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Carbon sequestration in sediments containing ferric iron

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CICCS [centre for innovation in carbon capture and storage]

Outline

Introduction

- Carbon dioxide capture and storage (CCS)
- CO_2 geological storage
- Estimates of CO_2 storage costs

Part 1

- Ferric-iron bearing sediments
- Objectives
- Study samples

Part 2

- Research plan
- Novel experimental set-up and methodology
- Preliminary results

Conclusions

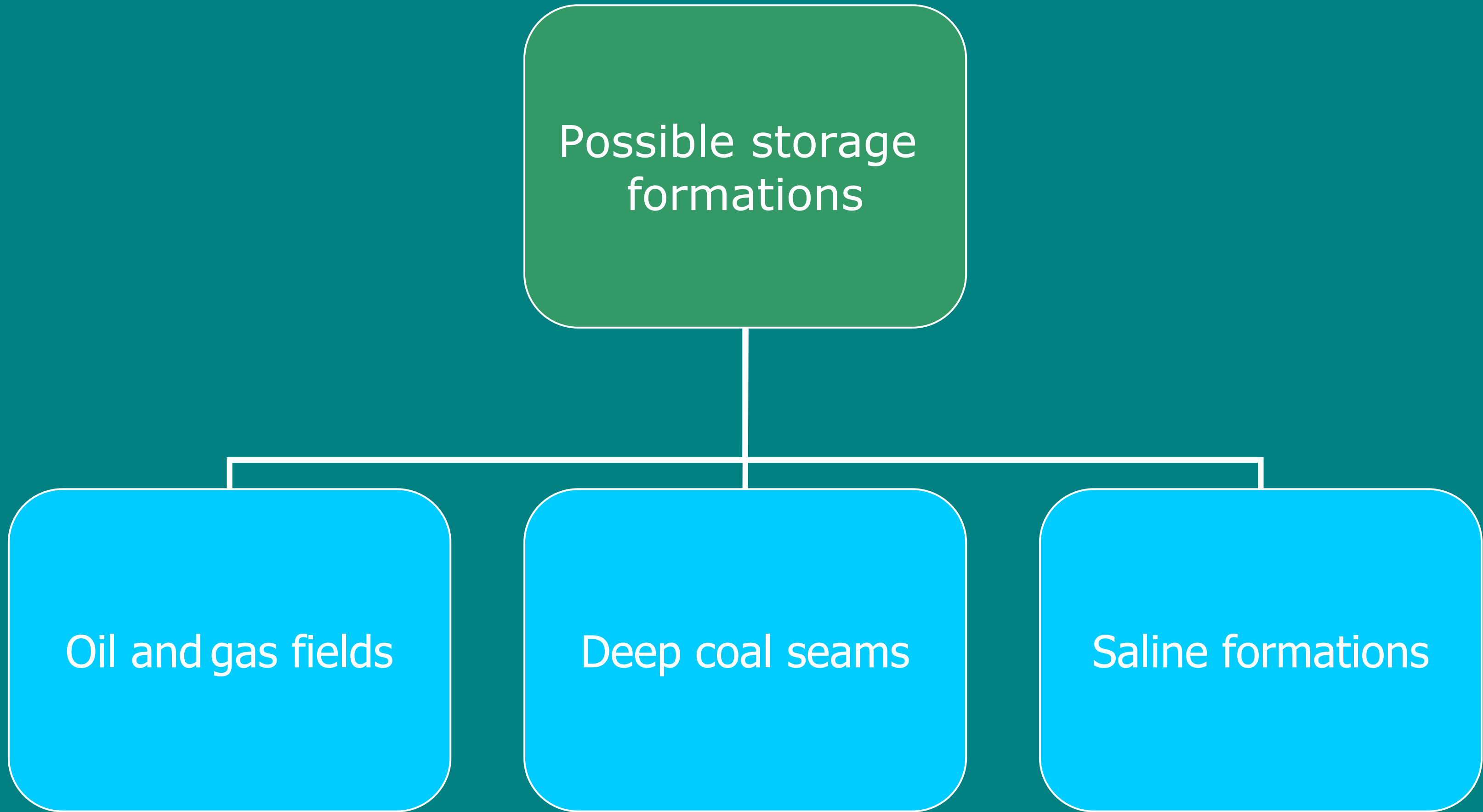
CO_2 capture and geological storage

1. Capture from a large point source
2. Injection into suitable deep rock formations

A **FOUR STEP** PROCESS:

Capture → *Compression* → *Pipeline transport* → *Underground injection*

CO_2 Geological Storage



Global capacity of geological reservoirs

Emissions from combustion of fossil fuels = 22 Gt CO_2/year

Reservoir type	Lower estimate of storage capacity ($GtCO_2$)	Upper estimate of storage capacity ($GtCO_2$)
Oil and gas fields	675[a]	900[a]
Unminable coal seams (ECBM)	3-15	200
Deep saline formations	1,000	Uncertain, but possibly 10^4

[a] These numbers would increase by 25% if 'undiscovered' oil and gas fields were included in this assessment.

Source: IPCC Special Report on CCS, 2005

Estimates of CO_2 storage costs

Option	Representative Cost Range (US$/tonne CO_2 stored)	Representative Cost Range (US$/tonne C stored)
Geological - Storage[a]	0.5-8.0	2-29
Geological - Monitoring	0.1-0.3	0.4-1.1
Ocean[b]		
Pipeline	6-31	22-114
Ship (Platform or Moving Ship Injection)	12-16	44-59
Mineral Carbonation[c]	50-100	180-370

[a] Does not include monitoring costs.

[b] Includes offshore transportation costs; range represents 100-500 km distance offshore and 3000 m depth.

[c] Unlike geological and ocean storage, mineral carbonation requires significant energy inputs equivalent to approximately 40% of the power plant output.

Source: IPCC Special Report on CCS, 2005

CO_2 Geological Storage

- CO_2 storage mechanisms in geological formations

Physical trapping: Hydrodynamic trapping

Geochemical trapping:

1. Solubility trapping ⇒

$CO_2\ (g) \leftrightarrow CO_2(aq)$
$CO_2 + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

2. Mineral trapping ⇒

$Ca + HCO_3^- \leftrightarrow CaCO_3 + H^+$

- Sediments considered so far:

Ca-bearing arkosic

Mg-bearing illitic

FeII-bearing glauconitic

Ferric-iron bearing sediments

- Their potential usage has been suggested lately (*Palandri, J.L. et al, 2005*)

- Advantages versus sediments considered so far:
  - Widespread geographic distribution and great thickness
  - High porosity and permeability
  - Less expensive/less energy demanding CO_2 capture process

- Reductant agent needed for the process to take place → SO_2

Acid gas injection

- Acid gas: mixture of H_2S and CO_2 with minor amounts of hydrocarbon gases
- It occurs at 44 different locations across the Alberta Basin (Alberta and British Columbia)

→ Mature and safe technology

HOWEVER…

- It has not been developed as a CO_2 sequestration approach
- *More research is needed*

Reaction of CO_2-SO_2 gas mixtures with ferric iron and water

- Dissolution process

$4\ SO_2(g) + 4\ H_2O(l) \leftrightarrow H_2S(aq) + 3\ H_2SO_4\ (aq)$
$CO_2\ (g) \leftrightarrow CO_2(aq)$

$CO_2 + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

- Reduction process

$8\ Fe^{3+} + HS^- + 4\ H_2O \leftrightarrow 8\ Fe^{2+} + SO_4^{2-} + 9\ H^+$

- Carbonation process

$H_2CO_3 + Fe^{2+} \leftrightarrow FeCO_3 + 2H^+$

Fe_2O_3 (hematite) + **$2\ CO_2$** + **SO_2** + $H_2O \leftrightarrow 2\ FeCO_3$ (siderite) + H_2SO_4 $\Delta G_R < 0$

2FeOOH (goethite) + **$2\ CO_2$** + **SO_2** $\leftrightarrow 2\ FeCO_3$ (siderite) + H_2SO_4 $\Delta G_R < 0$

Objectives

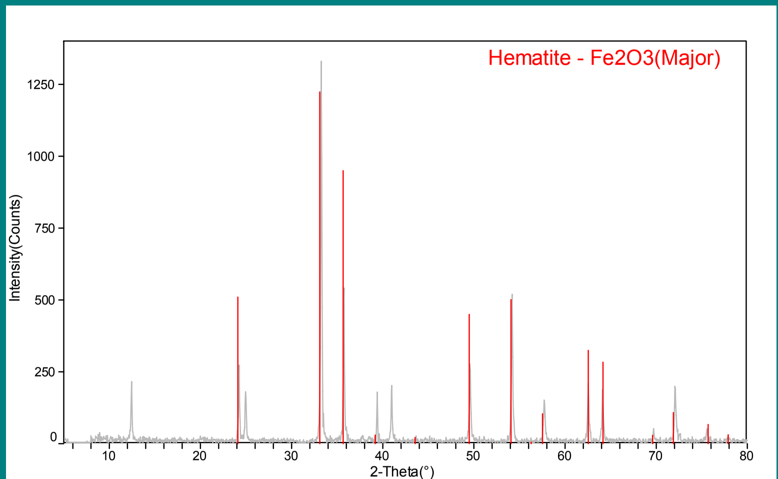
- Laboratory studies to proof the ferric-iron bearing sediments potential for CO_2 underground storage

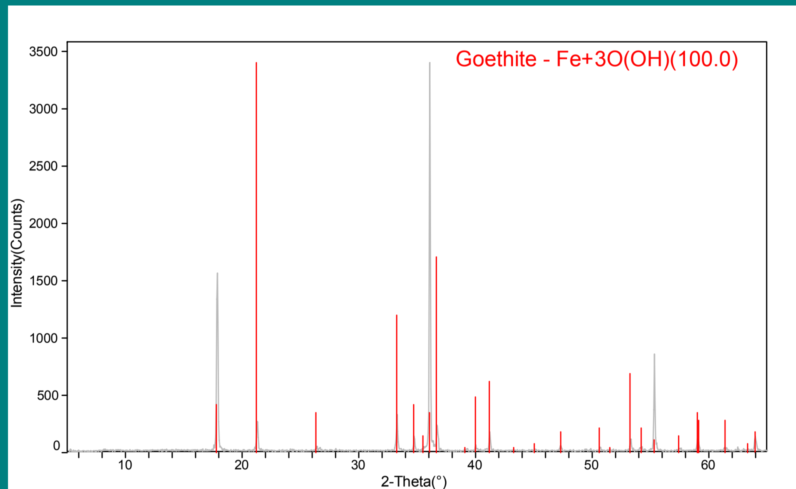
- Experimental set-up design to run tests under different geochemical conditions

- Research plan and development of the methodology

Study samples

- Previous researchers: Hematite sample from Gerais mines (Brazil)
- This research:
  - Hematite sample from Shishen mine (South Africa)
  - Goethite sample from El Paso County, Colorado (US)
  - Future samples: olivine, serpentine, granite and sandstone





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Research plan

Theoretical equilibrium geochemical simulations

Laboratory studies:

1. Reductive dissolution of iron oxides

- CO_2/SO_2 ratio (boiler, experiment, stoichiometric)
- Reaction time (1 day, 1 week, others)
- Solids concentration (25g/L, 67g/L, 100g/L)
- Reaction temperature (50°C, 100 °C, 150 °C)
- Reaction pressure (100 bar, 200 bar, 350 bar)
- Particle size (<38 µm, 38-150 µm, 150-300 µm)

2. Carbonation conditions

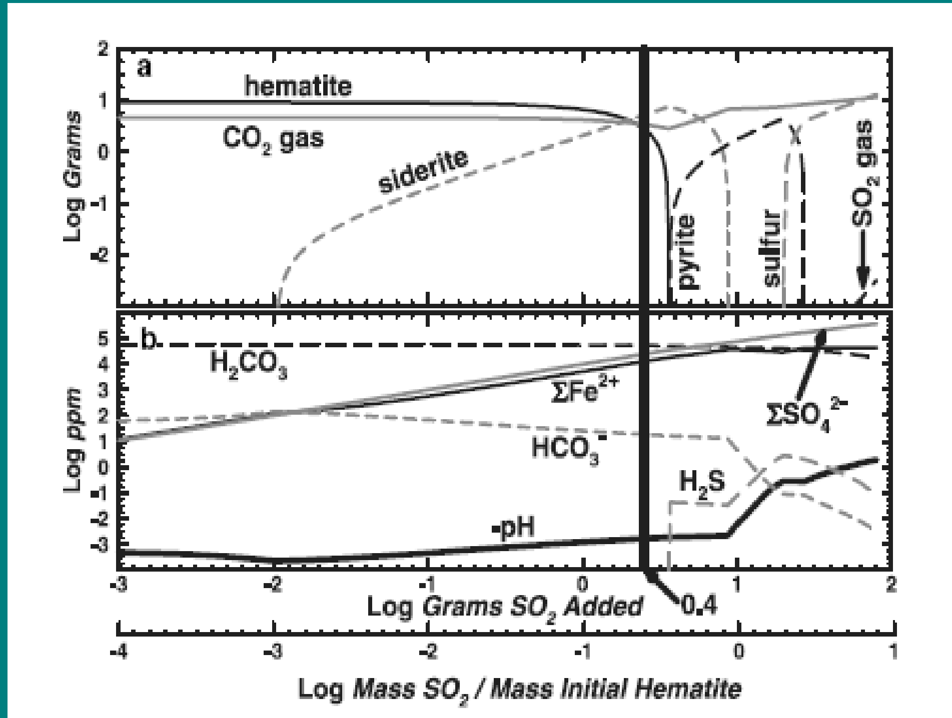
3. Optimization of reductive dissolution and carbonation processes

Theoretical equilibrium geochemical simulations

Computer program: Chiller

Compute reaction path in geologic systems by changing one of the systems variables incrementally and re-computing equilibrium at each step.

Follow-up of work by Palandri J.L, Rosenbauer R.J. and Kharaka Y.K.



Results summary from simulation at 150°C and 300 bar of the CO_2-SO_2 reaction with 10 gr of hematite in 156 gr of 1.0m NaCl brine using 14 gr (excess) CO_2 (Palandri J.L. et al, 2005)

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Previous experimental work

- **Experimental apparatus**

Autoclave containing a flexible Au-Ti reaction cell with ~ 200 ml total volume.

- **Experimental conditions**

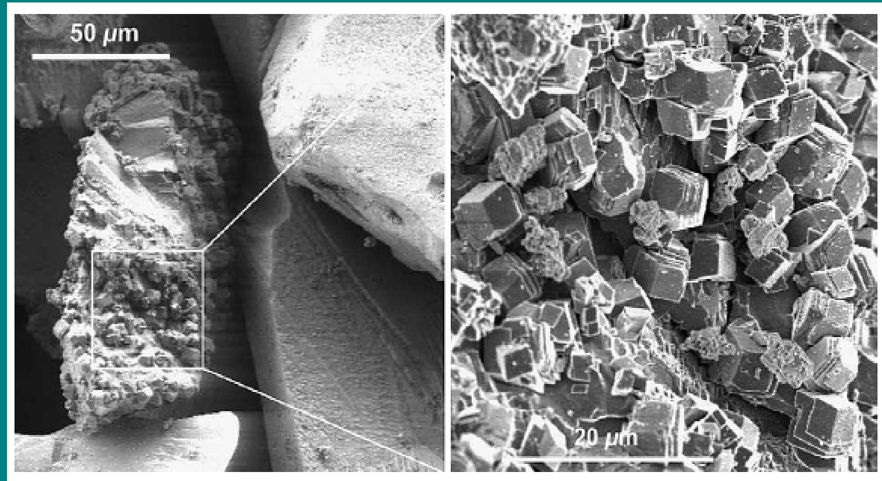
Temperature = 150°C

Pressure = 300 bar

CO_2/SO_2 ratio ~ 9:1

Brine volume (1.0 m NaCl)= 150 ml

Solids concentration = 67 g/L



Experimental results, solids: siderite on etched hematite (Palandri J.L. et al, 2005)

Only ONE experiment reported so far …

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CO_2/SO_2 ratios

- **Boiler ratio**

	By Mass		By Volume	
	From boiler	Stack	From boiler	Stack
CO_2	17.527%	17.159%	11.765%	11.340%
N_2	70.204%	68.559%	73.987%	71.137%
Ar	1.188%	1.160%	0.878%	0.845%
O_2	6.531%	6.374%	6.030%	5.795%
H_2O	4.447%	6.739%	7.291%	10.879%
SO_2	0.101%	0.009%	0.046%	0.004%
HCl	0.002%	0.000%	0.002%	0.000%
	100.000%	100.000%	100.000%	100.000%
0.68% Sulphur Coal				

→ **99.6% CO_2** **0.4% SO_2**

CO_2 ↓ ↑ SO_2

- **Experiment ratio** → **CO_2/SO_2 ~ 9:1** → **90% CO_2** **10% SO_2**
- **Stoichiometric ratio** → **2 mol CO_2** **1 mol SO_2** → **66.3 % CO_2** **33.7 % SO_2**

AND…What about the SO_2 needed?

Significant limitation: Flue gas typically contains less than 5%wt SO_2

Various options to overcome the problem:

1. Targeted sediments must contain other divalent metals (e.g., Ca, Mg, Fe^{II}).
2. Reduced S-bearing waste gas derived from other industrial processes could be added to the waste gas stream,e.g., H_2S from sour natural gas processing.

Research plan

Theoretical equilibrium geochemical simulations

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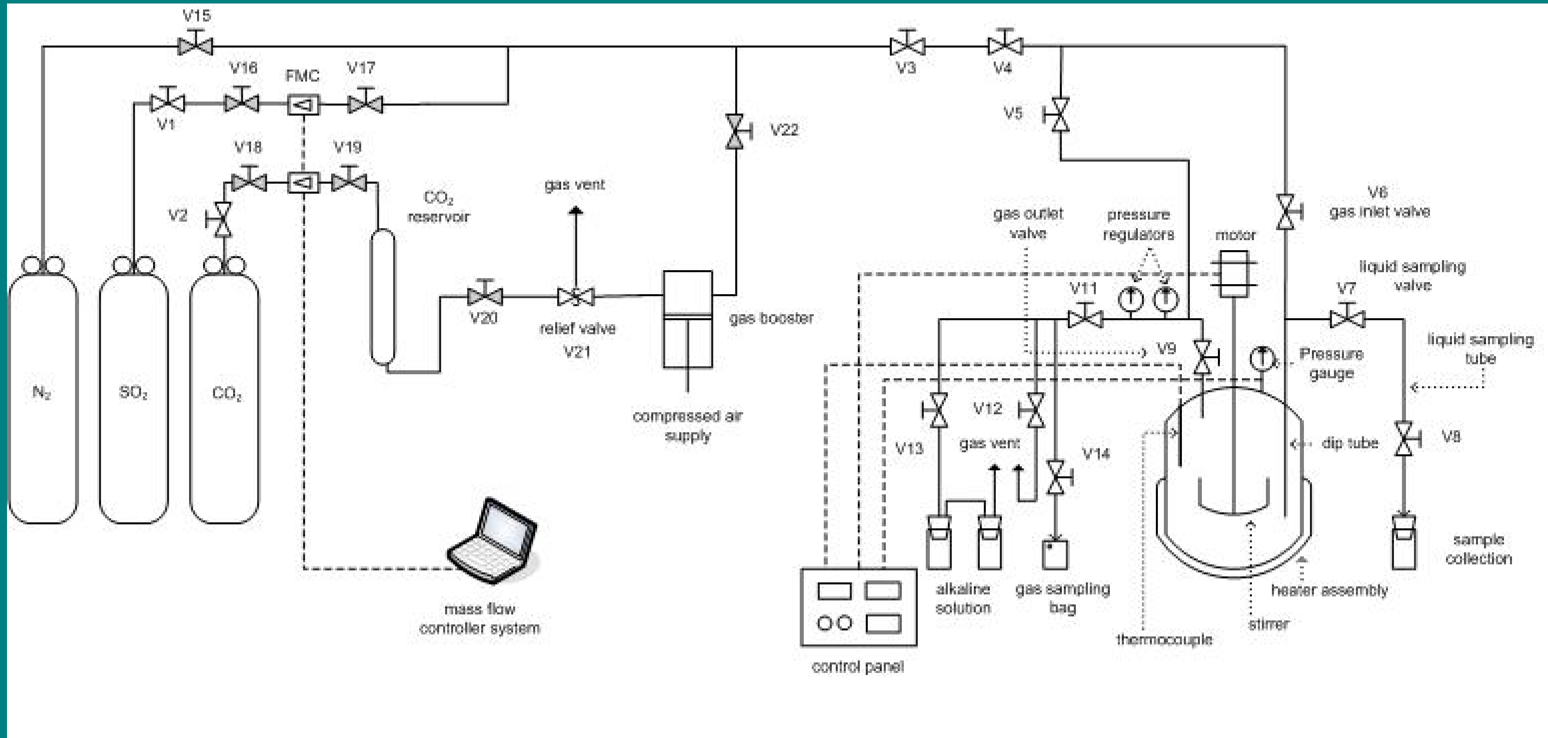
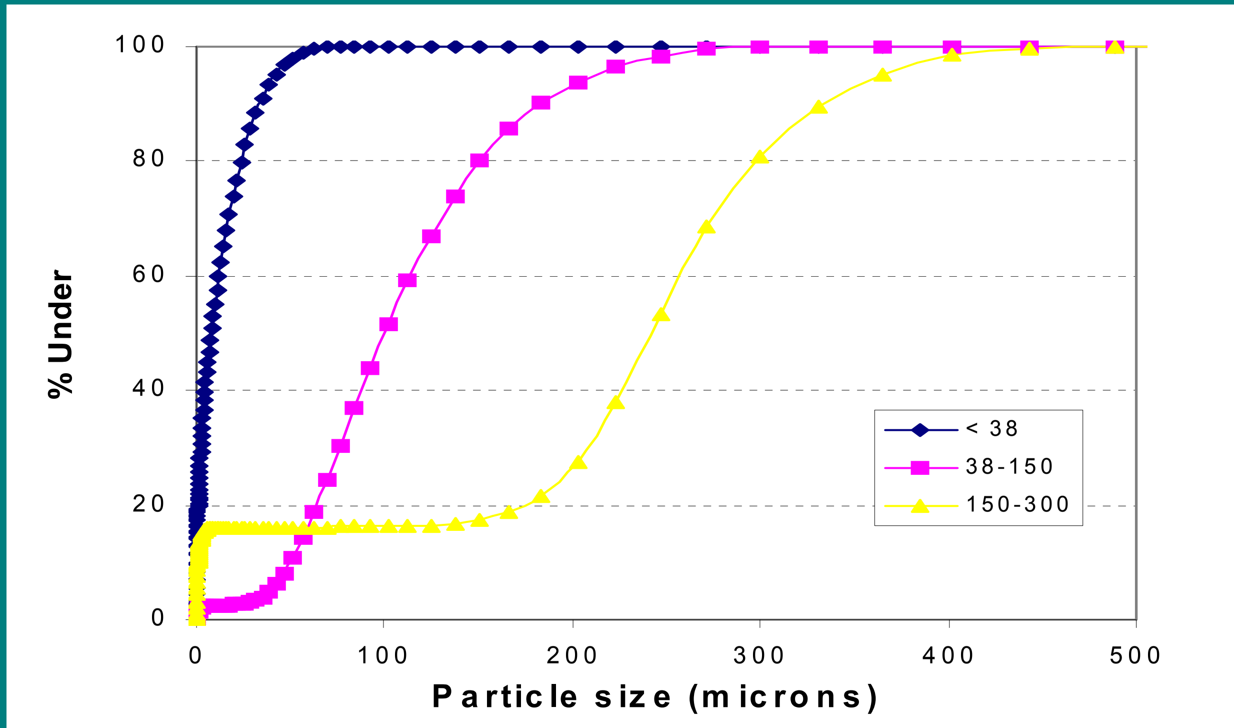
Novel experimental set-up and methodology



V15,V16,V17,V18,V19,V20,V22 : check valves
V1,V2,V4,V5,V8,V11,V14 : needle valves
V3,V6,V7,V9,V12,V13 : isolation (on/off) valves
V21 : relief valve

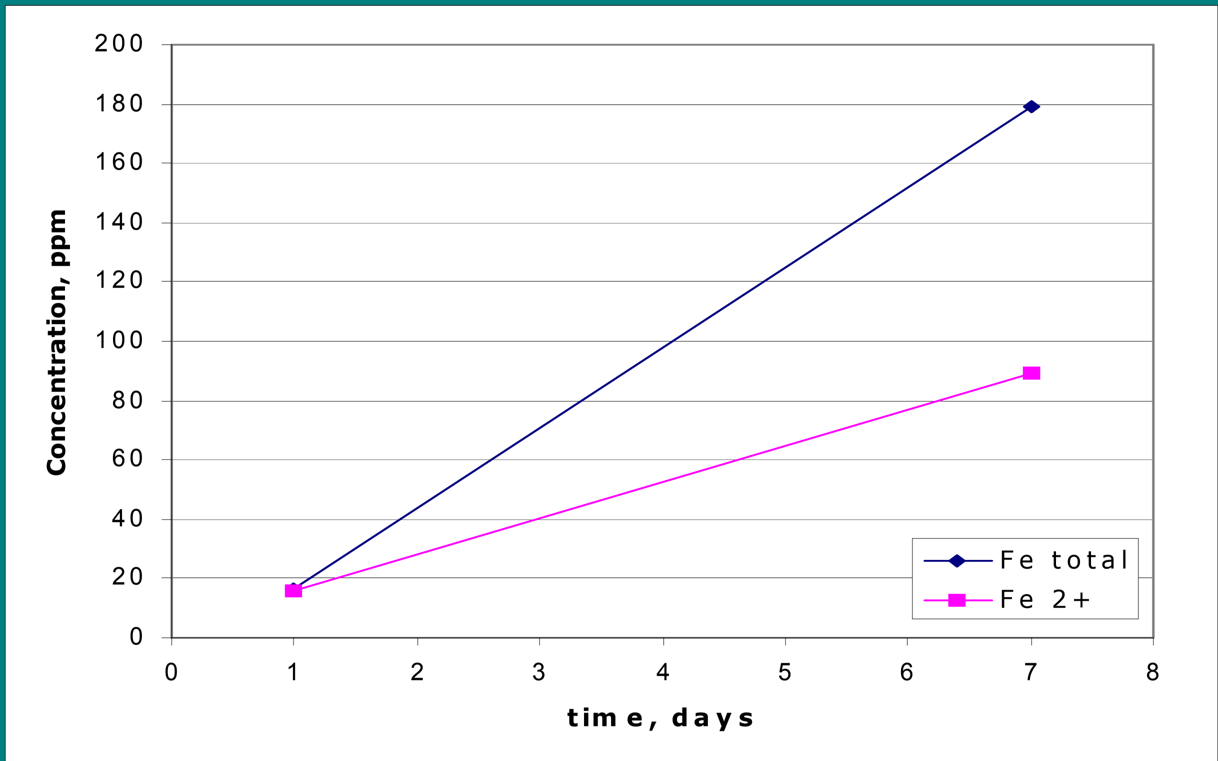
Preliminary results

Particle size distribution



Preliminary results

Experimental conditions		
T = 100 C P = 269 bar particle size = 38x150 100% CO_2 solids concentration = 25 g/L stirring speed = 350 rpm		
time, days	final pH	mass removal, wt %
1	5.25	1.5
7	5.43	5



Conclusions

- Experimental work is needed to assess the ferric-iron bearing sediments potential to become effective reservoirs for underground CO_2 storage.
- A state-of-the-art experimental set-up has been designed and assemblaged to test previous theoretical work.
- Different iron oxide samples have been obtained and characterized as well as other silicate samples already considered for CO_2 sequestration.
- This research will provide empirical and novel data concerning CO_2/SO_2 injection into saline aquifers with different rock formations.
- Data will help validation of the different geochemical simulations already conducted within the acid gas injection research field.

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