

Biogeochemical Processes Utilizing Fly Ash for Carbon Sequestration

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ABSTRACT

The objective of this study is to investigate biogeochemical processes to sequester CO₂ and metals utilizing metal-rich fly ash. Microbial conversion of CO₂ into sparingly soluble carbonate minerals has been studied using metal-rich fly ash under different pCO₂ and different bicarbonate concentrations. Scaling from test tube to fermentation vessels (up to 4-L) using metal-reducing bacteria and metal-rich fly ash have proved successful at sequestering carbon dioxide and metals. CO₂ sequestration via precipitation processes using metal-rich fly ash may complement the capture of carbon dioxide from fossil fuel plants while potentially stabilizing fly ash wastes.

INTRODUCTION

Perhaps one of the most stimulating scientific discoveries of the 20th-century was the observation that the concentration of atmospheric CO₂ and its rate of increase have both been increasing since the 1950s (e.g., as measured at Mauna Loa, Hawaii). These fundamental data, when combined with long-term records through glacial-interglacial cycles of atmospheric CO₂ recovered from trapped air in ice cores from Antarctica has led climate scientists, atmospheric chemists, oceanographers, geochemists, and a host of other diverse specialists to focus efforts towards understanding how carbon is cycled between the four large reservoirs of the continents, seawater, sediments, and the atmosphere. While understanding this carbon cycle remains the focus of much study, the consensus is that anthropogenically driven increases in atmospheric CO₂ will play a major role in climate forcing during the coming centuries.

The 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, accounting for about 85% of the emissions (Kane and Klein, 1997), the majority of which result from the use of fossil fuels. With viable replacement of fossil fuels remaining decades away, alternatives for reducing the impacts of atmospheric CO₂ accumulations will surely include carbon sequestration and carbon management. Current cost for carbon fixation 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). We need cost effective carbon sequestration technologies coupled with very low transport and disposal costs or more preferably, the derivation of useable products.

Biological uptake via reforestation and soil formation certainly represents low costs and known technologies. Unfortunately, complete reforestation of available areas may sequester <20% of the 1990 CO₂ 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 CH₄ and N₂O (Bachu et al., 1994). While injection of CO₂ 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) suggested that deep ocean injection may not immediately be applicable.

Many species of microorganisms, mainly anaerobic metal-reducing bacteria, are capable of reducing amorphous and crystalline Fe oxides (Zhang et al., 1997; Liu et al., 1997). Anaerobic metal-reducing bacteria precipitated magnetite (Fe₃O₄), siderite (FeCO₃), vivianite [Fe₃(PO₄)•2H₂O], or sulfide (FeS). Recent studies demonstrated that partial pressures of CO₂ and ionic species composition of aqueous media exhibited profound influences on the type of minerals precipitated in anaerobic microbial cultures

(Roh et al., 2003). The formation of siderite was favored in reducing environments and high CO₂ partial pressure (Zhang et al., 1997; Roh et al., 2003). Minerals precipitated under a nitrogen atmosphere were predominantly magnetite. In the presence of 20% headspace CO₂, a mixture of magnetite and iron rich carbonates such as siderite was formed. It has been reported that calcite (CaCO₃) and magnesite (MgCO₃) may be precipitated by bacteria, algae and yeast (Thompson and Ferris, 1990; Cicerone et al., 1999). Determining the potential importance of the biogeochemical processes on carbonate mineral precipitation and gaining a fundamental understanding of the controlling factors, rate and extent of carbonate mineral precipitation will significantly advance our understanding of carbon management and the science of coal utilization.

The objective of this study was to investigate biogeochemical processes to sequester CO₂ and metals utilizing metal-rich fly ash. Biogeochemical conversion of CO₂ into sparingly soluble carbonate minerals such as calcite (CaCO₃) and siderite (FeCO₃) 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.

MATERIALS AND METHODS

Microorganisms used for carbon sequestration. Biogeochemical conversion of CO₂ into sparingly soluble carbonate minerals (e.g., iron carbonate and calcium carbonate) has been studied using metal-reducing bacteria isolated from diverse environments in conjunction with low-value products such as metal-containing fly ash. Table 1 shows thermophilic, psychrotolerant, and alkaliphilic Fe(III)-reducing bacteria isolated by ORNL researchers from a variety of cold, hot, and alkaline environments such as deep marine sediments, sea water near a hydrothermal vent, deep subsurface environments, and a leachate-pond containing high levels of salt and boric acid. For these experiments, thermophilic (*Thermoanaerobacter ethanolicus*, TOR-39 and C1), psychrotolerant (*Shewanella* alga, PV-4; *Shewanella pealeana*, W3-6-1 and W3-7-1), alkaliphilic (*Alkaliphilus transvaalensis*, QYMF) metal-reducing bacteria (Table 1) were used to examine biogeochemical processes for CO₂ sequestration using metal-rich fly ash.

Biogeochemical conditions and fly ash chemistry. Culture medium contained the following ingredients (g/L): 2.5 NaHCO₃, 0.08 CaCl₂•2H₂O, 1.0 NH₄Cl, 0.2 MgCl₂•6H₂O, 10 NaCl, 0.4 K₂HPO₄•3H₂O, 7.2 HEPES (hydroxyethylpiperazine-N²-2-ethanesulfonic acid), 1.0 rasazurin (0.01%), 0.5 yeast extract, and 10 trace minerals and 1 vitamin solutions (Phelps et al., 1989). No exogenous electron carrier substance (i.e., anthraquinone disulfonate) and reducing agent (i.e., cysteine) were added to the medium. Biogeochemical precipitation of carbonate minerals was performed using metal-rich fly ash (Table 2) plus metal-reducing bacteria (Table 1) isolated from diverse environments. The metal-rich fly ash was obtained from several sources were selected based on mineralogical and chemical characterization.

Experiments were performed at 25°C for psychrotolerant and alkaliphilic cultures (*Shewanella pealeana*, W3-7-1; *Shewanella* alga, PV-4; *Alkaliphilus transvaalensis*, QYMF), and at 65°C for the thermophilic culture (*Thermoanaerobacter ethanolicus*, TOR-39) (Table 1). Experiments were terminated after 30 days of incubation for psychrotolerant and alkaliphilic bacteria and after 22 days for thermophilic bacteria.

Biogeochemical processes for carbon sequestration using metal-reducing bacteria isolated from diverse environments (Table 1) and metal-rich fly ash (Table 2) were examined in the presence of different pCO₂ including N₂, N₂-CO₂ (95% N₂-5% CO₂; 80% N₂-20% CO₂), H₂-CO₂ (80% H₂-20% CO₂), CO₂ (100% CO₂). Experiments with CO₂ pressure (0.05%CO₂) close to the atmospheric CO₂ content were also examined to see the influence of low CO₂ on carbon sequestration. In addition, the effects of bicarbonate buffer concentration (30 - 210 mM) on biogeochemical processes for carbon sequestration was also examined using different concentrations of HCO₃⁻ buffered media (30 - 210 mM). The pH of the medium with metal-rich fly ash was varied from 6.5 to 9.5. Hydrogen (80% H₂-20% CO₂), glucose (10 mM), acetate (10 mM), or lactate (10 mM) served as electron donors to examine biogeochemical sequestration of carbon dioxide.

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

Isolates	Growth condition	Site Description	Geology/ Sample Type	Genus & species	References
TOR-39	Thermophilic (40 – 75°C)	Taylorsville Triassic Basin, Northern Virginia	Shale, Siltstone, and Sandstone	<i>Thermo- anerobacter ethanolicus</i>	Liu et al., 1997
C1	Thermophilic (40 – 75°C)	Piceance Basin Wasatch Formation, Western Colorado	Cemented sandstone; cross-bedded siltstones and shales	<i>Thermo- anerobacter ethanolicus</i>	Liu et al., 1997
PV-4	Psychro-tolerant (0 – 37°C)	Naha vents, Coast of Hawaii	Iron-rich microbial mat associated with a hydrothermal vent	<i>Shewanella alga</i>	Stapleton et al., 2003
W3-7-1	Psychro-tolerant (0 – 37°C)	Deep Pacific Ocean Marine Sediments	Marine sediment	<i>Shewanella pealeana</i>	Stapleton et al., 2003
QYMF	Alkaliphilic pH = 8.0 - 11	Boron-rich sites at the U. S. Borax mine in Borax, CA	Leachate-pond containing high level of salt (~12 % NaCl) and boric acid (2 - 8 g/L B) at pH 9 –10.	<i>Alkaliphilus transvaalensis</i>	Ye et al., 2003

Table 2. Fly ash and lime currently investigated for carbon sequestration 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)
TVA ParadiseAsh Paradise, KY	11.8	41.7	18.3	13.4	13.5	3.0	Mullite (Al ₆ Si ₃ O ₁₅), Maghemite (Fe ₂ O ₃), Hematite (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)

Geochemical and mineralogical characterization. To examine biogeochemical processes such as dissolution and carbonation using metal-rich coal fly ash in the presence of different $p\text{CO}_2$ and bicarbonate buffer concentrations, supernatants and fly ash slurry were geochemically and mineralogically characterized. The redox potential (Eh) and pH values in bacterial cultures at the beginning and end of the experiments were measured at room temperature in an anaerobic chamber. The pH measurements used a combination of pH electrode and an ORION EA 920 expandable ion analyzer (Orion Research, Beverly, MA), standardized with pH buffer 7 and the appropriate buffer of either pH 4 or 10 (Roh et al., 2001). Eh values were measured using platinum micro-electrodes (Microelectrodes, Inc., Londonderry, NH) (Roh et al., 2001). The probe was placed directly into the sample tube and equilibrated for at least 5 min before recording the value. Water-soluble metals including Ca, Na, Fe, and other elements in the solution with fly ash were determined by inductively coupled plasma mass (ICP-MS) spectroscopy. Total carbon contents of the metal-rich fly ash were determined using a Leco CR-12 dry combustion furnace (Leco, St. Joseph, MI). The mineralogy of fly ash was determined using X-ray diffraction analysis (XRD). All XRD was performed using a Scintag (Scintag, Inc, Sunnyvale, CA) XDS 2000 diffractometer (40 kV, 35 mV) equipped with Co-K α radiation with a scan rate of $2^\circ 2\theta$ /min. Chemical compositions of the fly ash were determined using ICP-AES. A JEOL JSM-35CF (JEOL LTD, Tokyo, Japan) scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) was used for the analysis of fly ash particle morphology and elemental compositions.

RESULTS AND DISCUSSION

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_2 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 processes with a lower bicarbonate buffer (30 – 70 mM) (Fig. 1A), suggesting greater microbial reduction of Fe(III) in association with the increased bicarbonate buffering capacity.

Similarly, the microbial utilization of hydrogen under a H_2 - CO_2 atmosphere resulted in significantly lower Eh values (< -450 mV) than lactate utilization under a N_2 (~ 200 mV) and a N_2 - CO_2 (~ 300 mV) atmosphere (Fig. 1B), suggesting greater microbial reduction of Fe(III) in association with H_2 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_2 - CO_2 atmosphere was consistent with the Eh measurement. The presence of a H_2 - CO_2 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 in contrast to the N_2/N_2 - CO_2 atmosphere and low bicarbonate buffer (30 – 140 mM). Thus, the Eh-pH diagram shows that carbonate minerals including calcite and siderite precipitation is likely facilitated by the microbial alteration of Eh and pH conditions, or both, and creating conditions of potentially localized supersaturation with respect to a mineral phase (Zhang et al., 1997).

Chemical analysis of water-soluble metals in the culture medium after incubation revealed that the leaching of Ca and Fe from fly ash was significantly reduced in the presence of a H_2 - CO_2 atmosphere (Fig. 2b) and in HCO_3^- buffered media (> 140 mM) (data not shown). In addition to microbially facilitated precipitation of carbonate minerals using fly ash, biogeochemical processes produced sparingly soluble carbonate minerals contributing to direct or indirect precipitation and sequestration of redox sensitive metals. This effect was likely a consequence of microbial metal reduction and the (co)precipitation of carbonate minerals in the presence of appropriate electron donors such as hydrogen, lactate, and glucose.

Biogeochemical Carbon Sequestration Under Different $p\text{CO}_2$ and Bicarbonate Concentrations. The atmospheric composition and bicarbonate buffer concentration in conjunction with biogeochemical processes exhibited profound influences on the types of minerals and the rate of carbonate mineral precipitation as shown in Fig. 3. Bottles containing metal-reducing bacteria and an energy sources led to more biogeochemically facilitated precipitation of carbonate minerals with redox-labile metals.

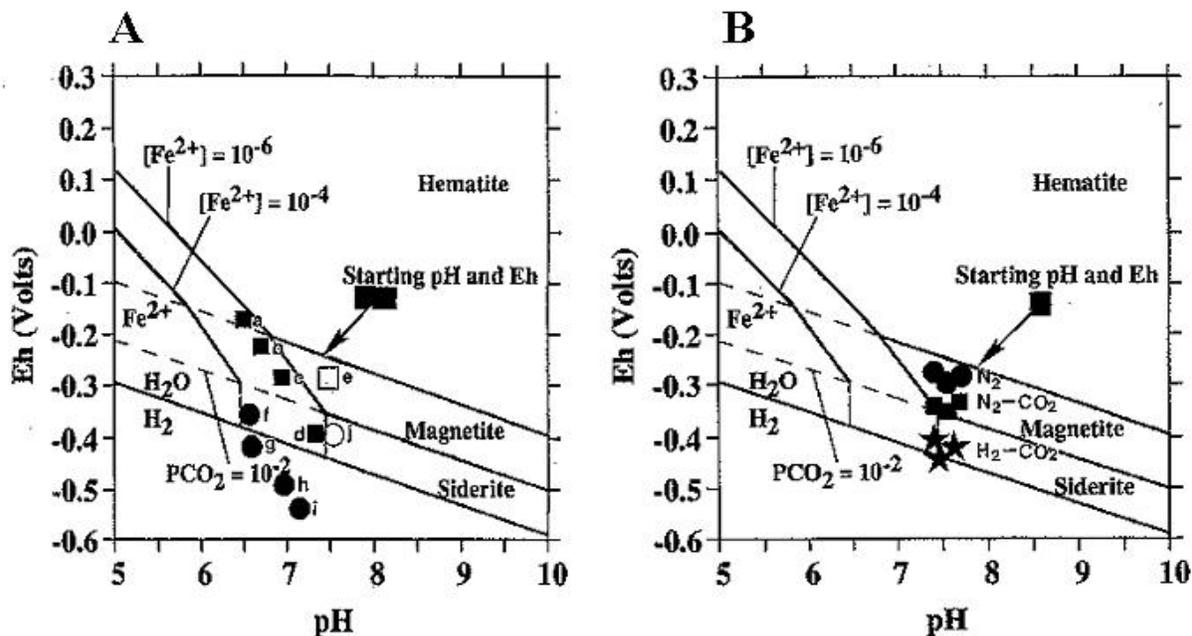
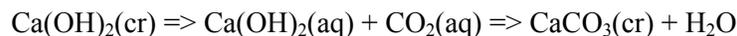
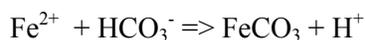


Figure 1. Eh-pH stability fields for hematite, magnetite, and siderite in the water-iron-CO₂ system at 25°C and 1 atm total pressure (modified from Zhang et al., 1997): (A) measured Eh and pH under different bicarbonate concentration (a: 30 mM HCO₃⁻, TOR-39; b: 70 mM HCO₃⁻, TOR-39; c: 140 mM HCO₃⁻, TOR-39; 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) and (B) measured Eh and pH under different atmospheric composition including N₂, N₂-CO₂ (80% N₂-20% CO₂), and H₂-CO₂ (80% H₂-20% CO₂).

XRD analysis (Fig. 4) showed that the biogeochemical processes induced precipitation of calcium carbonate, calcite (CaCO₃), using Ca-rich springville fly ash under the CO₂ atmospheres and with bicarbonate buffer at 60°C incubation temperature. SEM with EDX spectra also showed that biogeochemical processes precipitated calcium carbonate using Ca-rich fly ash under a H₂/CO₂ atmosphere and a high bicarbonate buffer (210 mM) (data not shown). No carbonate minerals formed using metal-rich fly ash without bacteria. The biogeochemical processes 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⁻) also 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 (data not shown). SEM with EDX spectra showed microbially-facilitated precipitation of iron carbonate with the Fe-rich fly ash under a H₂-CO₂ atmosphere (data not shown). In environments with high bicarbonate concentrations, the microbial production of Fe(II) from Fe-rich fly ash may stimulate siderite formation:



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 CO₂ 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.

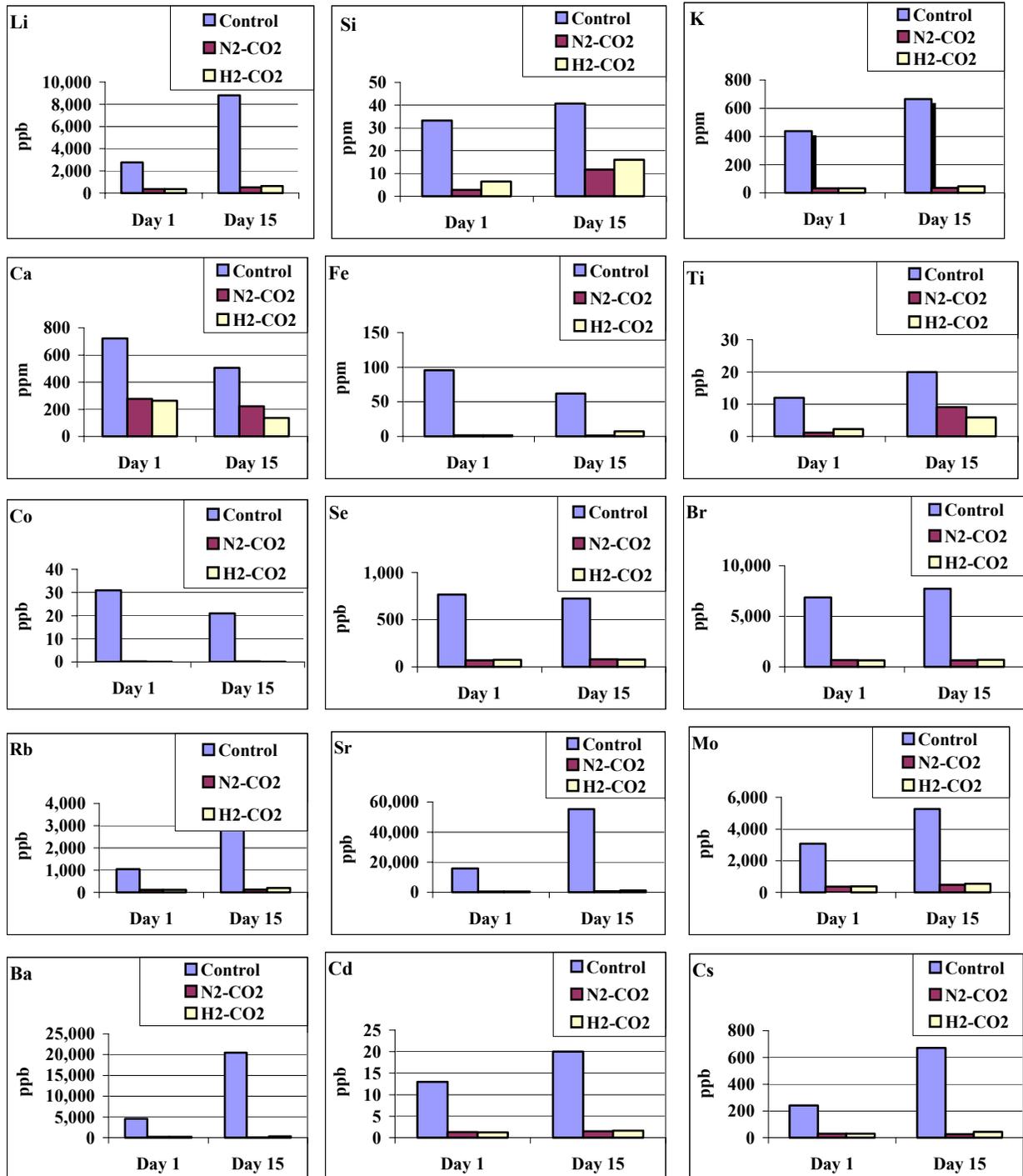


Figure 2. Water soluble metals in the culture media after incubation using Ca-rich Springerville fly ash and metal-reducing bacteria used for carbon sequestration (20% CO₂).



Figure 3. Scale-up carbon sequestration experiment using Fe-rich fly ash (left) and Ca-rich fly ash (right) with Fe(III)-reducing bacteria (TOR-35) at 60°C

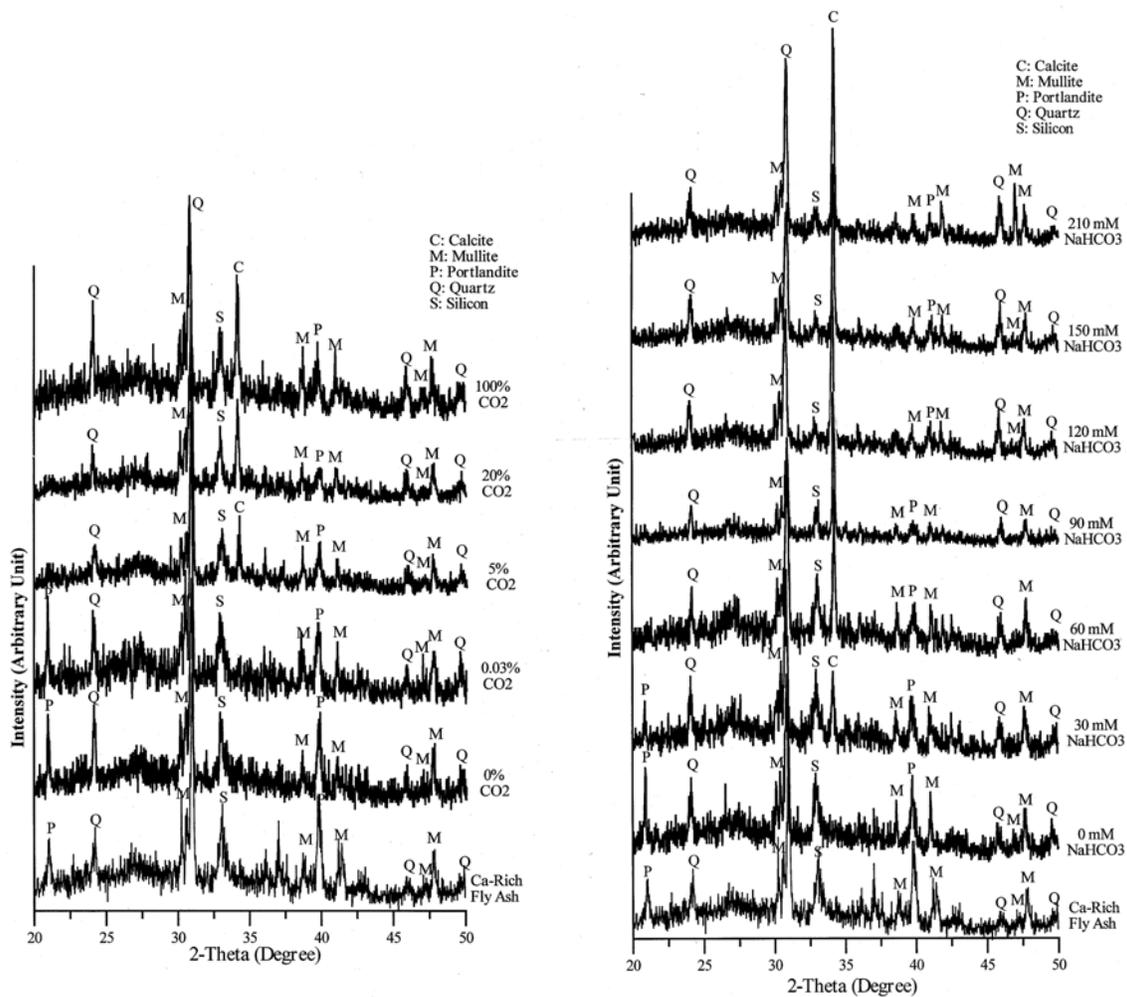


Figure 4. XRD analysis of Ca-rich fly ash used for carbon sequestration in the presence of different NaHCO_3 concentration (0 – 210 mM) (left) and difference pCO_2 (0 – 100% CO_2) (right).

Scale-up experiments (up to 4-L) using thermophilic and psychrophilic metal-reducing bacteria have proved successful at sequestering carbon while using Ca and Fe-rich fly ash. These upscaled experiments show potential for dramatic improvements of carbon and metal sequestration by complementing existing fly ash handling with biogeochemical processes. The capacity of biogeochemical processes using Fe(III)-reducing bacteria to precipitate carbonate minerals such as calcite and siderite using metal-rich fly ash creates the possibility of more effective CO₂ sequestration than would be possible with photosynthetic systems in alkaline ponds. This study indicates that siderite and calcite precipitation using metal-rich fly ash and 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 (Fredrickson et al., 1998; Zhang et al., 1998; Roh et al., 2003).

Metal-rich fly ash, rejected dust from cement kilns and non-regulated agricultural wastes or food processing wastes are often trucked and land filled at total disposal costs (including transportation) often exceeding \$50 per ton while carbon dioxide is liberated to the atmosphere. While previous strategies dealt with these as separate issues, there may be an opportunity to energyplex them into useful product lines in high ionic strength ponds. The high ionic strength would be provided by the fly ash (along with residual sulfate from the sulfur in the coal) and/or reject kiln dust. Carbon dioxide from the plant could be bubbled through the deep alkaline pond. Agricultural wastes could provide additional energy into the pond. Anaerobic bacteria fed by the organics in the wastes precipitate additional carbonates in the sediments. Within our labs different cultures of these bacteria produce siderite pellets in 5% salts at temperatures from 4°C to 75°C within days. Importantly, they also reduce other metals including chromium, manganese, uranium, and cobalt (Zhang et al., 1996). The product of our proposed process could therefore be a hydrated multi-metal limestone-like aggregates suitable for road fill materials or other uses.

IMPLICATIONS AND FUTURE ACTIVITIES

Sequestration mechanisms would include biogeochemical processes and abiotic geochemical precipitation. To the mixture of ash, agricultural wastes, water and bubbled carbon dioxide one could add of tons of waste cement kiln dust per day enhancing the bio- and geo-chemical precipitation and sequestration efficiency. Accordingly, a fraction of carbon per cubic foot of pond each day (one pound per day per 10 cubic ft of pond) could be sequestered. 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 the biogeochemical sequestration rates would dramatically increase. Using the same conservative 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.

Through this research supported by the DOE-FE program and the National Energy Technology Laboratory (NETL) we will further the science of coal utilization as it pertains to carbon and metal sequestration, stabilization of coal derived fly ash, and producing useable conglomerates while stabilizing fly ash. While microorganisms facilitated precipitating minerals, 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 discussing with the potential utility of engineered upscaling of both biogeochemical and geochemical mechanisms of increased carbon and metal sequestration in fly ash ponds. Scale-up experiments (1 - 5gal) in the laboratory are assessing potential upscaling and design parameters that could be pursued in field tests.

CONCLUSIONS

Given the abundance of Fe and Ca in metal-rich fly ash, the capacity of Fe(III)-reducing bacteria to precipitate carbonate minerals could have a significant impact on carbon sequestration. In addition to precipitation of carbonate minerals via biogeochemical processes, the microbial utilization of organic

matter and hydrogen also contributes to direct or indirect (co)precipitation of redox sensitive metals in fly ash ponds. The capacity of iron-reducing bacteria to precipitate carbonate minerals using fly ash creates the possibility of more effective CO₂ sequestration. In environments with high bicarbonate concentrations, the microbial production of Fe(II) from Fe-rich fly ash stimulates siderite formation. Biological carbonate mineral formation using fly ash indicates that biogeochemical processes may complement the capture of carbon dioxide from fossil fuel plants while potentially stabilizing fly ash wastes.

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