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Rates of microbial hydrogen oxidation and sulfate reduction in Opalinus Clay rock

Alexandre Bagnoud [a, b], Olivier Leupin [c], Bernhard Schwyn [c], Rizlan Bernier-Latmani [a, *]

[a] *Environmental Microbiology Laboratory, EPFL, Station 6, Lausanne 1015, Switzerland*
[b] *Stream Biofilm and Ecology Research Laboratory, EPFL, Station 2, Lausanne 1015, Switzerland*
[c] *NAGRA, National Cooperative for the Disposal of Radioactive Waste, Hardstrasse 73, Wettingen 5430, Switzerland*

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ABSTRACT

Hydrogen gas (H_2) may be produced by the anoxic corrosion of steel components in underground structures, such as geological repositories for radioactive waste. In such environments, hydrogen was shown to serve as an electron donor for autotrophic bacteria. High gas overpressures are to be avoided in radioactive waste repositories and, thus, microbial consumption of H_2 is generally viewed as beneficial. However, to fully consider this biological process in models of repository evolution over time, it is crucial to determine the *in situ* rates of microbial hydrogen oxidation and sulfate reduction. These rates were estimated through two distinct *in situ* experiments, using several measurement and calculation methods. Volumetric consumption rates were calculated to be between 1.13 and 1.93 μmol cm^{-3} day^{-1} for H_2, and 0.14 and 0.20 μmol cm^{-3} day^{-1} for sulfate. Based on the stoichiometry of the reaction, there is an excess of H_2 consumed, suggesting that it serves as an electron donor to reduce electron acceptors other than sulfate, and/or that some H_2 is lost via diffusion. These rate estimates are critical to evaluate whether biological H_2 consumption can negate H_2 production in repositories, and to determine whether sulfate reduction can consume sulfate faster than it is replenished by diffusion, which could lead to methanogenic conditions.

1. Introduction

Based on an international consensus, deep geological repositories are the preferred option for the disposal of radioactive waste (IAEA, 2003). An in-depth understanding of host rock processes relevant to safety is thus required, including the impact of microorganisms under repository relevant conditions. A few European countries have opted for a repository design that consists of waste sealed in carbon steel containers that are placed in a low-permeability Clay rock formation (ANDRA, 2005; Nagra, 2002). Steel is expected to corrode under reducing conditions at a rate of a few micrometers a year, producing iron oxide minerals (e.g., magnetite) and gaseous hydrogen (H_2) (King, 2008; Marsh and Taylor, 1988). Another source of H_2, but likely in lesser amounts, is the alpha-radiolysis of water after canister breaching (Le Caër, 2011). H_2 is believed to build up at higher rates than can be dissipated via diffusion. In this case, a free gas phase can form and migrate through the clay via two-phase flow or pathway dilation through the host-rock (Marschall et al., 2005). However, H_2 is also known to be an excellent source of energy that can support microbial growth and activity (Nealson et al., 2005). Thus, the consumption of H_2 by microbial activity could be beneficial to the long-term safety of the repository (Libert et al., 2011).

In Switzerland, Opalinus Clay, a clayey rock formation, is the current candidate to host a deep geological repository (Pearson et al., 2003). Results from an *in-situ* experiment on hydrogen diffusion through this rock formation that took place in the Mont Terri Underground laboratory, 300 m below the surface (Thury and Bossart, 1999), suggested that H_2 is being consumed by biological processes as it disappeared 20 times faster than accounted for by abiotic processes (Vinsot et al., 2014). A separate *in situ* experiment, carried out in the same facility, clearly showed that H_2 was oxidized microbiologically through a complex metabolic network (Bagnoud et al., submitted). Thus, it is expected that hydrogen gas might be utilized in a geological underground repository if the boundary conditions allow for it. The mechanism of hydrogen utilization in a repository have been discussed elsewhere (Nagra, in prep.) and are well established, but its rate of consumption remains uncertain.

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* Corresponding author.
E-mail address: rizlan.bernier-latmani@epfl.ch (R. Bernier-Latmani).

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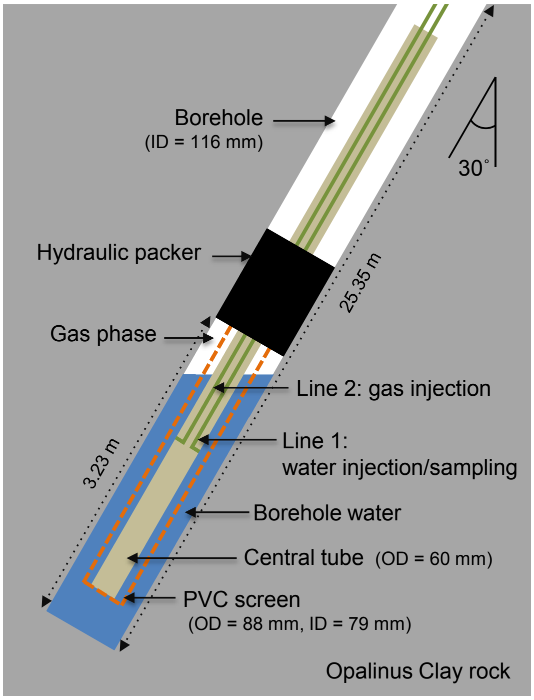

Fig. 1. Borehole equipment of BRC-3, which has an inclined descending orientation, forming a 30° angle with the zenith. Downhole equipment includes a central tube containing sampling lines (line 1 for water sampling and injection; line 2 for gas injection), a hydraulic packer and a PVC screen. Not to scale.

Determination of the *in situ* kinetics of H_2 oxidation is essential in order to complete the geochemical modeling of the repository and to account for biological contributions to H_2 consumption.

Furthermore, the rate of sulfate (SO_4^{2-}) reduction is a key parameter in evaluating whether sulfate depletion via hydrogen-fueled microbial sulfate reduction will exceed the influx of sulfate via diffusion from the rock. The depletion of sulfate, if it occurs, may enable the growth of methanogens. The establishment of a methanogenic microbial community would result in a lesser reduction of the gas pressure than sulfidogenic conditions due to the production of methane (CH_4), because the latter exhibits low solubility in water.

An experiment was carried out to characterize the microbial community that develops in response to H_2 amendments into a borehole within the Opalinus Clay formation (Bagnoud et al., submitted). While assessing rates of H_2 oxidation and sulfate reduction was not the primary goal of the experiment, it provided a unique opportunity to estimate these rates *in situ*. The collected data were evaluated using the differential rate (H_2, SO_4^{2-}) of consumption per time unit. The dependence of the consumption rates on hydrogen and sulfate concentrations as well as on the biomass was not obtainable. Nevertheless, the present work utilizes the data gathered from the H_2 amendment experiment to obtain a range of values for the rate of H_2 and sulfate consumption that could be of use to others in the nuclear waste disposal community as well as the subsurface H_2 storage community.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up was described previously by Bagnoud et al. (Bagnoud et al., submitted). Briefly, an inclined descending borehole (borehole BRC-3) at the Mont-Terri Underground Rock Laboratory (URL), producing 20 mL/day of porewater (due to a pressure differential between the rock formation and the borehole of about 10 bars), was equipped with a hydraulic packer in order to preserve reducing conditions and to enable a hydraulic pressure buildup (Fig. 1). Polyamide lines were connected to the surface through a series of lines and valves (referred to as surface equipment). This surface equipment allowed for water recirculation using a peristaltic pump (at a flow rate of 5 mL/min), water and gas sampling through needle valves, and hydrogen gas injection using a gas reservoir connected to the water circuit by a gas permeable membrane. A schematic representing the timescale set-up of the H_2 injection experiment is given in Fig. 2.

Bromide (Br^-) was amended to the borehole water as a conservative tracer in an initial pulse, before the start of the experiment. Hydrogen gas was then supplied to the circulating porewater for over 500 days (with some interruptions; Fig. 2). During the first 139 days, this amendment was delivered continuously as a gas

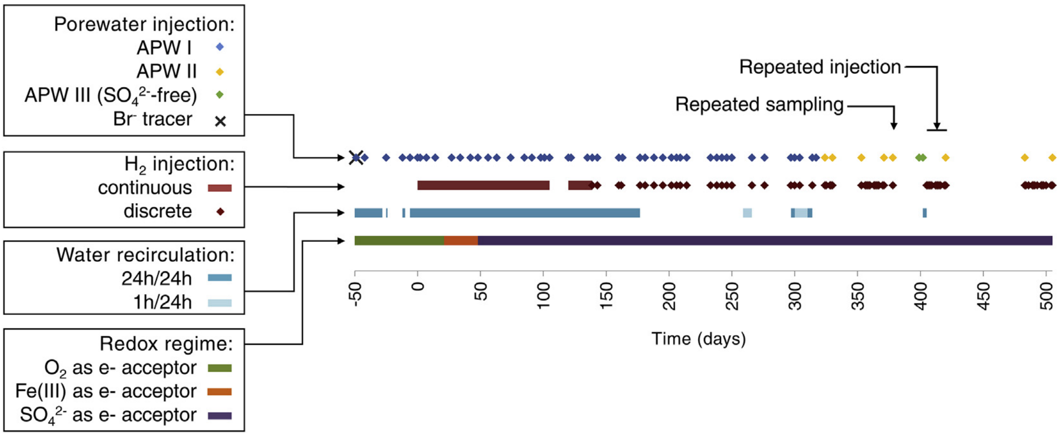

Fig. 2. Timeline of the H_2 injection experiment in BRC-3 borehole. Day 0 corresponds to the first injection of H_2 in borehole water. On the first line, the black cross indicates when the Br^- tracer was injected, the blue squares when APW I was injected, the yellow squares when APW II was injected and the green squares when APW III (sulfate-free) was injected into the borehole. On the second line, the red line indicates when H_2 was continuously injected to the borehole water (as dissolved phase), and the red diamonds indicate discrete H_2 injections into the borehole (as gas phase). On the third line, the dark blue line indicates when borehole water was continuously recirculated, and the light blue line when borehole water was recirculated 1 h per day. On the fourth line, the green line indicates when O_2 is the electron acceptor used by the microbial community, the orange line when Fe(III) is used, and the purple line when SO_4^{2-} is used (Bagnoud et al., submitted). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)