Comment on “Questioning the catalytic effect of Ni nanoparticles on CO₂ hydration and the very need of such catalysis for CO₂ mineralization from aqueous solutions by Ramsden et al. Chem. Eng. Sci., 2018, 175, 162”

Gaurav A. Bhaduri¹, Lidija Šiller²

¹Department of Chemical Engineering, School of Chemical and Civil Engineering, Manipal University Jaipur, Dhemi Kalan, Jaipur-303007, Rajasthan, India.
²Nanoscale Science and Nanotechnology Group, School of Engineering, Newcastle University, Newcastle upon Tyne, NE17RU, UK

Email: gaurava.bhaduri@jaipur.manipal.edu

The use of Ni nanoparticles (NiNPs) as the catalyst for CO₂ hydration for aqueous CO₂ capture and mineralization process, that was firstly suggested by Bhaduri and Šiller (2013), was recently questioned by Ramsden et al. (2018). They concluded that the mineral precipitation is the slowest step in mineralization process irrespective of catalyst used, which is contradictory to the experimental work reported by Bhaduri and Šiller (2013), Bhaduri et al. (2015, 2016), and an independent experimental study by Bodor et al. (2014), which has not been cited in the paper by Ramsden et al. (2018).

Firstly, we believe that this discrepancy is because the experimental methodology by Ramsden et al. (2018) has a big shortcoming. Although Ramsden et al. claim that they have repeated the experiment reported by Bhaduri and Šiller, the experimental procedure was modified by adding an external stirrer into the apparatus in their first experimental set up. From experience, we know that the use of an agitator in NiNPs suspension leads to the rapid settling of NiNPs from suspension due to increased rate of sedimentation in the presence of centrifugal force in solid-fluid systems. This has been extensively reported in literature by others (McCabe et al. 2005; Richardson et al. 2002, Foust et al. 1980). This is why Bhaduri and Šiller (2013), used a bubble column reactor without additional stirring. Additionally, Ramsden et al. only present data for the electrical conductivity changes when CO₂ is bubbled in pure DI water without NiNPs. The data are similar to that reported by Bhaduri and Šiller, 2013 (and see figure 2a in the paper by Ramsden), but Ramsden et al do not show any electrical conductivity data with suspended NiNPs in solution. Are both data sets similar (without and with NiNPs)? If they are, then this is probably due to the rapid settling time of NiNPs (due to the presence of the external stirrer), and there would of course be a lack of catalytic activity of NiNPs in water with CO₂ towards hydration reaction, because there would not be enough contact time between bubbled CO₂ gas and surface of NiNPs. Presently, the lack of conductivity data with NiNPs and the comparison with the same without NiNPs, leads to an ambiguous interpretation of their results.

We also note that the volume of liquid that Ramsden et al. used was 100 cm³. However, the volume used by Bhaduri and Šiller was 200 cm³. Considering that both experiments have identical bubblers, the dynamics of mixing of CO₂ gas with liquid is different. This is because, in a semi-batch process, the reactor volume determines the rate of mass transfer and reaction rate for any processes (Hill and Root, 2014). Consequently, the experimental conditions are clearly different.

In the second experimental set up, Ramsden et al. used a beaker (or Erlenmeyer flask), for observing the catalytic effect. The advantage of this setup was an accurate determination of gas-liquid interface area...
per unit volume. Again, the authors did not mention the settling time of the NiNPs in this second experimental set up. We suspect that due to the lack of significant change in the conductivity with NiNPs when compared to system without NiNPs (see figure 2b in the paper by Ramsden et al.), there was again a rapid settling of NiNPs from the suspension. We believe that this second experimental set up is good only for gas-liquid studies and not heterogeneous systems, due to forced sedimentation.

Concerning the settling time of NiNPs in solutions, here we would like to report that NiNPs can be dispersed in solutions by an ultrasonic horn or in ultrasonic bath. From experience, ultrasonic horn (Bandelin Sonoplus, Germany; at 50% power for 2 min), is better for the dispersion of NiNPs. They can stay in suspension up to 30 minutes without any settling.

One additional discrepancy might be the actual size of NiNPs powder. Although NiNPs are obtained from the same supplier as in the work by Bhaduri and Šiller, the actual size distribution of nanoparticles has not been analysed. Sometimes, different batches of nanoparticles, although made with the same method and provided by the same supplier, may have a different size distribution. This can also have an effect on the settling times of nanoparticles in suspension. The average size of NiNPs in the work from Bhaduri and Šiller was determined by high-resolution transmission electron microscopy (HRTEM), and it is ~ 46 nm (see ref Bhaduri and Šiller, 2013; Bhaduri et al, 2015). Therefore, one would like to know the actual average size of NiNPs in the work by Ramsden et al. (2018).

In summary, we think that the authors had problems in both experimental set ups, by not having nanoparticles in suspension for prolonged enough time to observe the catalyzed reaction of NiNPs towards CO2 hydration reaction.

In addition, Ramsden et al. have not referred to any previous kinetic studies on the hydration of CO2 in their paper. It is known that pH affects the kinetic rate of CO2 hydration reaction (Kern, 1960). Consequently, all previous published studies on kinetic rates of the catalytic hydration of CO2, have been carried out within a small and tight range of pH values. For example, in the case for NiNPs, Bhaduri and Šiller (2013), Bodor et al. (2014), Bhaduri et al. (2015), and Bhaduri et al. (2016), have presented both catalytic and noncatalytic data for the same reaction. In buffer studies using Carbonic Anhydrase as a catalyst for hydration reaction of CO2, the same methodology has been applied (Bond et al. 2001, Mirjafari et al. 2007, Kim et al. 2011, Yadav et al. 2010), although the buffer effect makes difficult a quantitative kinetic analysis. Validation for the NiNPs catalyst, using the above mentioned technique for CA activity analysis, was reported by Bhaduri et al, 2015. Additionally, Bodor et al. have reported a two-fold enhancement of CaO and MgO mineralization and Bhaduri et al. (2014), have observed a two-fold enhancement of CO2 absorption in K2CO3 solution in the presence of NiNPs and control. All these studies show that NiNPs are effective catalysts on high pH values, and kinetics play an important role in mineralization and carbon capture, contradicting the conclusions presented by Ramsden et al. Additionally, Han et al. (2015), have reported catalytic activity of immobilized NiNPs on aerogel support that have also not been considered by Ramsden et al.

The CO2[\text{aq}] concentration will depend on pH of solution. The equilibrium model that Ramsden et al. have presented was solved at pH 4 (where [CO2[\text{aq}]] \approx 0.037 \pm 0.003 \text{ M}), when the CO3^2- ion concentration is low (see figure 1 in their paper). Whereas, in the figure 3 they have solved it at higher pH and they do not explicitly mention the pH value or the solution details i.e. the CO2[\text{aq}] concentration. It should be noted that, the kinetic constants and equilibrium constants for CO2 hydration are pH dependent and the data for k2-k4 have been simulated for pH 6 (Mitchell et al, 2010), and should not be used for equilibrium
calculations for pH 4, which have been used by Ramsden et al. (In summary, their basic assumption is wrong: authors should use data of kinetic constants at pH 4 and not pH 6).

Recently, a pH independent kinetic study was done by Wang et al. (2010), solving highly complex model systems for homogeneous solutions of bicarbonate, carbonic acid and hydrochloric acid by fitting experimental data using a stop flow spectrophotometer. However, this method could not be applied to heterogeneous systems because the pH indicators reacted with the surface of NiNPs (Bhaduri et al, 2013; see Supplementary information), and there was an absorption peak overlap with the dye absorption band and the NiNPs.

In conclusion, we believe that the claims made by Ramsden et al. are not supported with relevant experimental or simulation data.

Acknowledgments:
We would like to acknowledge Dr. Miriam Baldwin for proof reading this manuscript.

References:


Han, X.; Williamson, F.; Bhaduri, G.A.; Harvey, A.; Šiller, L; Synthesis and characterization of ambient pressure dried composites of silica and Aerogel matrix and embedded nickel nanoparticles. J. Supercritical Fluids, 106, 2015, 140.


Ramsden, J.J.; Sokolov, I.J.; Malik, D.J.; 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, Chem. Eng. Sci., 2018, 175, 162.


Secondly, Ramsden et. al. have misunderstood what was reported in the paper by Bhaduri and Šiller (2013). The reported three-fold enhancement of CO₂ dissolution in water in presence of nickel nanoparticles was measured by titration and it is not a result of pH and conductivity measurements. Furthermore, the significant enhancement of dissolution of CO₂ in the presence of NiNPS was also confirmed by Bodor et. al. but this work was not cited, or commented on, in the paper by Ramsden et. al.