

## Opportunities for Low-Cost CO<sub>2</sub> Mitigation in Electricity, Oil, and Cement Production

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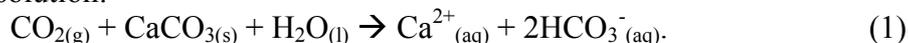
### Abstract

Several low-cost opportunities exist for scrubbing CO<sub>2</sub> from waste gas streams, utilizing spontaneous chemical reactions in the presence of water and inexpensive or waste alkaline compounds. These reactions convert CO<sub>2</sub> to bicarbonate or carbonate in dissolved or solid form, thus providing CO<sub>2</sub> capture and low-risk CO<sub>2</sub> storage underground, in the ocean, or in some cases on land. Useful by-products and co-benefits can also be generated by these processes. In certain settings this approach will be significantly less energy intensive, less costly, and less risky than "conventional" molecular CO<sub>2</sub> capture and geologic storage.

**Keywords:** CO<sub>2</sub>, bicarbonate, carbonate, limestone, water

### Introduction

Our research seeks to exploit the thermodynamically favored chemical reactivity of CO<sub>2</sub> to inexpensively capture this gas and convert it into storable or useable forms. For example, excess CO<sub>2</sub> can be reacted with water and solid mineral carbonates (e.g., limestone) to spontaneously form bicarbonates in solution:



The resulting bicarbonate-rich effluent can be disposed of in the ocean or in underground aquifers. This carbonate dissolution approach effectively sequesters the CO<sub>2</sub> in a safe, ionic state, avoiding the expense and risk of CO<sub>2</sub> capture, purification, and storage in molecular form.

Because the global abundance of water (i.e., seawater) and carbonate is orders of magnitude larger than the global reservoir of fossil fuels [1], all anthropogenic emissions of CO<sub>2</sub> could in theory be mitigated by reaction 1. Indeed, over geologic time scales significant, natural increases in atmospheric CO<sub>2</sub> have been moderated and consumed via carbonate weathering, and given enough time the same process will eventually absorb the majority of anthropogenic CO<sub>2</sub> as well [2,3]. But if we wait for Nature to perform this task, the earth in the meantime would be subjected to much higher atmospheric CO<sub>2</sub> than at present, and for many thousands of years. Thus it is worth considering proactively speeding up this carbonate weathering and CO<sub>2</sub> uptake process.

It has been previously shown that industrial-scale accelerated weathering of limestone, AWL, can effectively convert a significant fraction of US CO<sub>2</sub> emissions to long-term storage as bicarbonate in the ocean [4-8]. Being analogous to the successful, wide-spread use of wet limestone to desulfurize flue gas [9], AWL reactors could be retrofitted to existing power plants at a cost possibly as low as \$3-\$4/tonne CO<sub>2</sub> mitigated [5]. Such low costs would especially pertain to coastal power plants where an average of 3x10<sup>4</sup> tonnes of seawater per GWh<sub>e</sub> are already pumped through for cooling [10], and where the majority of coastline (at least in the US) is within 400 km of limestone sources [11]. In particular the southern and eastern US seaboard have the highest density of coastal US power plants and coastal electricity-related CO<sub>2</sub> production. More than 20 GW of power (≈ 100 million tonnes CO<sub>2</sub> emitted/yr) is generated by coastal power plants in Florida alone [7], a state that is also almost entirely underlain by carbonate deposits [12].

A CO<sub>2</sub> capture and sequestration cost of \$3-\$4/tonne CO<sub>2</sub> mitigated by this method would significantly out-compete most other current or proposed abiotic technologies and is near the US DOE target of \$2.73/tonne CO<sub>2</sub> mitigated [13]. The number of ideal sites and hence the volume of CO<sub>2</sub> that could be treated at this very attractive cost would, however, be small. Nevertheless, it has been estimated that 12% of CO<sub>2</sub> emission from US power production could be mitigated by the AWL method at <\$30/tonne CO<sub>2</sub> avoided [4,5,7], still below current cost estimates for the capture and geologic storage (in molecular form) of CO<sub>2</sub> emitted from conventional power plants [e.g., 14].

In addition to low-cost CO<sub>2</sub> mitigation, disposal of the resulting bicarbonate-enriched water into the ocean could benefit marine life. The acidity of seawater is currently increasing and carbonate alkalinity decreasing because of the ongoing passive, air-to-sea diffusion of excess anthropogenic CO<sub>2</sub> into the ocean [15,16]. Projecting business-as-usual CO<sub>2</sub> emission rates through this century, significant chemical alteration of the ocean is expected and will likely have dire consequences for shell-forming marine organisms that occupy essential niches in the marine ecosystem [15,16]. The addition of AWL effluent to the ocean could be used to counteract this loss of biological calcification, as demonstrated by the enhancement of marine shell production with experimental amendments of bicarbonate [17,18].

However, further research is required to better understand the costs, benefits, and impacts of this approach. For example, unless the waste gas steam being treated is relatively free of contaminants (e.g., from natural gas combustion), negative downstream environmental impacts by these dissolved constituents could ensue. The rate at which CO<sub>2</sub> can be removed from a waste gas stream will be dictated by the gas's contact surface area and residence time with water and limestone [4-7], and optimum gas contactor designs need to be found. We point out, however, that in some countries flue gas scrubbing with flow-through seawater is already employed for SO<sub>2</sub> removal [19,20], and lessons learned from this technology could readily translate to AWL applications. The following describes further opportunities for similar CO<sub>2</sub> mitigation approaches and benefits as applied to the oil and cement industries.

### **Capture and Storage Using Water Co-Produced With Oil**

On average 10 barrels of water are brought to the surface with each barrel of oil produced, and the majority of this water is simply pumped back into the reservoir. Our preliminary analysis [21] suggests that most of this water is significantly undersaturated in CO<sub>2</sub> relative to industrial waste gas streams that are typically 10% to 20% CO<sub>2</sub>. Furthermore, such waters can contain significant carbonate ion concentrations, meaning they have an enhanced capacity to react with excess CO<sub>2</sub> to form dissolved bicarbonates (e.g. reaction 1).

Using schemes such as that depicted in Figure 1, we roughly calculate that the average dissolved inorganic carbon content of produced water can be increased by some 170% through simple equilibration with a 15% CO<sub>2</sub> waste gas stream [21]. Further dissolution of waste CO<sub>2</sub> is possible via reaction 1 if additional carbonate (e.g., waste precipitate or limestone, Fig. 1) were added. The water can thus be significantly carbon-enriched prior to its routine re-injection underground. The overall approach allows simple, low-cost CO<sub>2</sub> capture combined with safe geologic storage of waste carbon that is mostly in dissolved, ionic forms. While the US capacity of this CO<sub>2</sub> mitigation approach is modest (perhaps 2x10<sup>6</sup> tonnes/yr) and is best suited to treat CO<sub>2</sub> waste streams in the immediate vicinity of the water production, the cost of such CO<sub>2</sub> mitigation could be extremely low, perhaps <\$1/tonne CO<sub>2</sub>.

Co-benefits of CO<sub>2</sub> addition to produced water would be the reduction (via lowered pH) of internal pipeline scale formation, a common and expensive problem in the industry. Also, CO<sub>2</sub> addition could enhance the oil-water separation process, may reduce downstream microbial fouling, and might enhance oil recovery. Further work is needed to better evaluate the cost/benefit and potential market of this CO<sub>2</sub> mitigation approach.

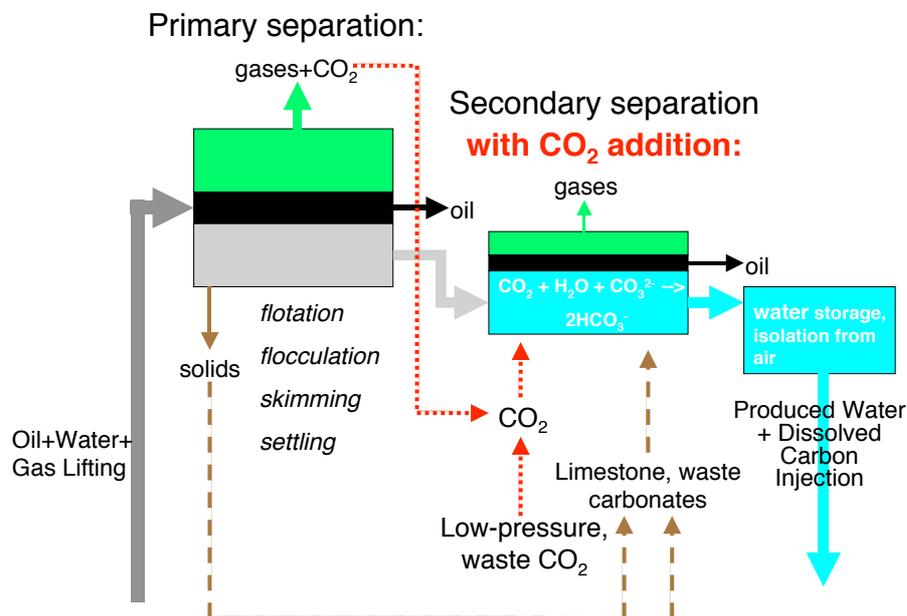


Figure 1. General scheme of water degassing, separation, and re-injection typically employed in oil production. By introducing CO<sub>2</sub> to this water prior to re-injection, low-cost CO<sub>2</sub> capture and sequestration can be effected. If desired, CO<sub>2</sub> uptake can be enhanced (via reaction 1) with the addition of alkalinity, such as limestone or the carbonate solids initially precipitated from the produced water. (From Rau et al. [21]).

## Application to CO<sub>2</sub> Mitigation in the Cement Industry

The manufacture of cement is a very carbon-intensive process that generates globally some 1.4 Gt CO<sub>2</sub>/year [22]. This CO<sub>2</sub> is largely produced in the calcination process wherein limestone is decarbonised at high temperature to produce lime, CaO. The resulting waste gas stream can contain >30% CO<sub>2</sub>. In addition, waste solids (cement kiln dust, or CKD) are generated, composed of a complex, highly alkaline mixture of Ca, Na, Mg, and K salts, silicates, oxides, and hydroxides. Many cement plants have a significant kiln dust management and storage problem with associated environmental issues.

One potential approach to the mitigation of both CO<sub>2</sub> and CKD from cement production would be to employ chemistry akin to AWL. An example would be to dissolve in water the soluble components of the alkaline kiln dust, in particular the metal oxides (e.g., CaO), to form hydroxides such as Ca(OH)<sub>2</sub>. Equilibration of the CO<sub>2</sub> waste gas stream with this solution would form dissolved metal carbonates and bicarbonates and would significantly lower solution pH, e.g.:  $2\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ . Subsequent exposure of the solution to low-CO<sub>2</sub> air would cause partial CO<sub>2</sub> degassing and loss from the solution, elevation of pH, and resulting CaCO<sub>3</sub> saturation and precipitation. The process could be controlled to allow the much more soluble sodium and potassium carbonates formed to remain in solution. Decanting or draining the solution would leave behind a CaCO<sub>3</sub>-enriched precipitate that could be harvested as feed for further cement production, or that could be stored above ground as a CO<sub>2</sub> sequestrant. Alternatively, because cement production already requires large volumes of mineral carbonate, additional limestone, especially waste fines, could be used to capture, transform, and sequester waste CO<sub>2</sub> in solution via reaction 1, followed by ocean or aquifer effluent storage.

## **Conclusions**

The magnitude and urgency of the global CO<sub>2</sub> problem coupled with the unlikely existence of a single, “magic bullet” solution requires that we broadly, aggressively, and objectively evaluate all CO<sub>2</sub> mitigation options. The preceding provides examples of how in certain settings the chemical reactivity of CO<sub>2</sub> can be used to allow inexpensive and safe CO<sub>2</sub> capture and storage with possible additional co-benefits. However, further research is clearly needed to better evaluate the costs, benefits, and impacts of these CO<sub>2</sub> mitigation approaches. The fact that wet limestone scrubbing is already a widely used, mature technology for acid gas removal suggests that similar industrial-scale chemistry could be applied to point-source CO<sub>2</sub> mitigation.

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