Journal of Nanochemistry & Electrochemistry
Spring 2021. Vol. Issue 1

Research Paper

High purity calcium carbonate production from FGD gypsum

Amin Azhdarpour[1], Masoumeh Emadi[2]
1 Department of Petroleum Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran.
2 Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran.

Received: 2021.8.19
Revised: 2021.10.1
Accepted: 2021.10.4

Keywords:
FGD Gypsum, CaCO3, High purity, Mersberg process, CO2 sequestration

Abstract: Increasing fossil fuel consumption due to industrialization and development of many countries in the 21st century emits more greenhouse gases (GHGs) and in particular carbon dioxide (CO2) into atmosphere. These activities have increased the concentration of the major component of the GHGs from 280 ppm in the 1750s to 396.8 ppm in 2013. Mineral carbon dioxide sequestration provides a leakage free and permanent method of CO2 disposal to produce environmentally benign and stable solid carbonates. Natural minerals and industrial by-products rich in calcium (Ca) and magnesium (Mg) are the most favorable feedstocks for mineral carbonation processes. Flue gas desulfurization (FGD) gypsum as a source of calcium was proposed as the potential feedstock in this study. The purpose of this laboratory study was to investigate the effect of reaction parameters such as CO2 pressure, reaction temperature, particle size, ammonia solution concentration, reaction time, and solid to solution ratio on calcium carbonate purity through Mersberg process. Increasing the reaction temperature as well as the pressure was very effective in improving the calcium carbonate purity. High purity calcium carbonate was produced when reaction temperature was increased to 400 °C and 70 bar, resulting in 93% and 94% purity, respectively. Experimental results showed that reducing particle size was also effective in enhancing the calcium carbonate purity in which the smallest particles produced higher purity calcium carbonates rather than larger particles. Increasing the reaction time from 30 to 60 minutes resulted in further completion of the reactions and better conversion of calcium into carbonate form.

Citation: High purity calcium carbonate production from FGD gypsum. Journal of Nanochemistry & Electrochemistry,

Introduction

Continuous increment of global carbon dioxide (CO_2) due to combustion of fossil fuels leads to steady rise of global mean temperature. As a consequence, the global climate has been changed to unfavorable situation for human and animal being. This alarming situation warns us to reduce the pumping of CO_2 into the atmosphere. These activities have resulted in increasing the CO_2 concentration from 280 ppm in the 1750s to 396.8 ppm in 2013. Increasing the global main temperature by 1.8 to 4 °C has been predicted by 2100 due to rapid emission of CO_2 into atmosphere [1-6].

Dissolution of CO_2 in rain water and then neutralization with alkaline minerals to form carbonates is called natural rock weathering. Mineral carbon dioxide sequestration that is an exothermic reaction mimics the natural rock weathering. In this process, CO_2 reacts with metal oxides to produce environmentally benign, permanent and stable solid carbonates with no chance of CO2 release after the reaction [7-10]. Calcium and magnesium oxides can undergo carbonation reactions. Pure magnesium and calcium oxides are very rare in nature and they usually appear in silicate forms [11]. Olivine (Mg_2SiO_4), wollastonite ($CaSiO_3$), and serpentine ($Mg_3Si_2O_5(OH)_4$) are the most common types of natural minerals rich in magnesium and calcium for carbonation process [11-15]. Industrial by-products rich in calcium and magnesium can be considered as potential feedstock of mineral carbonation experiments. A comprehensive effort has been paid to investigate the efficiency of these solid residues to date and nearly promising results have been achieved. Steelmaking slags, cement, MSWI bottom and fly ash, coal fly ash, blast furnace slag, electric arc furnace slag, and paper bottom ash are the most common and widely used of industrial by-products for mineral carbonation purposes [9,16]. The process of SO_x removal from power plant flue gas produces flue gas desulphurization (FGD) gypsum. This industrial by-product contains approximately 32% CaO that makes it a potential feedstock for mineral carbonation purposes. The produced FGD gypsum can be directly used as the mineral carbonation feedstock without any required grinding process since it is in a fine powder form [17-18]

Using Ca/Mg–rich minerals or solid residues to produce a carbonate in a single step is called direct mineral carbonation. This method is the simplest mineral carbonation, in which the extraction of metal ions and the precipitation of carbonate take place in one single step. Carbonation can proceed through gas-solid carbonation or aqueous carbonation [16]. Extensive studies have been carried out on direct aqueous carbonation in last couple of years, however results indicate that Ca/Mg conversion rate to carbonate form is not fast and significant through direct carbonation and in most of the cases low carbonation rate was achieved [19-21]. Therefore, in this study, we tried to utilize the Mersberg approach to enhance the conversion of calcium into carbonate form to produce high purity calcium carbonate.

Based on Mersberg process ammonium sulfate is produced through the chemical reaction of ammonium carbonate and natural gypsum [22]. However, the ammonium sulfate production is not a concern here and this study investigates the mineral CO_2 sequestration and high purity calcium carbonate production using FGD gypsum as the calcium source.

FGD gypsum with four different particle sizes of 45, 100, 200, and 400 micron representing a wide range of particle size were used as the feedstock. Pressures of 1, 30, 50, and 70 bar and temperatures of ambient, 150, 250, and 400 °C were chosen to represent a wide range of temperature and pressure. The choice of 400 °C and 70 bar as the maximum temperature and pressure was due to the limitations associated with experimental apparatus, however for the future work pressures and temperatures higher than 70 bar and 400 °C should be investigated to have clear trend of the carbonation rate. The whole experiments were conducted with 0.1, 0.5, 1, and 5 M ammonia concentration. In all experiments only 10 grams of FGD gypsum was used and solid to solution ratio was changed to 15, 30, 40, and 50%.

Materials and Methods

The FGD gypsum was taken from a thermal power plant in Malaysia. The physical and chemical properties of FGD gypsum were characterized using X-ray Fluorescence (XRF) and BET analysis. Result showed that calcium sulfate dihydrate (CaSO4.2H2O) is the major constituent of the FGD gypsum. The chemical composition of FGD gypsum was analyzed using XRF and results are presented at table 1. Results showed that FGD gypsum has purity more than 99% and consists of some major components such as CaO (32.22%), SO3 (41.12%) and some impurities such as SiO2 (0.89%), Fe2O3 (0.15%), and Al2O3 (0.51). These results prove that FGD gypsum could be a potential feedstock for mineral carbonation process since it contains high amount of calcium oxide. Particle size of FGD gypsum was analyzed using BET analyzer. Result showed that FGD gypsum particles are in a range of 20 to 100 micron with the average (d50) particle size of 56.03 micron.

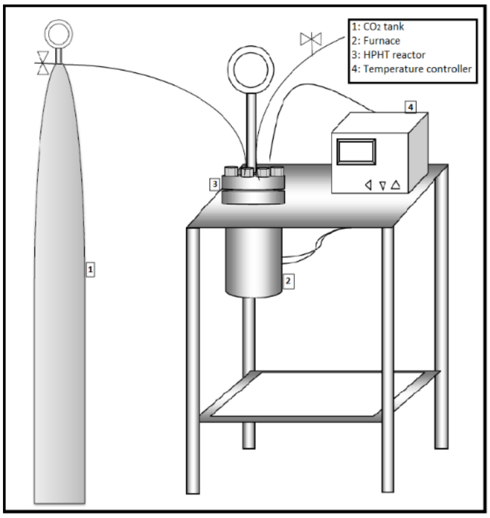

Figure 1: Schematic diagram of carbonation experiments

An 100 ml high pressure and temperature (HPHT) autoclave reactor was used for the carbonation experiments. Figure 1 shows the schematic diagram of carbonation experiment at HPHT conditions. The ammonia concentration (0.1-5 M), pressure up to 70 bar, temperature up to 400 °C, and particle size of 45, 100, 200, and 400 micron, and variable solid to solution ratio (15-50%) were utilized and their effects on calcium carbonate purity were investigated. Samples of FGD gypsum with specified particle size were poured in a beaker. The initial slurry was prepared by the addition of ammonia hydroxide solution (NH4OH) to FGD gypsum. After this step, slurry sample with known solid to solution ratio was taken and placed in the HPHT reactor and CO2 was injected to the reactor at the desired conditions of pressure and temperature. After giving 30 and 60 minutes time for each experiment, reaction was stopped and samples were collected for further analyses by TGA. The purity of produced calcium carbonate was measured using Thermogravimetric analyzer (TGA). After giving the required time each sample was taken and analyzed using TGA. Purity of calcium carbonate can be calculated using equation 1.

$$P_{CaCO3}(\%) = \frac{\Delta W(\%) \times Mw_{CaCO3}}{Mw_{CO2}} \qquad (1)$$

Results & Discussion

1. Effects of temperature on CaCO3 purity

The effect of temperature on calcium carbonate purity was investigated using four different temperatures (25, 150, 250, and 400 °C) in conjunction with variable ammonia concentrations. In these experiments 10 grams of 100 micron FGD gypsum was used with constant solid to solution ratio of 30%. Figure 2 and 3 represent the purity of calcium carbonate as a function of temperature with variable ammonia concentration (0.1-5 M) at atmospheric pressure after 30 and 60 minutes, respectively.

Experimental results showed calcium carbonate purity is in a direct relationship with temperature; however slightly low purity calcium carbonate was achieved at ambient temperature. Increasing temperature enhances the calcium carbonate purity. Purity was much higher when reaction temperature increased to its maximum value (400 °C) rather than ambient temperature, 150, and 250 °C. Increasing ammonia concentration was also effective in enhancing the calcium carbonate purity in which the highest ammonia concentration resulted in highest calcium carbonate purity. In general, increasing temperature was completely compatible with increasing ammonia concentration. Calcium carbonate purity of 93% and 82% were achieved after 60 and 30 minutes when temperature increased to 400 °C and 5M ammonia was used and it was at its lowest value

(20% purity after 30 minutes and 24% after 60 minutes) when only 0.1M ammonia was used at ambient temperature. The enhancement of calcium carbonate purity with increasing temperature observed after both 30 and 60 minutes, however experimental results showed that increasing the reaction time is very effective in producing higher purity calcium carbonates. The chemical reaction of ammonia slurry with CO2 will generate some ammonium salts including ammonium carbonate, ammonium carbamate, and ammonium bicarbonate besides the calcium carbonate formation. Higher temperatures facilitate the generation of these salts and consequently calcium carbonate production. In general, increasing the temperature enhances the chemical reactivity and this may result in improving the carbonation rate and producing higher purity calcium carbonates [23]. Therefore, carbonation rate is higher at higher temperatures rather than lower temperatures. Increasing ammonia concentration had significant effect on calcium carbonate purity as well, in which 5M ammonia gave the best result as compared to lower ammonia concentrations. The addition of higher ammonia solutions would be beneficial in producing high purity calcium carbonates and stabilizing the reaction [22].

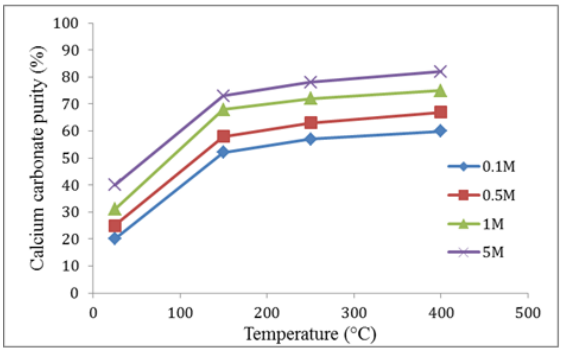

Figure 2: Effects of temperature on calcium carbonate purity after 30 minutes

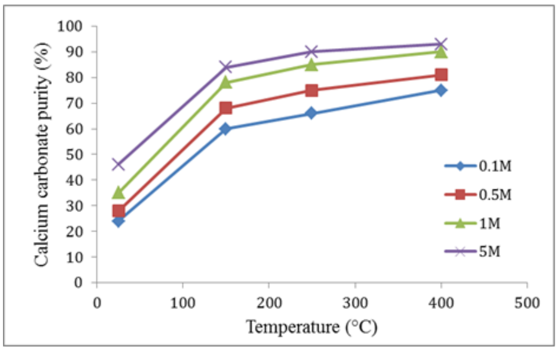

Figure 3: Effects of temperature on calcium carbonate purity after 60 minutes

2. Effects of pressure on CaCO3 purity

The effect of pressure on calcium carbonate purity was investigated at 1, 30, 50, and 70 bar pressure. Experiments were conducted using variable (0.1-5 M) ammonia concentrations at ambient temperature. In these experiments FGD gypsum with average particle size of 100 micron was used with constant solid to solution ratio of 30%. Figure 4 and 5 show the experimental results of calcium carbonate purity as a function of operating CO2 pressure after 30 and 60 minutes, respectively.

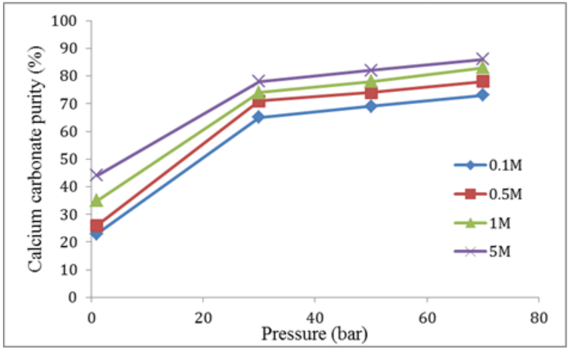

Figure 4: Effect of pressure on calcium carbonate purity after 30 minutes

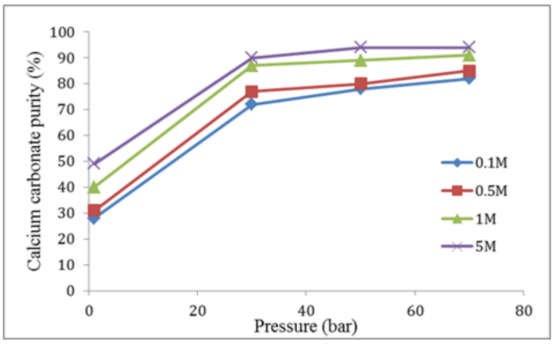

Figure 5: Effect of pressure on calcium carbonate purity after 60 minutes

Experimental results showed that calcium carbonate purity is in a direct relationship with pressure and increasing pressure enhances calcium carbonate purity significantly. The lowest purity was achieved at atmospheric pressure and the highest value was achieved at 70 bar pressure. It is due to the fact that CO2 dissolution and carbonation kinetics may be facilitated at elevated pressures. Therefore, increasing pressure drives the reaction forward faster and this would result in enhancing the carbonation rate [9]. Ammonium concentration also affected the carbonation rate and product purity. The least purity was achieved with 0.1M ammonia concentration and the most value was achieved when 5M ammonia solution was used. This trend was found with all pressure conditions while the highest product purity (86% purity after 30 minutes and 94% after 60 minutes) was achieved at 70 bar pressure and 5M ammonia concentration and the lowest carbonate purity (23% purity after 30 minutes and 29% after 60 minutes) resulted with 0.1M ammonia concentration at atmospheric pressure. The reaction of CO2 with ammonia hydroxide will produce ammonia salts and this rate is faster especially at higher CO2 pressures and ammonium concentrations [22]. In general samples collected after 60 minutes had higher purity as compared to samples after 30 minutes. The reason is that increasing the residence time of reaction gives more time to reactants to be in reaction, therefore more calcium ions will be converted to carbonate and higher purity calcium carbonate will be produced.

3. Effect of particle size on CaCO3 purity

FGD gypsum with three different particle sizes of 45, 200, and 400 micron were used at ambient temperature and atmospheric pressure with variable ammonia concentrations 0.1-5 M. Solid to solution ratio was used constantly 30% in all experiments. Each sample was given 30 and 60 minutes to react with CO2 and then samples were taken and send for further analyzes using TGA. Figure 6 and 7 shows the calcium carbonate purity of different particle size with variable ammonia concentrations after 30 and 60 minutes, respectively.

Particle size reduction was also effective in increasing the purity of calcium carbonate; however this improvement was not significant at ambient temperature and atmospheric pressure. The best results were observed when 45 micron particles were used while increasing the particle size toward 400 micron reduced calcium carbonate purity significantly. Reducing particle size to 45 micron resulted with calcium carbonate purity of 35% after 30 minutes and 47% after 60 minutes when 5M ammonia solution was used and purity was reduced to its lowest value when particle size of 400 micron was used with 0.1 M ammonia solution. The calcium carbonate purity for this case was found to be 9% and 14% after 30 and 60 minutes, respectively. Small particles have larger total surface are than the big particles. The overall reaction rate of calcium to carbonate is a function of total specific area of particles [24]. Therefore, increasing the total surface area by reducing the particle size can enhance the carbonation rate and calcium carbonate purity significantly. In general, particle size of 45 micron with 5M ammonia concentration showed the highest calcium carbonate purity and particle size of 400 micron with 0.1M ammonia concentration resulted in lowest calcium carbonate purity.

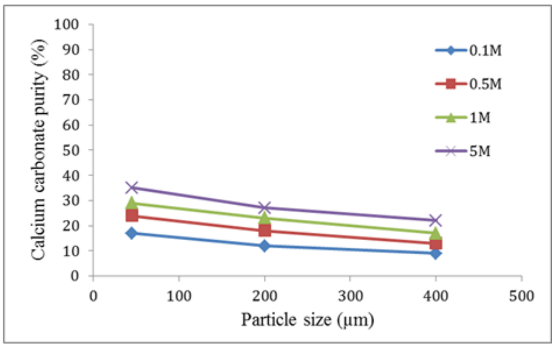

Figure 6: Effect of particle size on calcium carbonate purity after 30 minutes

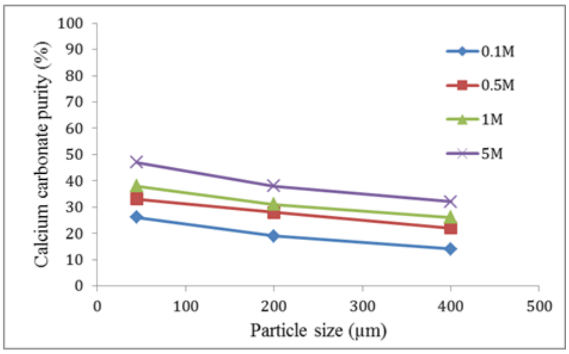

Figure 7: Effect of particle size on calcium carbonate purity after 60 minutes

Conclusion

High purity calcium carbonate production through Mersberg was proposed as one of the promising methods of reducing CO2 concentration. The effects of variable parameters such as reaction time, temperature, pressure, and particle size were studied and the effects of each parameter on calcium carbonate purity was investigated. Increasing reaction temperature and operating pressure resulted in high purity calcium carbonate production. Experimental results showed that other parameters such as particle size had minimal effect on calcium carbonate purity; however particle size reduction was still effective in improving the calcium carbonate purity. In all experiments, increasing the reaction time from

30 to 60 minutes resulted in increasing the calcium carbonate purity.

Ethical Considerations

Compliance with ethical guidelines

All subjects fulfill the informed consent.

Acknowledgments

We gratefully acknowledge the financial support of this work by Marvdasht Islamic Azad University.

Authors' contributions

Design and conceptualization, methodology, data analysis and final writing: Amin Azdarpour.

Conflicts of interest

The author declared no conflict of interest.

References

[1] IPCC. 2000. *Special report on emissions scenarios: a special report of working group III of the intergovernmental panel on climate change*. Cambridge: Cambridge University Press.

[2] Raupach, M. R., Marland, G., Ciais, P., Que´re, C. L´., Canadell, J. G., Klepper. G., Field, C. B. 2007. Global and regional drivers of accelerating CO_2 emissions. Proceedings of the National Academy Sciences of United States of America 104:10288–10293.

[3] Canadell, L. G., Quéré, C. L., Raupach, M. R., Field. C. B., Buitenhuis. E. T., Ciais, P., Conway, T. J., Gillett, N. P., Houghton, R. A., Marland, G. 2007. Contributions to accelerating atmospheric CO2 growth from economic activity, carbon intensity, and efficiency of natural sinks. Proceedings of the National Academy Sciences of United States of America 104: 8866–8870.

[4] IPCC (Intergovernmental Panel on Climate Change). 2007. *Carbon dioxide capture and storage. IPCC Special Report*. Metz, B., Davidson, O., Bosch, P., Dave, R., and Meyer, L. (Eds.). Cambridge: Cambridge University Press.

[5] IPCC. 2007. *Climate change 2007: Synthesis report, contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change*. Cambridge: Cambridge University Press.

[6] Earth System Research Laboratory, Global Monitoring Division: http://www.esrl.noaa.gov/gmd/ccgg/trends/

[7] Lackner, K. S. 2002. Carbonate chemistry for sequestering fossil carbon. *Annual Reviews of Energy and the* Environment 27:193–232.

[8] Huijgen, W. J. J., Comans, R. N. J. 2003. Carbon dioxide sequestration by mineral carbonation. Petten, NL: Energy Research Centre of the Netherlands.

[9] Bobicki, E. R., Liu, Q., Xu, Z., Zeng, H. 2012. Carbon capture and storage using alkaline industrial wastes. *Progress in Energy and Combustion Science* 38: 302–320.

[10] Maroto–Valer M. M., Kuchta, M. E., Zhang. Y., Andrésen, J. M., Fauth, D. J. 2005. Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. *Fuel Processing Technology* 86: 1627–1645.

[11] Lackner, K. S., Wendt, C. H., Butt, D. P., Joyce, L. E., Sharp, D. H. 1995. Carbon dioxide disposal in carbonate minerals. *Energy* 20: 1153–1170.

[12] Klein, F., Garrido C. J. 2011. Thermodynamic constraints on mineral carbonation of serpentinized peridotite. *Lithos* 126: 147–160.

[13] Andreani, M., Luquot, L., Gouze, P., Godard, M., Hoisé, E., Gibert, B. 2009. Experimental study of carbon sequestration reactions controlled by the percolation of CO_2-rich brine through peridotites. *Environmental Science & Technology* 43: 1226–1231.

[14] Boschi, C., Dini, A., Dallai, L., Ruggieri, G., Gianelli, G. 2009. Enhanced CO_2-mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malentrata. *Chemical Geology* 265: 209–226.

[15] Fagerlund, J., Teir, S., Nduagu, E., Zevenhoven, R. 2009. Carbonation of magnesium silicate mineral using a pressurised gas/solid process. *Energy Procedia* 1: 4907–4914

[16] Sipilä J., Teir S., Zevenhoven, R. 2008. *Carbon dioxide sequestration by mineral carbonation: literature review update 2005–2007*. Heat Engineering Laboratory, Faculty of Technology, Abo Akademi University, Finland.

[17] Choi, J. W. 1986. *A study on the production of ammonium sulfate from by-produced gypsum*. Ph.D. Thesis, Seoul National University, South Korea.

[18] Chou, M. M., Bruinius, J. A., Benig, V., Chou, S. F. J., Carty, R. H. 2005. Producing ammonium sulfate from flue gas desulfurization by-product. *Energy Sources* 27: 1061–1071.

[19] O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Rush, G. E., Walters, R. P., Turner, P. C. 2001. Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status. *First National Conference on Carbon Sequestration*, Washington, DC, May 14–17.

[20] O'Connor, W. K., Dahlin, D. C., Rush, G. E., Gerdemann, S. J., Penner, L. R., Nilsen, D. N. 2005. *Aqueous mineral carbonation: mineral availability, pretreatment, reaction parametric*

and process studies. Final report to Office of Fossil Energy US DOE, United States.

[21] Lackner, K. S., Butt, D. P., Wendt, C. H. 1997. Progress on binding CO_2 in mineral substrates. *Energy Conversion and Management* 38: 259–264.

[22] Lee, M. G., Jang, Y. N., Ryu, K. W., Kim, W., Bang, J. H. 2012. Mineral carbonation of flue gas desulfurization gypsum for CO_2 sequestration. *Energy* 47: 370–377.

[23] Darde, V. 2011. *CO_2 capture using aqueous ammonia*, Ph. D. Thesis, Technical University of Denmark, Denmark.

[24] Huijgen, W. J. J., Witkamp, G. J., Comans, R. N. J. 2006. Mechanisms of aqueous wollastonite carbonation as a possible CO_2 sequestration process. *Chemical Engineering Science* 61: 4242–4251.