Review

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# Mineral $CO_2$ sequestration by environmental biotechnological processes

**Shiva S. Salek[1], Robbert Kleerebezem[1], Henk M. Jonkers[2], Geert-jan Witkamp[1], and Mark C.M. van Loosdrecht[1]**

[1] Department of Biotechnology, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands
[2] Department of Materials and Environment, Microlab, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands

**$CO_2$ sequestration may be an avenue to mitigate climate change. $CO_2$ sequestration by mineral carbonation can be achieved by the reaction of $CO_2$ with alkaline silicates. Here, we evaluate how alkaline silicate mineral-based $CO_2$ sequestration can be achieved using environmental biotechnological processes. Several biotechnological processes rely on the sequence of (i) an acid-producing reaction such as nitrification and anaerobic fermentation and (ii) an alkalinity-producing reaction such as denitrification and methanogenesis. Whereas the acid-producing reaction can be used to enhance the dissolution of, for example, alkaline calcium silicates, the subsequent alkalinity-producing step can precipitate $CaCO_3$. We quantitatively evaluate the potential of these processes for $CO_2$ sequestration and propose that optimization of these processes could contribute to climate change mitigation strategies.**

## Stabilization of atmospheric $CO_2$ levels by natural mechanisms

$CO_2$ accumulation in the atmosphere has been suggested to result in global climate change, which along with disturbance of the nitrogen cycle and biodiversity loss have been identified as the main environmental challenges facing humanity today [1]. A variety of strategies have been proposed to mitigate climate change by reducing the atmospheric $CO_2$ concentration. A closer look at the global carbon cycle shows that from the total amount of carbon entering the atmosphere every year (213 gigatons of carbon, GtC), only 2.5–3% has an anthropogenic origin (5.4 GtC). The remainder of the carbon is a result of natural activities (Figure 1) [2–5]. Most of the carbon released is returned to the lithosphere and hydrosphere by several natural mechanisms, stabilizing the atmospheric $CO_2$ concentrations over the geological timescales. This implies that only a minor increase in the uptake rate of one of these natural mechanisms can compensate for the extra anthropogenic $CO_2$ emissions. Mineral carbonation of $CO_2$ (often referred to as mineral $CO_2$ sequestration) is one of the natural negative feedback mechanisms. It reduces the atmospheric $CO_2$ concentration by $CO_2$ reaction with alkaline silicate minerals to form carbonate minerals [6]. The durability of this process is evident from the distribution of carbon in the lithosphere of the Earth (Figure 1) where approximately half of the total carbon (42% wt/wt) is in the form of limestone ($CaCO_3$) and other types of carbonates [4]. However, a portion of the limestone has metamorphic and igneous origins; the large sedimentary portion of these carbonate rocks shows that mineral $CO_2$ sequestration is a geologically stable process with a high potential for $CO_2$ sequestration [7,8]. The effectiveness of the process for mitigation purposes has however been limited due to the slow kinetics of the $CO_2$–silicate reactions [9]. The idea of distributing finely powdered alkaline silicate minerals over land areas as a geo-engineering solution is to enhance the efficiency of mineral $CO_2$ sequestration by increasing the reactive surface area [10]. Model-based analysis demonstrated that applying this technique can raise the pH of the rivers, which in turn negatively influences the natural environment and decreases the mineral dissolution rates in the long term [11]. Besides using natural ecosystems, specific man-made ecosystems could be particularly suitable for implementing the mineral $CO_2$ sequestration strategy. Examples of such systems are environmental biotechnological processes such as wastewater treatment facilities that are essentially enhanced natural processes. Here, we introduce a new application of various biotechnological processes (i.e., wastewater, waste, and gas treatment facilities) for mineral $CO_2$ sequestration.

## Challenges for application of mineral $CO_2$ sequestration

Mineral $CO_2$ sequestration is a process where atmospheric $CO_2$ is fixed in the form of carbonates. For carbonate ions to precipitate as carbonate minerals, a suitable counter ion should be present. The most common carbonate minerals on Earth contain $Ca^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$, or $Sr^{2+}$ as counter ion [12]. These divalent cations, in addition to the alkalinity required for $CO_2$ conversion to carbonate ions can be considered as the main raw materials for the mineral $CO_2$ sequestration process (Equation 1). Alkaline silicate minerals such as wollastonite can potentially provide

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Corresponding author: Salek, S.S. (S.S.ShayeganSalek@tudelft.nl).

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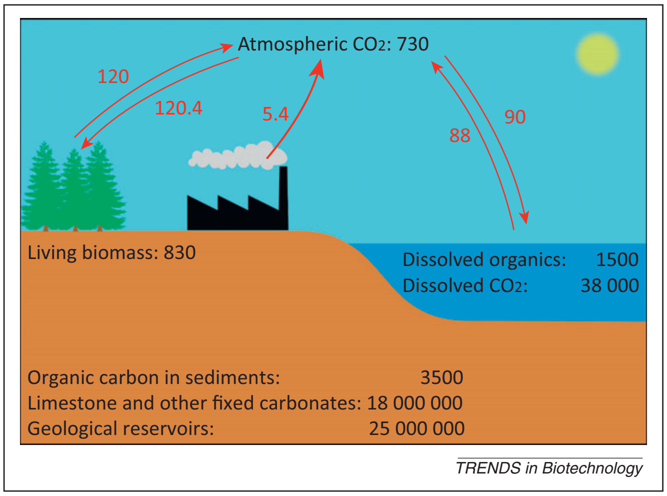

**Figure 1**. Global carbon reservoirs and fluxes [2–4]. Reservoirs are expressed as gigatons of carbon (GtC) and fluxes are in GtC/year.

the divalent cation and alkalinity needed for the capture and sequestration of $CO_2$ at ambient environmental conditions (Equation 2) [13]. There are far more sufficient alkaline silicate materials available to sequester the equivalent $CO_2$ of the total known amount of fossil fuels [14–16]. However, the slow release rate of divalent cations from these minerals under neutral and alkaline pH conditions, the same pH at which the carbonate ion ($CO_3{}^{2-}$) can form from $CO_2$ in water, is one of the main reasons for limited application of the mineral carbonation process to date [17,18]. Therefore, obtaining divalent cations and alkalinity at a high rate is considered among the main challenges for mineral $CO_2$ sequestration process [19,20].

$$(\mathrm{Ca/Mg})^{2+}(\mathrm{aq}) + \mathrm{CO_2} + 2\mathrm{OH^-} \rightarrow (\mathrm{Ca/Mg})\mathrm{CO_3(s)} + \mathrm{H_2O(aq)} \qquad [1]$$

$$\mathrm{CaSiO_3} + \mathrm{CO_2} \rightarrow \mathrm{CaCO_3} + \mathrm{SiO_2}$$
$$\Delta G_r(\mathrm{kJ/mol}) = -37,\ \ \Delta H_r(\mathrm{kJ/mol}) = -87 \qquad [2]$$

### *Enhancing divalent cation and alkalinity release rate of alkaline silicates*

To obtain substantial $CO_2$ sequestration by mineral carbonation, the problem of slow release of alkalinity and divalent cations from alkaline silicate minerals should be overcome. This can be accomplished by introducing chemical compounds such as specific complexing agents or acids to a solution in which alkaline silicates particles are suspended [21–23]. Another possibility is to activate the mineral reactants by thermal and mechanical means, that is increasing the surface area [24]. However, the high costs and intensive energy needs associated with such chemical or physical treatments of silicate minerals have been mentioned as the main drawbacks for application of these methods [19,20,25,26]. Therefore, recently, the application of biological processes as a more cost-efficient method for enhancing the dissolution of alkaline silicates has been investigated [27–31]. Microbial processes can primarily increase the dissolution rate of silicate minerals by modifying the environmental conditions such as pH reduction by, for example, production of organic acids [28,32]. Nitrification and carbohydrate fermentation to volatile fatty acids (VFA) are examples of acid-producing microbial processes that are widely applied in the field of environmental biotechnology. Hence, integration of alkaline silicate minerals into these processes can potentially enhance their dissolution rate [33]. The increase of dissolution rate of alkaline silicates can provide the divalent cations needed for the carbonate precipitation. However, the acidity produced by the biological process consumes the alkalinity, which is required for carbonate mineral formation (Equation 1). Therefore, the process should be combined with a process that generates alkalinity in order to enable carbonate mineralization.

### *Alkalinity source for conversion of $CO_2$ to carbonate ions*

Mineral sequestration of $CO_2$ requires alkalinity to form carbonate ion ($CO_3{}^{2-}$) from the $CO_2$ gas (Equation 1). Various sources of alkalinity have been suggested for $CO_2$ sequestration purposes. For example, alkaline solid residues from different industries such as steel slag [34,35], cement kiln dust [36], and fly ashes [37,38], have been identified as alkalinity sources. The quantity and distribution of these alkaline solid wastes is however limited on a global scale [34]. The large deposits of carbonate sediments found in lakes and seas are a result of various alkalinity-producing metabolic processes such as denitrification, methane production, and sulfate reduction [39]. Such microbial processes also occur in widely applied environmental biotechnologies such as biological nitrogen removal and anaerobic digestion (AD). In these processes, degradation of organic carbon by denitrifiers and methanogenic bacteria results in a pH increase that stimulates the carbonation of the liquid. Once the divalent cations are provided (e.g., by dissolution of alkaline silicates in an acid-producing process) to the alkaline-producing processes, mineral carbonation of $CO_2$ can take place.

## Integration of mineral $CO_2$ sequestration into two-stage biotechnological processes

There are a number of biotechnological processes that involve a sequence of an acid- and an alkalinity-producing step. Such reaction sequences enable mineral $CO_2$ sequestration by silicate dissolution and carbonate formation processes. Enhancement of alkaline mineral dissolution can be obtained in the first acid-producing stage, whereas the second alkali-producing stage yields carbonate formation (Figure 2).

Biological waste/wastewater technologies that are characterized by the sequence of an acid- and an alkalinity-producing step are typically conducted in a single stage reactor in order to prevent large pH variations. Separation of the steps would amend a traditional waste handling facility with $CO_2$ sequestration capacity. Example treatments are: (i) AD – substrate fermentation to volatile fatty acids and subsequent methanogenesis; (ii) biological nitrogen removal – aerobic nitrification and subsequent anoxic denitrification degrading organic carbon. Other examples of sequential acid- and alkalinity-producing steps in biotechnological processes are: (iii) flue gas desulfurization – weak