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Understanding the Chemistry of Direct Aqueous Carbonation with Additives Through Geochemical Modelling

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Abstract

Amongst possible mineral carbonation strategies, direct aqueous mineral carbonation using organic salts is perhaps the most promising one. By going to and from between geochemical modelling and experimental results, this paper reviews key findings and conclusions to date about this process. With the magnesium silicate – oxalate system, the paper makes a strong case for the necessity to characterize both solid and liquid phases in order to analyze any aqueous mineral carbonation test results. It is shown that partial information about reaction products, such as liquid phase analysis without characterization of the associated solid phase, can easily lead to flawed conclusions. Proper analysis of solid products is recognized however to complicate experimental work considerably, with many analytical techniques being required to reveal the true nature of the solid phases present in aqueous mineral carbonation chemical systems. Given the complexity of such systems, geochemical equilibrium modelling is found to be an invaluable companion tool for planning and interpretation of experimental results. However, in contrast with the performance of geochemical simulation tools available today, such as the CHESS package used in this work, the lack of thermodynamic data necessary to simulate the behaviour of relevant chemical systems is a real issue that must be addressed.

1. Introduction

Ex-situ mineral carbonation is considered a possible alternative to geological storage for CO_2 mitigation. Its strongest asset is that it converts a CO_2 gas stream into CO_2's most thermodynamically stable form: solid carbonates. Historically, mineral carbonation was first investigated under dry conditions, however kinetics was invariably found to be slow [1]. Then, investigations shifted almost entirely towards aqueous mineral carbonation, with two distinct schools of thought. The first one seeks to develop an indirect process with two sequential steps [2,3,4], so they can be optimised individually. The first step is the dissolution of (Mg, Ca)-bearing solids – either naturally occurring such as (Mg,Ca) silicates, or industrially produced such as mining wastes or slags – under strongly acidic conditions, followed by a carbonates precipitation step under basic conditions. The most severe problems with this process include a considerable consumption of acids and bases, and, to a lesser extent, a potentially high energy requirement [2]. The second school of thought, to which this work belongs, seeks to develop a direct process whereby dissolution of (Mg,Ca)-bearing solids and precipitation of carbonates can occur under the same near-neutral pH conditions. This is made possible by using specific catalyst-like additives that promote silicate dissolution under such conditions, without being consumed by the process.

Contrary to CO_2 capture and geological storage, development of direct aqueous mineral carbonation is still in its early stages. Nevertheless, the practical question we would like to answer is whether current knowledge is sufficient

for considering practical developments. This question underlies the purpose of this article, which, by going to and from between geochemical modelling and experimentation, reviews and discusses some of the main findings and conclusions to date about this particularly interesting CO_2 mitigation process.

Direct aqueous mineral carbonation has been a focal point for several research teams throughout the world. In this paper, we base our analysis on key contributions made by research teams from the National Energy Technology Laboratory (NETL), Arizona State University (ASU) and Columbia University.

2. Review and analysis of current state of knowledge on direct aqueous mineral carbonation

Direct aqueous mineral carbonation is based on the co-occurrence of dissolution of (Mg,Ca) silicates and precipitation of carbonates. With protons as the dissolution driver, a number of additives have been proposed and tested to compensate for the lack of protons under the near-neutral pH conditions which precipitation of carbonates demands. We shall restrict our discussion to the case of magnesium silicates.

2.1. Main published results and conclusions

Direct aqueous mineral carbonation has been a focal point for several research teams, in particular from NETL [5,6,7], ASU [8,9,10,11,12,13] and Columbia University [14,15].

Research carried out at NETL, which started in the 90s, paved the way for direct aqueous carbonation of magnesium silicates with additives; mainly, they aimed to quantify the overall process costs, and to obtain the highest possible extent of reaction. Their work was based on a solution with 0.64M $NaHCO_3$ and 1M NaCl [5]. Comprehensive insights about the effect of these inorganic additives is given by Chen *et al*. [6]. Under a CO_2 pressure of 170 atm, addition of 0.64M of bicarbonate increases the concentration of carbonate ions in solution by a factor 10^5 compared to the reference case with water only. This in turn reduces the minimum Mg concentration necessary to form magnesite (which is dictated by the solubility product K_{sp}). In addition, at such a high CO_2 pressure, the bicarbonate buffer maintains a more alkaline pH (5.4 against 2.8 with distilled water), which also promotes magnesite precipitation. NaCl is added to lower the activity of ions in solution (such as Mg^{2+}), which further improves the dissolution of Mg silicates. With this system, NETL scientists investigated all key process parameters [5,7]: ore type (olivine, serpentine lizardite and antigorite), particle size (grinding), thermal pretreatment of hydrated silicates, concentration of additives ($NaHCO_3$/NaCl), reaction time, CO_2 partial pressure and temperature. With several ore types, they showed using XRD that magnesite was the dominant species amongst reaction products, which confirmed the possibility of achieving dissolution of magnesium silicates and precipitation of carbonates in a single step. By testing the effect of particle size on reaction kinetics, they showed that kinetics was surface-controlled, and concluded that Mg dissolution with olivine followed a shrinking core model. With thermally activated (i.e. dehydroxylated) serpentine, reaction rate was found to slow down significantly beyond 50% conversion. A research team from ASU [8,9,13] eventually confirmed and discussed the formation of passivating layers around reacting olivine particles.

The NETL team identified the conditions leading to the highest carbonation rate in 1 hour: temperature between 155 and 180 °C, CO_2 pressure between 115 and 150 bar, particle size finer than 75 microns, and solid concentration around 15 wt%. Under such conditions, in a stirred reactor, they were able to convert 50% of a dehydroxylated serpentine in 1 hour, and 65% in 12 hours [7]. McKelvy *et al*. [12] completed these results by testing different inorganic salts ($AHCO_3$ and ACl where A = Li, Na, K) at various concentrations in order to improve the conversion of olivine. All in all, with the ($NaHCO_3$/ACl) system, NETL research led to energy intensive operating conditions, with high pressures and temperatures, in addition to thermal pretreatment and fine grinding of magnesium silicates.

Logically, the team from Columbia University looked at reducing these penalties by investigating other additives, aiming to achieve comparable conversion and kinetics with coarser particles, and without thermal pretreatment. With dissolution being the rate limiting step under near-neutral pH conditions, Krevor et Lackner [14,15] focused their efforts more specifically on testing organic salts to accelerate dissolution of a serpentine antigorite. They chose to operate at 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. By monitoring changes in Mg^{2+} concentration in solution during reaction, they showed that citrate, oxalate and EDTA ligands yielded significantly higher initial dissolution rates than inorganic salts. They found however that sodium acetate had a very small effect in comparison, which fits the conclusions by Olsen and Rimstidt [20] about efficiency of poly-acids versus mono-acid on the dissolution of oxides and silicates. 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%. Overall, their results proved the efficacy of polyacid organic salts on the dissolution kinetics of magnesium silicates. They also showed that the efficiency of the additives was strongly related to their concentration.

2.2. Analysis of current state of knowledge using preliminary geochemical simulations

The recent work by Krevor et Lackner [14,15] has made a definite contribution to the issue of dissolution kinetics of magnesium silicates using organic salts in the context of direct aqueous mineral carbonation. However, since their work relied upon analysis of the liquid phase only, their results do not provide a clear picture of the changes that could occur in the solid phase. In particular, it is not known whether magnesium carbonates formed during their experiments, even under the dilute solid concentration and low CO_2 partial pressure they used. Let us recall that the very principle of the process is to operate under near-neutral pH (or weakly acidic) conditions, such that dissolution of silicates and precipitation of carbonates may coexist.

We make the point in this paper that it is critical to complete their findings with an analysis of the solid phase, as well as of all species in solution, Si in particular. In addition, we reflect upon the effect of additives concentration and operating mode. It is worth noting that interactions between a number of organic ligands and magnesium silicates have received a great deal of attention in the geochemical literature [16,17,18,19,20], since it is also a natural weathering mechanism for silicates. Olsen and Rimstidt [20] conclude that the oxalate ion accelerates forsterite leaching (dissociation of Mg-O-Si bonds) by protons. It is purely a surface mechanism in which the oxalate ion bonds with the Mg atom, which weakens the Mg-O bond more efficiently than water alone, thereby increasing dissolution kinetics. This implies that ions concentration, relative to the reactive surface area of particles, is a key parameter for the problem at hand. Finally, we may add that formation of Si-oxalate complexes, in solution and/or at the surface, has also been suggested to explain the improved kinetics of quartz dissolution with these ligands [21]. Such complexes could therefore possibly contribute to the overall dissolution of magnesium silicates, although their formation remains controversial [22]. In this study we chose to limit our analysis to the oxalate case.

In order to analyse experimental results properly, we strongly believe in coupling experimentations and associated measurements with a geochemical analysis of the systems under investigation. In this paper, we analyse and discuss predictions of solid-liquid equilibria at abovementioned temperatures and pressures, in water or in aqueous solution with disodium oxalate, made with the CHESS geochemical modelling package [23,24].

Overall, geochemical simulations applied to direct aqueous mineral carbonation have highlighted two recurring problems. One is that a number of species from the corresponding chemical systems do not necessarily appear in every thermodynamic database. For instance, the database we chose for our simulations - CTDP (Common Thermodynamic Database Project) V.1.0.2 [25] - did not account for all the possible interactions in solution between the magnesium ion and oxalate ligand. For example, we had to add the $Mg(C_2O_4)_{(aq)}$ complex to the database using the SUPCRT [26,27] package, which allowed us to calculate the corresponding equilibrium constants at different temperatures. A second and more critical problem is that many thermodynamic data specific to the direct aqueous mineral carbonation systems are often simply unavailable or incomplete. For example, magnesium can also form a precipitate with oxalate - glushinskite (or magnesium oxalate dihydrate) – for which the solubility product K_{sp} is mostly referenced at 25°C : $K_{sp}=(4.86\text{-}5.08)\cdot10^{-6}$ [28,29]. Very few articles deal with the formation of glushinskite. Lichstein et Brescia [29,29] report the heat of dissolution, calculated from K_{sp} values measured at 25°C et 35°C ($\Delta H° = 7607.6$ J/mol). In order to extrapolate K_{sp} at higher temperatures, Van't Hoff's law was used with neglecting the variations of $\Delta H°$ with temperature. Despite the assumptions made to complete the thermodynamic database, we are confident that the modified thermodynamic database gives us a reasonable idea of the behaviour of the oxalate – magnesium silicate system as a function of temperature.

Using the antigorite already available in CTDP, with stoichiometry $Mg_3Si_{2.125}O_{9.188}H_{3.875}$, we predicted the equilibrium under the test conditions used by Krevor and Lackner, namely 3 g/L of solid and 0.1M of disodium oxalate [15]. This stoichiometry is in a relatively close match to the oxide composition of the ore they used in their work, with 45.0 wt% SiO_2 against 37.9 wt% reported, and 42.7 wt% MgO against 39.1 wt%.

We also deemed important to show the equilibrium predictions with water without additives, as the reference case. Simulation results are given in Table 1. In these simulations, we let precipitation occur when the ratio between the

product of activities of species in solution and the solubility constant $\Omega = ([M^{q+}]^p[X^{p-}]^q)/K_{sp}$ equals 1, as if reaction water was already loaded with magnesite nuclei.

		Simulated system		
		Case 1: Water	Case 2: Oxalate 0.1M	Case 3: Water with only 8% of « reactive » antigorite
Solid phase	Antigorite	0	0	2.76 g (92.0% Mg, Si)
	Magnesite	2.34 g (87.5% Mg)	0.05 g (1.9% Mg)	0
	Quartz	1.28 g (94.7% Si)	1.28 g (94.7% Si)	0.04 g (2.7% Si)
Liquid phase	Total $Mg_{(aq)}$	0.0040 mol/kg$_{water}$ Mg^{2+} (10.6% Mg) $MgHCO_3^+$ (1.9% Mg)	0.031 mol/kg$_{water}$ $MgC_2O_{4(aq)}$ (97.3% Mg) Mg^{2+} (0.5% Mg) $MgHCO_3^+$ (0.3% Mg)	0.0025 mol/kg$_{water}$ (8.0% 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)	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) $HC_2O_4^-$ (3.1% oxalate)	N/A

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 $\Omega = 1$). In Case 3.92% of the antigorite is considered as inert. Percentages in parentheses indicate the proportion of initial element content (Mg or Si) in the corresponding phase. Quartz was used in the simulation as an approximation for amorphous silica.

A number of things can be learned from these simulations. Firstly, simulations of equilibrium predict total antigorite dissolution in all cases, with and without oxalate. Even under such dilute conditions and low CO$_2$ pressure, reference Case 1 with water only should yield significant amounts of magnesite and quartz, excluding the possibility of any kinetic barrier. These would account for 87.5 mol% of total Mg and 94.7 mol% of total Si respectively. The final solid mass would also be very close to the initial antigorite mass, so that even accurate measurement of final solid mass would not carry useable information about the actual antigorite conversion. Case 2 with oxalate, on the other hand, exhibits unfavourable thermodynamics with respect to the formation of magnesite, due to the existence of a strong magnesium – oxalate complex in the liquid phase. In this case, very low amount of magnesite should form (if magnesite precipitation is disabled in the simulation, its saturation index SI, defined as log(Ω), is equal to 0.12) and more than 97% of the initial Mg is complexed with oxalate. Also, there is hardly any Mg(aq) as Mg^{2+}, whereas there is still mostly free oxalate as $C_2O_4^{2-}$. This implies that much higher solid concentration is required to potentially form magnesite under such conditions. About silica, its split between solid and liquid phases remains the same in all cases, as the thermodynamic database does not include any "Si-oxalate" complex.

Let us turn our attention to the water case in order to analyse the sensitivity of magnesite formation to a possible kinetic barrier. Assuming the thermodynamic data base is complete and reliable, prediction of species in solution at equilibrium is reliable. On the other hand, given the difficulty in predicting dissolution and precipitation reactions, the presence of solids in the system adds a great deal of uncertainty to prediction of geochemical equilibria. Not only solid-liquid reactions are very much governed by kinetic effects, but dissolution and precipitation reactions themselves are controlled by complex processes and poorly known equilibrium constants.

First a complementary simulation was made using $\Omega = 50$ as a necessary oversaturation for magnesite precipitation (which is the order of magnitude commonly found in the literature), so that magnesite would precipitate only at a Mg concentration significantly higher than that given by K$_{sp}$. This value of Ω gives identical results to those of Case 1, with precipitation of magnesite. Based on the conclusions from Krevor and Lackner [15] who obtained only 8% dissolution of antigorite in 7 hours, another simulation scenario can be considered, referred to as Case 3 in Table 1. Allowing only 8% of the antigorite to react (assuming equilibrium precipitation of magnesite), magnesite no longer precipitates, as the overall quantity of magnesium in the system is insufficient. In both Cases 1 and 3, total Si concentrations in solution are equal, and Mg concentrations are not very different, so that their measurement alone is not sufficient to conclude about the actual antigorite dissolution as one could possibly miss the precipitation of carbonates.

All the above observations lead to the important conclusion that it is imperative to characterise both solid and liquid phases during an experiment in order to compare the efficiency of different systems on dissolution of silicates. In addition, we think that geochemical simulation is useful for planning experiments. Already, simulations of equilibrium indicate that it should be necessary to operate under higher solids concentration in order to potentially form magnesite with the oxalate system. Literature shows however that such conditions are not favourable from a kinetics viewpoint since, as reported earlier, a key parameter in this case is the concentration of additives relative to the reactive surface of particles. We thought necessary at this stage to complete and confirm the above analysis with few well-chosen experiments at low and high solid concentrations.

3. Experimental analysis

3.1. Experimental set-up and materials

The experimental set-up comprises a 300 mL stirred autoclave reactor with a Teflon inner jacket and Hastelloy internals. The CO_2 pressure inside the reactor is regulated using a CO_2 ballast tank, and instantaneous CO_2 consumption by the liquid-solid suspension is monitored by recording temperature and pressure inside the ballast. The slurry is stirred by a gas inducing turbine that achieves high gas-liquid mass transfer. Slurry temperature is monitored and PID controlled.

An ore from New Caledonia was used in the experiments, which is composed mainly of lizardite with traces, or low amounts, of forsterite, enstatite and diopside. Its chemical composition (wt% oxides) is as follows: SiO_2: 40.0%, Al_2O_3: 0.6%, CaO: 0.6%, MgO: 41.1%, MnO: 0.1%, Fe_2O_3: 7.8%. Loss on ignition at 1000°C is 9.1 wt%.

The ore was first ground, then sieved below 100 μm and sampled using a rotary splitter, resulting in 4.2 μm Sauter diameter lots. Such a fine particle size is used to achieve a high reactive surface area, hence fast dissolution kinetics [15].

3.2. Experimental results and discussion

A typical test run consists in contacting CO_2 with the liquid-solid dispersion under constant pressure for 24 hours. After reaction, the system is cooled down to room temperature and pressure is released. The slurry is then passed through a 0.2 μm micropore filter and filtered solids are oven dried. Mg and Si concentrations in the filtrate are measured by ICP-AES. Solid phase characterization is more complex and different complementary techniques are thus used to get both qualitative and quantitative results: microscopy (FEG/SEM coupled with EDX analysis), thermogravimetry (TGA coupled with IR analysis of released gases), and Raman spectroscopy. From SEM/EDX an elemental mapping of the solids can be provided. Thermogravimetry analysis, performed under N_2 flow (with a heating rate of 10°C/min from room temperature to 1000°C), yields the total amount of CO_2 in the solids after reaction. From analysis of TGA/IR spectra for the initial material and a commercial 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. Raman spectroscopy was used to delineate the nature of solid products.

The aforementioned experimental conditions were used: 20 bar of CO_2 and 120°C. Without additives, operating temperatures higher than 100°C should yield precipitation of magnesite rather than hydromagnesite [30], which is expected to simplify subsequent analysis of the solid phase after reaction. The benefit of precipitating one or the other in an actual carbonation process is not clear-cut. Experiments were performed with a low solid concentration of 3 g/L$_{water}$ (0.3 wt%) as per Krevor and Lackner [15], and a high solid concentration of 250 g/L$_{water}$ (20 wt%). Tests were carried out using either osmosed water (for high solid concentration only) or 0.1 M disodium oxalate solution (for both low and high solid concentrations). As before, the corresponding geochemical simulations were made to understand the thermodynamic behaviour of all investigated systems and conditions. Simulations were done using the "chrysotile" model solid defined in the CTDP database, with stoichiometry Mg(3)Si(2)O(9)H(4), which matches SiO_2 and MgO composition of the ore (see above).

Experimental and simulation results for the 3 g/L$_{water}$ and 250 g/L$_{water}$ cases are reported in Tables 2 and 3 respectively. The second line in Table 2 corresponds to the equilibrium conditions predicted at 25°C, starting from the equilibrium conditions calculated at 120°C/20 bar of CO_2. As this calculation is used later in the paper for interpretation of the analyses of reaction products sampled after cooling, CO_2 fugacity is allowed to evolve freely during the simulations. The final predicted CO_2 fugacity is 5.7 bar, which is comparable to that measured experimentally. The same applies for Table 3.

	Solid phase, g				Liquid phase, mol/kg$_{water}$	
Eq. predictions	**Antigorite**	**Magnesite**	**Quartz**	**MgC$_2$O$_4$.2H$_2$O**	**Total Mg(aq)**	**Total Si(aq)**
Oxalate 0.1M 120°C, f$_{CO2}$ = 20 bar	0	0.035 g (8.2% Mg)	0.19 g (94.7% Si)	0	0.031 g (91.8% Mg)***	0.0012 g (5.3% Si)
Oxalate 0.1M 25°C, f$_{CO2}$ = 5.7 bar	0	0	0.20 g (99.6% Si)	0.44 g (58.4% Mg)	0.014 g (41.6% Mg)***	0.0001 g (0.4% Si)
Oxalate 0.1M exp. results (after cooling)	Solid mass after experiment: 0.74 g MgC$_2$O$_4$.2H$_2$O: 0.57 g* (79.6% Mg), MgCO$_3$: not detected (Raman)				0.006 g** (19.4% Mg)	0.01 g** (48.2% Si)

Table 2. Experimental and simulation results for the 3 g/L$_{water}$ case (Initial mass of solid: 0.47 g in 150 g of water, Ω = 1).

	Solid phase, g				Liquid phase, mol/kg$_{water}$	
Eq. predictions	**Antigorite**	**Magnesite**	**Quartz**	**MgC$_2$O$_4$.2H$_2$O**	**Total Mg(aq)**	**Total Si(aq)**
Oxalate 0.1M 120°C, f$_{CO2}$ = 20 bar	0	33.88 g (98.85% Mg)	16.27 g (99.9% Si)	0	0.031 g (1.15% Mg)***	0.0012 g (0.1% Si)
Oxalate 0.1M 25°C, f$_{CO2}$ = 4.1 bar	0	33.16 g (96.8% Mg)	16.28 g (99.99% Si)	1.56 g (2.6% Mg)	0.018 g (0.6% Mg)***	0.0001 g (0.01% Si)
Oxalate 0.1M exp. results (after cooling)	Solid mass after experiment: 38.46 g MgC$_2$O$_4$.2H$_2$O: 1.06 g* (1.87% Mg), MgCO$_3$: 0.84 g* (2.60% Mg)				0.009 g** (0.34% Mg)	0.004 g (0.26% Si)
Eq. predictions	**Antigorite**	**Magnesite**	**Quartz**	**MgC$_2$O$_4$.2H$_2$O**	**Total Mg(aq)**	**Total Si(aq)**
Water 120°C, f$_{CO2}$ = 20 bar	0	34.22 g (99.9% Mg)	16.27 g (99.9% Si)	0	0.004 g (0.1% Mg)	0.0012 g (0.1% Si)
Water 25°C, f$_{CO2}$ = 5.0 bar	0	33.92 g (99.0% Mg)	16.28 g (99.99% Si)	0	0.027 g (1.0% Mg)	0.0001 g (0.01% Si)
Water exp. results (after cooling)	Solid mass after experiment: 37.5 g MgCO$_3$: 0.62 g* (1.9% Mg)				0.022** (0.85% Mg)	0.007** (0.44% Si)

NB: values in brackets are molar percentages relative to the total amount present in the system.
* calculated from TGA weight loss;** total element concentration measured by ICP/AES; *** mainly as MgC$_2$O$_4$(aq)

Table 3. Experimental and simulation results for the 250 g/L$_{water}$ case (Initial mass of solid: 37.5 g in 150 g of water, Ω = 1).

For the 3 g/L$_{water}$ experiment with 0.1M oxalate, TGA/IR analysis of the solid product identified a significant water release (about 20 wt%) in the temperature range of 125-300°C, which was not observed with the original silicate, as well as a CO/CO$_2$ release in the temperature range of 300-600°C (about 40 wt%). These weight losses fit precisely the stoichiometry of glushinskite (MgC$_2$O$_4$, 2H$_2$O), whose formation was confirmed by Raman spectroscopy with bands at 1660 (ν(C=O)), 1637, **1471** (ν(C-O)), 1450, 919 (ν(C-C)), 864, 590, 529 (ν(Mg-O)), 266, 239 and 227 cm^{-1} [31]. Raman spectra did not show any of magnesite characteristic bands (1762, 1444, **1094**, 738, 329 and 213 cm^{-1} [32]) in the final product as expected from equilibrium simulation. Finally a mass balance based on TGA and ICP measurements found that almost all the magnesium (99%) was in the form of glushinskite and dissolved species (cf. Table 2, line 3). SEM images and EDX mapping of the final solid product (Figure 1a) showed magnesium-rich but silica-free sharp-edged rhomboedral particles, which correspond to the glushinskite. Fewer silica-rich magnesium-depleted zones were also found inside particles whose size resembles that of the original particles. This would indicate that few not fully dissolved silicate particles remained in the system, which is in slight disaccord with the mass balancing results. At the time of writing, XRD analyses are being made to verify whether the ore was fully converted, although both analyses show that conversion was total or near-total. Whereas geochemical equilibrium simulations (Table 2, line 1) predicted a full conversion of the ore with precipitation of a small quantity of magnesite at 120°C under these conditions, they also predicted (Table 2, line 2) the formation of magnesium oxalate only unpon cooling to 25°C. In fact, detailed thermodynamic calculations of equilibria predict the precipitation of glushinskite below 54°C, while magnesite becomes undersaturated below 110°C. Therefore, comparison between experimental and simulation results leads to the conclusion that glushinskite did precipitate spontaneously during cooling of the solution. We cannot tell from our data whether some magnesite did actually form at 120°C in the experiment; however, if such were the case, it had to have dissolved during cooling and reprecipitated as glushinskite. Ideally solid and liquid should be sampled at reaction temperature and pressure, which can be difficult. Overall, because of both the formation of a Mg-oxalate complex in the liquid phase, and the precipitation of glushinskite at low temperature, we conclude that the thermodynamics of the oxalate system do not favour the formation of magnesite at low solid concentration.

For the 250 g/L$_{water}$ experiment with 0.1M oxalate, interestingly enough, equilibrium simulations predicted that magnesite should remain (over)saturated over the whole temperature range (25-120°C), with glushinskite starting to co-precipitate below 64°C. In this case, one would expect magnesite redissolution to be negligible during cooling of the slurry from 120 to 25°C, and only a small amount of glushinskite to precipitate (cf. Table 3, lines 1 and 2). The corresponding experiment yielded very limited leaching of the magnesium silicate in 24 hours, with only 0.3 mol% of total magnesium in solution and 4.5 mol% in the form of glushinskite and magnesite (Table 3, line 3). Although Figure 1b confirms that the reaction product is almost entirely made up the original silicate particles, Raman spectroscopy did confirm the presence of both magnesite and glushinskite. The quantity of glushinskite formed was determined from the additional water loss measured by TGA/IR in the temperature range of 125-300°C. The corresponding CO and CO$_2$ weight loss was then deduced from the overall TGA weight loss in the 300-600°C zone, yielding the amount of magnesite present in the final reaction product. In this case, the dissolution yield was not very different from that observed with water only (about 3 mol% when adding the liquid phase and magnesite contributions). The strong difference between experimental and simulation results, in the 250 g/L$_{water}$ case with oxalate, suggests that the ligand concentration, relative to the reactive surface area of particles (80 times less than in the 3 g/L$_{water}$ case), is insufficient to accelerate the dissolution of magnesium silicate. This result is a confirmation that surface specific oxalate concentration, as reported in the geochemical literature and as predicted by our earlier simulations, is a key process parameter.
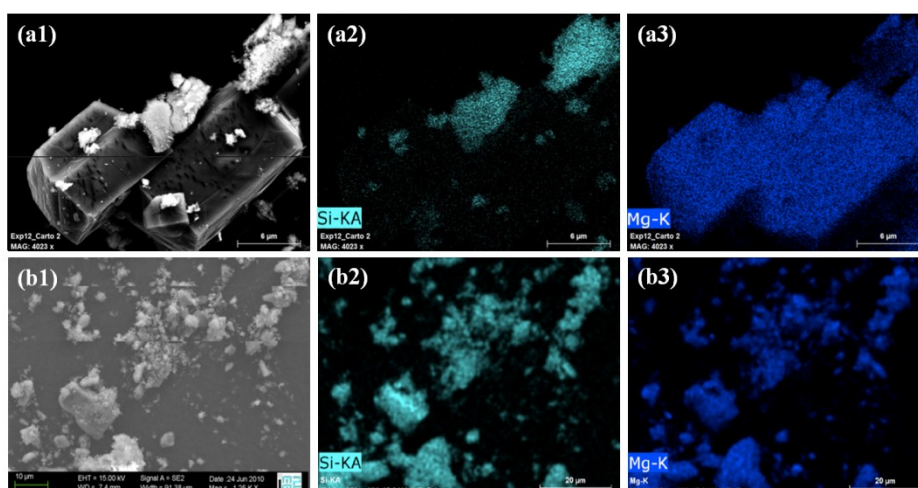

Figure 1. Example of SEM/EDX images for reaction products with 0.1M oxalate. (a): 3 g/L$_{water}$ case, (b) 250 g/L$_{water}$ case. From left to right: (1) SEM image, (2) Si EDX map, (3) Mg EDX map.

4. Conclusions et perspectives

A critical review of the current state of knowledge about direct aqueous mineral carbonation with organic salts was conducted using geochemical modelling and few well chosen experiments. It revealed that, notwithstanding the significant new body of knowledge that has been derived about this process in recent years, further research is required before such a process can be considered as a potential candidate for industrial development. One important issue that has been identified in this work is the lack of attention that has been paid to analysis of solid products formed after reaction. Through prediction of geochemical equilibria and laboratory tests, it was shown that no or insufficient analysis of the solid phase can easily lead to erroneous conclusions about the performance of given process parameters, such as the real value of a given additive. However, analysis of solids adds a significant workload to analysis of results, as a combination of analytical techniques must be used to conclude about the nature of the precipitates found in the reaction products.

Looking at the magnesium silicate – oxalate system, this work finds that oxalate ligand can yield to nearly total conversion of serpentine-like materials. However, under diluted slurry conditions, this system is not favourable for precipitation of magnesite, as Mg forms a complex in solution with the oxalate ligand. This complex was also found to precipitate upon cooling and yield to glushinskite, as predicted by geochemical equilibrium modelling. Ideally liquid and solid phases should be sampled at reaction temperature and pressure. Analysis of the whole solid-liquid system, by geochemical modelling and experimental work, confirmed that oxalate concentration, relative to the

reactive surface area of particles, is a key process parameter. Testwork carried out at high solids content, i.e. low oxalate concentration per unit area of particles, did yield very low conversion of the lizardite ore used in the work.

It was recognized during this work that combination of geochemical modelling and experimentation is a powerful approach for investigating such complex chemical systems. Indeed, geochemical equilibrium modelling is deemed to be a necessary companion tool for planning and interpreting testwork results. It was also found that thermodynamic data were not readily available for predicting the behaviour of magnesium silicate – oxalate systems. The lack of thermodynamic data that pertains to aqueous mineral carbonation systems seems to be an important issue that ought to be addressed.

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