Sequestration of inorganic carbon in groundwater of arid saline-alkali area

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Abstract. It has been reported that the saline/alkaline groundwater aquifer is a potentially large active inorganic carbon pool. This paper reviews the formation mechanism and the carbon storage path of inorganic carbon in groundwater of arid saline-alkali area. The geochemical carbon sequestration processes (CO2-water-rock interaction and mineral capture) known as the "capture-reaction" model, are considered to be the most effective means of long-term CO2 storage, since the saline aquifers are covered with thick saline-alkali soils, once CO2 is involved in rock weathering or mineralization, it will become a part of the geological structure that can hardly be released again. This review provides an important reference for the carbon sequestration mechanism of arid underground saline-alkali aquifers, and is helpful for the estimation of regional carbon balance and the mitigation of Greenhouse Effect.

1. Introduction

Global warming effect and carbon cycle has attracted much attention. How to mitigate anthropogenic CO2 emission and increase carbon storage capacity is of great significance to global climate change. Recently, some widely publicized paper about aquifers hidden beneath saline/alkaline soils as possible CO2 sinks suggested that have found a missing carbon cycle, that is bicarbonate entering shallow groundwater, based on carbon sink studies by Li et al. (2015) and Ma et al. (2014) [1-2]. Monger et al. (2015) also has indicated that groundwater as a carbon storage sink is larger than soil carbonate (695~940 Pg C), containing at least 1404 Pg C[3]. This stimulated much interest in the possible mechanisms for that carbon sequestration. Relevant researches have shown that, globally, the flux of dissolved inorganic carbon into groundwater in the form of HCO3− has been estimated to capture 0.2–0.36 Pg C/yr with a residence time is as long as the groundwater itself, possibly hundreds to thousands of years[3-4]. Yet, despite general agreement about saline/alkaline soil solution as a carbon sink, there is still controversy over the potential mechanisms and carbon reserves to absorb atmospheric CO2[5-7].

By introducing the concept of generations pedogenic carbonate, Monger et al. (2015) shows that soil carbonate can permanently sequester atmospheric CO2 when calcium comes from silicate minerals. However, when calcium comes from pedogenic carbonate or limestone minerals, the consecutive dissolution and reprecipitation of carbonate is not carbon sequestration, is just carbon exchange, while in groundwater, carbon can be reserved as HCO3− no matter whether calcium is from silicates or carbonates[3]. Ma et al. (2014) and Schlesinger et al. (2017) reported that it is reasonable that the CO2 can be absorbed by the saline/alkaline soil solution and be washed downward into the groundwater body with fluctuations in the groundwater table[2,5]. Li et al. (2015) points out that saline aquifers in the enclosed arid basins have no outlet and no hydrological link to river-ocean system. Any places with soil
pH > 7 (roughly half of the earth's coverage) can have obvious DIC deposition into groundwater, as long as there is groundwater recharge[1].

The potential and the capacity of the saline-alkali aquifer collecting and fixing the atmospheric CO2 are faced with the challenge and the pressure to compensate the greenhouse gas emission reduction of the industrial greenhouse, but, at present, the understanding of the groundwater and inorganic carbon pools in the arid and saline-alkali areas is still lacking[8-10]. By reviewing the formation mechanism and the carbon storage path of its inorganic carbon, the purpose of this paper is to provide the theoretical guidance and important reference for groundwater Carbon sequestration in arid saline-alkali areas.

2. Carbon sequestration mechanism

2.1. Atmosphere-soils–groundwater pathway
In arid saline-alkali area, in order to slow down the harm of saline and alkali to crops, the generally accepted practice is overirrigation to leach the salt away, the leaching of soil layer by water flow in the process of irrigation and salt washing, which makes the excess salt and alkali of soil and the main anion and cations enter the groundwater, the saline/alkalinegroundwater aquifers are formed[1-2]. Figure 1 illustrates the dissolved inorganic carbon (DIC) leaching and transport in an interior basin of an arid region[1]. It is widely believed that CO2 captured by saline-alkali soil will produce bicarbonate through irrigation of oasis farmland, salt-leaching and flood of desert area and fluctuation of groundwater, bringing into underground aquifer and become a carbon sink[1-2,5,11].

The CO2 migration process of atmosphere-soils-groundwater shows that the saline-alkali aquifer has the potential to serve as long-term CO2 sink, by means of aggravates the weathering dissolution of minerals and mineralization[12-13]. The carbon sequestration mechanism proposed by the researchers involves the following three geochemical processes: (1) dissolved capture: CO2 is directly dissolved and absorbed by water; (2) CO2-water-rock interaction: sequestration in saline aquifers and is involved in weathering dissolution of carbonate and silicate minerals; (3) mineral capture: carbon dioxide enters the aquifer and reacts with bivalent cations (Ca2+, Mg2+ etc.) or existing rock reactions to form new stable minerals.

2.2. Dissolved capture
CO2 is dissolved absorption by water as dissolved species in four existence forms of CO2, H2CO3, HCO3-, CO32-, that is the so-called DIC, which is widely distributed in groundwater and its transformation relationship is as follows:

\[
CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}
\]
The form of existence of DIC depends on the range of changes in pH in the water, and the reaction moves to the right when pH is high; at the pH value of 7–9, most of the carbon in the groundwater exists in the form of HCO$_3^-$; when pH is higher, DIC in solution is dominated by CO$_3^{2-}$ ion[14-15].

2.3. CO$_2$-water-rock interaction
Once CO$_2$ dissolves in geosphere water, it forms a weakly acidic solution and triggers a series of geochemical reactions that may eventually capture the CO$_2$ as dissolved species (such as HCO$_3^-$) [16]. CO$_2$-water-rock interaction generally include weathering dissolution of silicate and carbonate minerals (Figure 2). Dissolution of silicate minerals can consume CO$_2$ and release HCO$_3^-$ into solution, if the pH is high enough, can lead to the reprecipitation of carbonate phases, trapping the CO$_2$ in secondary minerals[17-19].

DIC is derived from weathering dissolution of silicate minerals (unidirectional reaction):

\[
2\text{CO}_2 + 3\text{H}_2\text{O} + \text{CaSiO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{H}_4\text{SiO}_4
\]  
(2)

DIC is derived from weathering dissolution of carbonate minerals (equilibrium reaction):

\[
\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + 2\text{HCO}_3^- 
\]  
(3)

It can be seen that half of the HCO$_3^-$ by carbonate dissolution and the entire HCO$_3^-$ by the silicate weathering are from the atmosphere or the soil CO$_2$ (the soil CO$_2$ is also primarily the cause of the atmosphere). The reaction of CO$_2$ and carbonate minerals dissolved in water is fast (days), but the weathering of the silicate minerals is quite slow (hundreds to thousands of thousands of years)[20]. Therefore, whether CO$_2$ is directly dissolved in water or involved in weathering dissolution of carbonate and silicate minerals, groundwater can indeed retain a large amount of CO$_2$ in the form of HCO$_3^-$.

![Figure 2. Carbon sequestration pathways by CO$_2$-water-rock interaction.](image)

2.4. Mineral capture
Mineral capture is also called Geochemical trapping (i.e., mineralization) is considered to be the most efficient way for long-term CO$_2$ storage[21-23]. Although the atmosphere CO$_2$ has long been considered to be relatively stable in chemical properties and not directly involved in the chemical process of diagenetic process, rocks surface have high porosity and can capture part of CO$_2$[23-24]. The basic idea of mineral capture is to mimic a naturally occurring process called weathering, where carbon dioxide enters the aquifer and reacts with bivalent cations (Ca$^{2+}$, Mg$^{2+}$ etc.) or existing rock to form new environmentally benign and stable calcium/magnesium carbonates minerals[20,25]. The common view is that the reaction process takes hundreds of years, however, recent Jihui Jia et al. (2019) have demonstrated that it only took 2 years to convert CO$_2$ to carbonates in reactive basaltic
reservoirs[26].

CO₂ mineralization involves the carbonation of natural silicate minerals that contain alkaline-earth oxides like magnesium oxide (MgO) and calcium oxide (CaO). The captured CO₂ is carbonized into environmentally stable solid carbonates, which can be described by the following chemistry[21-22]:

\[
\begin{align*}
\text{CaO} (s) + \text{CO}_2 (g) & \rightarrow \text{CaCO}_3 (s) \\
\text{MgO} (s) + \text{CO}_2 (g) & \rightarrow \text{MgCO}_3 (s) \\
\text{Mg}_2\text{Si}_2\text{O}_4(s) + 2\text{CO}_2 (g) & \rightarrow 2\text{MgCO}_3 (s) + \text{SiO}_2 (s) \\
\text{CaSiO}_3 (s) + \text{CO}_2 (g) & \rightarrow \text{CaCO}_3 (s) + \text{SiO}_2 (s)
\end{align*}
\]

3. Conclusion

In summary, for the carbon sequestration of groundwater in arid saline-alkali area, it is considered that atmosphere CO₂ is absorbed by saline-alkali soil and dissolved in recharge water (irrigation and salt washing, etc.) and transported down into the deep groundwater system through the soil belt. It will be involved in the geochemical interaction between rocks and water, and stored in saline-alkali groundwater aquifers in the form of DIC, or be captured by minerals to form new stable minerals. Arid saline-alkali area in the world is large, and the saline/alkaline groundwater aquifer is widely distributed. Compared with other carbon pools, the carbon sequestration can not be ignored. It is an important carbon sink produced by the global water cycle and a part of carbon fluxes in arid and semi-arid ecosystems. The long-term DIC sequestration in saline/alkaline aquifers is worthy of further study.

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