U.S. Department of ENERGY


# Carbon Conversion Multi-Year Program Plan

December 2024

# Table of Contents

# 1. Overview

## 1.1 Introduction and Background

The U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) supports investments in research, development, demonstration, and deployment (RDD&D) of carbon management technologies, including point source carbon capture, carbon transport and storage, carbon conversion, and carbon dioxide ($CO_2$) removal. To maximize the probability that these technologies are successful, it is necessary to have an informed, coherent, durable, and actionable Multi-Year Program Plan (MYPP) to move carbon management technologies towards successful commercialization. This document outlines the MYPP for FECM's Carbon Conversion Program.

The Carbon Conversion Program invests in research, development, and demonstration of technologies that convert captured carbon oxides, primarily $CO_2$, into economically valuable products such as chemicals, fuels, building materials, plastics, and bioproducts. These conversion technologies are among a portfolio of approaches required to address climate change. Such pathways play a critical role in accelerating the future decarbonization of our economy, particularly by providing solutions for hard-to-abate sectors. This Program, originally named Carbon Use and Reuse, began in 2012 as a sub-technology area under FECM's Carbon Storage Program. Since then, the Program has expanded the support it is able to provide researchers and industry. Notably, the recent expansion to the program via the Bipartisan Infrastructure Law and its Carbon Utilization Procurement Grants provision (Sec. 40302 Carbon Utilization Program) aims to accelerate the adoption of conversion technologies by making funds available to states, local governments, and public utilities to purchase products derived from converted carbon emissions.

Carbon conversion represents one mechanism to ameliorate rising atmospheric $CO_2$ levels and can be thought of as leveraging recycled anthropogenic $CO_2$ as the carbon feedstock for products that have lower lifecycle greenhouse gas emissions than incumbents. Within the context of FECM's Carbon Conversion Program, "anthropogenic $CO_2$" includes both concentrated $CO_2$ generated through human activity, such as power and industrial operations, as well as legacy emissions already present within the atmosphere, such as those concentrated through technologies such as direct air capture. Technologies supported by the Program fall into three broad categories based on the conversion mechanism:

- **Mineralization pathways** focus on thermodynamically favorable processes where $CO_2$ mineralizes with alkaline reactants to produce inorganic products like bicarbonates, synthetic aggregates, and other building materials.
- **Biological pathways** leverage agriculture, fermentation, and genetic engineering expertise to convert $CO_2$ into products via microorganisms, including algal systems and non-photosynthetic microbes.

- **Catalytic pathways** utilize thermochemical, electrochemical, photochemical, reactive capture, and plasma-assisted (thermal and non-thermal) approaches to transform $CO_2$ into synthetic fuels, chemicals and products.

The MYPP will detail the status, challenges, and future goals for the three pathways described above and will describe how these technologies align the Carbon Conversion Program with higher level DOE goals.

## 1.2 Alignment with DOE and FECM

The Biden Administration has set ambitious goals to ensure that America and the world can meet the urgent demands of climate change. Central to these goals is achieving "*a carbon pollution-free power sector by 2035 and … a net-zero economy by 2050.*"[1] Because the U.S. power generation, manufacturing, agricultural, chemical, and transportation sectors are heavily dependent on fossil fuels and $CO_2$-intensive industrial processes, achieving net-zero carbon emissions will require advancements in novel clean energy and industrial technologies, including carbon management technologies.

The FECM Strategic Vision serves as the foundational document for this MYPP and defines the Vision Statement for the Carbon Conversion Program: "*Research, develop, and demonstrate a broad suite of technologies that convert $CO_2$ into environmentally responsible, equitable, and economically valuable products, and enable low-carbon supply chains to meet the goal of a decarbonized economy by 2050.*" The Strategic Vision outlines the path to realizing this vision statement through program goals (near-, mid-, and long-term), stakeholder and policy engagement, and a high-level description of technical strategy.

In support of the vision for a net-zero economy, the Carbon Conversion Program is a key participant in the DOE's Energy Earthshots Initiative. Specifically, the Clean Fuels & Products Shot aims to meet projected fuel demands in 2050, including 100% of aviation fuel; 50% of maritime, rail, and off-road fuel; and 50% of carbon-based chemicals by using sustainable carbon resources, such as captured $CO_2$. Efficient carbon conversion will be a critical component of meeting these goals, especially for hard-to-decarbonize sectors. Carbon conversion technologies also play a role in supporting the Carbon Negative Shot, which calls for innovation in $CO_2$ removal pathways that will capture $CO_2$ from the atmosphere and store it at gigaton scales for less than $100/net metric ton of $CO_2$-equivalent.

Carbon conversion is also a key use case highlighted in the DOE Carbon Management Strategy, which identified four primary use cases for carbon management technologies: carbon removal, industrial decarbonization, sustainable fuels and products, and grid decarbonization; both sustainable fuels and products and industrial decarbonization directly tie into goals for the carbon conversion program, for example by applying carbon capture to ethanol and similar biofuel production processes and using captured $CO_2$ as a potential feedstock to make fuels. The DOE Industrial Decarbonization Roadmap also identifies a similar role for conversion technologies and the use of $CO_2$ as a chemical feedstock.

[1] E.O. 14057: "Catalyzing America's Clean Energy Economy Through Federal Sustainability." FACT SHEET: President Biden Signs Executive Order Catalyzing America's Clean Energy Economy Through Federal Sustainability | The White House

Consistent with the FECM Strategic Vision, the Carbon Conversion Program MYPP describes goals within each technology pathway (Biological, Mineralization, and Catalytic) and differentiates between goals that are near-term (less than five years), mid-term (five to ten years), and long-term (more than ten years). Section 1 of the MYPP will detail overall goals and strategy for the Program. Section 2 will present a Technical Plan that describes the key technologies for each pathway that need to be developed and the challenges that must be overcome. Section 2 will also present several pathway-specific programmatic goals for advancing the technology for eventual deployment. In summary, the MYPP aims to serve as the tactical plan for the Carbon Conversion Program and provide guidance to ensure that Program activities are aligned with the FECM Strategic Vision and the overall objective of a decarbonized economy by 2050.

## 1.3 Overarching Goals and Strategy

Commercial viability is an essential part of technology deployment, and novel products or pathways seeking to displace incumbents must be improved and de-risked to a reasonable degree to compete with existing technologies. Thus, **the overarching goal of the Carbon Conversion Program is to identify, support, and demonstrate carbon conversion technologies that yield products which are cost-competitive and more sustainable than incumbents.** Identifying suitable technologies for RD&D investment requires integration of life cycle analysis (LCA) and techno-economic analysis (TEA) to ensure that technologies have both 1) a lower carbon intensity and 2) an accurate assessment of their real-world cost and performance. Additionally, an understanding of what types of RD&D can be conducted in a reasonable timeline and budget is essential to designing an RD&D program. Finally, moving high-potential technologies from conceptual design to actual deployment requires execution in the development of funding opportunities, management of awarded projects, and reporting/integration of project results to inform future program decisions.

**Goal #1: Research, develop, and demonstrate a broad suite of technologies that convert $CO_2$ into economically valuable and environmentally responsible products, which will provide mitigation solutions for sectors of the economy that are otherwise difficult to decarbonize.**

Given the uncertainties surrounding technology development and the future energy and market landscape of the United States, it is necessary to explore numerous conversion technologies that could be successful under a wide range of scenarios. Uncertainties in the future availability of resources such as clean hydrogen, low carbon electricity, or water would directly impact the viability of certain conversion pathways. Thus, it is important to build a diverse RD&D portfolio that covers multiple routes for converting $CO_2$ across the technology readiness scale. These technologies, which are described in more detail later in the document, will enable low-carbon solutions for sectors of the economy that cannot easily shift away from using carbon, such as chemicals, building materials, and fuels for the heavy-duty transportation sector.

**Goal #2: Create publicly available TEA and LCA tools to accurately inform stakeholders of the state-of-the-art and create verifiable carbon accounting foundations to support technology development and policy formation.**

The advancement of novel technologies requires the best possible and most realistic understanding of the process being proposed and the impact it has on people and the environment. TEA and LCA are the leading mechanisms to gain such insight into cutting edge processes. Such analyses can provide a thoughtful evaluation of the scientific and economic feasibility of carbon conversion pathways, as well as the carbon intensity of the products generated from them. An understanding of these parameters is important for building an effective RD&D portfolio and providing the public and policymakers with the information needed to make decisions.

Creating open TEA and LCA tools increases familiarity with the impact of carbon conversion, its limitations, and its uses across the economy. The Carbon Conversion Program is committed to enabling such tools and supporting a community-wide model for LCA. It is of specific interest to the Program to increase the probability that such a model will be utilized correctly and enable confidence and stability in the private sector to incorporate LCA data into their decision-making. For example, the Conversion Program has worked closely with NETL in supporting LCA reviews for the 45Q tax credit for utilization and promoting tools developed for the Carbon Utilization Procurement Grants (UPGrants) program to bolster and consolidate LCA support for both incentive programs. Such efforts align with guidance from the Council on Environmental Quality on the need for collaboration as carbon management technologies advance (see Federal Register: Carbon Capture, Utilization, and Sequestration Guidance.) These tools are critical in highlighting the benefits of, and driving investment in, technology supported under the Carbon Conversion Program.

**Goal #3: Accelerate the deployment of large-scale conversion of CO2-derived fuels, chemicals, and products that help achieve net-zero emissions and provide economic and environmental benefits to communities.**

The adoption of novel technologies is often slow, especially those that operate in sectors of the economy that have established incumbents. In addition, the time to commercial deployment increases with the complexity of the production pathway and the risks associated with new product performance. Large-scale carbon conversion will require the capacity to cost-effectively produce commodity products from a novel feedstock ($CO_2$), making deployment a serious challenge.

Mature carbon conversion technologies will require piloting and demonstration activities to establish their commercial potential and demonstrate that their production does not cause adverse effects to local communities or consumers. Activities such as longer campaigns to validate the durability and robustness of novel unit operations, as well as product performance testing for safety and standards development, are required in several markets that are key targets for the Carbon Conversion Program. This includes advancing mineral carbonation for building materials, finding ways to accelerate the pathway to net-zero chemical refineries, and developing $CO_2$-based synthetic fuel solutions for aviation and heavy-duty transportation. For technologies and products that are further along toward commercialization, the Program established the BIL-funded UPGrants program, which makes $100M available via a 50% cost share for eligible entities to purchase products derived from carbon utilization. The program aims to alleviate cost barriers which may hinder early adopters and manufacturers and enable products and manufacturers to better establish a successful track record of use, especially in the public procurement space.

**Goal #4: Engage with industry, academia, policymakers, and communities to facilitate the efficient and equitable adoption of effective carbon conversion technologies.**

Decarbonization of the chemicals, fuels, and materials sectors of the economy will require the research, development, and deployment of novel technologies across the country. The infrastructure associated with this emerging industry can not only mitigate carbon emissions but also facilitate significant economic development. Meaningful public involvement is a necessity to ensure such technology deployment is not just effective and efficient but also beneficial to local communities.

Increasing public understanding of the complex tradeoffs between different conversion technologies is also of interest. The Program will support public engagement activities, such as public meetings and workshops. In addition, the Program will help develop user-friendly tools for exploring various technology pathways so that interested stakeholders and decisionmakers can understand the cost and benefits and what support is still needed for commercial deployment.

# 2 Technical Plan

There are several challenges that are common across technologies in the Carbon Conversion portfolio. While some are not specific technological challenges, they involve critical enabling technologies and resources, such as availability of decarbonized electricity. These are essential considerations when developing and executing an effective research and development strategy. Specific RD&D challenges that are of interest to the Carbon Conversion Division are discussed under each highlighted conversion pathway.

## 2.1 Introduction

As the U.S. seeks to transition to a decarbonized, net-zero economy by 2050, carbon conversion and carbon-based products will serve as an important bridge to producing a range of products with lower carbon emissions. Products derived from $CO_2$ also offer opportunities to store carbon for long timescales in durable products (i.e., cement and concrete). Carbon conversion and utilization may play an especially critical role in "hard-to-decarbonize sectors," such as long-haul aviation and chemicals, which are heavily reliant on hydrocarbon feedstocks and not suitable for other decarbonization strategies, like electrification.

While carbon conversion can support a broad swath of products and sectors, some challenges are common across technologies. Products and processes that rely on $CO_2$ are subject to the availability of suitable $CO_2$ feedstocks (either transported or on-site emissions). Currently, few carbon utilization technologies are capable of using all emissions generated from a large, industrial emitter, necessitating additional storage options. Many carbon conversion technologies are currently energy intensive and rely on a decarbonizing grid to maximize emissions reductions. Some challenges, like the uncertainty in scaling and commercialization of earlier stage technologies, can be addressed through integrated pilot and demonstration facilities to derisk the technology. Others are heavily dependent on buildout of supporting infrastructure, such as $CO_2$ transport. Below is a summary of several challenges that affect most $CO_2$ conversion pathways.

### 2.1.1 Availability of $CO_2$ feedstock

Today, there are several point sources of $CO_2$ that are suitable for conversion; however, most conversion strategies require those $CO_2$ streams to be cleaned up, concentrated, and transported at an acceptable cost relative to where conversion will take place. Significant progress has been made into making point source carbon capture and transportation a reality, and the FECM Point Source Capture (PSC) and Carbon Transport and Storage programs tackle these challenges. Technologies for carbon capture exist today, and thus there are economically viable routes to obtaining $CO_2$ feedstock. $CO_2$ may also be sourced from direct air capture facilities. While both point source and direct air capture are seeing robust commercial interest today, they are still only minimally present in our economy and their further deployment will be crucial to making $CO_2$ conversion a reality.

The Carbon Conversion Program will continue to analyze $CO_2$ availability to better inform future opportunities. This will include working across FECM's portfolio of carbon management technologies to address challenges such as $CO_2$ capture and transportation, purity, flexible operation of capture systems, and integrating capture and conversion research, development, and demonstration.

### 2.1.2 Long-term low-carbon electricity availability and cost

Many carbon conversion technologies require a significant amount of decarbonized electricity to meet the ambitious lifecycle greenhouse gas emissions targets required for inclusion in decarbonization strategies. This includes routes that directly use electricity to catalyze $CO_2$ conversion, such as electrocatalysis, as well as pathways that indirectly rely on electricity to supply the required hydrogen ($H_2$) or heat needed to perform $CO_2$ reduction. The cost of renewable or otherwise low-carbon electricity is consistently shown to be the key technoeconomic driver of different $CO_2$ conversion pathways. Thus, the continued buildout of low-carbon energy technologies is critical to supporting the widespread deployment of carbon conversion technologies.

### 2.1.3 Competitive marketplace for carbon-based products

Carbon conversion can support the manufacture of a variety of products including chemicals and fuels, important intermediary chemicals such as methanol, and consumer products such as building and construction materials (see Figure 1 for a summary of products produced from $CO_2$). Sectors such as fuels and chemicals often rely on high volumes of low-profit-margin materials and require large scales of production to be economic. This can pose a challenge for emerging carbon utilization products, as they must compete with heavily cost-driven sectors and may incur additional upfront costs such as new supply chains or infrastructure investments needed to use $CO_2$ feedstocks. Such products must also have certainty of demand to support any upfront investment needed. The markets for building materials and construction materials are among the most developed; however, performance testing and standards development is critical for wider adoption as it allows for new materials to meet performance and safety standards set for incumbent products.

**Figure 1:** Summary of carbon conversion products, estimated market size, and $CO_2$ consumption

| $0.5 – $2 trillion / year opportunity | 2 – 8 Gigatons of $CO_2$ / year | |
|---|---|---|
| | Annual Market Opportunity (Billion USD) | Annual $CO_2$ Comsumption (Million Tons) |
| **Construction Materials**<br>Concrete, aggregates | 165 – 550 | 900 – 5000 |
| **Fuels**<br>Natural gas replacement, gasoline, diesel fuel, jet fuel | 10 – 250 | 700 – 2100 |
| **Chemicals**<br>Solvents, detergents | 200 – 750 | 135 – 565 |
| **Engineered Materials**<br>Carbon fiber, carbon nanotubes, graphene, carbon ceramics | 140 – 400 | 30 – 84 |
| **Polymers**<br>Plastic foils, containers, furniture, plastic housings, toys | 2 – 25 | 1 – 20 |
| **Agriculture and Food**<br>Fertilizer, protein for human consumption, animal feed | >25 | >40 |

National Academies of Sciences, Engineering, and Medicine. 2023. Carbon Dioxide Utilization Markets and Infrastructure: Status and Opportunities: A First Report. Washington, DC: The National Academies Press. https://doi.org/10.17226/26703.

Conversely, $CO_2$ products may also be viable in niche, high value markets with smaller scales of production. Some startups are also adopting this strategy, beginning with high-margin, low-volume products. This may also allow emerging conversion technologies to establish a track record that may then be capable of expanding into high-volume, low-margin industrial and commodities sectors. The Carbon Conversion program aims to support intermediate processes and products that can then support a wide range of final products, as well as understanding needs in performance testing and scaling that are critical for market adoption.

## 2.2 Mineralization

### 2.2.1 Overview

Mineral carbonation technologies for $CO_2$ conversion rely on the naturally occurring mineralization reaction, where atmospheric $CO_2$ dissolved in rainwater reacts with alkaline earth minerals, such as calcium or magnesium silicates, to form stable carbonate rocks. This natural carbonation reaction is often termed "natural rock weathering" and contributes to the historical removal of $CO_2$ from the atmosphere over geological time scales with relatively slow reaction kinetics. Mineralization technologies can be distinguished between in-situ and ex-situ carbonation. In-situ carbonation describes the purposeful injection of $CO_2$ in silicate-rich geologic formations and the subsequent conversion of that rock into carbonates. Ex-situ carbonation describes the exposure of a pretreated feedstock or waste stream to a captured $CO_2$ source. In this process, $CO_2$ mineralizes with alkaline reactants to produce inorganic materials, such as aggregates, bicarbonates, and associated inorganic chemicals. These carbonate materials provide both an effective long-term storage option for $CO_2$ as well as the foundation for the manufacture of high-value products that can be used in various industries such as construction and chemical manufacturing. Understanding the technical hurdles to producing these products in a cost-effective and sustainable manner is of significant importance to the Carbon Conversion Program.

Beyond the technical aspects of mineralization, clear regulations and standards for $CO_2$-derived building materials are necessary to ensure safety and performance. This concern includes building codes, environmental regulations, and sustainability certifications. In addition, education is vital to ensure that the general public and those that procure such products are aware of the environmental and carbon removal benefits of $CO_2$ mineralization. To this end, the Carbon Conversion Program also recognizes and explores the regulatory framework and market demand for building materials made from $CO_2$.

*Carbonation of traditional cementitious materials for development of sustainable concrete*

Concrete materials offer a particularly attractive opportunity for $CO_2$ utilization, and incorporating $CO_2$ into concrete can occur via a variety of mechanisms. These routes include mixing carbonation (injecting $CO_2$ during concrete mixing), carbonation curing (replacing water or steam with $CO_2$ during the curing of precast concrete), and by the production of synthetic aggregates that have been manufactured from minerals or waste via $CO_2$ carbonation themselves.

### *Mixing carbonation*

Mixing carbonation is used for ready-mix concrete, which is usually delivered to construction sites by barrel trucks. This process consists of injecting $CO_2$ into the concrete mix during batching, which leads to the formation of nano-scale solid calcium carbonate ($CaCO_3$) particles distributed evenly throughout the mix and stores carbon for the lifetime of the concrete.[2] A relatively small dose of $CO_2$ can lead to improvements in performance, specifically an increase in the compressive strength of the finished concrete. Since concrete strength is primarily proportional to the amount of cement in the mix, this increase in strength enables a corresponding reduction in cement content to achieve the same overall performance.

Mixing carbonation also has favorable impacts on other concrete properties, including decreasing set time and increasing durability. In addition, mixing carbonation requires only minor process changes to conventional concrete production with low-cost additional equipment, making it relatively easy to adopt by most concrete producers. This technology has proven to be commercially deployable. However, there are still optimization challenges and barriers due to outdated specification practices in most worldwide markets.

### *Carbonation curing of precast concrete or concrete masonry*

Carbonation curing is primarily applicable to precast and masonry concrete products, which are conventionally cured using steam in closed reactors shortly after casting. Carbonation curing partly or completely replaces this steam with pure $CO_2$ gas. During conventional curing of ordinary Portland cement (OPC), reactions between water and cement produce calcium-silicate-hydrate (C-S-H) crystals—whose interlocking structure provides strength—and calcium hydroxide. In carbonation curing, C-S-H is still produced, but instead of calcium hydroxide, the reaction generates particles of solid calcium carbonate ($CaCO_3$), sequestering carbon in solid form within the concrete in a manner similar to mixing carbonation.[2] Recent demonstrations have shown the feasibility of using $CO_2$ to cure precast concrete blocks at a commercial scale.[3] This shows the possibility of adopting the technology at facilities such as concrete plants throughout the U.S. However, it has yet to see wider adoption on a level comparable to mixing carbonation.

### *Synthetic aggregates*

Aggregates typically make up 60%–80% of the volumetric composition of concrete.[4] While natural resources such as sand, gravel, and crushed stone make up the majority of aggregates used today, carbon mineralization can be used to produce synthetic aggregates to replace them. The process for generating synthetic aggregates involves inorganic material with sufficient alkalinity, typically from available $Ca^{2+}$ or $Mg^{2+}$ or their oxides, reacting with $CO_2$ to form durable carbonates that could be considered for use as aggregates or for things like fillers in paper or porcelain production. Materials such as steel slag, cement kiln dust, and fly ash contain a significant amount of alkaline material readily available for direct reaction with $CO_2$, while some natural minerals can also serve as feedstocks but require chemical processing to make the alkaline materials

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[2] David Sandalow, Roger Aines, Julio Friedmann, Peter Kelemen, Colin McCormick, Ian Power, Briana Schmidt, Siobhan (Sasha) Wilson, Carbon Mineralization Roadmap (ICEF Innovation Roadmap Project, November 2021)

[3] John Williams. CarbonBuilt and Blair Block Announce Commercial Production & Sale of World's First Ultra-low Carbon Concrete Blocks. CarbonBuilt. [May 17, 2023]; [08/02/2024]. https://carbonbuilt.com/low-carbon-concrete-blocks-in-production

[4] Ning Li, Liwu Mo, Cise Unluer. Emerging $CO_2$ utilization technologies for construction materials: A review. J CO2 UTIL 65 (2022) 102237. https://doi.org/10.1016/j.jcou.2022.102237

available.[5] In addition, concrete from demolition waste can be treated with $CO_2$ to improve their strength and generate recycled concrete aggregates in a process known as "carbon conditioning." There is an example of outstanding commercial-level technology for using recycled concrete aggregates to replace natural aggregates.[6] More work is needed to bring all possible feedstocks for synthetic aggregates to the level to replace natural aggregates worldwide.

### *Carbonation of supplementary cementitious materials (SCMs) and non-traditional infrastructure materials for development of sustainable concrete*

One additional route to decarbonization of concrete is to replace Ordinary Portland Cement (OPC), the most widely used cement in the world, with some type of supplementary cementitious material (SCM). OPC is produced by heating limestone ($CaCO_3$), causing it to undergo calcination to generate calcium oxide (CaO) and releasing a significant amount of $CO_2$. The use of SCMs can reduce the overall demand for OPC and thus associated $CO_2$ emissions.

SCMs contribute to the properties of hardened concrete via cementitious or pozzolanic properties and can be used individually with OPC, in blended cement, or various combinations.[7] Cementitious properties refer to the ability for a material to set and harden when hydrated; the pozzolanic reaction of an SCM refers to the byproduct of cement hydration (calcium hydroxide) reacting with silica (pozzolanic matter) in an SCM to form C-S-H material in concrete. Materials that can fill this role include carbonated wastes (fly ash, slag, or silica wastes), biochar, or non-traditional calcium silicates. Such SCMs improve the economics of concrete and are beneficial for reducing permeability, enhancing strength development, and improving other concrete properties.[7]

### *Calcium-rich biochar for use as a filler in concrete*

Certain biomass wastes (such as mushroom substrate[8] and crustacean shells[9]) produce calcium-rich biochar from pyrolysis with good carbonation potential that may be suitable as a filler for concrete mixtures. Carbonated biochar can fill voids within concrete, thus improving the packing of solid particles, reducing porosity, and enhancing mechanical properties. In addition, biochar used as a filler in pervious concrete can positively impact water retention and cooling effects through evaporation as well as thermal and acoustic properties in typical concrete mixtures. RD&D is necessary to understand the long-term implications, risks, and $CO_2$ conversion efficiency and the carbonation potential of calcium-rich biochar derived from pyrolysis or impregnated with calcium ions.

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[5] Ning Li, Liwu Mo, Cise Unluer. Emerging $CO_2$ utilization technologies for construction materials: A review. J $CO_2$ UTIL 65 (2022) 102237. https://doi.org/10.1016/j.jcou.2022.102237

[6] Blue Planet Systems. Products, Blue Planet produces coarse and fine aggregates containing sequestered CO , transforming the global built environment into a carbon sink. Blue Planet Permanent Carbon Capture, 2024. [08/02/2024]. https://www.blueplanetsystems.com/products

[7] Portland Cement Association, American Cement Manufactures. "Supplementary Cementitious Materials". https://www.cement.org/cement-concrete/concrete-materials/supplementary-cementing-materials, [7/9/2024]

[8] Haibo Zhang, Long Su, Caiping Cheng, Hongyan Cheng, Mingchang Chang, Fenwu Liu, Na Liu, and Kokyo Oh. A new type of calcium-rich biochars derived from spent mushroom substrates and their efficient adsorption properties for cationic dyes. Front Bioeng Biotechnol. 2022; https://doi.org/10.3389/fbioe.2022.1007630

[9] Lichun Dai , Furong Tan , Hong Li , Nengmin Zhu, Mingxiong He , Qili Zhu, Guoquan Hu, Li Wang, Jie Zhao. Calcium-rich biochar from the pyrolysis of crab shell for phosphorus removal. J Environ Manage. 2017 Aug 1;198(Pt 1):70-74. https://doi.org/10.1016/j.jenvman.2017.04.057

*Industrial solid wastes*

Certain waste streams from industrial processes are suitable for carbonation reactions. Slag from steelmaking is a notable SCM due to the substantial quantities of CaO and MgO present for subsequent carbonation. In addition, other wastes that have carbonation potential include fly ash, incineration bottom ash, wastewater sludge ash, and glass powder. Several byproducts from ore processing are also amenable to carbonation, such as phosphogypsum, red gypsum, and red mud (wastes from the processing of phosphate, titanium, and bauxite ore, respectively). Continued investigation is needed to fully understand the reactivity of these waste streams and the structural properties they impart on concrete.

*Non-traditional infrastructure materials*

Other materials may be suitable as binders for concrete applications which are not traditionally used in infrastructure. For example, there are certain “non-hydraulic” calcium silicates (e.g., wollastonite and rankinite) that do not readily undergo a hydraulic reaction in the presence of water to serve as a binder in traditional concrete production. However, such non-hydraulic calcium silicates can undergo carbonation in the presence of $CO_2$, heat and water, generating a mix of calcium carbonate and amorphous silica that serves as a calcium silicate cement. This cementitious material can perform as a novel binding agent for making concrete, which incorporates additional $CO_2$ during the curing process.

Other innovative technologies involve approaches that do not incorporate cement to produce concrete or use captured $CO_2$ in their non-traditional cement binder production. One technological approach is producing cement-free concrete by creating basalt-based or zeolite-based concrete that captures $CO_2$ during curing.[10, 11] Another non-traditional concrete production technique is capturing $CO_2$ from the calcination process of limestone in a kiln and using it to produce a non-traditional cement binder.[12] Those approaches reduce the carbon intensity of concrete manufacturing. Further research, development, or demonstration is needed to ensure widespread deployment of promising technologies

### 2.2.2 Challenges

*Availability of raw materials and cost of carbonated products*

The use of industrial solid wastes as feedstocks for mineralization is attractive since it capitalizes on a waste stream that could be abundant and inexpensive. However, leveraging such materials for carbon mineralization would need to compete with other uses that they already have. For example, ground granulated blast furnace slag, a byproduct of steelmaking, is already used as an SCM. The $CO_2$ emissions avoided through its use as an SCM could be greater than the emissions avoided by carbonating it for use as an aggregate. In addition, the collection, transport, and processing of such waste streams requires

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10 Brehm, Denise. “C-Crete Technologies Develops and Deploys the World’s First Zeolite-Based Concrete Devoid of Carbon Dioxide Emissions.” C-Crete Technologies, 2018, [29 July 2024], C-Crete Technologies Develops and Deploys the World’s First Zeolite-Based Concrete Devoid of Carbon Dioxide Emissions – C-Crete Technologies (ccretetech.com).

11 Brehm, Denise. “C-Crete Pours Word’s First Basalt-Based Concrete, A Zero-Emission Product Free of Portland Cement.” C-Crete Technologies, 2018, [29 July 2024], C-Crete Pours Word’s First Basalt-Based Concrete, A Zero-Emission Product Free of Portland Cement – C-Crete Technologies (ccretetech.com)

12 Fortera. “How We Do It.” Fortera, 2024, [28 July 2024], How We Do It - Fortera Corporation (forteraglobal.com).

additional labor and equipment which can quickly reduce the carbon or economic benefit of using a "waste" material. Depending on the source, there are differences in the chemical composition and morphological characteristics of wastes like steel slags, which necessitates case-by-case assessments for adequate carbonation, $CO_2$ curing efficiency, and any process optimizations to ensure its applicability as a construction material after mineralization. Continuous optimization and analysis of the economic feasibility of large-scale deployment of industrial solid waste mineralization technologies are necessary to develop a less complex and low-cost approach.

### *Carbonation reaction and processing challenges for traditional cementitious materials for development of sustainable concrete*

Further research is needed to optimize accelerated carbonation processes such as mixing carbonation and $CO_2$ curing. This includes a need to understand the tradeoffs between mixing carbonation and carbonation curing approaches and the appropriate conditions for each. For these approaches, understanding how different SCMs impact carbonation is essential as well as the carbonation extent of materials and their performance properties. Careful assessment is also needed to understand the long-term effects all the way through to final demolition and disposal. Furthermore, life-cycle and technoeconomic analyses of these carbonation processes and their products will provide the quantitative basis to evaluate their environmental and economic performance.

Table 1 that follows highlights specific challenges for concrete carbonation approaches:

**Table 1:** Challenges for the $CO_2$ mixing carbonation and precast curing approaches[13]

| Approach | Challenge |
|---|---|
| $CO_2$ curing | Development of curing protocols to increase compressive strength and reduce cement use |
| | Understanding impacts on concrete durability |
| | Understanding the effects on steel reinforcement susceptible to corrosion |
| Mixing carbonation | Increase $CO_2$ loading in the mix and maintain compressive strength gain |
| | Increase $CO_2$ loading in the mix and maintain favorable properties in low-load mixes |

### *Challenges of carbonation of calcium-rich biochar for use in concrete*

Challenges to incorporating biochar into conventional concrete must be addressed before widespread deployment. The study of the long-term durability of biochar in concrete mixtures is necessary to confirm practical suitability and reliability and validate its performance in real-world construction applications. The feasibility of using carbonated biochar in different concrete applications should be assessed on a case-by-case basis to understand attributes like the optimal use ratio for a concrete mixture and intended application in diverse conditions.[14]

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13 David Sandalow, Roger Aines, Julio Friedmann, Peter Kelemen, Colin McCormick, Ian Power, Briana Schmidt, Siobhan (Sasha) Wilson, Carbon Mineralization Roadmap (ICEF Innovation Roadmap Project, November 2021)

14 Barbhuiya, S., Bhusan Das, B., Kanavaris, F., "Biochar-concrete: A comprehensive review of properties, production and sustainability." Case Studies in Construction Materials, 20 (2024), e02859, ISSN 2214-5095, https://doi.org/10.1016/j.cscm.2024.e02859

Further work is needed on enhancing the substitution rate of biochar, its carbonation degree, and its performance in concrete. Moreover, the potential adverse effects of biochar in concrete should be elucidated. Some potential unwanted performance impacts are reduced workability, increased porosity, strength reduction, extended setting time, and any impact on the aesthetic appearance of concrete surfaces.[14]

### *Carbonation reaction and processing challenges for non-traditional infrastructure materialsfosustainable concrete*

There are many challenges to deploying non-traditional materials for sustainable concrete. Using mixtures of non-hydraulic calcium silicates with other hydraulic silicate minerals is preferred in terms of carbonation; however, differences in reaction rates, crystalline phases, and product structures of the different components can impact the microstructural and mechanical development.[15] Furthermore, a high concentration of $CO_2$ is required to achieve fast carbonation reaction kinetics for non-hydraulic calcium silicates.[16] Thus, the development of specific procedures for the efficient carbonation of non-traditional materials should be actively investigated.

In addition, there is a need to optimize the performance of carbonated non-hydraulic calcium silicates as a binder.  Early research shows that by doping a low-lime calcium silicate with sodium, carbonating the material, and then subjecting it to hydration, the overall strength of the material and the speed of the process can be improved.[17] Because non-hydraulic calcium silicates generally exhibit weaker hardening properties, further RD&D on innovative methods may enable more non-hydraulic calcium silicate binders that perform closer to traditional cement binders.

### *Developing models for the carbonation process of mineralization products*

Some models for predicting the carbonation of cement-based materials have already been developed. Modeling has been developed to mimic the accelerated carbonation of cementitious materials at a specific temperature to understand the influence on certain aspects of carbonation.[18] Such work can lead to a better understanding of carbonation; however, more work should be done to model temperatures with external relative humidity controls. Also, assessing the effects of other parameters such as gas flow rate, $CO_2$ concentration, and initial moisture content would lead to a more in-depth understanding of carbonation. This type of modeling could help with evaluating alternative compositions and various types of cementitious material.[18]

### *Developing construction codes and standards for mineralization products*

Since they are often incorporated into lived structures, products from mineralization technologies are required to meet robust performance and durability standards.  Government leadership in facilitating or

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15 Ning Li, Liwu Mo, Cise Unluer. Emerging $CO_2$ utilization technologies for construction materials: A review. J CO2 UTIL 65 (2022), https://doi.org/10.1016/j.jcou.2022.102237

16 National Academies of Sciences, Engineering, and Medicine 2019. Gaseous Carbon Waste Streams Utilization: Status and Research Needs. Washington, DC: The National Academies Press. https://doi.org/10.17226/25232.

17 Luyi Sun, Songhui Liu, Yuli Wang, Saisai Zhang, Jianping Zhu, Xuemao Guan, Gaijun Shi. Further hydration hardening behavior of $CO_2$ -cured sodium-doped calcium silicate compacts. Case Stud. Constr. Mat. 20 (2024), https://doi.org/10.1016/j.cscm.2024.e03143

18 Farah Kaddah, Ouali Amiri, Philippe Turcry, Harifidy Ranaivomanana, Emmanuel Roziere. Coupled thermos-hydro chemical modeling of accelerated carbonation of cement-based materials: Application of CO2 uptake. Journal Build. Eng. 93 (2024), https://doi.org/10.1016/j.jobe.2024.109819

expediting certification and standardization processes via support for the appropriate product testing can help carbon mineralization products penetrate the market. Such support can enable efficient demonstrations in compliance with industry quality standards before broad adoption. Rigorous life cycle assessment and product labeling, such as the Leadership in Energy and Environment Design (LEED) program, can indicate environmental benefits and increase the demand for carbonation products as construction materials.

The implementation of programs such as this would be difficult, since they need to cross numerous state, local, and federal jurisdictions. However, this type of support could help the safe and reliable scale-up of mineralization technologies and enable a regulatory sector for carbon-based products.

### 2.2.3 Goals/Milestones for Mineralization

*Near-term (< 5 years)*

- Develop cost-effective cement additives to improve reaction rates and kinetics in mineralization
- Support partnering with national standard certifying agencies, e.g., American Society for Testing and Materials but its more widely known as ASTM and National Institute of Standards & Technology (NIST), to identify applications for non-traditional concrete incorporating $CO_2$, which are potentially viable to demonstrate compliance with technical parameters via performance testing, ensuring widespread adoption
- Demonstration of a high technology readiness level (TRL) (engineering-scale prototypical validation in a relevant environment) for mineralization technologies yielding concrete with 5%-10% lower greenhouse gas emissions
- Support R&D of lower TRL (laboratory-scale) mineralization technologies that need component integration work as a system that enables concrete with <10% lower greenhouse gas emissions

*Mid-term (5-10 years)*

- Demonstrate long-term structural stability and durability of $CO_2$-cured products and their ability to meet performance standards
- Support the piloting of non-traditional concrete produced with $CO_2$ carbonation technologies to meet appropriate performance standards
- Demonstration of mineralization technologies yielding concrete with at least 10% lower greenhouse gas emissions than baseline
- Support R&D that enables concrete with 25% lower greenhouse gas emissions than baseline

*Long-term (10+ years)*

- Support the adjustment of concrete standards and establishment of testing protocols to include $CO_2$ cured precast concrete, mixtures with cement incorporating $CO_2$, or concrete without cement
- Operation of carbon mineralization activities on a megaton scale or greater
- Demonstration of mineralization technologies coupled with capture technologies (co-location sites and optimization of the process design)
- Demonstration of mineralization technologies yielding concrete with at least 25% lower greenhouse gas emissions than baseline

## 2.3 Biological Conversion

### 2.3.1 Overview

Biological routes for $CO_2$ utilization can use natural systems that leverage renewable energy in order to perform $CO_2$ conversion. In the case of autotrophic organisms such as algae, this occurs via photosynthesis. The resulting biomass produced in algal systems can be processed and converted to a wide variety of fuels and products. Similarly, other organisms can perform autotrophic $CO_2$ conversion using other forms of energy, such as hydrogen or other inorganic electron donors. While biomass can be used in this way to perform dedicated carbon removal (as in the Carbon Dioxide Removal Program), the Carbon Conversion Program is interested in exploring and understanding the cost, benefits, and potential for the many different routes to biologically convert $CO_2$ into products.

*Algae uptake*

Algae represents a large group of organisms, including unicellular microalgae; macroalgae like kelp and seaweed; and cyanobacteria. They are efficient photosynthetic organisms that can produce a large amount of biomass for fuels, chemicals, or other products like animal feed, soil amendments, or fine specialty items. Cultivation systems for producing large volumes of algae span from large open raceway ponds to a series of smaller, enclosed photobioreactors. Captured $CO_2$ is delivered to these systems to achieve a high biomass yield.

There are numerous aspects of algae growth, harvesting, and conversion that the Conversion Program explores. This includes productivity and cultivation improvement, community robustness, dewatering and concentration of algal biomass, and efficient nutrient and water use. The scale up of algae production from small-scale to commercial relevance will require maintaining consistent growth conditions, preventing contamination, and improving downstream processing.

*Non-photosynthetic biological $CO_2$ conversion*

Biological systems can also perform carbon reduction through chemosynthesis, which refers to the use of energy sources other than direct sunlight to convert $CO_2$. This can be achieved by certain bacteria or archaea through the oxidation of inorganic compounds to generate the energy required to drive carbon fixation. The reducing agents that can perform this task include hydrogen gas, ammonia, or various iron or sulfur containing compounds. In addition, biological systems can also be engineered to directly use electrical energy on the surface of an electrode or to consume an intermediate derived from $CO_2$ chemical reduction, like carbon monoxide or formic acid.

The organisms which can perform non-photosynthetic $CO_2$ uptake can be harnessed and engineered for $CO_2$ conversion into fuels, chemicals, or products. Using such biological catalysts can exploit the durability and high selectivity of biochemical conversion, as well as longstanding capabilities in fermentation and microbial engineering. When these systems for biological $CO_2$ conversion are coupled to decarbonized energy to supply the necessary reducing power, products of greatly reduced carbon intensity can be achieved.

### 2.3.2 Challenges

*Kinetically slower than abiotic approaches*

Carbon utilization via biological conversion is a complex process and is typically slower than catalytic $CO_2$ conversion to similar products. Biological pathways for $CO_2$ fixation require multiple enzymatic steps in various metabolic pathways, each with their own regulatory mechanisms and rate-limiting steps. While such pathways can generate very specific, multi-carbon products of low carbon intensity, they are often slow and can be affected by factors such as pH, temperature, and substrate concentration. Generating such a product must balance growth and maintenance pathways within algae or other microbial systems. Significant process engineering, optimization and microbial engineering is required to ensure the rate of growth or product formation is suitable for commercialization. Finding solutions to such challenges is of significant interest to the Carbon Conversion Program.

*Water and nutrient use requirements*

A challenging aspect of sustainable algae cultivation is mitigating the enormous amounts of water and nutrients such as nitrogen required to grow and process algal feedstocks.[19] The requirements for water use for biomass production will vary depending on the algal strain, desired growth conditions, and the region of cultivation. For large-scale algae production, the impact on existing water use and community infrastructure must be considered to avoid the misuse of resources for successful algae cultivation scale-up. In addition to algae cultivation, other biological routes, like large-scale fermentation, can also have significant water demands and nutrient requirements. All of these must be managed to minimize the cost and carbon intensity of the process.

Algae systems can use alternative water resources, such as wastewater or salt water, reducing the strain on water and nutrients needed to grow effectively. Effective wastewater recycling via algae can minimize freshwater and nutrient consumption while also providing an environmental service. Wastewater can also be leveraged as a nitrogen source for non-photosynthetic biological systems. Such use of treated or untreated wastewater is appealing, but more work needs to be done to develop and demonstrate the viability of this approach for large-scale applications.

*Improvements in $CO_2$ utilization efficiency in open raceway ponds*

One major limitation in the use of open ponds for algae cultivation is the loss of delivered $CO_2$ to the atmosphere. Aquaculture often uses long, narrow channels that promote continuous circulation of water for the growth of aquatic organisms. Most of the physicochemical and hydrodynamic process parameters related to mass transfer of $CO_2$ in such raceway ponds have important effects on microalgal growth. However, the detailed reaction mechanisms of carbon uptake by algae in ponds, including under novel conditions like the presence of carbonic anhydrase or high pH, remain unclear and need further RD&D.

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[19] Lieve M.L. Laurens, James D. McMillan et. al. State of Technology Review- Algae Bioenergy, An IEA Bioenergy Inter-Task Strategic Project. https://doi.org/10.13140/RG.2.2.11770.90560

Additionally, the scale required to utilize all the $CO_2$ emitted from large point-sources requires an immense land footprint and, for cost reasons, this dictates a need for open ponds for algae cultivation in such situations. The cost of transport of $CO_2$ from the facility to the site of cultivation, as well as $CO_2$ storage at night or other times when algae are inactive, puts another large economic burden on open raceway ponds. Understanding the costs and benefits to operating open ponds, as well as learning how to optimize these systems, is essential to enabling large-scale algae cultivation.

*Improvements in photobioreactors*

Algae cultivation in open raceway ponds typically uses sunlight and minimal temperature control, meaning that the growth of biomass greatly depends on weather conditions and ambient temperatures.

Because of these limitations, open ponds are restricted to certain parts of the world that already have a suitable environment. Photobioreactors enable tighter control of temperature, $CO_2$ delivery, and sunlight. A photobioreactor typically has a transparent or translucent barrier, which allows sunlight in while simultaneously protecting the algae population from the environment.[20] There is typically no direct exchange of gases or fluids between bioreactors and thus contamination of the cultivation systems is greatly reduced. Such photobioreactors can enable tightly controlled microalgae production systems.

Though progress has been made in developing photobioreactors for mass production of microalgae, more effort is still required for further reactor improvements and cost reduction. More durable, reliable, and transparent materials for the design of closed photobioreactors is necessary to enhance cultivation efficiency and to reduce the cost of photobioreactors.

*Improved fermentation of $CO_2$ and intermediates*

The fermentation of $CO_2$ and $H_2$ is a promising route to generating sustainable fuels and products and it can leverage organisms that have proven commercial success, such as acetogens and methanogens. However, challenges of gas mass transfer, safety, and organism tolerance remain. Further improvements are required to enable efficient $CO_2$ gaseous fermentation, including strain optimization for targeted products, fermentation monitoring and control, reactor design, and ensuring safety when handling $H_2$ gas in a reactor.

A related pathway to biological $CO_2$ conversion relies on the fermentation of intermediates derived from $CO_2$, such as carbon monoxide and formic acid. Such routes have the advantage of reducing or removing the need for $H_2$ in the fermentation and providing a more reduced form of carbon for biological uptake; however, they rely on other $CO_2$ conversion technologies to generate the intermediates that are fed to the microorganism. In addition, such routes require additional microbial strain development, reactor design, and fermentation optimization.

*Improved microbial electrosynthesis and the use of novel inorganic reducing agents*

Microbial electrosynthesis (MES) is a process where certain autotrophic microorganisms use direct electrical current from an electrode to drive the conversion of CO2. This merger of microbiology and electrochemistry

[20] Zhang, Xing. Microalgae removal of $CO_2$ from flue gas. © IEA Clean Coal Centre. http://dx.doi.org/10.13140/RG.2.2.26617.77929

can offer a direct route for using biology and decarbonized electricity to generate sustainable products in a single step with potentially higher efficiency and precise control of reaction conditions. Such routes are still in the early stages of development and require an improved understanding of the unique organisms that can perform microbial electrosynthesis, including genetic engineering tools to improve electron transfer, enable conversion to desired products, and ensure robustness to harsh reactor conditions. In addition, MES will require electrodes that are robust, have high surface area, and can allow for efficient interface with microorganisms.

Beyond MES, chemosynthesis can also occur using various novel electron donors such as ammonia and reduced iron or sulfur compounds. The optimization of the unique set of organisms that can use such reducing agents to convert $CO_2$ is an emerging area that must be scrutinized to understand if chemosynthetic routes can ever achieve commercial relevance.

### 2.3.3 Goals and Milestones for Biological Conversion

*Near-term milestones (< 5 years)*

- Improvements in methods to enhance light exposure and $CO_2$ delivery to algae culture
- Improvements in photobioreactors
- Microbial engineering for improving non-photosynthetic biological $CO_2$ conversion routes
- Explore emerging microbial electrosynthesis routes and novel chemosynthesis pathways

*Medium-term milestones (5-10 years)*

- Improvements in algae harvesting techniques to minimize the harvesting cost
- Integration of wastewater into algae systems
- Improvements in reactor design for $CO_2$+$H_2$ gaseous fermentation
- Piloting of non-photosynthetic biological $CO_2$ conversion routes

*Long-term milestones (10+ years)*

- Launch large-scale demonstration projects that show a reduction of water, energy, nutrient, and land use footprints for an integrated operation
- Launch projects demonstrating on-site processing or separation of algae biomass into lipid, carbohydrate, and/or protein or conversion into products
- Launch large-scale demonstration of the integration of catalytic $CO_2$ conversion to intermediates and the biological upgrading of such intermediates to fuels and chemicals

## 2.4 Catalytic Conversion

### 2.4.1 Overview

Catalytic Conversion pathways generally involve the reduction of $CO_2$ using a catalyst. These processes target concentrated streams of $CO_2$ and include thermochemical, electrochemical, photochemical, and non-thermal plasma-assisted routes. In addition, the Carbon Conversion Program also explores integrated systems that combine the process of $CO_2$ capture from a dilute gas stream and catalytic $CO_2$ conversion into value-added products without requiring a purified $CO_2$ stream.

Some catalytic conversion technologies have achieved a higher level of technology readiness and are more widely accepted by industry and academia than other routes. This is because they have achieved higher scale and produced more data on full system design, including optimizing post-reaction stream separation and recycle stream integration. Such advanced strategies are generally thermochemical in nature and rely on $H_2$ to provide the energy for carbon reduction, while some electrocatalytic technologies are achieving higher TRL as well. Conventional thermochemical processes that have achieved commercial relevance with $CO_2$ as a feedstock include $CO_2$ hydrogenation and carboxylation reactions to produce a variety of products such as syngas, methane, methanol, and ethanol. Such technologies align well with current efforts to produce low-carbon hydrogen in the FECM Hydrogen with Carbon Management Program. Shifting these thermochemical systems to leverage low carbon electricity, while also optimizing them to operate at more modular scale, is the core challenge of the field. Additionally, some electrocatalytic $CO_2$ reduction technology has shown promise at roughly the pilot scale. While promising, challenges remain for each of these higher TRL technologies, especially as they are further scaled up and integrated.[21, 22]

#### *Thermochemical $CO_2$ conversion*

Thermochemical $CO_2$ conversion is currently the most mature catalytic pathway for $CO_2$ conversion and generally refers to technologies that use a catalyst with heat and pressure to produce valuable products. The driving forces for an effective thermochemical reaction are usually temperature and pressure to overcome an activation barrier, while the catalyst material determines the product formation. For example, $CO_2$ hydrogenation to formate uses a metal active site (Pd, Au, Ir, or Pd and Cu) adsorbed to an oxide ($CeO_2$ and ZnO) or ceramic support. Many such processes have been proven at the industrial scale, including $CO_2$ hydrogenation to methanol, an important feedstock chemical, and $CO_2$ conversion to carbon monoxide via the reverse water gas shift reaction, which converts hydrogen and captured $CO_2$ into water and carbon monoxide that can be further processed into liquid fuels or for industrial applications by utilizing other processes such as Fisher-Tropsch. Similarly, methanol generated via $CO_2$ hydrogenation can serve as a feedstock for producing other chemicals or as a fuel itself.[23]

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21 Navarro-Jaén, S., Virginie, M., Bonin, J. et al. Highlights and challenges in the selective reduction of carbon dioxide to methanol. Nat Rev Chem 5, 564–579 (2021). https://doi.org/10.1038/s41570-021-00289-y

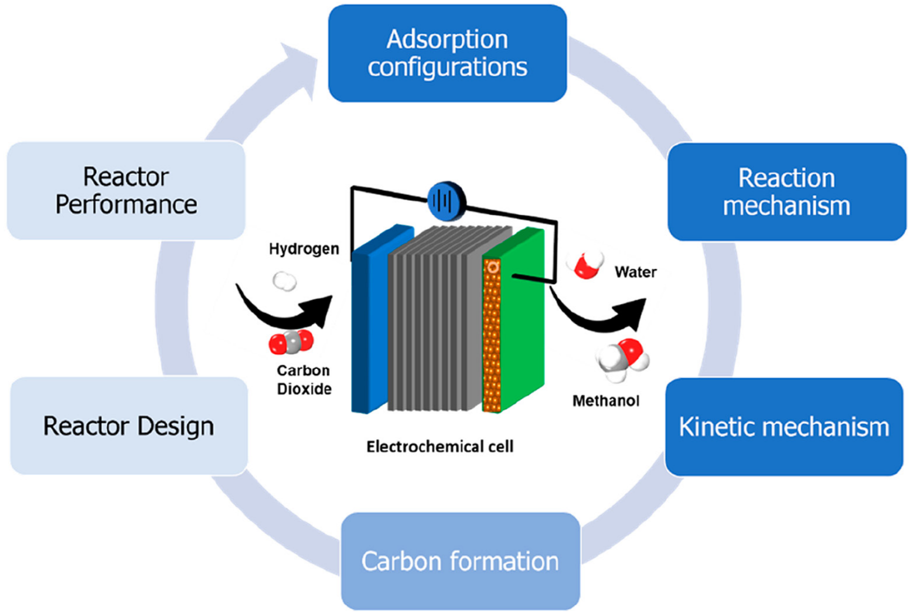
22 Kothandaraman, J., Goeppert, A., Czaun, M., Olah, G. A. & Prakash, G. K. (2016) Conversion of $CO_2$ from air into methanol using a polyamine and a homogeneous ruthenium catalyst. J. Am. Chem. Soc. 138, 778–781, https://doi.org/10.1021/jacs.5b12354

23 Gao J., et al. (2023) Reduction of CO2 to chemicals and Fuels: Thermocatalysis versus electrocatalysis, Chemical Engineering Journal, vol. 472, 145033 https://doi.org/10.1016/j.cej.2023.145033

### *Electrocatalytic $CO_2$ reduction*

The electrocatalytic conversion of $CO_2$ to products involves an external voltage that is applied across a pair of electrodes to add electrons to a molecule of $CO_2$, thus reducing its oxidation state. Electrocatalytic $CO_2$ reduction is considered an adaptable conversion technology with the availability to convert $CO_2$ into products dependent primarily on the type of catalyst used. This technology can be coupled with low carbon electricity towards offering a promising route for decarbonizing chemical manufacturing processes and displacing fossil fuels.[24] The most developed electrocatalytic technology is the high temperature solid oxide electrocatalytic reduction of $CO_2$ to C1 products (e.g., CO, formic acid). This high temperature electrolysis (HTE) requires high heat but can operate with high efficiency and relatively low voltage. On the other hand, low temperature (>100˚C) electrocatalytic (LTE) conversion is currently at a lower TRL, yet it is improving quickly with the help of modeling, and durability testing.[25] Figure 2 illustrates a general methodology of utilizing modeling tools to help in the understanding of catalyst and reactor performance. LTE technology does not need an external source of heat and offers an attractive option for directly using electricity to provide the energy needed for $CO_2$ reduction. Both types of electrochemistry have advantages and disadvantages, and both are of interest to the Carbon Conversion Program.

**Figure 2:** Process flow showing how modeling tools can help in understanding catalyst performance and the aligned reactor design for electrocatalytic systems[26]




[24] De Luna, P., Hahn, C., Higgins, D., Jaffer, S.A., Jaramillo, T.F., and Sargent, E.H. (2019). What would it take for renewably powered electrosynthesis to displace petrochemical processes? Science 364, p. 3506. https://doi.org/10.1126/science.aav3506

[25] Rainer Küngas (2020) J. Electrochem. Soc. 167 044508, https://doi.org/10.1149/1945-7111/ab7099

[26] Lourdes F. Vega, Daniel Bahamon, and Ismail I. I. Alkhatib ACS Sustainable Chemistry & Engineering 2024 12 (14), 5357-5382 https://doi.org/10.1021/acssuschemeng.3c07133

### *Plasma-induced $CO_2$ conversion*

Plasma-induced $CO_2$ conversion is an emerging process which uses a non-thermal plasma (NTP), typically created by exposing gas to an electric field, to overcome the high energy barrier for $CO_2$ reduction. One advantage of this process includes straightforward integration with the variability of renewable electricity without significant degradation of the reactor. Additionally, it is possible for NTP reactions to occur in the entire volume of a reactor, as opposed to occurring solely at the electrode surface. Further research is still needed to fully understand the complexity of the plasma physics and chemistry to achieve high product selectivity, energy efficiency, and to understand specific safety concerns to go beyond the bench scale.[27]

### *Photocatalytic $CO_2$ conversion*

Photocatalytic $CO_2$ conversion is a multistep electron transfer process that uses photon absorption on a photocatalytic material to overcome the large energy barrier to: (1) break the carbon-oxygen double bond; (2) break the oxygen-hydrogen bond; and (3) selectively form the desired products from the intermediates. The photocatalytic conversion of $CO_2$ to valuable products and fuels has been studied for over 40 years; however, the technology remains primarily at the laboratory scale.[28] Much of the current research is focused on identifying photocatalytic materials with higher selectivity toward value-added products and improved apparent quantum yield.[29] Currently, these technologies have achieved relatively small scale, and significant research of photoconversion materials and processes will be needed before photocatalytic reduction of $CO_2$ can be practically deployed.[30]

### *Reactive Capture and Conversion (RCC)*

Reactive capture and conversion is defined as the integration of two processes: (1) separation of $CO_2$ from a dilute gas stream and (2) conversion of $CO_2$ to a value-added product. Compared to separate capture and conversion processes, RCC does not require regeneration of the capture media, purification, and compression of the captured $CO_2$ intermediate, or $CO_2$ transport and storage. Additionally, RCC can be optimized to have an overall reduction in unit operations and capital expenditures by using fewer steps, a single reactor, and an overall simpler process intensification.[31]

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[27] Bogaerts A., Centi G. (2020) Plasma Technology for $CO_2$ Conversion: A Personal Perspective on Prospects and Gaps, Front. Energy Res., Vol. 8, https://doi.org/10.3389/fenrg.2020.00111

[28] Inoue, T., Fujishima, A., Konishi, S. et al. (1979) Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. Nature 277, 637–638 https://doi.org/10.1038/277637a0

[29] Gui M. M., Lee W.P., Putri L. K., Kong X. Y., Tan L. L., Chai S.-P. (2021) Photo-Driven Reduction of Carbon Dioxide: A Sustainable Approach Towards Achieving Carbon Neutrality Goal, Frontiers in Chemical Engineering, vol. 3, https://doi.org/10.3389/fceng.2021.744911

[30] Global Roadmap for Implementing $CO_2$ Utilization, $CO_2$ Sciences and The Global $CO_2$ Initiative (2016) innovation for Cool Earth Forum

[31] Rachel E. Siegel, Santanu Pattanayak, and Louise A. Berben. Reactive Capture of $CO_2$: Opportunities and Challenges. ACS Catalysis 2023 13 (1), 766-784 https://doi.org/10.1021/acscatal.2c05019

### 2.4.2 Challenges

*Thermochemical optimization and industrial integration*

Several challenges remain for thermochemical $CO_2$ conversion processes, such as their reliance on large scales for economic viability, dependence on high temperature and pressure, and competing reactions which reduce catalyst selectivity to the desired product. Improving these technologies such that they can operate at the appropriate scale associated with distributed $CO_2$ sources at high selectivity and the appropriate carbon intensity will require continued scale-up efforts focusing on optimizing energy consumption, catalyst development, and process integration leading to optimum product concentration.

*Low temperature electrolyzer scale-up*

Low temperature electrolyzers used to convert $CO_2$ to valuable products are complicated and more variable than water electrolyzers in their design, materials, membrane electrode assembly (MEA) processing, and operating conditions. The catalytic materials alone can differ greatly depending on the intended product and selectivity. A key need for deploying this technology quickly is well-balanced and thoughtfully designed verification of various electrolyzer architectures and performance. The Carbon Conversion Program is exploring accelerated durability testing and modeling to understand the degradation mechanisms of larger scale electrolyzer systems. Standardization of electrolyzer and component durability testing will reduce the costs of scaling up low temperature $CO_2$ electrolysis and facilitate commercialization at the industrial scale.

*Scaling NTP beyond the laboratory*

Moving non-thermal plasma (NTP) $CO_2$ conversion from the laboratory toward an industrial scale will require significant improvements. According to literature, there is an energy efficiency and conversion trade-off for $CO_2$ splitting in different plasma reactors. NTP will need to increase energy efficiency to be competitive with other conversion technologies while also improving conversion efficiency simultaneously.

Additionally, plasma has a very reactive nature that is not as selective. One potential remedy is to combine plasma with a catalyst either in the same reactor or as a series of reactors. However, multi-reactor systems could increase capital costs and scalability could be an issue. NTP could have a large potential impact if these and other, more nuanced, challenges are met with innovative solutions using a knowledge-based approach with systematic and reproducible testing.

*Photocatalytic $CO_2$ conversion challenge*

Photocatalytic conversion of $CO_2$ needs to overcome various challenges including mass transfer limitations, photon transfer limitations, lack of reaction pathway control, and proper product identification through discerning true product formation from that of advantageous carbon impurities. Although there have been intensive R&D efforts to overcome these challenges, photocatalytic conversion remains at the laboratory scale. Ensuring the measurement of carbonaceous product formation originates from feedstock $CO_2$ and not contamination from other sources should be investigated and verified early for each testing facility. Improving the process of materials development, photocatalyst design, and photoreactor system development could help reach higher conversion efficiency to be competitive with other conversion technologies.

*RCC commercialization challenges*

The advantage of RCC over separated capture and conversion processes is the reduction of capital and operational cost requirements. RCC can complement separate capture and conversion technologies as another tool to help optimize the carbon management portfolio. Currently, most of the materials and processes used in RCC remain at the laboratory scale, and a standardized accelerated stress test must still be developed to ensure long term materials durability. Challenges towards commercialization can be mitigated with targeted applied research and development to derisk existing technologies and diversify the products that can be produced with additional efforts toward standardizing the metrics used to develop TEA/LCAs. The end goal, in cooperation with the Point Source Capture Program and the Carbon Dioxide Removal Program, is to promote effective market penetration by creating balanced process economics, lifecycle profiles, and value-added products.

## 2.4.3 Goals and Milestones

*Near-term (< 5 years)*

- Support research on accelerated stress tests (ASTs) to test durability of low temperature electrocatalysis that is relevant at multiple scales
- Support thermochemical conversion routes that can operate at smaller scale
- Conduct initial studies to define engineering and economic parameters for industrial integration of $CO_2$ conversion
- Support early-stage R&D of emerging catalytic technologies such as photocatalysis and plasma catalysis

*Mid-term (5-10 years)*

- Conduct integrated field tests of high-temperature electrochemical and thermochemical conversion technologies to validate approaches
- Evaluation of front-end engineering design (FEED) studies: construction and operation/ demonstration of first-generation technologies

*Long-term (10+ years)*

- Optimizing low temperature electrochemical reactor design at the pilot scale
- Demonstrating thermal catalytic conversion at a mature industrial chemical plant
- Integration of pilot scale electrochemical conversion technologies at an industrial chemical plant
- Evaluate novel pilot scale CO2 catalytic conversion pathways

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