

MOLECULAR HYDROGEN : AN ENERGY SOURCE FOR BACTERIAL ACTIVITY IN NUCLEAR WASTE DISPOSAL

M. Libert*, L. Esnault

CEA-Cadarache, 13108 St Paul lez Durance, France (marie.libert@cea.fr)

NATURAL ORIGIN OF H₂

Hydrogen is a common product of microbial metabolism, large number of bacteria are able to use it as energetic substrate in subsurface ecosystems. Moreover H₂ is known as one of the most energetic substrates for deep subsurface ecosystem. It could be produced in different ways mainly volcanic activity (basalts iron rich volcanic rocks) or natural radiolysis of water or even fermentation (Lin *et al.*, 2005). The millimolar concentrations of H₂ observed in the ground waters are consistent with the activity of a large variety of hydrogen-oxidising bacteria as described in the following Table. Electron acceptors are identified as O₂, CO₂, NO₃⁻, SO₄²⁻ or Fe³⁺. Aerobic, anaerobic, obligate and facultative autotrophs are included. Numerous of these bacteria are thermophilic bacteria. This bacterial activity leads to the production of methane, acetate, nitrogen, hydrogen sulphur or ferrous oxides. In anoxic environments, H₂ concentrations are governed by microbial metabolism. In most cases, H₂ producing microorganisms are thermodynamically controlled by the abundance of H₂, and survive thanks to H₂ consumers, a metabolism called interspecies H₂ transfer. Metabolism of H₂ is catalysed by hydrogenase as cytoplasmic enzymes or membrane bound enzymes.

Examples of H₂ oxidation by aerobic or anaerobic microorganisms

Reaction	Microorganisms species
$2 \text{H}_2 + \text{O}_2 \Rightarrow 2 \text{H}_2\text{O}$	Aerobic hydrogen bacteria (<i>Ralstonia sp.</i>)
$4 \text{H}_2 + \text{CO}_2 \Rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$	Methanogens bacteria (<i>Methanobacterium sp.</i>)
$4 \text{H}_2 + 2 \text{CO}_2 \Rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2\text{O}$	Acetogens bacteria (<i>Acetobacterium sp.</i>)
$5 \text{H}_2 + 2 \text{NO}_3^- + 2 \text{H}^+ \Rightarrow \text{N}_2 + 6 \text{H}_2\text{O}$	Denitrifying bacteria (<i>Paracoccus denitrificans</i>)
$4\text{H}_2 + \text{SO}_4^{2-} + 2 \text{H}^+ \Rightarrow \text{H}_2\text{S} + 4 \text{H}_2\text{O}$	Sulfate reducing bacteria (<i>Desulfovibrio sp.</i>)
$\text{H}_2 + 2 \text{Fe}(\text{OH})_3 + 4 \text{H}^+ \Rightarrow 2\text{Fe}^{2+} + 6\text{H}_2\text{O}$	Iron reducing bacteria (<i>Shewanella sp.</i>)

H₂ IN NUCLEAR WASTE DEEP REPOSITORIES

Several situations of H₂ production will occur in nuclear waste repository:

- Radiolysis of water.
- Radiolysis of organic matter (such as bitumen, in case of B waste), H₂ production due to gamma radiolysis of bitumen is evaluated to 1 L H₂/kg of bitumen /MGy.
- Corrosion of metal containers (in deaerated solutions).

Large amount of H₂ are predicted in some situations, and will select the development of hydrogen species.

Then, aerobic hydrogen bacteria oxidising hydrogen could be found in basins containing irradiating waste, or during the oxic period of storage, denitrifying bacteria or sulfate reducing bacteria will develop near the bitumen waste. Groundwater of the Callovo-Oxfordian will support sulfate reducing bacteria or methanogen bacteria. Iron reducing activity could develop near containers or in argillite.

Several examples and results of kinetic of H₂ consumption by microorganisms are here presented:

- The development of bacteria using oxygen and H₂ from radiolysis of water in basin containing irradiating waste (Galés *et al.*, 2004).

- The development of denitrifying bacteria using nitrates and H₂ in the environment of bituminized embedded waste (Figure 1, B waste, Libert *et al.*, 1999). In presence of H₂, bacteria will reduce the released nitrates from bituminized waste: the limiting factor of the kinetic is the amount of released nitrates.
- The development of iron reducing bacteria using ferric iron and H₂ from container corrosion products (Figure 2, C waste, Esnault *et al.*, 2009). *Shewanella* sp is able to oxidise 1.2 mmol of H₂/day by iron reduction.

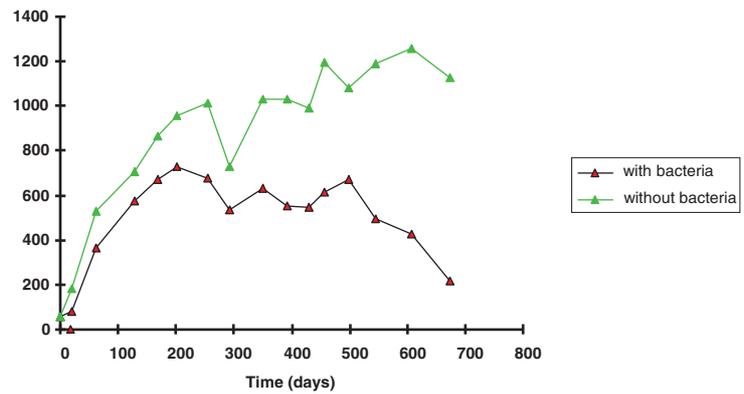


Figure 1: Activity of nitrate reducing bacteria oxidizing H₂ as a function of time, measured by the decrease of nitrate concentration (medium contains embedded bitumen leachates, NO₃ reducing bacteria, 10% of H₂).

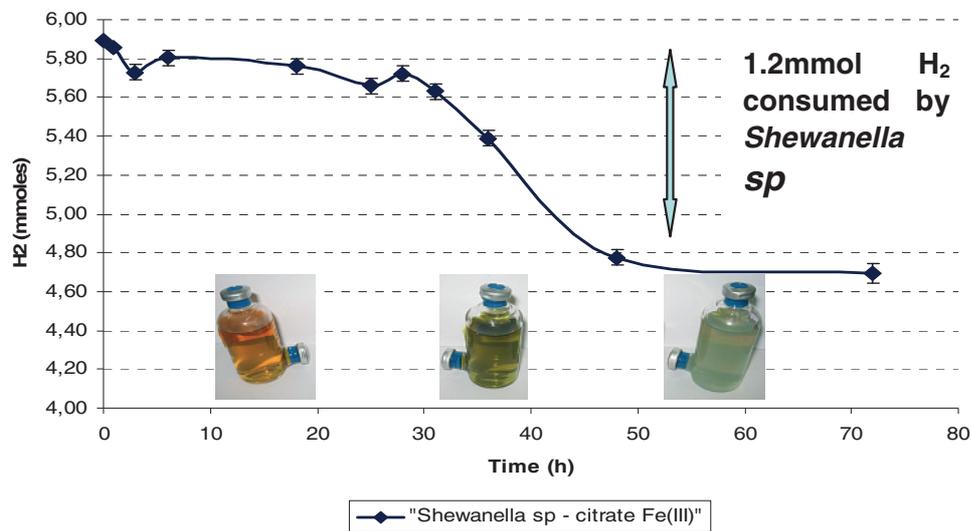


Figure 2: Consumption of H₂ by iron reducing bacteria in presence of Fe(III).

The consequences of the development of H₂ oxidising bacteria are discussed in terms of physico-chemical modifications in geological disposal: biomass production, gas production and consumption, biocorrosion.

References:

- Esnault, L., Libert, M., Mustin, C., Jullien, M., 2009. Availability of nutrients sources for bacterial development in deep clayed environments. *Geochimica Cosmochimica Acta*, Special Issue Goldschmidt 2009 A338.
- Gales, G., Libert, M., Sellier, R., Cournac, L., Chapon, V., Heulin, T., 2004. Molecular hydrogen from water radiolysis as an energy source for bacterial growth in a basin containing irradiating waste. *FEMS Microbiol Lett* 240(2), 155-162.
- Libert, M., Sellier, R., Marty, V., 1999. Hydrogen consumption by denitrifying bacteria in nuclear environment. *International Symposium Subsurface Microbiology*. Vail-Colorado (1999).
- Lin, L. H., Slater, G. F., Lollar, B. S., Lacrampe-Couloume, G., Onstott, T. C., 2005. The yield and isotopic composition of radiolytic H₂, a potential energy source for the deep subsurface biosphere. *Geochimica Cosmochimica Acta* 69(4), 893-903.