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Stability of calcium carbonate and magnesium carbonate in rainwater and nitric acid solutions

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Abstract

Carbonation of magnesium and calcium silicates has emerged as an interesting option for long term storage of captured CO₂. However, carbonated minerals are not stable in acidic environments. This study was conducted to determine if synthetically carbonated minerals dissolve in acidic rain and release CO₂. Synthetic magnesium and calcium carbonates were leached in nitric acid solutions of various acidities, as well as rainwater, and the stability of the minerals was investigated with various methods. The experimental study was complemented with thermodynamic equilibrium calculations using Gibbs energy minimization software (HSC 4.0). The leaching of base ions from the two carbonate minerals was found to behave similarly and depend mainly upon the acidity of the solution. The fraction of Mg and Ca dissolved after several days of stabilization in separate solutions with initial pH 1 was 9% for both carbonates, while the fraction of dissolved minerals in a solution with initial pH > 2 was less than 1%. FT-IR analyses of the reactor atmosphere revealed that CO₂ gas was more rapidly released from calcium carbonate than from magnesium carbonate. However, only 1.5% of the CO₂ stored in the calcium carbonate was released as gas at pH 1 against 0.0% for magnesium carbonate. No notable CO₂ release occurred when leaching magnesium and calcium carbonates in solutions of pH 2. The solid residue analyses showed that the fixed CO₂ content of the carbonates that had been exposed to nitric acid was even higher than before the treatment.

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1. Introduction

The increasing concentration of carbon dioxide (CO₂) and other greenhouse gases in the atmosphere due to human activities is a major reason for the warming observed during the last 50 years. During the industrialized era, the CO₂ concentration in the atmosphere has risen 31% from 280 ppm in the period of years 1000–1750 to 368 ppm in the year 2000 [1]. Capture and storage of CO₂ from industrial processes and power plants is one of

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the direct mitigation options that are considered and studied world wide. One of the capture and storage options under development is the accelerated carbonation of magnesium and calcium silicates, or simply mineral carbonation [2,3].

Minerals that could be carbonated for the purpose of large scale CO₂ storage include alkali or alkaline earth metal oxide bearing compounds. Since alkali carbonates dissolve too easily in water, alkaline earth metals are more suitable for carbonation. Several other metal oxide bearing compounds can also be carbonated, but most of them are too rare or valuable, such as iron. Magnesium and calcium are the most common alkaline earth metals. Their oxides and hydroxides are well suited for carbonation, but the availability of these is very limited. However, magnesium and calcium are also found in silicates, which can be used for carbonation since silicic acid is a weaker acid than carbonic acid [2].

According to Lackner [4], the silicate mineral reserves on Earth have a storage capacity of 10 000–1 000 000 Gt CO₂ (more than all the CO₂ that could possibly be generated by combusting fossil fuel) and a storage time of at least 50 000–1 000 000 years. This potential is superior to any other known CO₂ capture and storage method. Although the capacity of mineral reserves can be measured, the storage time is hard to verify. Since carbonate minerals have a lower energy state than their reactants (silicates and CO₂) at ambient conditions, they are thermodynamically stable and could theoretically store CO₂ for billions of years, i.e., permanently.

In order to use mineral carbonation for reducing atmospheric CO₂ emissions, not even a small re-release or leakage rate can be accepted, since it would reduce the effective amount of captured and stored CO₂. For example, if 10% of the registered CO₂ emissions in Finland released during 2003, i.e., 7 Mt, were stored as carbonates, the amount of CO₂ released would be 700 000 t if 1% were released. Apart from atmospheric emissions, any CO₂ leaking from carbonate minerals used for storing CO₂ could also affect the local surroundings. A sudden release of CO₂ gas could be hazardous, since it is heavier than air and can cause death by asphyxiation. Even a gradual leakage would be environmentally dreadful through accumulation in soils or in populated areas.

The verified thermodynamic stability of carbonates shows that there should not be any possible leakage of CO₂ when exposed to water. However, although carbonate minerals are only sparingly soluble in water they dissolve readily in strong acids [2]. Therefore, there is a risk that CO₂ gas could be released after contact of the carbonate mineral with acid rain, for example. Rain is normally slightly acidic (pH 5–7) through reactions with atmospheric CO₂ and natural emissions of sulfur and nitrogen oxides and certain organic acids. Human activities continuously produce more of these acidifying compounds, resulting in the formation of sulfuric and nitric acid in rainwater. Because of these strong acids, the pH of rain becomes less than 5. According to Brownlow [5], the pH of acid rain can occasionally be below 2.4. In Finland, where emissions of sulfur and nitrogen oxides are strictly controlled, the lowest monthly mean value of rainwater was between pH 3.9 and pH 4.5 during the years 2000–2002, while the lowest daily mean value was pH 3.6 [6].

Although carbonate minerals can be dissolved by acids, the amount of sulfur and nitrogen oxides emitted are far lower than the scale of CO₂ emissions. Natural carbonate mineral reserves are estimated at 90 million gigatons [2], which also proves the stability of carbonates. However, natural carbonate minerals have been produced in a geological time scale, and most of this natural reserve is underground. Manufactured magnesium and calcium carbonates will be produced in a time scale of hours or less, presumably by precipitation, and would, therefore, be in the form of a powder, which, due to its particle size, would be more easily soluble than large blocks of natural carbonate minerals. Therefore, acid rain could possibly cause local CO₂ releases from carbonate mineral storage sites. Since there is no literature available on magnesium and calcium carbonate stability from the perspective of using carbonates as a means to store very large amounts of CO₂, we have studied the stability of manufactured magnesium and calcium carbonates in nitric acid solutions and a rainwater sample from Finland. Sulfuric acid was not used in the tests because it is known that a skin of insoluble calcium or magnesium sulfate is produced when limestone or dolomite reacts with sulfuric acid rain [7], which may inhibit the cores of the particles from dissolving.

2. Theoretical basis

When magnesium carbonate (MgCO₃) and calcium carbonate (CaCO₃) come in contact with water, their lattice ions, Ca²⁺ and CO₃²⁻ for calcium carbonate and Mg²⁺ and CO₃²⁻ for magnesium carbonate, partly

dissolve. After the lattice ions have dissolved, hydrolysis of the cations occurs, producing MgOH^+ and $\text{Mg}(\text{OH})_2$ for magnesium carbonate dissolution and CaOH^+ and $\text{Ca}(\text{OH})_2$ for calcium carbonate dissolution. The anion is subject to proton reactions, producing, for example, HCO_3^- and H_2CO_3 . The dissolution of the lattice ions leads to a change in the pH of the solution. In an open system, the atmospheric CO_2 also affects the solution pH by producing CO_3^{2-} , HCO_3^- and H_3O^+ upon dissolution in water. Therefore, the mineral solubility is more accurately measured as the total cation concentration in the solution. However, the presence of acid (nitric acid in our study) will also affect the equilibrium of the system.

In reaction with water, nitric acid forms oxonium ions (H_3O^+) by



The concentration of the oxonium ions can be calculated from the solution pH as

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad (2)$$

The oxonium ions react with carbonate minerals, dissolving lattice ions into the solution. For magnesium and calcium carbonates, this reaction path is



where M represents Ca or Mg [8]. An important aspect for the use of carbonates as CO_2 storage is whether the CO_3^{2-} ions eventually form CO_2 gas or not, and if gas is produced, how much will be formed? CO_2 gas formation could be estimated according to reactions (6)–(8).



Although the ion concentration at equilibrium could be calculated using the equilibrium constants of the various reactions, as in the solubility study of Chen and Tao [9], a deeper understanding of the solution chemistry involved is needed in order to select the most dominating reactions. Calculating the solution equilibrium using software based on Gibbs free energy minimization should produce similar results, since the equilibrium constant of a reaction, K_a , can be related to the Gibbs free energy change, ΔG , of the reaction, if the temperature of the reaction is known, as

$$\Delta G = -RT \ln K_a \quad (9)$$

with R , universal gas constant and T , reaction temperature. The theoretical results might also be more exact using Gibbs free energy minimization, since software can take all possible compounds into account for which thermodynamic data exists in its database.

3. Equilibrium composition calculations using software

In order to calculate the theoretical cation concentrations at equilibrium conditions in aqueous HNO_3 solutions at different pH values, Outokumpu HSC 4.0 was used. This software calculates the equilibrium composition based on Gibbs free energy minimization. In these calculations, the amounts of magnesium (or calcium) carbonate, HNO_3 and water for the system were set as input data at 25 °C, and the software calculated the concentrations of all possible products (ionic, aqueous and gaseous) with given inputs using Gibbs free energy minimization. In order to be able to approximate the amount of gaseous CO_2 released from the carbonates, the calculations were performed for a closed system, which does not take into consideration the interaction between the solution and CO_2 present in the atmosphere. The theoretical Mg (or Ca) concentration was calculated by summing up the concentration of all the aqueous products that consisted of Mg (or Ca) components (excluding $\text{MgCO}_3(\text{aq})$ and $\text{CaCO}_3(\text{aq})$, since their dissolved lattice ions are included). However, only

a few components made significant contributions to the Mg (or Ca) concentration. For the magnesium carbonate solution, the theoretical Mg concentration was simplified as

$$c_{\text{Mg,theor.}} = [\text{Mg}^{2+}] + [\text{Mg}(\text{NO}_3)_2(\text{aq})] \text{ (mg l}^{-1}\text{)} \quad (10)$$

The theoretical Ca concentration was similarly simplified as

$$c_{\text{Ca,theor.}} = [\text{Ca}^{2+}] + [\text{Ca}(\text{NO}_3)_2(\text{aq})] + [\text{CaHCO}_3^+] \text{ (mg l}^{-1}\text{)} \quad (11)$$

These formulas differ only on one element, since the ion MgHCO_3^+ was missing from the HSC database. However, leaving out CaHCO_3^+ from Eq. (11) reduces c_{Ca} only about 0–1%, so the error for c_{Mg} should be of the same magnitude.

4. Experimental methods

Magnesium carbonate and calcium carbonate stability in acidic solutions was tested in sterilized water (aqua ad iniectionem) with various concentrations of nitric acid (HNO_3), which is present in acid rain besides sulfuric acid. Synthetic magnesium carbonate (grain size $<40 \mu\text{m}$, MgO content = 42.1%¹) and synthetic calcium carbonate (grain size $<10 \mu\text{m}$, $\text{CaCO}_3 \geq 99\%$) were used in the experiments. The Mg, Ca and CO_3^{2-} content of the synthetic carbonate minerals were also analyzed. The carbonates were put into solutions of nitric acid (HNO_3), and sterile water with pH values of 0.9–7.1. One experiment for each carbonate was also performed using rainwater, which had been recovered at Espoo, Finland in August–September 2004. The pH of the rainwater was in the range 4.9–5.8. No pH buffers were used, which allowed the pH of the batch experiment solution to change freely. The amount of carbonate mineral batch used was 1 mole l^{-1} of solution. Therefore, 10.0 g of calcium carbonate or 8.4 g of magnesium carbonate was put into a 100 ml decanter glass containing the solution. The batch was measured using scales with an accuracy of ± 0.1 g. During the course of the magnesium carbonate experiments, we started to suspect that the mixing was inadequate. Therefore, the calcium carbonate tests were performed at 500 rpm, while the magnesium carbonate tests were performed at 300 rpm. After stirring for 1–3 h, the stirrer was turned off and the batch was left to stabilize in an open container for 3–11 days. The particles had then formed a sediment layer, allowing the clear liquid to be separated and analyzed. The filtration residue was also recovered, of which a few selected samples were analyzed. One experiment with each mineral was also scaled up (800 ml of nitric acid solution with an initial solution pH of 1) in order to attempt to monitor the weight change online. Although the weight change was eventually too small to be registered by the equipment, the solution obtained was analyzed as well.

The solution pH was measured with a Hanna HI 1333B pH-electrode, which has an accuracy of ± 0.2 pH. However, by shielding the electrode, we received a much better accuracy, roughly ± 0.01 pH. The temperature of the solution was also measured using a PT-100 platinum resistance thermometer. The temperature and pH were monitored and recorded online using a data logger. Ca and Mg concentrations in the solutions were measured after the tests using a Varian 600 atomic absorption spectrophotometer (AAS).

Synthetic magnesium carbonate, synthetic calcium carbonate and the filtration residues from the tests with lowest initial pH (pH 1–2) were analyzed for their Mg, Ca and CO_3^{2-} content using the AAS, sample fusion and acid digestion, modified ASTM method and CO_3 internal method with acid digestion and GC. The carbonate degree (CD) was calculated from these results as

$$\text{CD} = \frac{\frac{m'_{\text{CO}_3^{2-}}}{M_{\text{CO}_3^{2-}}}}{\frac{m'_{\text{Me}}}{M_{\text{Me}}}} \quad (12)$$

¹ The quality definition of commercially available magnesium carbonates is based on the MgO content of the carbonate. Higher quality carbonates are difficult to obtain, since precipitation of magnesium carbonates usually results in hydrated magnesium carbonates or magnesium hydroxide carbonates [10].

where subscript Me represents Ca or Mg, M stands for molar mass (g mole^{-1}) and m'_i is the mass fraction of element i in the sample. XRD (X-ray diffraction) analyses were also performed on these samples.

The proportional weight loss of cations released from the mineral to the initial amount stored in the mineral carbonate, D_{Me} , was calculated by comparing the concentration of cations in the solution, c_{Me} (g l^{-1}), to the original mass fraction of the element in the synthetic carbonate (m'_{Me}):

$$D_{\text{Me}} = \frac{V \cdot c_{\text{Me}}}{m_{\text{batch}} \cdot m'_{\text{Me}}} \quad (13)$$

where V (l) is the initial volume of the solution and m_{batch} (g) is the mass of the mineral batch. This is equal to the amount of CO_2 dissolved per mass of initially stored CO_2 in the synthetic carbonate, D_{CO_2} .

The experiments were repeated for nitric acid solutions of pH 1–2, where most leaching of Mg and Ca occurred, in order to measure how much of the CO_2 stored in the solid escapes as gas. Fifty gram of CaCO_3 and 42 g of MgCO_3 were leached in separate tests using 250 ml of nitric acid solutions of pH 1 and pH 2 at 20–22 °C. The atmosphere in the 250 ml glass reactor housing the solution was analyzed online using a FT-IR gas analyzer (Gasetm DX4000), which pumped continuously 2 l min^{-1} of air out of the glass reactor. The suction of the FT-IR pump was estimated to be strong enough to prevent any released CO_2 from escaping through the air inlet of the glass reactor. The accuracy of the FT-IR was about ± 200 ppm $\text{CO}_2(\text{g})$. The experiments were performed as long as the FT-IR indicated a higher concentration of CO_2 in the air coming from the reactor than the concentration in reactor air prior to the addition of carbonate to the aqueous nitric acid solution.

5. Results and discussion

The temperature of the solutions was observed to continue to increase slowly during the experiments. When the test series had been conducted, we discovered that the temperature rise had been caused by a broken heating element in the stirrer. Because of this equipment failure, the temperature of the experiments varied between 18 and 32 °C. Since the solubility is dependent on temperature, it also affected the online measurements and initial solution pH measurements. Fortunately, a temperature deviation of only 14 °C will not significantly affect the solubility of the species studied. Moreover, the solutions were left to stabilize for several days in a storage room, and the AAS analyses were performed at the same temperature for all samples.

The results from the carbonate mineral analysis (Table 1) shows that the CO_3^{2-} contents of the filtration residues are actually larger than that of the untreated carbonate minerals. It is possible that this re-carbonation occurred when the samples were dried after the experiments. The higher carbonate content cannot be a result of removal of any other possible compounds (as crystal water, hydrocarbonates or impurities), since the magnesium content of the residue would then also be higher than that of the untreated carbonate, which is not the case (Table 1). Calculations based on the sample analysis using Eq. (12) indicated that the magnesium elements of the synthetic magnesium carbonate are only carbonated to a degree of 72.2%, while the synthetic calcium elements in the calcium carbonate are carbonated to a degree of 92.1%. However, the results from the XRD analyses showed that the crystal structure of magnesium carbonate used in the experiment is partly $\text{MgCO}_3 \times 5\text{H}_2\text{O}$, lansfordite, which explains why the calculated carbonate degree was too low for being pure magnesite, MgCO_3 . The crystal structure of the calcium carbonate used indicates pure calcite, CaCO_3 . The XRD analyses verified that the crystal structure of magnesium carbonate and calcium carbonate

Table 1
Filtration residue analysis of dissolution experiments in pH 1–2

Sample	m'_{Mg} (g kg^{-1})	m'_{Ca} (g kg^{-1})	m'_{CO_3} (g kg^{-1})	CD (%)
Filter residue from MgCO_3 dissolution in pH 1	260		485	75.5
Filter residue from MgCO_3 dissolution in pH 2	259		485	75.8
Pure MgCO_3 for comparison	261		465	72.2
Filter residue from CaCO_3 dissolution in pH 1		410	593	96.6
Filter residue from CaCO_3 dissolution in pH 2		410	583	95.0
Pure CaCO_3 for comparison		409	564	92.1

was not affected by the acid treatment (Fig. 1, graph to the left), with one exception: the XRD-graph of the filter residue from CaCO_3 in a solution with an initial pH of 1 revealed that a small amount of another crystal structure (most likely $\text{Ca}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$, according to the XRD analysis database) had formed (Fig. 1, right hand side graph).

The results from the AAS analysis are shown in Figs. 2–4. Two samples from each test were analyzed using the AAS for the total amount of dissolved Mg (for the experiments where magnesium carbonate was leached, Fig. 2) and dissolved Ca (for the experiments where calcium carbonate was leached, Fig. 3). If the initial pH values (prior to the addition of carbonate minerals) of the solution are converted to H_3O^+ concentrations using Eq. (2), we notice that the dissolution of base ions depends almost linearly on the initial H_3O^+ concentration of the solution (Fig. 4) for solution pH 0.9–7.1. The lower the initial pH is, the higher is the final Mg and Ca concentration. The calculated Mg and Ca concentrations predict a lower solution concentration than was achieved experimentally. This may be caused by the limitations of the calculations, since they were

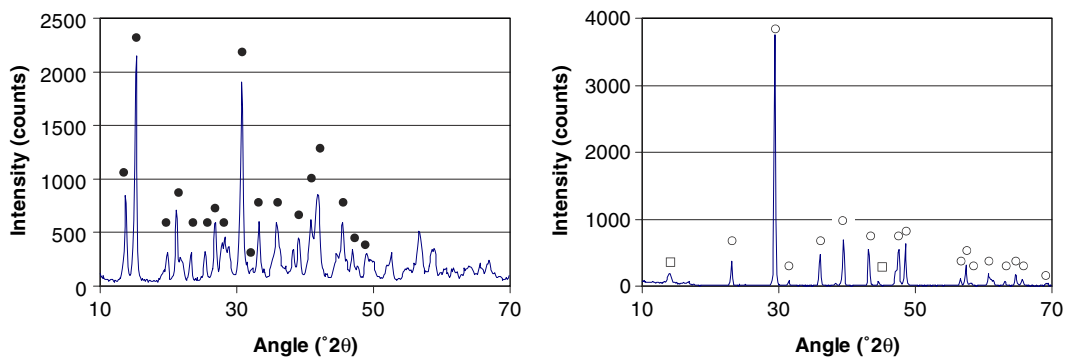


Fig. 1. X-ray diffraction (XRD) patterns of filter residue from MgCO_3 (left) and CaCO_3 (right) dissolution experiments (solution pH 1). ● corresponds to $\text{MgCO}_3 \times 5\text{H}_2\text{O}$, lansfordite (ICPDS 35-680, reference data available only for $2\theta < 50$); ○ corresponds to CaCO_3 , calcite (ICPDS 5-586); □ corresponds to $\text{Ca}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$ (ICPDS 20-229).

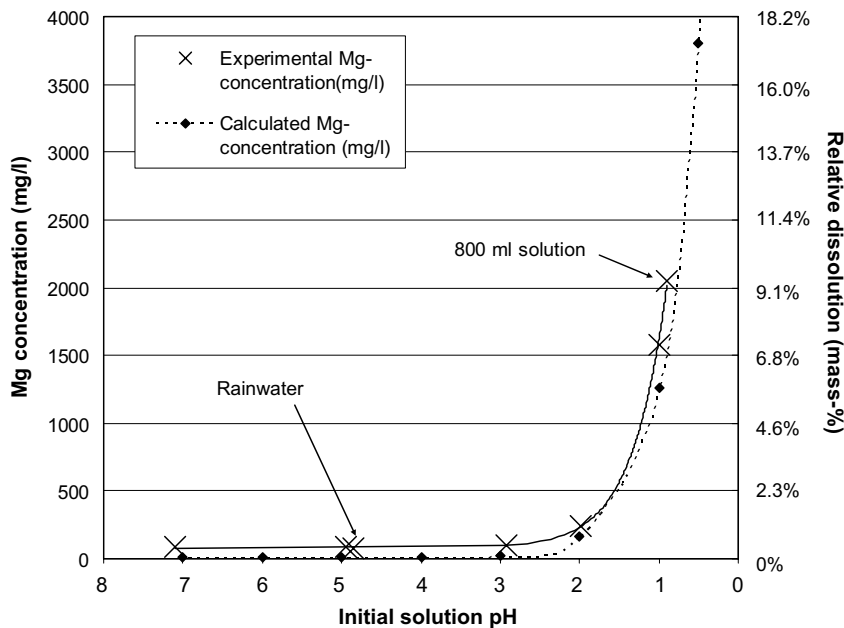


Fig. 2. AAS analysis results of dissolved Mg from MgCO_3 in solutions of different initial acidities. The results from the scaled up experiment and the experiment with rainwater are indicated.

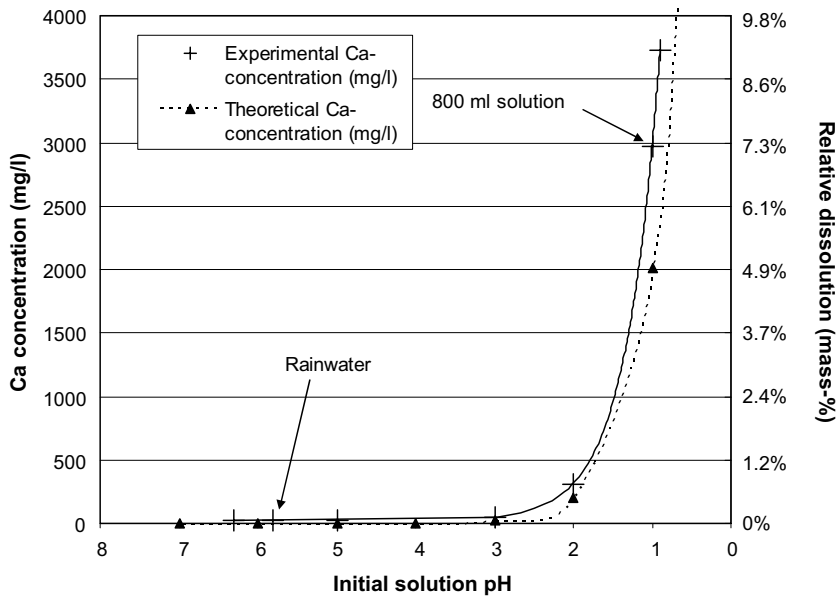


Fig. 3. AAS analysis results of dissolved Ca from CaCO₃ in solutions of different initial acidities. The results from the scaled up experiment and the experiment with rainwater are indicated.

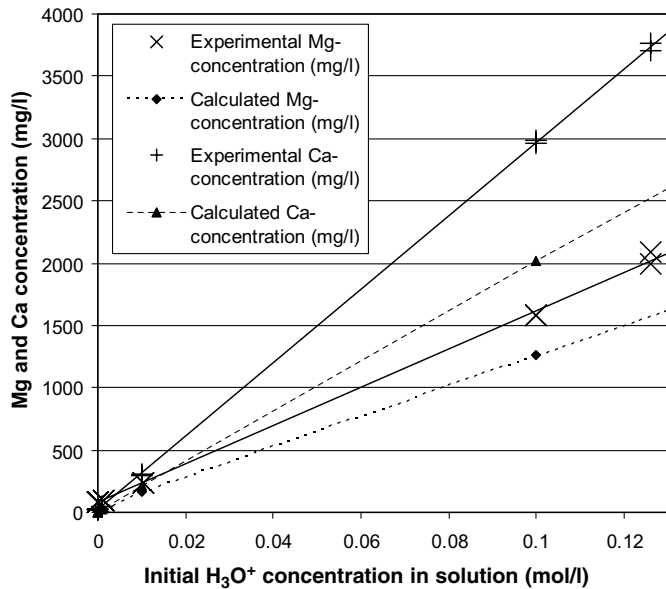


Fig. 4. Results from Figs. 2 and 3 plotted as functions of initial solution H₃O⁺ concentration calculated using pH.

performed for a closed system and exclude any interaction from carbon dioxide in the air. The concentrations of Ca and Mg in the tests conducted with rainwater were found to be very similar to those of the experiments conducted with nitric acid at the same acidity. Using the content of Mg in magnesium carbonate (Table 1), the relative dissolution of the magnesium carbonate could be compared, i.e., the mass of Mg dissolved per original mass of Mg in the batch. Similar reasoning was used for calcium carbonate. As can be seen in Figs. 2 and 3, the highest measured relative dissolution, 9.3% for MgCO₃ and 9.1% for CaCO₃, occurred in a solution with initial pH 0.9, which was the most acidic solution used in the experiments. Solution acidity does not seem to

have an effect upon the leaching of carbonates in solutions with initial pH > 3: for these tests, the relative dissolution (calculated using Eq. (13)) was 0.4% for CaCO_3 and much lower, 0.06%, for MgCO_3 . The relative dissolution of Mg and Ca is roughly equal to the ratio of CO_2 dissolved per CO_2 originally stored in the carbonate, since for each mole of Mg (or Ca) dissolved from the mineral, 1 mole of CO_2 is released. As part of the dissolved CO_2 remains in solution and part is released as gas, the relative dissolution is the maximum fraction of stored CO_2 that could have been released from the mineral.

Results from the online measurements performed with FT-IR gas analysis are shown in Figs. 5 and 6 (the peaks in the continuous parts of the pH curves are due to electrical disturbances in the pH electrode). The pH

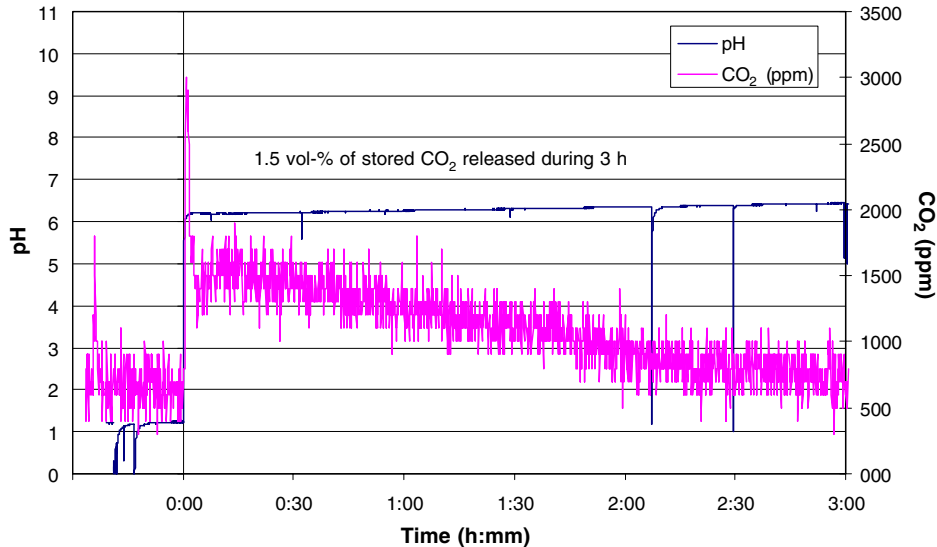


Fig. 5. Online measurements of pH change and CO_2 gas release when adding 50 g CaCO_3 to 250 ml solution of 33.3% HNO_3 and 66.7% H_2O (pH 1). Two liter of air per minute was pumped from the reactor to the FT-IR.

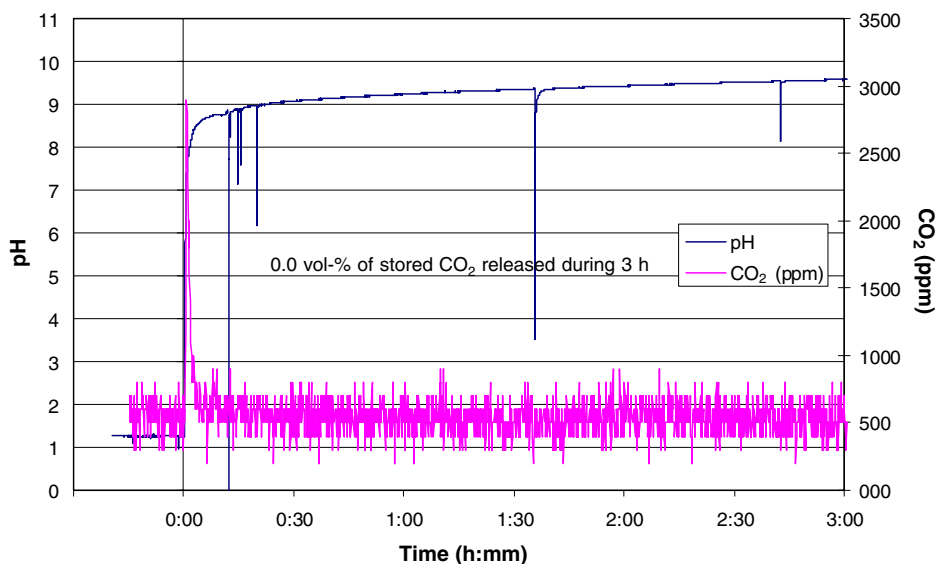


Fig. 6. Online measurements of pH change and CO_2 gas release when adding 50 g MgCO_3 to 250 ml solution of 33.3% HNO_3 and 66.7% H_2O (pH 1). Two liter of air per minute was pumped from the reactor to the FT-IR.

of the calcium carbonate solutions rose much faster to the level after which it rose more slowly than the pH of the magnesium carbonate solutions did. Using the thermodynamic equilibrium composition calculated with HSC, the net amount of gaseous CO_2 formed at thermodynamic equilibrium for the solution was first estimated. The results from the calculations predicted that gaseous CO_2 is thermodynamically stable over a certain H_3O^+ concentration, which is $0.120 \text{ mole l}^{-1}$ for CaCO_3 , and $0.126 \text{ mole per liter}$ for MgCO_3 . This corresponds to $\text{pH} < 0.92$ for CaCO_3 and $\text{pH} < 0.90$ for MgCO_3 . However, thermodynamic equilibrium calculations do not reveal intermediate products. Therefore, it is possible that CO_2 gas is released before it re-carbonates Mg or Ca compounds at $\text{pH} > 0.9$. The results from the experiments with online FT-IR analysis revealed a slow release of CO_2 gas when adding CaCO_3 to pH 1 nitric acid (Fig. 5). By integrating the area surrounded by the signal after time = 0:00 and the normal CO_2 content of the air (average value from air analysis 10 min prior to adding the carbonate batch) and multiplying with the amount of gas pumped, the total gas release can be calculated. The ratio of CO_2 gas released per amount of CO_2 originally stored in the mineral was calculated using the carbonate data in Table 1 for CaCO_3 . Thus, approximately 1.5 vol% of the CO_2 stored in CaCO_3 was released during 3 h of mixing in pH 1. At pH 2, only 0.1% of the CO_2 stored in CaCO_3 was released during 20 min. The corresponding experiment with MgCO_3 registered only a brief emission of CO_2 gas directly after the addition of the carbonate batch (at time = 0:00) at pH 1 (Fig. 6). However, after 3 h, the net amount of gas released amounted to zero. At pH 2, CO_2 was not released from MgCO_3 and 0.1% of the CO_2 originally stored in CaCO_3 seemed to be absorbed into the solution during 20 min. (the experiments were conducted as long as the FT-IR registered a higher CO_2 level than normal of the air coming from the reactor). However, it is not certain that any CO_2 was released at all for the experiments performed at pH 2, since the very small emission values registered could also be due to uncertainties in the accuracy of the equipment. Still, the results from the experiments show that the carbon dioxide gas release from leaching MgCO_3 and CaCO_3 is insignificant for nitric acid solutions of initial $\text{pH} > 2$.

6. Conclusions

The results from the various analyses of the experiments performed indicate that a relevant dissolution of magnesium carbonates and calcium carbonates occurs only for nitric acid solutions with an initial $\text{pH} < 2$, which is safely below the pH range for acid rains. It is also shown that magnesium carbonate is a more stable option than calcium carbonate for storing CO_2 . However, even at pH 1, the release of CO_2 is very low for calcium carbonate and even insignificant for magnesium carbonate. The higher carbonate content of leached carbonate minerals, similar crystal structure (unless $\text{pH} < 2$), and the measured CO_2 gas release, imply that acid rain should not affect the amount of CO_2 stored negatively. More research is needed to investigate why the content of CO_2 trapped in the mineral increases after leaching, but from a CO_2 storage perspective and the scope of this research, the important fact is that it does not decrease. When taking into account the relatively low acidity of rain water and the very low rates and amounts of CO_2 gas emitted from nitric acid solution leaching of carbonates, the local environmental effects of CO_2 emissions from a carbonate mineral storage site should be insignificant.

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