Permanent Sequestration of CO_2 in Industrial Wastes/Byproducts

A techno-economic investigation commissioned by the members of the

Carbon Dioxide Capture and Conversion (CO_2CC) Program

Report Completed: September 2021

TCGR The Catalyst Group Resources™
Vision > Intelligence > Impact

INTRODUCTION

- Fossil fuels are an essential source of energy accounting for approximately 80-85% of the global energy consumption, and they are projected to remain the main source of energy worldwide for the coming decades.
- CO_2 is an important constituent of our atmosphere and is believed to have the greatest adverse impact on the observed greenhouse effect causing approximately 55% of global warming, and the rise in the average earth surface temperature is known to correlate well with the amount of CO_2 in the atmosphere.
- CO_2 can be utilized and converted into valuable products or used in mitigating different kinds of solid wastes.
- Reducing the harmful effects of CO_2 emissions can be achieved through improving the current combustion technologies and by developing novel effective technologies that can utilize CO_2 as a valuable commodity rather than harmful emissions.

Urgent solutions are required to combat the ever-increasing CO_2 emissions. Carbon Capture and Storage or Sequestration (CCS) technologies are proposed as tools with a paramount importance to mitigate CO_2 emissions

SCOPE

- Permanent sequestration of CO_2 through mineral carbonation (MC) is a process that involves the reaction of CO_2 with alkaline compounds such as calcium and magnesium oxides and has the potential to sequester considerable amounts of CO_2 with a capacity that can be scaled to match the amount of CO_2 emissions released from several industries.
- MC is one of the most sustainable approaches for CO_2 sequestration. It ensures leakage-free fixation of carbon dioxide and generates valuable products such as calcium and magnesium carbonates, which can be utilized in different applications, such as adsorbent materials and cement additives.
- This techno-economic report investigates CCS and MC with unprecedented depth and detail. After a comprehensive Introductory **first chapter**, **chapter two** discusses the fundamental principles of mineral carbonation starting from natural processes to engineering systems. The chapter also lays the foundation for all the different mineral carbonation techniques that reader will encounter in the following chapters.
- The **third chapter** introduces the use of industrial wastes/byproducts as a viable and effective feedstock for the mineral carbonation process. Parameters affecting the carbonation process are rigorously examined to form the basis of the technical discussion in the following chapter.
- **Chapter four** is the major chapter in the report as it includes detailed techno-economic analyses of numerous carbonation techniques that a utilize variety of industrial wastes in terms of their technical performance, economic feasibility, and life cycle.
- The **report concludes** with a presentation and discussion of current and potential industrial applications of CO_2 sequestration using solid wastes.

MINERAL CARBONATION

The Mineral Carbonation (MC) technique has the potential to sequester CO_2 through the process of natural weathering or by accelerated carbonation. MC has a CO_2 sequestration capacity that can be scaled to match the amount of CO_2 emissions released from several industries. In addition, MC is considered the only permanent CO_2 sequestration technique. All these factors combined make MC an attractive option for CO_2 sequestration.

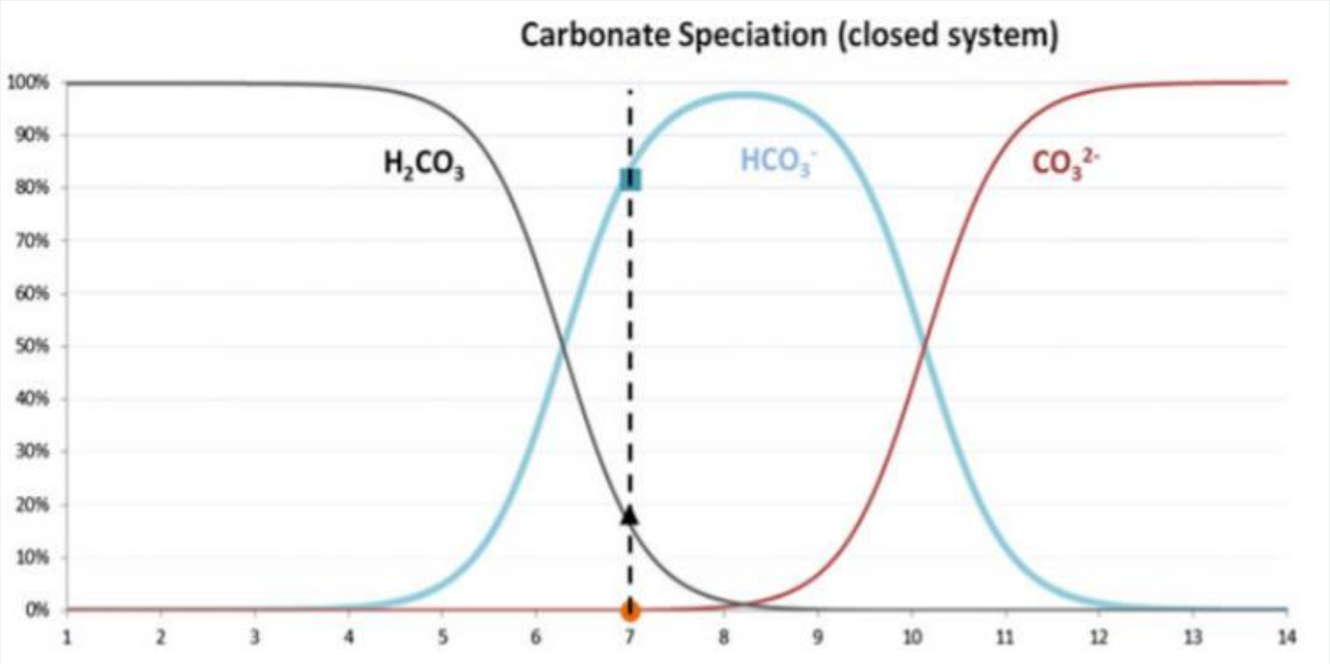


Figure 1. Bjerrum plot of carbonate speciation versus pH in aqueous solution (Kawi, 2019).

This report discusses in detail the difference between various MC routes and their implications. It also includes an extensive explanation of the chemistry, thermodynamics and kinetics involved in the mineral carbonation process.

MINERAL CARBONATION

EX-SITU MINERAL CARBONATION MECHANISM

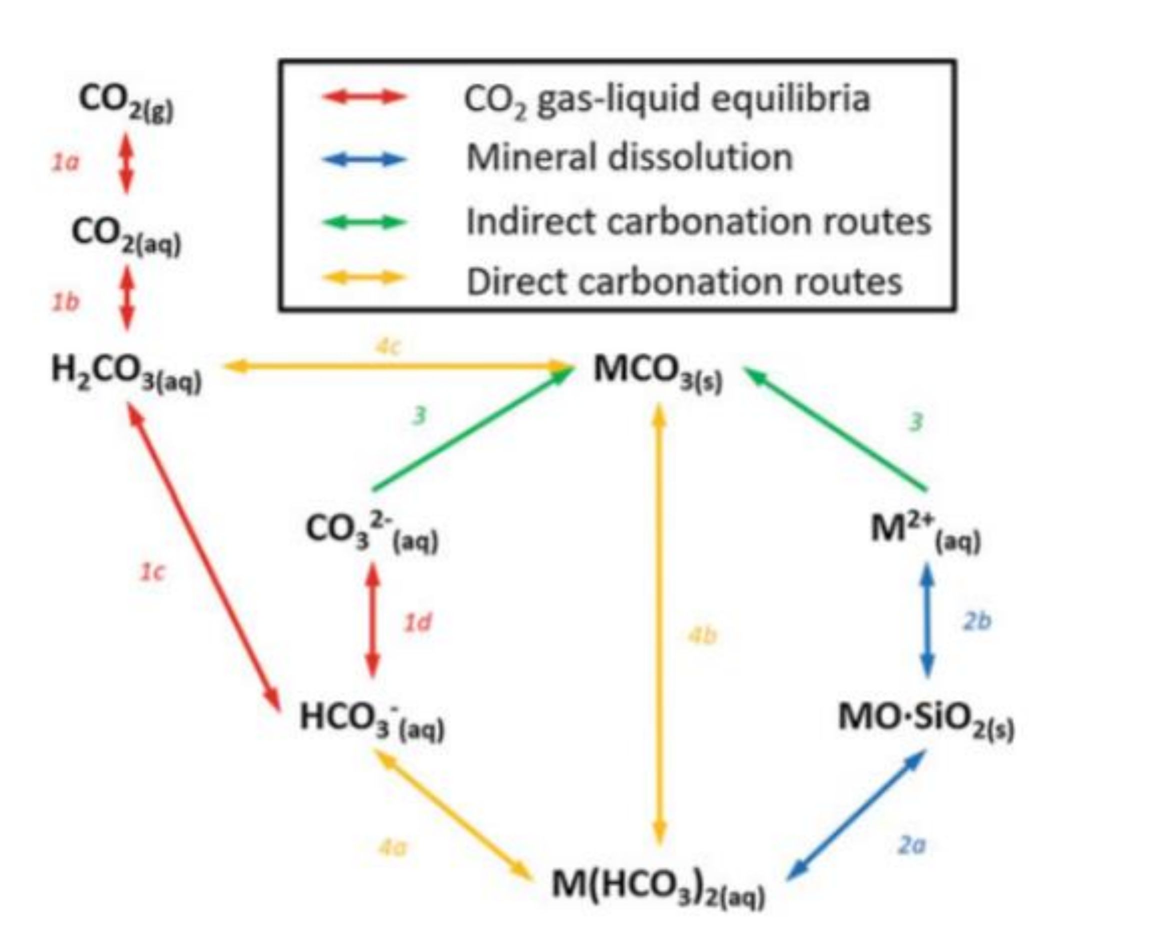


Figure 2. Reaction pathways of different carbon species (Kawi, 2019).

- There is a common misconception that carbon dioxide can be a difficult molecule to utilize in different chemical processes. This is not true. CO_2 has the ability to participate in different arrays of chemical reactions. Most notably, CO_2 can lead to the gradual erosion of calcium and magnesium silicates through a simple chemical reaction.
- It is worth noting that since the carbonic acid is a weak acid, the deprotonation process can take up considerable time and happen over a prolonged pH range (4-12) (strong acid deprotonation happens noticeably quickly and over a narrower pH range). The slow deprotonation results in the coexistence of several inorganic carbon species within the solution.
- Although the reaction between CO_2 and alkali-earth metal rocks happens spontaneously in the environment, the reaction rate is considerably slow and does not match the rate of industrial CO_2 emissions. These unmatched rates between release and sequestration lead to the accumulation of CO_2 emissions in the atmosphere causing global warming.

MINERAL CARBONATION

Recent Literature Survey

- The recent publications on industrial waste were surveyed using SCOPUS search engine. Figure 3 shows that 703 papers were published on the topic of mineral carbonation from 2016 to 2021. Out of the 703 published, 130 focused on industrial waste carbonation.
- The Figure also confirms the increasing interest of the scientific community in the field of mineral carbonation and industrial waste carbonation. Despite this increasing interest, there is still a limited amount of work on life cycle assessments (LCA) and technoeconomic evaluation of industrial waste carbonation.

Conclusions & Remaining Hurdles

- Carbon sequestration can be carried out through numerous techniques that can possibly sequester large amounts of carbon dioxide which can greatly mitigate the harmful impacts of CO_2. The mineral carbonation process has the potential to capture considerable amounts of CO_2 and then to turn it into useful commodities.
- An optimization approach for all the different intricacies in the MC process is a key to achieve the best CO_2 uptake and eventually the optimum sequestration conditions. Reaching the optimum operating conditions for each feedstock is the main challenge facing the MC process.
- Studying the reaction mechanism of different wastes and the interplay between CO_2 the alkaline components will provide more insights on how to increase the amount of CO_2 sequestered per mass of used waste.

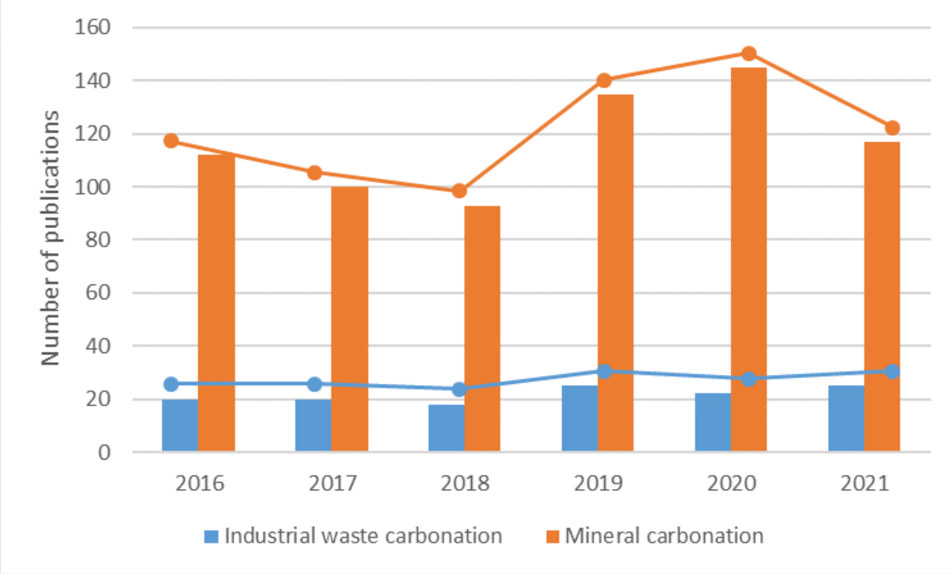


Figure 3. Recent publications on industrial waste carbonation against total publications on mineral carbonation generated from SCOPUS.

INDUSTRIAL WASTES/BYPRODUCTS

Sources of Different Feedstocks

Several industries produce wastes or byproducts that can be used as a suitable feedstock for the MC process. These wastes include steel dusts and slags, cement and construction materials waste, red mud, and coal and fly ash. Although these wastes are generated from several industries involving different processes, they share numerous inherent features such as:

- Rich alkali-earth metal content
- The need to stabilize the waste
- The manufacturing process produces considerable amounts of CO_2

These wastes consist of mixtures of many elements that are often present in different phases such as calcium, iron, silicon, aluminum, and magnesium oxides. Figure 4 shows the composition range of these wastes with their annual production.

Sequestration Potential and Regional Availability

Out of this total emission reduction, 43.5% of the reduction is attributed to the use of steelmaking industrial wastes followed by cement waste and mining waste representing 13.5% each. Fly ashes generated from the coal industry had the lowest contribution with 12.3%.

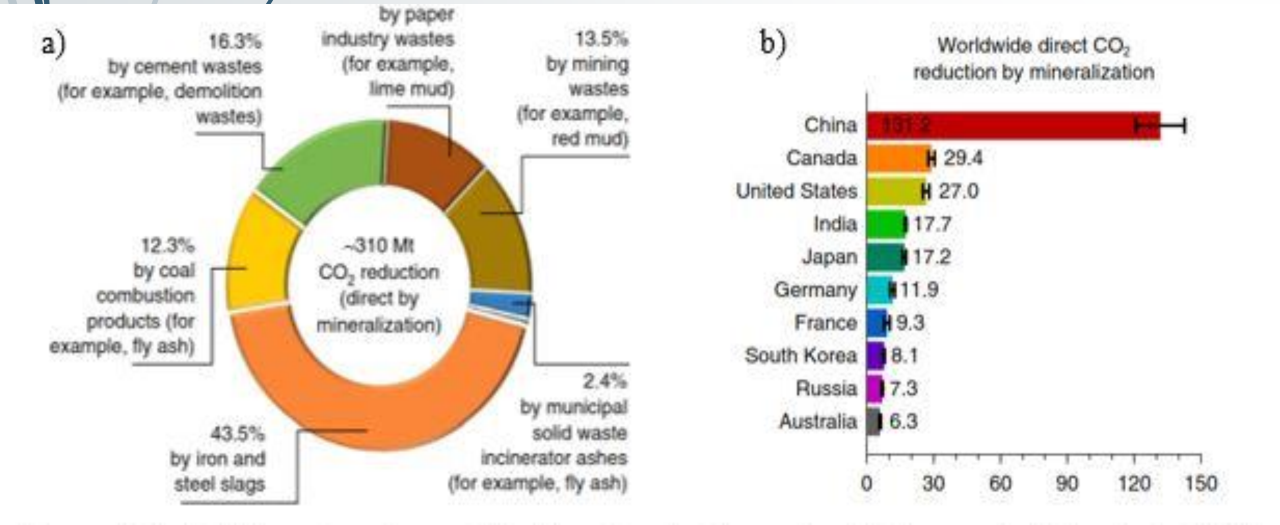


Figure 4. a) different wastes) combination **b) r**eduction potential by county (Pan et al., 2020)

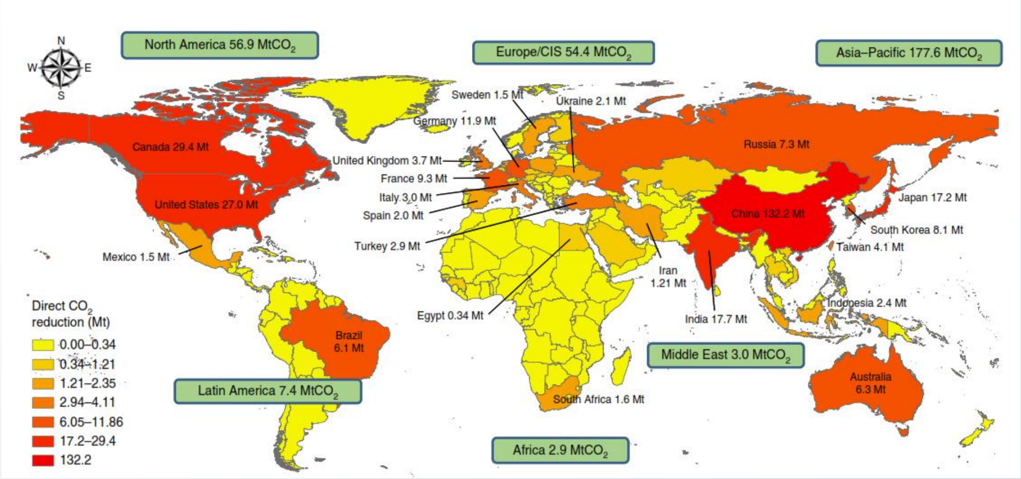


Figure 5. Estimates of the regional CO_2 reduction potential using industrial alkaline waste (Pan et al., 2020)

INDUSTRIAL WASTE AS A FEEDSTOCK

The steel industry produces different types of wastes that can be used as a feedstock for the MC process due to their high alkalinity. Each waste is named after the stage at which it is generated. Producing one ton of steel generates, on average, 250 kg of alkaline waste. These include:

Steel Slag - Solid waste/byproduct that is generated from the steel-making process. There are different oxides that can exist in the slag, but it mainly includes between 30 to 60% calcium and magnesium oxides and the balance can be a mixture of iron oxide (Fe_2O_3), silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3)

Blast Furnace Slag – Iron and steel can be generated by the blending of slagging agents with the different impurities that are produced during different stages of steel manufacturing. Blast furnace slag (BFS) is one of the major solid byproducts that are generated in the steel manufacturing process.

Basic Oxygen and Electric Arc Furnace Slag - Generated in their respective furnaces during the steelmaking process; these furnaces are the most widely used processes for steel manufacturing.

Ladle Furnace Slag - Generated in the last phase of the steel-making process, which is known as the secondary metallurgy process where the produced steel is desulfurized in the transport ladle.

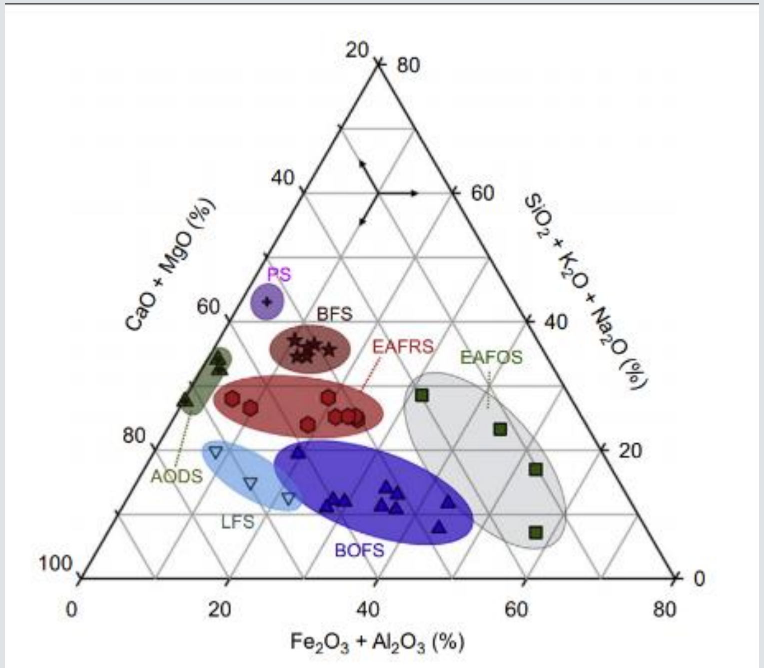


Figure 6. Tertiary diagram showing the composition of different industrial wastes (Yildirim and Prezzi, 2011).

INDUSTRIAL WASTE AS A FEEDSTOCK

Lab-Scale Application - The applicability of mineral carbonation on steel slags for both direct and indirect routes is primarily dependent on its mineral extraction efficiency, mineral carbonation efficiency and CO_2 loading capacity (uptake) of the carbonation process. These factors are in turn affected by various operating parameters, such as particle size, temperature and pressure, liquid to solid ratio, reaction time as well as the reagents used for extraction or carbonation. Over the last few years, a considerable number of studies have been conducted in lab-scale with the aim to elucidate the effects of the aforementioned factors on the steel slag carbonation process.

Red Mud: Availability and Composition - Red mud is a solid waste that is often generated during the processing of bauxite into aluminum. The global reserves of bauxite, which is a sedimentary rock with very high aluminum content, are estimated to be around 55-75 billion tons. The distribution of these reserves is the following: 32% in Africa, 23% in Oceania, 21% in South America and the Caribbean, 18% in Asia and 6% are disturbed in other locations. Approximately 90% of these reserves are in tropical and sub-tropical regions.

Paper Mill Waste: Lab-Scale Implementation - A different route for utilizing LM in CO_2 sequestration is to use it as a feed for the calcium looping process. Calcium looping involves capturing CO_2 by calcium oxide from LM. Li et al. (2012) investigated the use of LM to sequester CO_2 and SO_2 in a calcium looping process. In order to remove the different impurities from LM, it was washed using distilled water. This wash was found to enhance the CO_2 sequestration capacity over the long run. The prewashed LM was found to have 1.8 higher uptake capacity than the unwashed LM and 4.8 times higher than that of the conventional limestone.

INDUSTRIAL WASTE AS A FEEDSTOCK

Cement Kiln Dust: Lab-Scale Implementation

Huntzinger et al. (2009) carried out a series of column experiments on several extracted segments of a landfilled CKD from a real landfill site. Experimental parameters such CO_2 gas flowrate and water content in the samples have been varied to test the effect of each parameter. A flowrate range between 45 to 61 mL/min and CO_2 concentration range of 35,600 to 84,900 ppm were used. The authors observed that the efficiency was higher in columns that have lower water content.

In a different work, the same authors studied the carbonation of CKD by carrying out batch experiments. The overall carbonation efficiency was 60% that was achieved after 8 hours. The authors revealed that the reaction followed the shrinking core model, and it was controlled by the diffusion rate.

Fly Ash: Lab-Scale Implementation and Utilization

Dananjayan and co-workers (2016) applied both the dry and wet routes in their investigation of mineral carbonation of coal fly ash. The carbonation capabilities of fly ash samples increased with an increase in CO_2 pressure and within 1 hour of the experimental time, CO_2 uptake of the fly ash samples increased from 5 kg to 26 kg CO_2 per ton of fly ash at pressure of 2 and 10 bars, respectively. While studying the effect of reaction time, they reported that the sequestration capabilities of the fly ash rapidly increased and stabilized after an hour of reaction beyond which no change in CO_2 uptake was observed. They suggested that the observed stabilization in CO_2 uptake capacities of fly ash samples was primarily due to passivation.

Fly ashes are commonly utilized in the production of materials for construction sector which include materials for cement clinkers, waste stabilization, waste solidification, supplementary cementitious materials and as a geopolyme.

INDUSTRIAL WASTE AS A FEEDSTOCK

Availability and Composition of Concrete/Building Material

The cement industry contributes approximately 7% of the overall CO_2 emissions worldwide. The waste concrete generated throughout the manufacturing process can be used as a suitable feed for the MC process due to its large availability and high alkalinity due to the presence of calcium hydroxides.

There can be different types of concretes based on the composition, preparation method, and hydration reaction.

In general, concrete approximately consists of 70% aggregates and 30% hydrated cement in addition to chemically inactive stones and sands. Hydrated cement contains several alkaline chemicals, such calcium hydroxide and calcium silicates in additions to other minerals.

Due to the high alkalinity of these wastes, a proper disposal method or utilization method is required. This makes MC one of the most suitable management techniques to address the concrete wastes.

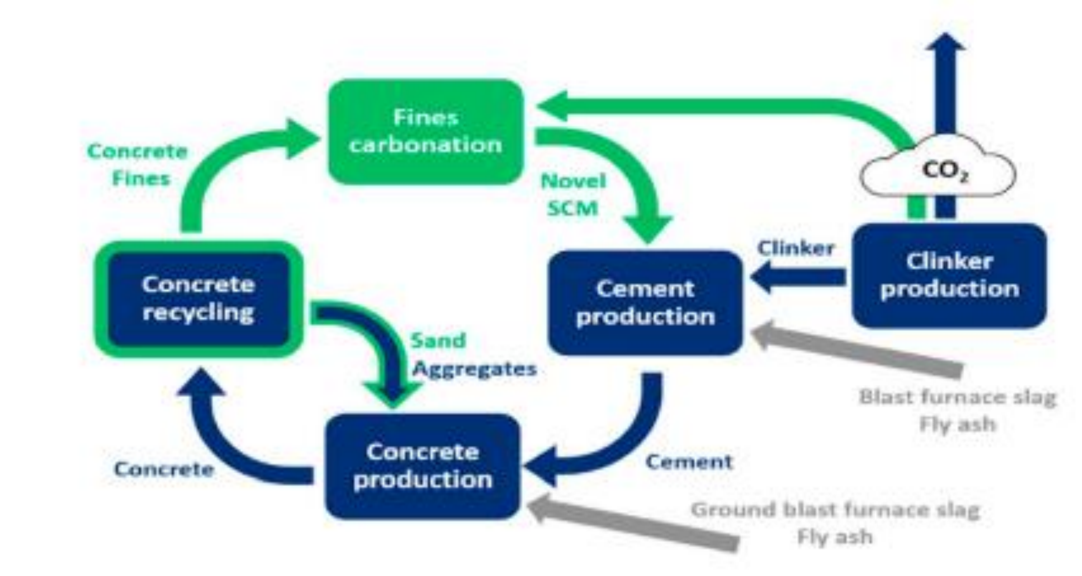


Figure 7. A schematic diagram for the proposed cement manufacturing utilizing aqueous MC (Skocek et al., 2020).

INDUSTRIAL WASTE AS A FEEDSTOCK

Mine Tailing: Nickel Tailings

Over the last few years, there has been increasing interest in studying the tailings generated during the extraction of Nickel from ores. Nickel tailings typically contain very high concentrations of magnesium oxides (≤ 40 wt%) along with other alkaline oxides.

Canada is on one of the top five producers of Nickel around the world with good number of active mining projects. The Dumont Nickel Project (DNP) is one of them and it is considered to the one of largest nickel sulfide producer of the world. The mining operations, during the lifetime of the project, are expected to generate around 1.2 billion metric tons of brucite rock tailings along with 514 million metric tons of ultramafic waste rocks.

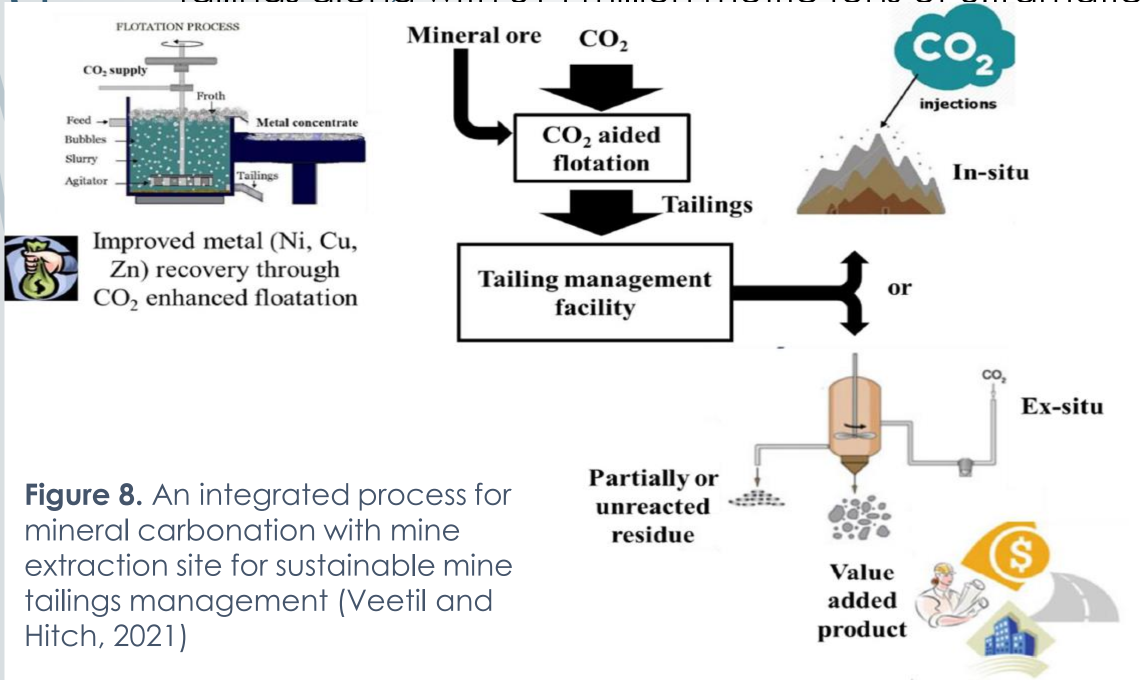


Figure 8. An integrated process for mineral carbonation with mine extraction site for sustainable mine tailings management (Veetil and Hitch, 2021)

Several studies have investigated the techno-economics of mineral carbonation of mine tailings in Canada. Veetil and Hitch (2021) performed a techno-economic assessment on the application of mechanical activation step in an integrated process for mine tailings carbonation. The mining tailings were obtained from the drill core at the Turmagain project, Hard Creek Nickel, Canada. Their study showed inclusion of a mechanical activation step increased the carbonation efficiency of the process by 60%, increasing the potential CO_2 capture capacity of the process which translated to around 14.6 million tons of CO_2 per year during the 28 years lifetime of the project. They further noted that the operating cost of the process was $107 per ton of mine wastes, which was reduced to $104 when mine tailings were used instead.

CURRENT & POTENTIAL INDUSTRIAL APPLICATIONS OF MC PROCESSES

Several carbon capture technologies have reached different levels of maturity and industrial implementation. Figure 9 illustrates the maturity of each carbon technology and their current level of industrial implementation. The figure shows that there are several technologies that have been deployed on a large industrial scale and others that are still in the research stage.

Cement Industrial Waste - Cement industries have attempted to capture CO_2 that is released from the process and reuse it or react it with the generated waste throughout the entire process. These uses include curing and manufacture and modification of cementitious construction materials. Some of the technologies have been commercialized.

Steel Industrial Waste - The research group "Energy Engineering and Environmental Protection" at Aalto University in Finland designed, constructed, and evaluated the world's first MC pilot plant to produce calcium carbonates by reacting the slag with CO_2. The plant can operate in batch or continuous mode. In batch mode, the pilot plant has a capacity of 20 kg of steelmaking slag ($\leqslant$250 μm) and 190 liters of the extraction agents. At these capacities, the pilot can produce 10 kg of $CaCO_3$. The extraction agent (ammonium salt solvents) can be regenerated to be used again to extract the calcium from the slag helping in reducing the overall cost of the process.

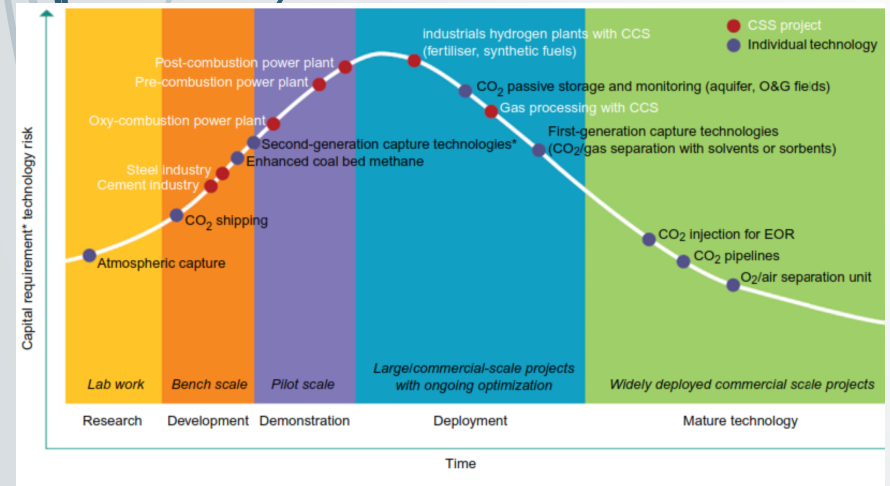


Figure 9. Maturity of several carbon capture technologies and their deployment level 1 (Bennaceur, 2014).

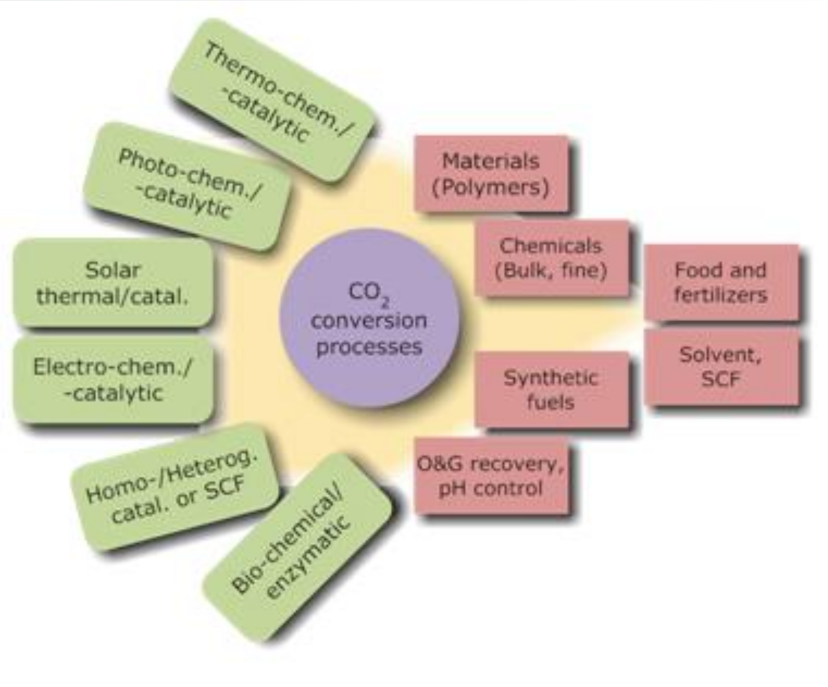
Other Industrial Large-scale Implementations - Phosphogypsum (PG) is as an industrial waste that is generated from wet processing of phosphoric acid manufacturing. China is the largest producer of PG with an annual production of 5×10^7 tons, yet only 15% of this waste is used in other applications, such as cement or brick manufacturing. This leaves huge quantities of PG unutilized without a suitable disposal method which can lead to numerous environmental hazards especially for nearby water bodies.

Remaining Hurdles and Future Perspectives - The area of industrial waste mineral carbonation is rapidly evolving and expanding in different directions depending on the type of the waste and the process, but only in lab or bench scale. Major industrial wastes emitting industries, such as steel and cement manufacturing, have yet to get seriously involved in MC efforts at a large scale, as this can be seen in the low number of industrial and pilot scale MC implementation using the wastes. Nonetheless, utilizing various types of wastes can offer an attractive route for the problematic waste disposal and at the same time mitigate CO_2 emissions and produce value added products.

CONCLUSIONS & OUTLOOK

- Life cycle assessment of steel slag in the US showed that it can sequester 7.5 million tons of CO_2 annually of which 7 million tons are from direct CO_2 capture from the mineralization process and 0.5 million tons from the avoided emissions by using the MC products.
- Although studies on life cycle assessments (LCA) of solid waste utilization are rather limited and often restricted to case studies on a specific waste, all assessments seem to confirm the economic feasibility and profitability of utilizing solid wastes for MC.
- Despite the growing interest in MC, most recent studies are still in the bench scale stage and only a few studies have evaluated industrial demonstration units of MC process using industrial wastes.
  - This could be attributed to the limited research funding for pilot scale applications as well as lack of regulatory policies for the application of the solid products.
  - It could also be attributed to the fact that experts often discuss carbon capture and sequestration in terms of geological storage, which pushes CO_2 mineralization to the margins making it less likely to be included in policymaking.
- In general, the main challenges for MC research and development are increasing the CO_2 uptake and decreasing the energy requirements and cost.
- This can be addressed through effective optimization of the process by identifying the most influential parameters that can mainly affect the overall efficiency.
- Hence, taking a holistic approach towards the MC process optimization can be very insightful and set the future direction for MC research.
- In addition, more studies on lifecycle and technoeconomic assessments are needed to pave the way for technically and economically viable large-scale applications.

Carbon Dioxide Capture and Conversion (CO_2CC) Program



The **Carbon Dioxide Capture and Conversion (CO_2CC) Program** is a membership-directed consortium, launched in January 2010, whose members are involved in developing, monitoring and utilizing the "state-of-the-art" in technological progress and commercial implementation of carbon dioxide capture and conversion.

The program's objective is to document and assess technically and commercially viable options for the capture/clean-up/utilization of CO_2 and its mitigation via energy efficiency gains which meaningfully address the challenges posed by CO_2 life-cycle and overall sustainability issues. Included in the program's scope are:

- Global decarbonization efforts towards net zero or negative carbon emissions
- Industrial process technology shifts towards renewable, circular and sustainable practices
- CO_2 capture and/or separation
- CO_2 concentration, purification and/or other post-treatment
- CO_2 utilization/conversion (e.g., CO_2 as a feedstock) for use as a fuel or intermediate, including enhanced oil recovery (EOR)
- Energy requirements (and other costs), including energy efficiency
- Industrial process improvements and energy saving initiatives which mitigate CO_2 production
- Bottom-line financial (income) impacts resulting from CO_2 reduction programs
- Life-cycle considerations and sustainability of CO_2 applications
- GHG/CO_2 regulation and "cap and trade" developments

By the direction of the member companies (through balloting and other interactive means) and operated by TCGR, the program delivers weekly monitoring communications via email (**CO_2CC Communiqués**), three techno-economic reports (highly referenced and peer reviewed) and scheduled meetings of members (either in-person or via webinar). **Access to deliverables is exclusive to members.**

In addition to the program deliverables, TCGR works with members to identify and foster competitive advantage and opportunity. This value-added relationship, along with active participation by the membership, leads to improved (or unique) external R&D and commercial investment possibilities.

Contact & More Information

More information about this and other services of the **CO_2CC Program** can be seen at http://www.catalystgrp.com/php/tcgr_co2cc.php.

Call +1-215-628-4447 or e-mail John Murphy, President jmurphy@catalystgrp.com, and we'll be happy to discuss these and other interesting membership benefits.

www.CatalystGrp.com

The Catalyst Group Resources (TCGR), a member of The Catalyst Group Inc., is dedicated to monitoring and analyzing technical and commercial developments in catalysis as they apply to the global refining, petrochemical, fine/specialty chemical, pharmaceutical, polymer/elastomer and environmental industries.

TCGR The Catalyst Group Resources™

Vision > Intelligence > Impact