Gas-Water-Rock Interactions in Saline Aquifers Following CO_2 Injection: Results from Frio Formation, Texas, USA

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To investigate the potential for the geologic storage of CO_2 in saline sedimentary aquifers, ~16 million kg of CO_2 were injected at ~1,500-m depth into a 24-m sandstone section of the Frio Formation—a regional brine and oil reservoir in the U. S. Gulf Coast. Fluid samples obtained from the injection and observation wells before, during and post CO_2 injection, show a Na-Ca-Cl type brine with 93,000 mg/L TDS and near saturation of CH_4 at reservoir conditions. As injected CO_2 became the dominant gas at the observation well, results showed sharp drops in pH (6.5 to 5.7), pronounced increases in alkalinity (100 to 3,000 mg/L as HCO_3) and Fe (30 to 1,100 mg/L), and significant shifts in the isotopic compositions of H_2O, DIC and CH_4. Geochemical modeling indicates that brine pH would have dropped lower, but for the buffering by dissolution of carbonate and iron oxyhydroxides. The low pH values resulting from CO_2 injection could cause rapid dissolution of carbonate and other minerals creating pathways for CO_2 and brine leakage. Dissolution of some minerals, especially iron oxyhydroxides could mobilize trace metals and other toxic components. Also, where residual oil and other organics are present, the injected CO_2 may mobilize organic compounds, some may be environmentally toxic. The $\delta^{18}O$ values for brine and CO_2 samples indicate that supercritical CO_2 comprises ~45% of fluid volume in Frio sandstone near injection well ~6 months after end of injection. Post-injection sampling, coupled with geochemical modeling, indicate the brine gradually returning to its pre-injection composition.

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Topics Discussed

- Energy, CO_2 levels and global warming
- Composition of water and gases in the Frio– Baseline, during and post injection results.
- How are such data obtained and why are they important to CO_2 sequestration?
- Water-mineral-CO_2 interactions in the Frio.
- Environmental implications of post injection results.
- Future plans and concluding remarks.

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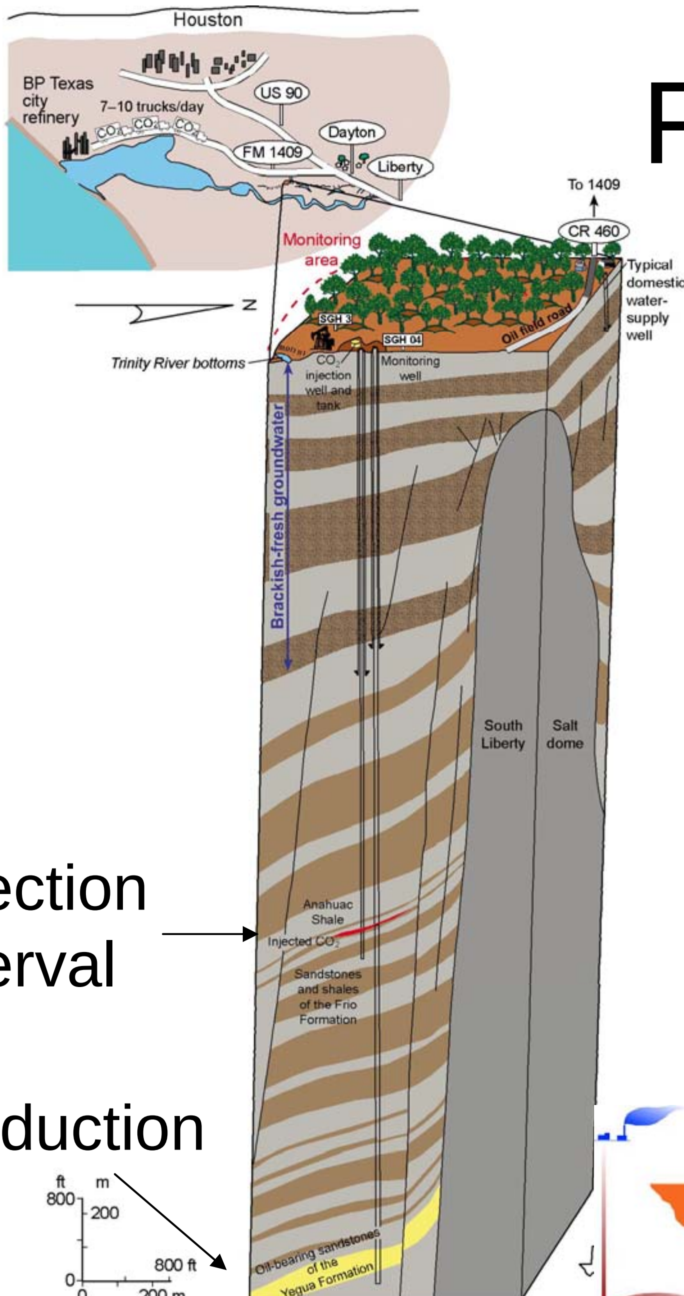
Frio Brine Pilot



Injection interval

Oil production

- Injection interval: 24-m-thick, mineralogically complex Oligocene reworked fluvial sandstone, porosity 34%, Permeability 2-3 Darcys
- Seals – numerous thick shales, small fault block
- Depth 1,500 m
- Brine-rock system, no hydrocarbons
- 67°C; 150 bar

Hovorka et al., 2004

Bureau of Economic Geology

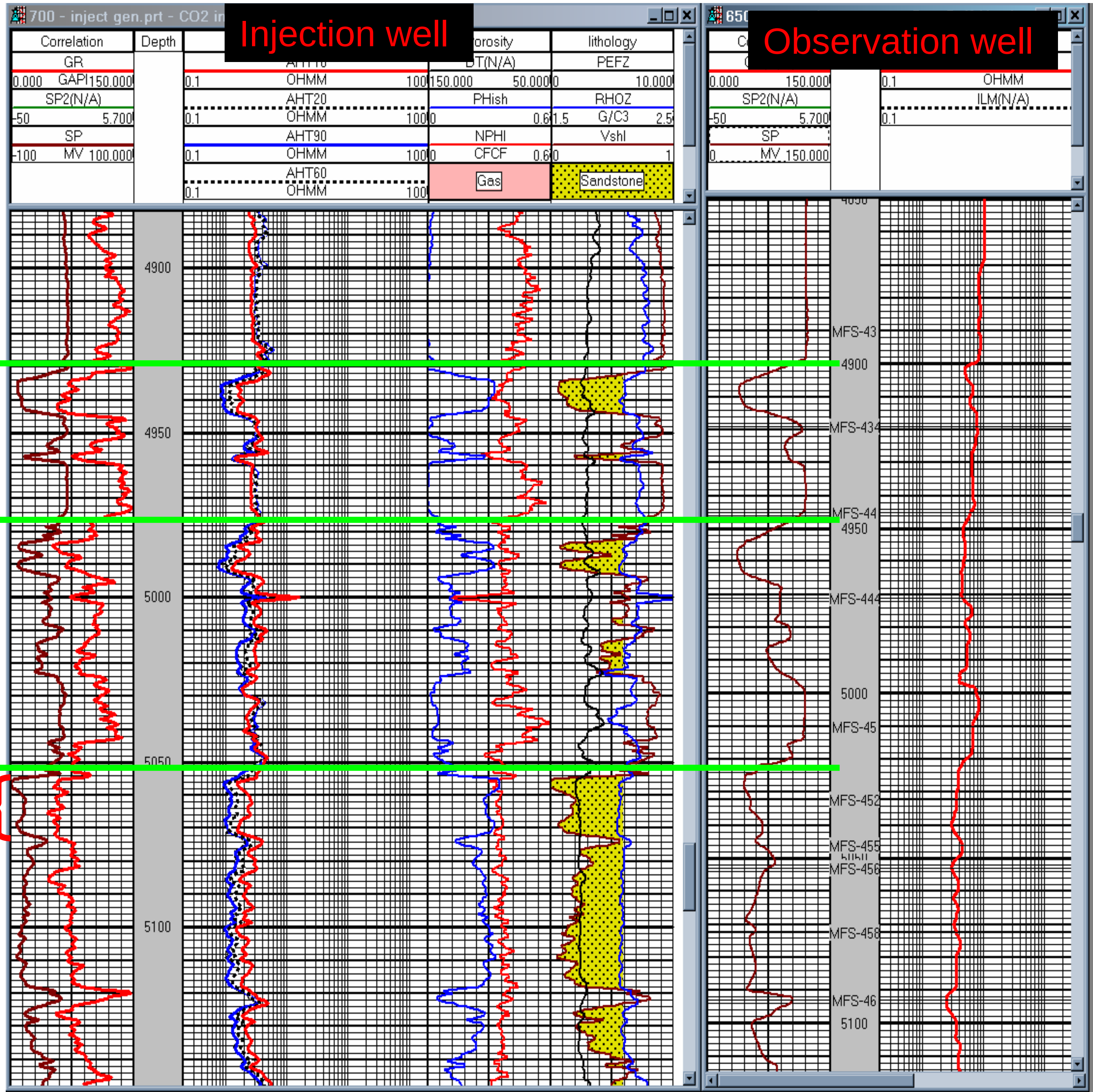
Open Hole logs

Top A ss

Top B ss

Top C ss

Proposed injection zone



Hovorka et al., 2004


PRAXAIR

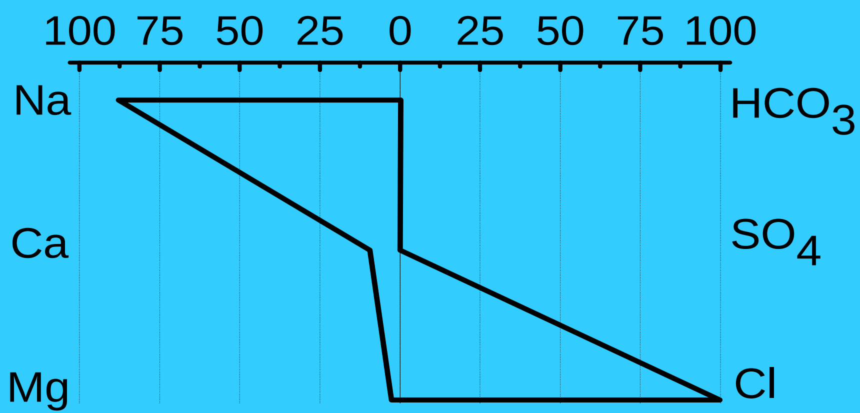
Frio CO_2 Field sampling

Drilling & test water tagged with dye tracers

Date	Site	Sampling info	Sample series
June 3, 2004	injection well	MDT tool	04FCO_2-100
Jul 23-Aug 2, 2004	injection well, monitoring well & gw wells	surface sampling (N_2), Kuster, submers.pump	04FCO_2-200
Oct 4-7, 2004	monitoring well	U-tube	04FCO_2-300
Oct 29-Nov 3, 2004	monitoring well	U-tube	04FCO_2-400
April 4-6, 2005	injection well & monitoring well	surface sampling (N_2) & Kuster	05FCO_2-100

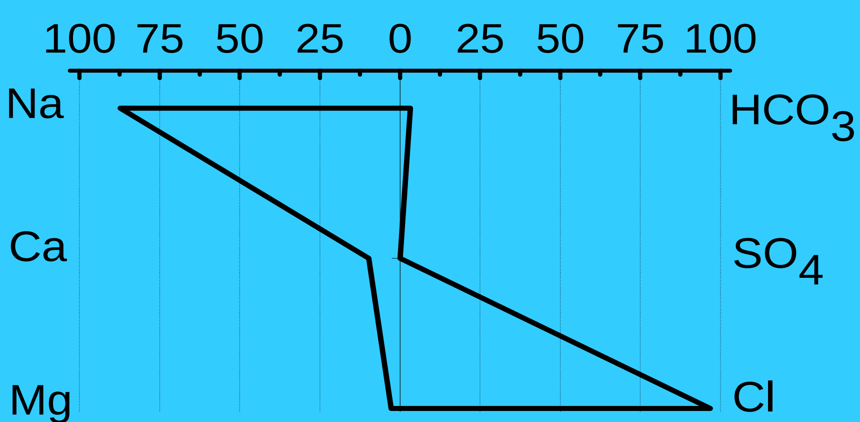
Salinity and normalized conc. of major cations and anions

04FCO2-218 (observation; pre-injection)



pH = 6.7; TDS = 93,800 mg/L

04FCO2-337 (observation; post-injection)

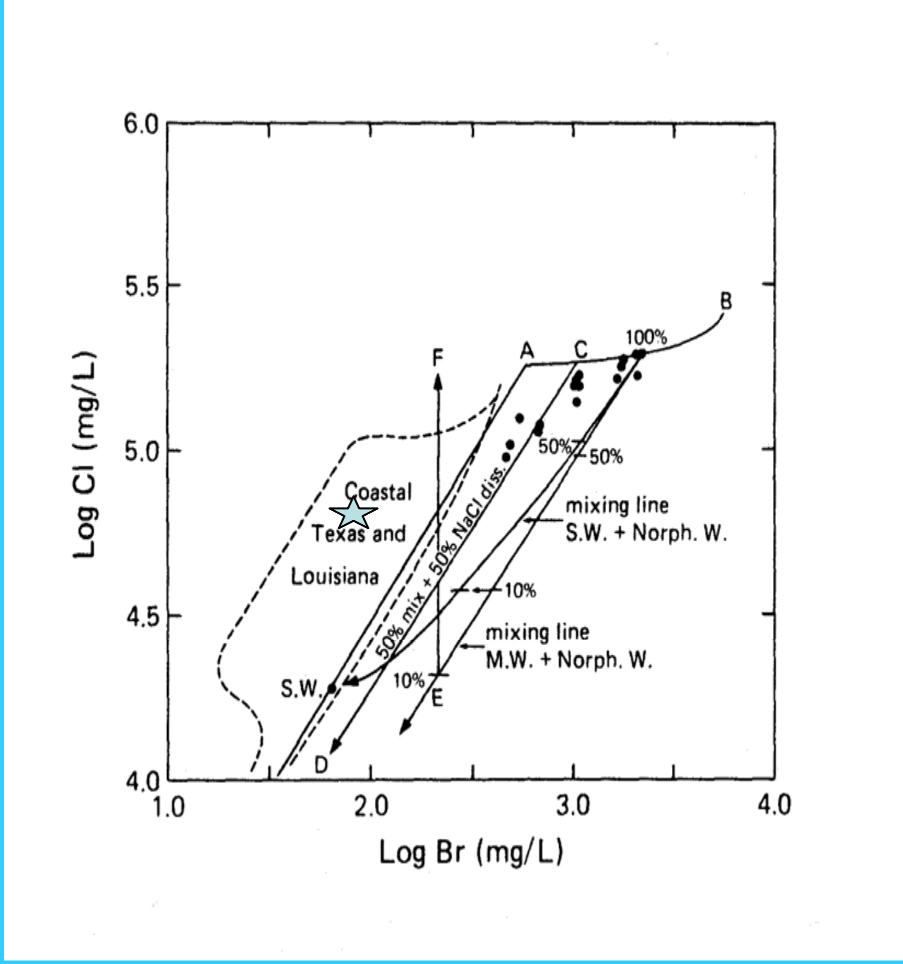


pH = 6.03; TDS = 92,600 mg/L

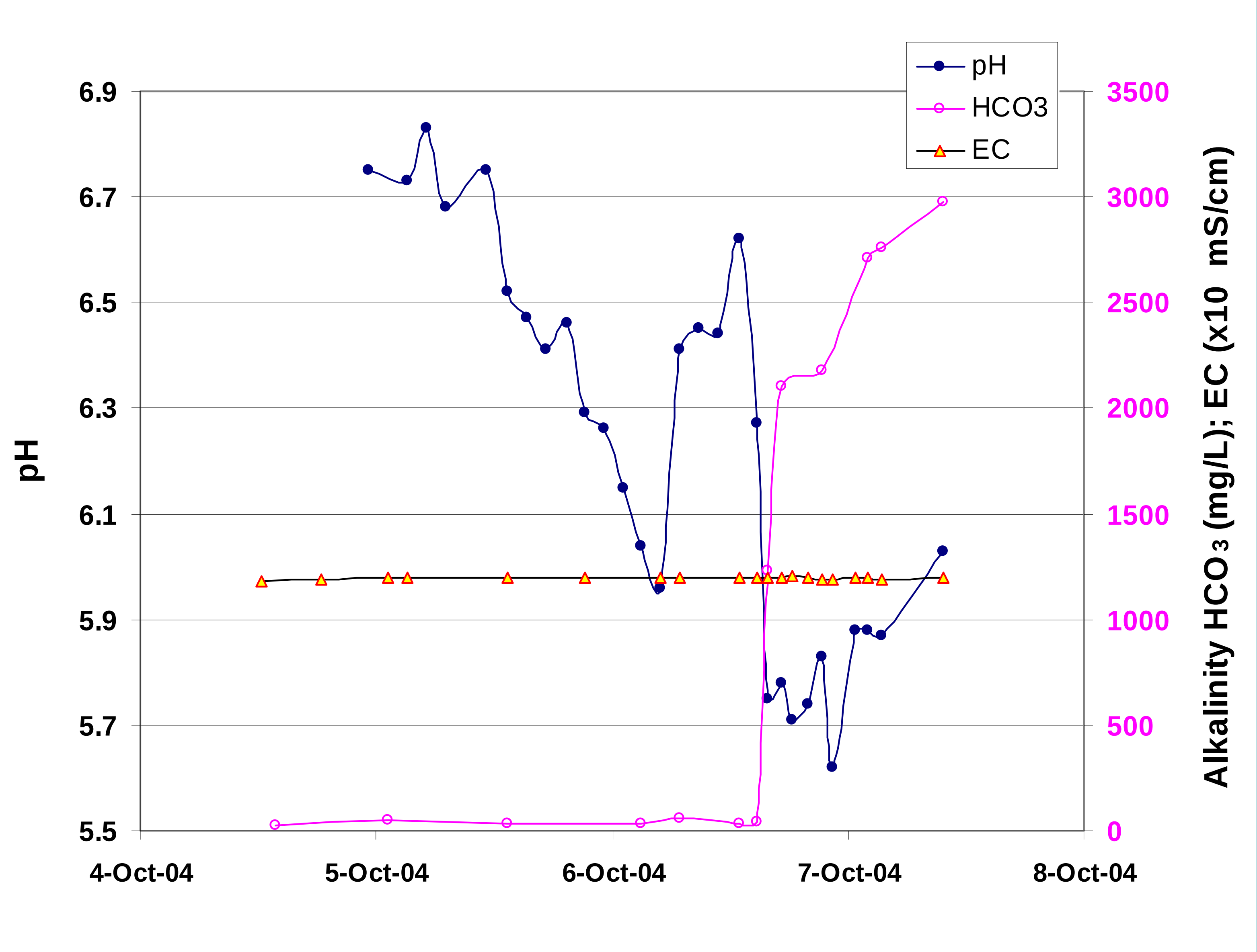
Br-Cl, indicator of solute origin

(* Frio value)

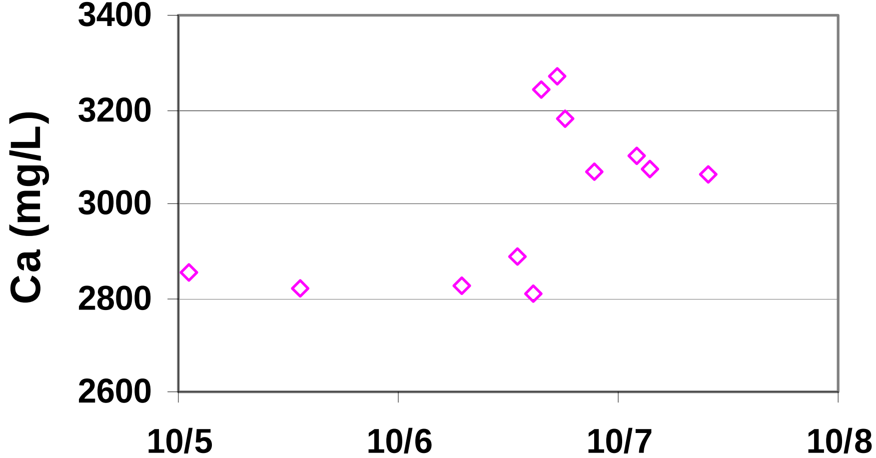
Kharaka & Hanor, 2004



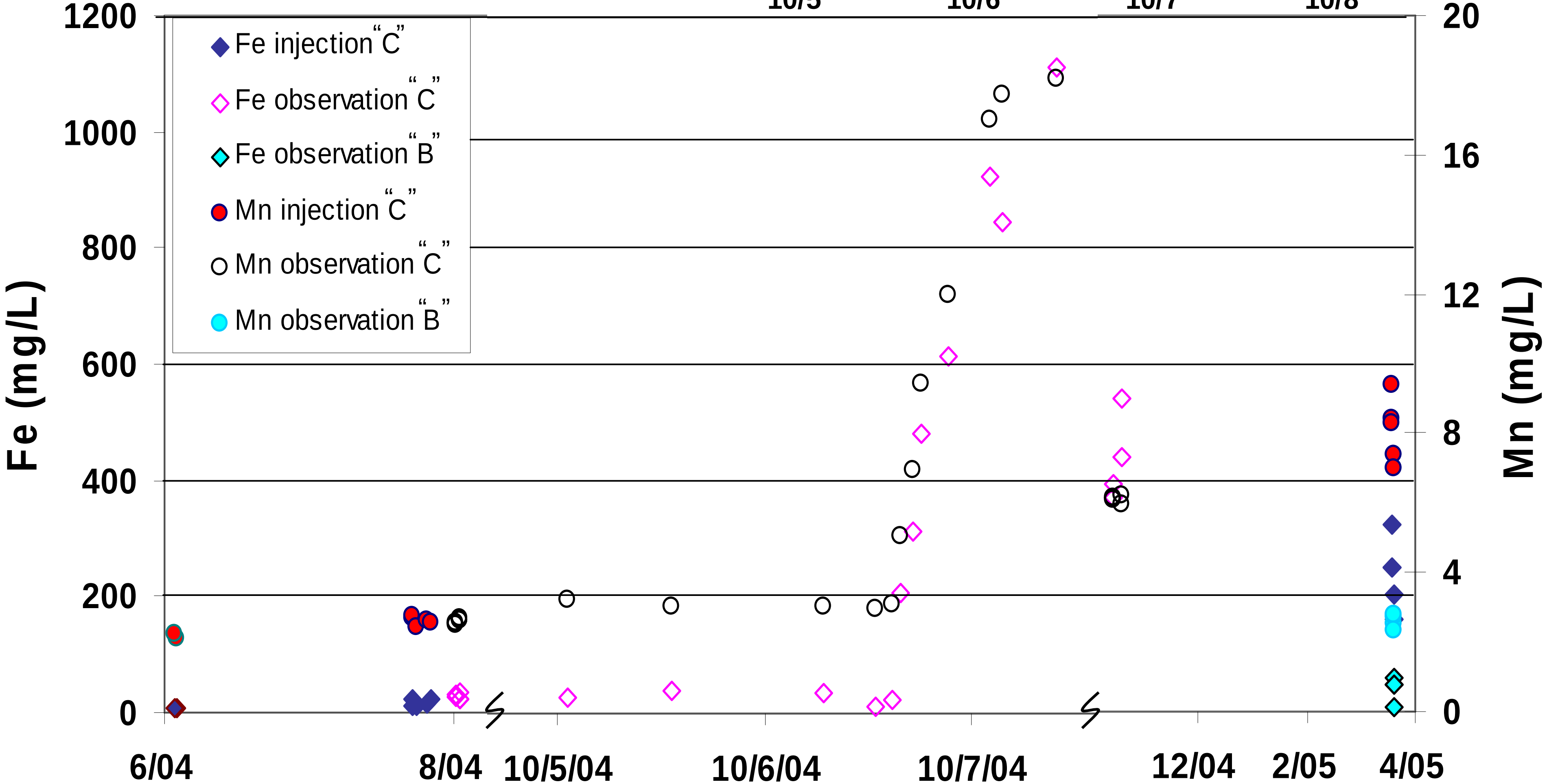
Selected chemical data from monitoring well during CO2 injection



Frio: Ca, Fe & Mn

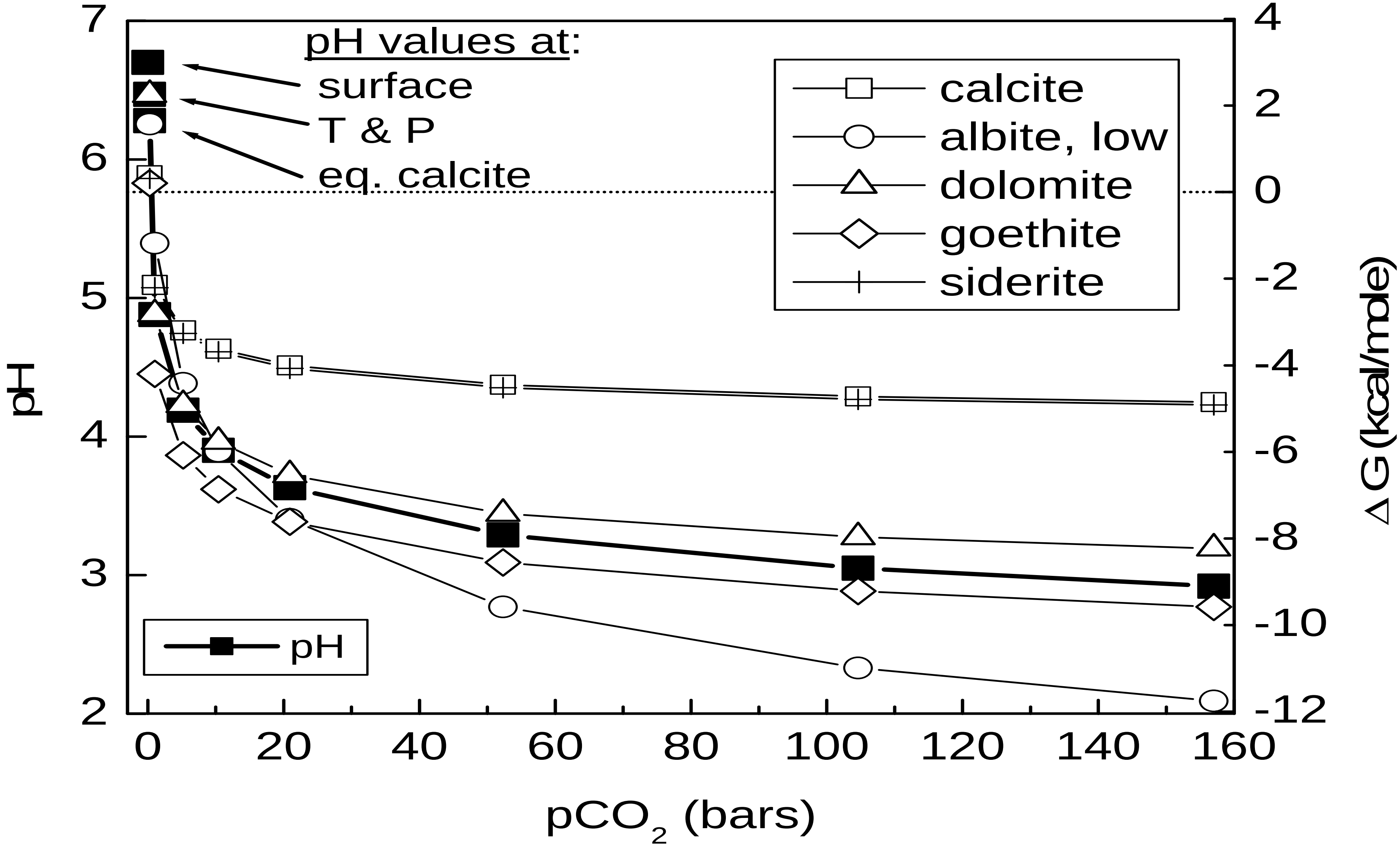


3400
3200
3000
2800
2600
Ca (mg/L)
10/5
10/6
10/7
10/8



1200
1000
800
600
400
200
0
Fe (mg/L)
20
16
12
8
4
0
Mn (mg/L)
Fe injection "C"
Fe observation "C"
Fe observation "B"
Mn injection "C"
Mn observation "C"
Mn observation "B"
6/04
8/04
10/5/04
10/6/04
10/7/04
12/04
2/05
4/05

Computed pH and saturated states of selected minerals at T & P



Important Mineral-Water-Gas Interactions in Frio

$CO_{2\,(gas)} + H_2O \Leftrightarrow H_2CO_3^{o}$ ------ (1)

$H_2CO_3^{o} \Leftrightarrow HCO_3^- + H^+$ ------ (2)

$CO_{2\,(gas)} + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^-$ ------ (3)

$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$ ------ (4)

$H^+ + FeCO_3 \Leftrightarrow Fe^{++} + HCO_3^-$ ------ (5)

$4Fe^{++} + O_2 + 10H_2O \Leftrightarrow 4Fe(OH)_3 + 8H^+$ ------ (6)

$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$ ------ (7)

$4.8H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 3.2H_2O \Leftrightarrow$

$.2Ca^{++} + .8Na^+ + 1.2Al^{+++} + 2.8H_4SiO_4$ ------ (8)

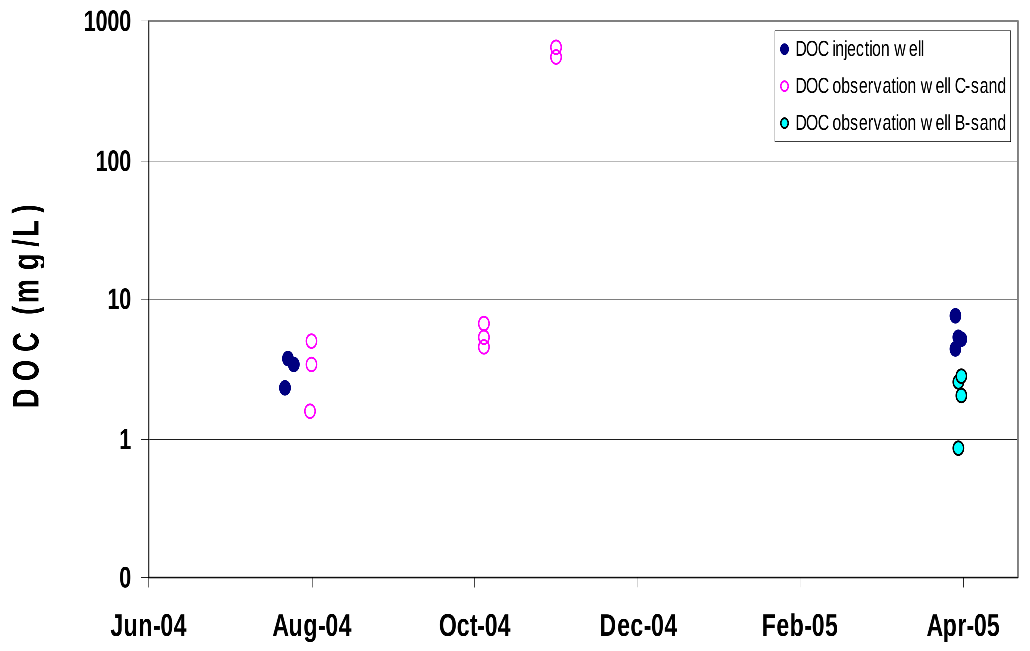
$0.4H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 0.8CO_2 + 1.2H_2O \Leftrightarrow$

$.2Ca{+}{+} + .8NaAlCO_3(OH)_2 + 0.4Al(OH)_3 + 2.8SiO_2$ --- (9)

Organics in Oil-Field Water

(mg/L)

Frio DOC (6/04-4/05)



ACETATE & OTHER ACID ANIONS	10,000
BTEX	60
PAHs	10
PHENOL	20
4 – METHYL PHENOL	2
BENZOIC ACID	5
4 – METHYL BENZOIC ACID	4
2 – HYROXY BENZOIC ACID	0.2
3 – HYDROXY BENZOIC ACID	1.2

Kharaka & Hanor, 2004

Chemical Composition of Frio Gases

Frio formation water at saturation with CH_4

	Injection well before CO_2 injection 04FCO2-102	Monitoring well before CO_2 injection 10-7-04 @ 2:15 am	Monitoring well after CO_2 injection 10-13-04 @ 20:37	Monitoring well "B" sand 05FCO2-110
He	0.0077	0.0026	0	0.0124
H_2	0.0401	1.36	0.191	0.285
Ar	0.0418	0.0207	0	0.0608
O_2	0.0719	0	0	0.748
CO_2	0.31	0.0040	96.8	0.208
N_2	4.15	3.60	0.037	5.17
CO	0	0	0	<0.001
CH_4	93.4	94.8	2.94	93.4
C_2H_6	0.149	0.161	0.0052	0.103
C_3H_8	0.0086	0.0021	0	0.0012
C_4H_{10}+	1.76	0.0037	0	<0.0005

volume%, normalized

Brine/CO2 volume ratio at reservoir conditions

	^{18}O shift	^{18}O shift	Brine/CO_2
Date*	Brine	CO_2	vol. ratio
10-5-04	0	0	$\rightarrow \infty$
10-6-04	0.37	32	59
10-6-04	0.69	32	32
10-6-04	0.77	32	29
10-6-04	1.22	32	18
10-7-04	2.24	32	10
11-3-04	1.43	32	15
11-3-04	1.74	32	12
4-4-05	11.2	22	1.4
5-4-05	11.7	22	1.3
6-4-05	11.9	22	1.3

$$X_{brine}/X_{CO2} = \frac{\delta^{18}O^{f}_{CO2} - \delta^{18}O^{i}_{CO2}}{\delta^{18}O^{i}_{H2O} - \delta^{18}O^{f}_{H2O}}$$

Isotopic mass balance equation, where the superscripts “i” and “f” are the initial and final δ values for brine and CO2, respectively, and X is the atomic oxygen in the subscipted omponent.

Summary and Conclusions

1- The Frio brine is saturated with CH_4 has a salinity of ~93,000 mg/L TDS, and is a Na-Ca-Cl type water.

2- Alkalinity and pH determinations are excellent and rapid field methods for tracking injected CO_2.

3- The low pH values resulting from CO_2 injection could have important environmental implications:

a)-Dissolution of minerals, esp. iron oxyhydroxides could mobilize toxic components;

b) dissolution of minerals may create pathways for CO_2 and brine leakage.

4- Where residual oil and other organics are present, CO_2 may mobilize organic compounds; some may be toxic.

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