# FINAL REPORT

Project Title: **$CO_2$ MINERALIZATION USING POROUS CARBON AND INDUSTRIAL WASTES TO MAKE MULTIFUNCTIONAL CONCRETE**

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**EXECUTIVE SUMMARY:**

Along with substantial benefits and promises of carbon capture and storage (CCS) technologies, significant challenges exist in developing scalable materials and methods for capture and of $CO_2$. The overarching objective of this project is to provide a *system* approach for developing a new $CO_2$ capture and utilization technology using porous carbon and industrial wastes to make a low-cost, scalable and multifunctional concrete product. The objective of Phase I of this project is to develop and fine-tune activated carbons from different wastes such as plastic wastes to offer a cheap, abundant and scalable feedstock for $CO_2$ uptake. The objective of Phase 2 is creating a facile protocol to develop a concrete prototype comprising $CO_2$ adsorbed activated carbon (e.g. from plastic wastes), followed by product validation, life-cycle analysis, and bench-scale testing. The project objectives are designed to specifically obtain a final product and technology that directly addresses the main goals of the DOE's CCS programs.

**Project Description:**

This project develops a new protocol integrating a collection of advanced synthesis and characterization techniques, a thorough combination of lab-simulation and bench tests, as well as life-cycle analysis, thereby providing a *system approach* to achieve the most beneficial and cost effective technology for use of $CO_2$ in value-added and scalable products. The core synthesis strategy is based on capturing $CO_2$ in activated carbon from wastes (e.g., plastic wastes) to efficiently lock $CO_2$ for making multifunctional concrete products. Characterizations and testings comprise of a myriad of probes and techniques including advanced electron microscopies, spectroscopies, conductivity measurements, mechanical analysis, and bench-scale testing. Our technical results will be coupled to life-cycleanalysis, incorporating materials/method cost structures, and risk and environmental priorities to quantitatively evaluate the impact and benefits of our new product and technology.

**Key Outcomes and Impact:**

This project results in the following value propositions:

1) A completely new phase space that provides a revolutionary new paradigm for effective $CO_2$ capture using wastes such as plastic wastes.
2) A concrete materials technology that uses the $CO_2$ adsorbed activated carbon (e.g. from plastics wastes) at scale
3) A final $CO_2$ capture and utilization technology and concrete manufacturing protocol that will be easily integrable to existing power plants (thus minimally system-intrusive) to efficiently store their $CO_2$ without generating additional $CO_2$ footprint.

Essentially, this project solves two mega environmental issues: $CO_2$ in the atmosphere and plastic waste pollution, with a goal of using them in concrete, the most man-made material on the planet.

## 1. Introduction

Ever-raising carbon dioxide ($CO_2$) level is among the top environmental concerns of the 21st century.[1-3] The concentration of $CO_2$ in the atmosphere has increased from preindustrial value of ~280 ppm to 401 ppm in 2018.[3] This increase in $CO_2$ levels is believed to be primarily due to the continuous combustion of fossil fuels and the lack of economical $CO_2$ capture technologies. Nonetheless, fossil fuels are expected to remain the least expensive energy source for the next 40 years because of the slow development of green and renewable energy sources.[4, 5] To lessen the impact caused by fossil fuel consumption, efficient and economic post-combustion $CO_2$ capture technologies are needed to replace the expensive and energy intensive amine-based chemical absorption that has been practiced in industry for years.[6] Developing novel $CO_2$ capture technologies using waste feedstocks such as plastic wastes is a key goal of this project, which will be discussed shortly.

### 1.1 Utilization of $CO_2$ from Power Plants

Coal-fired power plants are considered as a large point sources of $CO_2$ release, in addition to the generation of solid industrial wastes, such as fly ash and bottom ash, which are potent source of Ca and Mg. Currently, majority of captured $CO_2$ from power plants is mainly used to act as a solvent in enhanced oil recovery (EOR), because it is miscible with crude oil, and is inexpensive. In addition, the injected $CO_2$ for EOR can be partially stored underground which will contribute to the reduction in green house gas (GHG) emissions. However, still about half of the injected $CO_2$ cannot be sequestrated and are released to the atmosphere. Furthermore, the injected $CO_2$ which is stored underground can escape through the micro/nano-cracks in the wellbores over the time.

The other application of captured $CO_2$ is in carbonation of plastic materials. Traditional monomers, such as ethylene and propylene, can be combined with $CO_2$ to produce polycarbonates, such as polyethylene carbonate and polypropylene carbonate.[32-34] Polycarbonate plastics are lightweight, high-performance plastics that possess a unique balance of toughness, optical clarity, and excellent electrical resistance. However, producing polycarbonate requires high processing temperatures, making it quite costly to manufacture. Consequently, the price of polycarbonate exceeds that of standard acrylonitrile butadiene styrene (ABS) general-purpose plastic resin. Also, polycarbonate is susceptible to degradation when exposed to processing equipment, alkaline solution and solvent for an extended period. There are a number of industrial efforts to make use of $CO_2$ to make useful solid products such as concrete. Examples include Solidia Technologies, Carbicrete, et. However, so far these technologies have not been commercialized in large scales and competitive prices, in part due to expensive and complex processes.

## 2. State of the Art

Amine-based technologies for $CO_2$ capture rely on the chemical reaction between amines and $CO_2$ to form a carbamate complex.[6-8] Carbamates are stable and require heating up to 125 °C to regenerate the amine, making it an extremely energy intensive technology given the high heat capacity of aqueous amine solution.[9] On top of the high regeneration cost, aqueous amines are corrosive and cause continuous equipment failures in the $CO_2$ capture units, degrade upon heating, are expensive to replace, and produce large amounts of wastewater and sludge as byproducts. Thus, the development of a greener and cheaper technology is sought after. [10]

Solid adsorbents have received more interest in recent years due to their low heat of regeneration and high thermal stability.[11, 12] Out of all reported solid adsorbents, activated carbons are cheap, non-toxic, and have resilient structure,[13-18] making it a great candidate for applications with severe and harsh conditions including: crude oil desulfurization,[19, 20] gas storage,[21] and high-pressure $CO_2$ capture.[11] The surface area and pore volume of carbonaceous materials can be tuned easily and economically.[15, 22] Moreover, carbonaceous materials can be synthesized from various feedstocks ranging from a renewable biomass like glucose [15] to industrial carbon waste like asphalt, [23] which makes the precursors of carbonaceous material highly abundant

With the increasing awareness of the harmful effects of microplastic and plastic waste, [24, 25] new technologies for plastic waste utilization are being pursued. One of the proposed technologies to treat plastic waste is pyrolysis of plastic, also called chemical recycling.[26] This method involves heating plastics in an inert atmosphere, a process which breaks up the plastic into smaller molecules and oils.[26, 27] Plastics decompose into char, oils, gas, and waxes when heated around 600 °C in an inert atmosphere.[27] The waxes and oils products are further cracked over acidic zeolites or bentonite clay to obtain high value petrochemicals and fuels.[28-30] One of the drawbacks of pyrolysis methods for plastic handling is the formation of large amounts of char that currently has no significant use.[31]

There have been also a number of experimental simulation and approaches that focus on injection of compounds that react with $CO_2$ or supercritical $CO_2$ in an effort to form solid materials. In these instances, methods such as solid precipitation may be used to form precipitates such as calcium carbonate or magnesium carbonate, gel formation could be used by employment of time/pH dependent gelling polymer or sodium/colloidal silica, or even microbial films could be used but with the probability of success being quite low.[35] In all such approaches, the key is to store the captured $CO_2$ in materials that can physically/chemically bond with $CO_2$ molecules and make new useful products with various features, for example by converting $CO_2$ into a solid minerals or other high-value chemicals. However, the $CO_2$ mineralization using available feedstock, namely Ca- and Mg-based silicate minerals such as olivine, serpentine, and wollastonite are impractical due to the high cost of about \$ 54 $t^{-1}$ $CO_2$ stored and requirements of large amounts of minerals. Using alternative and inexpensive feedstock of minerals that are mainly from industrial waste still remains a challenge due to slow chemical kinetics of the process and requirements of high activation energy. Therefore, a key technical challenge that must addressed in this regard is enhancing the reaction kinetics and efficiency of the process. This could be accomplished by changing the mechanism of $CO_2$ uptake through pretreatment of waste materials that can capture $CO_2$ within its pores and subsequent usage in concrete.

### 3. Project Objectives

The overarching objective of this project is to provide a *system* approach for developing a new $CO_2$ capture and utilization technology using porous carbon and industrial wastes to make multifunctional concrete products. More precisely, by integrating various advanced syntheses, high-level characterizations, testings, and life-cycle analysis, the project objectives are designed to specifically address the main goals of the DOE's CCS programs. Each project objective are performed with an overall goal of producing a final commercial product and technology that can be integrated to coal-fired power plants and produces a stable, efficient, cost-effective and scalable $CO_2$ capture and utilization technology.

The first objective of our project was to develop activated carbons from different wastes such as plastic wastes to offer a scalable solution to $CO_2$ capture. This objective contained numerous synthesis optimization procedures and advanced characterizations to allow for an effective sorbent targeted at maximizing $CO_2$ uptake efficiency, scalability and cost-effectiveness. To this end, we tuned several parameters such as reaction kinetics, ratio of the reagents, and utilize several alternative plastic wastes (e.g. high density polyethene , low density polyethylene, Polyethylene terephthalate, Polyvinyl chloride, Polypropylene, Polystyrene, Polyacrylonitrile, etc., or any combination thereof known as mixed plastic wastes) as the carbon source to find the optimum conditions such as porous nano/meso/microstructure in which the activated carbon materials possess desired performances such as highest $CO_2$ uptake, specially near room conditions and/or at low pressure, such as 0.1 bar, in line with the actual pressure of the flue gas in power plants.

The second objective was to create a facile protocol to prepare concrete products comprising $CO_2$ adsorbed activated carbon materials (e.g. from plastic wastes), and other industrial wastes such as flyash, slag, etc., and testing them in accordance with the standards to confirm and optimize the enhanced properties of the final composites induced by porous carbon additives.

The third objective was life-cycle analysis, technology gas analysis, and bench-scale testing via synthesis flue gas containing ~85% $CO_2$ and 15% $N_2$ to ensure that our technology can be integrated to power plants.

## 4. Key Project Achievements:

**1)** we developed an alternative approach to plastic pyrolysis, resulting in obtaining a porous carbon that has high $CO_2$ capture capacity. The developed approach also results in thermal cracking of the polymer, yielding the typical chemicals and fuels that are usually produced with the conventional pyrolysis. The advantage of this technology over conventional pyrolysis is the elimination of unusable char and the production of an effective $CO_2$ adsorbent, which solves two of the mega environmental issues: $CO_2$ levels in the atmosphere and plastic waste pollution.

**2)** The improved mechanical properties of the concrete with $CO_2$ adsorbed activated carbon (e.g. from plastic wastes) make it an excellent filler/reinforcing agents in making high performance concrete materials. Increasing the average strength of concrete by using $CO_2$ adsorbed activated carbon leads to more efficient use in smaller quantities (to do more with less) and thus lower $CO_2$ emissions; recall that cement manufacturing is responsible for 5-10% of overall $CO_2$ emissions worldwide.

**3)** The improved electrical and thermal properties of concrete using activated carbon have a variety of applications including anti-static flooring, roadway deicing and cathodic protection of reinforcing steel in concrete structures. Given that the traditional concrete is a poor electrical conductor, the high thermal and electrical conductivity of our concrete product can be used to design novel structural materials with de-icing capability for use in pavements and bridges. For instance, applying a voltage to thin layer of our concrete can prevent ice formation on the bridge and eliminate 10-15% of roadway accidents that occur due to the weather conditions.

**4)** The inherent hydrophobicity of our concrete makes our product more durable when compared to conventional concrete. The uniform distribution of inexpensive activated carbon in the bulk of concrete provides hydrophobicity, giving rise to water repellency and therefore reduces the chance of water penetration into the possible micro/nanocracks, which can cause failure of the concrete

**5)** Besides $CO_2$, our technology can employ several other by-products of coal-fired power plants (flyash, bottom ash, coal waste from mining, and water waste) to make our concrete product and technology quite cost-effective and offset the cost of waste disposals. As one of the key by-products of coal combustion, flyash is conventionally used as a supplementary cementitious material (SCM) to displace cement and increase the durability of concrete. Coal waste from mining is also a combination of coal and rock with tiny pores, which is a good source of *in-situ* $CO_2$ uptake.

**6)** Our technology can be easily integrated to power plants to capture $CO_2$ directly from the flue gas (e.g. our activated carbon from plastic waste has great selectivity to $CO_2$ versus $N_2$ at flue gas conditions) and/or use power plant wastes such as fly ash or bottom ash to make concrete. Thus, from the view point of co-locating $CO_2$ capture and use of power plant industrial wastes (fly-ash and bottom ash), this project has great synergy.

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