



# An Inexpensive, Safe CO<sub>2</sub> Capture and Storage Option Using Groundwater Co-Produced with Oil



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## SUMMARY:

Roughly 3x10<sup>9</sup> tonnes of water are annually brought to the surface during US oil production. After oil separation and other treatment, the majority of this water is then reinjected into the subsurface to maintain reservoir pressure and/or to avoid disposal and contamination in surface waters. Using chemical analysis of 500 produced water samples from W. Texas (USGS, 2002) we estimate that on average the inorganic carbon content of such water could be increased by about 170% when equilibrated with a 0.15-atm CO<sub>2</sub> waste gas stream. An additional 40% net increase in mean waste CO<sub>2</sub> uptake could be achieved by equilibration with a carbonate mineral such as limestone. Thus, without any costly pressurization or exotic chemistry, equilibration of produced water with waste CO<sub>2</sub> streams could conservatively capture and sequester some 2x10<sup>8</sup> tonnes of CO<sub>2</sub>/yr at an estimated cost of <\$1/tonne CO<sub>2</sub>.

Further potential benefits of produced water/waste CO<sub>2</sub> equilibration include:

- ▶ Enhanced oil/water separation via CO<sub>2</sub> bubbling/scavenging and lowered pH.
  - ▶ Reduction or elimination of scaling and particle formation and hence reduction or elimination of the need for anti-scaling chemicals, due to CO<sub>2</sub>-lowered pH.
  - ▶ Reduction or elimination of acid-intolerant microbes and therefore reduction or elimination of the need for anti-microbial treatments, due to the biocidal effects of CO<sub>2</sub>.
- Further chemical analysis, modeling, and experimentation are needed to fully evaluate the costs, benefits, and market niche of this CO<sub>2</sub> mitigation approach.

See panels at right for details

## PRODUCED WATER GENERATION AND HANDLING:

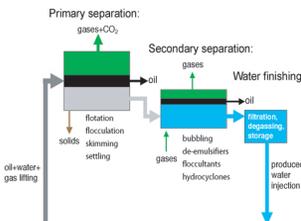
On average 10 barrels of water are generated per barrel of oil produced, and about 65% of this water is reinjected into the subsurface (USGS, 2002). Past the well head the oil, water, and gases are separated in one or more separators that employ gravity, gas bubbling, flocculation, centrifugal force, and/or other means (Fig. 1). Further chemical treatment is often necessary to prepare water for reinjection.

The preceding actions lead to a significant reduction in the water's CO<sub>2</sub> and carbonate ion content because of:

- 1) equilibration with CO<sub>2</sub>-depleted air or purge gas, and
- 2) carbonate precipitation (e.g., scale formation) due to the preceding CO<sub>2</sub> loss and subsequent pH elevation.

By modeling the degassing of in situ formation waters (Palandri and Reed, 2002), we estimate that some 10<sup>8</sup> tonnes CO<sub>2</sub>/yr are potentially lost to the atmosphere via mechanism 1 above. What then is this water's CO<sub>2</sub> uptake potential prior to reinjection? See panel on right →

Figure 1. General scheme of current produced water treatment:



## PRODUCED WATER CHEMISTRY AND CO<sub>2</sub> UPTAKE POTENTIAL:

Summary of produced water carbon chemistry and CO<sub>2</sub> uptake potential:

	pH	T, deg. C	pCO <sub>2</sub> , atm	Total dissolved inorganic carbon, mM	waste CO <sub>2</sub> consumed, mM
mean of 500 W. Texas produced waters (USGS data):	6.93	25°	0.0193*	6.6	0
as above and equilibrated with waste gas @ pCO <sub>2</sub> = 0.15 atm	6.41*	25°	0.150*	17.8*	11.2*
as above and equilibrated with excess limestone	6.64*	25°	0.150*	22.8*	13.7*

■ Averaging the chemistry profiles of 500 W. Texas produced waters (USGS, 2002) we found this water to be on average 170% undersaturated in CO<sub>2</sub> relative to a hypothetical 0.15 atm waste CO<sub>2</sub> stream.

■ Equilibrating this gas and the water (in a geochemical model) increased the water's total dissolved inorganic carbon load from 6.6 mM to 17.8 mM. Further equilibrating this water with limestone added an additional 2.5 mM of carbon from CO<sub>2</sub>. In all cases the predominant dissolved carbon form was ultimately bicarbonate, HCO<sub>3</sub><sup>-</sup>.

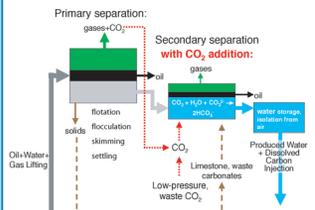
■ Extrapolating this uptake, we conservatively estimate that the US potential for CO<sub>2</sub> capture and storage by this method is 2x10<sup>8</sup> tonnes CO<sub>2</sub>/yr.

■ These are probably underestimates of the CO<sub>2</sub> uptake potential because the water chemistries in the USGS data base are not representative of fully degassed waters prior to injection (E.g., Palandri and Reed, 2002; Kharaka and Hanor, 2005). Indeed, our calculate mean pCO<sub>2</sub> for the initial water is 0.0193 atm (Table above), or some 50 times higher than atmospheric pCO<sub>2</sub>.

## PROPOSED CO<sub>2</sub> MITIGATION SCHEMES USING PRODUCED WATER:

We envision capturing and sequestering waste CO<sub>2</sub> by contacting such waste streams with produced water at some point prior to water reinjection. Local CO<sub>2</sub> sources would be the cheapest to mitigate and include: 1) CO<sub>2</sub> stripped from produced water in the course of oil/water/gas separation, 2) CO<sub>2</sub> generated in flaring of volatile hydrocarbons, 3) CO<sub>2</sub> produced in local internal combustion engines.

Figure 2. Possible scheme for CO<sub>2</sub> addition to produced Water.



Waste CO<sub>2</sub> sources external to the well such as power plants, cement plants, etc. could also be transported for mitigation with produced water as dictated by cost/benefit.

Since produced water is already commonly subjected to gas stripping/purging (Fig. 1), we suggest including the waste CO<sub>2</sub> in the purge gas to facilitate CO<sub>2</sub> and bicarbonate charging of the water prior to injection (e.g., Fig. 2). Further CO<sub>2</sub> uptake could be chemically achieved by the addition of solid carbonate (e.g. waste precipitate from upstream water degassing or externally supplied limestone).

Engineering an optimised system as well as evaluating potential CO<sub>2</sub> mitigation markets and capacity require further research including more thorough chemical characterization of waters, experimentation, and modeling.

## COSTS AND BENEFITS:

### Costs:

Considering that gas ventilation is already common practice in treating produced water, including CO<sub>2</sub> in the purge gas stream could potentially be very easily and inexpensively implemented. Based on cost estimates for seawater-based systems (Rau and Caldeira, 1999; Sarv and Downs, 2002), the total cost may be <\$1/tonne CO<sub>2</sub> mitigated (i.e. below DOE point-source targets and substantially below conventional CO<sub>2</sub> capture and geologic storage). However, this cost will rise as the following are encountered:

- Transportation and treatment of non-local CO<sub>2</sub> waste streams.
- Increased metal corrosion via aqueous CO<sub>2</sub> oxidation (requiring plastic coatings).
- Increased pre-injection water compression costs due to presence of CO<sub>2</sub>.

### Benefits:

- CO<sub>2</sub> is chemically captured and geologically sequestered without the need for gas separation, purification, and pressurization.
- The CO<sub>2</sub> is largely converted to HCO<sub>3</sub><sup>-</sup> (= chemical trapping prior to injection) due to reactions with water, carbonate ions, and metal cations. This means reduced leakage risk and greater safety for the stored CO<sub>2</sub>.
- Easier oil removal/flocculation due to CO<sub>2</sub> bubbling and lowered pH.
- Reduced scaling (carbonate and hydroxide precipitation) in water stream due to CO<sub>2</sub>-lowered pH.
- Reduction of acid-intolerant microbes due to CO<sub>2</sub> addition.

Further research is needed to better quantify cost/benefit.

## THE BOTTOM LINE:

Prior to injection underground, much of the 3x10<sup>9</sup> tonnes/yr of water co-produced with US oil presents an unexploited opportunity for very safe, inexpensive geochemical capture and sequestration of CO<sub>2</sub>, possibly at a cost <\$1/tonne CO<sub>2</sub> mitigated. Reduction in the need for anti-scaling, -microbial, and -emulsion chemicals in treating produced water could actually result in a net operational cost savings. The CO<sub>2</sub> sources amenable to such mitigation may be limited, but let's find out. Implementation of this technology could at least help mitigate the local CO<sub>2</sub> intensity associated with oil production. Further research, water chemistry analysis, experimentation, and modeling are needed.

**Comments? Criticism? Or care to partner with us?** – Contact: Greg Rau rau4@llnl.gov, 925-423-7990

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