



## Feasibility study of net CO<sub>2</sub> sequestration using seawater desalination brine with profitable polyproduction of commodities

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### Abstract

To limit mean global temperature rise to 2 °C (2DS) in accordance with the 2015 Paris Agreement, integrated assessment models indicate that a greenhouse gas neutral society is necessary in the second half of the century, with concomitant realization of negative emissions at the gigatonne scale. Research into CO<sub>2</sub> capture and storage (CCS) methods has been relatively diverse, exploring capture from fossil fuel-fired power plants, cement manufacture, iron and steelmaking, bio-energy with carbon capture and storage (BECCS), direct air capture (DAC). On the other hand, the sequestration method of CO<sub>2</sub> has been largely limited to underground injection, CO<sub>2</sub> utilization (CCU), and to a lesser extent, the enhanced weathering of Ca/Mg-bearing minerals (EW). The focus on injection and CCU is primarily due to the unpriced/underpriced externality of carbon disposal in the global markets. The current market then implicitly requires CO<sub>2</sub> sequestration to be profitable via the generation of products (e.g., enhanced oil recovery (EOR), CCU). Unfortunately, EOR is forecast to provide at most only 4-8% of the CO<sub>2</sub> sequestration required for 2DS. Additionally, the impact from CCU-derived products (e.g., fuel, plastics) is negligible due to the short half-life of carbon stored in these compounds. BECCS offers a potential method to offset sequestration costs, but may be hindered by competition over land use, water use, and much lower energy production costs from renewables. Thus, the physical constraints of the Earth system combined with the financial constraints of current global markets indicates that the CO<sub>2</sub> sequestration options beyond injection, EOR, and CCU may be necessary.

The main alternative to CO<sub>2</sub> injection has been EW, which has the advantage of providing failsafe, permanent sequestration. Despite two decades of research focus, EW has failed to gain strong acceptance due primarily to the need for extensive grinding, pretreatment via chemical or thermal 'activation' of the source rock, and pH-controlled reactions. The need for such process enhancements derives from the slow kinetics of silicate-rock dissolution and the formation of a passivating layer of silicates and carbonates as CO<sub>2</sub> mineralization reactions proceed. Unfortunately, the CO<sub>2</sub> emissions associated with these enhancements can nullify or exceed the CO<sub>2</sub> mineralization achieved. To circumvent the issues of EW, we examine the feasibility of using desalination brine as a feedstock of (Mg,Ca) for CO<sub>2</sub> mineralization.

Though the CO<sub>2</sub> mineralization potential of the ocean is 6-7 orders of magnitude more than that required by 2DS, the low concentration of (Mg,Ca) and the coexistence of (Na,K) complicates their utilization. Recovery of such a low concentration resource is inherently difficult and prone to the utilization of substantial energy with concomitant emission of CO<sub>2</sub>. Currently, efficient concentration of seawater is achieved as a consequence of fresh water production via desalination, resulting in a brine that is 2-3 times concentrated over seawater. Further concentration of brines to

recover (Mg,Ca) is typically accomplished using pH-based precipitation. However, for the purpose of CO<sub>2</sub> sequestration, utilization of chemicals would induce the same net CO<sub>2</sub> emissions as has occurred in EW. Likewise, further concentration of brines via evaporation produces precipitates wherein (Mg,Ca) and (Na,K) are mixed, making them unsuitable for CO<sub>2</sub> mineralization. It is clear then that a method that changes the chemical composition of brine while regenerating additives is necessary.

We propose a reaction pathway for seawater desalination brines that separates (Mg, Ca) species from (Na, K)-species without the addition of consumable additives. The reaction scheme begins with solar heated concentration of seawater desalination brine to ~10 times seawater concentration. By controlling the temperature and pressure ~87% of the Ca content is precipitated as high purity Ca<sub>2</sub>SO<sub>4</sub>\*2H<sub>2</sub>O (gypsum). Following removal of precipitated gypsum, further evaporative precipitation is applied to remove 97% of the initial water content of seawater. Temperature and pressure control is again employed to precipitate 95% of the remaining Ca as CaSO<sub>4</sub>\*2H<sub>2</sub>O and 87% of the Na content as NaCl and Na<sub>2</sub>SO<sub>4</sub>. To produce a high purity Mg stream for use in CO<sub>2</sub> mineralization, the remaining non-Mg cations are precipitated via addition of HCl. Sparging with HCl induces precipitation by reducing the dielectric constant and increasing the common ion effect. Mg ions remain in solution due to their strong double-hydration shell. After precipitate removal, nearly anhydrous HCl is recovered from the remaining brine by addition of low hydration MgCl<sub>2</sub> along with vacuum heating; water preferentially binds with Mg<sup>2+</sup> ions over protons due to the small ionic diameter and divalent charge of Mg. The generated nearly anhydrous HCl is recirculated to the next brine batch. Roughly 22% of the resultant high purity MgCl<sub>2</sub> slurry is diverted to CO<sub>2</sub> mineralization, while the remaining portion is dehydrated via vacuum drying prior to recirculation for HCl distillation.

To ascertain the net energy and CO<sub>2</sub> footprint of the process, we modeled the system using Aspen Plus<sup>®</sup>, supported by data from lab-scale testing of each of the subsystems. The produced Mg-carbonates are saleable as construction aggregate. Current, global seawater desalination brine capacity could generate ~0.30 Gtonne,MgCO<sub>3</sub>/y (~12% of the aggregate market) with a value of ~\$2.84B/year. Globally, ~0.10 Gtonne,CaSO<sub>4</sub>\*2H<sub>2</sub>O/y could currently be produced, offsetting declining gypsum production from coal fired power plants, and generating a value of ~\$0.93B/year. Roughly 0.22 Gtonne/y of NaCl of sufficient purity for industrial and de-icing use could be generated, providing ~\$1.77B/year in revenue. Most critically, the process would yield an additional ~30.5 Gtonne,H<sub>2</sub>O/y with a value of \$26-46B/y, dependent on location. The net result is a profit of \$201-330/tonneCO<sub>2</sub>,sequestered. Due to increasing strains on fresh water supply from population growth and climate change, the global seawater desalination capacity is projected to increase 2.9-8.6 times current levels by 2050; the equivalent negative emissions potential of brine-based CO<sub>2</sub> mineralization would be 4.5% to 16% of the ~10 GtonneCO<sub>2</sub>/y sequestration required to meet 2DS. In this paper we demonstrate the process using seawater desalination brines, though application to basinal and industrial brines is straightforward, increasing the potential for reducing CO<sub>2</sub> emissions across a range of industries.