

# Influence of Sediment Acidification on Water Quality in Carbonate Environments

## A Laboratory Experiment

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### Abstract

A sediment leaching experiment was conducted in a controlled laboratory setting. The sediments were collected from a carbonate-rich waste mine tailings site in MO. Dissolved inorganic carbon (DIC), major ions, and stable carbon isotope ratios of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) leachate were analyzed. The purpose was to investigate the carbon dioxide produced from acid neutralization by carbonate-rich sediments that may occur at an acid mine drainage contaminated site (e.g. parts of Neosho County, SE Kansas) during the loss of  $\text{CO}_{2(\text{g})}$  from groundwater discharge. Results show that there is rapid decrease in DIC and an increase in pH during the first 48 hours of leaching the tailings with 0.1N sulfuric acid. The decrease in DIC is due to the loss of excess carbon dioxide  $\text{CO}_{2(\text{aq})}$  that dissolved in water as neutralization is occurring. This loss of  $\text{CO}_{2(\text{g})}$  leads to a kinetic enrichment of the stable carbon isotopes  $\delta^{13}\text{C}_{\text{DIC}}$ . The magnitude of the  $\delta^{13}\text{C}_{\text{DIC}}$  enrichment is determined to depend on the (1) initial concentration of the excess  $\text{CO}_{2(\text{aq})}$  (at time =  $t_{0+1}$ ) in the leachate, (2) the amount of DIC and (3) the rate at which the  $\text{CO}_{2(\text{g})}$  is lost from the reactor. These results are important in our understanding of the long-term effect from the exploitation of natural resources that can generate carbon dioxide in the environment.

### Introduction

Acidification is a major environmental problem caused by activities such as mining, industrial processes and emissions from vehicles, volcanoes etc. that release acid to the environment.

- Acidity decreases the pH of fluids below the neutral value of 7. This can have effects on plants, aquatic life, people, their property and the environment. In the United States and across the world, the acidity leaches into water bodies (e.g. lakes, streams, oceans and groundwater) and circulates in the environment.
- The cause of acidification in the environment is mostly from intense weathering of acid-causing minerals such e.g. pyrite ( $\text{FeS}_2$ ) in the presence of water and oxygen, or atmospheric gases e.g. sulfur dioxides ( $\text{SO}_2$ ) dissolved in precipitation.



Fig. 1: "Yellowboy" acidification by acid mine drainage stream, Huntsville, Missouri

In areas with significant amounts of carbonate ( $\text{CO}_3^{2-}$ ) rocks, acid waters can be quickly neutralized by the minerals in these rocks e.g. calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) according to the reaction:



The bicarbonate can further react with protons from the acid to produce carbonic acid that dissociates into water and carbon dioxide according to:



If the concentration of  $\text{CO}_{2(\text{aq})}$  produced in the water is elevated, the the  $\text{CO}_2$  will be lost by diffusion to the atmosphere adding to the carbon budget.

### Objectives

**The objective of this study is to simulate the leaching of carbonate-rich sediments under high acidic conditions.**

The approach is to investigate and model changes in the chemical concentrations of ions, the inorganic carbon content and stable carbon isotope ratios of leachates.

The purpose of the research is to characterize the changes in water quality and quantify the extent of acidification that occurs during the neutralization of acid as it interacts with carbonate sediments and generates  $\text{CO}_{2(\text{g})}$ .

### Material and Methods

#### Field setting

##### Sediment sampling

- Samples were collected from the Federal Tailings Pile (Fig.1) in the Old Lead Belt mining district in SE Missouri. The tailings were produced from more than 100 year long lead mining activities.

- About 1000 mg of the fine grained sediments were acid digested, processed and analyzed for metals using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Fig.3)



Fig. 2: Tailings Pile where sediments were collected for leaching experiment



Fig. 3: A Perkin Elmer Optima™ 2000DV ICP-OES used for sediment analysis

#### Laboratory setting

##### Experimental setup

- A 20 liter reactor (HDPE Fort-Paks® plastic container) was partially filled with sediment and saturated with a high purity 18.2  $\Omega\text{m}$  deionized water (fig. 4).

- The cap of the reactor was modified by fitting with a septum seal to insert syringes for adding acid and sampling and tube fitted with a three way stop cork connected to a vacuum pump to degas the reactor (fig. 4).

##### Experimental Procedure

- Excess 0.1N sulfuric acid was added (once) via a glass syringe to the sediments in the air-tight reactor. The reactor was then mechanically agitated and water parameters measured and sampled for ions and DIC over time.

- The physical parameters (temperature, pH, specific conductance (SPC), oxidation reduction potential (ORP)) of water in the reactor were measured using a Yellow Spring Instrument (YSI) multi-parameter probe. Alkalinity was titrated using the Hach Digital Titrator (Hach, 1992) (fig. 5).

- Water was sampled for chemical analysis at different times until no change in physical parameters was observed over sustained interval after 172 hours.

##### Water sample analysis

- Water samples were collected for the analysis of major ions, dissolved inorganic acid and stable carbon isotopes.

- Major cations and anions were analyzed using a Dionex Reagent-Free™ Ion Chromatography System. Triplicates of each sample were averaged and compared to a standard calibrated to greater 99.5% accuracy

-  $\text{CO}_2$  was extracted as described by Atekwana and Krishnamurthy (1998) and sealed in pyrex tubes, for isotopes analysis using an Inductively coupled plasma mass spectrometry (ICP-MS). Bicarbonate was calculated from alkalinity. Samples were analyzed in the geochemistry lab at OSU- Stillwater OK.

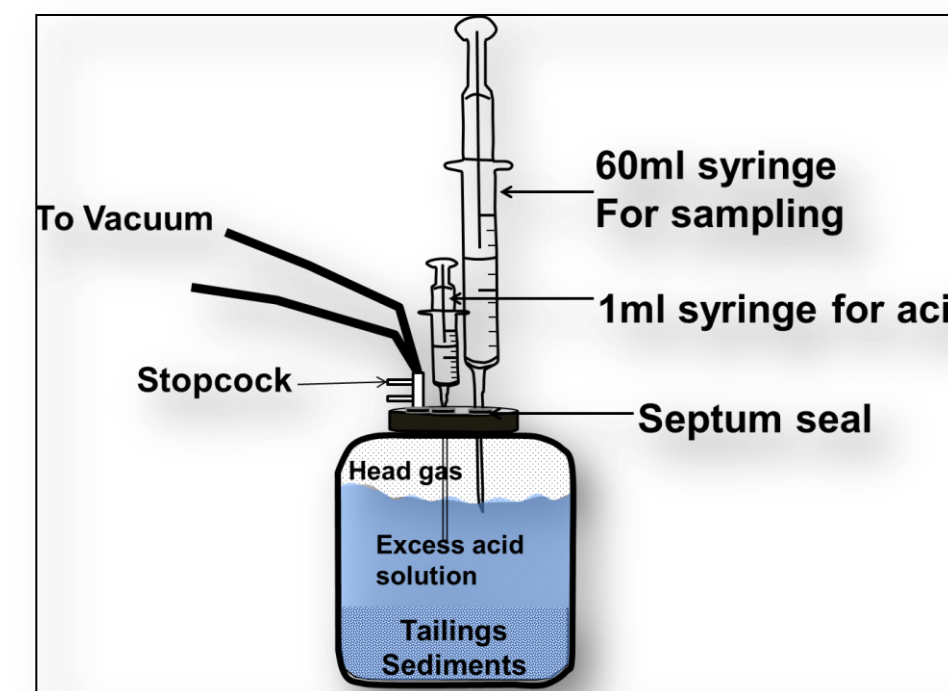


Fig. 4: Experimental reactor modification and setup

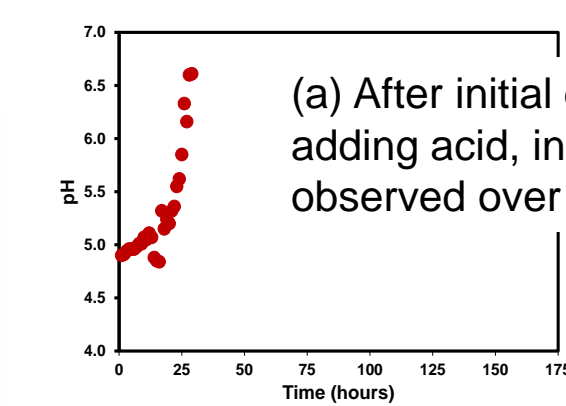


Fig. 5: Multi-parameter probe (a) and Hach digital titrator used for physical parameters and alkalinity

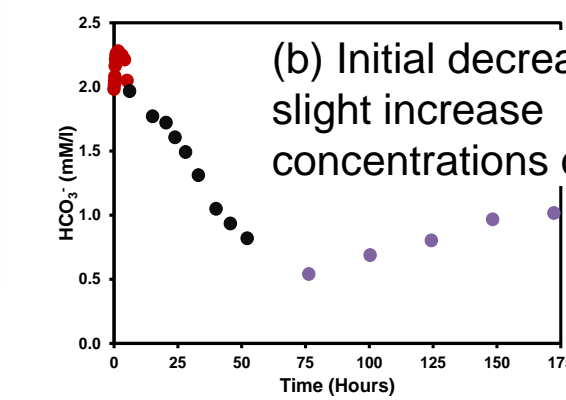


Fig. 6: Dionex Reagent-Free™ Ion Chromatograph used for ions analysis

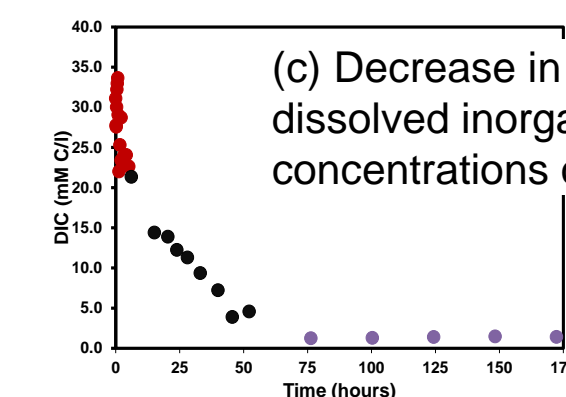
### Results and Discussion



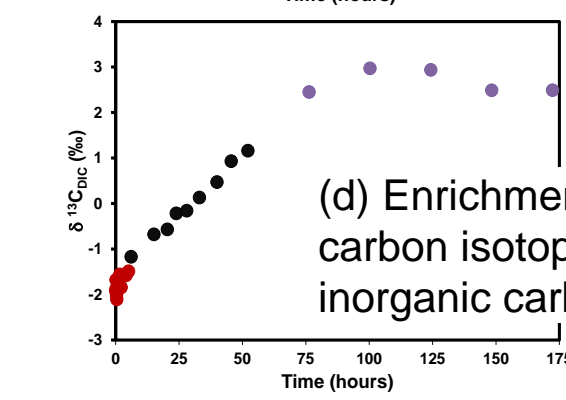
(a) After initial drop from adding acid, increase in pH observed over time



(b) Initial decrease followed by slight increase in bicarbonate concentrations over time



(c) Decrease in total dissolved inorganic carbon concentrations over time



(d) Enrichment in the stable carbon isotope of dissolved inorganic carbon over time

Fig. 7: Changes in concentrations of (a) pH (b)  $\text{HCO}_3^-$ , (c) DIC and (d)  $\delta^{13}\text{C}_{\text{DIC}}$  over time

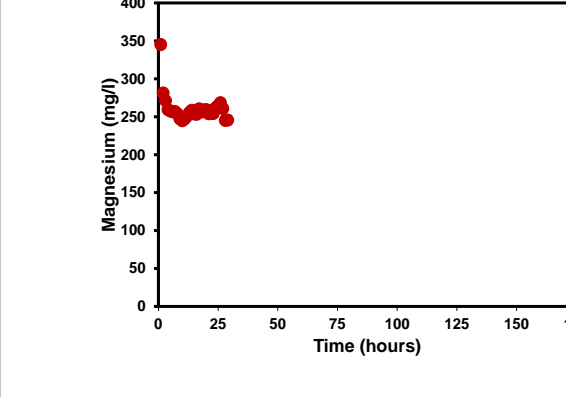
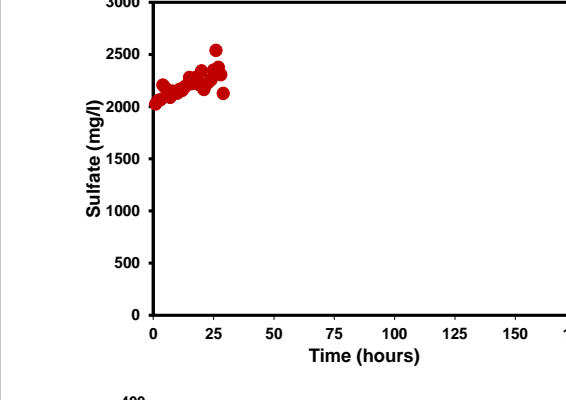
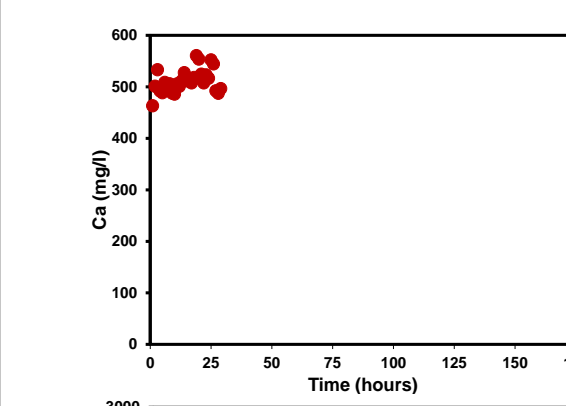
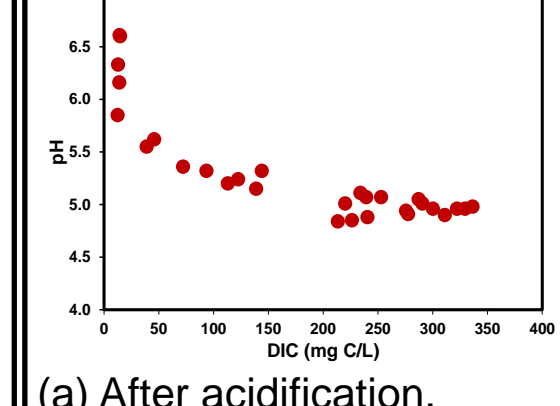
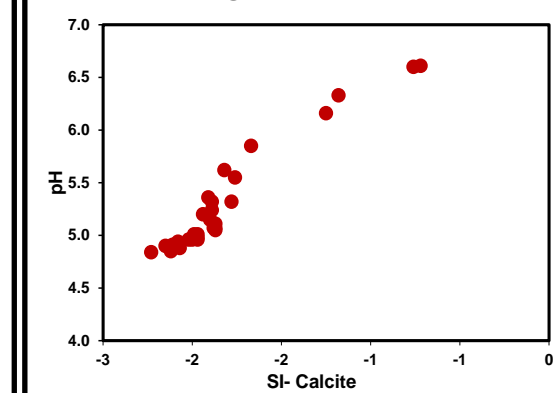


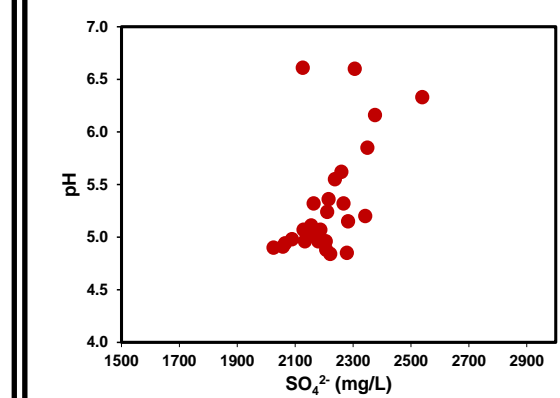
Fig. 8: Concentrations of non carbonate components e.g. Ca, Mg and Sulfate show no significant changes over time



(a) After acidification, increasing pH accompanied by decreasing DIC concentrations



(b) Increasing pH accompanied by increased saturation with calcite



(c) High sulfate concentrations after acidification did not vary much with increasing pH

Fig. 9: Crossplots of pH and (a) DIC, (b) saturation index of calcite and (c) sulfate content

### Interpretation

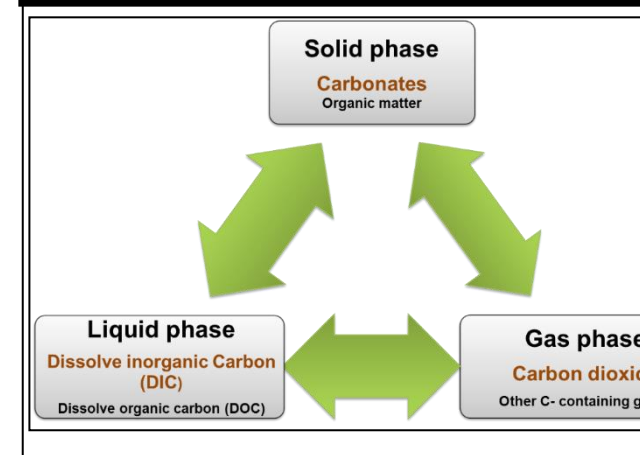


Fig. 10: Physical state of inorganic Carbon in the environment

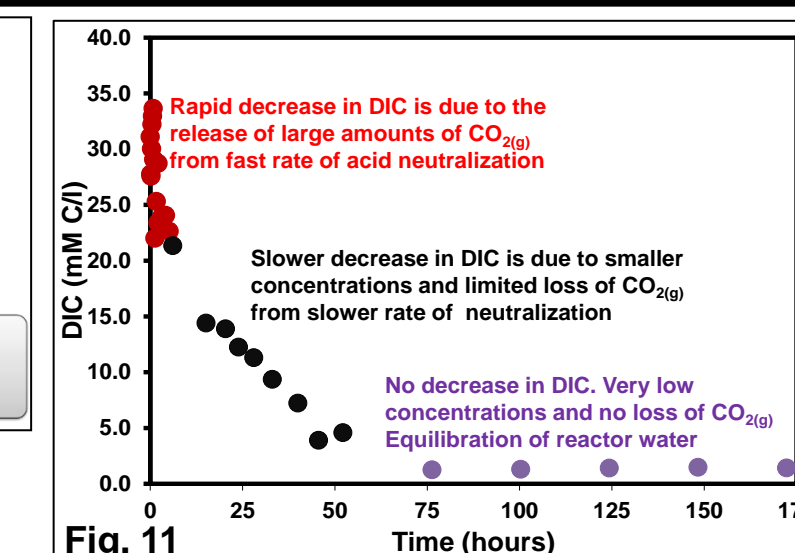


Fig. 11

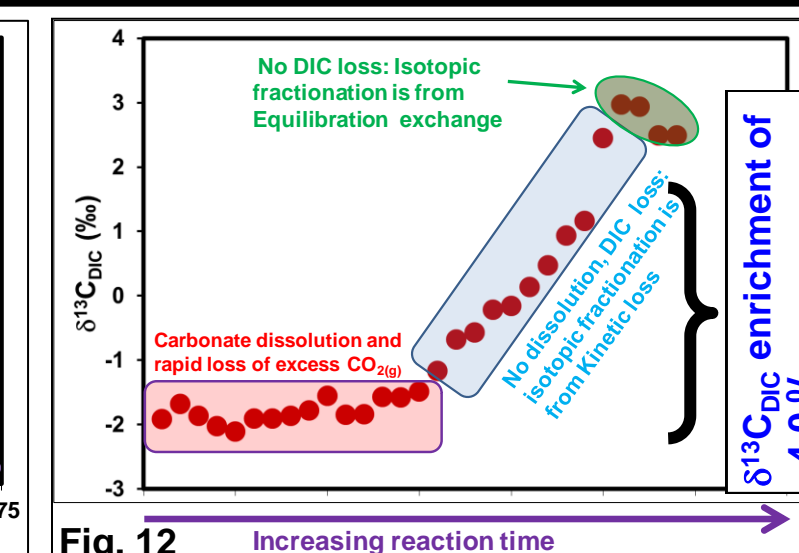


Fig. 12

During the neutralization of acids by carbonates, inorganic carbon is first converted from the solid state sediments (e.g. calcite) to the liquid state as DIC (e.g. bicarbonate) and ultimately to the gaseous phase ( $\text{CO}_{2(\text{g})}$ ) (fig.11). These transformations are accompanied by changes in the  $\delta^{13}\text{C}_{\text{DIC}}$  (fig.12). This information can be used to better understand the processes involved in the cycling of inorganic carbon in the environment.

### Conclusions and references

- Acidification of carbonates does not show decreasing pH over time due to neutralization.
- Evidence of acidification is observed in the enrichment of  $\delta^{13}\text{C}_{\text{DIC}}$ , and increased saturation with respect to calcite.
- Neutralization by carbonates is accompanied by the rapid release of large amounts of carbon dioxide.
- The carbon dioxide released from neutralization need to be factored in atmospheric  $\text{CO}_2$  budgets.