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Short Communication

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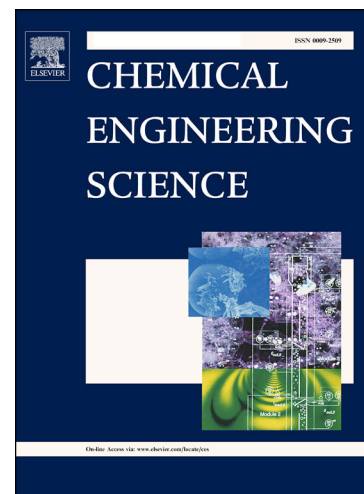
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Questioning the catalytic effect of Ni nanoparticles on CO₂ hydration and the very need of such catalysis for CO₂ capture by mineralization from aqueous solution.Jeremy J. Ramsden^a, Ilya J. Sokolov², Danish J. Malik^{2*}^a *Collegium Basilea (Institute for Advanced Study), Basel, Switzerland.*^b *Chemical Engineering Department, Loughborough University, Loughborough LE11 3TU, England.*

ABSTRACT

Recent publications claimed a significant catalytic effect of nickel nanoparticles on hydration of CO₂ to carbonic acid. Others have claimed that such catalysis can significantly accelerate the overall process of CO₂ capture by mineralization to CaCO₃ from aqueous solution. Having repeated the experiments as closely as possible, we observed no catalytic effect of Ni nanoparticles. Numerical modelling revealed that hydration is not the slowest reaction in the chain ending with mineralization; hence its catalysis cannot have a significant effect on CaCO₃ formation.

1. Introduction

There is a great deal of scientific research activity in the field of CO₂ capture and sequestration, stimulated by various programs aiming to reduce CO₂ emission. Capturing CO₂ from flue gases in an aqueous solution and converting it to a mineral such as CaCO₃ looks attractive, especially in the light of a reportedly cheap and reliable catalyst (Ni nanoparticles) for this process. This study aims to corroborate recent findings by reproducing published experiments and undertaking numerical simulations on the feasibility of using Ni nanoparticles for CO₂ hydration and mineralization in an industrial process for CO₂ capture.

2. Numerical model

Table 1 presents the full set of reactions and corresponding differential equations for CaCO₃ production from CO₂ representing a way of capturing and storing CO₂.

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Table 1. Reactions and equations for CaCO₃ production from CO₂.

	Reactions							← Equations
	(R1)	(R2)	(R3)	(R4)	(R5)	(R6)	(R7)	
	absorption CO _{2(g)} ⇌ CO _{2(aq)}	hydration CO _{2(aq)} + H ₂ O ⇌ H ₂ CO ₃	bicarbonation H ₂ CO ₃ ⇌ H ⁺ + HCO ₃ ⁻	carbonation HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ²⁻	dissociation H ₂ O ⇌ H ⁺ + OH ⁻	CO _{2(aq)} + OH ⁻ ⇌ HCO ₃ ⁻	mineralization Ca ²⁺ + CO ₃ ²⁻ ⇌ CaCO ₃	
	k ₁	k ₂ = 6 · 10 ⁻² s ⁻¹	k ₃ = 1 · 10 ⁷ s ⁻¹	k ₄ = 3 s ⁻¹	k ₅ = 2 · 3 · 10 ⁻⁵ s ⁻¹	k ₆ = 7 · 7 · 10 ³ M ⁻¹ s ⁻¹	k ₇ = 2 M ⁻¹ s ⁻¹	
	k ₋₁	k ₋₂ = 2 · 10 ¹ s ⁻¹	k ₋₃ = 5 · 10 ¹⁰ M ⁻¹ s ⁻¹	k ₋₄ = 5 · 10 ¹⁰ M ⁻¹ s ⁻¹	k ₋₅ = 1 · 3 · 10 ¹¹ M ⁻¹ s ⁻¹	k ₋₆ = 2 · 9 · 10 ⁻⁴ s ⁻¹	k ₋₇ = 1 · 10 ⁻³ s ⁻¹	
Ref. →	(Mitchell et al., 2010) †					(Eigen and de Maeyer, 1995) †		(Palmer and van Eldik, 1983) †
[CO _{2(aq)}] ' =	+k ₁ [CO _{2(g)}] - k ₋₁ [CO _{2(aq)}]	-k ₂ [CO _{2(aq)}] + k ₋₂ [H ₂ CO ₃]				+k ₋₆ [HCO ₃ ⁻] - k ₆ [CO _{2(aq)}] [OH ⁻]		(1)
[H ₂ CO ₃] ' =		+k ₂ [CO _{2(aq)}] - k ₋₂ [H ₂ CO ₃]	-k ₃ [H ₂ CO ₃] + k ₋₃ [H ⁺] [HCO ₃ ⁻]					(2)
[H ⁺] ' =			+k ₃ [H ₂ CO ₃] - k ₋₃ [H ⁺] [HCO ₃ ⁻]	+k ₄ [HCO ₃ ⁻] - k ₋₄ [H ⁺] [CO ₃ ²⁻]	+k ₅ [H ₂ O] - k ₋₅ [H ⁺] [OH ⁻]			(3)
[OH ⁻] ' =					+k ₅ [H ₂ O] - k ₋₅ [H ⁺] [OH ⁻]	+k ₋₆ [HCO ₃ ⁻] - k ₆ [CO _{2(aq)}] [OH ⁻]		(4)
[HCO ₃ ⁻] ' =			+k ₃ [H ₂ CO ₃] - k ₋₃ [H ⁺] [HCO ₃ ⁻]	-k ₄ [HCO ₃ ⁻] + k ₋₄ [H ⁺] [CO ₃ ²⁻]		-k ₋₆ [HCO ₃ ⁻] + k ₆ [CO _{2(aq)}] [OH ⁻]		(5)
[CO ₃ ²⁻] ' =				+k ₄ [HCO ₃ ⁻] - k ₋₄ [H ⁺] [CO ₃ ²⁻]			-k ₇ [Ca ²⁺] [CO ₃ ²⁻] + k ₋₇ [CaCO ₃]	(6)
[Ca ²⁺] ' =							-k ₇ [Ca ²⁺] [CO ₃ ²⁻] + k ₋₇ [CaCO ₃]	(7)
[CaCO ₃] ' =							+k ₇ [Ca ²⁺] [CO ₃ ²⁻] - k ₋₇ [CaCO ₃]	(8)
Rate and equilibrium constants from other sources								
		k ₂ = 3 · 7 · 10 ⁻² s ⁻¹ k ₋₂ = 25 s ⁻¹ (Wang et al., 2010)				k ₆ = 1 · 2 · 10 ⁻⁴ k ₋₆ = 4 · 10 ⁻⁴ (Wang et al., 2010)		
						k ₆ = 8 · 5 · 10 ³ M ⁻¹ s ⁻¹ (Kucka et al., 2002; Pohorecki and Moniuk, 1988)		

Hereafter [...] denotes concentration, [...]'=d[...]/dt, t is time, $M = \text{mol}\cdot\text{dm}^{-3}$, $[\text{H}_2\text{O}]=55.5\text{M}$, k_2 is a pseudo first order coefficient based on the assumption that the concentration of water is constant.

For a well-mixed solution the rate of absorption from the gas phase into liquid, reaction (R1), can be described as $\kappa\alpha([\text{CO}_{2(\text{aq})}]_s - [\text{CO}_{2(\text{aq})}])$, where $\alpha=A/V$ is liquid interfacial area/volume ratio, κ is a coefficient depending on many unknown parameters, and $[\text{CO}_{2(\text{aq})}]_s$ is CO_2 concentration in the thin layer of the water contacting gaseous CO_2 . In fact it is the "Henry's law concentration", i.e., the solubility of the gas in the liquid. In Table 1 $[\text{CO}_{2(\text{g})}]=[\text{CO}_{2(\text{aq})}]_s$, and we used $[\text{CO}_{2(\text{g})}]=0.037\text{M}$, which is the approximate concentration of saturated CO_2 solution in water at 22°C . For this model of absorption $k_1=k_{-1}=\kappa\alpha$.

Up to reaction (R6) only water is needed. Reaction (R7) needs a source of a metal ion whose carbonate is insoluble but, depending on the intended fate of the end-product, very low cost waste materials such as concrete rubble or pulverised fuel ash might be usable as the source.

3. Experimental section.

Setup 1. Pure CO_2 was bubbled through a porous sparger into 100cm^3 of deionised stirred water in a 150cm^3 beaker covered with a lid allowing gas to escape. This allowed high, albeit ill-determined, ratios α and mass transfer rates of the gaseous CO_2 to be achieved. Higher flow rates resulted in bigger α and higher mass transfer rates.

Setup 2. Flow of pure CO_2 was introduced into the headspace of either a beaker or an Erlenmeyer flask partly filled with stirred water. This allowed small, but well-determined gas/liquid interfacial areas, $\alpha \approx 0.11\text{cm}^{-1}$ and $\alpha \approx 0.0077\text{cm}^{-1}$ accordingly, to be achieved.

In both setups the reactions at room temperature ($\sim 22^\circ\text{C}$) were followed using a conductivity meter.

Nickel nanoparticles were purchased from Nano Technologies, Daejeon, Korea (spheroidal, nominal size 100nm , dry powder). 60mg were dispersed in 50cm^3 of deionised water and sonicated for 5min , then diluted into 2dm^3 water to make a final concentration of $30\text{mg}\cdot\text{dm}^{-3}$.

4. Results and discussion.

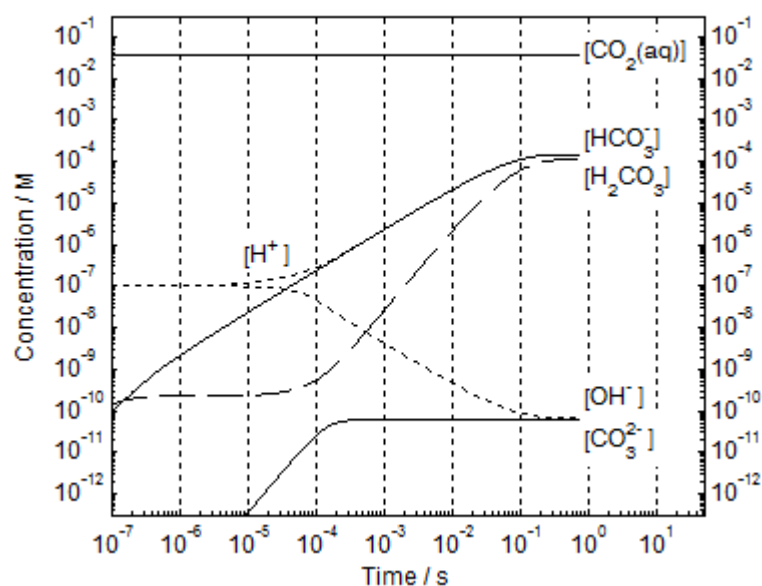


Fig. 1. Numerical simulation of CO_2 hydration.

Fig. 1 shows the results of integrating numerically differential equations (1)-(6) describing reactions (R2)-(R6) in a batch reactor without absorption ($k_1=k_{-1}=0$) and with the following initial conditions: $[\text{CO}_{2(\text{aq})}]_0=0.037\text{M}$; $[\text{H}^+]_0=[\text{OH}^-]_0=10^{-7}\text{M}$; $[\text{H}_2\text{CO}_3]_0=[\text{HCO}_3^-]_0=[\text{CO}_3^{2-}]_0=0$; $[\text{Ca}^{2+}]_0=[\text{CaCO}_3]_0=0$. An explanation of why equilibrium concentrations $[\text{H}^+]$ and $[\text{HCO}_3^-]$ are about identical for any $[\text{CO}_{2(\text{aq})}]_0$ is given in Appendix 1.

Hydration is a relatively slow reaction, but not the slowest in the chain of reactions of CO_2 mineralization. As Fig. 1 demonstrates, it takes all reactions of CO_2 with water, (R2)-(R6), less than 1s to reach equilibrium. $[\text{CO}_3^{2-}]$, which ultimately determines the rate of mineralization, reaches its equilibrium value, $[\text{CO}_3^{2-}]=6.0 \cdot 10^{-11}\text{M}$, even faster, within 10^{-3}s .

The reaction (R1), absorption, is relatively slow, but does not constitute a problem, especially on an industrial scale. Under laboratory conditions (Setup 1) it takes just minutes of bubbling CO_2 through water to get close to saturation, as the solid lines in Fig. 2a demonstrate.

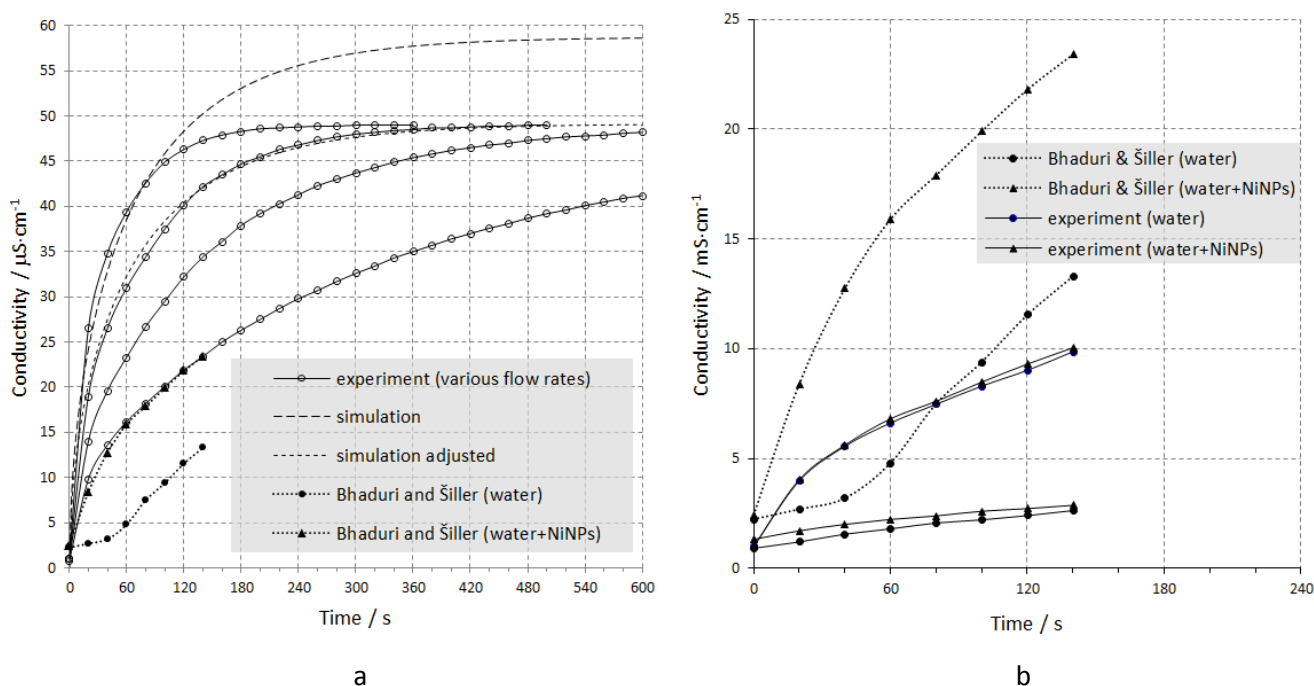


Fig. 2. Experimental and numerical results of conductivity change as a result of CO_2 absorption by deionised water.

As the output parameter is conductivity, the curves represent the combined result of simultaneous CO₂ absorption and reactions with water, but the latter is a much faster process as Fig. 1 reveals.

The four solid lines in Fig. 2a correspond to four different flow rates of CO₂: 10, 50, 100 and 300mL/min.

The conductivity K is a result of the ions H⁺, OH⁻, HCO₃⁻ and CO₃²⁻ present in the solution:

$$K = \lambda_1[\text{H}^+] + \lambda_2[\text{CO}_3^{2-}] + \lambda_3[\text{HCO}_3^-] + \lambda_4[\text{OH}^-]. \quad (9)$$

Here $\lambda_1 = 3.50 \cdot 10^5 \mu\text{S/M}$, $\lambda_2 = 1.39 \cdot 10^5 \mu\text{S/M}$, $\lambda_3 = 4.45 \cdot 10^4 \mu\text{S/M}$, λ_4 is much smaller; ≈ 0 (Lide, 2004).

The long-dashed line in Fig. 2a shows the result of numerical integration of equations (1)-(6) with $k_1 = k_{-1} = 0.0095\text{s}^{-1}$ and conductivity calculated according to (9). The asymptotic conductivity is slightly higher than the experimental one. The discrepancy can be easily explained by the implicit inaccuracy (lack of significant digits) of the coefficients k_1 - k_7 and k_{-1} - k_{-7} , e.g. up to 50% for k_3 . Appendix 1 provides further information.

The short-dashed line in Figure 2a shows the simulation result for the same system with $k_3 = 0.7 \cdot 10^7$ thus achieving a close match with one of the experimental curves. The adjustment is within the accuracy of the original value of k_3 .

The adjustment of the rate coefficients needed to bring the simulation results into line with the experiments is a useful reminder about the accuracy and the reliability of the values given in Table 1. There is, in fact, no unique way of carrying out the adjustment; the value of $(k_2/k_{-2}) \cdot (k_3/k_{-3})$ needs to be adjusted by a factor of about 0.7. Smaller changes in the values of several or all of the coefficients k_2 , k_{-2} , k_3 and k_{-3} would suffice to achieve that.

However, the mineralization reaction (R7) is very slow because of the very low equilibrium concentration [CO₃²⁻]. The maximum theoretical rate can be estimated as

$$[\text{CaCO}_3]' = k_5[\text{CO}_3^{2-}][\text{Ca}^{2+}] = 2\text{M}^{-1}\text{s}^{-1} \cdot 6.0 \cdot 10^{-11}\text{M} \cdot 6.7\text{M} \approx 8 \cdot 10^{-10}\text{M/s}. \quad (10)$$

In this calculation we used the equilibrium concentration [CO₃²⁻] (Fig. 1) and the solubility limit of CaCl₂ at room temperature (Lide, 2004). At this rate it will take more than 24 hours to reach the solubility limit $7 \cdot 10^{-5}\text{M}$ of CaCO₃ (Mitchell et al., 2010), at which precipitation in principle starts. In practice the rate will be much smaller as it drops in a batch reactor and only much lower concentrations [Ca²⁺] would be used, mainly because this is economically feasible only when waste materials, e.g. flue ash, are used.

Some authors (Bond et al., 2001; Mirjafari et al., 2007; Kim et al., 2011; Bhaduri and Šiller, 2013) suggest that mineralization can be accelerated by catalysing hydration (R2). In our view this cannot be the case as such catalysing does not change the equilibrium concentration [CO₃²⁻] and, hence, the rate of the slowest reaction (R7) in the chain, mineralization.

Kim et al. (2011) in their experiments used carbonic anhydrase (CA), a natural enzyme known to enormously accelerate the reaction of hydration. They observed a significant increase in the rate of mineralization, allegedly caused by the enzyme. However, they used a pH buffer (0.1 M tris-HCl, pH 7.0) to maintain the pH of the solution in order for the delicate enzyme to remain active. However, the buffer on its own dramatically affects reactions of CO₂ with water. This feature was neglected, leading to misinterpretation of their experimental results.

As Fig. 1 demonstrates, pH drops as a result of the reactions. The rising concentration of H⁺ ions is the main factor limiting the equilibrium concentration [CO₃²⁻] because of the increasing rate of the reverse reaction. As Fig. 3 shows that if pH is maintained at a constant level in a batch reactor, [CO₃²⁻] keeps rising to a much higher level than otherwise and so will the rate of mineralization if Ca²⁺ ions are added. In this case the equilibrium concentration [CO₃²⁻] $\approx 1.9 \cdot 10^{-5}\text{M}$ results in the maximum production rate $[\text{CaCO}_3]' \approx 2.5 \cdot 10^{-4}\text{Ms}^{-1}$. At this rate it takes less than 1s to reach the solubility limit of CaCO₃.

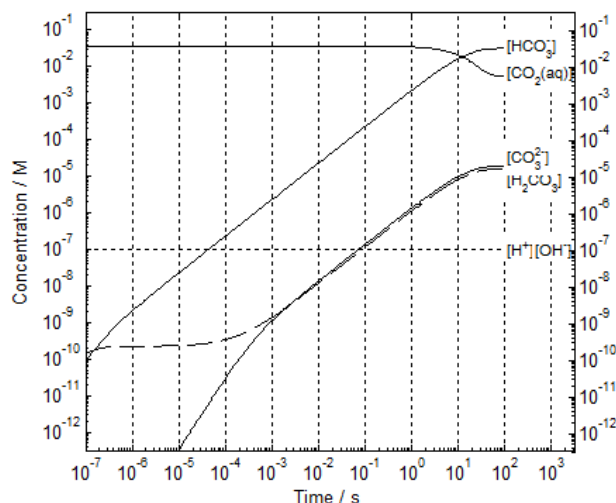


Fig. 3. Numerical simulation of CO₂ hydration at fixed pH.

However, even the buffer used by Kim et al. (2011) cannot fully explain the apparent enhancement of calcium carbonate formation and the observed precipitation within the first seconds of mixing solutions of CO₂ and CaCl₂. There are ambiguities and lacunae in descriptions of their experiments, but the authors seem to have used significantly lower concentrations of CaCl₂ (0.1M). At this concentration, even ignoring dilution due to mixing with another solution, the rate would be $[CaCO_3]' \approx 3.8 \cdot 10^{-6} Ms^{-1}$ and it would take about 20s to reach the solubility limit of CaCO₃.

Fragile and expensive carbonic anhydrase, even if it were efficient for enhancing mineralization, makes any industrial process using it wholly impractical because of the cost of the enzyme. Bhaduri and Šiller (2013) announced that they had discovered a cheap, stable inorganic catalyst for reaction (R2), with the additional advantages of remaining stable over a wide range of pH and of being magnetic. The catalyst was nickel nanoparticles (NiNPs). The published results don't allow direct comparison with carbonic anhydrase, but reportedly a "threefold enhancement in the dissolution of CO₂ in water was observed in the presence of NiNPs (30ppm)." In Figures 2a,b the dotted lines (with filled round and triangular markers for deionised water without and with NiNPs respectively) show their basic results that we have attempted to reproduce both experimentally and numerically. The paper lacks detailed description of the experimental setup, but it would appear that the rate of absorption in their experiment was much lower than in our original experiments (Setup 1) even with the lowest flow of CO₂. That was why we undertook another experiment with much lower and better controlled rate of CO₂ transfer (Setup 2).

Solid lines with filled round markers in Fig. 2b show our results for deionised water and $\alpha \approx 0.0077 cm^{-1}$ (bottom line) and $\alpha \approx 0.11 cm^{-1}$ (top line). As expected, both lines, despite being close to the results of Bhaduri and Šiller (2013) in terms of the time scale and absolute values of conductivity, were not sigmoidal. We also note that sigmoidicity was questioned by Britt (2013). Solid lines with filled triangle markers show our results for the same experiments repeated with NiNPs added to the water this time at the concentration identical to that used by Bhaduri and Šiller (2013) and supplied by the same company (which confirmed that they were the same type). Our results cast grave doubts on the reproducibility of the reported catalytic effect of NiNPs.

5. Conclusions

We were unable to reproduce experimentally the results of Bhaduri and Šiller (2013) that indicated that NiNPs can catalyse hydration of CO₂. Regardless, our numerical model confirms that catalysis of this reaction alone cannot facilitate the process of CO₂ capture by mineralization.

The apparently enhanced carbon dioxide sequestration reported in papers by Kim et al. (2011) and Bhaduri and Šiller (2013) are in all likelihood misinterpretation of observations, some of which may be explained in the light of the simulation results reported in this paper.

Acknowledgement

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Appendix 1

Effect of the rate constants on conductivity.

At equilibrium all concentrations stop changing and right parts of differential equations (1)-(6) have to be zero.

The equilibrium concentrations can be found as a solution of the system of algebraic equations

$$\begin{aligned} -k_2 [\text{CO}_2(\text{aq})] + k_{-2} [\text{H}_2\text{CO}_3] + k_{-7} [\text{HCO}_3^-] - k_7 [\text{CO}_2(\text{aq})] [\text{OH}^-] &= 0 \\ k_2 [\text{CO}_2(\text{aq})] - k_{-2} [\text{H}_2\text{CO}_3] - k_3 [\text{H}_2\text{CO}_3] + k_{-3} [\text{H}^+] [\text{HCO}_3^-] &= 0 \\ k_3 [\text{H}_2\text{CO}_3] - k_{-3} [\text{H}^+] [\text{HCO}_3^-] + k_4 [\text{HCO}_3^-] - k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] + k_6 [\text{H}_2\text{O}] - k_{-6} [\text{H}^+] [\text{OH}^-] &= 0 \\ k_6 [\text{H}_2\text{O}] - k_{-6} [\text{H}^+] [\text{OH}^-] + k_{-7} [\text{HCO}_3^-] - k_7 [\text{CO}_2(\text{aq})] [\text{OH}^-] &= 0 \\ k_3 [\text{H}_2\text{CO}_3] - k_{-3} [\text{H}^+] [\text{HCO}_3^-] - k_4 [\text{HCO}_3^-] + k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] - k_{-7} [\text{HCO}_3^-] + k_7 [\text{CO}_2(\text{aq})] [\text{OH}^-] &= 0 \\ k_4 [\text{HCO}_3^-] - k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] &= 0 \end{aligned}$$

Here $[\text{CO}_2(\text{aq})]=0.037\text{M}=\text{const.}$

It is not easy for this system to investigate analytically how the roots depend on the parameters. Solving the original differential equations shows that the reactions (R5) and (R6) don't have visible effect on the equilibrium conductivity. Fortunately, the reduced system of algebraic equations ($k_7=k_{-7}=0$, $k_6=k_{-6}=0$) can be investigated analytically:

$$\begin{aligned} -k_2 [\text{CO}_2(\text{aq})] + k_{-2} [\text{H}_2\text{CO}_3] &= 0 & (\text{A1}) \\ k_2 [\text{CO}_2(\text{aq})] - k_{-2} [\text{H}_2\text{CO}_3] - k_3 [\text{H}_2\text{CO}_3] + k_{-3} [\text{H}^+] [\text{HCO}_3^-] &= 0 & (\text{A2}) \\ k_3 [\text{H}_2\text{CO}_3] - k_{-3} [\text{H}^+] [\text{HCO}_3^-] + k_4 [\text{HCO}_3^-] - k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] &= 0 & (\text{A3}) \\ k_3 [\text{H}_2\text{CO}_3] - k_{-3} [\text{H}^+] [\text{HCO}_3^-] - k_4 [\text{HCO}_3^-] + k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] &= 0 & (\text{A4}) \\ k_4 [\text{HCO}_3^-] - k_{-4} [\text{H}^+] [\text{CO}_3^{2-}] &= 0 & (\text{A5}) \end{aligned}$$

From equation (A1) it can be found that

$$[\text{H}_2\text{CO}_3] = k_2/k_{-2} \cdot [\text{CO}_2(\text{aq})]. \quad (\text{A6})$$

From mass conservation for reactions $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ and $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ it follows that

$$[\text{H}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}]. \quad (\text{A7})$$

As $[\text{CO}_3^{2-}]$ is much smaller than $[\text{H}^+]$, this explains why the equilibrium concentrations $[\text{H}^+]$ and $[\text{HCO}_3^-]$ were almost indistinguishable in the simulations.

(A3),(A4) and (A7) yield the following cubic equation for $[\text{H}^+]$:

$$[\text{H}^+]^3 - A [\text{H}^+] - 2AB = 0. \quad (\text{A8})$$

Here $A = k_3/k_{-3} \cdot [\text{H}_2\text{CO}_3] = k_2 k_3/k_{-2} k_{-3} \cdot [\text{CO}_2(\text{aq})]$, $B = k_4/k_{-4}$.

The roots of equation (A8) depend on A and B and, hence, on $k_2 k_3/k_{-2} k_{-3}$ and k_4/k_{-4} . Figure A1,a below shows how the only positive root depends on the relative variations A/A_0 (solid line) and B/B_0 (dashed line). A_0 and B_0 are the values calculated for the rate constants given in Table 1. For small variations the root depends on A only, i.e. on $k_2 k_3/k_{-2} k_{-3}$. Figure A1,b shows this dependence in more detail and explains the k_2 correction by 0.7 used to make the simulation results close to the experimental one.

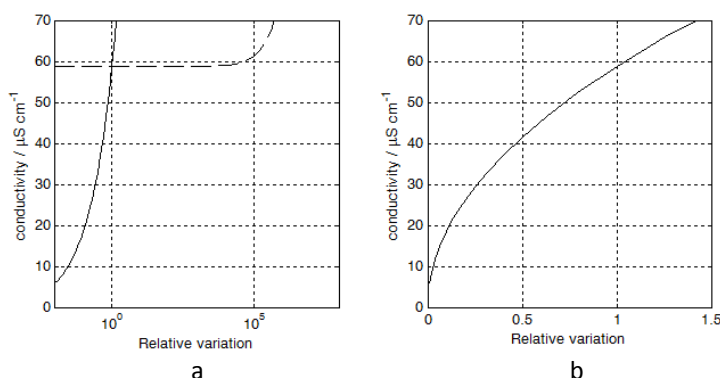


Figure A1. Affect of varying rate constants on conductivity.

Highlights

- Numerical simulation of carbonation reactions for CaCO_3 production from aqueous carbon dioxide in a batch reactor.
- Production of protons limits the equilibrium carbonate ion concentration which remains low.
- Catalysing the hydration process in the sequence of carbonation reactions isn't the rate limiting step in mineralization of CO_2 to metal carbonates.