

CO₂ Sequestration in Mining Residues

– Probing Heat Effects Associated to Carbonation

By MSc student
Aksenova Diana

Department of Chemical Engineering

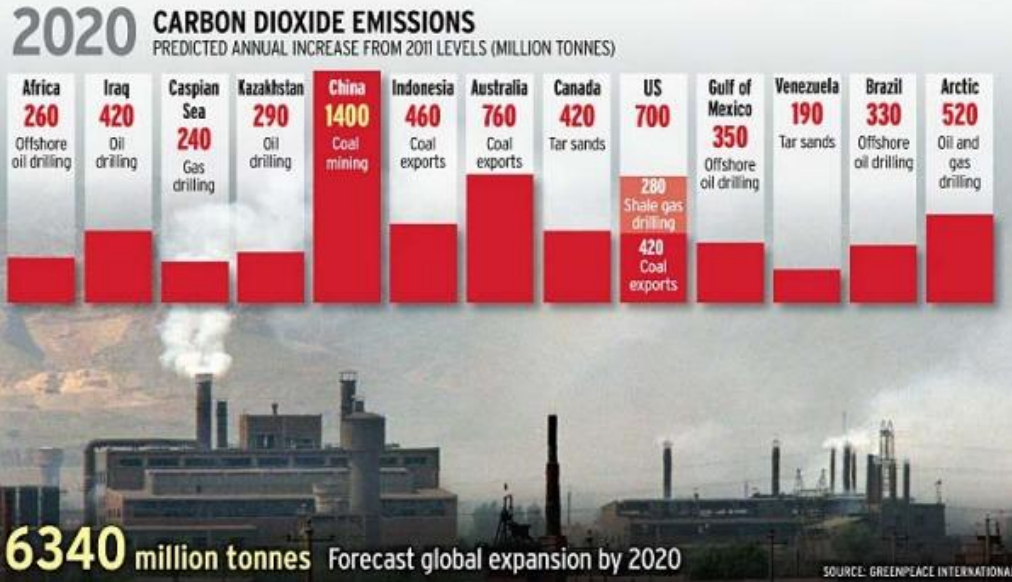
Supervisor: Prof. Faical Larachi
Co-Supervisors: Prof. Xavier Maldague
and Prof. Georges Beaudoin

Content

- Raison d'être du travail / Purpose of the project
- Bibliographie et problématique / Literature review
- 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

CO₂ emissions



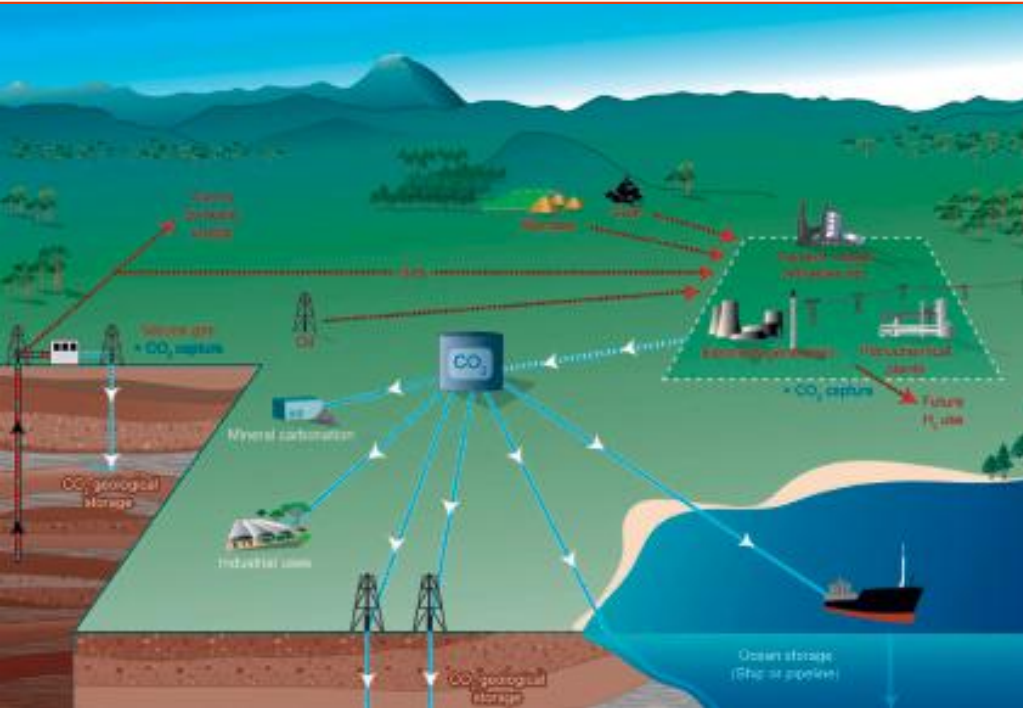
March, 2016 – 404,83 ppm

If CO₂ 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°C contains potential significant damage to the ecosystems upon which we depend directly.

Literature review

CO₂ 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)
- Biological (algae, cyanobacteria)

Storage:

- Geological
- Ocean
- **Mineral**

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

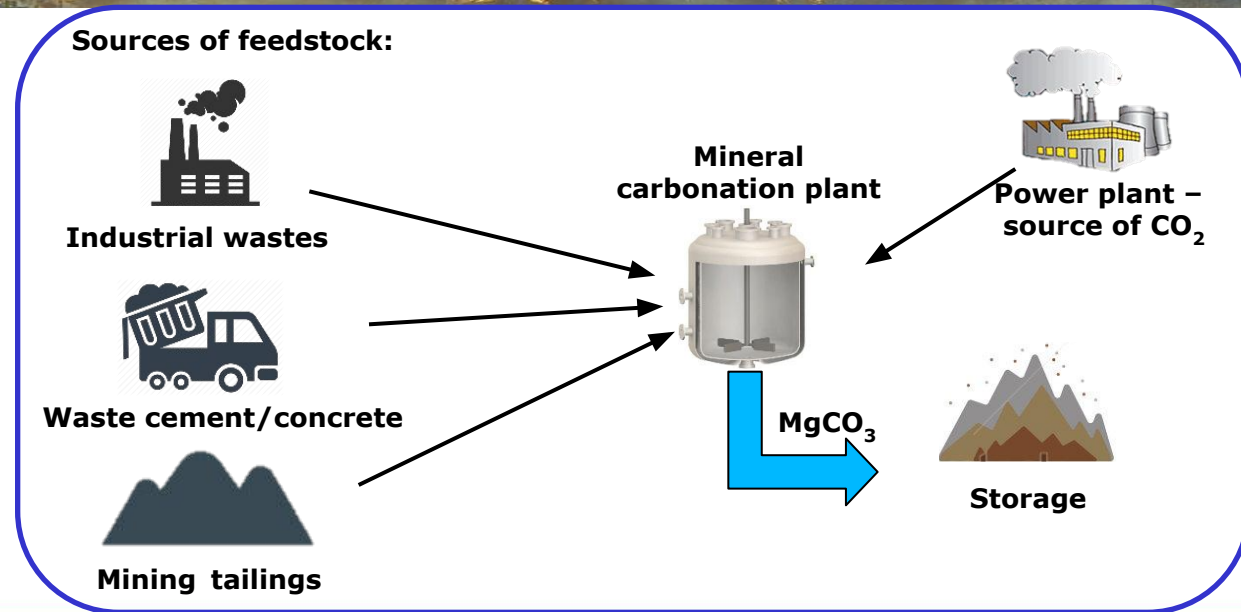
Indirect carbonation

Involves the extraction of reactive components (Mg²⁺, Ca²⁺) from the minerals, using acids or other solvents, followed by the reaction of the extracted components with CO₂ either in the gaseous or aqueous phase

Active carbonation concept



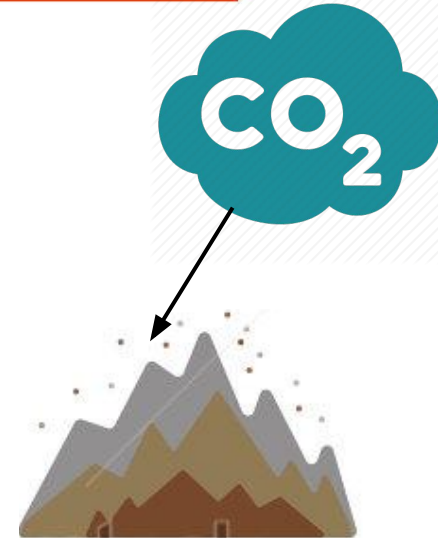
- The Netherlands
- Finland
- Japan
- China
- U.S. and Canada
- Switzerland
- Australia



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

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 CO₂ 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 CO₂ 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

Description of the project

Primary challenge



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

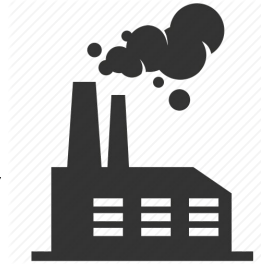
What's new?

Science



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

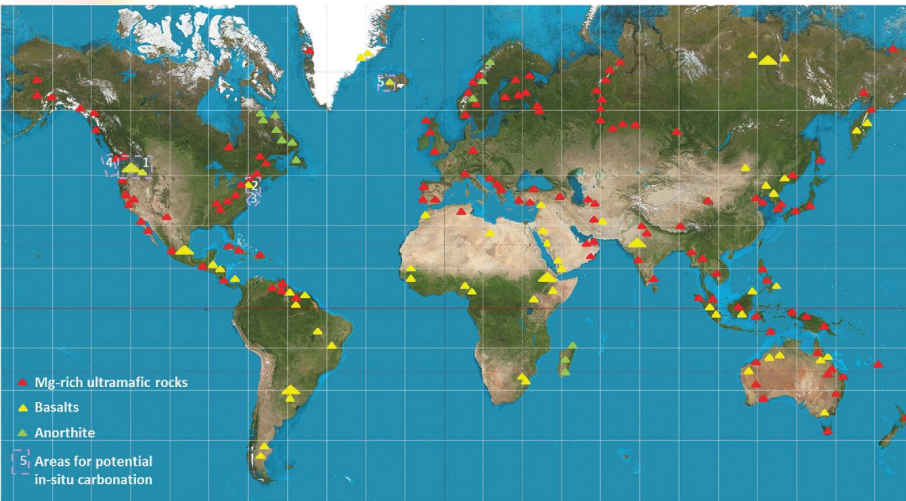
Industry



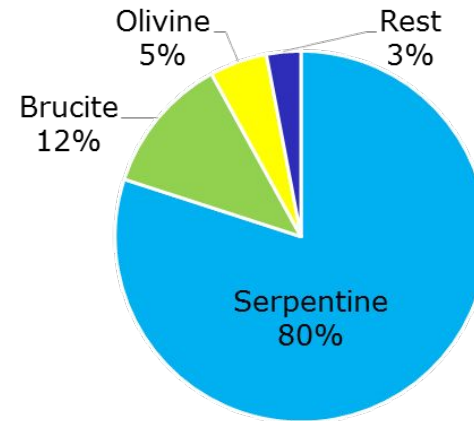
- The way to get back some energy and use it for an industrial needs

Mining tailings

Mafic and ultramafic residues are the best feedstock for the CO₂ 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

- $T = -20 \dots 0^{\circ}\text{C}$
- $\text{H}_2\text{O sat. (snow)} = 50 \dots 100\%$

Spring/Autumn

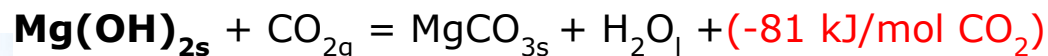
- $T = 0 \dots +15^{\circ}\text{C}$
- $\text{H}_2\text{O sat. (rain)} = 50 \dots 100\%$

Summer

- $T = +15 \dots +30^{\circ}\text{C}$
- $\text{H}_2\text{O sat. (rain)} = 0 \dots 50\%$

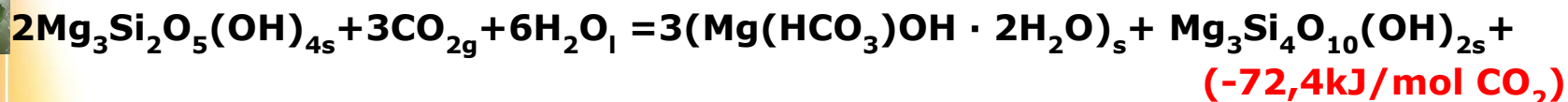
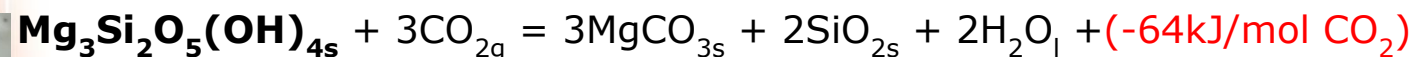
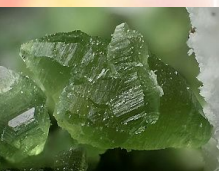
Theoretical & real carbonation reactions

Brucite



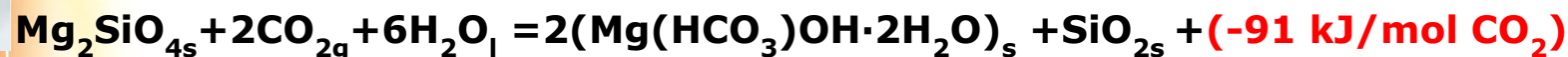
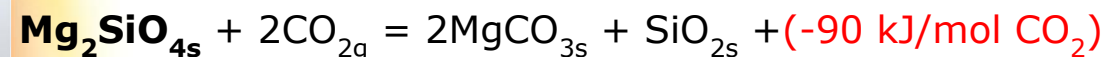
-1,95 MJ/kg of CO2

Lizardite



-1,64 MJ/kg of CO2

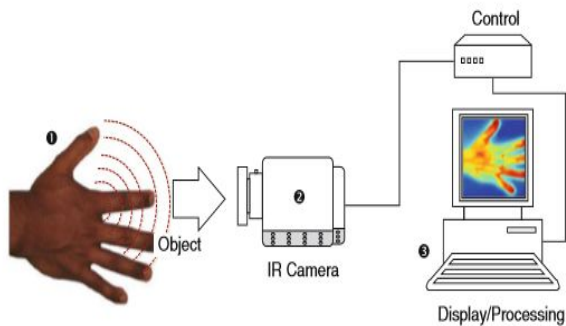
Forsterite



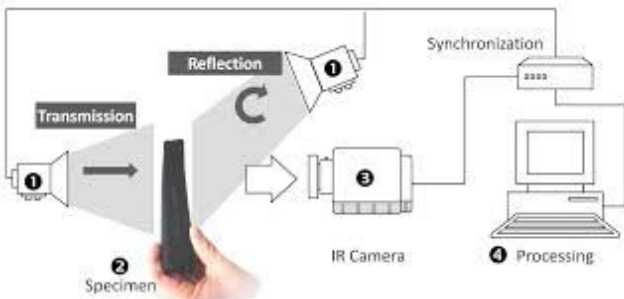
-2,07 MJ/kg of CO2

Infrared thermography

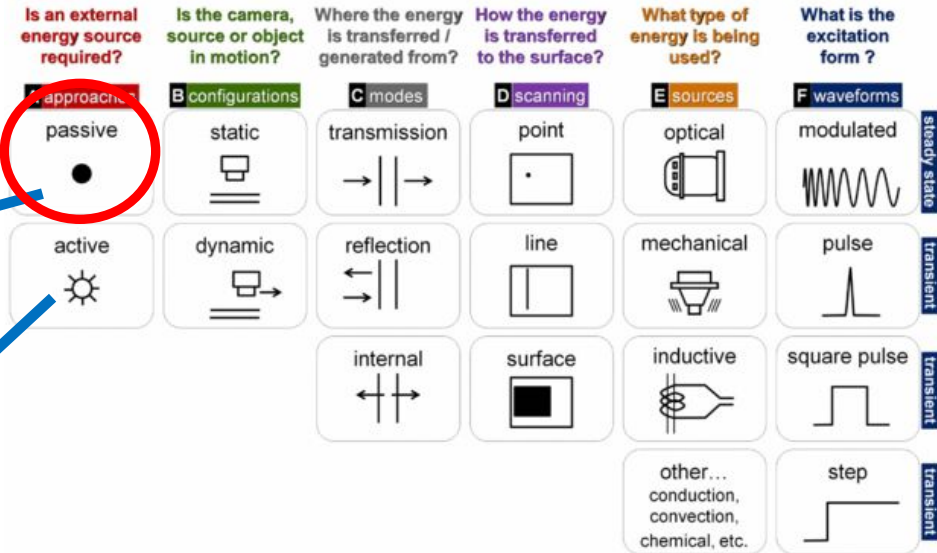
Radiation coming from the target object is measured without any external heat stimulation



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



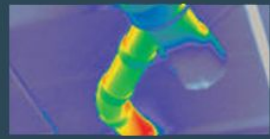
(Infrared Thermography for NDT: Potentials and Applications, X. P. V. Maldague, slide 19)



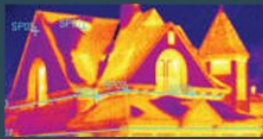
(Infrared Thermography, C. Ibarra-Castanedo and X. P. V. Maldague, p. 180)

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

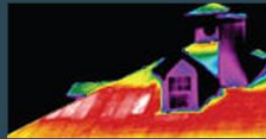
Infrared camera



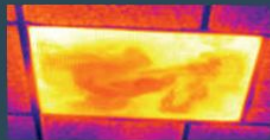
Blockage in Pipes



Residential Heat Loss



Missing Insulation in
Roof/Rafters



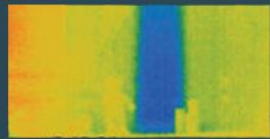
Cold Air Return



Water Damage



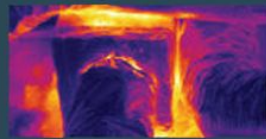
Ceiling Leaks



Uninsulated Stud Bay



Circuit Breaker Problems



Loose HVAC Junction

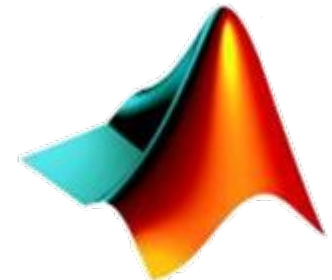
(<http://fiveboroughhomeinspection.com/inspection-service/infrared-camera-inspection-service/>)

**Thermal image data is colored
up pixel by pixel based on
 $T^{\circ}\text{C}$.**

Indigo Phoenix Thermal Camera



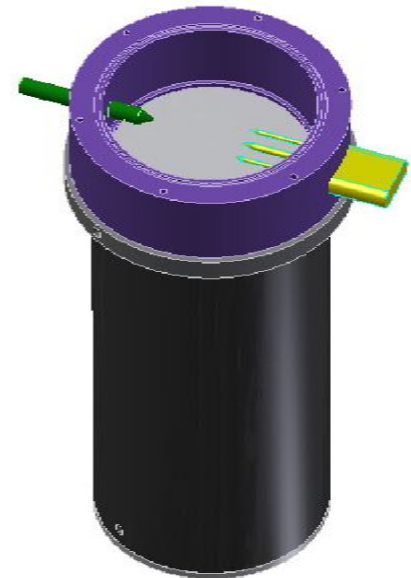
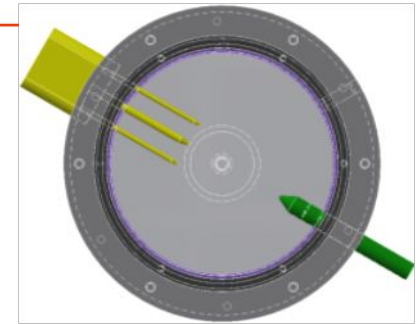
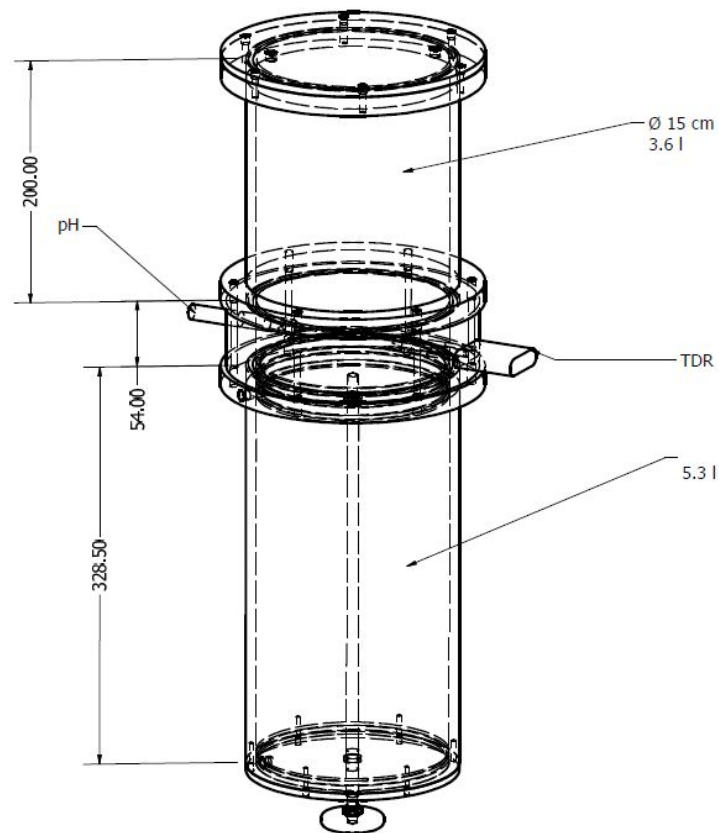
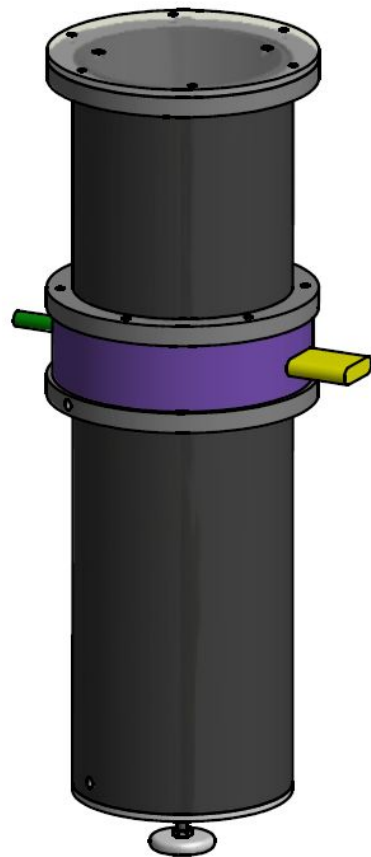
(<http://www.rliir.com/legacy/view/?id=51542>)



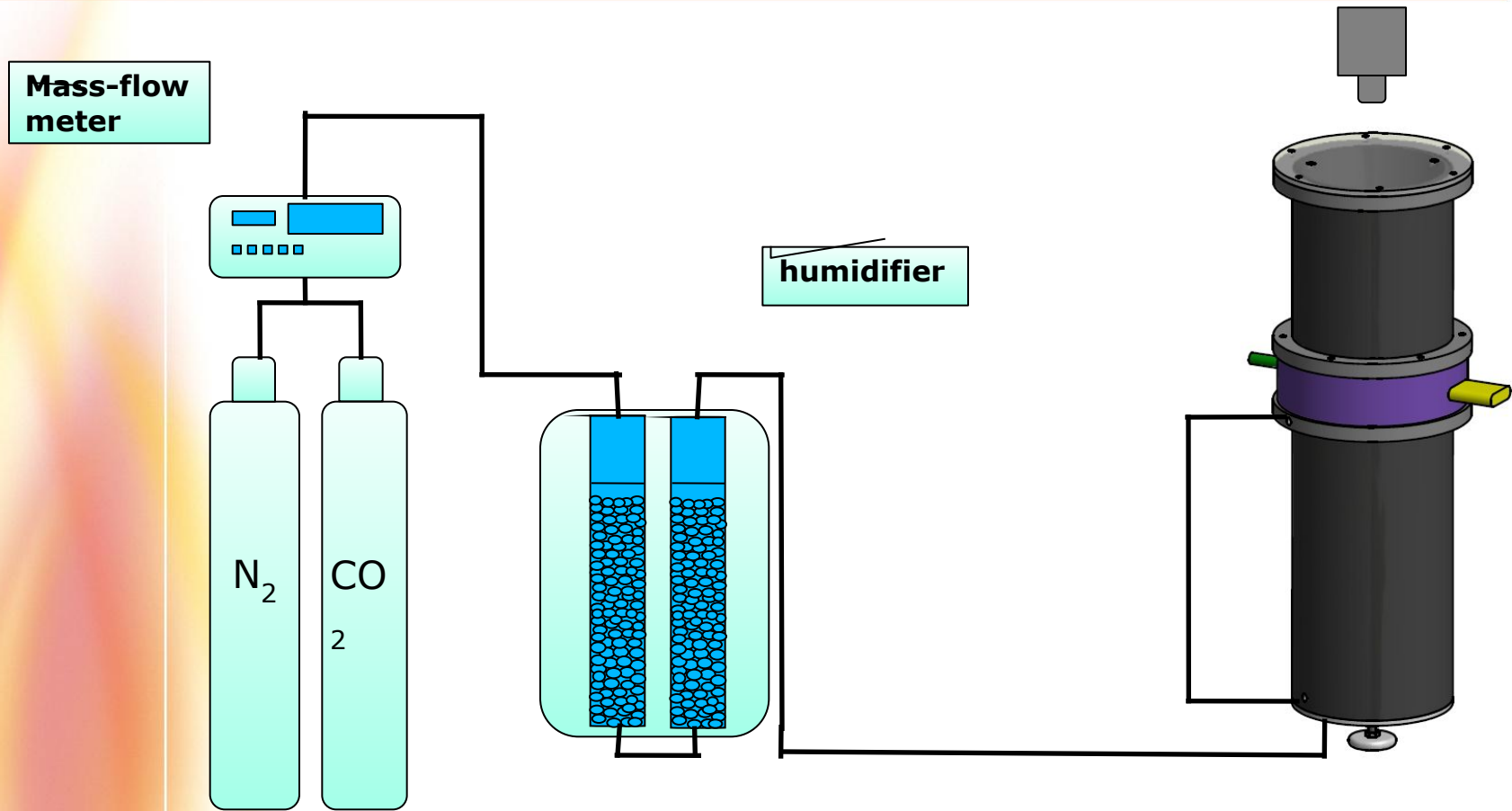
MATLAB

Methodology

Design of the setup



Carbonation setup



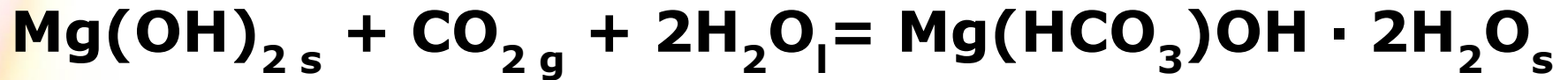
Chemistry of the laboratory process

50 g of ORE + 0,047 mol of CO₂ (1,06 l), 50% water saturation :

	CO ₂ , mol	Q, J	Cp(prod.), J/mol*K	ΔT, K
Mg(OH)_{2s} + CO_{2g} + 2H₂O_l = Mg(HCO₃)OH · 2H₂O_s + (-86 kJ/mol)	0,0078	669,52	301,71	2,22
2Mg₃Si₂O₅(OH)_{4s} + 3CO_{2g} + 6H₂O_l = 3(Mg(HCO₃)OH · 2H₂O)_s + Mg₃Si₄O₁₀(OH)_{2s} + (-72,4 kJ/mol)	0,0234	1492,79	1226,84	1,38
Mg₂SiO_{4s} + 2CO_{2g} + 6H₂O_l = 2(Mg(HCO₃)OH · 2H₂O)_s + SiO₂ + (-91 kJ/mol)	0,0156	1418,26	647,99	2,19

9 g of ore will react with 1,02 l of CO₂

Carbonation reaction with brucite



Laboratory conditions: $\omega(\text{CO}_2) = 20\%$, $T = 298\text{K}$,
50% saturation

$$V_{\text{CO}_2} = 1,06 \text{ litres}$$

$$n(\text{CO}_2) = 0,047 \text{ mol}$$

$$\Delta_r H = -85836 \text{ J/mol of CO}_2$$

$$Q = -\Delta_r H \cdot n = 4061,88 \text{ J}$$

$$Q = C_p \cdot \Delta T$$

$$\Delta T = 13,46\text{K}$$

Ambient conditions(mine site): $\omega(\text{CO}_2) = 400\text{ppm}$, $T = 298\text{K}$,
50% saturation

$$V_{\text{CO}_2} = 0,00212 \text{ litres}$$

$$n(\text{CO}_2) = 9,46 \cdot 10^{-5} \text{ mol}$$

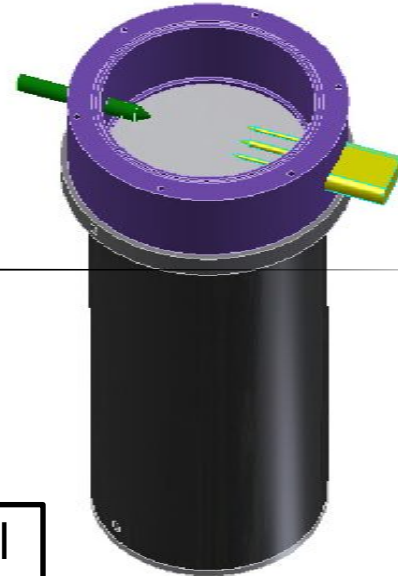
$$\Delta_r H = -85836 \text{ J/mol of CO}_2$$

$$Q = -\Delta_r H \cdot n = 8,12 \text{ J}$$

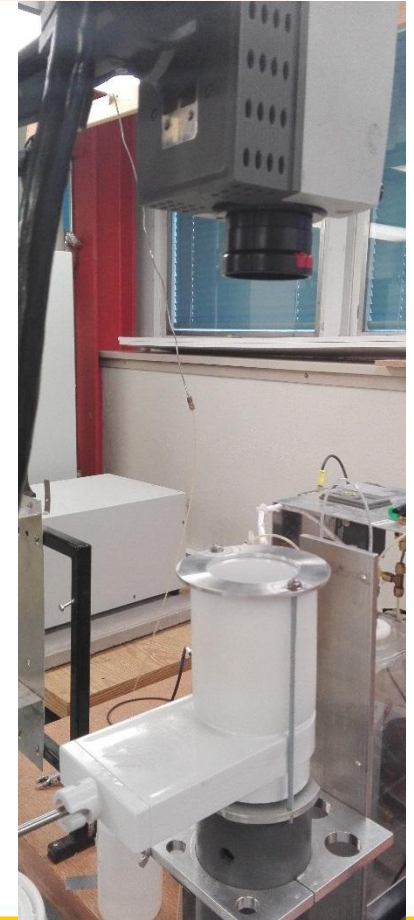
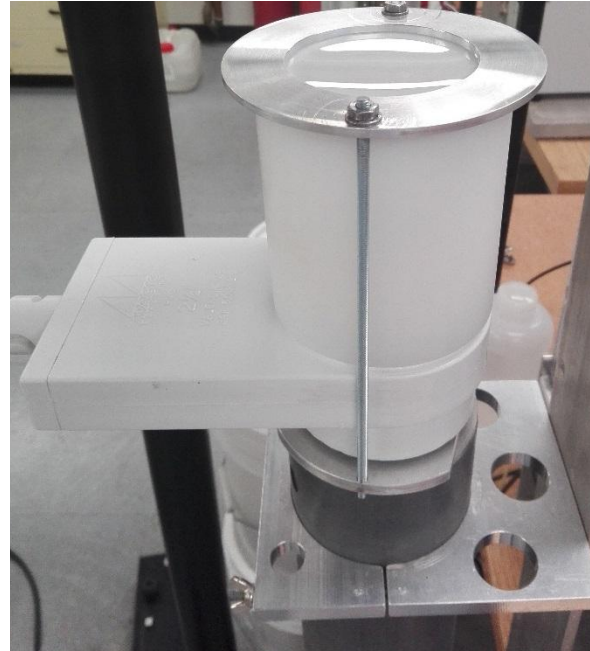
$$Q = C_p \cdot \Delta T$$

$$\Delta T = 0,027\text{K}$$

$$V_{\text{total}} = 5,3 \text{ l}$$



Reactor available in the laboratory of Prof. Larachi

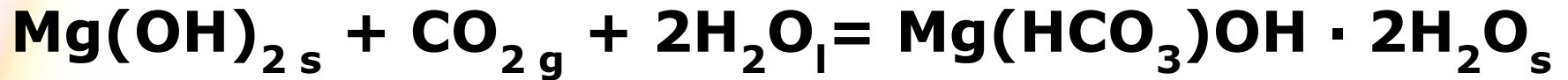


Estimation for A. Entezari Zarandi setup

35 g of ore + 0,009 mol CO₂ (50% water saturation)

	CO ₂ , mol	Q, J	Cp(prod.), J/mol*K	ΔT, K
Mg(OH)_{2s} + CO_{2g} + 2H₂O_l = Mg(HCO₃)OH · 2H₂O_s + (-86 kJ/mol)	0,0015	128,75	301,71	0,43
2Mg₃Si₂O₅(OH)_{4s} + 3CO_{2g} + 6H₂O_l = 3(Mg(HCO₃)OH · 2H₂O)_s + Mg₃Si₄O₁₀(OH)_{2s} + (-72,4 kJ/mol)	0,0045	287,07	994,27	0,26
Mg₂SiO_{4s} + 2CO_{2g} + 6H₂O_l = 2(Mg(HCO₃)OH · 2H₂O)_s + SiO₂ + (-91 kJ/mol)	0,003	272,74	647,99	0,42

Carbonation reaction with $\text{Mg}(\text{OH})_2$



Laboratory conditions: $\omega(\text{CO}_2) = 10\%$, $T = 298\text{K}$, 50% saturation

$$V_{\text{CO}_2} = 0,2 \text{ litres}$$

$$n(\text{CO}_2) = 0,009 \text{ mol}$$

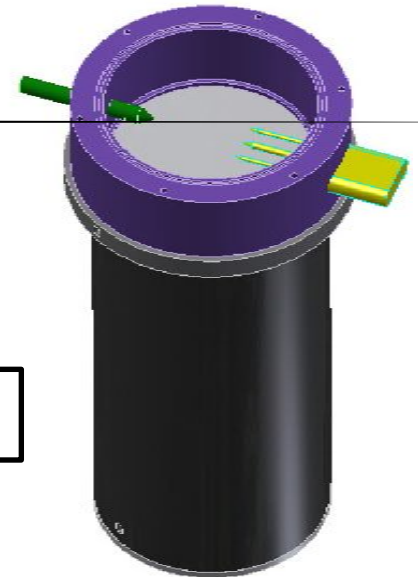
$$\Delta_r H = -94714 \text{ J/mol of CO}_2$$

$$Q = -\Delta_r H \cdot n = 766,39 \text{ J}$$

$$Q = C_p \cdot \Delta T$$

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

$$V_{\text{total}} = 2 \text{ l}$$



Summary table for brucite

% CO₂	400ppm -ambient amount of CO₂	20% - new setup	10%- Ali's setup
V (total), l	5,3	5,3	2
V (CO₂), 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

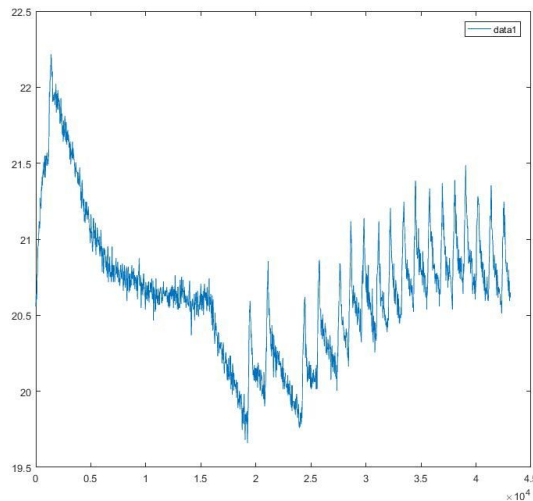
35g Mg(OH)₂ (11%)+SiO₂

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

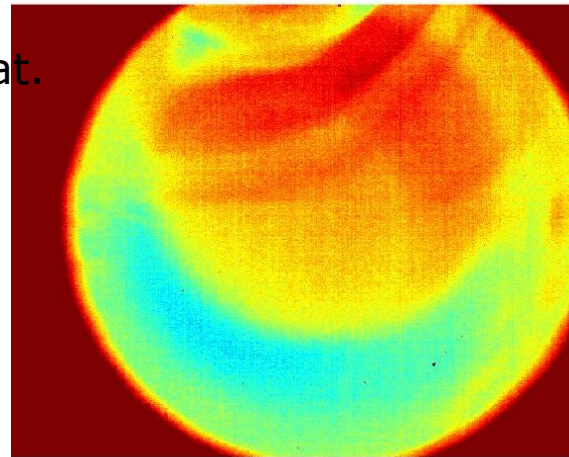
First results - ORE

35 g of the ore

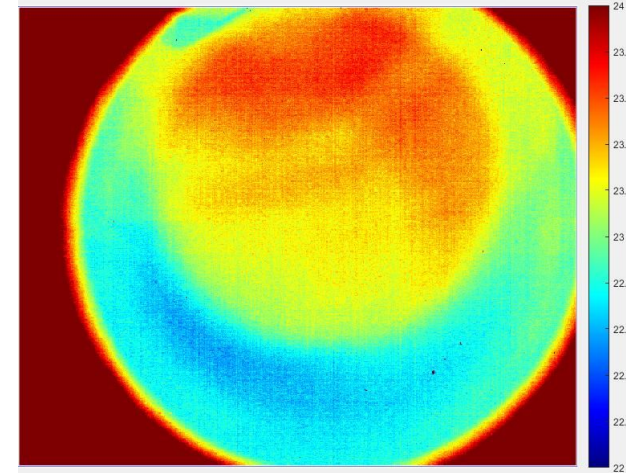
- 4,37 ml of H₂O = 50% sat.
- 9.83% of CO₂
- Duration = 9 h



15 min



30 min



33 min: $T = 22.25\text{ C}$, $\Delta T = 1.65\text{ C}$

Summary

- Investigate
- Get
- Utilize



(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

CO₂ Sequestration in Mining Residues

– Probing Heat Effects Associated to Carbonation

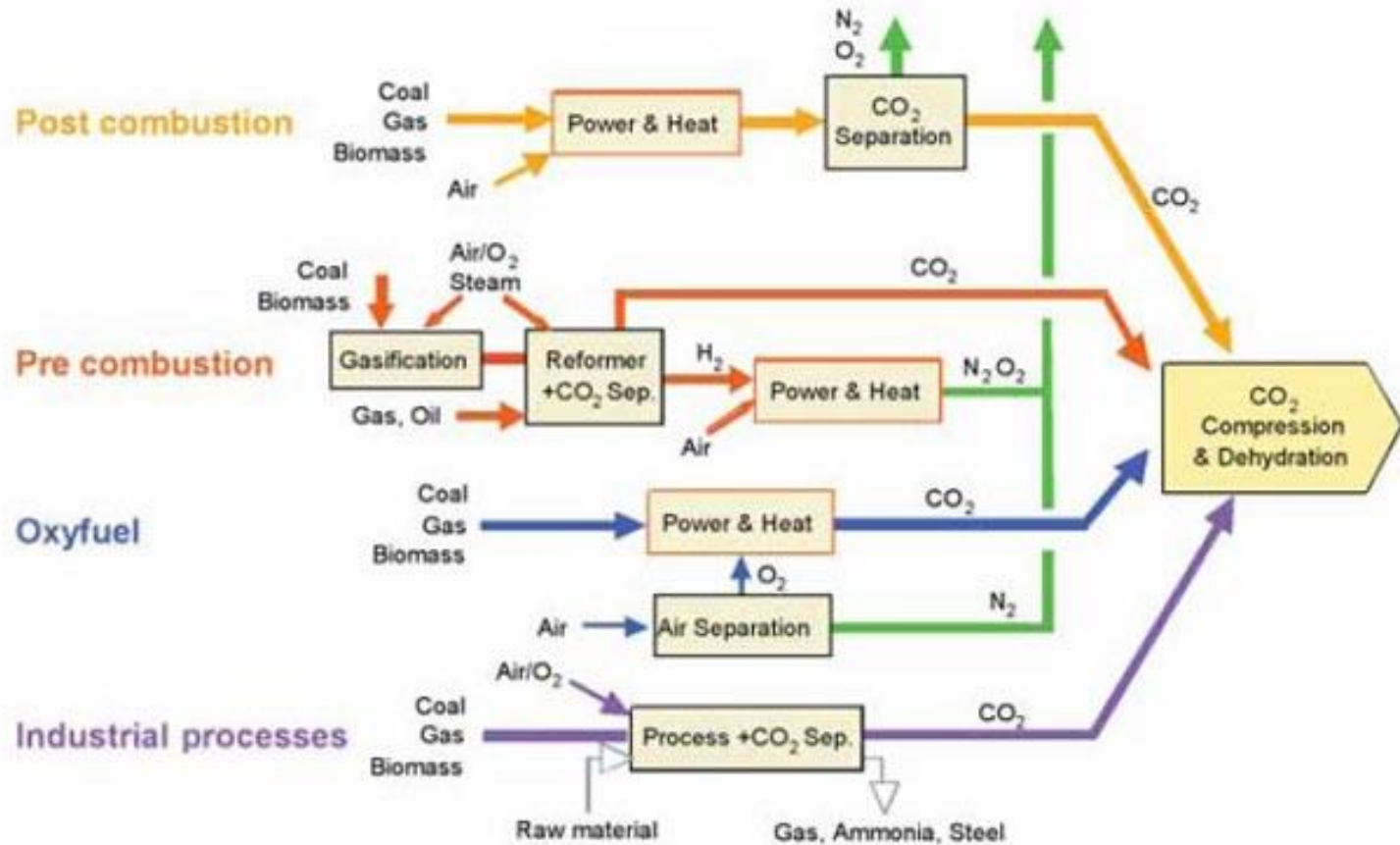
By MSc student
Aksenova Diana

Department of Chemical Engineering

Supervisor: Prof. Faical Larachi
Co-Supervisors: Prof. Xavier Maldague
and Prof. Georges Beaudoin

Questions

CCS



Carbon Dioxide Capture and Storage: Technical Summary (2005)

Active carbonation concept

Ex-situ

Sources of feedstock:



Mineral
carbonation plant



OR

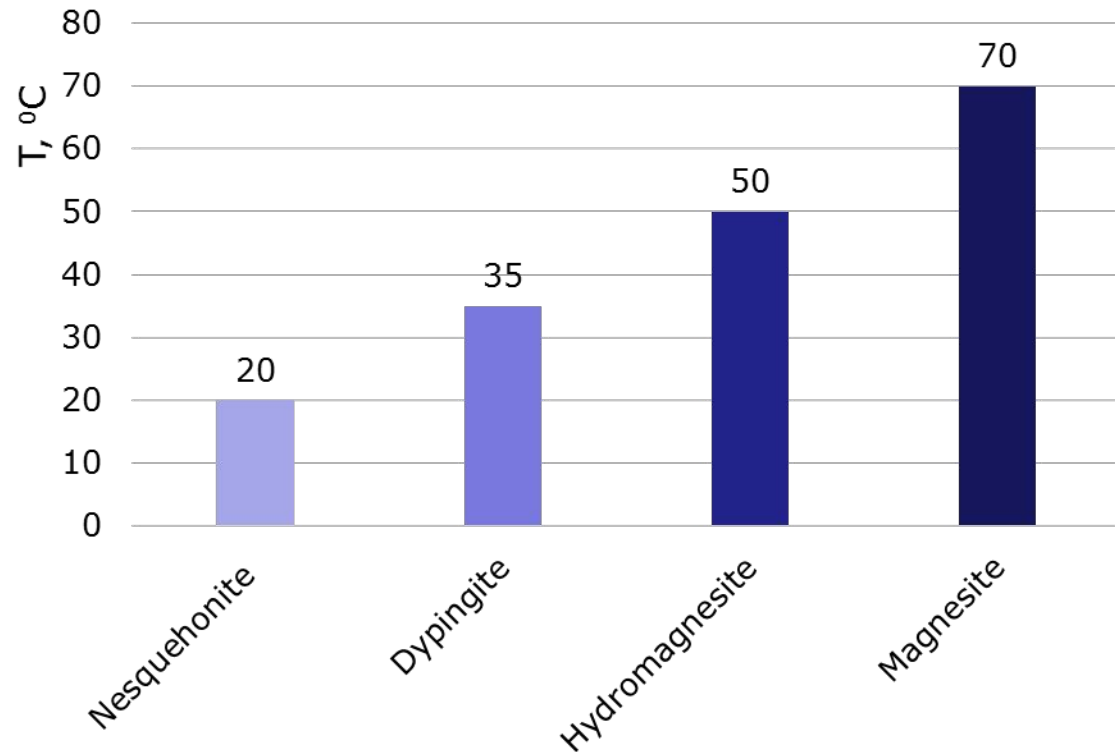
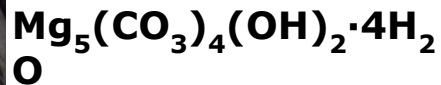
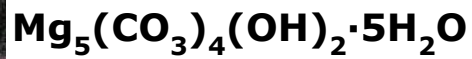
In-situ



injections

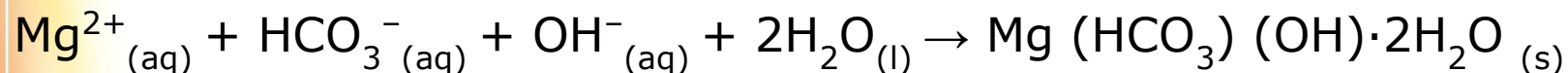
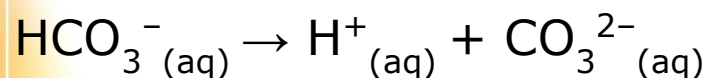
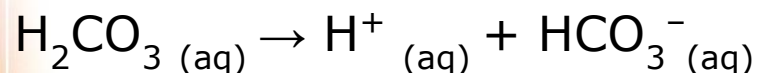
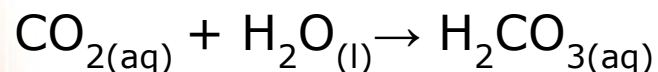
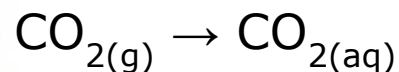


Reaction products of sequestration

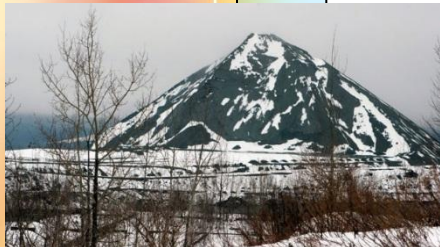
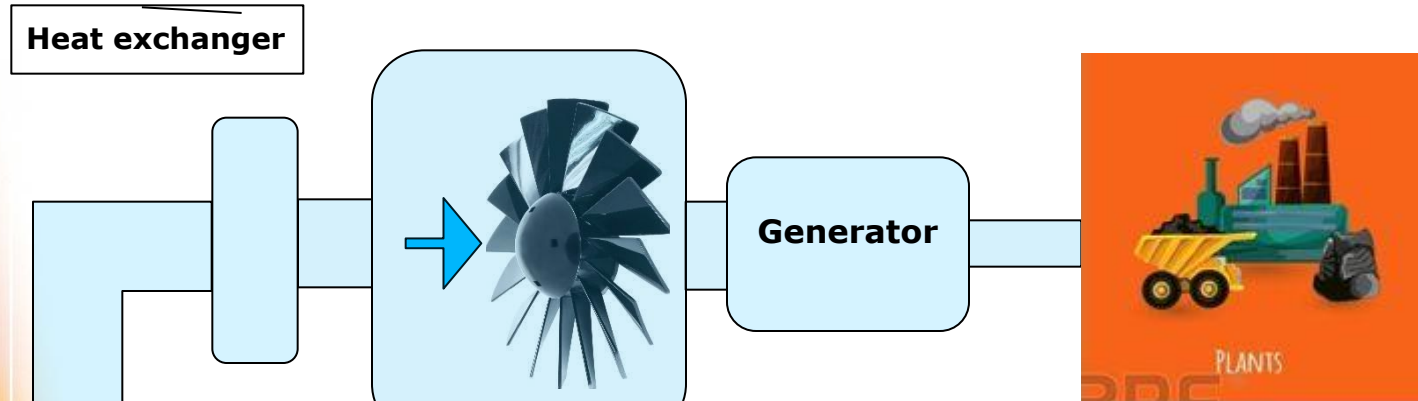


(<http://www.mindat.org/min-1979.html>)

Mg²⁺ – series of the reactions



Future investigations



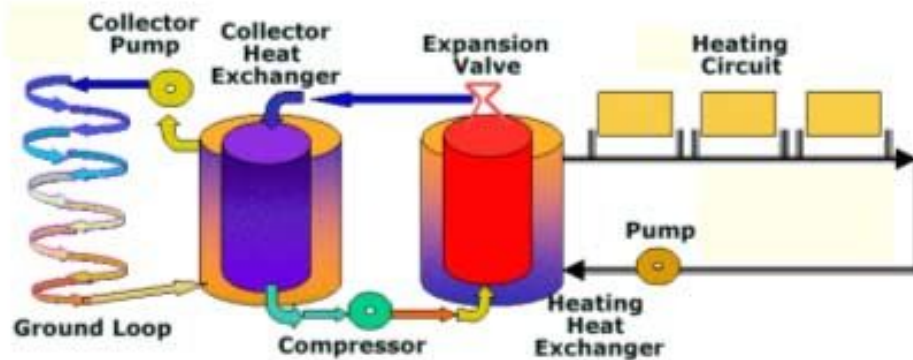
(<http://www.ctvnews.ca/canada-s-last-asbestos-mine-about-to-run-out-of-asbestos-1.674045>)

Geothermal heat exchangers
underground loop (probes)
or cluster geofield



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

Future investigations



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

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%

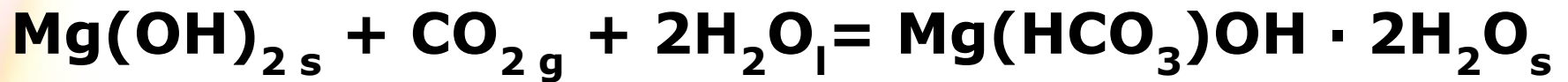
Heating Costs Comparison

Estimates based on the following energy costs:
Electricity - \$.09/ KWh; Oil - \$3.26 / gallon; Propane - \$1.95/ gallon; Dry Wood - \$210 / full cord; Natural Gas - \$.098 / therm



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

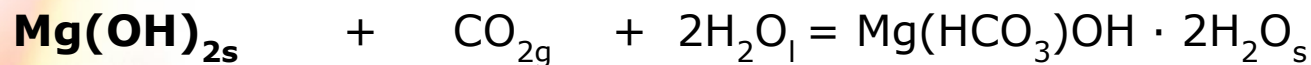
Detailed calculations for $\text{Mg}(\text{OH})_2$



Mg(OH)₂:				
Mg(OH)_{2s} + CO_{2g} + 2H₂O_l = Mg(HCO₃)OH · 2H₂O_s				
Brucite Nesquehonite				
ω (CO₂), %	0,04	20	10	$V(\text{CO}_2) = \frac{\omega \cdot V(\text{total})}{100\%}$
V(total), l	5,3	5,3	2	
V(CO ₂), l	0,00212	1,06	0,2	$n(\text{CO}_2) = \frac{V(\text{CO}_2)}{V_m}$
V _m , l/mol	22,4	22,4	22,4	
n(CO ₂), mol	9,46429E-05	0,047	0,009	$Q = -\Delta rH \cdot n$
ΔrH , J/mol CO ₂	-85836	-85836	-85836	
Q, J	8,12	4061,88	766,39	$Q = C_p \cdot \Delta T$
C _p (products), J/mol*K	301,71	301,71	301,71	
ΔT, K	0,027	13,463	2,540	

Chemistry of the laboratory process

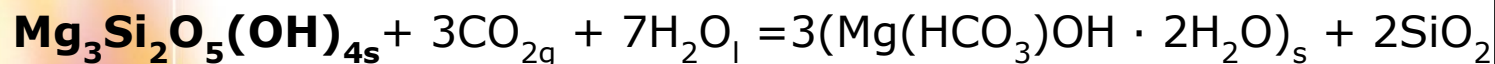
50 g of ORE + 0,047 mol of CO₂ (1,06 l) :



Brucite

Nesquehonite

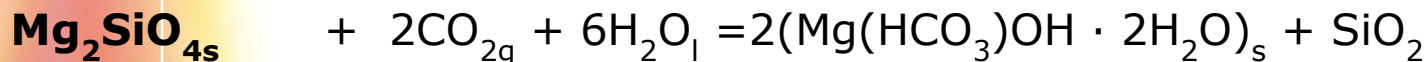
0,103 mol (6g – 12%) 0,0078 mol



Lizardite/chrysotile

Nesquehonite

0,145 mol (40 g – 80%) 0,0234 mol



Forsterite

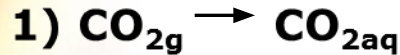
Nesquehonite

0,0286 mol (4 g – 8%) 0,0156 mol

**9 g of ore
will react
with
1,02 l of
CO₂**

Carbonation reaction with $\text{Mg}(\text{OH})_2$

Laboratory conditions: $\omega(\text{CO}_2) = 10\%$, $T = 298\text{K}$, 50% saturation



$$\Delta_r H = -23298 \text{ J/mol}$$

$$C_{p(\text{CO}_2)\text{aq}} = 243 \text{ J/mol}\cdot\text{K}$$

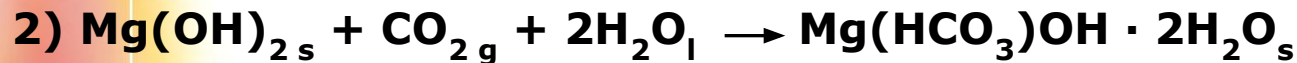
$$n(\text{CO}_2) = 0,009 \text{ mol}$$

$$Q = -\Delta_r H \cdot n = 209,68 \text{ J}$$

$$Q = C_{p(\text{CO}_2)\text{aq}} \cdot \Delta T$$

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

$$V_{\text{total}} = 2 \text{ l}$$



$$V_{\text{CO}_2} = 0,2 \text{ litres}$$

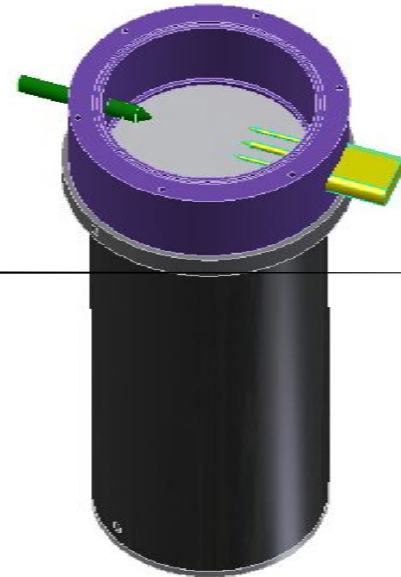
$$n(\text{CO}_2) = 0,009 \text{ mol}$$

$$\Delta_r H = -94714 \text{ J/mol of CO}_2$$

$$Q = -\Delta_r H \cdot n = 766,39 \text{ J}$$

$$Q = C_p \cdot \Delta T$$

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



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