Bio-electrochemical conversion of carbon dioxide to methane in geological storage reservoirs

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ABSTRACT

Geological storage of carbon dioxide (CO_2) as currently conceived is not commercially viable. To promote deployment of CO_2 capture and storage (CCS), substantial value must be added to CCS operations. We have proposed a subterranean carbon plantation that involves storing CO_2 in a geological reservoir, biologically converting the stored CO_2 to methane *in situ*, and harvesting the biogenic methane as a recycled energy source. To examine the durability of methanogenic metabolism under storage reservoir conditions, the methanogenic activity of *Methanothermobacter thermautotrophicus* (a representative subsurface methanogen) was assessed under nutrient-limited and reduced-pH conditions in actual formation-water-based media. Moreover, to examine the possibility of electrochemically supplying the source of reducing power into the reservoir, methanogen was also incubated in absence of exogenously supplied molecular hydrogen with applied voltage. Applied-voltage-dependent methanogenesis was observed, suggesting that methanogen can utilize electrons and protons as a reducing-power source to reduce CO_2 to methane. Towards practical deployment of the electromethanogenic system to utilize CCS reservoirs as energy-reserving tanks, further studies are required to enhance the bio-electromethanogenic activity and optimize well configurations.

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1. Introduction

Geological storage of carbon dioxide (CO_2) is a promising technology to mitigate greenhouse gas (GHG) emissions from large-scale fossil fuel use. For instance, in a scenario of reducing GHG emissions by 50% by 2050 (the IEA BLUE Map scenario), it is estimated that a hundred CO_2 capture and storage (CCS) projects need to be globally deployed by 2020 and over 3000 projects by 2050 [1]. Other options for CO_2 storage such as mineral carbonation and chemical industrial uses of CO_2 have also been proposed [2]. However, in terms of cost effectiveness, storage potential, and technological maturity, geological CO_2 storage is technologically superior to those alternatives (which remain largely underdeveloped) and is at the stage of large-scale demonstration or precommercialization. Nonetheless, deployment of CCS over the world, at present, is limited to only eight fully integrated operations, namely, the Sleipner, Snohvit, In Salah, Weyburn, Shute Creek, Val Verde, Enid Fertilizer, and Century projects [3]. Such sluggish deployment is attributed to several factors, including, but not limited to, legal and regulatory aspects, public acceptance, and financial issues.

With regard to costs for employing CCS systems with fossil-fired power plant and various industrial processes, although a fairly wide range of expenses has been reported [3], it is certain that CCS is a capital-intensive technology. The BLUE Map scenario through 2050 requires an additional investment of over 30% more than equivalent non-CCS plants [1]. Financing mechanisms such as GHG reduction incentives and tax rebates need to be established to incentivise commercialization of CCS.

Because CCS alone would not be commercially viable and requires financial support to outweigh the cost of deployment, value-added options such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coal-bed methane (ECBM) recovery have been suggested for partially offsetting the costs of CCS operations [2,4–6]. Various geological settings in sedimentary basins are suited for geological storage. Hydrocarbon pools, coal beds, and saline formations are all possible candidates, among which the value-added options are applicable to oil fields, gas fields, and coal beds, which, however, have limited storage capacity and geographic distribution [7]. In contrast, saline aquifers are believed to have by far the largest storage capacity and exist all over the globe [2], but value-added options have not yet been proposed for them. Therefore, it is desirable to develop a means to add substantial value to CO_2 storage in saline aquifers.

As an economic incentive for saline aquifer storage, conversion of CO_2 to a handy energy source, methane, is considered in this

study by virtue of microbial metabolism. Although the impacts of CO_2 on subterranean and near-surface microbial ecosystems have attracted considerable attention [8–10], active utilization of microbial organisms in CCS operations is rarely discussed in the literature. A few exceptions include the utility of biofilms as a means of reducing permeability of cap rocks [11] and the utility of hydrogenotrophic methanogen for converting CO_2 and hydrogen to methane [12]. The current study considers the possibility of microbial conversion of CO_2 and electrical current to methane in storage reservoirs—the core technology of a subterranean carbon plantation that could utilize the storage reservoirs as energy-reserving tanks.

2. Subterranean carbon plantation

2.1. Geological storage reservoirs as natural bioreactors for methane production

The concept of the subterranean carbon plantation proposed herein has the geological storage of CO_2, *in situ* biological conversion of the stored CO_2 to methane, and harvest of the biogenic methane as a recycled energy source as its sequence (Fig. 1). Geological storage reservoirs provide huge volumes of water-filled pore space maintained at geothermal temperatures. When supplied with CO_2 through CCS operations, such reservoirs could function as natural bioreactors that prompt methanogens to convert CO_2 to methane.

As is the case with the formation of petroleum reservoirs [13], migration and trapping are the key mechanisms that form methane accumulation worth developing. Primary migration is the expulsion of converted methane from a water phase into a permeable carrier bed. Expulsion can be achieved by virtue of the less-soluble nature of methane in groundwater. Under usual pressure and temperature conditions for geological storage, methane solubility in groundwater is an order of magnitude lower than that of CO_2. For higher values of salinity, often encountered in saline aquifers or petroleum reservoirs, solubility is further reduced [14]. Thus, methane converted from CO_2 tends to be transferred to a gas phase that can easily flow through a carrier bed.

Once methane is expelled from a water phase, subsequent movement, that is, secondary migration, is driven by buoyancy. Gaseous methane is much lighter and more mobile than groundwater; thus, methane can displace groundwater downward and moving itself upward. Buoyant force is proportional to the product of the height of the methane column and the density difference between the groundwater and methane [13]. Coalescence of the methane globules after expulsion increases their ability to move upward through water-filled pore space.

Upward buoyant force is opposed by capillary pressure, which is the resistance to entry of the methane gas globule into pore throats. When buoyant force is greater than capillary pressure, the globule squeezes into the pore throat and continues moving upward. Capillary pressure increases as the pore throat reduces. If the methane gas globule encounters a tight bed with tiny pore throats, capillary pressure may exceed buoyant force, and secondary migration eventually ceases. Such an impermeable bed is called a cap rock, beneath which gaseous methane is trapped. In the site selection process for geological CO_2 storage, cap rocks are essential for preventing CO_2 leakage from storage reservoirs into overlying beds, which also provide an efficient trapping mechanism for biogenic methane converted from CO_2.

2.2. Subterranean methanogenesis

Carbon atoms exhibit oxidation states ranging from +4 to −4, occurring mostly in the +4 (oxidized) state in CO_2 and carbonates. The most reduced form of carbon is methane, with an oxidation number of −4 [15]. Methane is generated by two main processes: biogenic and abiogenic. The former is microbial methanogenesis, and the latter includes thermal cracking of kerogen and pyrolysis or inorganic reaction of water with hot ultramafic rocks and metals [16]. Biogenic methane has been found all over the world [17], and at least 20% of the known natural gas resources are estimated to have been generated by microbes [18].

The Earth crust is inhabited from the surface down to more than 3000 m below ground by microorganisms [19]. Active microbial populations are recognized in various sedimentary environments such as gas hydrate sediments, sedimentary rocks, unconsolidated sediments, petroleum-contaminated aquifers, and petroleum reservoirs. Many subterranean environments are anoxic and appropriate for anaerobic microorganisms. Methanogens are a phylogenetically diverse group of obligate anaerobic microorganisms belonging to the *Euryarchaeota* phylum of the *Archaea* domain. Pore space in sedimentary environments is sufficient for methanogens, which have an average size of 1 μm, to thrive. In comparison with their surface relatives, subterranean methanogens are smaller, tolerate higher salt concentrations, and grow at a wider range of temperatures [16].

Methanogens generally compete with three other major anaerobic metabolic groups for their substrates in natural habitats: sulfate-reducing bacteria, acetogens, and ferric iron reducers. In habitats where the electron donor is limiting, there is a hierarchy for competition for electron donor in which ferric iron reducers outcompete other organisms if their electron acceptor is present, followed by sulfate-reducing bacteria, methanogens, and acetogens [20]. When only CO_2 is available as an electron acceptor, however, methanogens and acetogens dominate habitats. At low H_2 concentrations, a pH of less than 7, and high temperatures, acetogenic bacteria channel acetic acid into H_2 and CO_2 formation. Methanogens then finally convert acetate, H_2, and CO_2 into methane [21].

Energy metabolism of methanogens has been considered to be restricted to the formation of methane from CO_2/H_2, formate, methanol, methylamines, and/or acetate [21]. Among these limited metabolic reactions, the two main methanogenic pathways are CO_2 reduction and acetate fermentation, as shown below, respectively:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (1)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (2)$$
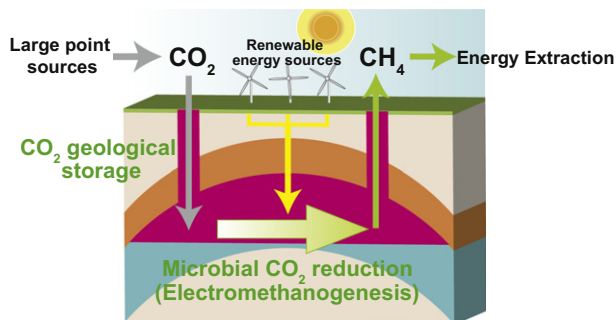
Fig. 1. Concept of carbon plantation using electromethanogenesis. CO_2 is captured from large point sources (such as fossil-fuel power plants) and stored in geological reservoirs. The stored CO_2 is then reduced to methane by electromethanogenic microorganisms within the reservoir. Electrical current generated by renewable energy sources is used as a reducing-power source in electromethanogenic reduction of CO_2 and thereby stored as methane. The resulting methane can be recovered from the reservoir in a manner similar to that for natural-gas production.