Use of Gas Phase Tracers for Monitoring CO_2 Injection at the Frio Test Site

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K. Pruess
B. Freifeld
M. Kennedy
C. Oldenburg
T. J. Phelps
M. C. van Soest

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Use of Gas Phase Tracers for Monitoring CO_2 Injection at the Frio Test Site

Karsten Pruess[1], Barry Freifeld[1], Mack Kennedy[1], Curt Oldenburg[1], Tommy J. Phelps[2] and M.C. van Soest[1]

[1] Earth Sciences Division, Lawrence Berkeley National Laboratory
[2] Oak Ridge National Laboratory

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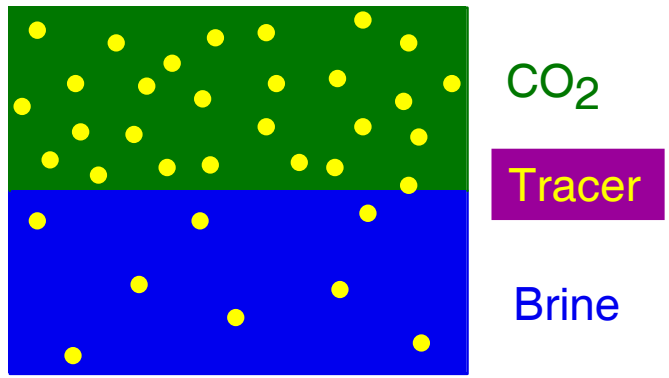
Outline

- Phase-partitioning tracers
- Issues for CO_2 injection into brine aquifers
- Tracer migration and analysis
- Test design
- Results
- Concluding Remarks

Phase-Partitioning Tracers (I)

Chemical species that are both water soluble and volatile



- non-condensible gases (O_2, CO_2, CH_4)
- noble gases
- SF_6; volatile organic chemicals (e.g., halogenated hydrocarbons)

Henry's law

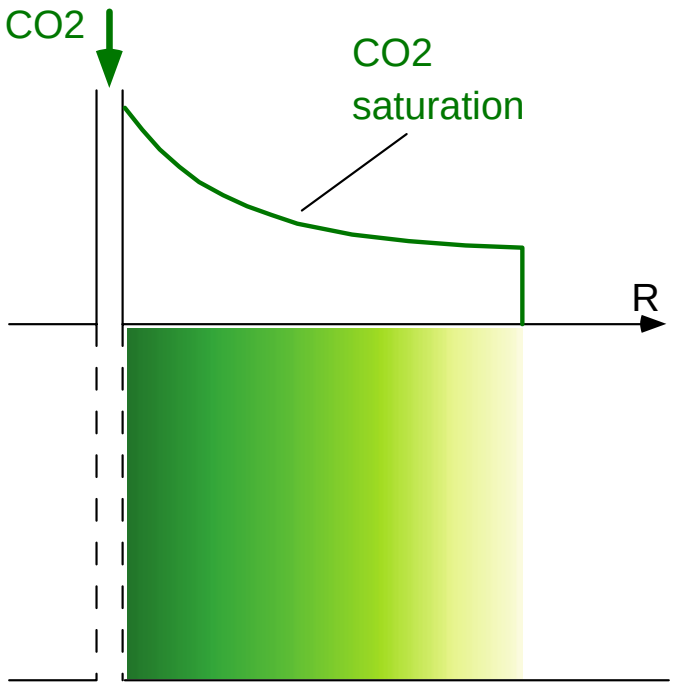
$$P_{gas}^{tracer} = K_h \, x_{aq}^{tracer}$$

- determine reservoir processes and conditions (phase saturations, boiling, fracture-matrix interaction)
- find fast preferential flow paths

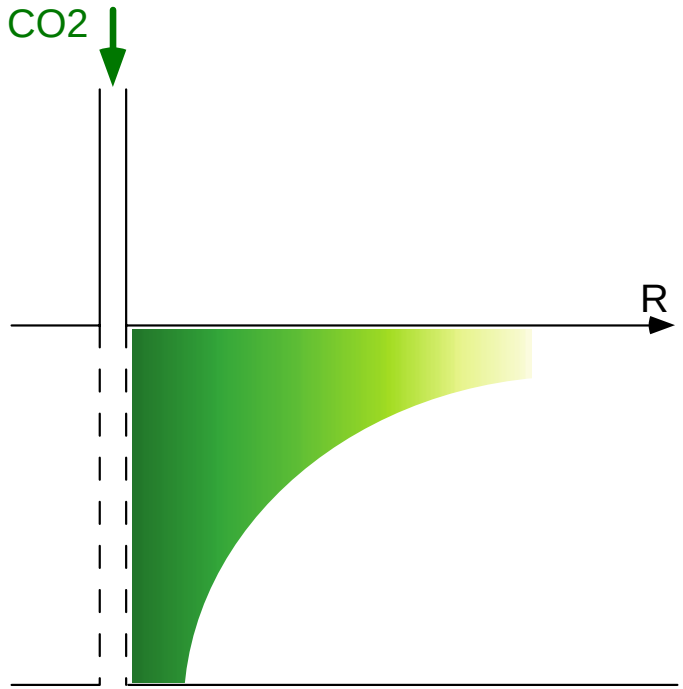
Phase-Partitioning Tracers (II)

- Typical application is for multiphase systems, with one mobile and one or more immobile fluid phases.
- Tracer migration is retarded (slowed) relative to an inert (insoluble) tracer by partitioning into immobile phases.
- The ratio of travel times is the retardation factor, $R = t_{PPT}/t_{inert}$.
- R is given by the (local) ratio of total tracer inventory to tracer inventory in the mobile phase.
- From known phase partitioning behavior (solubility, volatility), observations of tracer retardation can be used to infer the average volume fractions of different fluid phases along the flow path.
- Applications of phase-partitioning tracers have been made for different purposes, including:
    - determination of residual oil in petroleum reservoirs
    - estimation of non-aqueous phase liquid (NAPL) contamination
    - characterization of trapped gas in groundwater systems
    - determination of boiling processes in geothermal reservoirs

Displacement of Brine by CO_2 (I)

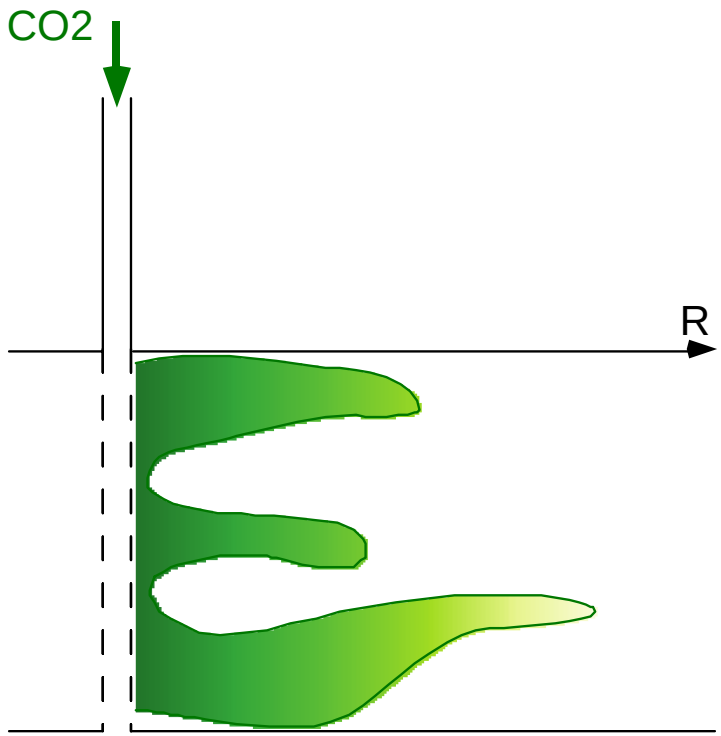


uniform displacement
(Buckley-Leverett)



gravity override

Displacement of Brine by CO_2 (II)



non-uniform sweep

- formation heterogeneity
- hydrodynamic instabilities

Issues in Displacement of Brine by CO_2

- how does CO_2 invade and occupy the pore space?
- where does the CO_2 go, and how much brine is left behind?
- geometry of the displacement process
- utilization of subsurface space
- available storage capacity

Gas Tracers

Tracer transport in single-phase gas conditions

$$\frac{\partial \phi C_g^t}{\partial t} = -\mathrm{div} C_g^t v_g + \mathrm{div} \phi \tau D_g^t \nabla C_g^t$$

with ϕ = porosity

C_g^t = tracer concentration in gas (partial density; kg/m^3)

v_g = gas velocity

τ = tortuosity

D_g^t = tracer diffusivity

Tracer transport in two-phase conditions with immobile liquid

$$\frac{\partial \phi \left[S_g C_g^t + S_a C_a^t \right]}{\partial t} = -\mathrm{div}\, C_g^t v_g + \mathrm{div}\, \phi \tau_g D_g^t \nabla C_g^t = \frac{\partial \phi R_t S_g C_g^t}{\partial t}$$

R_t is the retardation factor, given by

$$R_t = \frac{\left[S_g C_g^t + S_a C_a^t \right]}{S_g C_g^t} = 1 + \frac{S_a \zeta_t}{1 - S_a}$$

with $\zeta_t = C_a^t / C_g^t$ an aqueous-gas distribution coefficient (solubility)

Retardation Factor

From a known (observed) retardation factor, aqueous phase saturation can be calculated:

$$S_a = \frac{R_t - 1}{R_t - 1 + \zeta_t}$$

R_t is the ratio of tracer transit (or travel) time for a phase-partitioning tracer t to that for a hypothetical insoluble tracer i

$$R_t = t_t / t_i$$

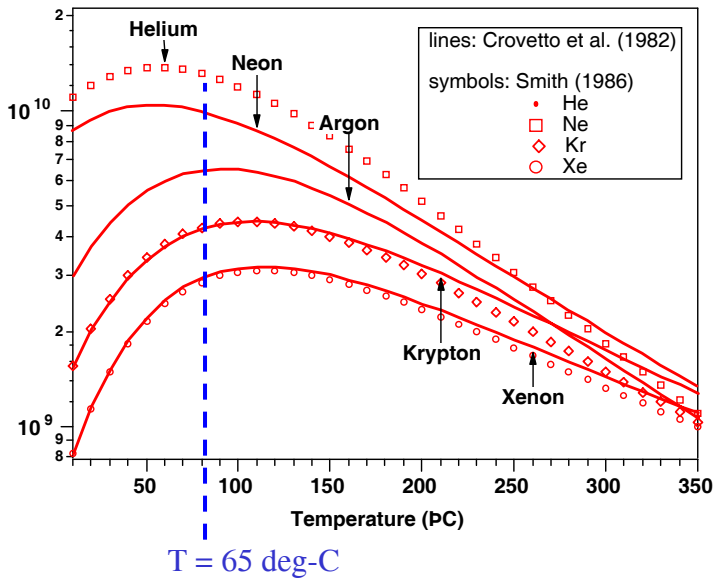
- all tracers are soluble to some extent, so t_i is not observable, and neither is R_t
- from two different phase-partitioning tracers t and u, obtain t_t and t_u
- then have two equations for the unknowns t_i and S_a
- eliminating t_i gives aqueous phase saturation as

$$S_a = \frac{1 - t_t/t_u}{1 - t_t/t_u + \zeta_u\, t_t/t_u - \zeta_t}$$

Advantages of Noble Gas Tracers

- no significant subsurface sinks or sources
- chemically inert, non-hazardous
- abundance can be measured with great precision

Henry's coefficient as function of temperature



Henry's law: $P_t = K_H \bullet x_t$

Isotope	Partial pressure in air, Pa	Dissolved mass fraction in water at T = 10 deg-C	Henry's coefficient, Pa	
			T = 10 deg-C	**T = 65 deg-C**
^{22}Ne	0.170	2.440e-11	8.510e9	**10.20e9**
^{36}Ar	3.184	2.134e-9	2.981e9	**6.141e9**
^{84}Kr	0.0658	1.990e-10	1.542e9	**3.860e9**
^{132}Xe	2.370e-3	2.142e-11	8.110e8	**2.634e9**

Data from Crovetto et al., 1982

Field Equipment for Gas Tracer Tests

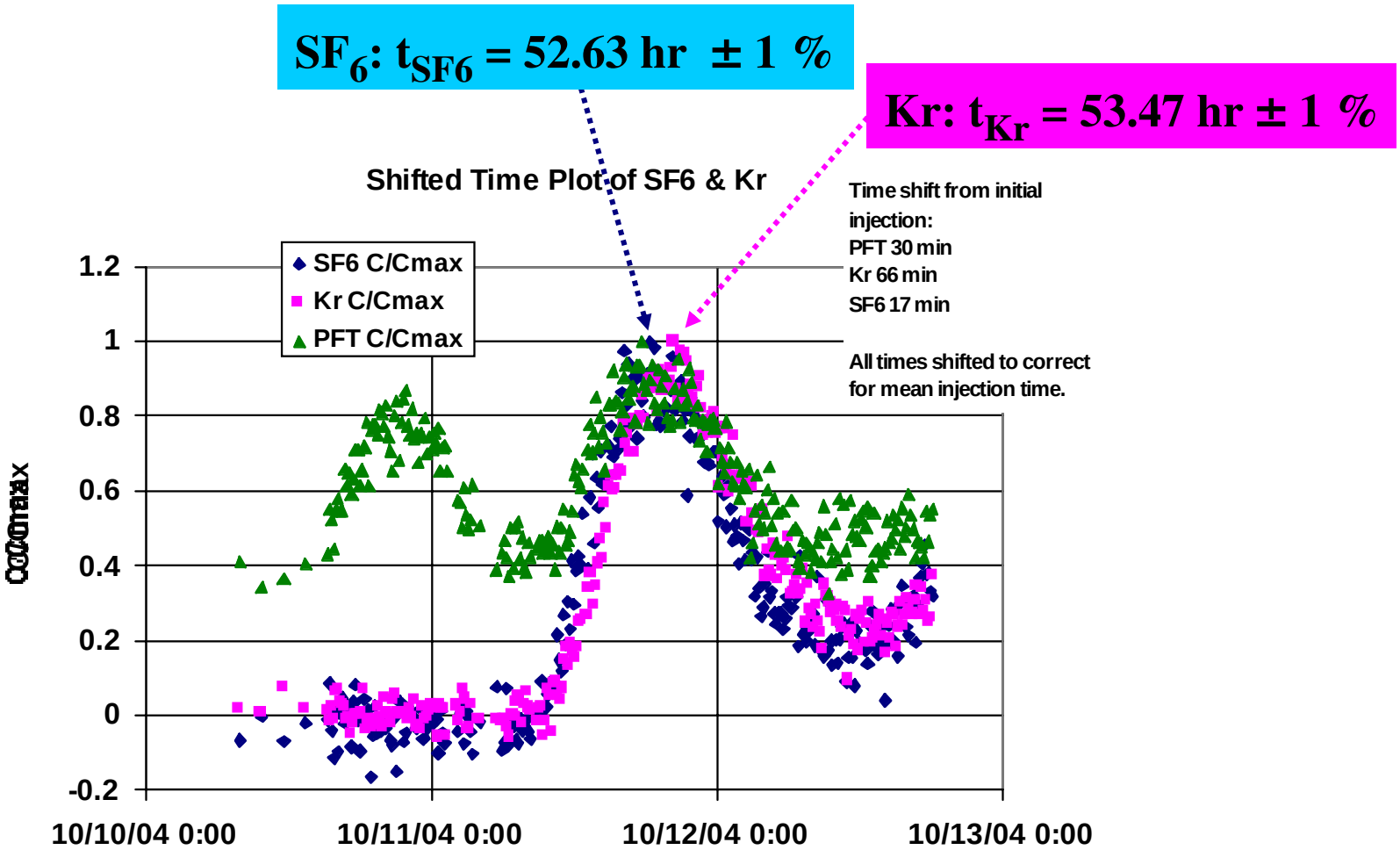
- Gas samples collected using the U-Tube sampling system
- Gas-phase was sampled off top of high pressure sample cylinders

- Sample gas processed in real-time using quadrupole mass spectrometer
- Complete collection and analysis cycle occurred every 11 minutes once sample stream became self-lifting

Gas Tracer Observations

Component	Mass Injected	Injection Time (Rel. time hr.)	Injection Duration (hr)	Arrival Time (Rel. time hr.)	Peak Time (Rel. time hr.)	Travel time (hr.)
CO_2	3 kg/s*	4 Oct 11:34 (0.00+0.0/-2.0)	N/A	6 Oct 14:28 50.90+0.0/-2.0	N/A	50.9+0.0/-2.0
PMCH, PTCH	3.1 kg	4 Oct 13:26 (1.87)	3.9	6 Oct 14:28 50.90+0.0/-2.0	6 Oct 15:20 (51.8±0.9)	48.0±0.9
PMCP, PDCH	0.3 kg	8 Oct 18:19 (102.75)	1.0	10 Oct 15:32 (147.97±0.5)	10 Oct 22:52 (155.3±0.5)	50.22±0.5
PMCH, PTCH	0.3 kg	9 Oct 11:37 (120.05)	1.0	11 Oct 11:42 (168.13±0.5)	11 Oct 18:36 (175.03±0.5)	52.67±0.5
SF_6	< 200g‡	9 Oct 11:37 (120.05)	0.58	11 Oct 10:26 (166.87±0.5)	11 Oct 18:22 (174.80±0.5)	52.63±0.5
Kr	83.8 g	9 Oct 12:39 (121.08)	0.13	11 Oct 10:37 (167.05±0.5)	11 Oct 20:01 (176.45±0.5)	53.47±0.5

Observed Tracer Breakthrough Curves



Analysis

$$S_a = \frac{1 - t_t/t_u}{1 - t_t/t_u + \zeta_u\, t_t/t_u - \zeta_t}$$

$t_{SF6}/t_{Kr} = 52.63/53.47 = 0.984 \pm 1\ \%$

Solubilities at T = 65 deg-C

tracer	brine* molality	Henry's coefficient (Pa)	solubility ζ
Kr	1.55	6.27e9	2.440e-2
	0	3.86e9	3.964e-2
SF_6	0	3.29e10	4.650e-3

* modeled as pure NaCl

Inferred aqueous phase saturations
(different assumptions for solubilities)

Kr	SF_6	**S_a**
1.55 m brine	pure water	**45.2 %**
1.55 m brine	insoluble	**40.0 %**
pure water	pure water	**31.8 %**

Uncertainty in Breakthrough Time

- t_{SF6}/t_{Kr} = 0.984 ± 1 %; range: 0.975 – 0.993
- assume 1.55 m NaCl brine for Kr solubility; SF_6 insoluble
- t_{SF6}/t_{Kr} = 0.975; ==> S_a = 51.2 %
- t_{SF6}/t_{Kr} = 0.993; ==> S_a = 22.4 %

===> small uncertainty in relative tracer arrival times translates into large uncertainty for aqueous phase saturation

Concluding Remarks

- Conducted successful gas tracer tests at Frio site.
- More water-soluble tracer (krypton) is retarded relative to less soluble SF_6.
- From krypton retardation relative to SF_6, estimate in situ water saturation in CO_2 plume of approximately 40 %.
- Interpretation (conceptual model) is not unique:
  - analysis assumes simplest model: phase-partitioning according to local equilibrium
  - how about non-equilibrium dissolution and subsequent diffusion in aqueous phase?
  - partitioning into additional phases? (oil phase, sorption on solids)
- Ambiguities may be reduced by using several different tracers
- Additional data analysis is underway.

Determining Tracer Travel Time