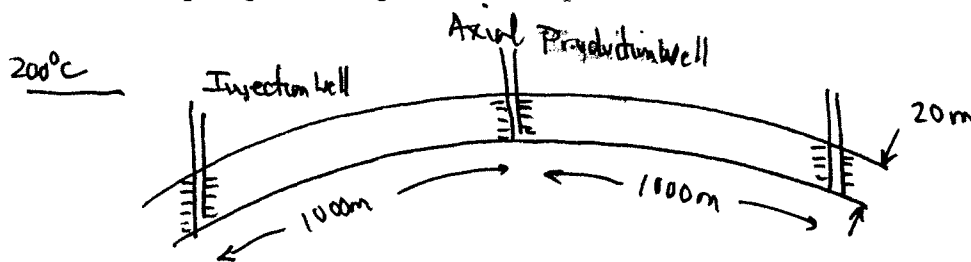


Invention Disclosure

This is to disclose that on May 18 during dinner conversations with Martin Schoell of Chevron Petroleum Technology Corp. in San Diego at the Marriott Hotel Bayside, I conceived of a novel idea to strip CO₂ from a CO₂-CH₄ gas mixture. I told Martin of the idea on the condition that he would respect my invention rights. Since then I have checked the feasibility using published data and a hand calculator and I believe the concept is technically sound. Whether it could be an economic process of CO₂ removal depends on economics and whether it can be implemented in a suitable natural setting. The purpose of this disclosure is to document the date of the conception of the invention and build secure ownership rights to it so that discussions can be opened with Chevron or another oil company to explore its further development and implementation.

The idea envisions that minerals in natural sandstones will strip CO₂ from a gas mixture in a few days at 200°C. The CO₂ would be precipitated as carbonate with cations such as calcium supplied by alumino-silicates in the sandstone. The reactions would be entirely natural and in fact the reactions will be the inverse of the reactions that generated the CO₂ in the first place. There would be no unnatural byproducts, and the carbonates formed would be stable and innocuous. No additives are required, although it might be that some would be beneficial. Thus in its pure form the envisioned process of CO₂ removal will be an ideal way to strip CO₂ from a gas stream. The CO₂ problem is severe in south east Asia where great quantities of CO₂ will be co-produced with natural gas and released to the atmosphere if this, or some other means of economically stripping the CO₂ from the gas stream, is not invented.

The simplest manifestation of the concept would be to inject the mixed (CO₂-CH₄) gas into a permeable sand layer from ~4 wells perhaps ~100 m from the crest of a small anticline as shown below. The stripped gas would be recovered from a single well at the anticline crest. The 5-spot pattern could also be applied to a flat or dipping layer and many other implementations are possible, but an anticlinal form of the sand would facilitate complete and efficient recovery of the gas because buoyant forces could, if the sand were permeable enough, cause the gas to collect at the crest of the anticline. The sand layer should be at depths great enough that the temperature in the sandstone is about 200°C.



The concept embodied in the invention disclosed here is that the calcium, iron and magnesium silicate minerals in the sandstone will remove the CO₂ from the methane (and higher hydrocarbon)-CO₂ gas mixture, leaving only the combustible hydrocarbons. We believe that this process occurs in nature. We seek to utilize this natural processes of CO₂ precipitation to preferentially remove CO₂ from the injected gas. The stripping operation will be designed so that the gas spends several days moving to the crest of the anticline. In this time, or a greater or lesser time as may be required by the site-specific kinetics of the CO₂ precipitation reactions, the CO₂ will be largely removed from the injected gas, with

the result that the economic value and environmental acceptability of the gas will be greatly improved.

The slow kinetics, large residence times, high gas pressures, and large volumes of gas that must be put through the system each day in a realistic operation suggests that natural sandstone reservoirs will be most economical way to implement the novel CO2 removal process disclosed here. However the disclosure should be considered to include any suitable implementation, whether utilizing natural sandstones or chemical engineering constructs whether in the form of a surface or subsurface plant or facility.

There are several critical technical aspects of this invention. Perhaps the most fundamental is the rate at which CO2 may be precipitated under field conditions. I disclose below preliminary calculations that suggest that CO2 will be removed with an exponential decay time of about 1 day at 200°C. The second critical issue is whether a typical sand lens contains enough of the critical minerals to strip the volumes of CO2 required. A third issue is the amount of gas that would be tied up in the sand lens. How much methane and CO2 would be required to prime the system. Other issues concern the flow rates through the system, the gas saturation of the system, etc. Preliminary answers to these questions are offered in this disclosure. The calculations show that the idea disclosed has technical merit. It could work, but there are many uncertainties that need to be resolved. Recommendations are made for removing these uncertainties.

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/cm³-sec is:

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

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

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 known from geothermal system measurements. Formulae are given in Cathles et al. (1990, Loc. cit.). At 200°C, $C_{eq} = 4.3 \times 10^{-4}$ molal. The concentration of CO₂ in solution in a situation where CO₂-rich gas is in contact with water can be estimated from Henry's law. At 200°C Henry's law coefficient for CO₂, K_{CO_2} , is 107. Assuming a fluid pressure, P_f , of 220 bars, $C = 220/107 = 2.05$. Hence if $X_{CO_2} = 1$, the steamflooding analysis suggests that the consumption rate of CO₂ per cubic centimeter cubed of sandstone sediment is 0.21 moles/cm³-yr, as indicated above.

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

$$\rho_{gas} \phi_{gas} \frac{DX_{CO_2}}{Dt} = 0.21 X_{CO_2}$$

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 / cm³, and X_{CO_2} is the mole fraction of the gas that is CO₂. Taking $S_{gas} = 0.2$, $\phi = 0.2$, so that $\phi_{gas} = 0.04$, and $\rho_{gas} = (0.6 \text{ g/cc})(1/44 \text{ g/mole}) = 1.36 \times 10^{-2}$ moles/cc. The above equation may be solved for the change in X_{CO_2} over:

$$X_{CO_2} = X_{CO_2}^0 e^{-\frac{t}{\tau}}$$

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

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

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 where 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 10¹⁰ scf/year of gas is 50% CO₂, about 4 billion moles of CO₂ need to be reacted each year ($= R_{CO_2}$). 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 m³, but an arkosic sand would have enough silicate cations to precipitate only about 100 moles of CO₂ per m³ of sand. We will assume that a suitable greywacke sand can be located and take a titration capacity of 1000 moles CO₂/m³. With these numbers, the **volume of greywacke sand required** is of reasonable dimensions is required (1 km x 1 km x 20 m thick).

$$\begin{aligned} \text{CO}_2 \text{ Titration Capacity} &= T_{CO_2} = 1000 \text{ moles CO}_2 / \text{m}^3 \\ \text{Total CO}_2 \text{ treated} &= LR_{CO_2} = 4 \times 10^9 \text{ moles / yr} \times 5 \text{ yrs} = 20 \times 10^9 \text{ moles} \end{aligned}$$

$$\text{Volume of sand required, } V = LR_{\text{CO}_2} / T_{\text{CO}_2} = 2 \times 10^7 \text{ m}^3 = 20\text{m} \times 1\text{km} \times 1\text{km}.$$

One of the costs will be filling 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	=	$2 \times 10^7 \text{ m}^3$
Gas Delivery Rate, Q	=	$10^{10} \text{ scf/yr} \sim 8 \times 10^9 \text{ moles/yr}$
molar density, ρ_{gas}	=	$13,600 \text{ moles} / \text{m}^3$
Fill time	=	$V \rho_{\text{gas}} \phi S_{\text{gas}} / Q = 1.36 \text{ years}$

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	= $5 \text{ yrs} \times 3.15 \times 10^7 \text{ sec/yr}$
Q	=	production rate	= $6.7 \times 10^4 \text{ cc/sec}$
μ	=	fluid viscosity	= 0.005 poise
k	=	permeability	= 10^{-8} cm^2 (1 darcy)
b	=	sand thickness	= $20 \times 10^2 \text{ cm}$
κ	=	hydraulic diffusivity	= $k/\mu\phi c \sim 2 \times 10^5$

The injection rate accommodates the 8×10^{10} moles of gas per year, which at 44 g per mole and 0.6 g/cc density has a volume of $2 \times 10^{12} \text{ cc}$. 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 $12 \times 10^{12} \text{ cc/yr}$ or $6.7 \times 10^4 \text{ cc/sec}$. With these numbers the drawdown at the production well is $1.33 \text{ bars} (\ln 3.23 \times 10^{11} + 0.809) = 36 \text{ bars}$. **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**, $T_{\text{residence}}$ 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:

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

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, $\rho_{\text{gas}} = 0.6$, and ρ_f =density of water = 1.0, and $k = 1$ darcy, and S is the slope of the sand lens, is:

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

- 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:

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

- The two darcy flow rates will be close to equal if $S \sim 0.1$ and $k[\text{darcies}] = 10$. 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	= $(4 \times 10^9 \text{ scf})(\$0.05/\text{scf})$	= \$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:

- 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.

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