# Recent Investigations into Mineral Carbonation





## **Strategies to Sequester Carbon**

### Injection Processes

Enhance Natural Processes



### **Mineral Carbonation**



## **Mineral Carbonation**





Mineral carbonates

Material fluxes and process steps associated with the ex-situ mineral carbonation of silicate rocks or industrial residues (Energy Research Centre of the Netherlands (ECN)).

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### **Research highlights**

M. Maroto-Valer, D. J. Fauth, M.E. Kachta, Y. Zhang, J.M. Andresen *Fuel Processing Technology* 86 (2005) 1627-1645

- Previous studies (solid-gas interaction)
- Raw serpentine (7% wt increase. 155°C and 126 atm for 1 hour)
- Physical and chemical activation (Steam activated serpentine 60% wt increase).

•Sulphuric acid wash of serpentine (carbonation of Mg(OH)<sub>2</sub> solution at 20<sup>o</sup>C and 45 atm)

 $Mg_{B}Si_{2}O_{5}(OH)_{4} + 3H_{2}SO_{4} \rightarrow 3Mg^{2+} + 3SO_{4}^{2-} + 2SiO_{2} + 5H_{2}O_{4}$ 

 $Mg^{2+} + SO_4^{2-} + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$ 

 $Mg(OH)_2 + CO_2 + H_2O \rightarrow MgCO_3 + 2H_2O$ 

G. Alexander, M. Maroto-Valer, P Gafarova-Aksoy Fuel 86 (2007) 273-281

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Ferric iron-bearing sediments versus mafic rocks Susana Garcia PhD studies

 $(Mg, Ca)_x Si_y O_{x+2y} + xCO_2 \rightarrow x(Mg, Ca)CO_3 + ySiO$ 

 $Fe_2O_3$  (hematite) + 2 CO<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O  $\leftrightarrow$  2 FeCO<sub>3</sub> (siderite) + H<sub>2</sub>SO<sub>4</sub>

Widespread geographic distribution & great thickness
High porosity (storage potential) and permeability (injectivity requirements)

Increasing interest in co-injection processes



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### **Chemical Equations**

 $Fe_2O_3$  (hematite) + 2 CO<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O  $\leftrightarrow$  2 FeCO<sub>3</sub> (siderite) + H<sub>2</sub>SO<sub>4</sub>  $\Delta G_{R} < 0$ **2FeOOH** (goethite) + 2 CO<sub>2</sub> + SO<sub>2</sub>  $\leftrightarrow$  2 FeCO<sub>3</sub> (siderite) + H<sub>2</sub>SO<sub>4</sub>  $\Delta G_{P} < 0$ 

- **Reaction steps** ٠
- 1. Dissolution process

 $CO_2$  (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. Reduction process

$$4 \text{ SO}_2(g) + 4 \text{ H}_2\text{O}(I) \leftrightarrow \text{H}_2\text{S}(aq) + 3 \text{ H}_2\text{SO}_4 (aq)$$
$$\text{H}_2\text{S} \leftrightarrow \textbf{HS}^- + \text{H}^+$$

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

3. Carbonation process

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

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#### Modeling

- Thermodynamic model
- •Sediment systems
- $\bullet CO_2 SO_2$  gas mixture
- Aqueous phase
- Rock and precipitates

#### Two model-cases:

First model-case: 0.5m NaOH is added to simulate natural mineral buffering of pH.

Second model case: no NaOH is added.



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#### T=150 °C, P=300bar, 10g of goethite, 150mL of 1.0m NaCl solution

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First model-case: 0.5m NaOH is added

Second model-case: no NaOH is added



### Experimental

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### Experimental setup





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#### Conclusions

# Ferric iron-bearing minerals could have a great potential to geologically sequester CO<sub>2</sub> into a carbonate form:

✓ They offer several advantages vs sediments considered so far.

✓ Sulfur dioxide, SO<sub>2</sub>, could then be co-injected with CO<sub>2</sub> instead of expensively separated from the flue gas stream.
 ✓ Learning experience on injection of contaminants in subsurface repositories.

Thermodynamic equilibrium simulations have been performed and predict that siderite is the stable phase at equilibrium.

The influence of different reaction variables (P,T, time,  $CO_2/SO_2$  ratio, particle size, solids concentration) has been assessed:

✓ State-of-the-art experimental set-up designed and developed for the studies.

Effect of reaction time is crucial and very promising results are reported if they were to be extrapolated to a real-case scenario.
 Methodology can be applied to other potential host rocks.



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