



Procedia Environmental Science, Engineering and Management **8** (2021) (1) 1-6

Environmental Innovations: Advances in Engineering, Technology and Management,
EIAETM, 19th-23rd October, 2020

OPPORTUNITIES FOR CO₂ UTILISATION VIA CARBONATION*

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Abstract

This study focuses on describing the most important aspects of CO₂ carbonation processes. Furthermore, a novel proposal for classifying CO₂ carbonation alternatives is presented. The technologies are classified into two main categories: mineral CO₂ carbonation; and hydroxides, salts and waste carbonation. The carbonation of hydroxides, salts and waste presents advantages over the traditional mineral CO₂ carbonation. The most important one is the flexibility to be used in those places where there is not a mineral reservoir near to the installations. Moreover, softer conditions are needed in the cases where chemical regeneration of the solvent is chosen, showing also remarkable efficiencies (70-90%) and very good product quality.

Keywords: carbonates, CO₂ carbonation, CO₂ utilization, low-energy technologies, mineral carbonation

1. Introduction

During the last decades, the CO₂ concentration in the atmosphere has increased considerably. This fact can accelerate the very discussed climate change. Therefore, the reduction of CO₂ emissions is a crucial challenge in the forthcoming years (Zhang et al., 2020). Apart from increasing the use of renewable energy sources, the two main technologies to decrease CO₂ emissions are Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) (Baena-Moreno et al., 2019b). Even though CCS are considered an effective solution, some technical difficulties still remain, such as for example storage problems (Baena-Moreno et al., 2020a) . On the contrary, CCU technologies offer a valid

* Selection and peer-review under responsibility of the EIAETM

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solution for the short-medium term. The main problem associated to CCU technologies is the huge amount of final CO₂-based products in case of applying them on large emitters. In this sense, CCU technologies are more suitable for small-medium emitters, such as for example CO₂ coming from biogas upgrading (Baena-Moreno et al., 2020b).

There is a wide portfolio of CCU technologies which have proved to be ready either for imminent industrialization or for being scale-up towards demonstration (Baena-Moreno et al., 2020c). The main CCU technologies are collected in Fig. 1. The viability of some of them were proved many years ago, such as for example Enhanced Oil Recovery (EOR) or Methanation. Others, such as polymers production from CO₂ or the production of biofuels from CO₂, still need some technological improvements to be profitable alternatives. Among all the CCU alternatives, CO₂ carbonation presents potential to removed billions of CO₂ tonnes at a competitive price (Sanna et al., 2014).

In this work, a brief overview of CO₂ carbonation technologies is presented. This work is aimed to be a guide for those implicated in the industrial decarbonization via CO₂ carbonation. Moreover, this work proposes a classification of CO₂ carbonation technologies, based both in the raw material used and the number of stages of the processes. The categories in which this work proposes to divide CO₂ carbonation technologies are presented in Fig. 2.

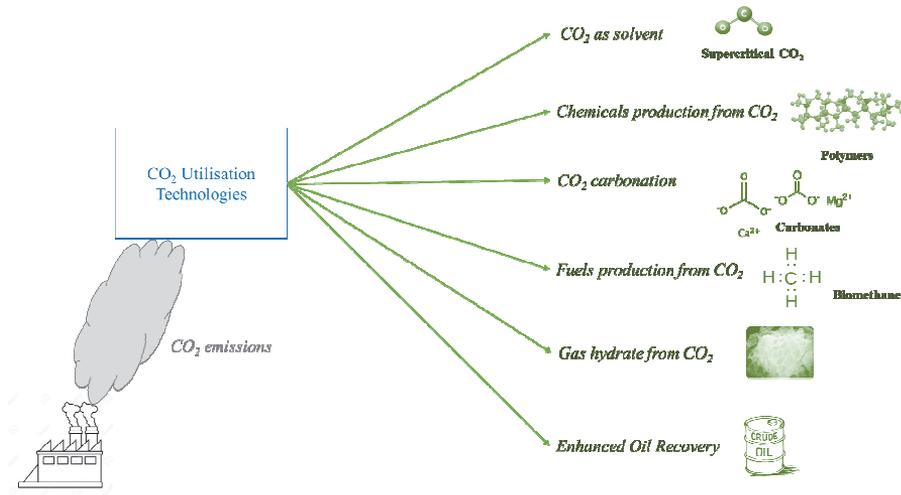


Fig. 1. CCU portfolio technologies

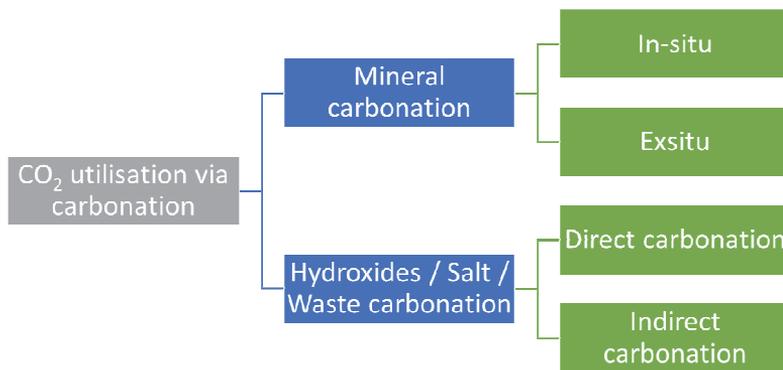


Fig. 2. Classification proposal for CO₂ carbonation alternatives

This work is divided in two main parts:

- Description of mineral CO₂ carbonation alternatives. Among these technologies highlight in-situ and ex-situ CO₂ carbonation.
- Description of hydroxides – salt – brines carbonation options, in which we can distinguish direct carbonation (solid-gas) and indirect carbonation (solid-aqueous-gas).

2. A review of CO₂ carbonation technologies

2.1. Mineral CO₂ Carbonation

There are commonly two Mineral Carbonation (MC) alternatives, which are in-situ and ex-situ MC. The first one requires CO₂ injection into underground reservoirs. Thus, the injected CO₂ reacts with the minerals contained into the reservoirs to give carbonates as products. Regarding ex-situ MC, this process takes mineral formations which are available above-ground and transform them in carbonates. This alternative requires a previous mining stage, then grinding the mineral extracted.

In-situ MC follows the scheme represented in Fig. 3. The typical minerals in which in-situ MC can be applied are peridotite and basalts natural deposits (Sanna et al., 2014). These mineral deposits are characterized for having a high percentage composition of magnesium and calcium silicates. In some natural locations is possible to find iron silicates, which can also serve as mineral source for CO₂ carbonation (Helwani et al., 2016).

When injecting CO₂ in peridotite mineral reservoirs, at a temperature of 90°C and a pressure of 100 bar, approximately 0.63 kg CO₂ / kg peridotite can be storage (Sanna et al., 2014). Afterwards, it would be necessary a drilling – extraction process to obtain the carbonates formed. Concerning basalt reservoirs, they can be found both onshore and offshore. The most important study carried out to date is the one offshore in the USA West Coast, “Juan de Fuca Plate basalts”. It is estimated that the storage potential of this reservoir is about 920 Gt of CO₂ (Goldberg et al., 2008). Other important reservoirs can be found in Papua New Guinea, New Caledonia or East of the Adriatic Sea (Sanna et al., 2014).

Ex-situ MC presents some disadvantages against in-situ MC. The most limiting one is the slower kinetics of the reactions. Environmental concerns are also among the negative points of ex-situ MC. The typical mineral for ex-situ MC carbonation are silicate rocks, which contains Mg and Ca. The silicates rocks which present these characteristics are serpentine, olivine and wollastonite.

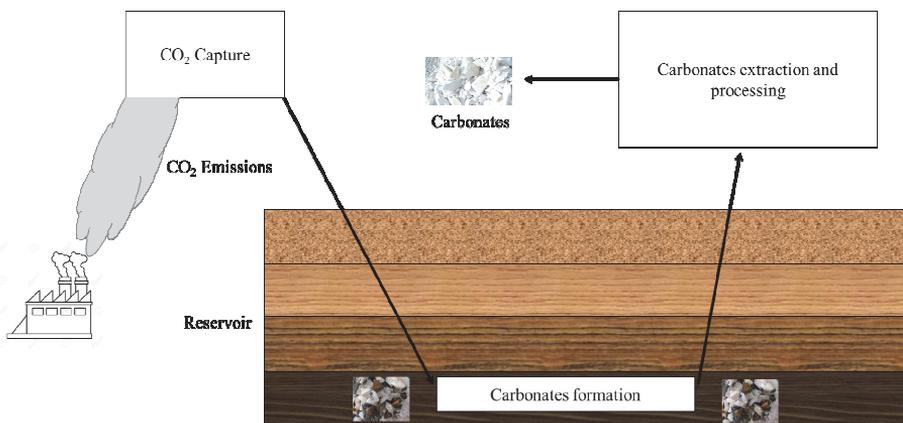


Fig. 3. In-situ MC process scheme

The first one is preferred because of its availability and the better carbonation outputs obtained. Examples of commercial ex-situ MC carbonation process developed to date are Calera process and Abo Akademi process (Sanna et al., 2014). All the developed processes present the common process layout represented in Fig. 4. Regarding typical operation conditions, very different parameter values can be found. This fact is mainly caused by the differences in the silicate rocks composition. Temperatures between 50-650°C and pressures between 1-200 bars can be found (Helwani et al., 2016). Even though very different efficiencies have been published, values around 50-60% are the average (Librandi et al., 2019).

Regarding the energy consumption of MC alternatives, it is strongly dependent on the location, the type of MC, and the operational conditions. Thus, it is difficult to quantify an exact number. However, some estimations reveal that energy consumption are in the range of 170-6030 kW h per t-CO₂ (Sanna et al., 2014). In order not to emit more CO₂, this energy should be produced by renewable sources.

2.2. Hydroxides, Salts and Waste Carbonation

The second alternative for CO₂ carbonation relies on a simpler process than MC, as can be seen in Fig. 5.

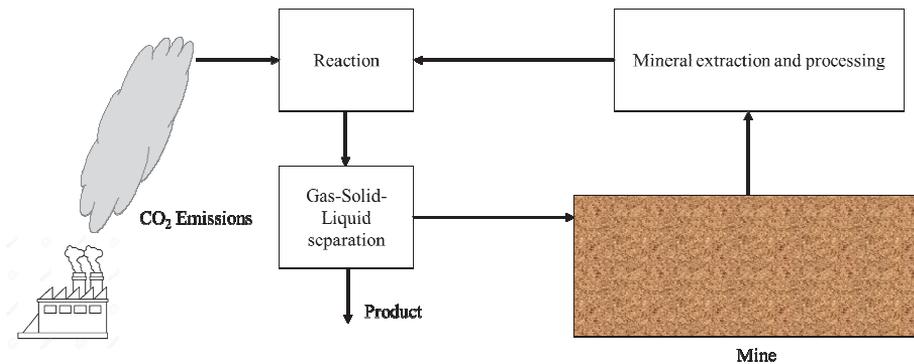


Fig. 4. Ex-situ MC process layout

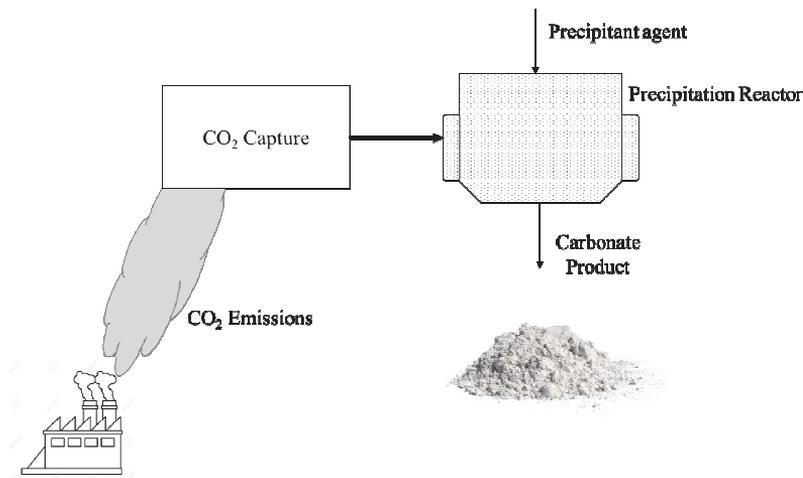


Fig. 5. Carbonation of hydroxides, salts and waste.

In this process, CO₂ is first capture from the emitting source and subsequently sent to a reactor in which the final carbonate is produced through the reaction between CO₂ and a precipitator agent. This precipitator agent can be a hydroxide (i.e. calcium hydroxide or magnesium hydroxide), a salt (i.e. calcium chloride or magnesium chloride) or a waste which can fulfil the same function that the previous ones (i.e. slag from steel manufacturing) (Baena-Moreno et al., 2019a).

The advantages of this process in comparison with MC are manifold.

- Firstly, the adaptability of the process to work with more than one precipitator material.
- Another important advantage is the flexibility of the installation to be located in places far from mines or reservoirs. Moreover, the process can be also adapted to the market needs regarding the type of carbonate desired (i.e. calcium or magnesium carbonate).

This alternative presents two main process schemes, depending on the technology chosen for CO₂ capture. Thus, carbonation reaction can be carried out by means of a gas-liquid or liquid-liquid reaction. If the CO₂ captured is release from the capture stage as gas, the first type is employed. This is the case of technologies such as for example membrane for CO₂ capture, or adsorption with zeolites. In those cases where CO₂ is chemically captured and separated from the flue gas (chemical absorption), there is an alternative to regenerate the spent solvent by means of chemical reaction. In these cases, both reactants are in liquid state (Bacocchi et al., 2012).

Process conditions and efficiencies vary according to two main parameters: type of precipitant agent and state of the CO₂ source in the reaction. Generally, when the reaction is gas-liquid, lower efficiencies than in the other alternative are found due to thermodynamic aspects. Therefore, liquid-liquid carbonation is attracting the attention of several research during the last decade. These processes can keep soft process conditions in comparison with other carbonation technologies. For example, pressure is kept at atmospheric value whereas temperature ranges between 20-70 °C (Bacocchi et al., 2013). Furthermore, reactions time are not very long (around 30-45 minutes). The challenge of this technology relays on the optimization of the molar ratio between precipitant agent and carbonated solvent. As the maximum efficiencies are around 90%, there are rest of calcium or magnesium agents that need to be removed before recirculating the solvent to the beginning of the process. This calcium – magnesium removal is costly and it needs further research to improve the overall economic performance of the process.

Regarding energy consumption, there is a lack of works dealing with this issue. It can be affirmed that the softer conditions than MC suppose lesser energy consumptions. This is a future point of further research for those collaborating in this area.

3. Concluding remarks

- Herein the main technologies available for CO₂ carbonation have been described. CO₂ carbonation is a promising path for both carbon storing and CO₂ utilization. Furthermore, in this work a novel proposal for classifying these technologies is presented. The technologies are classified into two main categories: Mineral CO₂ Carbonation; and Hydroxides, Salts and Waste Carbonation.

- The first category presents some disadvantages against the second one. The most important disadvantage is the poor flexibility regarding the location of the process, since both in-situ and ex-situ MC can only be performed near to mineral reservoirs to keep the cost as low as possible.

- The carbonation of hydroxides, salts and waste presents an opportunity for those industries which do not have a mineral reservoir near to their installations. Moreover, softer conditions are needed in the cases where chemical regeneration of the solvent is chosen, showing also remarkable efficiencies.

Acknowledgements

This work was supported by the University of Seville through V-PPTI.

References

- Baclocchi R., Carnevale E., Costa G., Gavasci R., Lombardi L., Olivieri T., Zanchi L., Zingaretti D., (2013), Performance of a biogas upgrading process based on alkali absorption with regeneration using air pollution control residues, *Waste Management*, **33**, 2694-2705.
- Baclocchi R., Costa G., Gavasci R., Lombardi L., Zingaretti D., (2012), Regeneration of a spent alkaline solution from a biogas upgrading unit by carbonation of APC residues, *Chemical Engineering Journal*, **179**, 63-71.
- Baena-Moreno F.M., Pastor-Pérez L., Wang Q., Reina T.R., (2020a), Bio-methane and bio-methanol co-production from biogas: A profitability analysis to explore new sustainable chemical processes, *Journal of Cleaner Production*, **265**, 121909.
- Baena-Moreno F.M., Pastor-Pérez L., Zhang Z., Reina T.R., (2020b), Stepping towards a low-carbon economy. Formic acid from biogas as case of study, *Applied Energy*, **268**, 115033.
- Baena-Moreno F.M., Rodríguez-Galán M., Reina T.R., Zhang Z., Vilches L.F., Navarrete B., (2019a), Understanding the effect of Ca and Mg ions from wastes in the solvent regeneration stage of a biogas upgrading unit, *Science of The Total Environment*, **691**, 93-100.
- Baena-Moreno F.M., Rodríguez-Galán M., Vega F., Reina T.R., Vilches L.F., Navarrete B., (2019b), Converting CO₂ from biogas and MgCl₂ residues into valuable magnesium carbonate: A novel strategy for renewable energy production, *Energy*, **180**, 457-464.
- Baena-Moreno F.M., Vega F., Pastor-Pérez L., Reina T.R., Navarrete B., Zhang Z., (2020c), Novel process for carbon capture and utilization and saline wastes valorization, *Journal of Natural Gas Science and Engineering*, **73**, 103071.
- Goldberg D.S., Takahashi T., Slagle A.L., (2008), Carbon dioxide sequestration in deep-sea basalt, *Proceedings of the National Academy of Sciences*, **105**, 9920-9925.
- Helwani Z., Wiheeb A.D., Kim J., Othman M.R., (2016), In-situ mineralization of carbon dioxide in a coal-fired power plant, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **38**, 606-611.
- Librandi P., Nielsen P., Costa G., Snellings R., Quaghebeur M., Baclocchi R., (2019), Mechanical and environmental properties of carbonated steel slag compacts as a function of mineralogy and CO₂ uptake, *Journal of CO₂ Utilization*, **33**, 201-214.
- Sanna A., Uibu M., Caramanna G., Kuusik R., Maroto-Valer M.M., (2014), A review of mineral carbonation technologies to sequester CO₂, *Chemical Society Reviews*, **43**, 8049-8080.
- Zhang Z., Liu Z., Pan Z., Baena-Moreno F.M., Soltanian M.R., (2020), Effect of porous media and its distribution on methane hydrate formation in the presence of surfactant, *Applied Energy*, **261**, 114373.