

# **BIOMINERALIZATION FOR CARBON SEQUESTRATION**

T. J. Phelps and Y. Roh

Environmental Sciences Division  
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge TN 37831-6036

## **ABSTRACT**

The objective of this study is to investigate biogeochemical processes utilizing metal-rich fly ash for carbon sequestration and metal immobilization. Metal-reducing bacteria enriched from fly ash ponds and extreme environments were capable of CO<sub>2</sub> conversion into sparingly soluble carbonate minerals using metal-rich fly ash and lactate as an energy source in the presence of different atmospheres (80% N<sub>2</sub>-20% CO<sub>2</sub>, 80% H<sub>2</sub>-20% CO<sub>2</sub>, 100% CO<sub>2</sub>) as well as in HCO<sub>3</sub><sup>-</sup> buffered media (30 - 240 mM). Chemical analysis of culture media after incubation revealed that the leaching of Ca and Fe from fly ash was significantly reduced in the presence of a CO<sub>2</sub> atmosphere. Microbial reduction of metals also plays an important role in immobilization of redox-labile trace metals including selenium (5 mM Se<sup>6+</sup>), cobalt (10 mM Co<sup>3+</sup>), and chromium (1 mM Cr<sup>6+</sup>) because these metals are readily reduced and/or coprecipitated with carbonate minerals. The use of metal-reducing bacteria facilitates the formation of carbonate minerals including calcite (CaCO<sub>3</sub>) and siderite (FeCO<sub>3</sub>) as well as sparingly soluble, reddish brown Se<sup>0</sup> precipitates. Slurries of metal rich fly ash exhibited a strong sequestration efficiency for CO<sub>2</sub> ranging upwards of ~ 50 g CO<sub>2</sub>/kg fly ash with concomitant precipitation and sequestration of several heavy metals such as As, Co, Cr, Se, and others. This work provides new biotechnological insights in potential carbon sequestration and metal immobilization in fly ash ponds.

## **INTRODUCTION**

One of the stimulating scientific discoveries of the twentieth century was the observation that the concentration of atmospheric CO<sub>2</sub> and its rate of increase have both been increasing since the 1950s (e.g., as measured at Mauna Loa, Hawaii). The amount of anthropogenic CO<sub>2</sub> emitted to the atmosphere, primarily because of expanding use of fossil fuels for energy, has risen from preindustrial levels of 280 ppm to present levels of over 365 ppm. These fundamental data, when combined with long-term records through glacial-interglacial cycles of atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> may play a major role in climate forcing during the coming centuries.

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 (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], or sulfide (FeS). Recent studies demonstrated that partial pressures of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>, a mixture of magnetite and iron rich carbonates such as siderite was formed. It has been reported that calcite (CaCO<sub>3</sub>) and magnesite (MgCO<sub>3</sub>) 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 is to investigate biogeochemical processes utilizing metal-rich fly ash for carbon sequestration and metal immobilization.

## MATERIALS AND METHODS

### MICROORGANISMS USED FOR CARBON SEQUESTRATION AND METAL

**IMMOBILIZATION.** Biogeochemical conversion of CO<sub>2</sub> 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 microbial mat near a hydrothermal vent, deep subsurface environments, and a boron leachate-pond containing high levels of salt and boric acid. For these experiments, thermophilic (*Thermoanaerobacter ethanolicus*, TOR-39 and C1), psychrotolerant (*Shewanella waksmanii*, PV-4), alkaliphilic (*Alkaliphilus transvaalensis*, QYMF) metal-reducing bacteria (Table 1) were used to examine biogeochemical processes for CO<sub>2</sub> sequestration using metal-rich fly ash.

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)	Taylorville Triassic Basin, Northern Virginia	Shale, siltstone, and sandstone	<i>Thermo- anaerobacter 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 waksmanii</i>	Stapleton et al., 2004
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., 2004

**BIOGEOCHEMICAL CONDITIONS AND FLY ASH CHEMISTRY.** 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 NaCl, 0.4 K<sub>2</sub>HPO<sub>4</sub>•3H<sub>2</sub>O, 7.2 HEPES (hydroxyethylpiperazine-N<sup>2</sup>-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 formation 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 and were selected based on mineralogical and chemical characterization.

Experiments were performed at 25°C for psychrotolerant (*Shewanella waksmanii*, PV-4) and alkaliphilic cultures (*Alkaliphilus transvaalensis*, QYMF) and at 60°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. To assess the capability of metal reduction by the metal-reducing bacteria, various electron acceptors such as cobalt(III)-EDTA (10 mM), potassium chromate (1 mM), and selenate (5 mM) were examined at 25°C or 60°C with lactate as an electron donor. 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 pCO<sub>2</sub> including N<sub>2</sub>, N<sub>2</sub>-CO<sub>2</sub> (95% N<sub>2</sub>-5% CO<sub>2</sub>; 80% N<sub>2</sub>-20% CO<sub>2</sub>), H<sub>2</sub>-CO<sub>2</sub> (80% H<sub>2</sub>-20% CO<sub>2</sub>), CO<sub>2</sub> (100% CO<sub>2</sub>). Experiments with CO<sub>2</sub> pressure (0.05%CO<sub>2</sub>) close to the atmospheric CO<sub>2</sub> content were also examined to see the influence of low CO<sub>2</sub> on carbon sequestration. In addition, the effects of bicarbonate buffer concentration on biogeochemical processes for carbon sequestration were also examined using different concentrations of HCO<sub>3</sub><sup>-</sup> buffered media (30 - 240 mM). The pH of the medium with metal-rich fly ash was varied from 6.5 to 9.5. Hydrogen (80% H<sub>2</sub>-20% CO<sub>2</sub>), glucose (10 mM), acetate (10 mM), or lactate (10 mM) served as electron donors to examine biogeochemical sequestration of CO<sub>2</sub>.

Table 2. Metal-rich fly ashes currently investigated for carbon sequestration 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
		-- % --					
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> )
TVA ParadiseAsh Paradise, KY	11.8	41.7	18.3	13.4	13.5	3.0	Mullite (Al <sub>6</sub> Si <sub>3</sub> O <sub>15</sub> ), Maghemite (Fe <sub>2</sub> O <sub>3</sub> ), Hematite (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> )

**GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION.** To examine biogeochemical processes such as dissolution and carbonation using metal-rich coal fly ash in the presence of different pCO<sub>2</sub> atmospheres 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 pH electrode and an ORION EA 920 expandable ion analyzer (Orion Research, Beverly, MA), standardized with pH 7 buffer and the appropriate buffer of either pH 4 or 10 (Roh et al., 2001). Eh values were measured using platinum microelectrodes (Microelectrodes, Inc., Londonerry, 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, Fe, and other elements in the fly ash slurries 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 radiation with a scan rate of 2° 2θ /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

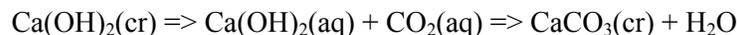
**MICROBIAL METAL REDUCTION.** The metal-reducing bacteria were able to reduce Co(III) [Co(III)-EDTA, 10 mM] to Co(II) and Cr(VI) ( $\text{K}_2\text{CrO}_4^{2-}$ , 1 mM) to Cr(III) with lactate (10 mM) as an electron donor, as indicated by the color change of the culture solution from purple [Co(III)-EDTA] and yellow (potassium chromate) to colorless at 25°C or 60°C. The bacteria were also able to reduce selenate [Se(VI), 5 mM] and precipitated reddish brown phases. SEM analysis showed the bacteria precipitated trigonal crystals or ball-like particles during selenate reduction using lactate as an electron donor at pH = 10. EDX analysis showed that the precipitated phases mainly consisted of Se, thereby demonstrating the reduction of Se(VI) to Se(0). These results indicated that the metal-reducing bacteria such as *Thermoanaerobacter ethanolicus* (TOR-39), *Shewanella waksmanii* (PV-4), and *Alkaliphilus metalliredigens* sp. (QYMF) can reduce several other transition metals as long as their concentrations are held below the toxic levels.

**SOLUTION CHEMISTRY.** Measurements of Eh and pH values were plotted 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. Microbial processes with lactate and fly ash under a higher bicarbonate buffer (140 – 240 mM) resulted in lower Eh values than microbial processes with a lower bicarbonate buffer (30 – 70 mM), 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, 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 ash in contrast to 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 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).

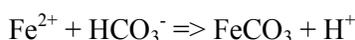
Chemical analysis of water-soluble metals in the culture medium after incubation revealed that the leaching of Ca and Fe from fly ash was significantly reduced in the presence of a CO<sub>2</sub> atmosphere and in HCO<sub>3</sub><sup>-</sup> buffered media (Figure 1). In addition to microbially facilitated 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 pCO<sub>2</sub> 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 efficiency of carbon sequestration as shown in Figures 2 and 3. Slurries of Ca-rich fly ash with metal reducing bacteria (TOR-39) exhibited a strong sequestration efficiency for CO<sub>2</sub> ranging upwards of ~40 g CO<sub>2</sub>/kg fly ash under CO<sub>2</sub> atmospheres and ~ 50 g CO<sub>2</sub>/kg fly ash under different bicarbonate concentrations. Bottles containing metal-reducing bacteria and an energy sources led to more biogeochemically facilitated precipitation of carbonate minerals with redox-labile metals.

XRD analysis (Figure 3) showed that the biogeochemical processes induced precipitation of calcium carbonate (Calcite,  $\text{CaCO}_3$ ) using Ca-rich Springerville fly ash under the  $\text{CO}_2$  atmospheres and with bicarbonate buffer at  $60^\circ\text{C}$  incubation temperature. SEM with EDX spectra also showed that biogeochemical processes precipitated calcium carbonate using Ca-rich fly ash under a  $\text{H}_2/\text{CO}_2$  atmosphere and a high bicarbonate buffer ( $> 60 \text{ mM}$ ). No carbonate minerals formed using metal-rich fly ash without bacteria. The biogeochemical processes facilitated calcite precipitation using Ca-rich fly ash under a  $\text{H}_2\text{-CO}_2$  atmosphere and high bicarbonate buffers ( $> 60 \text{ mM}$ ):



XRD analysis showed that increased bicarbonate buffer ( $210 \text{ mM HCO}_3^-$ ) also facilitated biomineralization of iron carbonate (siderite,  $\text{FeCO}_3$ ) using Fe-rich Johnsonville fly ash ( $25\% \text{ Fe}_2\text{O}_3$ ) under a  $\text{N}_2$  atmosphere at  $60^\circ\text{C}$  (data not shown). SEM with EDX spectra showed microbially-facilitated precipitation of iron carbonate with the Fe-rich Johnsonville fly ash under a  $\text{H}_2\text{-CO}_2$  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  $\text{CO}_2$  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.

Scale-up experiments (up to 4-L) using thermophilic, psychrophilic, and alkaliphilic 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. This study indicates that siderite and calcite precipitation using metal-rich fly ash is generally associated with the bacterial metabolism of organic matter and hydrogen coupled with microbial metal reduction in the presence of reducing environments and high bicarbonate buffer or a  $\text{CO}_2$  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  $4^\circ\text{C}$  to  $75^\circ\text{C}$  within days. The product of our proposed process could therefore be hydrated multi-metal limestone-like aggregates suitable for fill materials or other uses.

## IMPLICATIONS AND FUTURE ACTIVITIES

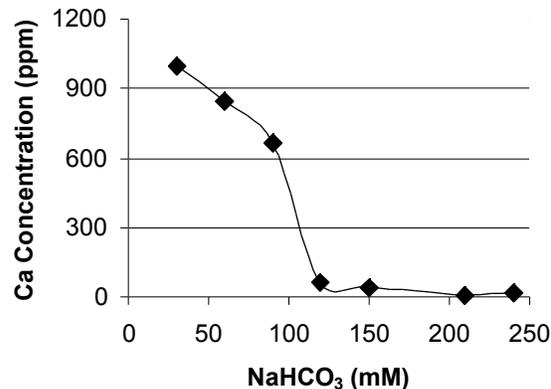
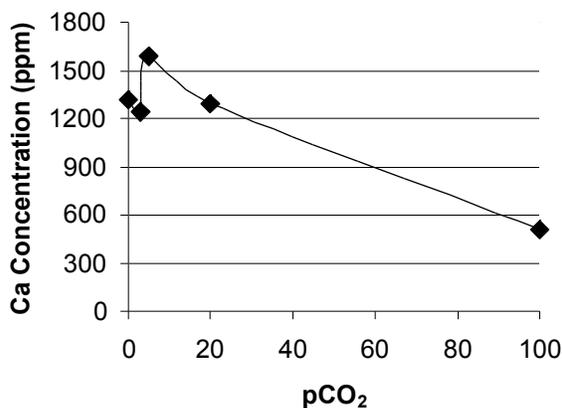
Sequestration mechanisms would include biogeochemical processes and abiotic geochemical precipitation. To the mixture of ash, agricultural wastes, water and bubbled carbon dioxide one could add

of tons of waste cement kiln dust per day enhancing the biogeochemical 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 develop 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 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 – 5 gal) 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 CO<sub>2</sub> 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.



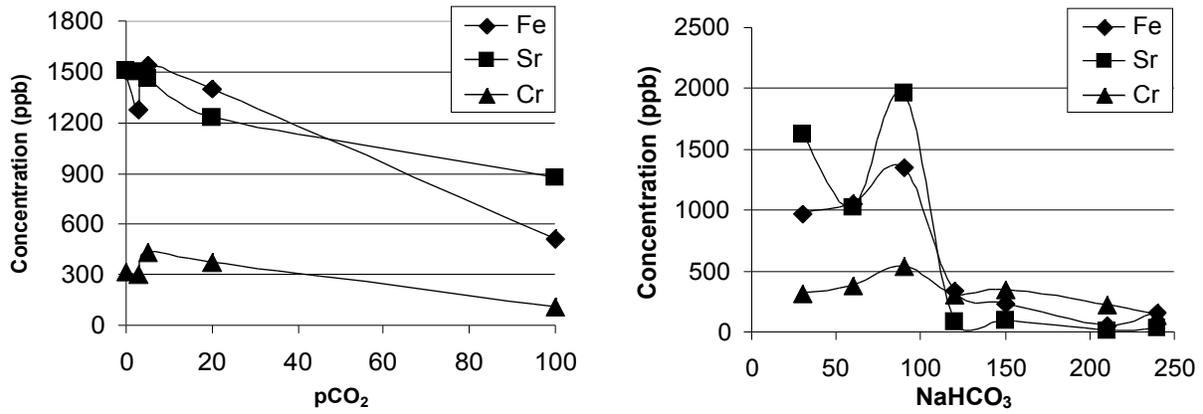


Figure 1. Water soluble metals in the culture media after incubation using Ca-rich Springerville fly ash and metal-reducing bacteria used for carbon sequestration under different pCO<sub>2</sub> atmospheres and NaHCO<sub>3</sub> concentrations.

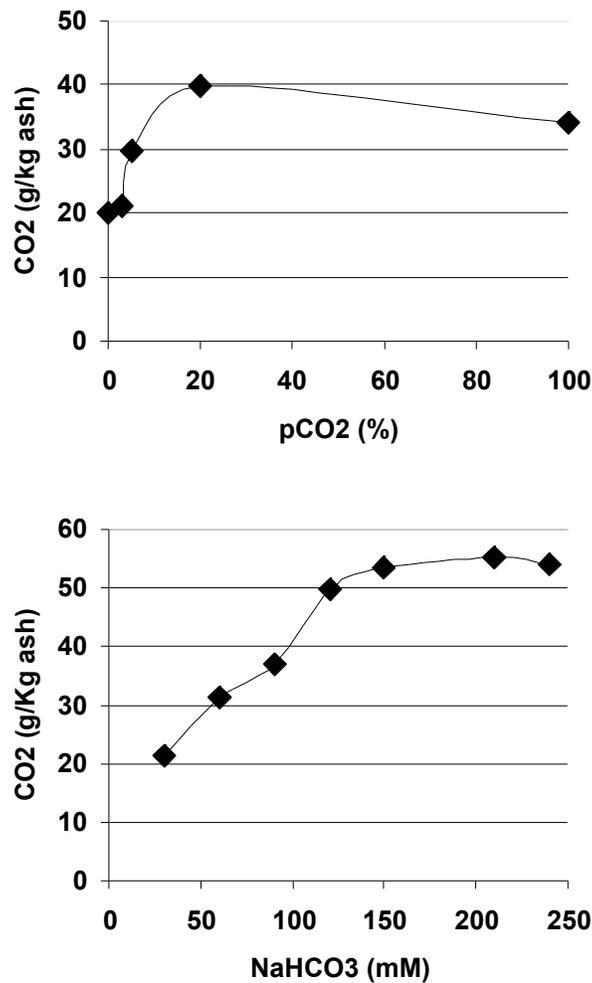


Figure 2. CO<sub>2</sub> sequestration efficiency using Ca-rich fly ash and metal-reducing bacteria (TOR-39) under different pCO<sub>2</sub> (0% - 100%) and different bicarbonate concentrations (30 - 240 mM NaHCO<sub>3</sub>).

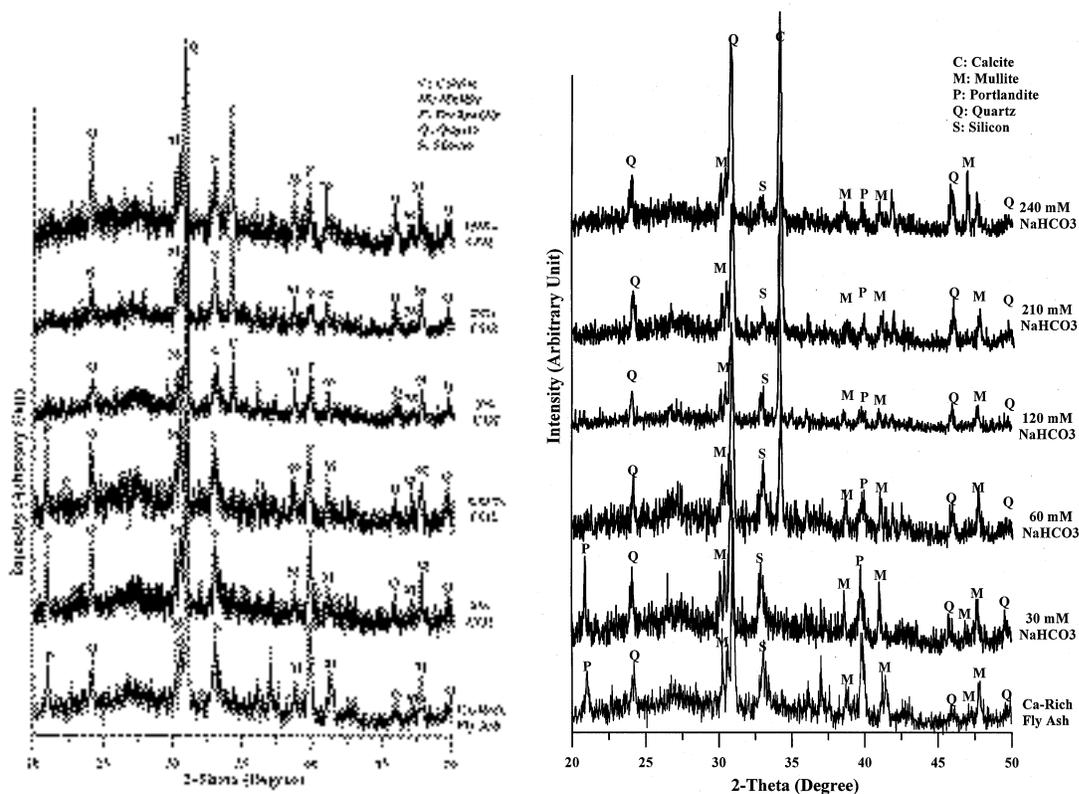


Figure 3. XRD analysis of Ca-rich fly ash used for carbon sequestration in the presence of different  $p\text{CO}_2$  (0 – 100%  $\text{CO}_2$ ) (left) and different  $\text{NaHCO}_3$  concentration (30 – 240 mM) (right).

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