Combining CO_2 valorization strategies to produce hydrogen and methane in a geological storage context

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1. Introduction

The dramatic increase of anthropogenic greenhouse gases concentrations in the atmosphere threatens the ecosystems equilibrium, including our way of life. The development of sustainable technologies in the frame of mitigation efforts to reduce anthropogenic CO_2 emissions remains an urgent need. A promising strategy consists in storing the CO_2 in deep geological formations, like deep saline aquifers. However, most of the considered methodology aim at forming carbonates to safely store CO_2 as a waste. Oppositely, it could be used as a raw material – and therefore valorized - for producing valuable resources such as hydrogen (through chemical reaction with Iron) or methane (through bioconversion). Far from being anecdotal, the transformation of part of the stored CO_2 into hydrogen or methane would lower the costs of capture and storage and change the paradigm of CO_2 geological storage.
Deep saline aquifers are porous environments, with temperature ranging between 40°C to 100°C and hydrostatic pressure up to 150 bar. When CO_2 is injected into these environment, several geochemical relations can proceed, in particular with iron-rich minerals, resulting in carbonation processes, which can also produce hydrogen. Besides, such reaction can be speeded up by considering the co-injection of CO_2 with iron wastes, which represent millions of tons of industrial wastes. This will results in: $Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2$. Meanwhile, methanogens microorganisms, which are part of the microbial population living in deep saline aquifers, and more particularly hydrogenotrophic methanogens, can transform CO_2 and H_2 into methane, through methanogenesis: $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$. Using their metabolisms would allow considering deep saline aquifers as macro (bio)reactors for an upgrading process of CO_2 to methane.

2. Materials and Methods

To investigate the transformation of CO_2 either in a biotic or in an abiotic way, we have developed multiscale high-pressure transparent biocompatible approaches (microfluidics and millifluidics) allowing to mimic deep environments at lab scale. The tools and approaches that we are developing and using make it possible to simulate these deep ecosystems, to estimate the yields of such approaches and the possibility of testing exploitation scenarios.
In the case of abiotic generation of hydrogen, iron powder was placed in a millifluidic reactor filled with DI or saline water and further pressurized with supercritical CO_2. The evolution of the gas phase was monitored with *ex situ* gas chromatography to access the reaction kinetics.
For the bioconversion of CO_2 to methane, microfluidics or millifluidics reactors were filled with an artifical groundwater medium, inoculated with a model microbial methanogen strain: *Methanococcus thermolithotrophicus*. This medium is then pressurized with a mixture of hydrogen and CO_2 (80/20 mol%) and the biofilm formation along with the gas production is monitored over time.

3. Results and discussion

We have determined the reaction kinetic of the abiotic production of hydrogen through iron corrosion in CO_2 / water medium, demonstrating quite fast reaction rates. Up to 80% of the iron is converted to carbonate, resulting in hydrogen production within few hours for pressure and temperature conditions ranging from $50 < p\ (bar) < 200$ and $25 < T(°C) < 130$.

Similarly, microbial CO_2 conversion to methane can reached high conversion rates at similar conditions and residence times. This is also linked with the development of biofilms inside the reactor, which was monitored using microfluidics approaches.
Finally, we have combined abiotic hydrogen generation with biotic CO_2 conversion by introducing iron powder in a microbial process, without introducing hydrogen. Depending on the CO_2 partial pressure, microbes can use the hydrogen production from iron corrosion to combine it with CO_2 and to form methane.

4. Conclusions

In brief, the promotion of the (bio)chemical conversion of CO_2 to hydrogen and methane in geological formations constitutes an advantageous long-term CCUS strategy. Besides the sole storage of CO_2, deep saline aquifers may also represent an interesting option for stable long-term energy generation and storage in addition to being cost-effective (bio)reactors for CO_2 valorization at a global scale. As the global energy economy remains hydrocarbon-based, this double valorization could aid in the transition to more sustainable sources of energy and raw materials.