#### Use of Gas Phase Tracers for Monitoring CO<sub>2</sub> Injection at the Frio Test Site

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

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## Outline

- Phase-partitioning tracers
- Issues for CO<sub>2</sub> 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<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>)
- noble gases
- SF<sub>6</sub>; 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<sub>2</sub>

- how does CO<sub>2</sub> invade and occupy the pore space?
- where does the CO<sub>2</sub> 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

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

with $\phi = \text{porosity}$  $v_g = \text{gas velocity}$  $C_g^t = \text{tracer concentration in gas}$  $\tau = \text{tortuosity}$ (partial density; kg/m³) $D_g^t = \text{tracer diffusivity}$ 

Tracer transport in two-phase conditions with immobile liquid

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

 $R_t$  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<sub>i</sub> 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





Isotope	Partial pressure in air, Pa	Dissolved mass fraction in water at T = 10  deg-C	Henry's co T = 10 deg-C	efficient, Pa T = 65 deg-C
<sup>22</sup> Ne	0.170	2.440e-11	8.510e9	10.20e9
<sup>36</sup> Ar	3.184	2.134e-9	2.981e9	6.141e9
<sup>84</sup> Kr	0.0658	1.990e-10	1.542e9	3.860e9
<sup>132</sup> 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 realtime using quadrupole mass spectrometer
- Complete collection and analysis cycle occurred every 11 minutes once sample stream became self-lifting

#### Gas Tracer Observations

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

## **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

Inferred aqueous phase saturations (different assumptions for solubilities)

tracer	brine* molality	Henry's coefficient (Pa)	solubility ζ
Kr	1.55	6.27e9	2.440e-2
	0	3.86e9	3.964e-2
SF <sub>6</sub>	0	3.29e10	4.650e-3

Kr	SF <sub>6</sub>	Sa	
1.55 m brine	pure water	45.2 %	
1.55 m brine	insoluble	40.0 %	
pure water	pure water	31.8 %	

\* modeled as pure NaCl

#### Uncertainty in Breakthrough Time

- $t_{SF6}/t_{Kr} = 0.984 \pm 1$  %; range: 0.975 0.993
- assume 1.55 m NaCl brine for Kr solubility; SF<sub>6</sub> 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.

