

## Utilization of Biomineralization Processes with Fly Ash for Carbon Sequestration

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### *Introduction*

The Department of Energy (DOE) Energy Information Administration estimates atmospheric greenhouse gas releases may exceed 8 billion metric tons by the year 2010 heightening its international environmental concern. Carbon dioxide will dominate the greenhouse gases (Kane and Klein, 1997) and the majority of these results from the use of fossil fuels. With viable replacement of fossil fuels remaining decades away, alternatives for reducing the impacts of atmospheric CO<sub>2</sub> accumulations will surely include carbon sequestration and carbon management.

Current cost for carbon sequestration scenarios range from approximately \$60-500 per ton of carbon dioxide captured plus additional costs for transport and disposal (\$4-600/t C) (Riemer and Ormerod, 1995). Cost effective carbon sequestration technologies demand low transport and disposal costs or more preferably the conversion to useable products. Biological uptake via reforestation and soil formation certainly represent low cost and known technologies. Unfortunately, complete reforestation of available area may sequester <20% of the 1990 CO<sub>2</sub> emissions (Riemer and Ormerod, 1995). Therefore, terrestrial primary production may be insufficient to resolve the problem. Though bio-fuels represent a sustainable option, there are cost penalties plus emissions of greenhouse gases such as CH<sub>4</sub> and N<sub>2</sub>O (Bachu et al., 1994). While injection of CO<sub>2</sub> into local geologic formations or sea floors may be a reasonable component for our carbon management strategy (Herzog et al., 1991; Bachu et al., 1994), Riemer and Ormerod (1995) correctly suggested that deep ocean injection is not immediately applicable due to a lack of information about the physiological effects of dissolved CO<sub>2</sub> on marine life as well as political complexities of deep sea disposal.

The focus of this research is to develop a fundamental understanding of the large-scale precipitation of carbonate-solids. The utilization of biological processes for the precipitation of low quality aggregates is an early example of energy-plexing; combining known diverse energy processes into a close-proximity constructive product line. We

envision an energy-plex gaining advantage from alkaline ecosystems analogous to the algal ponds of the Great Salt Lake during its low period of the 1970's. While the surface of the lake was algal rich, there was complex biogeochemical processing occurring in the waters facilitating the production of carbonate-rich deposits. We propose adding the carbonate precipitating aspects of high ionic strength microbial cultures with biogeochemically robust anaerobic microorganisms that precipitate carbonates in the water and sediments. Anaerobic Fe(III)-reducing bacteria precipitate or transform crystalline or amorphous iron oxides into crystalline Fe phases such as magnetite (Fe<sub>3</sub>O<sub>4</sub>), siderite (FeCO<sub>3</sub>), vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)•2H<sub>2</sub>O], iron sulfide (FeS), and maghemite (Fe<sub>2</sub>O<sub>3</sub>) (Zhang et al., 1997, 1998; Fredrickson et al., 1998; Roh et al., 2001). Biological conversion of CO<sub>2</sub> into sparingly soluble carbonate rocks such as siderite (FeCO<sub>3</sub>) and calcite (CaCO<sub>3</sub>) using metal reducing bacteria and metal containing fly ash plus other low-value products has potential for low cost carbon sequestration strategies (Roh et al., 2000).

**Objective**

The objective of this study is to examine biogeochemically facilitated carbonate precipitation processes using metal-rich fly ash in the presence of different atmospheres (N<sub>2</sub>, N<sub>2</sub>-CO<sub>2</sub>, and H<sub>2</sub>-CO<sub>2</sub>) as well as in HCO<sub>3</sub><sup>-</sup> buffered media (30 - 210 mM). Biological conversion of CO<sub>2</sub> into sparingly soluble carbonate minerals such as calcite (CaCO<sub>3</sub>) and siderite (FeCO<sub>3</sub>) 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 bonded conglomerates that could potentially be useful as fill materials or road construction aggregates.

**Approach**

Psychrotolerant (PV-4, W3-7-1), mesophilic (BrY), and thermophilic (TOR-39, C1) Fe(III)-reducing bacteria were used to examine biogeochemical processes such as

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 <sub>2</sub> , Formate
BrY	Estuary sediments	25°C Mesophile	Lactate, H <sub>2</sub> , Formate
W3-6-1	Oceanic sediments	0 – 37°C Psychrotolerant	Lactate, H <sub>2</sub> , Formate
PV-4	Sea water near hydrothermal vent	0 – 37 °C Psychrotolerant	Lactate, H <sub>2</sub> , Formate

dissolution and mineralization using fly ash in the presence of N<sub>2</sub>, N<sub>2</sub>-CO<sub>2</sub>, and H<sub>2</sub>-CO<sub>2</sub> headspace gases as well as in HCO<sub>3</sub><sup>-</sup> buffered media (30 - 210 mM). In this study, we examined the microbial formation of carbonate minerals using thermophilic (*Thermoanaerobacter ethanolicus*, TOR-39; ) (Liu et al., 1997), mesophilic (*Shewanella alga*, BrY) (Rossello-Mora et al., 1994), and psychrotolerant (*Shewanella alga*, PV-4; *Shewanella pealeana*, W3-7-1) (Stapleton et al., 2000) bacteria (Table 1).

Culture media contained the following ingredients (g/L): 2.5 NaHCO<sub>3</sub>, 0.08 CaCl<sub>2</sub>•2H<sub>2</sub>O, 1.0 NH<sub>4</sub>Cl, 0.2 MgCl<sub>2</sub>•6H<sub>2</sub>O, 10.0 NaCl, 7.2 HEPES, 1.0 resazurin (0.01%), 0.5 yeast extract, and 10 ml. Oak Ridge National Laboratory (ORNL) trace minerals, and 1 ml ORNL vitamin solutions (Phelps et al., 1989). No reducing agents were added to media. Table 2 shows the Fe- and Ca-rich fly ashes and lime chosen for this study. These Fe- and Ca-rich fly ashes were selected based on mineralogical and chemical characterization from several sources.

Table 2. Fly ash and lime currently investigated at ORNL

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

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 N<sub>2</sub>, N<sub>2</sub>-CO<sub>2</sub> (80% N<sub>2</sub>-20% CO<sub>2</sub>), and H<sub>2</sub>-CO<sub>2</sub> (80% H<sub>2</sub>/20% CO<sub>2</sub>) headspace. Effect of bicarbonate buffer concentration (30 - 210 mM) was also examined using those Fe(III)-reducing bacteria. The pH of the medium containing metal-rich fly ash was

adjusted from 6.5 to 9.5. Hydrogen (100% or 80% H<sub>2</sub>/20% CO<sub>2</sub>), glucose (10 mM), or lactate (10 mM) served as an electron donor (Table 1). Experiments were performed at 25 °C for psychrotolerant cultures (W3-7-1, PV-4) and for the mesophilic culture (BrY), and at 60 - 65°C for the thermophilic culture (TOR-39, C1). Experiments were terminated after 30 days of incubation for the psychrotolerant and mesophilic bacteria and after 21 days for the thermophilic bacteria.

Eh and pH values in the media were determined at room temperature in an anaerobic chamber (Zhang et al., 1997). Water-soluble metals including Ca and Fe in the media with fly ashes were determined by inductively coupled plasma (ICP) spectroscopy. Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDX) was used for the analysis of fly ash particle morphology and elemental compositions. The mineralogical composition of the fly ashes was determined using X-ray diffraction analysis (XRD).

### **Results**

**Solution chemistry:** Measurements of Eh and pH values were plotted (Fig. 1) on Eh-pH stability fields for hematite, magnetite, and siderite in the iron-water-CO<sub>2</sub> system at 25°C and 1 atm total pressure (Zhang et al., 1997). During the growth of the Fe(III)-reducing bacteria, pH decreased from 8.0 to 6.5 and Eh decreased from ~40 mV to -550 mV (Fig. 1). 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. 1), suggesting greater microbial reduction of Fe(III) in association with the increased bicarbonate buffering capacity.

Similarly, the microbial utilization of hydrogen under a H<sub>2</sub>-CO<sub>2</sub> atmosphere resulted in significantly lower Eh values (< -450 mV) than lactate utilization under a N<sub>2</sub> (~200 mV) and a N<sub>2</sub>-CO<sub>2</sub> (~300 mV) atmosphere (data not shown), suggesting greater microbial reduction of Fe(III) in association with H<sub>2</sub> oxidation. The observation of microbial siderite and calcite formation using metal-rich fly ash in a higher bicarbonate buffer (210 mM) and under a H<sub>2</sub>-CO<sub>2</sub> atmosphere was consistent with the Eh measurement. The presence of a H<sub>2</sub>-CO<sub>2</sub> 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 ashes than did the N<sub>2</sub>/N<sub>2</sub>-CO<sub>2</sub> atmosphere and low bicarbonate buffer (30 – 140 mM). Thus, the Eh-pH diagram shows that precipitation of carbonate minerals including calcite and siderite is likely facilitated by the microbial alteration of Eh, pH, or both and creating conditions of localized supersaturation with respect to a mineral phase (Zhang et al., 1997).

Chemical analysis of water-soluble metals in the culture media after incubation revealed that the leaching of Ca and Fe from fly ash was significantly reduced in the presence of a H<sub>2</sub>-CO<sub>2</sub> atmosphere (Fig. 2) and in HCO<sub>3</sub><sup>-</sup> 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.

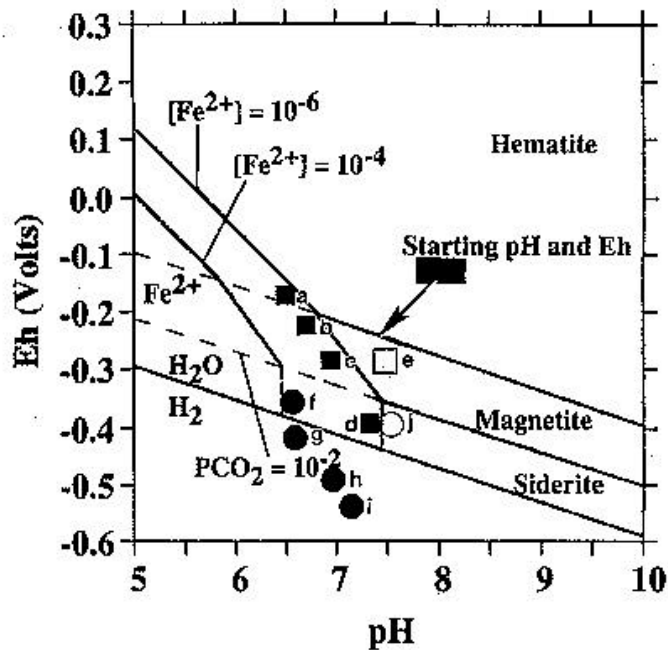


Figure 1. Eh-pH stability fields for hematite, magnetite, and siderite in the water-iron-CO<sub>2</sub> system at 25°C and 1 atm total pressure (modified from Zhang et al., 1997). (a: 30 mM HCO<sub>3</sub><sup>-</sup>, TOR-39; b: 70 mM HCO<sub>3</sub><sup>-</sup>, TOR-39; c: 140 mM HCO<sub>3</sub><sup>-</sup>, TOR-39; d: 210 mM HCO<sub>3</sub><sup>-</sup>, TOR-39; e: control; f: 30 mM HCO<sub>3</sub><sup>-</sup>, C1; g: 70 mM HCO<sub>3</sub><sup>-</sup>, C1; h: 140 mM HCO<sub>3</sub><sup>-</sup>, C1; i: 210 mM HCO<sub>3</sub><sup>-</sup>, C1; j: control)

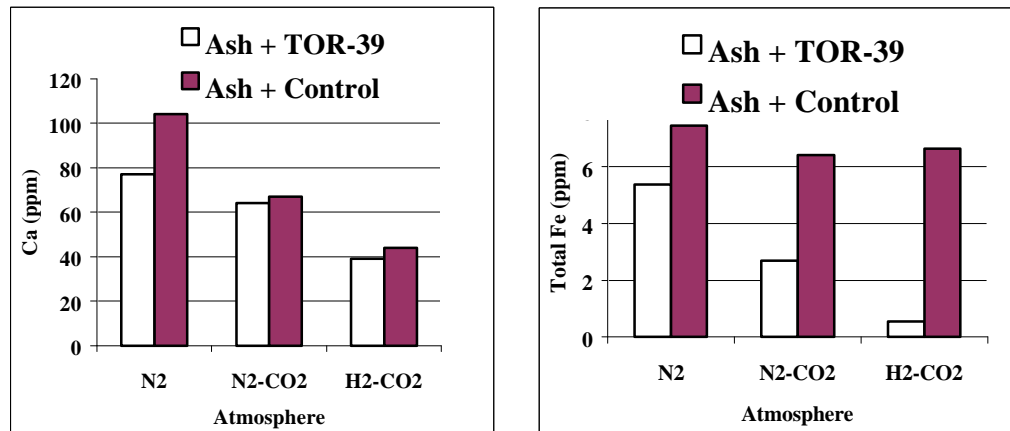
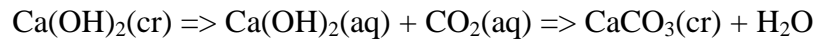
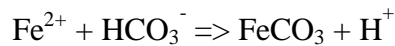


Figure 2. Water soluble Ca and Fe after microbial precipitation and mineralization processes using fly ash (left: ORNL steam plant fly ash (95%) + lime (5%); right: Johnsonville fly ash)

**Biom mineralization under the different atmospheres and bicarbonate concentrations:** XRD analysis (Fig. 3) showed that the Fe(III)-reducing bacteria precipitated calcium carbonate using Bull Run power plant fly ash (95%) with lime (5%) under a H<sub>2</sub>-CO<sub>2</sub> atmosphere at 60°C incubation temperature. SEM with EDX spectra showed that calcium carbonate precipitated by bacteria using fly ash and lime (Fig. 4). No carbonate minerals formed using fly ash and lime without bacteria (Fig. 4). SEM and EDX analysis also showed that the Fe(III)-reducing bacteria facilitated the precipitation of calcite using Ca-rich Springerville fly ash (15%) under a H<sub>2</sub>/CO<sub>2</sub> atmosphere and a high bicarbonate buffer (210 mM) (data not shown). The Fe(III)-reducing bacteria facilitated calcite precipitation using Ca-rich fly ash or Ca-poor fly ash plus lime under a H<sub>2</sub>-CO<sub>2</sub> atmosphere and a high bicarbonate buffer (210 mM):



XRD analysis showed that increased bicarbonate buffer (210 mM HCO<sub>3</sub><sup>-</sup>) facilitated biomineralization of siderite using Fe-rich Johnsonville fly ash (25% Fe<sub>2</sub>O<sub>3</sub>) and ORNL steam plant ash (15% Fe<sub>2</sub>O<sub>3</sub>) under a N<sub>2</sub> atmosphere at 65°C (Fig. 5). SEM with EDX spectra showed microbially-facilitated precipitation of iron carbonate with the Fe-rich fly ashes under a H<sub>2</sub>-CO<sub>2</sub> atmosphere (Fig. 6). 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 plus 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 H<sub>2</sub>/CO<sub>2</sub> 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 (Fredrickson, 1998).

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. 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<sub>2</sub> sequestration than would be possible with photosynthetic systems in alkaline ponds. In addition to precipitation of carbonate minerals, the microbial utilization of organic matter and hydrogen may also contribute to direct or indirect precipitation of redox sensitive metals in fly ash ponds.

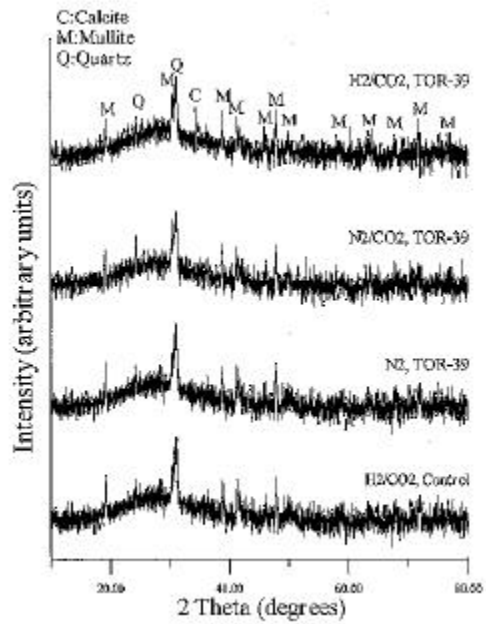


Figure 3. XRD analysis of fly ash used from microbial precipitation of carbonate minerals under different atmospheres

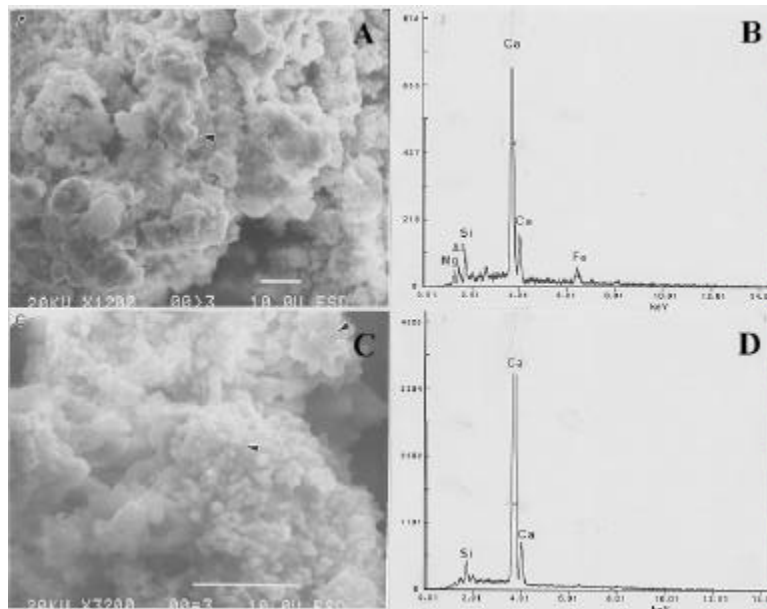


Figure 4. SEM/EDX analysis of fly ash plus lime used for microbial precipitation of carbonate minerals under a H<sub>2</sub>-CO<sub>2</sub> atmosphere (A and B: without bacteria; C and D: with bacteria).

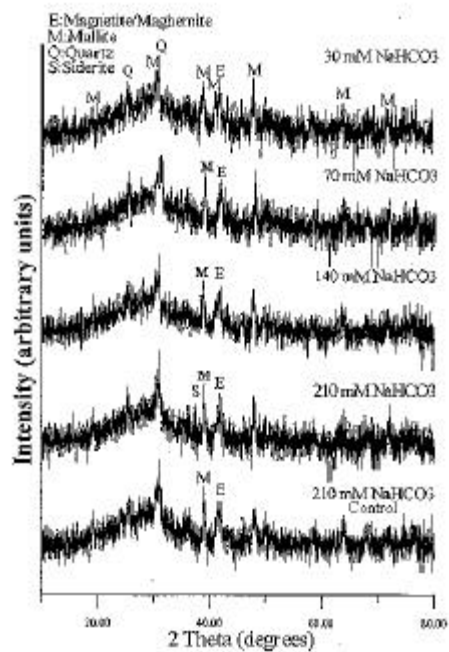


Figure 5. XRD analysis of fly ash used from microbial precipitation of carbonate minerals under different bicarbonate buffer concentrations.

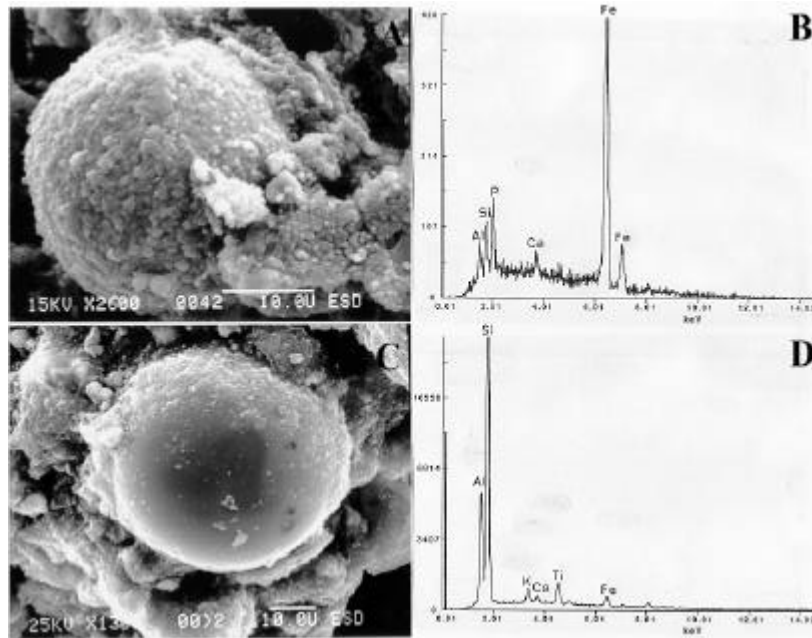


Figure 6. SEM/EDX analysis of Johnsonville Fe-rich fly ash used for microbial precipitation of carbonate minerals using 210 mM bicarbonate buffer (A and B: with bacteria; C and D: without bacteria).



### ***Application***

Assuming significant upscaling issues a set of fly ash ponds, 8 - 10 m (25 - 30 ft) depth with residence times of weeks, may handle 10,000 tons of ash per day (ash from >40,000 tons of coal per day). One may sequester 1/3 of the approximately 20,000 tons of carbon dioxide bubbled through the ponds each day as some will surely escape. Sequestration mechanisms would include algal precipitation, anaerobic microbial sequestration, and abiotic geochemical precipitation. To the mixture of ash, agricultural wastes, water, and bubbled carbon dioxide one could readily add hundreds of tons of waste cement kiln dust per day enhancing the bio- and geo-chemical precipitation of carbonate minerals and carbon dioxide sequestration efficiency. Accordingly, one could estimate sequestering a small fraction of a pound of carbon per cubic ft of pond each day (one pound per day per 10 cubic ft of pond). Such an efficiency would represent approximately 10% of the efficiency of our microbial cultures observed in the laboratory in the absence of significant abiotic geochemical precipitation. By circulating warm process waters and heating the deeper portions of the ponds to 30-45°C the biogeochemical carbon sequestration rates could increase. Using the assumptions field sequestration may represent less than 1% of the metabolic efficiency of our lab cultures. Therefore, use of warm recirculating waters to heat the ponds could accelerate rates of sequestration and/or require less land for the biogeochemical sequestration.

While most of the cost advantage represents offsets from disposal costs of fly ash the aggregate may have value as fill materials. Even with bulk discounts and close proximity the disposal costs from the waste streams often exceed \$35/ton. Added to the value of the product this process could represent a value gain of ~\$40/ton but more likely represent a gains of \$10-20 ton of aggregate or a net value gain of approximately \$2-5 per ton of sequestered carbon.

### ***Future Activities***

Through this research supported by DOE-FE carbon sequestration program through the National Energy Technology Laboratory (NETL) we will further the science of coal utilization as it pertains to carbon sequestration, stabilization of coal derived fly ashes, and producing usable conglomerates while stabilizing fly ashes.

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