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SUSTAINABLE INORGANIC MATERIALS MANAGEMENT

Innovation Concepts

Opportunities and developments on the intensification of chemical and geochemical processes by gravity pressure vessel technology

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ECCE9 ECAB2

Fourth European Process Intensification Conference
(EPIC 2013)

EFCE Working Party on Process Intensification

Outline

- Working principle
- History
- Opportunities under consideration
  - Mineral carbon sequestration
  - Asbestos remediation
  - Oil sand tailings treatment
- Developments of Innovation Concepts

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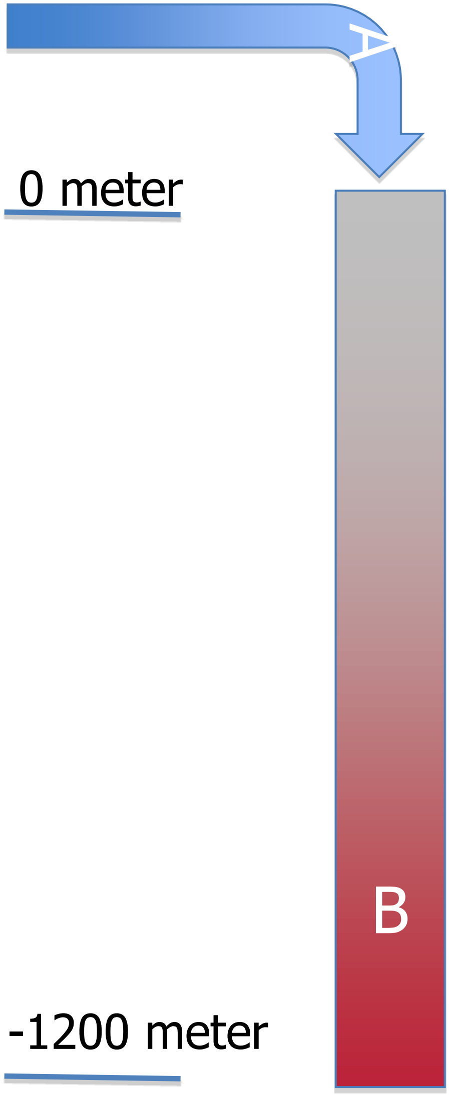
Working Principle

- Gravity pressure vessel (GPV) step by step

GPV 1



A: Incoming material

B: DownComer tube

Pressure increases

Pre-heating medium

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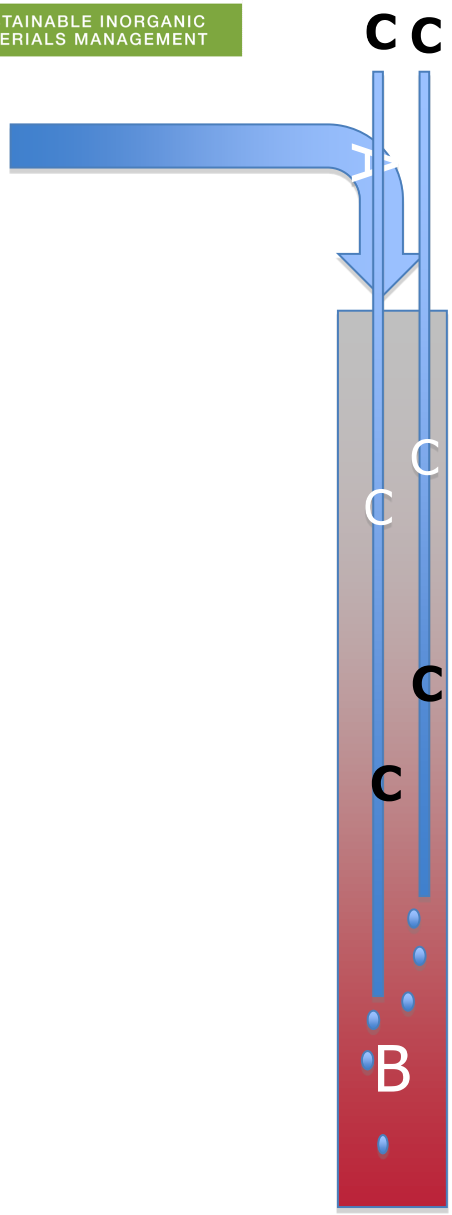
GPV 2

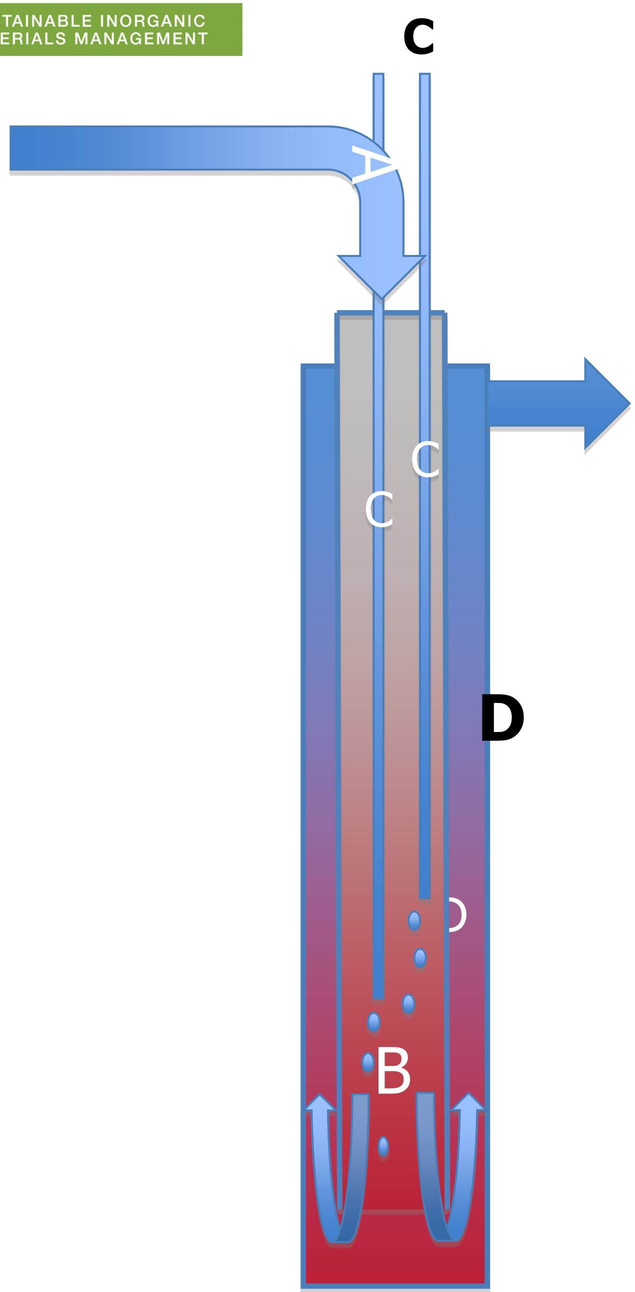


A: Incoming material

B: DownComer tube

C: Gas injection
Exothermic reaction -> Energy production

GPV 3



A: Incoming material

B: Downcomer tube

C: Gas injection

D: Upcomer tube:

- Releases energy to downcomer
- Pressure decreases
- Leaves the reactor

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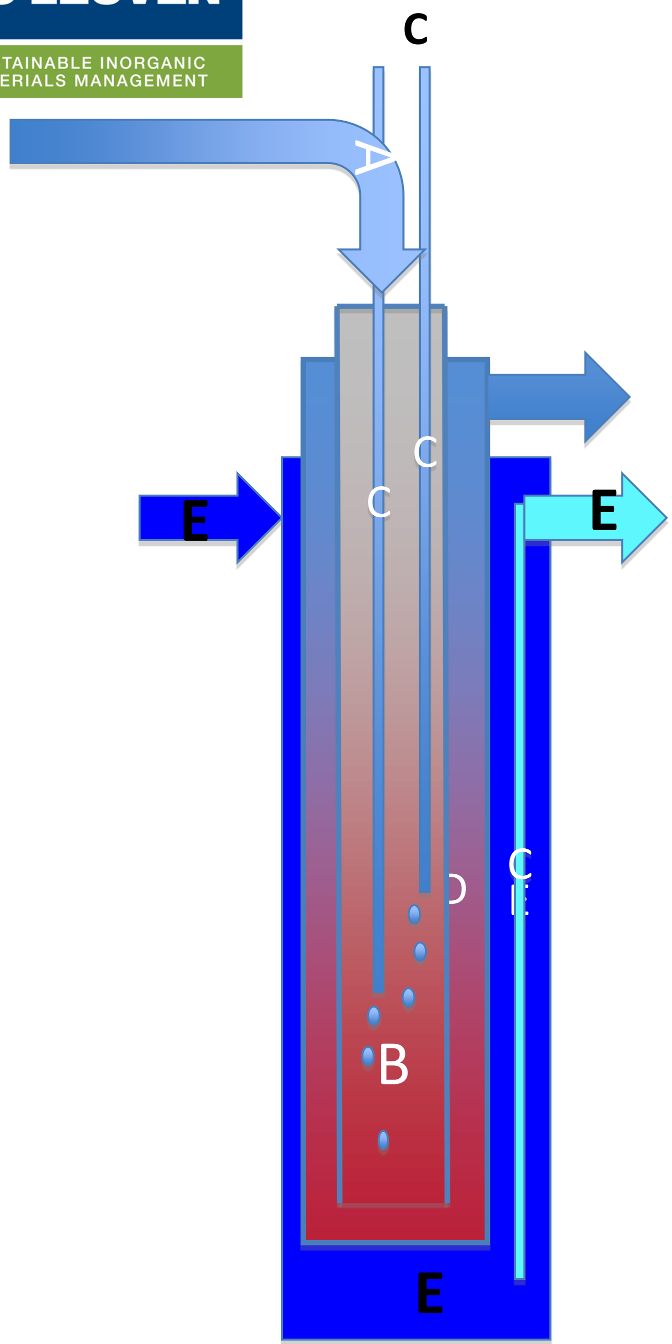
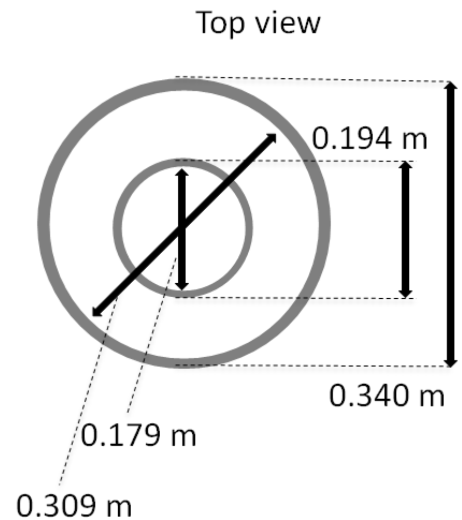
GPV 4





A: Incoming material

B: Downcomer tube

C: Gas injection

D: Upcomer tube:

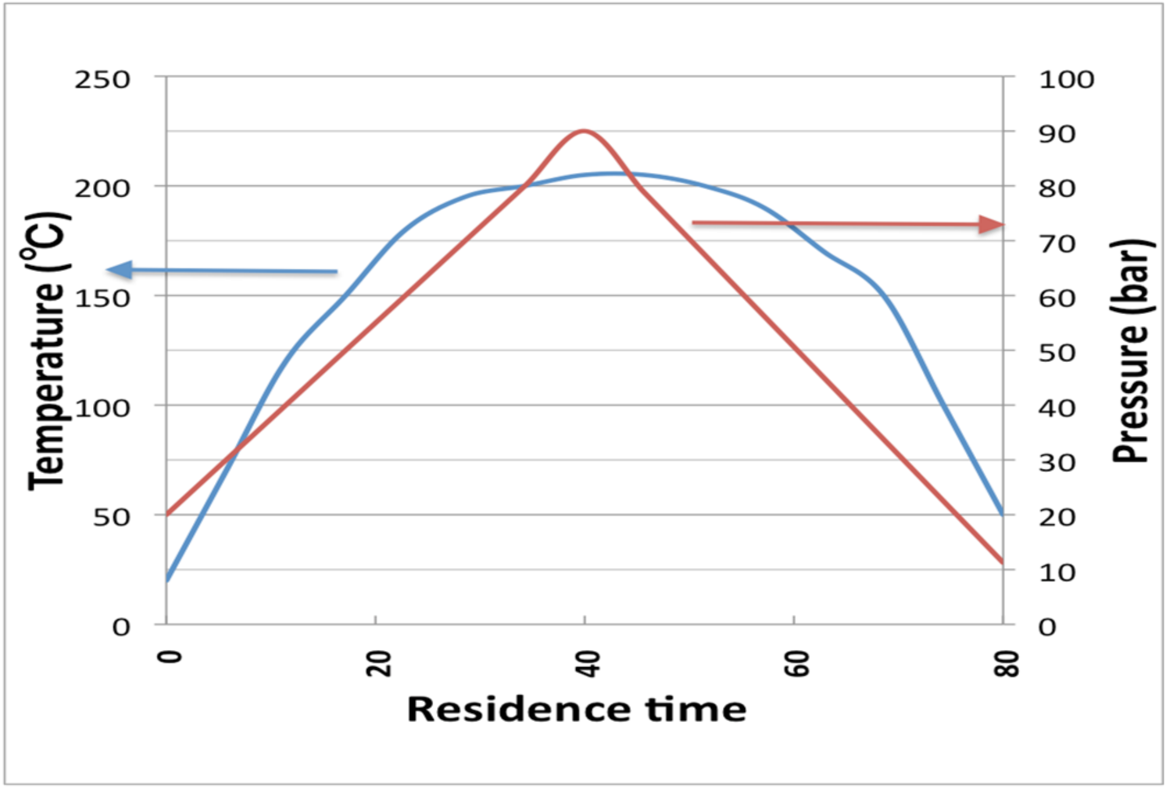
E: Surrounding tube

Start-up heating (ignition).

Steady-state (autothermic) cooling and energy harvesting.

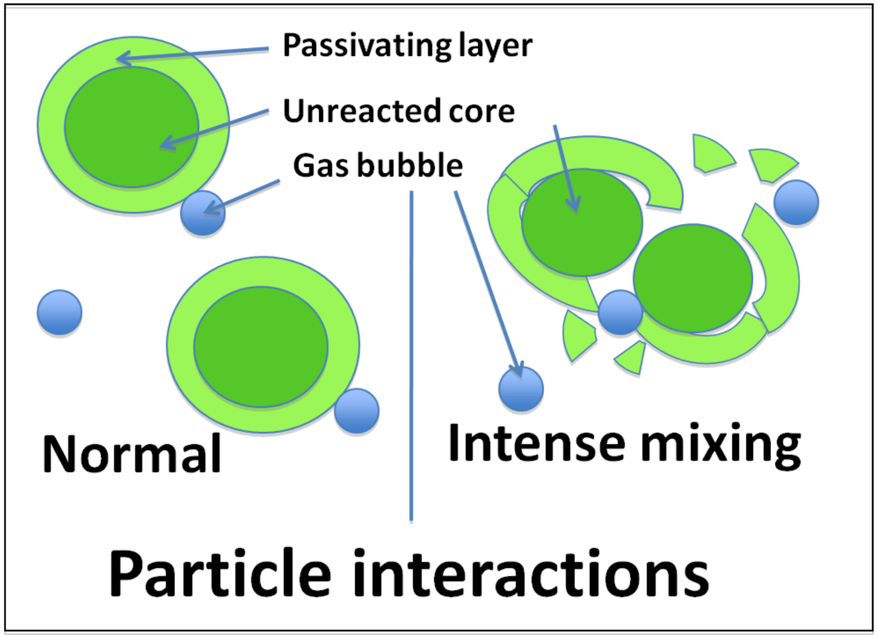
Advantages

- <u>built-in heat exchanger</u>: heat conservation, utilization and recovery.
- <u>hydrostatic pressurization</u>: low energy demand.



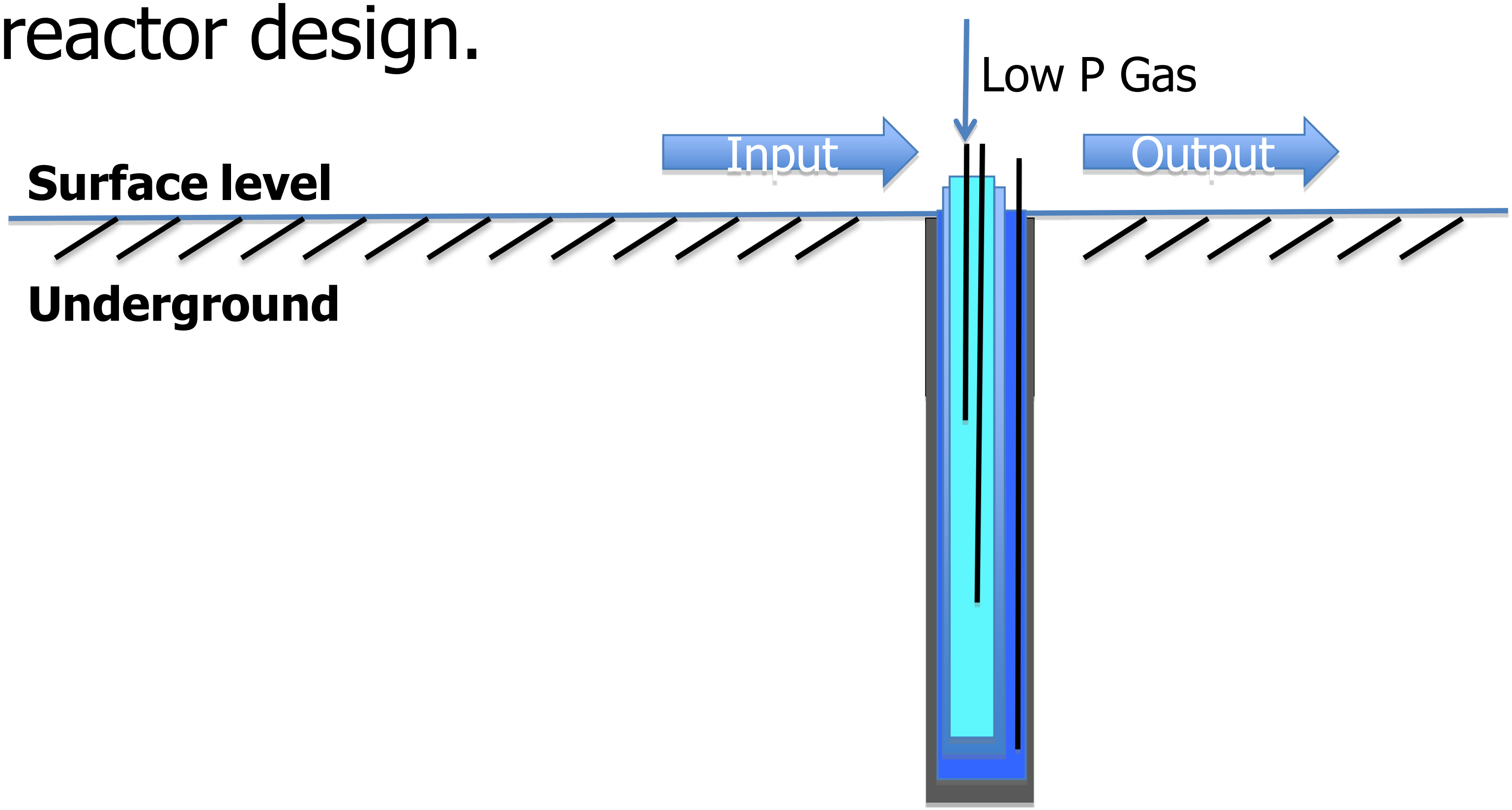
Advantages

- <u>turbulent three phase flow</u>: promotes heat and mass transfer, autogeneous milling and passivating layer erosion.



Advantages

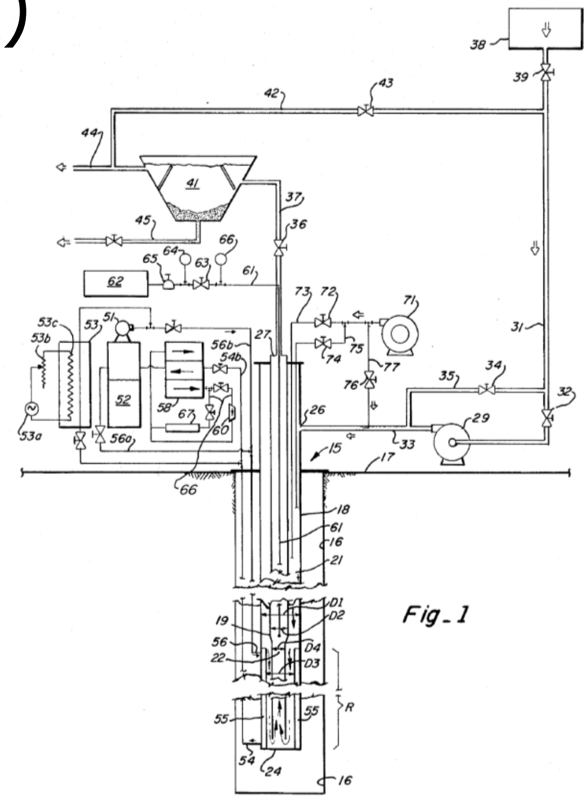
- <u>plug flow configuration</u>: continuous process, no moving parts.
- <u>underground installation</u>: safe/inexpensive reactor design.



History

- Patent 4,272,383, McGrew (1981)
  "Method and apparatus for effecting subsurface, controlled, accelerated chemical reactions"

- Sewage Sludge Wet Oxidation:
  – Longmont, Colorado (USA)
    - Moved to Apeldoorn
  – Apeldoorn (The Netherlands)
    - VerTech process
    - 1992-2004



US 4,272,383

History

- VerTech Process

Throughput	120 m^3/hr
Energy production Recovery	9.5 MW(th) 50% @ 260 °C
Energy density	340 J/kg
Gas injection	O_2: 2.4 tonne/hr
Max. temp Depth	270 °C 1200 m

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Installation

- Conventional drilling: Straight, 30”

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Commissioning

Opportunities

- Identification:
  - Accelerate reaction kinetics.
  - Integrate and recover exothermic reaction heat.
  - Valorize low value residues into products.

- Approach:
  - Focus towards full scale installation.
  - Build on existing R&D.
  - Harvest past experience.

Opportunities

- **Mineral carbon sequestration**:
  - Natural minerals: olivine, wollastonite, serpentine.
  - Industrial residues: slags, ashes, tailings.

- **Waste remediation**:
  - Asbestos containing-materials (mining tailings and construction materials).
  - Oil sand tailings.

Mineral Carbon Sequestration

- **Olivine:**

  $(Mg,Fe)_2SiO_4 + 2CO_2 \Rightarrow 2(Mg,Fe)CO_3 + SiO_2$

  [ΔH = **-89 kJ/mol CO_2**]

- **Wollastonite:**

  $CaSiO_3 + CO_2 \Rightarrow CaCO_3 + SiO_2$

  [ΔH = **-87 kJ/mol CO_2**]

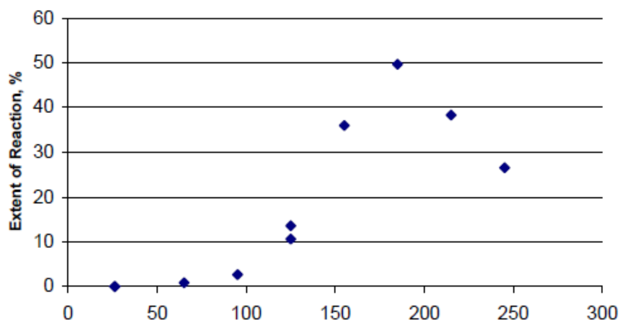
- **Serpentine:**

  $Mg_3Si_2O_5(OH)_4 + 3CO_2 \Rightarrow 3MgCO_3 + 2H_2O + 2SiO_2$

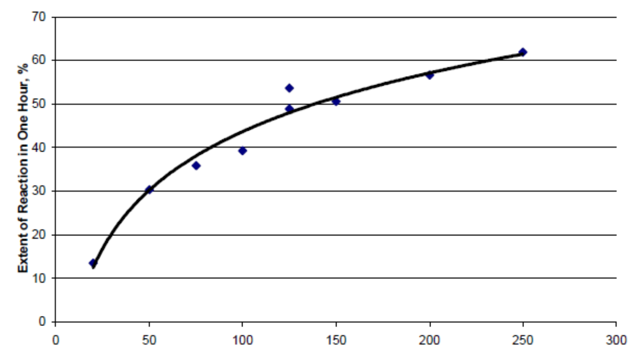
  [ΔH = **-64 kJ/mol CO_2**]

Mineral Carbon Sequestration

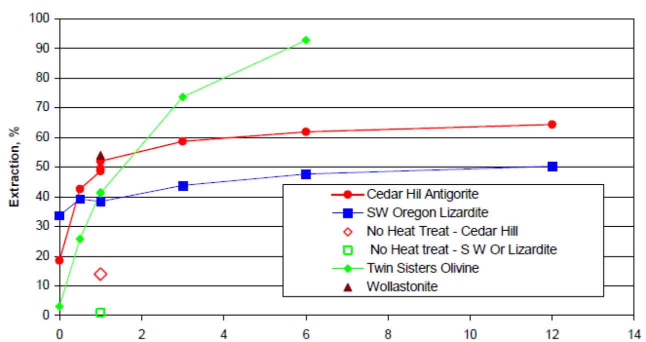
- Reaction rate



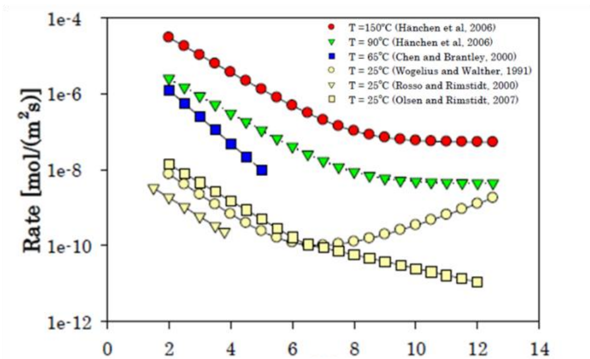
Temperature (°C)



Pressure (atm)



Time (hr)

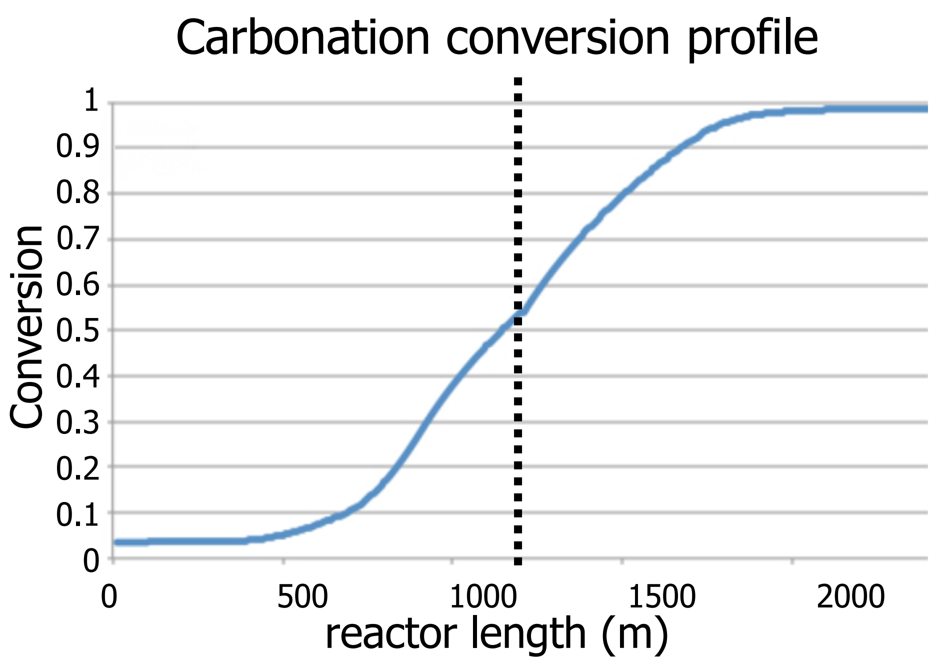


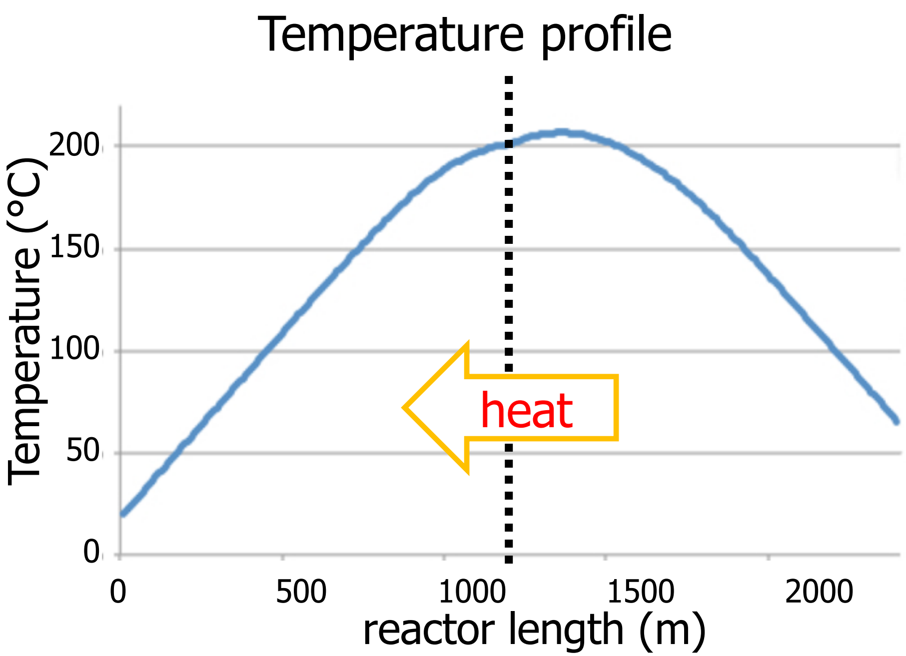
pH

T.A. Haug, 2010. *PhD Thesis*, NTNU.
S.J. Gerdemann et al., 2003. *Second Annual Conference on Carbon Sequestration,* Alexandria, VA, USA.

Mineral Carbon Sequestration

- Reaction profile





10 µm, 0.7 kg/kg

R.M. Santos et al. 2012. *11th International Conference on Greenhouse Gas Control Technologies*, Kyoto, Japan.

Mineral Carbon Sequestration

- Autothermic map

Outlet carbonation conversion (%)

solids loading (kg,solids/kg,liquid)

particle diameter (µm)	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8	2
10	4%	5%	100%	99%	96%	92%	89%	85%	82%	79%
20	4%	4%	4%	85%	80%	76%	72%	68%	65%	62%
30	4%	4%	4%	4%	69%	65%	61%	58%	55%	53%
40	4%	4%	4%	4%	4%	57%	54%	51%	49%	47%
50	-	-	-	-	-	4%	49%	46%	44%	42%
60		-	-	-	-	4%	4%	42%	40%	39%
70		-	-	-	-	4%	4%	4%	37%	36%
80	-	-	-	-	-	4%	4%	4%	4%	34%

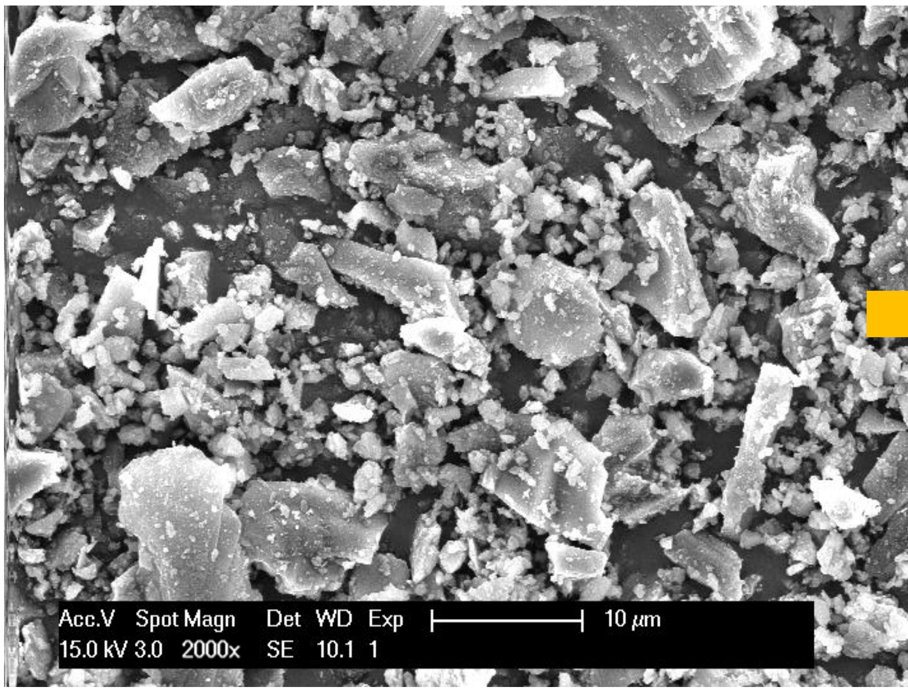
carbonation conversion

R.M. Santos et al. 2012. *11th International Conference on Greenhouse Gas Control Technologies*, Kyoto, Japan.

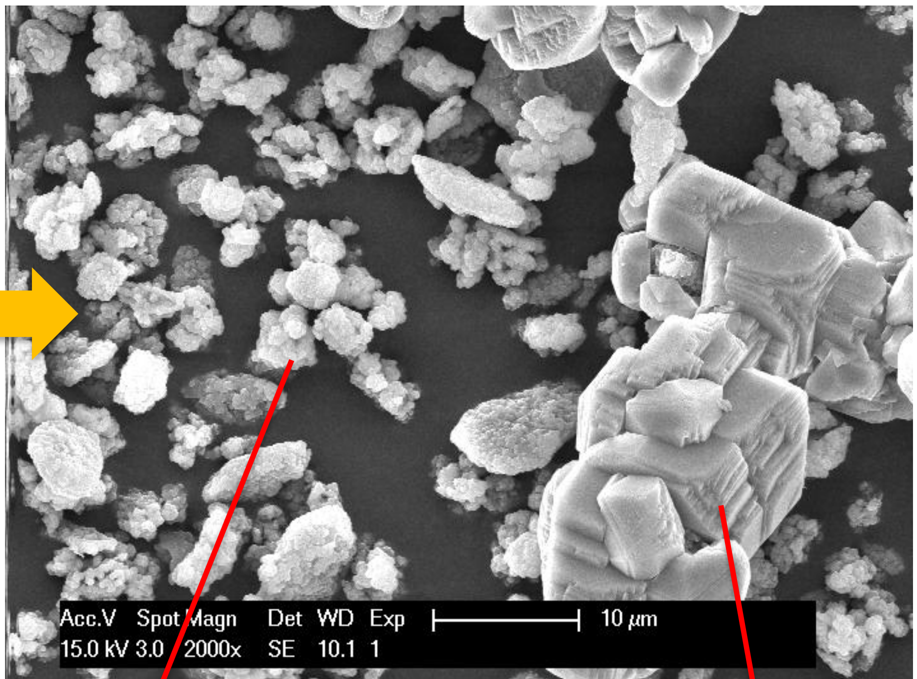
Mineral Carbon Sequestration

- Carbonation products

Fresh milled olivine



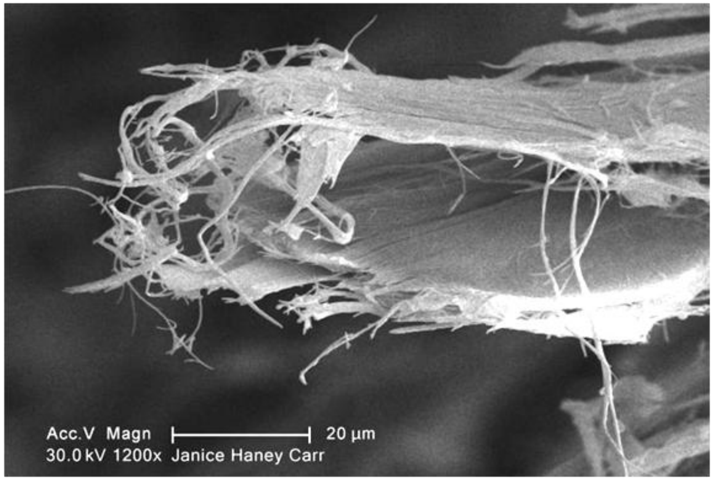
Fully carbonated olivine



amorphous silica (SiO_2) magnesite ($MgCO_3$)

Asbestos Remediation

- Chrysotile (white asbestos): $Mg_3(Si_2O_5)(OH)_4$
- Tremolite: $Ca_2Mg_5Si_8O_{22}(OH)_2$
- Fibre cement (historical): 90% cement, 10% chrysotile



http://en.wikipedia.org/wiki/File:
Chrysotile_SEM_photo.jpg

http://en.wikipedia.org/wiki/File:
Wellasbestdach-233-3354_IMG.JPG

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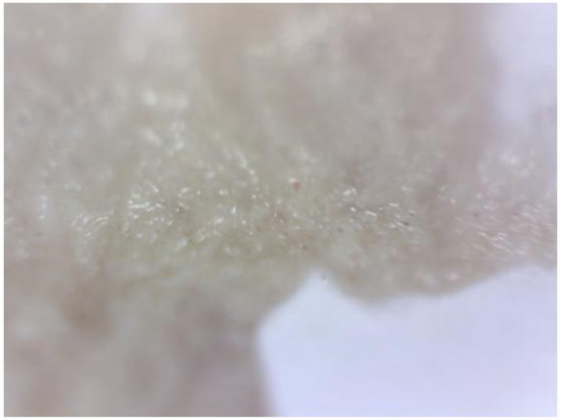
Asbestos Remediation



Original material

RPS: isolation material, 30-60%

XRD: 90% chrysotile, 4% chlorite

1 hour treated

RPS: carbonate, upper side 30-60%-interval

XRD: 80% chrysotiel, 16% carbonate, 1% pyroxene

5 hour treated

RPS: carbonate, lower side 30-60%-interval

XRD: 54% chrysotile, 25% carbonate, 13% pyroxene

Oil sand tailings Treatment

- Oil sand tailings: sand, clay, water and residual bitumen (‘tar’).
- MFT (Mature Fine Tailings) + O_2 =>

  TTT (Thermally Treaded Tailings)
- Aim:
  - reduce settling time;
  - oil and metals oxidation;
  - reduce contaminants leaching;
  - free water for re-use;
  - autothermic process.

http://en.wikipedia.org/wiki/File:
Syncrude_mildred_lake_plant.jpg

Oil sand tailings Treatment

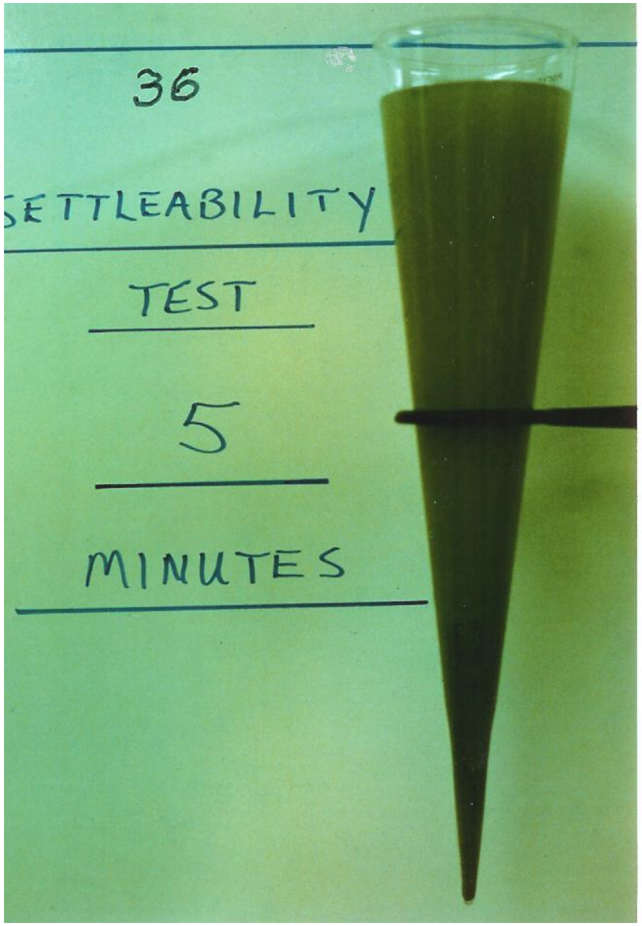
- COD reduction test

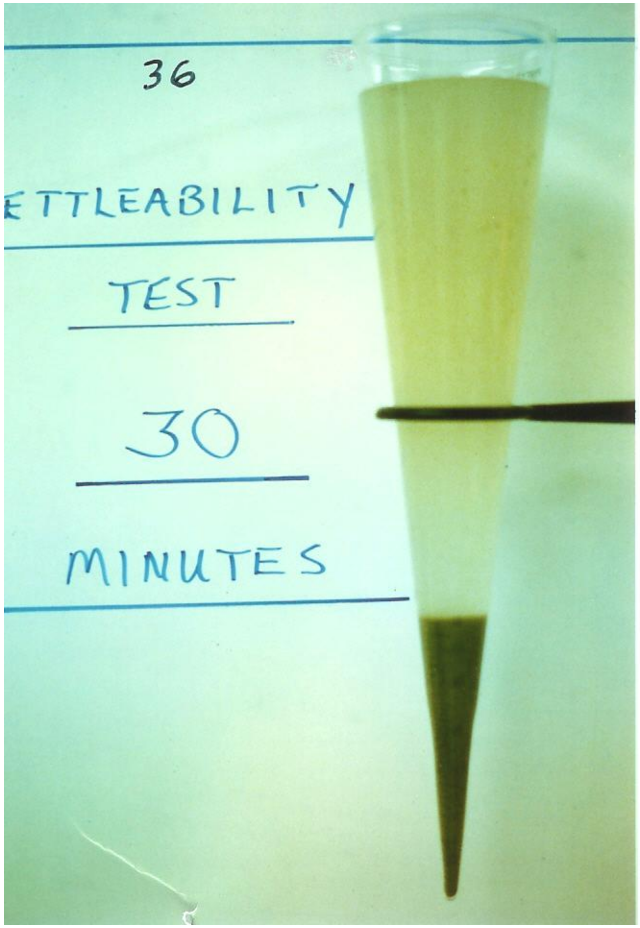
Temperature (°C)	350		300		250	
Time (min)	60	30	60	30	60	30
% COD reduction	86.3%	85.3%	82.9%	81.2%	70.6%	69.6%

P. Knops. 2011. *RemTech 2011*, Banff, Canada.

Oil sand tailings Treatment

- Settleability test





P. Knops. 2011. *RemTech 2011*, Banff, Canada.

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Developments

- Split into various stages:

✔ Patent application
✔ Batch autoclave
✔ Research consortium
☐ Continuous autoclave
☐ Pilot reactor
☐ Full scale

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(54) **Title**: METHOD FOR CONVERTING METAL COMPRISING SILICATE MINERALS INTO SILICON COMPOUNDS AND METAL COMPOUNDS

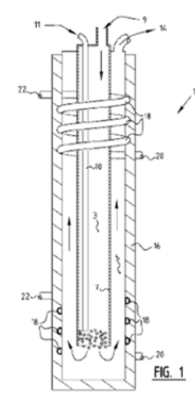

FIG. 1

(57) **Abstract**: Method for converting metallic silicate minerals to silicon compounds and metal compounds via a conversion reaction, characterized in that the conversion reaction is performed in a gravity pressure vessel (GPV), wherein: the GPV comprises two channels having separate entries on the upper side of the GPV and which channels are mutually connected on the bottom of the GPV, and wherein a dispersion of solid particles of the silicate minerals in water is carried into the GPV in a descending flow, one or more reactants for the conversion reaction are added to the dispersion, and the silicon compounds and metal compounds formed during the conversion reaction are carried away via an ascending flow of the GPV. The method provides a method for sequestration of carbon dioxide, wherein the heat produced can be utilized to form a concentrated gas flow of carbon dioxide prior to sequestration.

Developments

- Batch rocking autoclave (now under testing)

Simulate GPV characteristics:

- Tubular hydrodynamics.
- Transient T and P.

Generate fundamental understanding:

- Reaction rates.
- Particle exfoliation.
- Passivating layers.
- Product mineralogy.

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Developments

- Consortium agreement:
  - Sibelco (olivine producer) SIBELCO GLOBAL RESOURCES • LOCAL SOLUTIONS
  - Steel company (CO_2 producer)
  - Institute for Sustainable Process Technology (ISPT) ISPT
  - KU Leuven KU LEUVEN
  - Dutch University
  - Innovation Concepts (technology holder) Innovation Concepts

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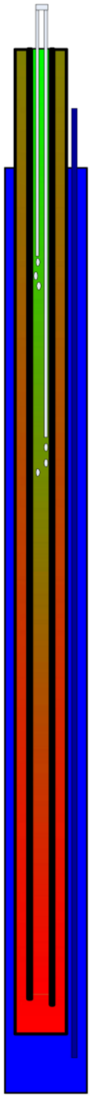

What else can a GPV intensify?

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Thank you for your attention!