

BIOMINERALIZATION FOR CARBON SEQUESTRATION

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INTRODUCTION

The purpose of this research is to develop an understanding of the mechanisms by which iron-reducing and carbonate-precipitating microorganisms sequester carbon dioxide into solid carbonate mineral phases and to use this knowledge to design biological processes to capture carbon dioxide from fossil fuel plants while stabilizing fly ash wastes. This research will develop a scenario by which fly ash is stabilized into carbonate solid conglomerates that could potentially be useful as fill materials or road construction aggregates. We envision an open system whereby ash collection ponds would be colonized with calcareous microorganisms capable of producing calcite, aragonite, and iron carbonates such as siderite. These carbonates would be formed in-situ, at depth by anaerobic carbonate producing bacteria. Results to date demonstrate that iron-reducing bacteria indeed convert CO_2 into sparingly soluble carbonate minerals such as calcite and siderite using metal containing fly ash and lime. Biological carbonate mineral formation using fly ash and lime materials indicated that bacteria may complement the capture of carbon dioxide from fossil fuel plants while potentially stabilizing fly ash wastes and bind the fly ash into solid materials. First, it would remove carbon from the atmosphere and immobilize it into a stable mineral phase. Second, it could turn waste ash into a useful product. Third, it could at the very least stabilize the ash to reduce the leaching of metals into the environment. Fourth, the process could be combined with a waste treatment strategy in which the carbonate forming microbes would use waste products from agriculture or food processing to supply energy for microbial growth. This would constitute energy plexing by combining multiple diverse waste streams into new products.

GOALS AND EXPERIMENTAL APPROACH

The objective of this research is to examine biogeochemically facilitated carbon sequestration processes using metal-rich fly ash in the presence of CO_2 atmosphere as well as in HCO_3^- buffered media. Biological conversion of CO_2 into sparingly soluble carbonate minerals such as calcite (CaCO_3) and siderite (FeCO_3) has been studied using Fe(III)-reducing bacteria in conjunction with metal containing fly ash and lime. This coal utilization research will develop a scenario by which fly ash is stabilized into carbonate solid conglomerates that could potentially be useful as fill materials or road construction aggregates.

Psychrotolerant (NV-1, W3-7-1), mesophilic (BrY), and thermophilic (TOR-39, C1) Fe(III)-reducing bacteria were used to examine biogeochemical processes such as dissolution and mineralization using fly ash in the presence of N₂, N₂-CO₂, and H₂-CO₂ headspace gases as well as in HCO₃⁻ buffered media (30–210 mM). In this study, we examined the microbial formation of carbonate minerals using thermophilic (*Thermoanaerobacter ethanolicus*, TOR-39), mesophilic (*Shewanella alga*, BrY), psychrotolerant (*Shewanella alga*, NV-1; *Shewanella pealeana*, W3-7-1), and alkaliphilic (CBS-011, *Alkaliphilus transvaalensis*) bacteria (Table 1).

Table 1. Microbial isolates chosen for current and ongoing investigations at ORNL

Organisms	Source	Incubation temperature	Electron donors used for growth
TOR-39	Subsurface sediments	45–75°C, Thermophile	Glucose, Lactate, Formate
C1	Subsurface sediments	45–75°C, Thermophile	Glucose, Lactate, Pyruvate, H ₂ , Formate
BrY	Estuary sediments	25°C, Mesophile	Lactate, H ₂ , Formate
W3-6-1	Oceanic sediments	0–37°C, Psychrotolerant	Lactate, H ₂ , Formate
NV-1	Sea water near hydrothermal vent	0–37°C, Psychrotolerant	Lactate, H ₂ , Formate
CBS-011	Boron-rich sites at the U.S. Borax mine in Borax, CA	High level of salt (~12% NaCl) and boric acid (2–8 g/L B) at pH 9–0, Alkaliphile	Lactate, H ₂ , Formate, Acetate

Table 2 shows the Fe- and Ca-rich fly ashes and lime chosen for biologically facilitated precipitation of carbonate minerals for carbon sequestration. These Fe- and Ca-rich fly ashes selected based on mineralogical and chemical characterization from several sources.

Table 2. Fly ash and lime currently investigated at ORNL

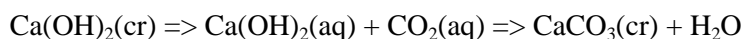
Material	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Mineralogy
ORNL Steam Plant Ash Oak Ridge, TN	7.7	34.4	19.1	15.2	1.8	0.4	Mullite (Al ₆ Si ₃ O ₁₅), Quartz (SiO ₂)
TVA Bull Run Ash, Oak Ridge, TN	6.4	48.1	24.4	8.4	1.6	0.9	Mullite (Al ₆ Si ₃ O ₁₅), Quartz (SiO ₂)
TVA Johnsonville Ash Chattanooga, TN	8.4	44.9	20.9	24.7	2.5	1.1	Mullite (Al ₆ Si ₃ O ₁₅), Maghemite (Fe ₂ O ₃), Quartz (SiO ₂)
Springerville Ash Joseph city, AZ	11.4	45.9	19.1	2.9	15.0	0.9	Mullite (Al ₆ Si ₃ O ₁₅), Portlandite [Ca(OH) ₂], Quartz (SiO ₂)
ORNL Inhouse Lime	11.7	8.9	1.5	0.7	44.8	22.9	Calcite (CaCO ₃), Quartz (SiO ₂)

The Fe(III)-reducing bacteria (Table 1) and metal-rich fly ashes (Table 2) were used to examine microbially facilitated precipitation and mineral formation in the presence of N₂, N₂-CO₂ (80% N₂-20% CO₂), and H₂-CO₂ (80% H₂/20% CO₂) headspace and different bicarbonate buffer concentration (30–210 mM). Experiments were performed at 25°C for psychrotolerant cultures (W3-7-1, NV-1), the alkaliphilic culture (CBS-011) and for the mesophilic culture (BrY), and at 60–65°C for the thermophilic culture (TOR-39, C1).

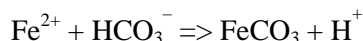
TECHNICAL PROGRESS

The Fe(III)-reducing bacteria (Table 1) and metal-rich fly ash (Table 2) were used to quantify the increased microbially facilitated precipitation and mineral formation in the presence of N₂ and CO₂ (80% N₂-20% CO₂ and 80% H₂/20% CO₂) headspace and under the different bicarbonate buffer concentration (30–210 mM). Under all conditions examined in batch systems of 15 ml to 4 liters the presence of microorganisms dramatically increased carbon sequestration.

XRD analysis showed that the Fe(III)-reducing bacteria precipitated calcium carbonate and iron carbonate using metal-rich fly ash with a H₂-CO₂ atmosphere and using bicarbonate buffer (>120 mM). SEM with EDX spectra showed that calcium carbonate precipitated by bacteria using fly ash and lime. No carbonate minerals formed using fly ash and lime without bacteria. SEM and EDX analysis also showed that the Fe(III)-reducing bacteria facilitated the precipitation of calcite using Ca-rich Springerville fly ash (15% Ca) under a H₂/CO₂ atmosphere and a high bicarbonate buffer (210 mM). The Fe(III)-reducing bacteria facilitated calcite precipitation using Ca-rich fly ash or Ca-poor fly ash plus lime under a H₂-CO₂ atmosphere and a high bicarbonate buffer (210 mM):



XRD analysis showed that increased bicarbonate buffer (210 mM HCO₃⁻) facilitated biomineralization of siderite using Fe-rich Johnsonville fly ash (25% Fe₂O₃) and ORNL steam plant ash (15% Fe₂O₃) under a N₂ atmosphere at 65°C. SEM with EDX spectra showed that microbially-facilitated precipitation of iron carbonate with the Fe-rich fly ashes under a H₂-CO₂ atmosphere. In environments with high bicarbonate concentrations, the microbial production of Fe(II) from Fe-rich fly ash may stimulate siderite formation:



This study indicates that siderite and calcite precipitation using metal-rich fly ash lime is generally associated with the bacterial metabolism of organic matter and hydrogen coupled with microbial Fe(III) reduction in the presence of reducing environments and high bicarbonate buffer or a H₂/CO₂ atmosphere.

High alkalinity and Fe(II) ions, as prompted by bacterial activity, seem important to biologically facilitated precipitation of carbonate minerals such as calcite and siderite. The microbial production of Fe(II) and lowered redox potential (Eh) also stimulates siderite precipitation.

The atmosphere and bicarbonate buffer concentration in conjunction with biomineralization processes exhibited profound influences on the types of minerals and the rate of carbonate mineral precipitation. Total carbon analysis of Ca-rich fly ash used for carbon sequestration showed that total carbon content in fly ash directly correlated with $p\text{CO}_2$ and NaHCO_3 concentration. The capacity of Fe(III)-reducing bacteria to precipitate carbonate minerals such as calcite and siderite using metal-rich fly ash creates the possibility of more effective CO_2 sequestration than would be possible with photosynthetic systems in alkaline ponds. In addition to microbially facilitated precipitation of carbonate minerals using fly ash, the microbial utilization of organic matter and hydrogen to produce sparingly soluble carbonate minerals may also contribute to direct or indirect precipitation of redox sensitive metals in fly ash ponds.

Scale-up experiments (up to 4-L scale experiment) using thermophilic metal-reducing bacteria have proved successful at sequestering carbon while using Ca and Fe-rich fly ash (Fig. 1). Biomineralization processes for carbon sequestration dramatically reduced water-soluble metals such as iron, calcium, and other metals under blankets of carbon dioxide. These upscaled experiments show potential for dramatic improvements of carbon and metal sequestration by complementing existing fly ash handling with biomineralization processes.

The capacity of iron-reducing bacteria to precipitate carbonate and metal containing minerals using fly ash creates the possibility of more effective CO_2 and metal sequestration than would be possible with photosynthetic systems in alkaline ponds and far greater than current technologies. In environments with high bicarbonate concentrations, the microbial production of Fe(II) from Fe-rich fly ash may stimulate siderite formation. Ca-rich fly ash or lime facilitated the calcium carbonate crystallization by the organisms altering local Eh, pH, and nucleation conditions. Biological carbonate mineral formation using



Fig. 1. Scale-up carbon sequestration experiment using Ca-rich fly ash and Fe(III)-reducing bacteria (TOR-35) at 60°C.

fly ash and lime materials indicated that bacteria may complement the capture of carbon dioxide from fossil fuel plants while potentially stabilizing fly ash wastes and solving red water problem in leachate from fly ash ponds. Interestingly, the results also suggest that many fly ash streams are less than saturated with respect to carbon dioxide. While biologically facilitated mineralization resulted in dramatic impacts, a significant portion of the total sequestration (30–60%) could be accomplished by saturating the fly ash waters with carbon dioxide. Future efforts will include discussions for the potential utility of engineered upscaling of both biotic and abiotic mechanisms of increased carbon and metal sequestration in fly ash streams.

Solution chemistry data showed pH decreased from 8.0 to 6.5 and Eh decreased from ~40 mV to -550 mV during the growth of the Fe(III)-reducing bacteria. Microbial processes with lactate and fly ash under a higher bicarbonate buffer (140–210 mM) resulted in lower Eh values than microbial process with a lower bicarbonate buffer (30–70 mM) (Fig. 2), suggesting greater microbial reduction of Fe(III) in association with the increased bicarbonate buffering capacity. Similarly, the microbial utilization of hydrogen under a H₂-CO₂ atmosphere resulted in significantly lower Eh values (< -450 mV) than lactate utilization under a N₂ (~200 mV) and a N₂-CO₂ (~300 mV) atmosphere, suggesting greater microbial reduction of Fe(III) in association with H₂ oxidation. The observation of microbial siderite and calcite formation using metal-rich fly ash in a higher bicarbonate buffer (210 mM) and under a H₂-CO₂ atmosphere was consistent with the Eh measurement. The presence of a H₂-CO₂ atmosphere and the high bicarbonate buffer (210 mM) provided more reducing conditions and significant buffering capacity allowing the complete reduction of Fe(III) in metal-rich fly ash than did the N₂/N₂-CO₂ atmosphere and low bicarbonate buffer

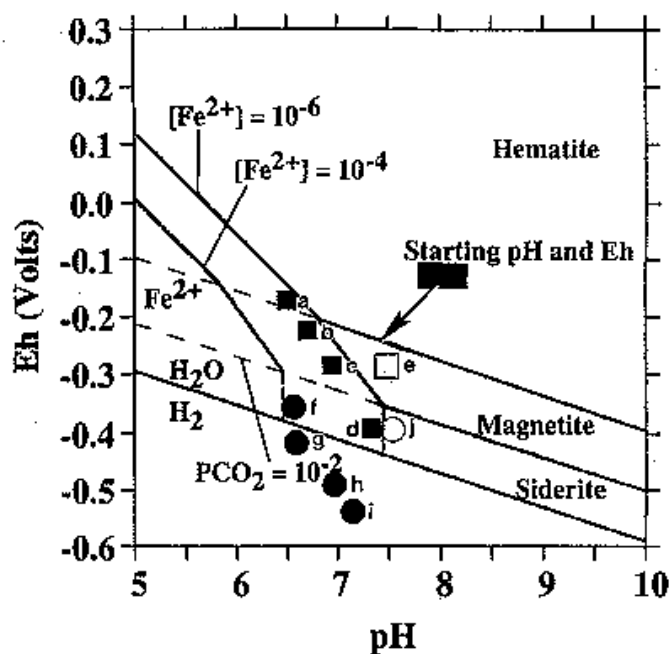


Fig. 2. Eh-pH stability fields for hematite, magnetite, and siderite in the water-iron-CO₂ system at 25°C and 1 atm total pressure (modified from Zhang et al., 1997). (a) 30 mM HCO₃⁻, TOR-39; (b) 70 mM HCO₃⁻, TOR-39; (c) 140 mM HCO₃⁻, TOR-39; (d) 210 mM HCO₃⁻, TOR-39; (e) control; (f) 30 mM HCO₃⁻, C1; (g) 70 mM HCO₃⁻, C1; (h) 140 mM HCO₃⁻, C1; (i) 210 mM HCO₃⁻, C1; (j) control.

(30–140 mM). Thus, the Eh-pH diagram shows that carbonate minerals including calcite and siderite precipitation is likely facilitated by the microbial alternation of Eh conditions, pH conditions, or both and creating conditions of potentially localized supersaturation with respect to a mineral phase.

Chemical analysis of water-soluble metals in the culture media after incubation revealed that the leaching of Li, Si, K, Ca, Fe, Ti, Co, Se, Br, Rb, Sr, Mo, Ba, Cd, and Cs from fly ash was significantly reduced in the presence of a CO₂ atmosphere (Fig. 3) and in HCO₃⁻ buffered media (>140 mM) (data not shown). This effect was likely a consequence of microbial metal reduction and the precipitation of carbonate minerals in the presence of appropriate electron donors such as hydrogen, lactate, and glucose. Water-soluble metals were expected sequestered into carbonate mineral during the mineralization of carbonate minerals.

APPLICATION

The capacity of iron-reducing bacteria to precipitate carbonate and metal containing minerals using fly ash creates the possibility of more effective CO₂ and metal sequestration than would be possible with photosynthetic systems in alkaline ponds and far greater than current technologies.

In environments with high bicarbonate concentrations, the microbial production of Fe(II) from Fe-rich fly ash may stimulate siderite formation. Ca-rich fly ash or lime facilitated the calcium carbonate crystallization by the organisms altering local Eh, pH, and nucleation conditions. Biological carbonate mineral formation using fly ash and lime materials indicated that bacteria may complement the capture of carbon dioxide from fossil fuel plants while potentially stabilizing fly ash wastes and solving red water problem in leachate from fly ash ponds. Interestingly, the results also suggest that many fly ash streams are less than saturated with respect to carbon dioxide. While biologically facilitated mineralization resulted in dramatic impacts, a significant portion of the total sequestration (30–60%) could be accomplished by saturating the fly ash waters with carbon dioxide. Future efforts will include discussions with TVA and the Paradise plant as to the potential utility of engineered upscaling of both biotic and abiotic mechanisms of increased carbon and metal sequestration in fly ash streams.

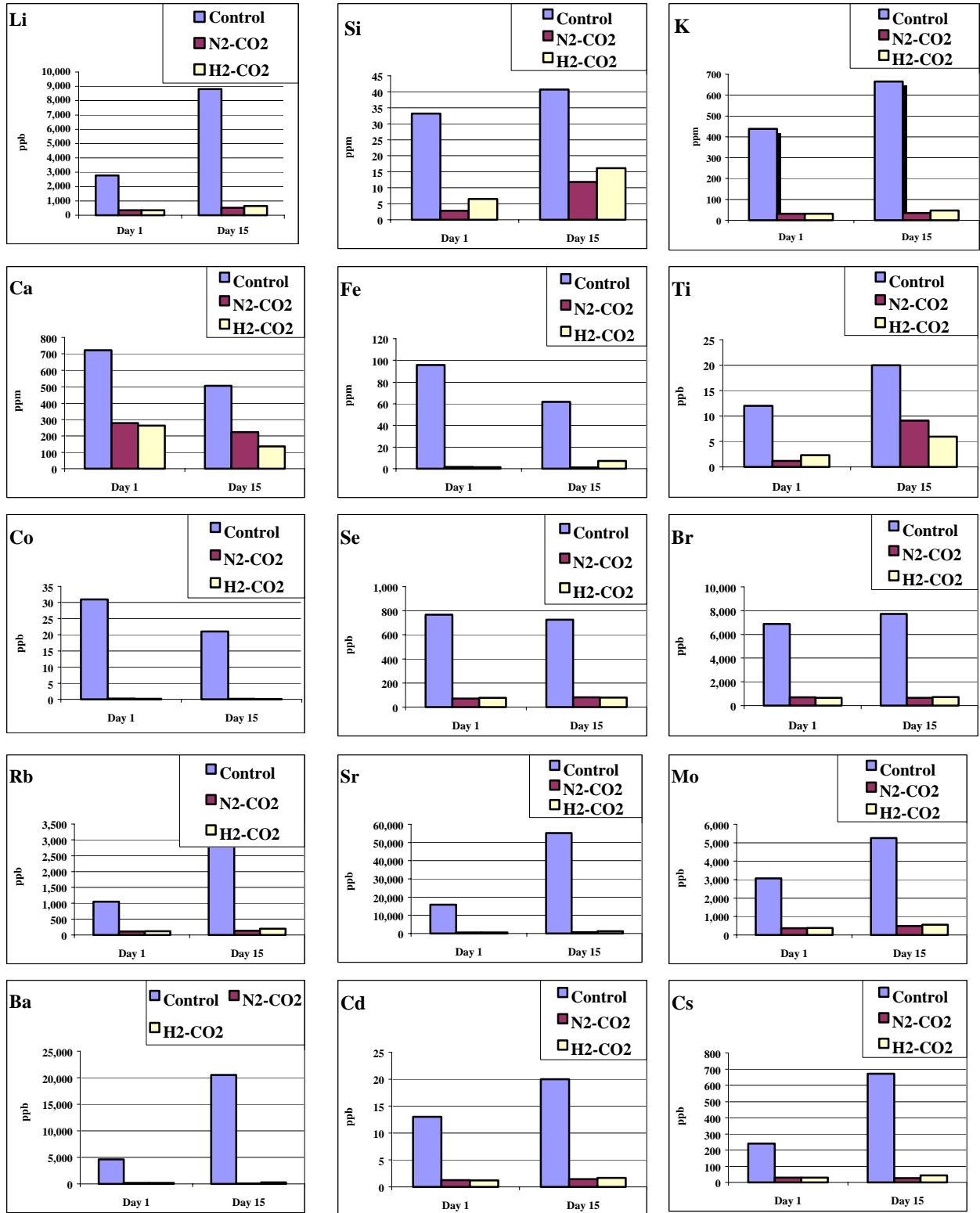


Fig. 3. Water soluble metals after Ca-rich Springerville fly ash used for carbon sequestration (20% CO₂).

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