CO_2 Sequestration in Mining Residues – Probing Heat Effects Associated to Carbonation

By MSc student
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and Prof. Georges Beaudoin

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Content

- Raison d’être du travail / Purpose of the project
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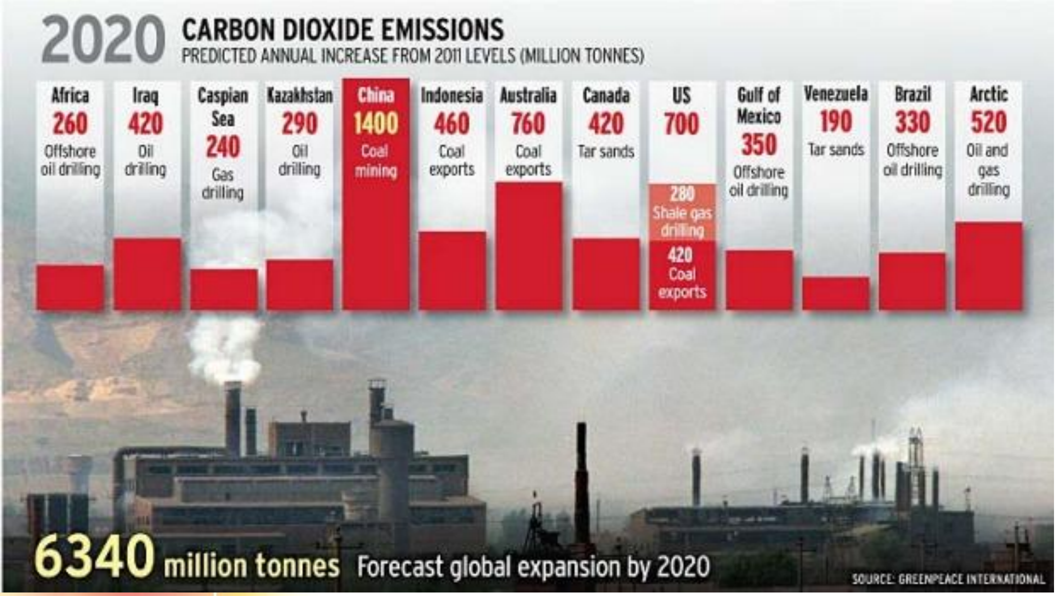
- Description du projet de thèse / Description of the project
- Méthodologie du projet proposé / Methodology
- Résultats préliminaires / First results
- Conclusion
- Échéancier envisagé / Education plan

Purpose of the project
CO_2 emissions



(http://www.smh.com.au/federal-politics/political-news/australian-coal-mining-threatens-co2-target-20130122-2d5ck.html)

March, 2016 – 404,83 ppm

If CO_2 emissions continue to rise, the enhanced greenhouse effect may permanently change the climate system in the world.

According to the IPCC association, an increase in the global average surface temperature more than 2^0C contains potential significant damage to the ecosystems upon which we depend directly.

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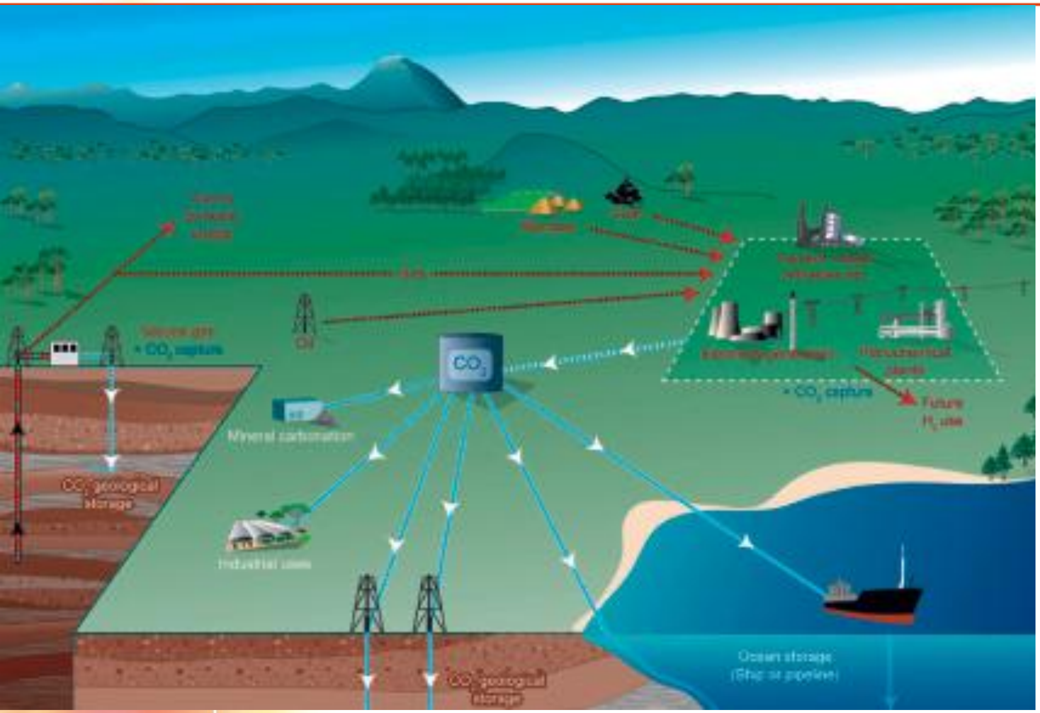
Literature review
CO_2 capture and storage



(IPCC Special Report on Carbon Dioxide Capture and Storage, p. 4)

Capture:

- Absorption (amines, carbonates, ammonia, hydroxide)
- Adsorption (metal organics, zeolites)
- Membranes (fibers, microporous)
- Bioligical (algae, cyanobacteria)

Storage:

- Geological
- Ocean
- **Mineral**

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Mineral sequestration

- **W. Seifritz,** *CO2 disposal by means of silicates (1990)*
- **H. Dunsmore,** *A geological perspective on global warming and the possibility of carbon dioxide removal as calcium carbonate mineral (1992)*
- **K. Lackner et al.,** *Carbon dioxide disposal in carbonate minerals (1995)*
- **O'Connor et al.,** *Carbon dioxide sequestration by direct mineral carbonation with carbonic acid (2000)*

Direct carbonation

Accomplished through the reaction of a solid alkaline mineral with CO2 either in the gaseous or aqueous phase

Indirect carbonation

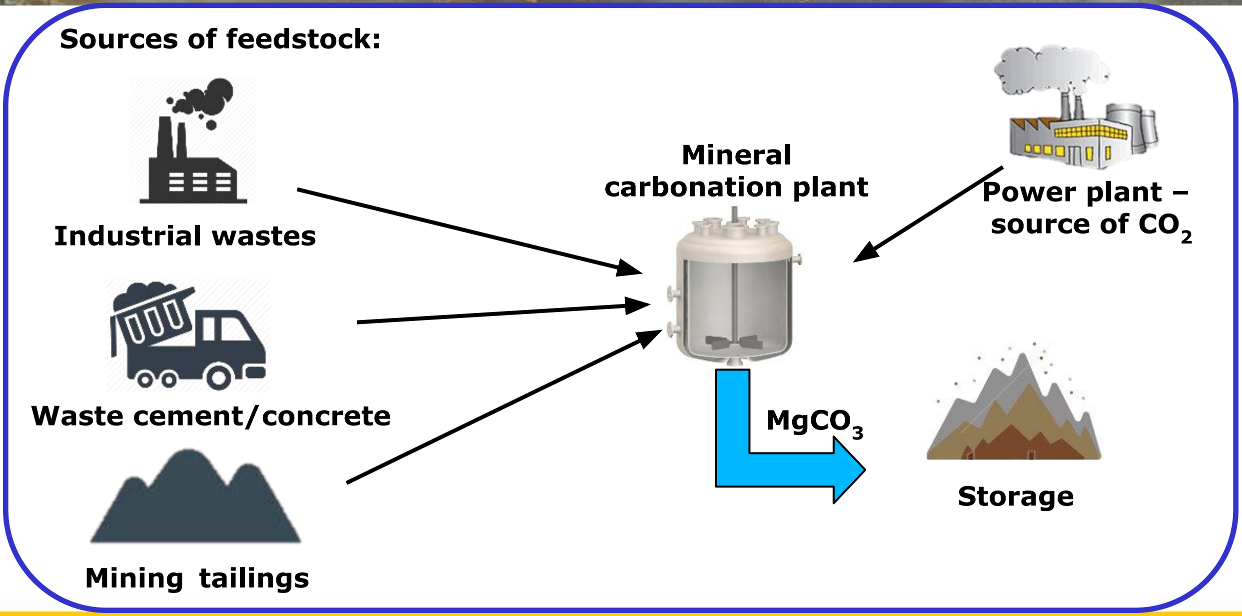
Involves the extraction of reactive components (Mg^{2+}, Ca^{2+}) from the minerals, using acids or other solvents, followed by the rection of the extracted components with CO_2 either in the gaseous or aqueous phase

A review of mineral carbonation technologies to sequester CO2 *(A. Sanna et al.)*
Carbon Mineralization: From Natural Analogues to Engineered Systems (*Ian M. Power et al.*),
Carbon Sequestration via Mineral Carbonation: Overview and Assessment *(H. Herzog)*

Active carbonation concept

- The Netherlands
- Finland
- Japan

- China
- U.S. and Canada
- Switzerland
- Australia



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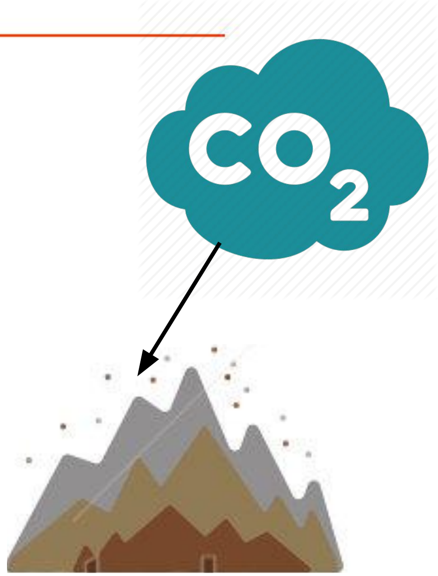
Accelerated Carbonation of Brucite in Mine Tailings for Carbon Sequestration *(Anna L. Harrison et al.)*
Passive offsetting of CO2 emissions at the Mount Keith Nickel Mine, Western Australia: A basis for geoengineering carbon neutral mines *(Siobhan A. Wilson et al.)*
Exploring The Mechanism That Control Olivine Carbonation Reactivity During Aqueous Mineral Carbonation *(Michael J. McKelvy et al.)*

Passive carbonation by tailings

1) Long term stability
2) Raw materials are abundant
3) Potential to be economically viable



1) Low speed of the process
2) No control under ambient conditions

A review of mineral carbonation technologies to sequester CO2 *(A. Sanna et al.)*
CO2-depleted warm air venting from chrysotile milling waste (Thetford Mines, Canada): Evidence for in-situ carbon capture from the atmosphere *(J. Pronost et al.)*

ULaval group

- **G. Assima:**

1) The presence of the T difference in a reactor between bed with NiMR and recirculating gas
2) Water content accelerates the process and leads to the bigger CO_2 capture
3) More alkaline carbonates are formed at elevated temperatures

- **J. Pronost:**

1) Hot-spots in the waste heap surface – the sign of the exothermic behavior of the reaction
2) Carbonation potential of ultramafic material depends on the brucite content

- **A. Entezari Zarandi:**

1) The rapid CO_2 uptake in the early minutes of reaction caused a sharp drop in pH
2) The highest carbonation reactivity is attained with 3% brucite doping of an already carbonated NiMR
3) Carbonation proceeds through formation of a porous flaky carbonate phase topping mainly the high-pH brucite surfaces

CO2 Sequestration in Chrysotile Mining Residues: Implication of Watering and Passivation under Environmental Conditions *(Assima, G. et al.)*
Fixation of CO2 by chrysotile in low-pressure dry and moist carbonation: Ex-situ and in-situ characterizations *(Larachi, F. et al.)*
Carbon sequestration kinetic and storage capacity of ultramafic mining waste *(Pronost, J. et al.)*
Multivariate study of the dynamics of CO_2 reaction with brucite-rich ultramafic mine tailings *(Entezari Zarandi, A. et al.)*

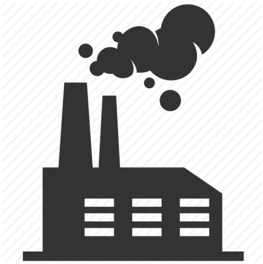
Description of the project
Primary challenge

(http://cdn1.buuteeq.com/upload/15348/asbestos-mine-tailings-mountain-1.jpg.1140x481_default.jpg)

What’s new?

Science 

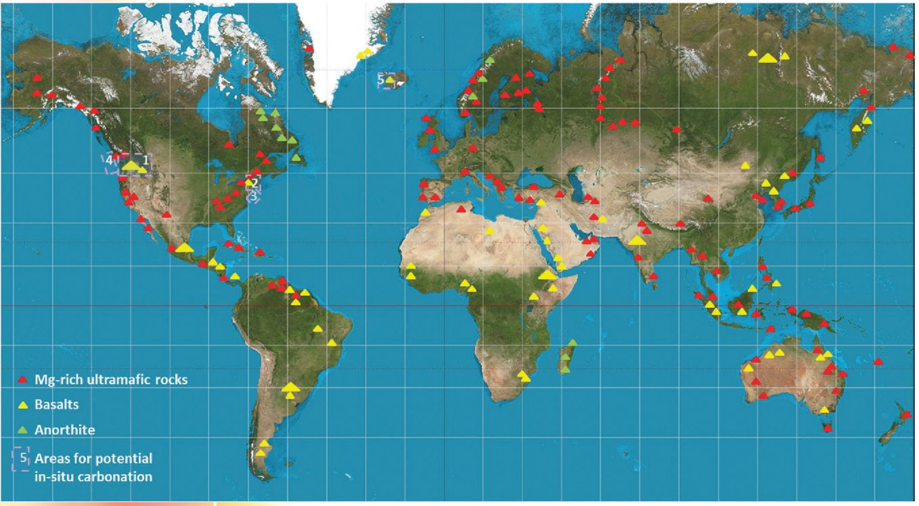
- Deep investigation of the ore behavior under ambient conditions by using IR thermography

Industry 

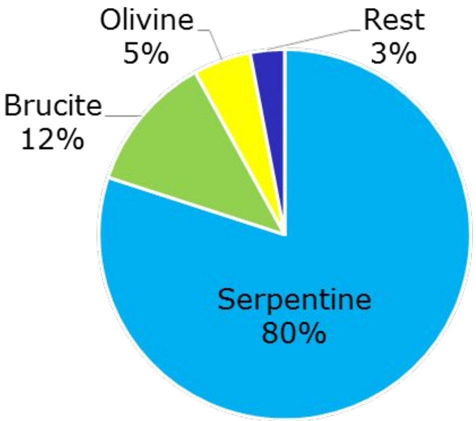
- The way to get back some energy and use it for an industrial needs

Mining tailings

Mafic and ultramafic residues are the best feedstock for the CO_2 sequestration.



(A review of mineral carbonation technologies to sequester CO2, www.rsc.org/csr)



- Serpentine group(Lizardite)~80-90%
- Brucite ~ 0-12%
- Olivine group (Forsterite) ~ 5%
- Rest ~ 3%

Group of minerals based on **Magnesium carbonate** is an environmentally stable and non-toxic.

Experimental procedure

(https://nuclear-news.net/information/wastes/)

Winter

- T = -20...0^0C
- H_2O sat.(snow)= 50...100%

Spring/Autumn

- T = 0...+15^0C
- H_2O sat.(rain) = 50...100%

Summer

- T = +15...+30^0C
- H_2O sat. (rain) =0...50%

Theoretical & real carbonation reactions

Brucite

$\mathbf{Mg(OH)_{2s}} + CO_{2g} = MgCO_{3s} + H_2O_l +$ (-81 kJ/mol CO_2)

$\mathbf{Mg(OH)_{2s} + CO_{2g} + 2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s +}$ **(-86 kJ/mol CO_2)**

-1,95 MJ/kg of CO2

Lizardite

$\mathbf{Mg_3Si_2O_5(OH)_{4s}} + 3CO_{2g} = 3MgCO_{3s} + 2SiO_{2s} + 2H_2O_l +$ (-64kJ/mol CO_2)

$\mathbf{2Mg_3Si_2O_5(OH)_{4s} + 3CO_{2g} + 6H_2O_l = 3(Mg(HCO_3)OH \cdot 2H_2O)_s + Mg_3Si_4O_{10}(OH)_{2s} +}$

(-72,4kJ/mol CO_2)

-1,64 MJ/kg of CO2

Forsterite

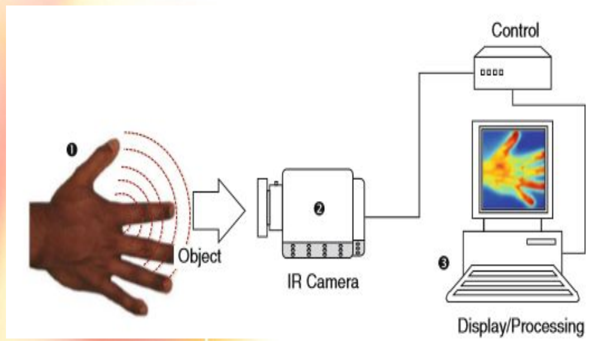
$\mathbf{Mg_2SiO_{4s}} + 2CO_{2g} = 2MgCO_{3s} + SiO_{2s} +$ (-90 kJ/mol CO_2)

$\mathbf{Mg_2SiO_{4s} + 2CO_{2g} + 6H_2O_l = 2(Mg(HCO_3)OH \cdot 2H_2O)_s + SiO_{2s} +}$ **(-91 kJ/mol CO_2)**

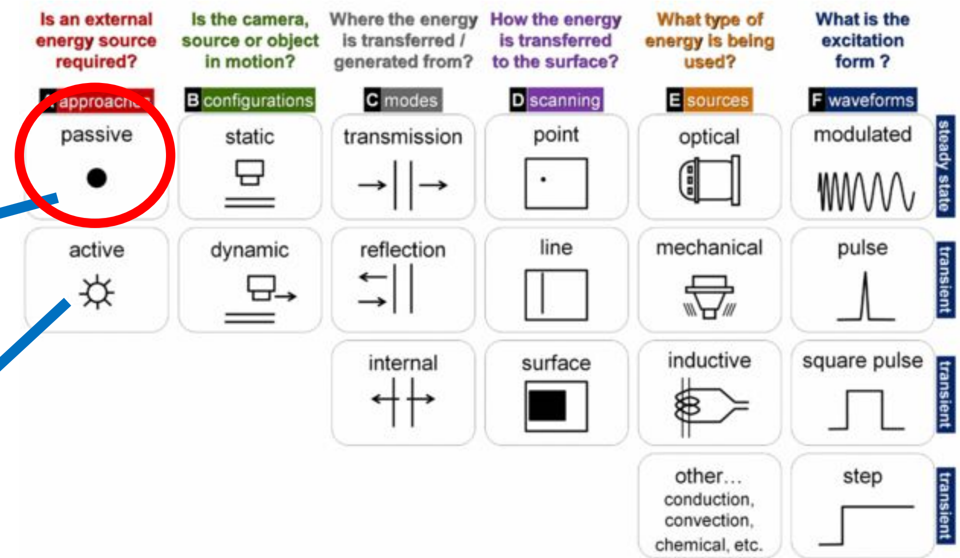
-2,07 MJ/kg of CO2

Infrared thermography

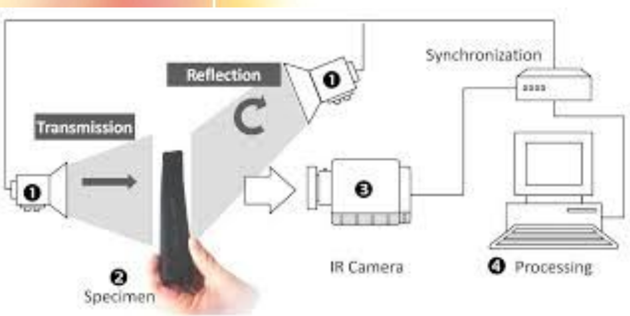
Radiation coming from the target object is measured without any external heat stimulation



(Infrared Thermography, C. Ibarra-Castanedo and X. P. V. Maldague, p. 178)



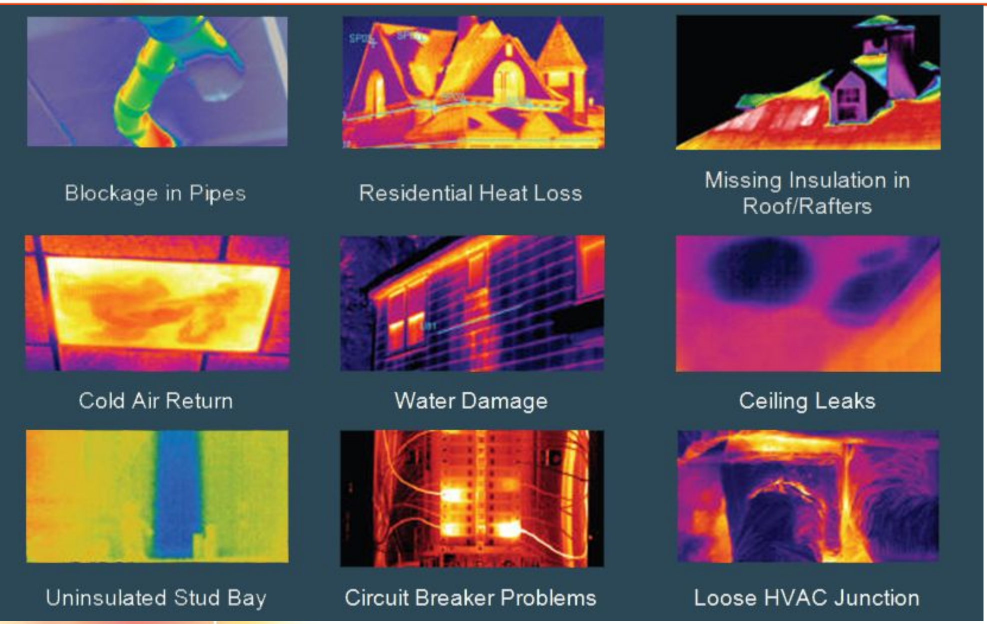
(Infrared Thermography, C. Ibarra-Castanedo and X. P. V. Maldague, p. 180)



Energy source is required to produce a thermal contrast between the feature of interest and the background

(Infrared Thermography for NDT: Potentials and Applications, X. P. V. Maldague, slide 19)

Infrared camera



(http://fiveboroughhomeinspection.com/inspection-service/infrared-camera-inspection-service/)

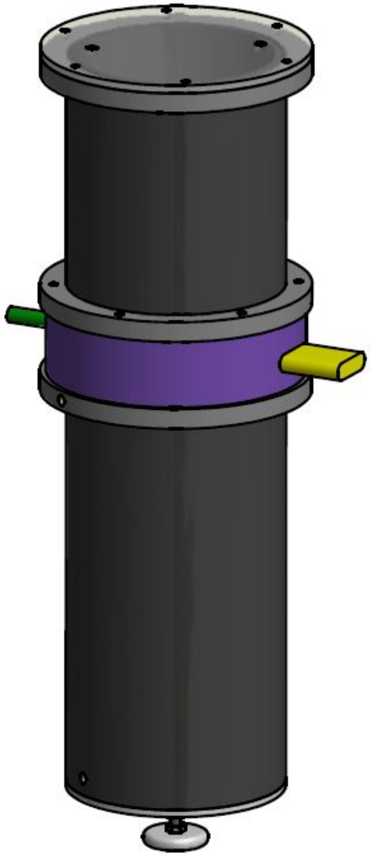
Indigo Phoenix Thermal Camera

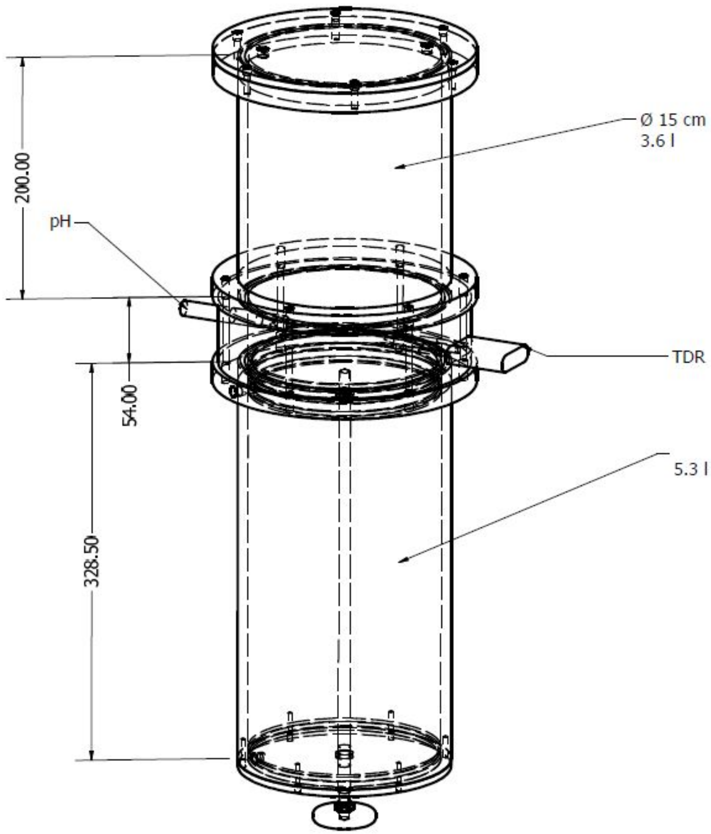
(http://www.flir.com/legacy/view/?id=51542)

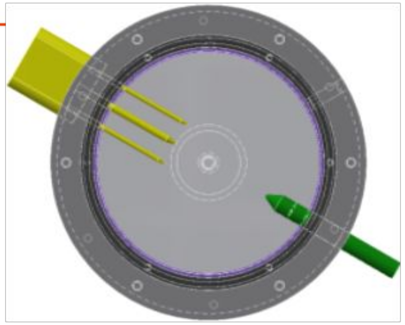
Thermal image data is colored up pixel by pixel based on $T^{0}C$.

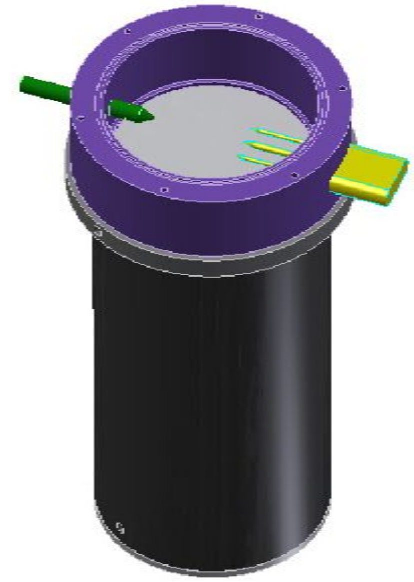
MATLAB

Methodology
Design of the setup

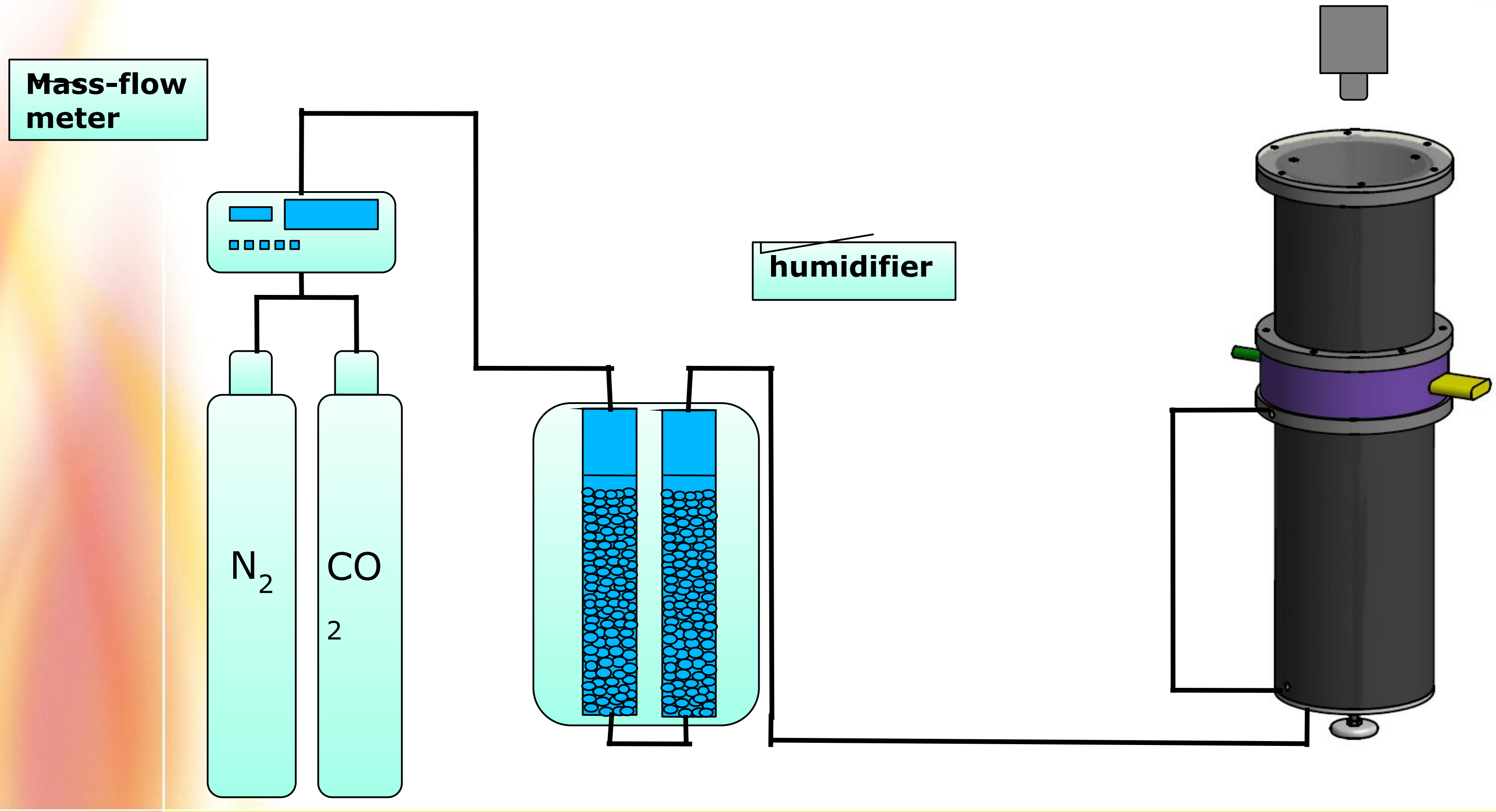








Carbonation setup



Chemistry of the laboratory process

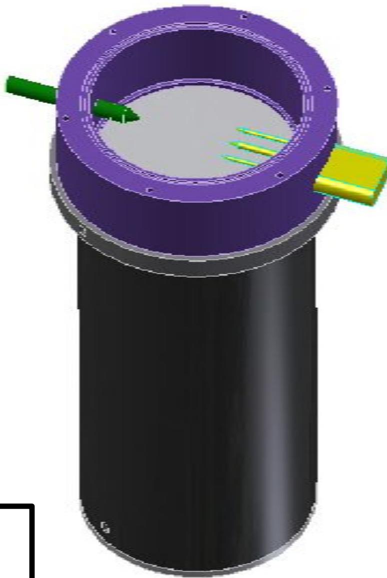
50 g of ORE + 0,047 mol of CO_2 (1,06 l), 50% water saturation :

	CO2, mol	Q, J	Cp(prod.), J/mol*K	ΔT, K
$\mathbf{Mg(OH)_{2s}}$ + CO_{2g} + $2H_2O_l$= $Mg(HCO_3)OH \cdot 2H_2O_s$ + **(-86 kJ/mol)**	0,0078	669,52	301,71	**2,22**
$\mathbf{2Mg_3Si_2O_5(OH)_{4s}}$+$3CO_{2g}$+$6H_2O_l$ =$3(Mg(HCO_3)OH \cdot 2H_2O)_s$ + $Mg_3Si_4O_{10}(OH)_{2s}$+ **(-72,4 kJ/mol)**	0,0234	1492,79	1226,84	**1,38**
$\mathbf{Mg_2SiO_{4s}}$ + $2CO_{2g}$ + $6H_2O_l$ =$2(Mg(HCO_3)OH \cdot 2H_2O)_s$ + SiO_2 + **(-91 kJ/mol)**	0,0156	1418,26	647,99	**2,19**

9 g of ore will react with 1,02 l of CO_2

Carbonation reaction with brucite

$$Mg(OH)_{2\,s} + CO_{2\,g} + 2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s$$



Laboratory conditions: ω(CO2) = 20%, T=298K,
50% saturation

V_{CO2} = 1,06 litres
n (CO_2) = 0,047 mol
$\Delta_r H$ = -85836 J/mol of CO_2
$Q = -\Delta_r H \cdot n$ = 4061,88 J
$Q = C_p \cdot \Delta T$

ΔT = 13,46K

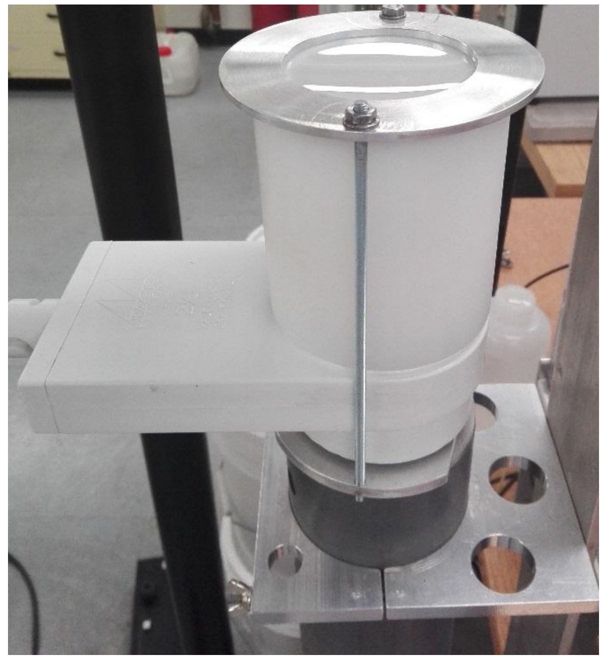
Ambient conditions(mine site):ω(CO2) = 400ppm, T=298K,
50% saturation

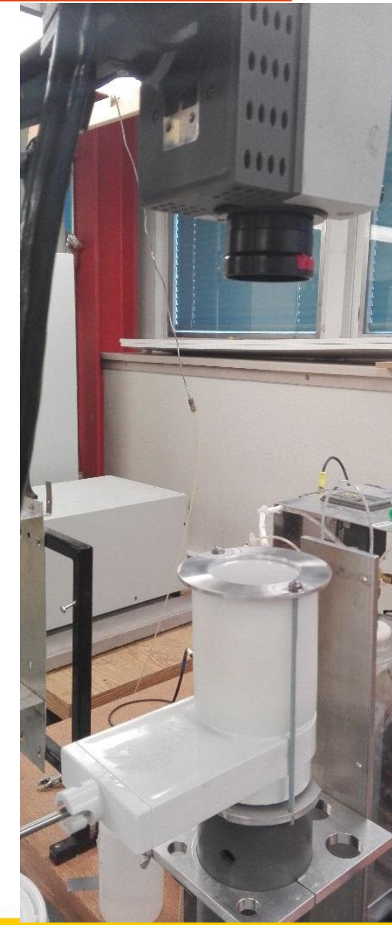
V_{CO2} = 0,00212 litres
n (CO_2) = $9{,}46 \cdot 10^{-5}$ mol
$\Delta_r H$ = -85836 J/mol of CO_2
$Q = -\Delta_r H \cdot n$ = 8,12 J
$Q = C_p \cdot \Delta T$

ΔT = 0,027K

V_{total} = 5,3 l

Reactor available in the laboratory of Prof. Larachi





Estimation for A. Entezari Zarandi setup

35 g of ore + 0,009 mol CO2 (50% water saturation)				
	CO2, mol	**Q, J**	**Cp(prod.), J/mol*K**	**ΔT, K**
$\mathbf{Mg(OH)_{2s}}$ + CO_{2g} + $2H_2O_l$= $Mg(HCO_3)OH \cdot 2H_2O_s$ + **(-86 kJ/mol)**	0,0015	128,75	301,71	**0,43**
$\mathbf{2Mg_3Si_2O_5(OH)_{4s}}$+$3CO_{2g}$+$6H_2O_l$ =$3(Mg(HCO_3)OH \cdot 2H_2O)_s$ + $Mg_3Si_4O_{10}(OH)_{2s}$+ **(-72,4 kJ/mol)**	0,0045	287,07	994,27	**0,26**
$\mathbf{Mg_2SiO_{4s}}$ + $2CO_{2g}$ + $6H_2O_l$ =$2(Mg(HCO_3)OH \cdot 2H_2O)_s$ + SiO_2 + **(-91 kJ/mol)**	0,003	272,74	647,99	**0,42**

Carbonation reaction with $Mg(OH)_2$

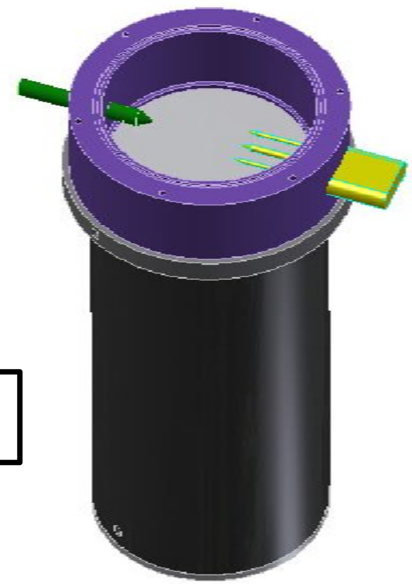
$$Mg(OH)_{2\,s} + CO_{2\,g} + 2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s$$

Laboratory conditions: ω(CO2) = 10%, T = 298K, 50% saturation

V_{CO2} = 0,2 litres
$n(CO_2)$ = 0,009 mol
$\Delta_r H$ = -94714 J/mol of CO_2
$Q = -\Delta_r H \cdot n$ = 766,39 J
$Q = C_p \cdot \Delta T$

ΔT = 2,54K

V_{total} = 2 l



Summary table for brucite

% CO_2	400ppm -ambient amount of CO_2	20% - new setup	10%- Ali's setup
V (total), l	5,3	5,3	2
V (CO_2), l	0,00212	1,06	0,2
Q, J	8,12	4061,88	766,39
ΔT, K	**0,027**	**13,46**	**2,54**

First results - Brucite

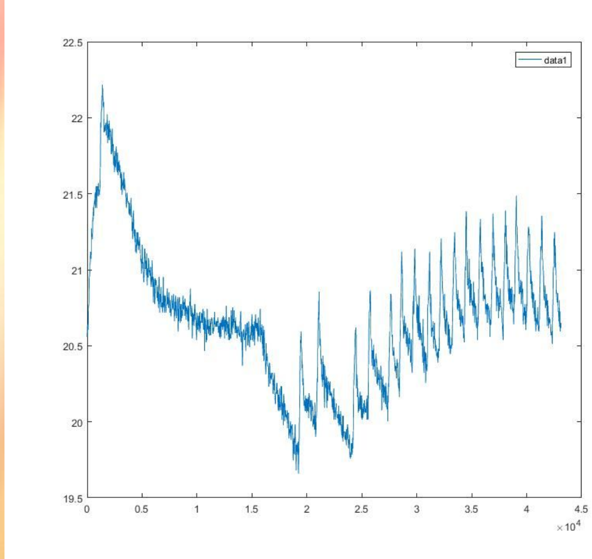
35g $Mg(OH)_2$ (11%)+SiO_2

- 5,25 ml of H2O = 50% sat.
- 9.69% of CO2
- Duration = 15 h
- 0.56% of CO2 left

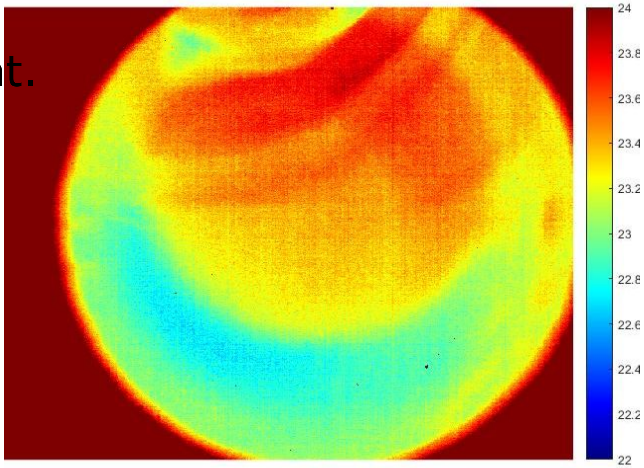
First results - ORE

35 g of the ore

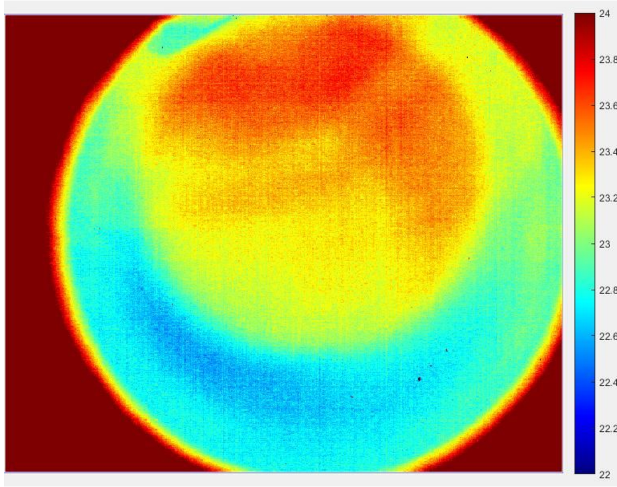
- 4,37 ml of H_2O = 50% sat.
- 9.83% of CO_2
- Duration = 9 h



15 min



30 min



33 min: T = 22.25 C, ΔT=1.65 C

Summary

- **Investigate**
- **Get**
- **Utilize**

Q

(http://cdn1.buuteeq.com/upload/15348/asbestos-mine-tailings-mountain-1.jpg.1140x481_default.jpg)

Education plan

	2016			2017
	Winter	Summer	Autumn	Winter
Literature search				
Experiments				
Courses	CHM- 6002		GCH-7011	GCH-6000 GIF-7006
Writing a thesis				

CHM-6002: Propriétés et réactivité des surfaces
GCH-7011: Planification et analyse des expériences
GCH-6000: Communication scientifiques orale et écrite I
GIF-7006: Vision en inspection industrielle

CO_2 Sequestration in Mining Residues – Probing Heat Effects Associated to Carbonation

By MSc student
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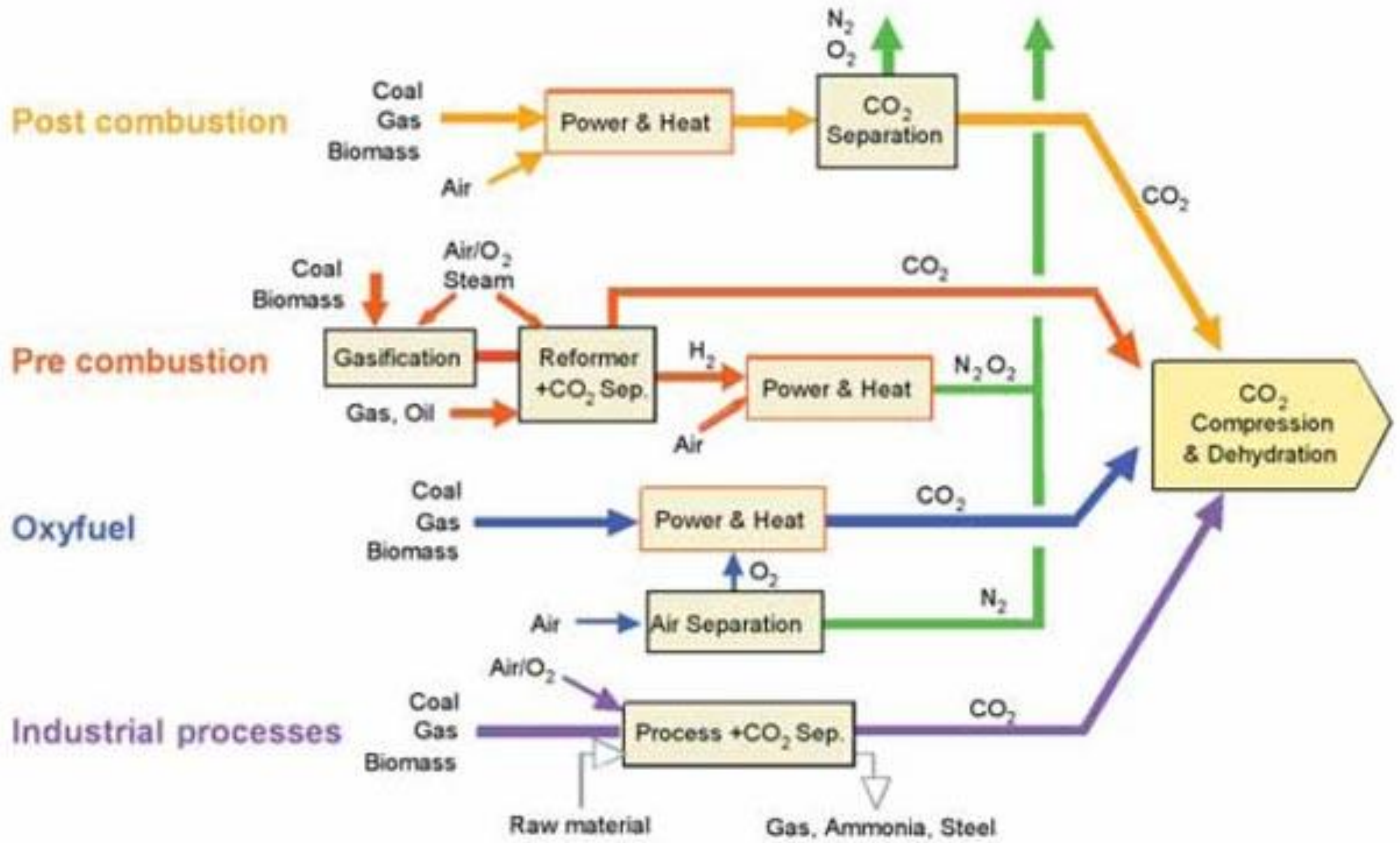
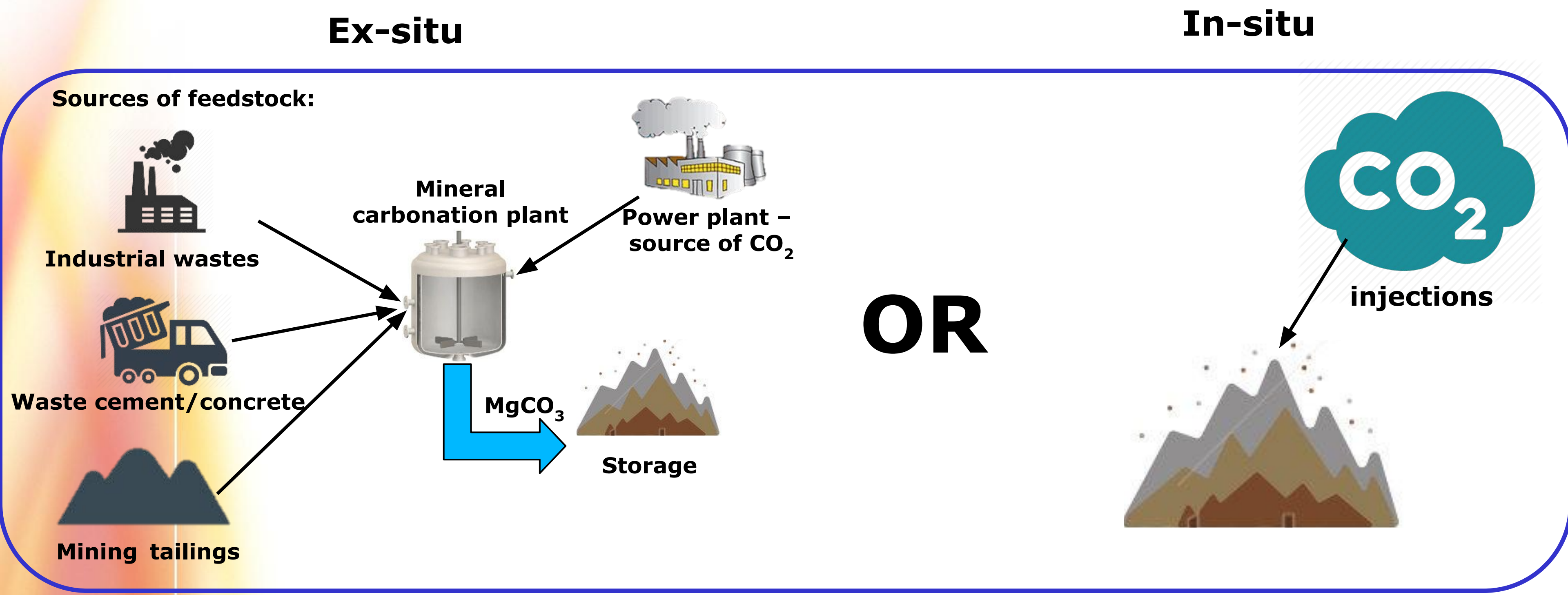
Questions

CCS



Carbon Dioxide Capture and Storage: Technical Summary (2005)

Active carbonation concept



Exploring The Mechanism That Control Olivine Carbonation Reactivity During Aqueous Mineral Carbonation *(Michael J. McKelvy et al.)*

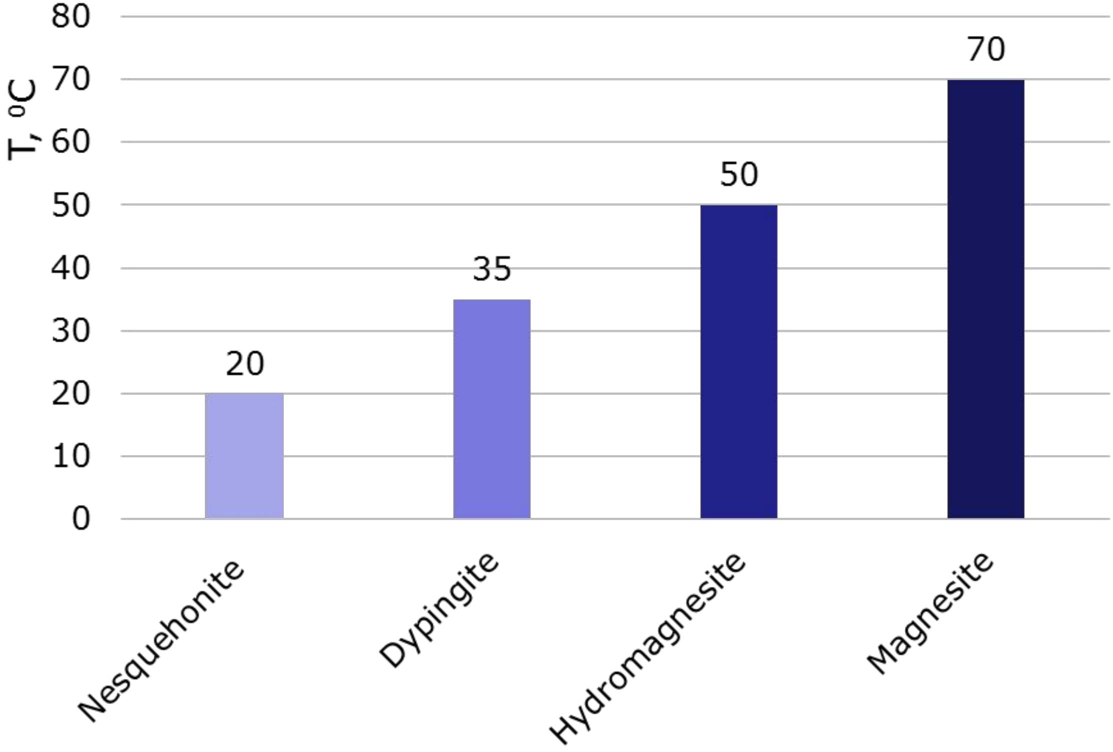
Reaction products of sequestration

$Mg(HCO_3)OH \cdot 2H_2O$

$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$

$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$

$MgCO_3$



(http://www.mindat.org/min-1979.html)

Mg^{2+} – series of the reactions

$$CO_{2(g)} \rightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$$

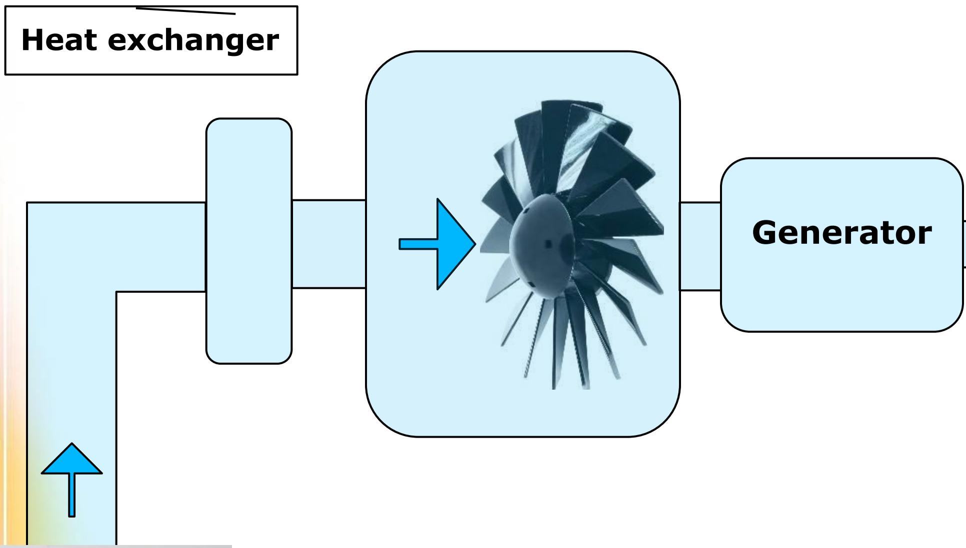
$$H_2CO_{3\ (aq)} \rightarrow H^+_{\ (aq)} + HCO_3^-{}_{(aq)}$$

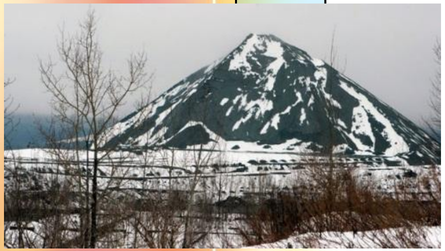
$$HCO_3^-{}_{(aq)} \rightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$Mg\ (OH)_{2(s)} + H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)} + OH^-_{(aq)}$$

$$Mg^{2+}_{(aq)} + HCO_3^-{}_{(aq)} + OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Mg\ (HCO_3)\ (OH)\cdot 2H_2O_{\ (s)}$$

Future investigations





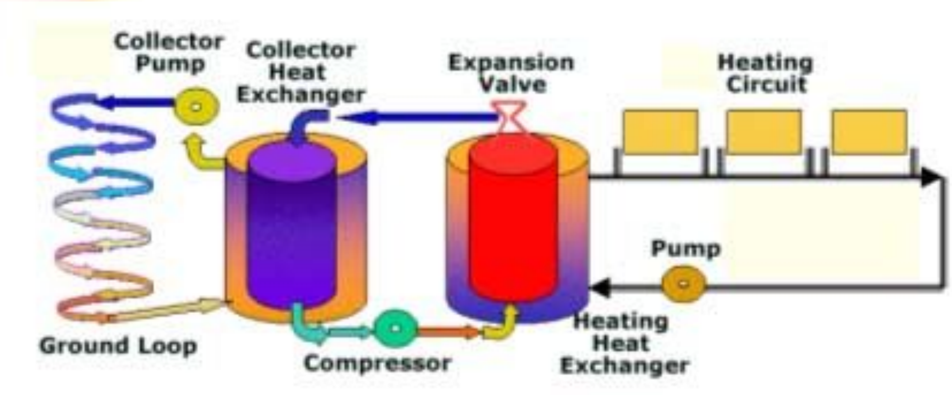
(http://www.ctvnews.ca/canada-s-last-asbestos-mine-about-to-run-out-of-asbestos-1.674045)

Geothermal heat exchangers underground loop (probes) or cluster geofield

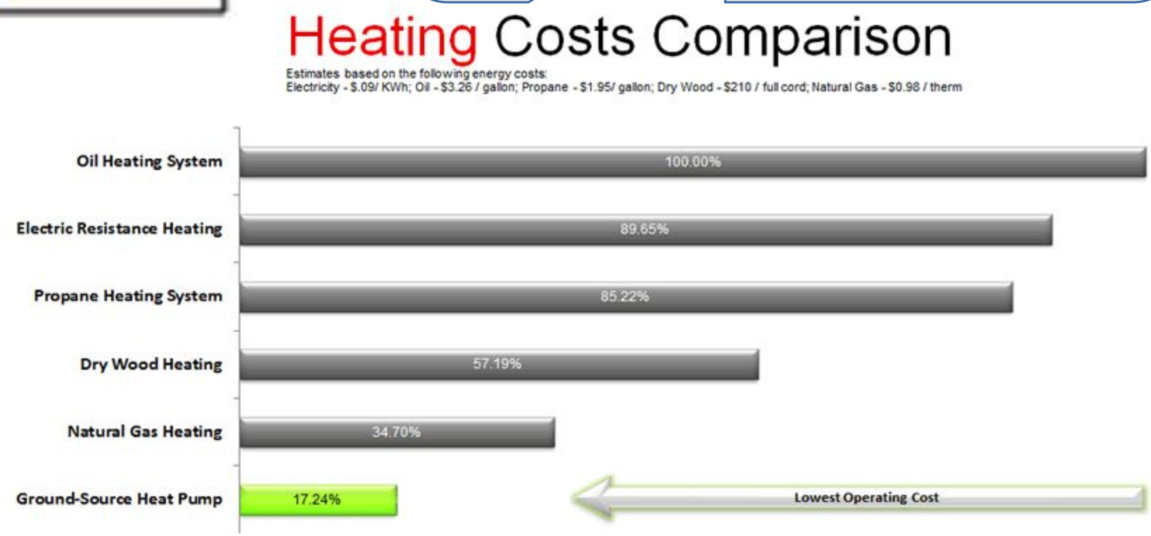
(http://www.geotherm.com.ua/about/closedloop/claster-loop.html)

Future investigations

Using the heat pump, 1 kW geothermal heat energy is converted into thermal energy in 4 kW and above,
there is an energy consumption - 25%



(http://www.diydoctor.org.uk/green-living/green-living-projects/ground-source-heat-pumps.htm)



(http://www.luxtherm.com/what-is-a-geothermal-heat-pump.html)

Detailed calculations for $Mg(OH)_2$

$$Mg(OH)_{2\,s} + CO_{2\,g} + 2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s$$

Mg(OH)2:

$$Mg(OH)_{2s} + CO_{2g} + 2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s$$

Brucite Nesquehonite

ω (CO2), %	**0,04**	**20**	**10**
V(total), l	5,3	5,3	2
V(CO2), l	0,00212	1,06	0,2
Vm, l/mol	22,4	22,4	22,4
n(CO2), mol	9,46429E-05	0,047	0,009
ΔrH , J/mol CO2	-85836	-85836	-85836
Q, J	8,12	4061,88	766,39
Cp(products), J/mol*K	301,71	301,71	301,71
ΔT, K	**0,027**	**13,463**	**2,540**

$$V(CO2) = \frac{\omega \cdot V(total)}{100\%}$$

$$n\,(CO2) = \frac{V(CO2)}{Vm}$$

$$Q = -\Delta rH \cdot n$$

$$Q = Cp \cdot \Delta T$$

Chemistry of the laboratory process

50 g of ORE + 0,047 mol of CO_2 (1,06 l) :

$Mg(OH)_{2s}$ + CO_{2g} + $2H_2O_l = Mg(HCO_3)OH \cdot 2H_2O_s$

Brucite — Nesquehonite

0,103 mol (6g – 12%) — 0,0078 mol

$Mg_3Si_2O_5(OH)_{4s}$ + $3CO_{2g} + 7H_2O_l = 3(Mg(HCO_3)OH \cdot 2H_2O)_s + 2SiO_2$

Lizardite/chrysotile — Nesquehonite

0,145 mol (40 g – 80%) — 0,0234 mol

Mg_2SiO_{4s} + $2CO_{2g} + 6H_2O_l = 2(Mg(HCO_3)OH \cdot 2H_2O)_s + SiO_2$

Forsterite — Nesquehonite

0,0286 mol (4 g – 8%) — 0,0156 mol

9 g of ore will react with 1,02 l of CO_2

Carbonation reaction with $Mg(OH)_2$

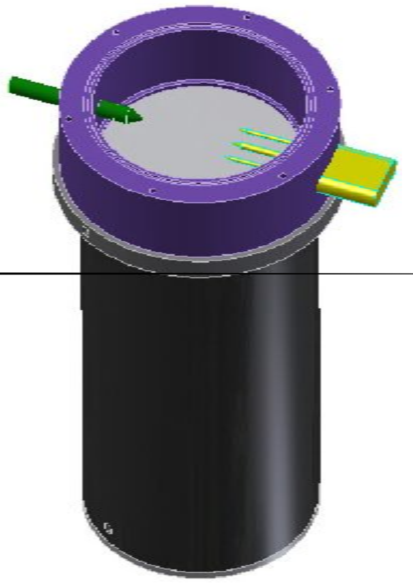
Laboratory conditions: ω(CO2) = 10%, T = 298K, 50% saturation

1) $CO_{2g} \rightarrow CO_{2aq}$

$\Delta_r H = -23298$ J/mol
$C_{p(CO2)aq} = 243$ J/mol·K
$n(CO_2) = 0{,}009$ mol
$Q = -\Delta_r H \cdot n = 209{,}68$ J
$Q = C_{p(CO2)aq} \cdot \Delta T$

$\Delta T = 0{,}86$ K

$V_{total} = 2$ l



2) $Mg(OH)_{2\,s} + CO_{2\,g} + 2H_2O_l \rightarrow Mg(HCO_3)OH \cdot 2H_2O_s$

$V_{CO2} = 0{,}2$ litres
$n(CO_2) = 0{,}009$ mol
$\Delta_r H = -94714$ J/mol of CO_2
$Q = -\Delta_r H \cdot n = 766{,}39$ J
$Q = C_p \cdot \Delta T$

$\Delta T = 2{,}54$K

Required equipment

Name	Company	Price, CAD
GMT221 Carbon Dioxide Transmitter for Incubators, Up to 20% CO2	Vaisala	1150
pH-meter	Hanna Instruments	300
T-couple*4	Omega	150
Valves	Swagelok	380
Mg(OH)2	Sigma Aldrich	220
SiO2(sand)	Sigma Aldrich	215
Al2O3	Sigma Aldrich	150
Data acquisition card (DAQ)	National Instruments	1000
PC		?
Overall costs		~3700