Lundy and Vinsot 2010). The spectrometer was a Kaiser Optical Systems' Raman Rxn3™ analyzer with a Kaiser Optical Systems AirHead™ probe. The Raman probe was calibrated for H_2 using three calibrated gas mixtures with hydrogen content of 1%, 3% and 5% (rest argon) at 1.5 bars. The hydrogen sensor was calibrated with an argon based mixture with 5% hydrogen by varying its pressure between 1.05 and 1.80 bar.

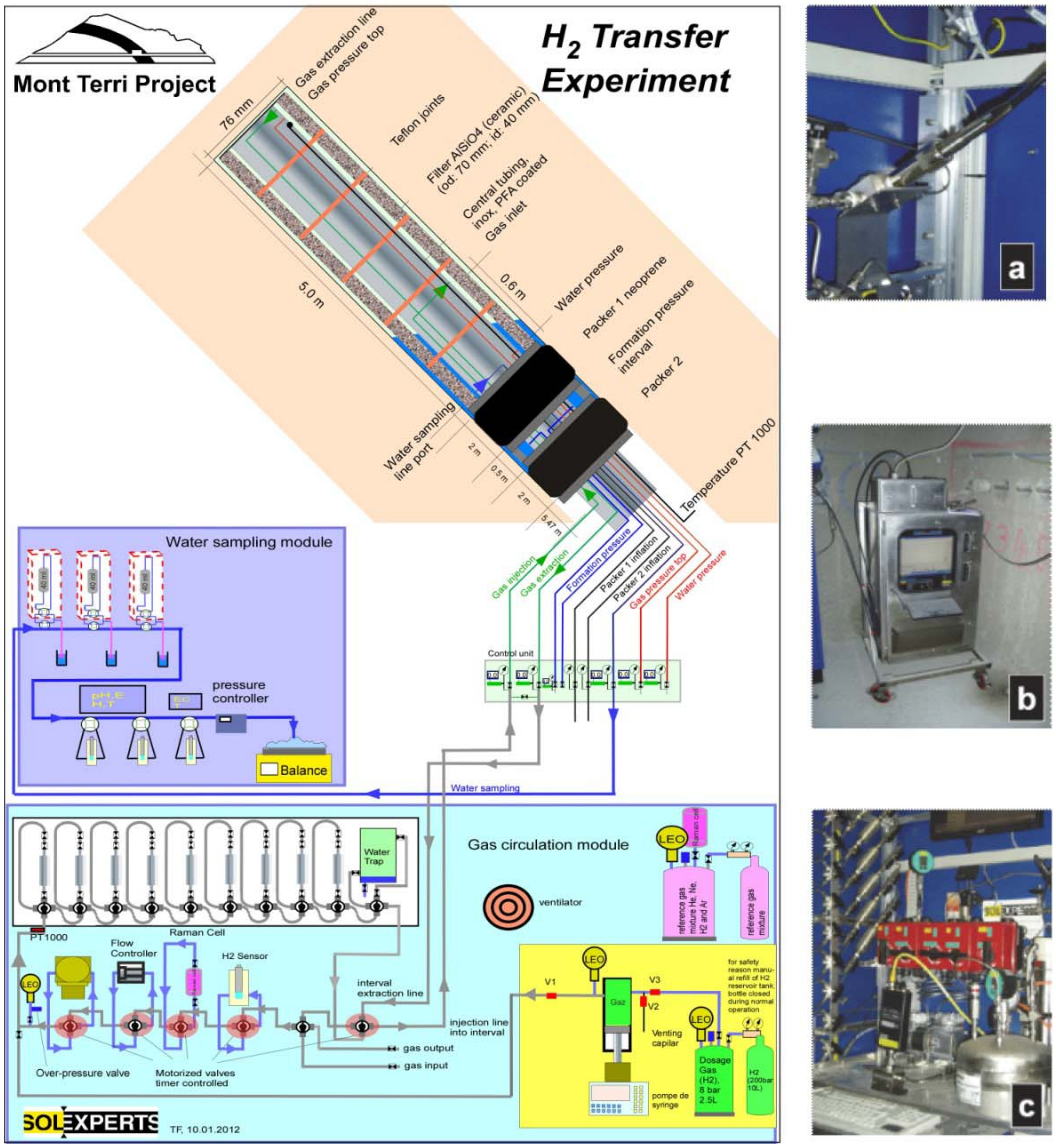

Figure 1: Schematic of the experiment setup. Photos: (a) Kaiser Raman probe; (b) Kaiser Raman spectrometer; (c) Gas circulation and dosage control/monitoring module

The gas tracer dosage equipment (yellow background, Figure1) was connected to the gas circuit module (light-blue background, Figure 1). The main component of the dosage module was the Teledyne Isco 500D syringe pump. A tightness tests of the standard cond syringe pump in the workshop using hydrogen gas showed higher than desired leakage rates. The following modifications considerably improved the pump's tightness with respect to hydrogen:

- A special piston with an o-ring seat (and not the standard ring seals)
- Replacement of the upper Teflon cylinder seal with a custom made double o-ring construction

The volume of the pump cylinder was 507 ml. The (extremely wide) range of adjustable flow rates was between 0.001 ml/min and 204 ml/min up to pressures of 258 bar. The pump was connected to a Teledyne Isco controller which interfaced with the Solexperts Dosage Control And Monitoring software (DCAM). The DCAM software managed the tracer gas dosage by controlling the syringe pump and three electro valves (Figure 2). The electro valves allowed the pump to dose the interval with tracer gas (inject), automatically refill and then equalize the pump pressure to the interval pressure before continuing the dosage.

DCAM monitored: internal pump pressure, external pump pressure, pump cylinder volume, borehole interval pressure, dosage gas pressure, reference gas pressure, and hydrogen volume percentage. Recording both injection pressure of tracer gas and injection flow rate allowed calculation of the injected tracer gas mass.

Each gas module bypass (circulation pump, flow meter, Raman probe, hydrogen probe, borehole) was remotely controlled and time scheduled via DCAM. The monitored values, the pump cylinder and value positions were numerically and graphically shown in real-time. Data was automatically transferred to the SAGD system (Tabani *et al.* 2010) and the Solexperts data visualization website (WebDAVIS) so the experiment's progress could be monitored by appropriate personnel using a web browser anywhere there is an internet connection.

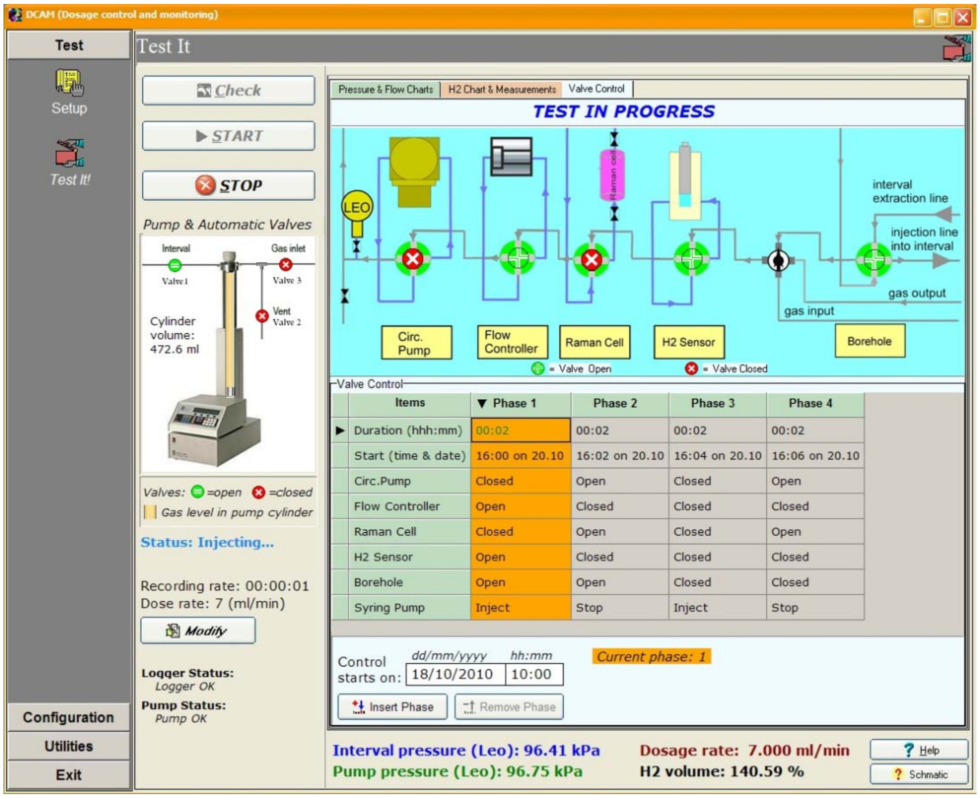

Figure 2: DCAM testing window with "Valve control" tab selected

Hydrogen Tightness Test

Before the first hydrogen injection, on-site tightness tests were conducted in the gas module (isolated from the borehole) with a mixture of gases of 2.2% hydrogen in argon at a total pressure of 1.1 bars over 200 days. The outcome of these tightness tests was an averaged total gas leakage rate of 0.5 mbar/day, corresponding to 0.5 mL/day STP. Hydrogen contributed to 9% of the leak. This rate was four times higher than the hydrogen content in the total gas. This result confirms that hydrogen leaks more easily than argon. The pure hydrogen leak was therefore estimated to be 0.04 mbar/day or 1.6 10^{-6} mol/day.

Chronology and Results of the Tests

Initial Phase

The borehole equipment was installed just after the drilling. Then, the test interval was filled with pure argon at a pressure of 2.3 (abs) bar and the circulation of the gas was started. The composition of the circulating gas was monitored over almost 2 years. It was observed that its composition evolved: nitrogen and light alkane concentrations increased with time. These gases were originally dissolved in the rock pore water. Over the year preceding the first injection of hydrogen, a water production flow rate from the surrounding rock between 10 and 20 mL/day was obtained in the borehole and the water composition was determined.

Hydrogen Injection Phase

The first hydrogen injection was performed by replacing the previous circulating gas by a mixture of gases containing 5% H_2, 5% He, 5% Ne and 85% Ar at a total pressure close to 1.5 bars. Because the previous gas was not completely eliminated after the gas replacement, the largest hydrogen partial pressure value was close to 0.06 bars. Helium and neon served as reference non-reactive gases since changes in their content should only depend on dissolution and diffusion processes in the rock pore water. They were used in the calibration of the transport part in the reactive transport model.

Following the first injection in the test interval, hydrogen concentration dropped below detection limits in the time frame of 65 days (Figure 3). In November 2011, pure hydrogen was added to the circulating gas to restore a hydrogen partial pressure of 0.06 bars in the test interval. Once again, hydrogen concentration decreased to less than detectable limits in 65 days (Figure 3).

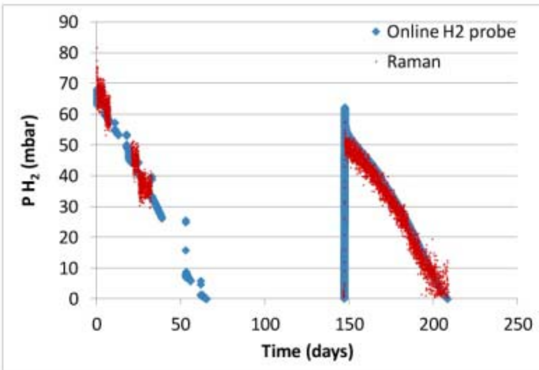

Figure 3: Measured evolution of H_2

In February 2012, a semi-continuous hydrogen injection phase was launched (Figure 4). This phase consisted in regulating the pure hydrogen injection phase time duration and frequency together with the hydrogen injection flow rate to maintain a partial pressure of hydrogen close to 0.06 bars in the test interval.

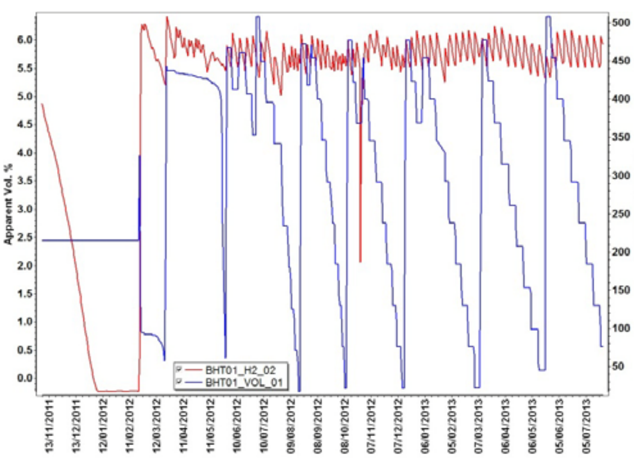

Figure 4: Recorded evolution of the Teledyne Isco syringe volume (blue line) and apparent volume fraction of hydrogen (H2scan specific sensor measurement, red line); the value of 6% for apparent volume fraction of hydrogen corresponds to hydrogen partial pressure of about 60 mbars.

Conclusions

- It was possible to inject H_2 in a borehole and to control the mass balance using a Teledyne Isco syringe pump and the DCAM software.
- The disappearance rate of H_2 observed was approximately one order of magnitude faster than the calculated rate assuming only dissolution and diffusion in the pore water. In contrast, He and Ne concentrations decreased as expected based on dissolution and diffusion processes alone. The modeling was carried out with the code PHREEQC in a one dimension radial configuration.
- The hydrogen loss rate was much higher than the helium loss rate and higher than the measured H_2 leak rate.
- The evolution of the borehole water composition suggests that hydrogen could have been consumed by a reaction involving sulfate reduction and catalyzed by microorganisms.

Partners

This experiment was performed within the Mont Terri project (www.mont-terri.ch). It was financed by the partners Andra (France), Nagra (Switzerland) and NWMO (Canada).

References

1. Delay J., Bossart P., Xiang Ling L., Blechschmidt I., Ohlsson M., Vinsot A., Nussbaum C., Maes N. (accepted). Three decades of Underground Research Laboratories. What have we learned? *Journal of the Geological Society of London*.
2. Lundy M. and Vinsot A. (2010). Implementation of Raman and mass spectrometry for on line measurement of gas composition in boreholes. In: Andra (Ed.), Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, 4th Intern. Meeting, Nantes, France, March 29–April 1st, 2010, Abstracts: 535-536.
3. Tabani P., Hermand G., Delay J., Mangeot A. (2010). Geoscientific Data Acquisition and management System (SAGD) of the Andra Meuse/ Haute-Marne research center. In: Andra (Ed.), Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, 4th Intern. Meeting, Nantes, France, March 29–April 1st, 2010, Abstracts: 253-254.
4. Thury M., Bossart P. (1999). Mont Terri Rock Laboratory. Results of the hydrogeological, geochemical and geotechnical experiments performed in 1996 and 1997. SNHGS Geol. Rep. 23, Swiss Nat. Hydrol. and Geol. Surv., Bern.
5. Vinsot A., Mettler S., Wechner S. (2008a). In-situ characterization of the Callovo–Oxfordian pore water composition. Physics and Chemistry of the Earth 33S1, S75–S86.
6. Vinsot A., Appelo C.A.J., Cailteau C., Wechner S., Pironon J., De Donato P., De Cannière P., Mettler S., Wersin P., Gäbler H.E. (2008b). CO_2

data on gas and pore water sampled in situ in the Opalinus Clay at the Mont Terri rock laboratory. Physics and Chemistry of the Earth 33, S54-S60.

7. Vinsot A., Appelo C.A.J., Lundy M., Wechner S., Lettry Y., Lerouge C., Fernandez A.M., Labat M., Tournassat C., De Canniere P., Schwyn B., McKelvie J., Dewonck S., Bossart P., Delay J. (accepted). *In situ diffusion test of hydrogen gas in the Opalinus Clay. Journal of the Geological Society of London*.

Last modified August 21, 2014

Teledyne Isco
P.O. Box 82531, Lincoln, Nebraska, 68501 USA
Toll-free: (800) 228-4373 • Phone: (402) 464-0231 • Fax: (402) 465-3091
E-mail: IscoInfo@teledyne.com

Teledyne Isco is continually improving its products and reserves the right to change product specifications, replacement parts, schematics, and instructions without notice.

TELEDYNE ISCO
Everywhereyoulook™