# Some aspects of CO2 Sequestration in Carbonate

Abstracted from a Memorandum to file written May 28, 1996
L. M. Cathles

The calculations recorded below are abstracted from a Memorandum to my personal files written May 28, 1996. The calculation use kinetic parameters deduced from a steamflood as reported in Cathles et.al., 1990, A kinetic model of CO2 generation and mineral and isotopic alteration during steamflooding, SPE Reservoir Engineering, p. 524-530). The analysis envisions injection into a sand reservoir as illustrated below and asks what temperature, permeability, and chemistry the reservoir should have to allow CO2 to be removed as a carbonate phase. At the time the hope was to remove CO2 from mixed CO2-CH4 gas. The remainder of the discussion is verbatim from the original memo.
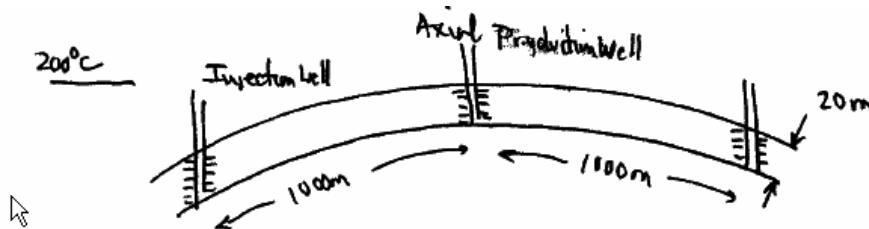
KINETICS OF THE CO2-ROCK REACTION

Constraints on the kinetics of CO2 precipitation come from models I have previously used to analyze the rate of CO2 generation during steam flooding (Cathles et.al., A kinetic model of CO2 generation and mineral and isotopic alteration during steamflooding, SPE Reservoir Engineering, Nov. 1990, p524-530). The model developed and calibrated against field tests treated the kinetics of CO2 generation and precipitation with the same equation, which is appropriate as they are essentially reversible forms of the same reactions. The generation kinetics were fairly well constrained; the precipitation reactions much less well constrained. The precipitation reactions in the model that fit the field results best were considered in that publication, for various reasons related both to true kinetics and also channeling, to occur at half the rate of the generating reactions.

Using the kinetics determined in the above-cited publication, **the rate of precipitation of CO2, j_c,** in moles/cm^3-sec is:

$$j_c = f\, k_o\, \rho\; e^{-E/RT}\, [c_{eq}(T) - C].$$

$$j_c = (0.5)\,(0.050)(1)(e^{-15,000/(2)(473.15)})(2.05) \qquad = 6.69 \times 10^{-9}\ \text{moles/cm}^3\text{-sec}$$
$$= 0.21\ \text{moles/cm3-yr.}$$

In this expression:

f	=	rate of precipitation compared with CO2 generation reactions = 0.5
k_o	=	kinetic pre-exponential factor = 0.050
ρ	=	density of water = 1.0
E	=	activation energy in cal/-mole = 15,000
R	=	gas constant in cal/°K-mole = 2
T	=	temperature in °K = 200 + 273.15 °K
C_{eq}	=	equilibr. concentr. of total dissolvd CO2 in moles CO2/g solution.
C	=	$P_{CO2}\, /\, K_{CO2} = X_{CO2}\, P_f\, /\, K_{CO2}$ = moles CO2/g solution.
X_{CO2}	=	mole fraction of CO2 in the gas
K_{CO2}	=	Henries Law constant for CO2 gas = 107 at 200°C

The values of all but two of the parameters were estimated in the CO2 steamflooding field trials. The values at 200°C are listed above. The equilibrium concentration of CO2 in aqueous solution, C_{eq} is know from geothermal system measurements. Formula are given in Cathles et.al. (1990, Loc. cit.). At 200°C, C_{eq} = 4.3 x 10^{-4} molal. The concentration of CO2 in solution in a situation where CO2-rich gas is in contact with water can be estimated from Henries law. At 200°C Henrie's law coefficient for CO2, K_{CO2}, is 107. Assuming a fluid pressure, P_f, of 220 bars, C = 220/107 = 2.05. Hence if X_{CO2} = 1, the steamflooding analysis suggests that the consumption rate of CO2 per cubic centimeter cubed of sandstone sediment is 0.21 moles/cm^3-yr, as indicated above.

The consumption of CO2 from a gas stream moving through a sediment can be written:

$$\rho_{gas}\varphi_{gas}\frac{DX_{CO2}}{Dt} = 0.21\ X_{CO2}\ ,$$

where ϕ_{gas} is the fraction of the pore space filled with gas which equals the total porosity ϕ times the gas saturation S_{gas}, the density of the gas in the pore space is ρ_{gas} in moles / cm^3, and X_{CO2} is the mole fraction of the gas that is CO2. Taking S_{gas} = 0.2, ϕ = 0.2, so that ϕ_{gas} = 0.04, and ρ_{gas} = (0.6 g/cc)(1/44 g/mole) = 1.36 x 10^{-2} moles/cc. The above equation may be solved for the change in X_{CO2} over:

$$X_{CO2} = X_{CO2}^0\ e^{\frac{-t}{\tau}}\ ,$$

where, for the values given above the **exponential reaction time** is:

$$\tau = \frac{\rho_{gas}\ \varphi_{gas} = 5.44\ x\ 10^{-4}moles/cm^3}{0.21\ moles.cm^3-yr} = 0.0025\ years = 1\ day.$$

A reaction time this short is encouraging. It means it should be possible to design a system to strip CO2 from a mixed gas, provided favorable geologic conditions can be found. In south east Asia it should be possible to find such conditions. For example, 90% of the CO2 in the input gas could be stripped if the gas had a residence time of 2 days in the sand lens. It should be emphasized that the kinetic data used are uncertain. However residence times substantially longer than a few days are probable in the geologic implementation (see below were a base case residence time of 36 days is estimated), and furthermore, the kinetics is strongly temperature sensitive and the rate of reaction can be doubled by finding a sand 10°C warmer. Thus favorable conditions are probable even if the kinetics are substantially slower than believed.

A BASE CASE COMMERCIAL OPERATION

The next questions concern the feasibility of a commercial operation. We consider the feasibility of a base case in which **10 billion standard cubic feet of gas is treated each year**. If the 10^{10} scf/year of gas is 50% CO2, about 4 billion moles of CO2 need to be reacted each year (= R_{CO2}). For a **design life, L, of 5 years** this is 20 billion moles of CO2 that must be precipitated. A greywacke sand has sufficient silicate cations to precipitate about 1200 moles of CO2 per m^3, but an arkosic sand would have enough silicate cations to precipitate only about 100 moles of CO2 per m^3 of sand. We will assume that a suitable greywacke sand can be located and take a titration capacity of 1000 moles CO2/m^3. With these numbers, the **volume of greywacke sand required** is of reasonable dimensions is required (1 km x 1 km x 20 m thick).

CO2 Titration Capacity =	T_{CO2}	= 1000 moles CO2 / m3
Total CO2 treated =	LR_{CO2}	= 4 x 10^9 moles / yr x 5 yrs = 20 x 10^9 moles

Volume of sand required, V $= LR_{CO2} / T_{CO2} = 2 \times 10^7$ m^3 = 20m x 1km x 1km.

One of the costs will be filing the sand lens reactor with gas. The cost will be **the time required to fill the sand**. For the parameters given above, and re-listed below, the time to fill the underground reactor is about 1.4 years:

Gas saturation, S_{gas}	=	0.2
Sand Porosity, ϕ	=	0.2
Reservoir volume, V	=	2×10^7 m^3
Gas Delivery Rate, Q	=	10^{10} scf/yr ~ 8×10^9 moles/yr
molar density, ρ_{gas}	=	13,600 moles / m^3
Fill time	=	V ρ_{gas} ϕ S_{gas} / Q = 1.36 years

The low gas saturation used in the above calculations controls the relatively short system priming time. The low gas saturation requires **that water and gas should be co-injected at least during the priming period**. The co-injection during this period should be in a ratio such that the gas will constitute about 20% of the total fluid volume at the bottom of the injection wells. During the priming period water produced from the axial well must be injected with the added gas at the four production wells.

The pressures required to inject and produce the required fluid volumes depend on the permeability of the sand lens and its thickness. A maximum estimate of the drawdown at the production well can be made assuming production from just that one well over the 5 year system life. The drawdown will of course be substantially reduced by injection from the surrounding four injection wells in the envisioned system. The governing equation from the standard reservoir engineering monograph by Mathews and Russel is:

$$p(r_w,t) = \frac{Q\mu}{4\pi kb}\left(\ln \frac{\kappa t}{r_w^2} + 0.809\right) \, ,$$

where

r_w	=	radius of the well bore =		10 cm
t	=	time in seconds	=	5 yrs x 3.15 x 10^7 sec/yr
Q	=	production rate	=	6.7 x 10^4 cc/sec
μ	=	fluid viscosity	=	0.005 poise
k	=	permeability	=	10^{-8} cm2 (1 darcy)
b	=	sand thickness	=	20 x 10^2 cm
κ	=	hydraulic diffusivity	=	$k/\mu\phi c$ ~ 2 x 10^5

The injection rate accommodates the 8 x 10^{10} moles of gas per year, which at 44 g per mole and 0.6 g/cc density has a volume of 2 x 10^{12} cc. The gas is injected with water in a volume ratio of 1 to 5, so if the fluid is recovered in the same proportion of gas to water, the total flow will be 12 x 10^{12} cc/yr or 6.7 x 10^4 cc/sec. With these numbers the drawdown at the production well is 1.33 bars (ln 3.23 x 10^{11} + 0.809) = 36 bars. **This is a very reasonable pressure drawdown but** it should be noticed that it depends very critically on the assumed 1 darcy permeability and the 20 m sand lens thickness.

The **residence time, $T_{residence}$** of the fluid in the envisioned system can be estimated from the ratio of the total fluid volume in the system and the balanced injection and production rates:

$$T_{residence} = \frac{V}{Q} = \frac{2\pi rb}{Q} = \frac{2\pi(1000 \times 10^5 cm)(20 \times 10^2 cm)}{12 \times 10^{12} cm^3/yr} = \frac{1.26 \times 10^{12}}{12 \times 10^{12}} = 0.1 \text{ yr} = 36 \text{ days}$$

This **residence time should give plenty of time for CO2 to be reacted** out of the gas if our estimates of reaction kinetics are close to being correct.

Finally buoyancy will help contain the gas and move it to the anticline axis if the permeability of the sand is in the 10 darcy range and the sand lens slope ~10%:

- The buoyancy-driven darcy flow rate for the gas phase, V_b, where μ=dynamic viscosity in poise, $\rho_{gas}= 0.6$, and ρ_f=density of water = 1.0, and k = 1 darcy, and S is the slope of the sand lens, is:

$$V_b = \frac{-k}{\mu}(\rho_{gas}-\rho_f)g = \frac{10^{-8}S}{.005}(0.4)(980) = 7.85 \times 10^{-5}S \text{ k[darcies] } g/cm^2\text{–sec}$$

- The mass flux of gas, V_{gas}, toward the axial production at a distance r = 1 km from the production well at a throughput Q of 2×10^{12} cc year is:

$$V_{gas} = \frac{Q}{2\pi rb} = \frac{(2 \times 10^{12} cm^3/yr)(1/3.15 \times 10^7 sec/yr)}{2\pi(10^5 cm)(20 \times 10^2 cm)} = 5.05 \times 10^{-5} cm/sec$$

- The two darcy flow rates will be close to equal if S~0.1 and k[darcies]=10. Buoyancy could help contain the gas if the sand permeability is high.

ECONOMIC CONSIDERATIONS

The **economics** of the stripping operation can be intuitively estimated from the following numbers:

Value of hc gas processed per year	= $(4 \times 10^9$ scf)($0.05/scf)	= $20 MM per yr.
Cost to fill reactor (10% interest, 1.4 years delay)		= $ 2.8 MM
Cost of 5 wells about 2 km deep		= $ 5 MM
Operating cost		= $ 0.5 MM/yr
Life of operation		= 5 years

These numbers are very rough (just guesses on my part) and highly uncertain, but it appears that the process could be economically feasible if the value added by CO2 removal is on the order of 20% of the value of the gas.

FURTHER REQUIRED DEVELOPMENTS

The above analysis suggests the following path for further research and development:

1. The economics of the stripping operation should be evaluated with more accurate numbers than I could supply above. A reservoir engineer should assess the validity of the 4% gas saturation I have assumed, the fact I have assumed the viscosity of high

pressure gas is similar to that of water, and provide better estimates of drilling and operating costs. If the operation appears feasible after this review, the following steps should then be taken:

2. The kinetics of CO2 precipitation as a function of temperature should be assessed by flow through hastler cell experiments at ~200°C in the laboratory. This should not be expensive and can be done quickly. If the kinetics are such that the operation continues to appear feasible, proceed:

3. The CO2 titration capacity of sand bodies in areas of interest should be determined both by calculating them from mineralogical analyses and by direct laboratory titration experiments.

4. A geologist should determine if a suitable sand unit can be found near a producing CO2-contaminated gas fields. The sand should be at depths where the fluid pressure is ~200 bars and the temperature ~200°C, and the sand should have darcy permeability and enough Ca, Fe, and Mg in clays or other silicate minerals to be an effective titrant for CO2.

5. If a suitable sand can be found, the economics of a pilot test of the concept outlined above with a follow-on stripping facility should be calculated.

6. If the pilot and subsequent stripping facility look economically feasible, a pilot test should be designed and carried out.

7. If the pilot test is successful, the plant should be made operational and the feasibility of replicating and/or licensing this kind of facility should be evaluated.

8. If replicating and licensing appear feasible the facility should be licensed as broadly as possible.

Written by L. M. Cathles on May 28, 1996.