To cite this version :
Bonfils, Benjamin and Julcour-Lebigue, Carine and Bourgeois, Florent and Guyot, François and Chiquet, Pierre (2010) *About the foundations of direct aqueous carbonation with dissolution enhancing organic salts.* In: ACEME10 (Accelerated Carbonation for Environmental and Materials Engineering 2010), December 2010, Turku, Finland. (Unpublished)

About the foundations of direct aqueous carbonation with dissolution enhancing organic salts

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ABSTRACT

Direct aqueous carbonation is a promising mineral carbonation route. Under mildly acidic conditions, this single-step carbonation process aims to simultaneously dissolve Ca/Mg-bearing silicates or wastes and precipitate Ca/Mg carbonates. By and large, since mineral dissolution is rate limiting due to the lack of protons at near-neutral pH, research has mainly been concerned with the issue of enhancing dissolution. By analysing the liquid phase, it has been established that polyacid organic salts can significantly enhance silicate dissolution under such unfavourable conditions.

Comparatively little attention has been paid to the investigation of the very basis of the whole process, *i.e.* the concomitance of silicate dissolution and carbonate precipitation. By taking a close look at the solid phases in lizardite and olivine slurries, this work confirms the co-occurrence of magnesium silicate dissolution and magnesite precipitation inside a stirred reactor operating at 120°C, 20 bar of CO_2 and 0.1M disodium oxalate, thereby bringing indisputable evidence that supports the foundation of direct aqueous carbonation with organic salts.

Introduction

Ex-situ mineral carbonation of silicates or industrial wastes is a CO_2 mitigation option that consists in converting CO_2 gas into thermodynamically stable solid carbonates. Amongst the process routes that have been investigated over the years - see literature review by Sipilä, Teir and Zevenhoven [1] – direct aqueous carbonation using organic salts as dissolution enhancing additives is a particularly interesting single-step process. It is based on achieving concomitant (Mg,Ca)-bearing solids dissolution and carbonate precipitation under the same near-neutral pH conditions.

Specific catalyst-like additives, in particular polyacid organic salts, play a pivotal role in this process. Indeed, they compensate for the lack of protons and promote silicate dissolution at pH greater than 5, without being consumed during the dissolution step. Dissolution being rate limiting under such conditions, research [2,3,4] has focused on screening organic salts to accelerate dissolution of magnesium silicates. Typical experiments relied on using dilute slurries with antigorite or olivine particles (e.g. 3 g/L in the case of [3]), such that the concentration of Mg in solution would be high enough for detection, and yet not exceed the saturation level required for precipitation of Mg-carbonates. With a temperature of 120 °C, a CO_2 pressure of 20 bar, and a solid concentration of 3 g/L with particles ground below 75 μm, Krevor and Lackner [3] found the highest dissolution rates of a serpentine antigorite with citrate, oxalate and EDTA ligands. After 24 hours, they accounted for 70% of the Mg contained in the ore into solution, with 0.1M $Na_2C_2O_4$ (disodium oxalate), 0.1M $Na_3C_6H_5O_7$ (trisodium citrate) or 0.1M $Na_2C_{10}H_{14}N_2O_8$ (disodium EDTA). By increasing citrate concentration to 0.5M, they even achieved a magnesium dissolution yield as high as 90%. Recently [4], dissolution kinetics has been measured with olivine particles under such conditions. Overall, the results to date have proven the efficacy of polyacid organic salts on the dissolution kinetics of magnesium silicates. They have also shown that the efficiency of the additives is strongly related to their concentration relative to the particle surface area. In addition, they have indirectly confirmed the conclusions by Olsen and Rimstidt [5] about efficiency of polyacids versus mono-acids on the dissolution of oxides and silicates as significantly lower dissolution rates have been measured with sodium acetate.

Because research has focused on dissolution under dilute solid conditions, only the liquid phase has been analysed and used to build up knowledge about the direct aqueous carbonation process with organic salts. Surprising as it may sound, the very foundation of the process, i.e. the co-occurrence of silicate dissolution and carbonate precipitation under the abovementioned conditions remains to be verified. Moreover, optimising dissolution of silicates may not necessarily point in the right direction. Indeed, it is conceivable that dissolved Mg may form stable complexes in solution with dissolution enhancing additives, and possibly hinder precipitation of magnesium carbonates. Aside from the knowledge that has been established to date about the effect of organic salts on silicate dissolution, it appears urgent to investigate the aqueous carbonation as a whole. To this end, both the liquid phase and the solid phase must be analysed.

In a recent publication [6], we made the point that analysis of the solid phase is essential for analysis and interpretation of direct aqueous carbonation experiments. With the CHESS geochemical modelling package [7,8], we carried out a number of "virtual" direct aqueous carbonation experiments which indicated that analysis of the liquid phase, even under undersaturated conditions, must be coupled with analysis of the solid phase for proper interpretation of experiments. Geochemical equilibrium simulations were done using an antigorite-like magnesium silicate with stoichiometry $Mg_3Si_{2.125}O_{9.188}H_{3.875}$, whose oxide composition matches the serpentine antigorite used by Krevor and Lackner [3]. Only key results are reported here, and the reader is invited to refer back to [6] for details about hypotheses, results and interpretation. Table 1 shows results from two simulation cases under dilute solid conditions (3 g/L), with Case 2 being a close match to the test conditions used by Krevor and Lackner [3].

		Case 1: Water	**Case 2: Oxalate 0.1M**
Solid phase	Antigorite	0	0
	Magnesite	2.34 g (87.5% Mg)	0.05 g (1.9% Mg)
	Quartz	1.28 g (94.7% Si)	1.28 g (94.7% Si)
Liquid phase	Total $Mg_{(aq)}$	0.0040 mol/kg_{water} Mg^{2+} (10.6% Mg)	0.031 mol/kg_{water} $MgC_2O_{4(aq)}$ (97.3% Mg)
	Total $Si_{(aq)}$	0.0012 mol/kg_{water} $SiO_{2(aq)}$ (5.3% Si)	0.0012 mol/kg_{water} $SiO_{2(aq)}$ (5.3% Si)
	Total $Oxalate_{(aq)}$	N/A	0.1 mol/kg_{water} $C_2O_4^{2-}$ (66.0% oxalate) $MgC_2O_{4(aq)}$ (30.9% oxalate)

NB: values in brackets are molar percentages relative to the total amount present in the system.

Table 1. Geochemical equilibrium simulation results for antigorite dissolution (solvent mass: 1 kg, antigorite mass: 3 g, temperature: 120°C, CO_2 fugacity: 20 bar, precipitation occurs as soon as saturation is reached $\Omega = 1$).

Many learnings can be made from Table 1 [6], of which only those that serve this paper are discussed here. In both Cases 1 and 2, geochemical equilibrium simulation predicts the complete dissolution of the magnesium silicate and the precipitation of magnesite. Under dilute conditions and low CO_2 pressure, reference Case 1 with water only yields significant amounts of magnesite and quartz. Case 2 with oxalate, on the other hand, exhibits unfavourable thermodynamics with respect to the precipitation of magnesite, due to the formation of a strong magnesium – oxalate complex in the liquid phase, which accounts for more than 97% of the initial Mg. However, geochemical equilibrium simulation still predicts the formation of a low amount of magnesite. If magnesite precipitation is disabled in the simulation, its saturation index SI defined as log(Ω), is equal to 0.12 only. The key point here is that in the absence of any kinetic hindrance, magnesite should precipitate despite the very low solid concentration of the slurry (3 g/L only). Such a small quantity of magnesite would remain undetected from liquid phase analysis alone. However, its measurement would suffice to validate the very basis of direct aqueous carbonation with organic salts. It is this simple observation that led us to conclude that characterisation of both solid and liquid phases is absolutely necessary for analysis and interpretation of any direct aqueous carbonation experiment. Moreover, this finding triggered our interest in finding out whether magnesite formation could actually be obtained under the conditions established by Krevor and Lackner [3], which are deemed favourable for direct aqueous carbonation of magnesium silicates from the viewpoint of extent and rate of dissolution. The high concentration of Mg-oxalate complex in solution that is predicted by geochemical simulation raises questions about how much magnesite can possibly be obtained by direct aqueous carbonation with the oxalate ligand.

Experimental validation of the direct aqueous carbonation process with oxalate salt

In the following section, we report experimental proof of precipitation of magnesite with disodium oxalate for lizardite and olivine ores, thereby confirming the very foundation of the direct aqueous carbonation process.

Materials and methods

The carbonation of the two following ores was investigated: a serpentine from New Caledonia, which is composed mainly of lizardite with traces - or low amounts - of forsterite, enstatite and diopside, and an olivine from Austria with traces - or low amounts - of enstatite. Their chemical composition is given in Table 2.

	Serpentine	**Olivine**
SiO_2	40.0	40.5
Al_2O_3	0.6	N/A
CaO	0.6	0.4
MgO	41.1	48.8
MnO	0.1	N/A
Fe_2O_3	7.8	9
Loss on ignition	9.1	0.1

Table 2. Mineral composition of investigated starting material, given as oxide wt%.

The starting materials were first ground to a P_{80} value of 100 µm, then sieved below this size and sampled using a rotary splitter. This procedure resulted in lots with 4.2 µm Sauter diameter for serpentine and 12.4 µm for olivine. Such a fine particle size was produced to give a high reactive surface area, hence fast dissolution kinetics [3]. The difference in particle size does not permit comparison of the reactivity of the ores on the basis of the results presented below. Ideally, tests should be conducted with narrow particle size classes for comparison purposes.

The experimental set-up comprised a 300 mL stirred autoclave reactor with a Teflon inner jacket and Hastelloy internals. The CO_2 pressure inside the reactor was regulated using a CO_2 ballast tank, and instantaneous CO_2 consumption by the liquid-solid suspension was monitored by recording temperature and pressure inside the ballast. The slurry was stirred by a gas inducing turbine that achieved high gas-liquid mass transfer. Slurry temperature was monitored and PID controlled.
A typical test run consisted in contacting CO_2 with the liquid-solid dispersion under constant pressure for 24 hours. After reaction, the system was cooled down to room temperature and pressure was released. The slurry was then passed through a 0.2 µm micropore filter and retained

solids were oven dried. Mg and Si concentrations in the filtrate were measured by ICP-AES. Solid phase characterization is more complex, hence different complementary techniques were used to get both qualitative and quantitative results: microscopy (FEG/SEM coupled with EDX analysis), X-ray diffraction, Raman and infrared spectroscopy and thermogravimetry (TGA coupled with IR analysis of released gases).

Thermogravimetry analysis, performed under N_2 flow (with a heating rate of 10°C/min from room temperature to 1000°C), yielded the total amount of CO_2 in the solids after reaction. From analysis of TGA/IR spectra for the initial material and pure magnesite, it was found that carbonates formed during reaction could be detected and quantified by the TGA weight loss in the temperature range 300-600°C. TGA/IR analysis was also used to quantify the amount of solid by-products, such as oxalate magnesium dihydrate (glushinskite), which first yields H_2O in the 120-300°C range, then CO and CO_2 at a slightly lower temperature than magnesite. When both glushinskite and magnesite co-precipitate, the quantity of glushinskite was determined from the water loss only (see *preliminary data analysis* section). The corresponding CO and CO_2 weight loss was then deduced from the overall TGA weight loss in the 300-600°C zone, the remaining CO_2 loss yielding the amount of magnesite present in the final reaction product.

Results and comments

Experiments were performed at 120°C under 20 bar of CO_2, first with a low solid concentration of 3 g/L_{water} (0.3 wt%) as per Krevor and Lackner [3], and then with a high solid concentration of 250 g/L_{water} (20 wt%). They were carried out using either osmosed water or 0.1M disodium oxalate solution.

Preliminary data analysis

The abovementioned analytical techniques gave access to a large amount of information and a preliminary analysis was required to check for their sensitivity and consistency.

For instance, both the thermogravimetry analysis of the final solid and the measurement of CO_2 consumption from the ballast should give an independent measurement of the carbonation yield. However the low amount of magnesite formed in the investigated cases accounted for less than 5% of the total CO_2 consumption. In other words, 95% of the CO_2 pressure drop from the ballast corresponded to the filling of the reactor and the dissolution of CO_2 in water. The calculation was therefore very sensitive to the amount of bicarbonate ions in solution. This latter value varied in between 0.2 ppm from simple CO_2 dissolution (according to equilibrium calculations) to about 150 ppm (measured) after 24 hours of reaction in water, as a consequence of pH increase. However nothing is known about the way it varied during an experiment. Consequently, the measurement of CO_2 consumption could only provide an order of magnitude of the amount of magnesite formed. Nevertheless it gave valuable information on the kinetics of the whole carbonation process (mainly limited by mineral leaching). An example of time-CO_2 consumption profile obtained after reactor filling and gas dissolution is given in Figure 1 for an experiment with olivine in water only. The figure shows a continuous slowing down of magnesite formation, which levels off after 12 hours or so under the given test conditions. Under these conditions, the carbonation yield after 24 hours reached only about 1% of that predicted from thermodynamic calculations, which indicates the presence of some form of a kinetic barrier.

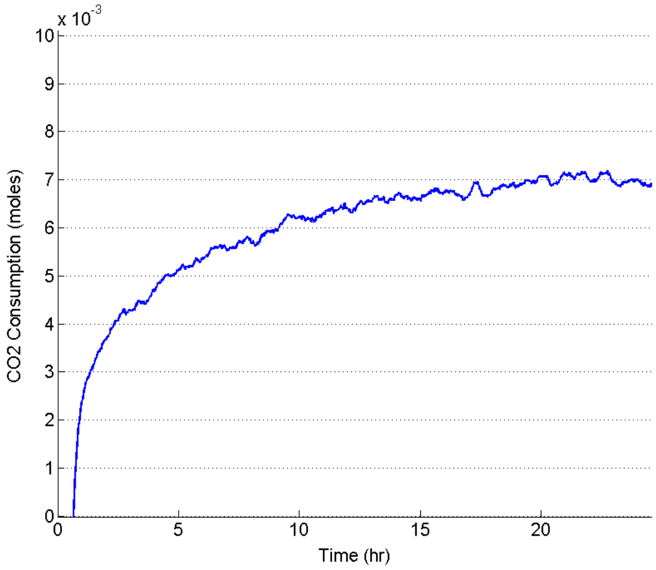
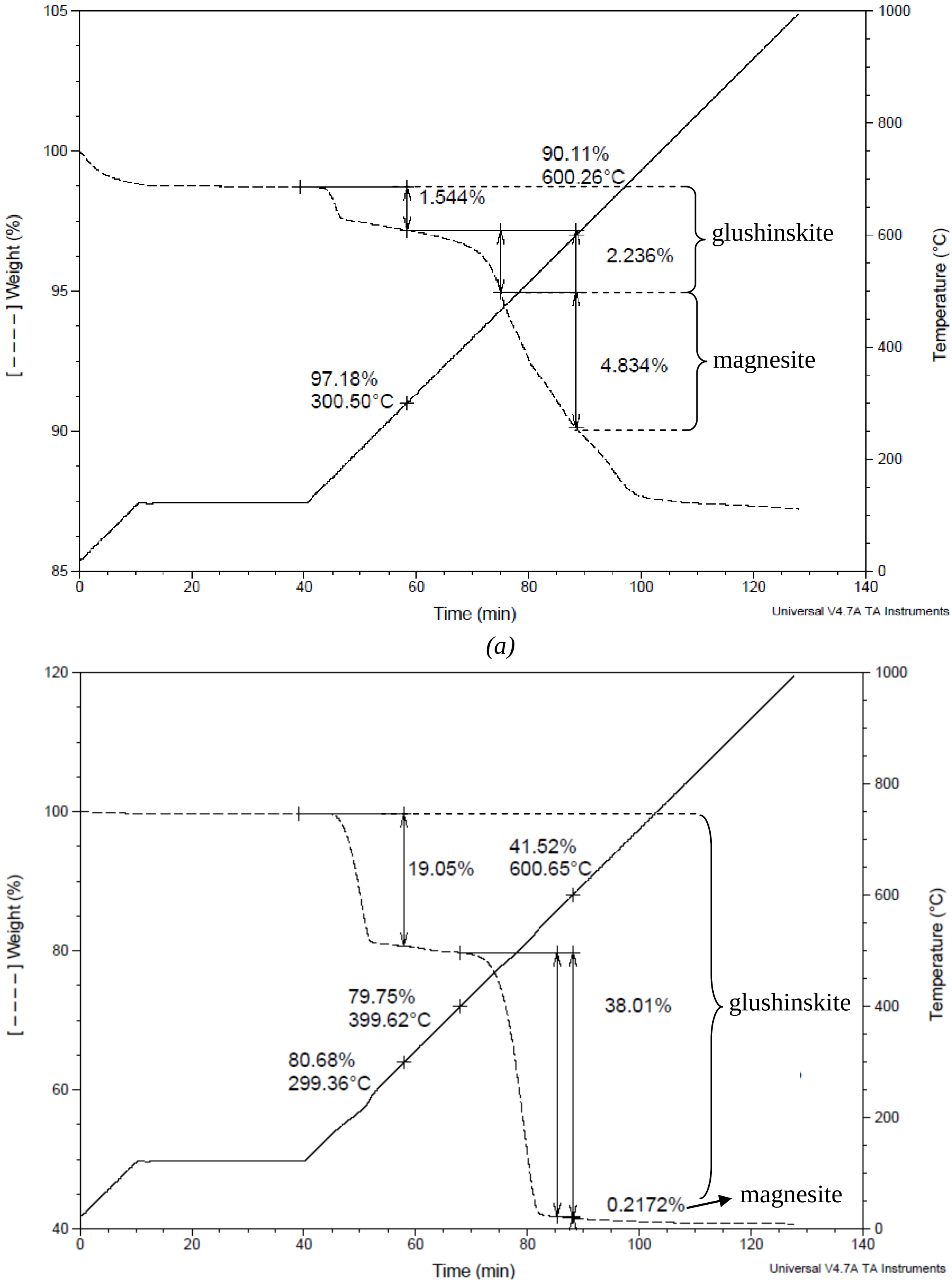


Figure 1 – Example of instantaneous consumption of CO_2, which corresponds to magnesite precipitation during an experiment with olivine (120°C and 20 bar CO_2, slurry concentration: 250g/L_{water}).

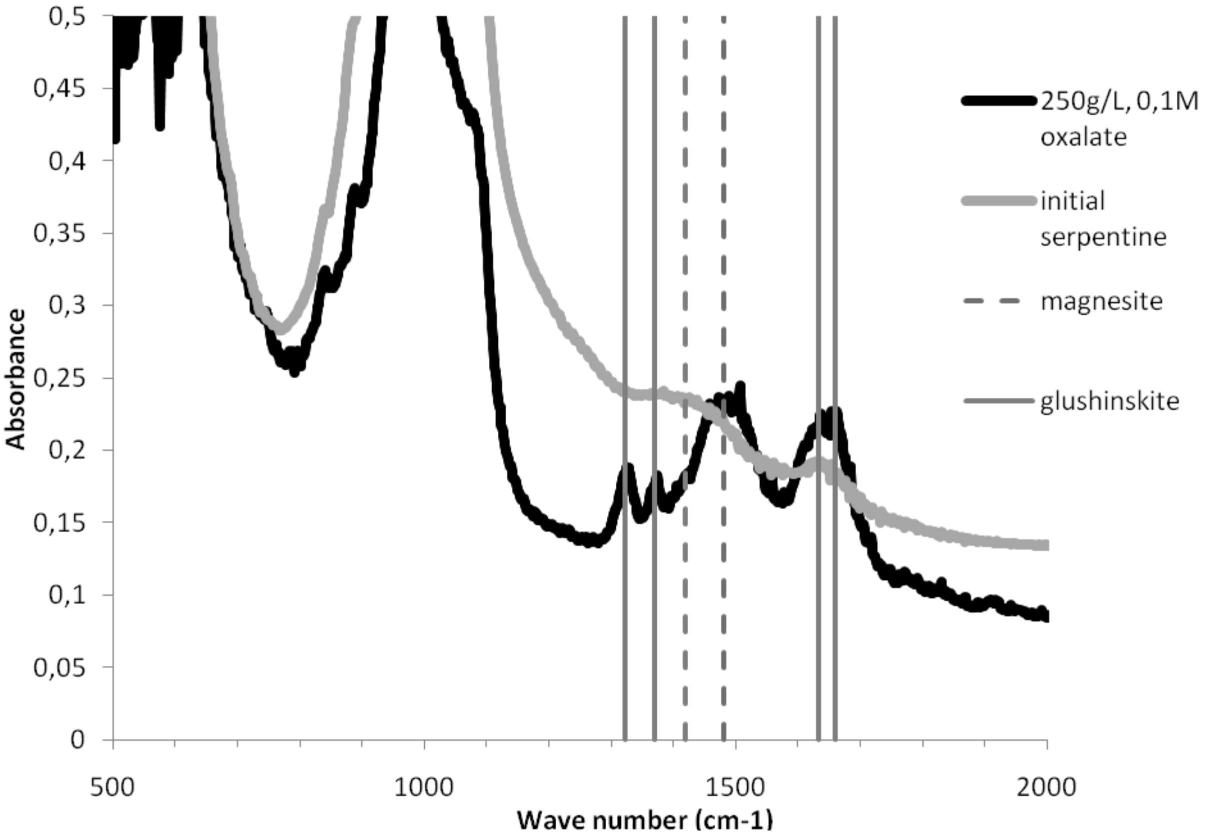
Provided that the composition of the starting material is homogeneous and well-known, mass balances can be calculated from ICP and TGA to give the magnesium extraction yield and its distribution amongst the different phases (see Figures 5 and 6). In order to delineate the nature of solid products and cross-check the interpretation of the thermograms, Raman and infrared were used. For materials with low conversion, Diffuse Reflectance IR spectroscopy (DRIFT) was also used to obtain information about carbonates that might have precipitated on the surface of the particles. First, we shall comment on the results obtained for the concentrated serpentine slurry with 0.1M oxalate (See Figures 2a and 3a). The thermogram shown in Figure 2a indicates both an additional water release in the temperature range of 120-300°C as compared to the original silicate, and a CO/CO_2 release in the 300-600°C temperature range (with two consecutive CO_2 release peaks). The Raman spectroscopy clearly confirmed that part of this weight loss is due to the decomposition of glushinskite, whose Raman bands were detected at 1660 ((C=O)), 1637, **1471** ((C-O)), 1450, 919 ((C-C)), 864, 590, 529 ((Mg-O)), 266, 239 and 227 cm^{-1} [9]. Detection of carbonates using Raman spectroscopy lacks representativity in cases where small amounts of carbonates are present inside the product mass, due to the analysis being highly localized. In this particular case, DRIFT analysis however gave evidence of the presence of magnesite, with a signal observed in the 1420-1480 cm^{-1} characteristic region (Figure 3a).



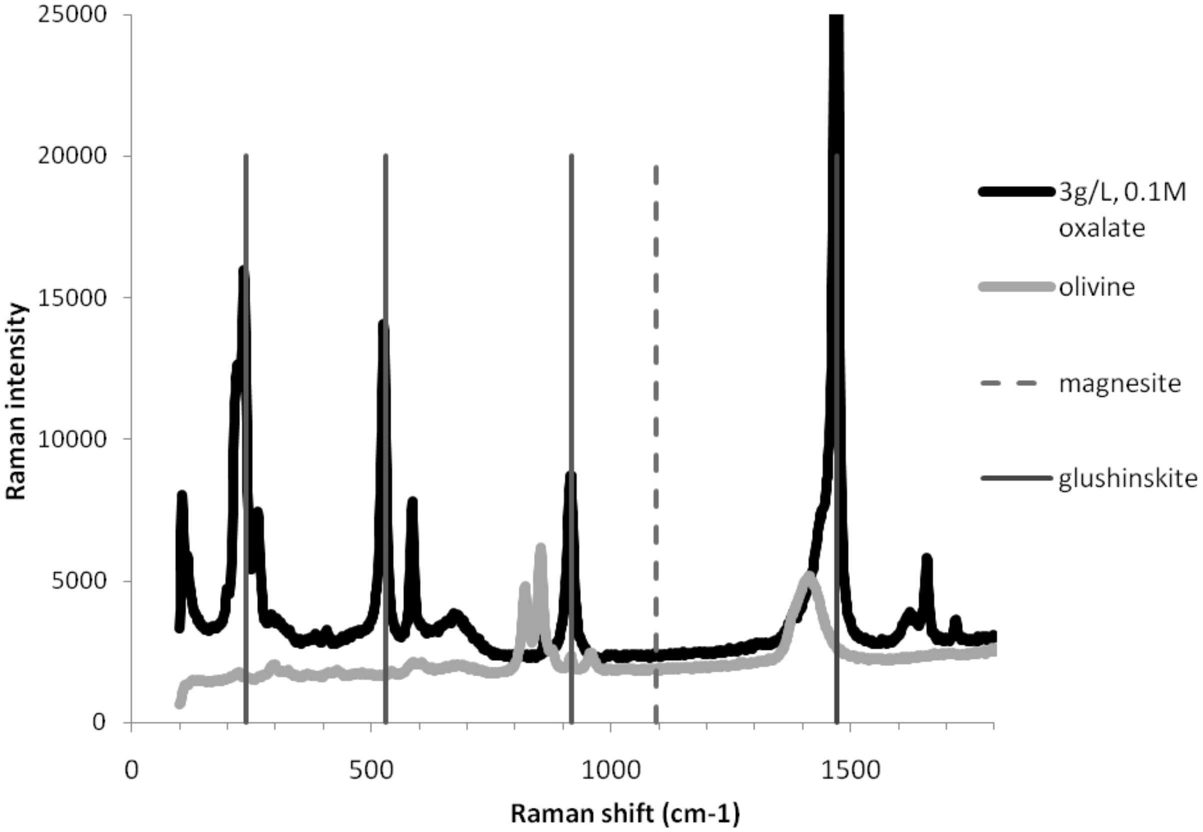
(a)

(b)

Figure 2 – Examples of thermograms used to evaluate glushinskite and carbonate amounts: (a) serpentine, 250 g/L$_{water}$ with 0.1M oxalate, (b) olivine, 3 g/L$_{water}$ with 0.1M oxalate.



(a)



(b)

Figure 3 – Examples of DRIFT and RAMAN spectra used to confirm carbonate and glushinskite precipitation: (a) serpentine, 250 g/L_{water} with 0.1M oxalate, (b) olivine, 3 g/L_{water} with 0.1M oxalate.

For the 3 g/L$_{water}$ experiment with 0.1M oxalate, mass balances revealed that almost all the magnesium was in the form of glushinskite and dissolved species. SEM/EDX was first used for elemental mapping of the solid products.

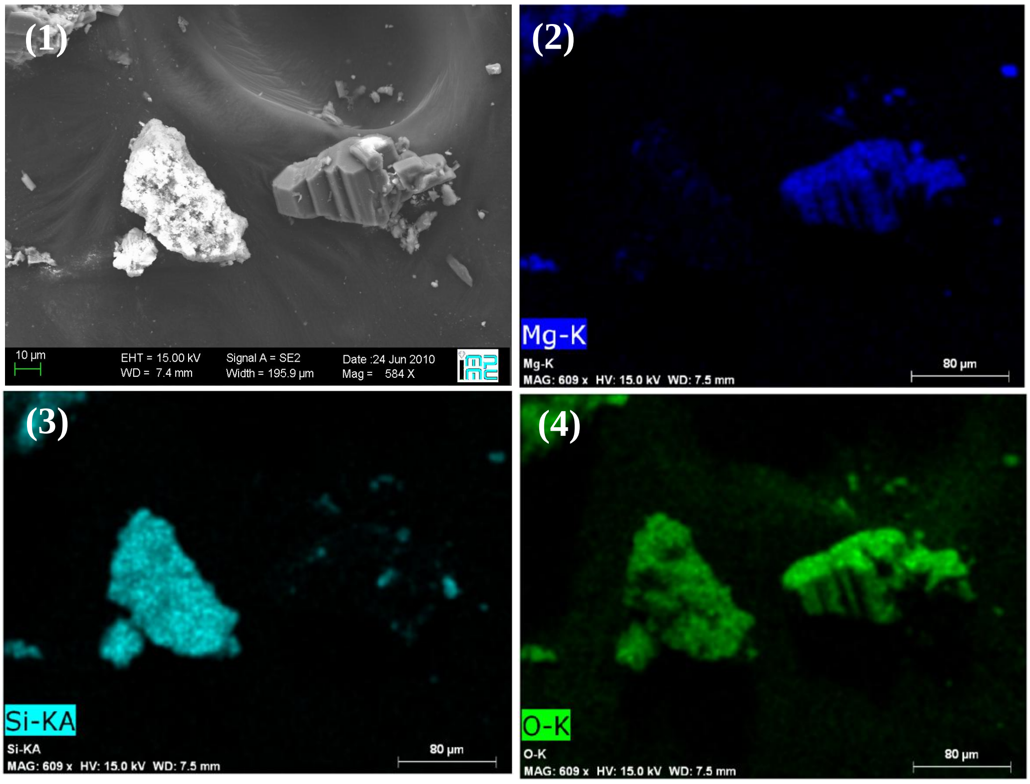


Figure 4 - Example of SEM/EDX images for reaction products with 3 g/L$_{water}$ of olivine and 0.1M oxalate: (1) SEM image, (2) Magnesium EDX map, (3) Silica EDX map, (4) Oxygen EDX map.

In Figure 4, we can identify two types of particles: rhomboedral magnesium oxalate particles (glushinskite) and silica-rich particles. The size of the later particles also resembles that of the original particles, which suggests that the leaching of magnesium could follow a shrinking core like mechanism.

A semi-quantitative EDX analysis made on a few particles confirmed that glushinskite precipitated separately and that the remaining silicate particles had a low magnesium content (7-10% wt.), as compared to the initial content of 30% wt. However the technique is known to be sensitive to surface defects (roughness, pores) and heterogeneity of the powder particles (the incident electrons have a relatively small penetration depth), so that it could not be used as a quantitative tool to measure silicate conversion. The representativity of the measurement is also questionable, as it was applied to a few large particles only.

Therefore X-ray diffraction was used to assess the extent of conversion of the ore, confirming that only traces of original magnesium silicate were present.

In this condition, the consecutive weight losses observed on the thermogram almost matched with the stoichiometry of the glushinskite. Thus the amount of magnesite deduced was close to the quantification limit of the method (Figure 2b). The spectroscopy techniques (Figure 3b) did not detect any carbonate either. Another technique is clearly needed to improve the detection limit for magnesite in such systems. We are currently developing an experimental technique for measuring low levels of magnesite in these systems, based on selective dissolution of the glushinskite precipitates.

Experimental results

Figures 5 and 6 summarise the dissolution and carbonation yields of serpentine and olivine respectively, for both the diluted (3 g/L) and concentrated (250 g/L) cases. We re-emphasise that our objective here is not to find the conditions that produce the greatest amount of magnesite, but to prove that the co-occurrence of silicate dissolution and magnesite precipitation can be obtained.

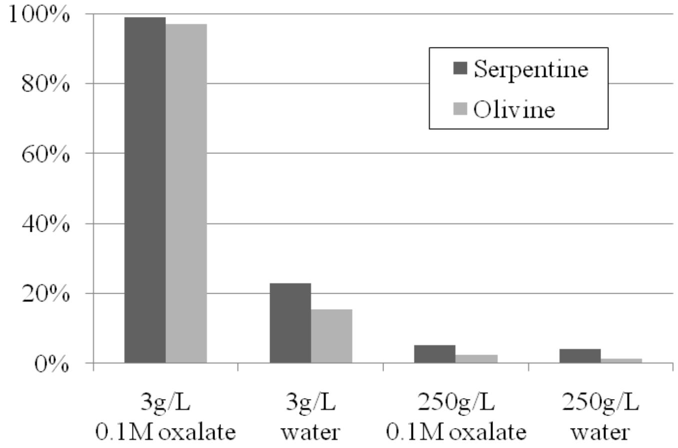
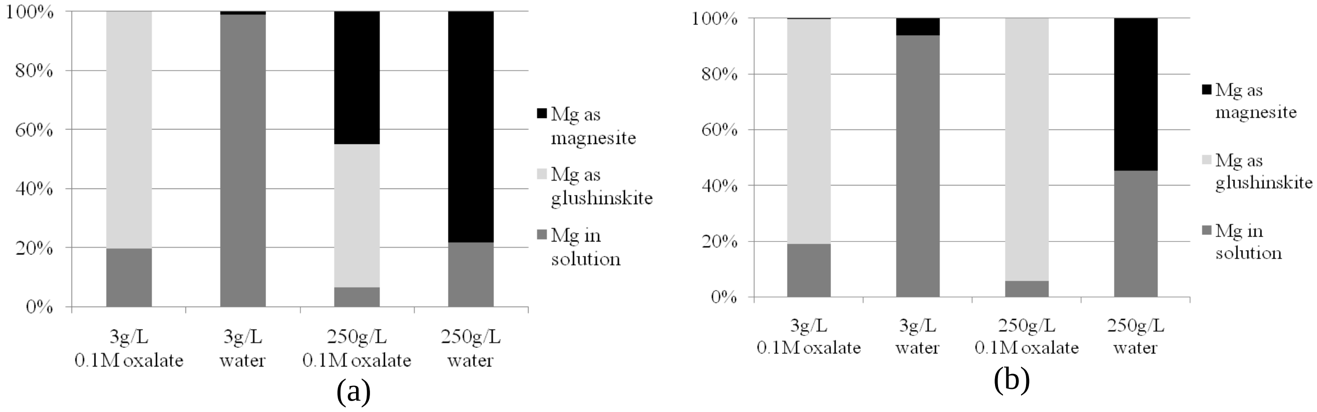


Figure 5 – Total magnesium extraction yield for the different experiments with both starting materials (based on the amount of Mg found in solution).



(a) (b)

Figure 6 – Speciation of extracted magnesium for the different operating conditions: (a) serpentine case, (b) olivine case.

From the data presented here, the following conclusions can be drawn with both ores:

(1) In dilute (3 g/L_{water}) slurry conditions, disodium oxalate yields almost complete dissolution of magnesium silicates (98-99%) within 24 hours (Figure 5), the magnesium being mainly in the form of glushinskite and dissolved species (Figure 6). As indicated by geochemical modelling, glunshinskite should not exist at the reaction temperature, but should precipitate from Mg-oxalate dissolved species during cooling of the solution below 50-60°C.

(2) Precipitation of magnesite is low to undetected in all dilute cases, for which modelling however indicates that oversaturation should be reached for magnesite under such conditions (*cf.* Table 2, right column). Precipitation of magnesite seems to be hindered by the presence of oxalate, as can be seen with olivine in Figure 6b.

(3) Accounting for experimental uncertainties, the dissolution enhancement due to the addition of oxalate salt was not conclusive with concentrated (250g/L_{water}) slurries. This suggests that for the 250 g/L_{water} slurry, the ligand concentration relative to the reactive surface area of particles (80 times less than in the 3 g/L_{water} case) was insufficient to accelerate the dissolution of magnesium silicate. The silicate/ligand ratio is certainly a key issue with optimisation of the process. Indeed, sufficient ligand must be added to the system for

enhancing dissolution; however dissolved Mg forms a strong complex with oxalate in solution, which may inhibit magnesite precipitation.

(4) The effect of solid concentration was also found significant when no ligand was added, probably as a consequence of the lack of protons in the system. Like [3], we saw earlier with the example of Figure 1 that dissolution rate is drastically reduced after a few hours, despite being far from equilibrium.

The olivine was found to be slightly less reactive than the serpentine. We think that this is particle size related. Indeed, from the Sauter diameter values, the specific surface area with serpentine is 3 times greater than that for the olivine sample. This could possibly explain why no magnesite was found for the 250 g/L_{water} case with oxalate, contrary to what could be expected from the composition of this ore (with a higher Mg content than in serpentine). With serpentine, spectroscopy techniques did confirm the presence of both magnesite and glushinskite (Figure 3a).

Conclusions

In this work, we have demonstrated with few well-chosen test conditions that magnesium silicate dissolution and magnesite precipitation can actually co-occur, which confirms the soundness of direct aqueous carbonation with organic salts. Conditions that were used included dilute solid conditions used in the literature for studying the dissolution step of the process, and concentrated conditions seemed well-suited for development of an industrial process. Unfortunately, only low amounts of magnesite were found in both cases, due to either too small an amount of solids in the 3 g/L case, and too small an amount of oxalate in the 250 g/L case. It seems likely that process conditions that lay somewhere between these 2 extreme cases could yield higher magnesite formation.

One point of significance for process feasibility is the formation of a strong Mg-oxalate complex in solution, which may in fact be detrimental to the precipitation of magnesite. This makes the point that optimising dissolution is possibly not the way to optimise the aqueous carbonation process as a whole. More work is clearly required on this critical issue. In order to compare test results for various ores, the effect of surface area that were discussed here mean that tests should be carried out on narrow particle size classes.

The following issue was not fully developed in the paper, but conclusive identification and quantification of the different solid species that may form during an experiment is not trivial by any mean. Some techniques are capable of conclusive identification (e.g. EDX), but they often analyse very few particles, hence their quantitative value is questionable. Other techniques such as TGA/IR can make quantitative measurements on representative subsamples of reaction products, however their capacity for conclusive delineation of solid species is limited. Overall, one must use many complementary analytical techniques, and account for their respective precision, threshold values and the representativity of the subsamples used in the analyses. A number of measures are currently being taken in order to reduce some critical threshold values, such as with the reduction of the dead volume above the slurry inside the reactor. Other experimental techniques are currently being tested for improving our ability to delineate solid species, such as with selective dissolution of the glushinskite that forms during cooling for more accurate measurement of magnesite formation.

Acknowledgements

This research work is being conducted as part of the CARMEX project n°ANR-08-PCO2-002, which is funded by the Agence Nationale de Recherche (the French National Research Agency) through the CO_2 Capture and Storage program. The authors also thank the oil and gas company TOTAL for funding the Ph-D grant of B. Bonfils.

Finally, they acknowledge Jean-Louis Labat, Alain Müller and Lahcen Farhi (LGC, INP Toulouse) for their contribution to the design and implementation of the experimental set-up, Thierry Augé (BRGM Orléans) for providing the starting material, Christine Rey-Rouch, Colin Fourtet, Marie-Line de Solan Bethmale (SAP, LGC Toulouse), Sandrine Desclaux, Sébastien Teychené, Nicolas Estime (LGC Toulouse), Philippe Besson (LMTG Toulouse), Serge Alamercery (SCA CNRS Lyon), Corinne Routaboul (SFTCM, UPS Toulouse), Véronique Jean-Prost (BRGM Orléans), Matthieu Galvez (IMPMC Paris), , Olivier Sissmann (IPG Paris) for the physico-chemical analyses of the solids and solutions.

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