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# Ex-situ mineral carbonation: resources, process and environmental assessment (Carmex project)

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## Abstract

This article presents the main results of the Carmex project (2009-2012), whose purpose was to review the feasibility of ex-situ mineral carbonation in terms of resource availability, performance of the aqueous mineral carbonation process and life cycle analysis criteria. This collaborative project looked at a wide range of generic issues about this CO<sub>2</sub> mitigation option, with particular views on assessing its potential in the context of New-Caledonia. Indeed, insularity and local abundance of 'carbonatable' rocks and industrial wastes (i.e. rich in MgO, CaO, if not Fe(II)O), coupled with significant GHG emissions from first-class nickel pyrometallurgical industries, make it a potential candidate for application of ex-situ mineral carbonation. The project conducted a worldwide analysis of the potential of ex-situ mineral carbonation using a dedicated SIG-based tool. Using a variety of materials the project also reviewed a number of critical issues associated with the aqueous mineral carbonation process itself, with promising perspectives. Finally, through life cycle analysis of the system as a whole, ex-situ mineral carbonation was compared to mainstream CSC solutions. It was concluded that the viability of this CO<sub>2</sub> storage option is located at the level of the process itself and lies with the optimisation of its operating conditions.

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## Introduction

Mineral carbonation, which involves trapping CO<sub>2</sub> by chemical reaction with carbonable mineral phases to form stable inert carbonates, can be considered as an alternative solution to geological CO<sub>2</sub> storage, which is at present the main, if not only, the solution for storing industrial CO<sub>2</sub> emissions on a large scale. With aqueous mineral carbonation, two distinct reactions occur: first the 'carbonatable' cations Mg<sup>2+</sup> (Ca<sup>2+</sup>, Fe<sup>2+</sup>) are leached out of the ore, and then they precipitate with dissolved CO<sub>2</sub> to form carbonates. The overall reaction is typically written as  $Mg_2SiO_4 + CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4$ . Depending on the conditions, serpentinization-like reaction can also occur:  $2Mg_2SiO_4 + CO_2 + 2H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3$ .

This article presents the main results of the French Carmex project (2009-2012), whose purpose was to review the industrial feasibility of ex-situ mineral carbonation, essentially in terms of resource availability, performance of the aqueous mineral carbonation process and life cycle analysis criteria.

## Worldwide potential for ex-situ mineral carbonation - Geographical Information System (GIS)

World data on (i) CO<sub>2</sub>-emission sites and (ii) ore deposits in mafic/ultramafic (M/UM) rock contexts have been cross-examined through a GIS (under ArcGIS) in order to identify sites of potential interest for implementing the ex-situ carbonation method on a worldwide scale. Applying criteria about the nature and quantity of mining wastes, volumes of CO<sub>2</sub> emissions, distance between mine and emission sites, and adding mining data from the literature, has led to a first selection of eight 'super large' potential ore deposits in an ultramafic rock context, all within a 300 km radius of coal-fired industrial plants emitting over 1Mt/year CO<sub>2</sub>. These sites are located in Botswana, South Africa, China, Russia and Kazakhstan<sup>1</sup>. Additional information is reported in Table 1 that indicates the level of accessibility of the sites (good/difficult/very difficult), considering the mining value of the residues – i.e. possible profitable recycling of rare metals- the total length of pipelines to transport the CO<sub>2</sub> from the emission sites, local topography – calculation of average slope parameter which results in evident access difficulties.

**Table 1.** First selection of 8 superlarge sites

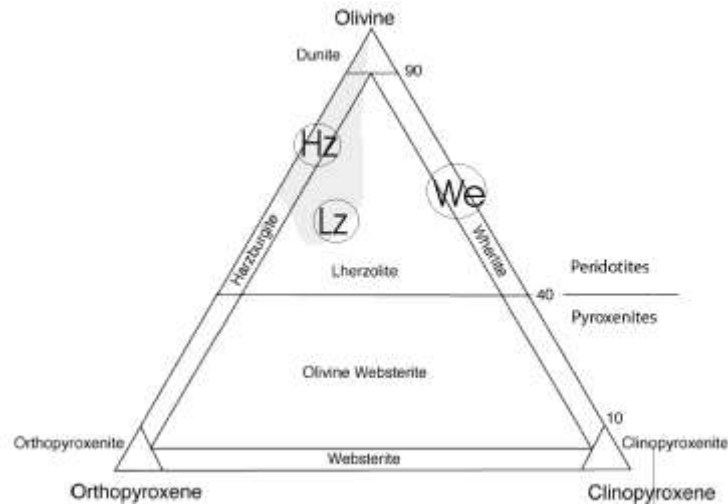
Superlarge (class 4) UM ore deposits			Parameters				CO <sub>2</sub> emission sites within 300 km			
Name	Country	Main commodity	Estimated volume of waste	Accessibility	Distances (km)	Average slope	Nb CO <sub>2</sub> sites	Country	Total CO <sub>2</sub> kt/y	Main fuel
PHALABORWA	South Africa	P <sub>2</sub> O <sub>5</sub>	> 1 Gt	Good	78 - 271	2,9 - 8,3 %	2	South Africa	11 571	COAL
BUSHVELD NORTH	South Africa	Cr <sub>2</sub> O <sub>3</sub>	> 1 Gt	Good	119 - 295	3 - 11,1 %	6	South Africa Botswana	80 748	COAL
PREMIER	South Africa	diamond	> 1 Gt	Difficult	98 - 256	3 - 6,6 %	1 4	South Africa	149 033	COAL
ORAPA	Botswana	diamond	~ 350 Mt	Difficult	230 - 262	0,1 - 0,5 %	1 2	Botswana Zimbabwe	7 865	COAL
JWANENG	Botswana	diamond	~ 250 Mt	Difficult	211 - 267	1,7 - 2 %	2	South Africa	7 547	COAL
PANZHUHUA	China	Fe	> 100 Mt	Very difficult	96 - 249	12 - 13,5 %	6 1	China India	47 404	COAL
KEMPIRSAI	Kazakhstan	Cr <sub>2</sub> O <sub>3</sub>	>100 Mt	Very difficult	111	0,80%	1	Russia	1 179	COAL
KACHKANARSKOYE	Russia	Fe, V <sub>2</sub> O <sub>5</sub> , TiO <sub>2</sub> , PGF	> 10 Gt	Very difficult	101 - 178	2 - 3,7 %	1	Russia	15 445	COAL

The criteria used above are rather drastic, hence the small number of sites that this analysis identified as early opportunities for ex-situ mineral carbonation. But this example was intended as a demonstration of the value of using modern SIG-based technology for decision-making about the value of implementing mineral carbonation around the globe. Indeed, other criteria can be used which would yield different potential sites, for example using shorter transport distances, using ultramafic and mafic resources instead of mining wastes, etc. It could also be further improved by

applying hydrographical, chemical and mineralogical and economic criteria. The outcomes of this analysis can be compared locally with the corresponding geological storage potential evaluation, which can be very interesting.

## Materials and methods

### Samples: chemical content and mineralogy



**Figure 1.** Ternary diagram showing the mineral proportion of the three types of rocks tested: harzburgite (Hz), Iherzolite (Lz) and wehrlite (We) in modal fraction of olivine, orthopyroxene and clinopyroxene. The grey zone corresponds to rocks commonly found in ophiolite and ultramafic complexes.

Three types of material were tested: natural peridotites (harzburgite Hz1, Hz2 and wehrlite We1 collected in New Caledonia and Iherzolite Lz1 from the French type locality – the proportion of each mineral in the three rock types without considering serpentine is given in Figure 1). Pure synthetic olivine from Magnolithe GmbH obtained after 1600°C calcination of natural serpentinite and Ni slag from SLN Doniambo pyrometallurgy plant in Nouméa were also studied.

Global chemical analyses expressed as oxides show that the selected rocks are rich in MgO and contain some CaO (Table 2). As confirmed by volumetric analysis, slags also contain potentially carbonable Fe(II)O. Like most peridotite in New Caledonia, Hz1 and Hz2 contain about 88 % serpentine (lizardite - LOI 9.1-10.4%) and 10 % olivine [average structural formulae  $(\text{Mg}_{1.83}, \text{Fe}_{0.07})\text{SiO}_4$ ] and rare occurrence of Mg, Fe pyroxenes –enstatite type. Wehrlite and Iherzolite are also composed of serpentinized olivine but to a lesser extent (LOI 5.6-6.2 %). They also contain Ca, Mg, Fe pyroxenes – diopside and augite type. Olivine Magnolithe composition varies between  $(\text{Mg}_{1.88}\text{Fe}_{0.12})\text{SiO}_4$  and  $(\text{Mg}_{1.82}, \text{Fe}_{0.18})\text{SiO}_4$ . Slags are composed of olivine/forsterite and an amorphous phase referred to as glass hereafter. Quench dendritic olivine and larger euhedral olivine  $(\text{Mg}_{1.90}, \text{Fe}_{0.1})\text{SiO}_4$  represent about 30 % of the slag but their

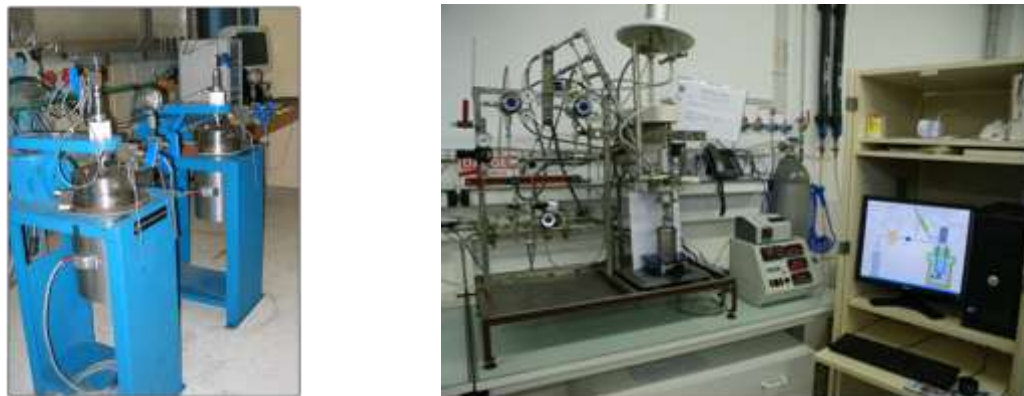
effect on the slag composition is low, its whole composition being close to its point (EPMA) composition (MgO 33.19%, CaO 0.2%).

**Table 2.** Chemical content of the samples (X-ray fluorescence after alkaline fusion)

	Hz1	Hz2	We1	Lz1	Olivine/ Magnolithe	slag
MgO	41.1	40.4	32	30.8	47.35	31.9
CaO	0.6	0.9	4.9	5.0	0.17	0.2
Fe <sub>2</sub> O <sub>3</sub> t	7.8	7.3	7.5	7.6	9.79	12.0 (Fell)
LOI (1000°C)	9.12	10.36	6.17	5.67	0.00	<0.1
Total (majors)	99.3	99.7	99.0	99.52	99.57	99.85
Total C (initial)	0.1	0.1	<0.1	0.12	0.04	0.13

### Experimental set-up

Two distinct test rigs (Figure 2) were used during this work, which differ in volume and range of possible operating conditions.



**Figure 2.** Experimental set-up used in CARMEX project: set-up1 (left) and set-up2 (right)

Set-up 1: the equipment is composed of a 2L stirred autoclave reactor with a Teflon inner jacket equipped with a magnetic stirrer that can maintain a rotating speed as high as 1500 rpm, is rated up to 200 bars and 343 °C. Starting with a standard liquid CO<sub>2</sub> bottle (with pressure around 50 bars), the CO<sub>2</sub> is compressed via a mechanical pressure booster to 200 bars. The whole compression system is assembled inside a dedicated closet that is kept at a temperature about 45°C, so that CO<sub>2</sub> remains supercritical in the system that feeds the autoclave. The control panel controls the operating total pressure inside the autoclave chamber via an electromagnetic CO<sub>2</sub> injection valve and the temperature via a heating coil.

Set-up 2: The experimental set-up comprises a 300 mL stirred autoclave reactor with a glass inner jacket and Hastelloy internals. The CO<sub>2</sub> pressure inside the reactor is regulated using a CO<sub>2</sub> ballast tank, and instantaneous CO<sub>2</sub> consumption by the liquid-solid suspension is monitored by recording temperature and pressure inside the

ballast. The slurry is stirred by a gas inducing stirrer that achieves high gas-liquid mass transfer. Slurry temperature is monitored and PID controlled.

### Water analyses and solid characterization

Throughout this project, it was found over and over that understanding of process performance required systematic and comprehensive analysis of both liquid and solid phases. Such analytical work is time and energy intensive, but investigation of one phase only, the liquid phase being simplest, is insufficient for sound analysis of aqueous mineral carbonation systems.

Set-up 1: after filtration at 0.2µm, pH and alkalinity was measured. Major anions and cations were analysed by ICP-AES and IC. Solid were dried and total inorganic carbon was measured. Powder and polished thin sections were observed on SEM coupled with elemental analysis (EDX). X-Ray diffraction was also performed. Set-up 2: after filtration using a 0.2 µm micropore filter liquid phase was analysed by ICP-AES to determine the amount of dissolved minerals (Mg, Fe, Si). Solid phase was characterized by different techniques: thermogravimetry coupled with IR detection of released gases to confirm the amount of carbonates, electronic microscopy (SEM and TEM) coupled with elemental analysis (EDX) to identify the different mineral phases, and laser diffraction particle size analysis.

The extent of carbonation (or initial Mg converted) is defined as the fraction of Mg from the initial solid that is extracted and forms MgCO<sub>3</sub>.

### Process development

Direct aqueous carbonation tests were performed with the equipment described above. Studies focused mainly on increasing the reactive surface through grinding, limiting the conditions for the formation of a passivation layer, thermally activating the serpentine (derived from the alteration of olivine), using organic or inorganic additives (including seawater) and studying the reaction kinetics.

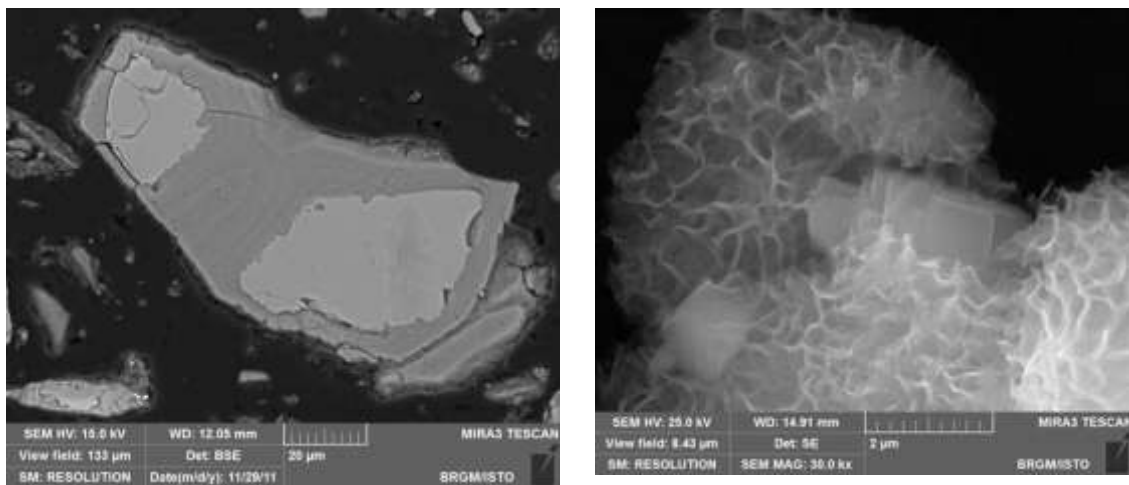
### Direct aqueous carbonation of rocks and slags

**Table 3.** Selective carbonation tests on rocks and slags

	Ref	Media	PCO <sub>2</sub>	t (h)	Final inorg C %	Final MgCO <sub>3</sub> calc %	Initial Mg converted
Hz2<100µm	test V	Dem.w.	10	10	0.41	2.88	2.58
Hz2<100µm	test H	Dem.w.	10	96	0.84	5.90	6.15
Hz2 HT 650°C	test U	Dem.w.	10	24	1.39	9.76	9.58
We1<100µ	test B	Dem.w.	10	96	0.07	0.5	0.73
Lz1<200µ	test C	Dem.w.	10	96	0.15	1.1	0.31
Slag <100µm	test J	Dem.w.	10	24	0.02	<b>0.1</b>	-
Slag <20µm	test S	Inorg.add.	10	24	2.33	<b>16.37</b>	24.45

Carbonation tests were performed on minerals and slag at 180°C (**Table 3**), and low pressure (10-20 bar CO<sub>2</sub>), 90 g/L in agreement with the operating conditions investigated through a dedicated PhD work<sup>2</sup>. Also addition of NaCl (sea water concentration) and inorganic additives –NaHCO<sub>3</sub>/NaCl, concentrations adapted from<sup>3</sup> was tested.

Test results reveal distinct reactivities with a greater responsiveness from the more serpentinized rocks (harzburgite > wehrlite) than from the slag. Slag reactivity was greatly increased however with the addition of NaCl/NaHCO<sub>3</sub>, by grinding to <20 μm and also by increased operating pressure (90 bar CO<sub>2</sub>). A working pressure around 10-20 bar CO<sub>2</sub> (as against 150 bar) enables carbonation of the materials. SEM pictures of slag alteration and MgCO<sub>3</sub> are given as examples (Figure 3).



**Figure 3.** SEM photographs of a) Altered and non altered glass in the slag (left), b) Precipitation of MgCO<sub>3</sub> crystals in proto-serpentine matrix (right)

Also carbonation kinetics of harzburgite was studied for reaction times between 10h and 96h. Geochemical modelling using Phreeqc and v2.18 with the Thermoddem thermodynamic database (<http://thermddem.brgm.fr/>) was performed to simulate experimental points.

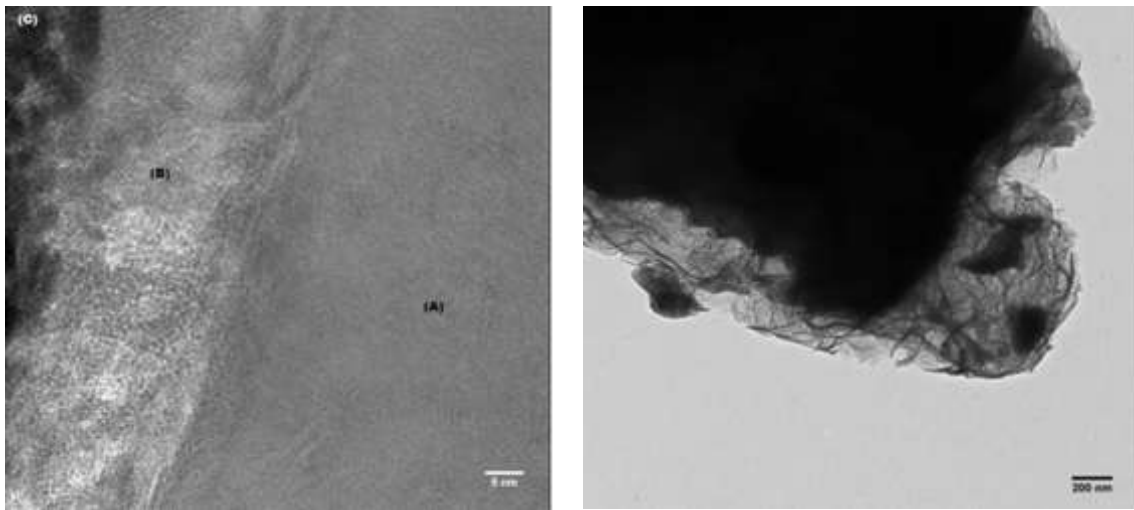
### **Influence of organic ligands/ mechanisms (set-up 2)**

Thus the value of direct aqueous mineral carbonation in the presence of organic ligands was thoroughly investigated<sup>2</sup>, using olivine (Magnolithe GmbH) and harzburgite Hz1 ground to minus 100 μm. While confirming that this additive-based solution to ex-situ mineral carbonation was efficient for mineral dissolution, it was shown to be a dead-end option which could not lead to formation of carbonates<sup>4,5</sup>. This work found that the Mg that would leach out of the ore invariably ended up forming a strong complex with the inorganic component of the additives, in solution and/or in solid form. Glushinskite would for example precipitate in the case of the oxalate additive, preventing any carbonate formation. This detailed piece of research led to a number of positive outcomes however. It demonstrated that sound research about such complex geochemical systems demands that all phases be analysed simultaneously using a

number of analytical techniques, and that the findings be systematically analysed via appropriate geochemical models and thermodynamic databases. It also allowed the research team to build up a strong expertise in analysis of the solid phases present in these systems.

### Comprehensive direct aqueous carbonation of rocks and slags (set-up 2)

Eventually, the work reverted to analysis of the carbonation process in water only, so as to build knowledge on the passivation that opposes the dissolution of magnesium-bearing ores in water. Figure 4 shows TEM cross-sections of olivine particles having been exposed to 20 bar of CO<sub>2</sub> at 120°C and 180°C.



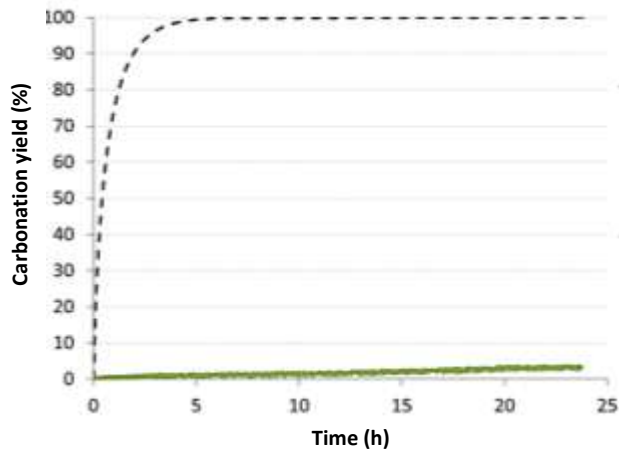
(A) olivine, (B) passivation layer composed of iron oxide and silica, (C) traces of gold from the FIB thin section preparation process.

Translucent passivation layer - Mg, Si and Fe phyllosilicate - covering unreacted olivine particle.

**Figure 4.** Visuals of the passivation layers that precipitate around the olivine particles during aqueous mineral carbonation reaction in water only -TEM pictures after reaction at a) 120°C (3 g.L<sup>-1</sup>, P<sub>CO<sub>2</sub></sub>=20 bar, 24h reaction time) and b) at 180°C (90 g.L<sup>-1</sup>, P<sub>CO<sub>2</sub></sub>=20 bar, 95h reaction time).

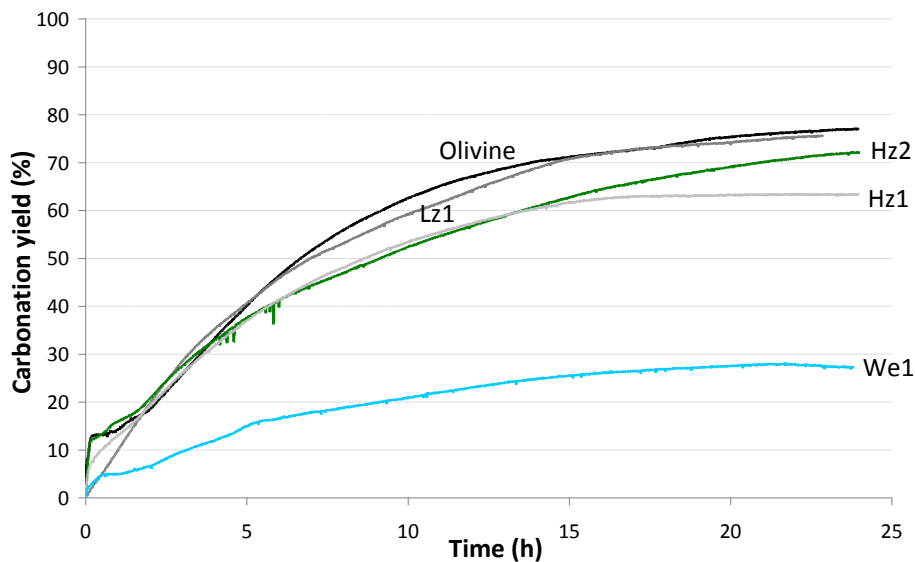
The passivation process always occurred, and the extent of carbonation, never exceeded 7% in 24 hours. The lower curve in Figure 5 shows a typical carbonation rate at 180°C, for olivine particles. The dotted line indicates the rate and extent of carbonation that could be obtained if one were able to prevent the formation of the passivation layer on the particle surface. This was estimated through geochemical modelling of the whole system applied to the olivine feed size distribution, using the dissolution rate of the fresh un-passivated surface of the ore. This rate was obtained by extrapolating the measured dissolution kinetics back to t=0, based on carbonate amount formed according to TGA/IR analysis.





**Figure 5.** Extent of carbonation for olivine as a function of time ( $180^{\circ}\text{C}$ ,  $P_{\text{CO}_2}=20$  bar,  $90\text{ g}\cdot\text{L}^{-1}$ ). The solid line shows a typical measurement for a magnesium silicate ore (minus  $100\mu\text{m}$ ), whereas the dotted line shows the theoretical kinetics expected without passivation.

Next, the research team investigated the idea of preventing the formation of the passivation layers, as a driving-concept for crossing the gap between the two curves from Figure 5. Following the earlier work of Béarat et al. (2006)<sup>6</sup>, a dedicated reactor was commissioned at the laboratory scale so as to exfoliate the passivation layers as they would form. Remarkable results were obtained, without optimisation of the process conditions, thereby leaving a significant margin for optimisation, both in terms of energy requirement of the overall process and kinetics. The results (Figure 6) were obtained with minus  $100\mu\text{m}$  particles for 5 distinct magnesium silicates also without any thermal pre-treatment for serpentine rich rocks.



**Figure 6.** Kinetics of carbonation as a function of time ( $180^{\circ}\text{C}$ ,  $P_{\text{CO}_2}=20$  bar,  $90\text{ g}\cdot\text{L}^{-1}$ ) obtained with 5 magnesium silicates with a continuous passivation layer exfoliation scheme.

Few modifications of this process were tested, including addition of the standard 1M NaCl + 0,64M NaHCO<sub>3</sub> inorganic solution<sup>3</sup>, which helped reach carbonation yields in excess of 90% in less than 24 hours. This process, which opens promising avenues for the development of ex-situ mineral carbonation, is the focus of new research that targets industrial feasibility and demonstration.

### Environmental assessment

The environmental assessment of ex-situ mineral carbonation has been performed based on LCA methodology (Figure 7). Three scenarios were defined and compared, using a coal-fired power station as the source of CO<sub>2</sub> emissions:

- (1) without CO<sub>2</sub> capture ;
- (2) with CO<sub>2</sub> capture and geological storage ;
- (3) with CO<sub>2</sub> capture and ex-situ mineral carbonation.

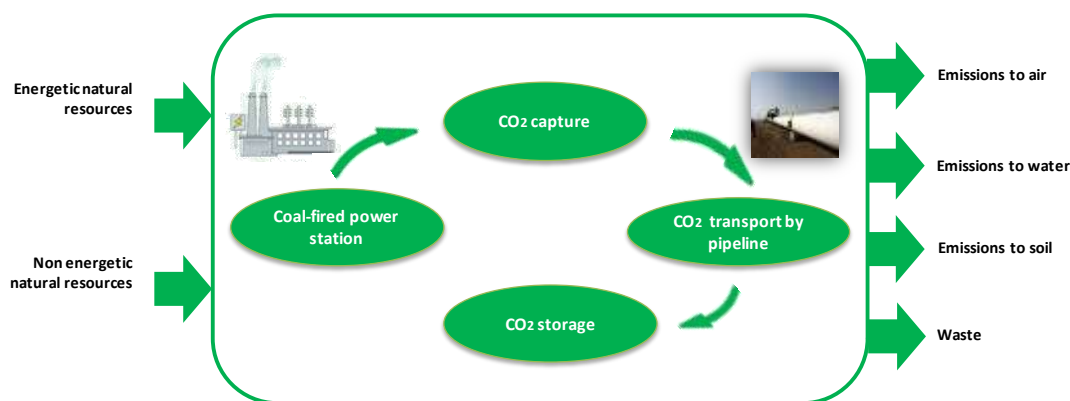


Figure 7. Life cycle of the system studied

Table 4. LCA results for each scenario studied

Environmental impact indicators	Units	Scenario (1)	Scenario (2)	Scenario (3) Best results obtained
Natural resources depletion	kg Sb eq.	6.70E+00	9.81E+00	1.20E+01
Non-renewable primary energy consumption	primary MJ	9.99E+03	1.47E+04	2.09E+04
Climate change	kg CO <sub>2</sub> - eq.	9.23E+02	2.98E+02	6.08E+02
Terrestrial acidification	kg SO <sub>2</sub> eq.	1.64E+00	1.22E+00	2.50E+00
Photochemical oxidation	kg NMVOC eq.	9.73E-01	1.34E+00	1.98E+00

The evaluation showed mixed results with pollution gains or transfers depending on the process and the studied impact indicators (Table 4). However, with the best set of operating conditions and performance obtained using the aqueous mineral

carbonation process, the net result from LCA for mineral carbonation shows promises. It is noted that the research work on the process itself was not optimised; hence there remains a significant margin of improvement. The analysis confirmed however that the viability of this CO<sub>2</sub> storage option is mainly at the level of the mineral carbonation process and optimization of its operating conditions.

## Conclusion

This article did propose an overview of the main outputs from the French Carmex project (2009-2012). This project reviewed the feasibility of ex-situ mineral carbonation in terms of resource availability, performance of the aqueous mineral carbonation process and life cycle analysis criteria. Firstly, the project demonstrated the value of SIG for identification and ranking of potential sites. Through a real team effort, the project was able to achieve significant conversion rates, using a process capable of preventing the formation of passivation layers around the particles. Life cycle analysis of the system as a whole led to the conclusion that the eligibility of ex-situ mineral carbonation as a practical solution to CO<sub>2</sub> mitigation depends primarily on the operating conditions of the process. This result indicates that more development work is required to optimise the process, however results obtained during this project suggest that admissible conditions are within reach, particularly in favourable situations such as with the New Caledonian context.

## Acknowledgements

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